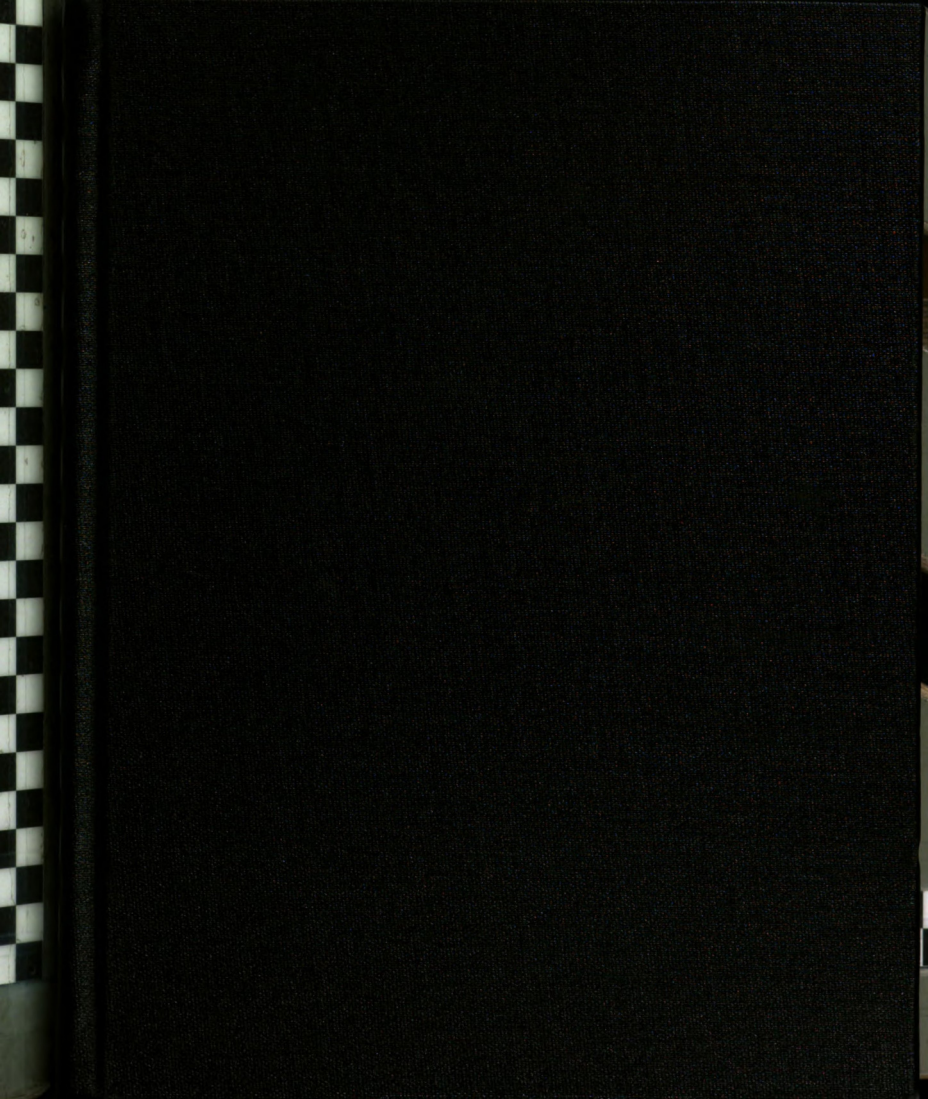




This is to certify that the

dissertation entitled

INVESTIGATIONS IN THE MULTINARY BISMUTH
CHALCOGENIDES SYSTEMS: SYNTHESIS,
CHARACTERIZATION AND THERMOELECTRIC PROPERTIES
OF BISMUTH CHALCOGENIDES

presented by

LYKOURGOS IORDANIDIS

has been accepted towards fulfillment
of the requirements for

Ph.D degree in Chemistry

Date

12/1/2000


Major professor

LIBRARY
Michigan State
University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

INVESTIGATIVE
SYSTEMS SY
P

INVESTIGATIONS IN THE MULTINARY BISMUTH CHALCOGENIDES
SYSTEMS: SYNTHESIS, CHARACTERIZATION AND THERMOELECTRIC
PROPERTIES OF BISMUTH CHALCOGENIDES

VOLUME I

By

Lykourgos Iordanidis

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

2000

Majority of

regulation due

to compounds of

metals and metalloids

Such compounds

primarily with the

environment as a

In view of

$t = K.Rt.Cs.B.$

$Q = S.$

normalized and

normalized compounds

In the term

$R.B.Seq. AB$

$R.B.Seq. B.B.$

related to the

ABSTRACT

INVESTIGATIONS IN THE MULTINARY BISMUTH CHALCOGENIDES SYSTEMS: SYNTHESIS, CHARACTERIZATION AND THERMOELECTRIC PROPERTIES OF BISMUTH CHALCOGENIDES

By

Lykourgos Iordanidis

Multinary bismuth chalcogenide systems have attracted a lot of attention during the past decade due to their emergence as a new class of thermoelectric materials. Several new compounds have been discovered that compete in performance with the best materials used today for thermoelectric cooling applications, alloys of Bi_2Te_3 .

Such compounds, however, are also interesting for other scientific reasons particularly with respect to their structural features, electronic properties and smooth interconversions which gives them the ability to form unusual homologous series

In view of these features we performed exploratory investigations in the $A/\text{Bi}/Q$ ($A = \text{K, Rb, Cs, Ba}$; $Q = \text{S, Se}$) and $A/M/\text{Bi}/Q$ ($A = \text{K, Rb, Cs, Sr, Ba}$; $M = \text{Pb, Sn, rare earth}$; $Q = \text{S, Se}$) systems. The resulting new phases were physicochemically characterized and these investigations enabled us to obtain a better understanding of this class of compounds.

In the ternary systems a large number of compounds such as $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$, $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$, ABi_3Q_5 , ($Q = \text{S, Se, Te}$), $\text{CsBi}_{3.67}\text{Se}_6$, $\text{A}_2\text{Bi}_8\text{Se}_{13}$, ($A = \text{Rb, Cs}$), $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$, BaBi_2Se_4 and $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{S}_{13}$ were found. The incorporation of rare earths resulted to the formation of the three-dimensional complex structures such as

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{Na}_2\text{O})_y(\text{K}_2\text{O})_z$

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{Na}_2\text{O})_y(\text{M}_2\text{O})_z$

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{Bi}_2\text{O}_3)_y(\text{Se}_2\text{O}_3)_z$

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{R}_2\text{O})_y(\text{P}_2\text{O}_5)_z$

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{M}_2\text{O})_y(\text{Se}_2\text{O}_3)_z$

$(\text{Li}_2\text{B}_2\text{O}_3)_x(\text{R}_2\text{O})_y(\text{S}_2\text{O}_3)_z$

We discovered

many blocks combi

many countless m

when the different

Several of the

existing thermolec

can be further app

Furthermore,

strongly bimodal

transformation p

removal of

spalling. We exp

quite good for ex

This disserta

properties of the

$ALn_{1\pm x}Bi_{4\pm x}S_8$ ($A = K, Rb$; $Ln = La, Ce, Pr, Nd$), $BaLnBi_2Q_6$ ($Ln = La, Ce, Pr$; $Q = S, Se$), $M_2La_xBi_{8-x}S_{14}$ ($M = Pb, Sr$), $Cs_2La_xBi_{10-x}S_{16}$, $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$, $Rb_4EuBi_6Se_{12}$ and $Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z}$. Reactions with Pb and Sn resulted in the formation of compounds such as $Rb_2PbBi_8S_{14}$, $Ba_xPb_{4-x}Bi_6S_{13}$, $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$, $APbBi_3S_6$ ($A = Rb, Cs$), $Rb_{2.5}M_{2x}Bi_{8.5}Se_{14}$ ($M = Pb, Sn$), $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$, $A_xPb_{4-x}Bi_6Se_{13}$, ($A = Sr, Eu$), $Ba_xPb_{6-x}Bi_6Se_{15}$, $Rb_xSn_{1-x}Bi_{6-x}Se_{10}$ and $Rb_{1.5-x}Sn_{2x}Bi_{7.5-x}Se_{12}$.

We discovered an amazing structural and compositional variety. Several different building blocks combine with each other, like "Legos", in various ways to create a seemingly countless number of novel phases. By examining the structural relationship between the different structure types, we found various homologous series.

Several of the synthesized compounds such as $Rb_2Bi_8Se_{13}$ and $BaBi_2Se_4$ possess interesting thermoelectric properties (including very low thermal conductivities) and will have to be further optimized.

Furthermore, a unique topotactic oxidative solid-state process was discovered in the ternary bismuth chalcogenides, $A_2Bi_4Se_7$, $A_3Bi_7Se_{12}$ and $Rb_4Bi_{10}Se_{17}$ ($A = Rb, Cs$). In this transformation process, we have the formation of Se-Se bond with the simultaneous de-intercalation of alkali metal ions from the Bi-Se framework, without loss of crystallinity. We expect that both the initial layered and final fully transformed products could be good ion exchange materials.

This dissertation describes the synthesis, structural relationships, characterization and properties of the compounds discovered.

To my family, Μάκης, Μαρία, Γιάννης and Jen

First I would

appreciate the

financial support and

also be involved in

I would also like

pay for their help in

making who helped in

Also I would like

especially grateful to

has served as from me

At MSU we need

University and the

for Microfabrication

reliability measure

colleagues at N

University of Michigan

Dr. Hagen and his group

Geographic Location

and Re-B, Se- and I

I would like to

my career and always

ACKNOWLEDGMENTS

First I would like to thank my advisor, Mercouri G. Kanatzidis for his help, support, encouragement and advice during the past 6 years. I especially appreciate the financial support and opportunity to work in such a well-equipped lab. I was also very lucky to be involved with an exciting research project.

I would also like to thank the past and current members of the Kanatzidis research group for their help and support throughout my time here at MSU. Especially Dr. Greg Marking who helped me very much in the beginning with many things in the lab.

Also I would like to thank the wonderful staff of the chemistry department. I am especially grateful to the members of the electronic shop, David, Ron and Scott. Their skills saved us from many "catastrophic" situations.

At MSU we made use of the SEM and TEM facilities at the Center for Advanced Microscopy and the majority of the Raman experiments were performed at the W. M. Keck Microfabrication Facility, a NSF MRSEC facility. The charge transport and thermal conductivity measurements would not have been possible without our hardworking collaborators at Northwestern University (Professor Kannewurf and his group), University of Michigan (Professor Uher and his group) and Michigan State (Professor Tim Hogan and his group). We would like also to thank Victor G. Young and the X-Ray Crystallographic Laboratory of the University of Minnesota for collecting the X-ray data set of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ and $\text{RbLa}_{0.84}\text{Bi}_{4.16}\text{S}_8$.

I would like to thank my parents and my brother for encouraging me throughout my career and always want me to have the best education I could get. And I would like

around my world

200

Early the 19

and support. C

also to thank my wonderful wife, Jen, for helping me during this long year of writing my thesis.

Finally the Office of Naval Research is gratefully acknowledged for generous financial support (Contracts N00014-94-1-0935 and N00014-98-1-0443).

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Chapter 1. Main body of the thesis

1. Introduction

1.1. Main body of the thesis

1.2. Thermoelectric

Chapter 2. A. B. N. S.

Chapter 3. Main body of the thesis

1. Introduction

2. Experimental

Reagents

Synthesis

B₂Se₃

Rh₂Bi₂Se₇

Cs₂Bi₂Se₇

CsBi₂Se₇

BaBi₂Se₇

3. Physical Me

Electron m

Differential

Infrared sp

Charge tran

Powder X-r

Single crys

Rh₂Bi₂Se₇

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES	xvii
LIST OF FIGURES	xxv
LIST OF ABBREVIATIONS.....	xxxiv
Chapter 1. <i>Multinary Bismuth Chalcogenides and Thermoelectric Concepts</i>	1
1. Introduction.....	1
1-1. Multinary Bismuth Chalcogenides.....	1
1-2. Thermoelectric concepts	11
Chapter 2. <i>A₂Bi₈Se₁₃ (A = Rb, Cs), CsBi_{3.67}Se₆ and BaBi₂Se₄: New Ternary Semiconducting Bismuth Selenides</i>	24
1. Introduction.....	24
2. Experimental Section	27
Reagents.....	27
Synthesis.	27
Bi ₂ Se ₃	28
Rb ₂ Bi ₈ Se ₁₃ (I)	28
Cs ₂ Bi ₈ Se ₁₃ (II).....	28
CsBi _{3.67} Se ₆ (III).....	29
BaBi ₂ Se ₄ (IV).....	29
3. Physical Measurements.....	30
Electron microscopy.....	30
Differential thermal analysis.....	30
Infrared spectroscopy	30
Charge-transport and thermal conductivity measurements.....	31
Powder X-ray diffraction	33
Single crystal X-ray crystallography.....	33
Rb ₂ Bi ₈ Se ₁₃ (I)	34

Cs₂B₁₂N₁₂

CsB₁₂N₁₂

BaB₁₂N₁₂

4 Results and

Synthesis

Structure

Rh₂B₁₂N₁₂

CsB₁₂N₁₂

BaB₁₂N₁₂

Energy gap

Charge transfer

Thermal

5 Concluding

Chapter 3. Structure

Notes

1. Introduction

2. Experiment

Reagents

Synthesis

B₁₂S₁₂

B₁₂Se₁₂

γ-Rh₂B₁₂N₁₂

α-Rh₂B₁₂N₁₂

β-Rh₂B₁₂N₁₂

γ-Rh₂B₁₂N₁₂

CsB₁₂N₁₂

Rh₂B₁₂N₁₂

Rh₂B₁₂N₁₂

3 Physical

$\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ (II).....	34
$\text{CsBi}_{3.67}\text{Se}_6$ (III).....	34
BaBi_2Se_4 (IV).....	35
4. Results and Discussion.....	43
Synthesis and thermal behavior.....	43
Structure description	44
$\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ (I) and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ (II)	44
$\text{CsBi}_{3.67}\text{Se}_6$ (III)	52
BaBi_2Se_4 (IV).....	56
Energy gaps	60
Charge transport properties	63
Thermal conductivity	76
5. Concluding Remarks.....	78
Chapter 3. <i>Structural Complexity in the ABi_3Q_5 ($A = \text{Rb}, \text{Cs}$; $Q = \text{S}, \text{Se}, \text{Te}$)</i>	
<i>Systems</i>	85
1. Introduction.....	85
2. Experimental Section	87
Reagents.....	87
Synthesis	88
Bi_2S_3	88
Bi_2Se_3	88
$\gamma\text{-RbBi}_3\text{S}_5$ (I).....	88
$\alpha\text{-RbBi}_3\text{Se}_5$ (II).....	89
$\beta\text{-RbBi}_3\text{Se}_5$ (III).....	89
$\gamma\text{-RbBi}_3\text{Se}_5$ (IV)	90
CsBi_3Se_5 (V).....	90
$\text{RbBi}_3\text{Se}_4\text{Te}$ (VI).....	90
$\text{RbBi}_3\text{Se}_3\text{Te}_2$ (VII)	91
3. Physical Measurements.....	91

Solid-State

Single-crystal

γ -RbB₂

α -RbB₂

β -RbB₂

γ -RbB₂

CsB₂S₃

RbB₂S₃

4 Results and

Synthesis

Energy gap

Structure

γ -RbB₂

α -RbB₂

β -RbB₂

γ -RbB₂

Comparison

5 Concluding

Figure 4. Overview

Transformations in

Borate Selenide

1. Introduction

2. Experiment

Reagents

Synthesis

Bi₂Se₃

Rb₂Bi₂

Cs₂Bi₂

Cs₂Bi₂S₃

Solid-State UV/Vis Spectroscopy	91
Single crystal X-ray crystallography	91
γ -RbBi ₃ S ₅ (I).....	92
α -RbBi ₃ Se ₅ (II).....	92
β -RbBi ₃ Se ₅ (III).....	93
γ -RbBi ₃ Se ₅ (IV)	93
CsBi ₃ Se ₅ (V).....	94
RbBi ₃ Se ₄ Te (VI).....	95
4. Results and Discussion.....	105
Synthesis and thermal behavior.....	105
Energy gaps	107
Structure description.	109
γ -RbBi ₃ S ₅ (I).....	109
α -RbBi ₃ Se ₅ (II).....	114
β -RbBi ₃ Se ₅ (III) and CsBi ₃ Se ₅ (V)	118
γ -RbBi ₃ Se ₅ (IV) and RbBi ₃ Se ₄ Te (VI).....	123
Comparison of the AM ₃ Q ₅ structures	128
5. Concluding Remarks.....	131

Chapter 4. *Observation of Topotactic Two-Dimensional to Three-Dimensional Transformations in the Solid State. Redox-Induced “Zipper” Action in Ternary Bismuth Selenide*.....

1. Introduction.....	138
2. Experimental Section	141
Reagents.....	141
Synthesis	141
Bi ₂ Se ₃	141
Rb ₂ Bi ₄ Se ₇ (I).....	141
Cs ₂ Bi ₄ Se ₇ (II).....	142
Cs ₃ Bi ₇ Se ₁₂ (III).....	142

Rh₂Bi₂Se₇

Rh₂Bi₂Se₇

ABi₂Se₆ (A)

A₂Bi₂Se₆

ABi₂Se₆

Rh₂Bi₂Se₇

3 Physical Measurements

Raman Spectroscopy

Single-crystal

Rh₂Bi₂Se₇

Cs₂Bi₂Se₆

Cs₂Bi₂Se₆

Rh₂Bi₂Se₇

Rh₂Bi₂Se₇

Rh₂Bi₂Se₇

Cs₂Bi₂Se₆

Cs₂Bi₂Se₆

Rh₂Bi₂Se₇

Cs₂Bi₂Se₆

Rh₂Bi₂Se₇

Rh₂Bi₂Se₇

4 Results and Discussion

Synthesis, structure

Structure determination

A₂Bi₂Se₆

ABi₂Se₆ (A)

A₂Bi₂Se₆

A₂Bi₂Se₆

ABi₂Se₆ (A)

Rh₂Bi₂Se₇

Rb ₃ Bi ₇ Se ₁₂ (IV).....	142
Rb ₄ Bi ₁₀ Se ₁₇ (V).....	143
ABi ₄ Se ₇ (A = Rb, Cs) (VI and VII)	143
A ₂ Bi ₇ Se ₁₂ (A = Cs, Rb) (VIII and IX).....	143
ABi ₇ Se ₁₂ (A = Cs, Rb) (X and XI).....	144
Rb ₂ Bi ₁₀ Se ₁₇ (XII).....	144
3. Physical Measurements.....	145
Raman Spectroscopy.....	145
Single crystal X-ray crystallography.....	145
Rb ₂ Bi ₄ Se ₇ (I).....	146
Cs ₂ Bi ₄ Se ₇ (II).....	147
Cs ₃ Bi ₇ Se ₁₂ (III).....	147
Rb ₃ Bi ₇ Se ₁₂ (IV).....	149
Rb ₄ Bi ₁₀ Se ₁₇ (V).....	149
RbBi ₄ Se ₇ (VI)	150
CsBi ₄ Se ₇ (VII)	152
Cs ₂ Bi ₇ Se ₁₂ (VIII)	152
Rb ₂ Bi ₇ Se ₁₂ (IX)	153
CsBi ₇ Se ₁₂ (X)	154
RbBi ₇ Se ₁₂ (I).....	154
Rb ₂ Bi ₁₀ Se ₁₇ (XII).....	154
4. Results and Discussion.....	174
Synthesis, thermal behavior and spectroscopy	174
Structure description	180
A ₂ Bi ₄ Se ₇ (II) (A = Cs, Rb) (I and II).....	180
ABi ₄ Se ₇ (II) (A = Cs, Rb) (VI and VII).....	187
A ₃ Bi ₇ Se ₁₂ (III) (A = Cs, Rb) (III and IV).....	189
A ₂ Bi ₇ Se ₁₂ (III) (A = Cs, Rb) (VIII and IX).....	194
ABi ₇ Se ₁₂ (III) (A = Cs, Rb) (X and XI).....	197
Rb ₄ Bi ₁₀ Se ₁₇ (V).....	199

1 Introduction

2. Experiment

Regents...

Synthesis



3. Physical M.

Magnetite

Powder X

Single cr



4. Results and

Synthesis

Structure

Charge 11

Magnetic

3. Concluding

Rb ₂ Bi ₁₀ Se ₁₇ (XII).....	201
Topotactic solid state chemistry and "zipper" action.....	205
Oxidation (closing the zipper)/reduction (opening the zipper) chemistry.	216
5. Concluding Remarks.....	220
 Chapter 5. $ALn_{1\pm x}Bi_{4\pm x}S_8$ ($A = K, Rb$; $Ln = La, Ce, Pr, Nd$) : New <i>Semiconducting Quaternary Bismuth Sulfide</i>	225
1. Introduction.....	225
2. Experimental Section	228
Reagents.....	228
Synthesis	228
KLa _{1.28} Bi _{3.72} S ₈ (I)	228
RbLa _{1±x} Bi _{4±x} S ₈ (II).....	229
RbCe _{0.84} Bi _{4.16} S ₈ (III).....	229
KCe _{1±x} Bi _{4±x} S ₈ (IV).....	229
KPr _{1±x} Bi _{4±x} S ₈ (V) and KNd _{1±x} Bi _{4±x} S ₈ (VI).....	230
3. Physical Measurements.....	230
Magnetic measurements	230
Powder X-ray diffraction	231
Single crystal X-ray crystallography.....	231
KLa _{1.28} Bi _{3.72} S ₈ (I)	231
RbCe _{0.84} Bi _{4.16} S ₈ (III).....	239
KCe _{1±x} Bi _{4±x} S ₈ (IV).....	242
4. Results and Discussion.....	244
Synthesis and thermal behavior.....	244
Structure description	246
Charge transport properties and energy gaps.....	254
Magnetic properties	257
5. Concluding Remarks.....	259

Chapter 6: A

Chapter 6: S. 20

1. Introd.

2. Exper.

Requ.

Sym.

B

P

S

C

3. Phys.

Sim.

4. Res.

Sy.

Sy.

5. Co

Chapter 7

Second

En. Sec.

1. In

2. E

F

S

Chapter 6. <i>Novel Quaternary Lanthanum Bismuth Sulfides $Pb_2La_xBi_{8-x}S_{14}$, $Sr_2La_xBi_{8-x}S_{14}$ and $Cs_2La_xBi_{10-x}S_{16}$ with Complex Structures</i>	263
1. Introduction.....	263
2. Experimental Section	265
Reagents.....	265
Synthesis	266
Bi_2S_3	266
$Pb_2La_xBi_{8-x}S_{14}$ (I).....	266
$Sr_2La_xBi_{8-x}S_{14}$ (II)	266
$Cs_2La_xBi_{10-x}S_{16}$ (III).....	267
3. Physical Measurements.....	267
Single crystal X-ray crystallography.....	267
$Pb_2La_xBi_{8-x}S_{14}$ (I).....	268
$Sr_2La_xBi_{8-x}S_{14}$ (II)	269
$Cs_2La_xBi_{10-x}S_{16}$ (III).....	271
4. Results and Discussion.....	280
Synthesis, thermal behavior and energy gaps.....	280
Structure description	282
$Pb_2La_xBi_{8-x}S_{14}$ (I).....	282
$Sr_2La_xBi_{8-x}S_{14}$ (II)	291
$Cs_2La_xBi_{10-x}S_{16}$ (III).....	294
5. Concluding Remarks	305

Chapter 7 <i>Synthesis and Characterization of the New Quaternary Bismuth Selenides: $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$, $A_xPb_{4-x}Bi_6Se_{13}$, ($A = Eu$ and Sr) and $Ba_xPb_{6-x}Bi_6Se_{15}$</i>	311
1. Introduction.....	311
2. Experimental Section	313
Reagents.....	313
Synthesis	313

Bi ₂ Se ₃	314
PbSe.....	314
EuSe.....	314
Eu _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (I).....	314
Sr _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (II)	315
Eu _x Pb _{4-x} Bi ₆ Se ₁₃ (III).....	315
Sr _x Pb _{4-x} Bi ₆ Se ₁₃ (IV).....	315
Ba _x Pb _{6-x} Bi ₆ Se ₁₅ (V)	316
3. Physical Measurements.....	316
Single crystal X-ray crystallography.....	316
Eu _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (I).....	317
Sr _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (II)	318
Eu _x Pb _{4-x} Bi ₆ Se ₁₃ (III).....	319
Sr _x Pb _{4-x} Bi ₆ Se ₁₃ (IV).....	319
Ba _x Pb _{6-x} Bi ₆ Se ₁₅ (V)	320
Bond Valence Calculations	321
4. Results and Discussion.....	331
Synthesis and thermal behavior	331
Structure description	333
Eu _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (I) and Sr _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ (II).....	333
Eu _x Pb _{4-x} Bi ₆ Se ₁₃ (III) and Sr _x Pb _{4-x} Bi ₆ Se ₁₃ (IV).....	342
Ba _x Pb _{6-x} Bi ₆ Se ₁₅ (V)	350
Energy gaps	358
Charge transport properties	360
5. Concluding Remarks.....	368

Chapter 8 <i>Synthesis and Characterization of β-K_{2.5}Bi_{8.5}Se₁₄, Rb₁₁Bi₁₅Se₂₈, Cs_{6-3x}Bi_{8+x}Se₁₅, Ba_{4-x}Bi_{6+2/3x}Se₁₃, K_xM_{4-2x-3y}Bi_{4+x+2y}S₁₀ (M = Pb, Eu), APbBi₃S₆ (A = Rb, Cs), Ba_xPb_{4-x}Bi₆S₁₃, Rb₄EuBi₆Se₁₂, Rb_{2.5-x}M_{2x}Bi_{8.5-x}Q₁₄ (M = Pb, Sn, Eu; Q = S, Se), Rb_xSn_{1-x}Bi_{6-x}Se₁₀, Rb_{1.5-x}Sn_{2x}Bi_{7.5-x}Se₁₂, BaLnBi₂Q₆ (Ln = La, Ce, Pr; Q = S, Se) and Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z}</i>	373
1. Introduction	373
2. Experimental Section	375
Reagents.....	375
Synthesis	376
Bi ₂ S ₃	376
EuS	376
Bi ₂ Se ₃	377
PbSe.....	377
β -K _{2.5} Bi _{8.5} Se ₁₄ (I)	377
Rb ₂ PbBi ₈ S ₁₄ (II)	377
Rb _{2.5-x} Pb _{2x} Bi _{8.5-x} Se ₁₄ (III).....	378
Rb _{2.5-x} Sn _{2x} Bi _{8.5-x} Se ₁₄ (IV)	378
Rb _{2.5-x} Eu _{2x} Bi _{8.5-x} S ₁₄ (V).....	378
Rb ₁₁ Bi ₁₅ Se ₂₈ (VI).....	379
Rb ₄ EuBi ₆ Se ₁₂ (VII).....	379
Cs _{6-3x} Bi _{8+x} Se ₁₅ (VIII).....	379
Rb _x Sn _{1+x} Bi _{6-x} Se ₁₀ (IX).....	380
Ba _{4-x} Bi _{6+2/3x} Se ₁₃ (X)	380
Ba _x Pb _{4-x} Bi ₆ S ₁₃ (XI)	380
Rb _{1.5-x} Sn _{2x} Bi _{7.5-x} Se ₁₂ (XII).....	381
K _x Pb _{4-2x-3y} Bi _{4+x+2y} S ₁₀ (XIII).....	381
K _x Eu _{4-2x-3y} Bi _{4+x+2y} S ₁₀ (XIV).....	381
RbPbBi ₃ S ₆ (XV).....	382
CsPbBi ₃ S ₆ (XVI).....	382
BaLaBi ₂ S ₆ (XVII).....	382

BaCeBi ₂ S ₆ (XVIII), BaPrBi ₂ Se ₆ (XIX) BaLaBi ₂ Se ₆ (XX)	382
Ba _{3-x} U _{x+y} Bi _{3-y} Se _{9-z} (XXI).....	382
3. Physical Measurements.....	383
Single crystal X-ray crystallography.....	383
β -K _{2.5} Bi _{8.5} Se ₁₄ (I)	385
Rb ₂ PbBi ₈ S ₁₄ (II)	385
Rb _{2.5-x} Sn _{2x} Bi _{8.5-x} Se ₁₄ (IV)	386
Rb _{2.5-x} Eu _{2x} Bi _{8.5-x} S ₁₄ (V).....	386
Rb ₁₁ Bi ₁₅ Se ₂₈ (VI).....	386
Rb ₄ EuBi ₆ Se ₁₂ (VII).....	387
Cs _{6-3x} Bi _{8+x} Se ₁₅ (VIII).....	387
Rb _x Sn _{1+x} Bi _{6-x} Se ₁₀ (IX).....	387
Ba _{4-x} Bi _{6+2/3x} Se ₁₃ (X)	388
Ba _x Pb _{4-x} Bi ₆ S ₁₃ (XI)	388
Rb _{1.5-x} Sn _{2x} Bi _{7.5-x} Se ₁₂ (XII).....	389
K _x Pb _{4-2x-3y} Bi _{4+x+2y} S ₁₀ (XIII).....	390
K _x Eu _{4-2x-3y} Bi _{4+x+2y} S ₁₀ (XIV).....	391
RbPbBi ₃ S ₆ (XV).....	391
CsPbBi ₃ S ₆ (XVI).....	391
BaLaBi ₂ S ₆ (XVII).....	392
Ba _{3-x} U _{x+y} Bi _{3-y} Se _{9-z} (XXI).....	392
Bond Valence Calculations	393
4. Results and Discussion.....	415
Synthesis, thermal behavior and energy gaps	415
Structure description	417
β -K _{2.5} Bi _{8.5} Se ₁₄ (I), Rb ₂ PbBi ₈ S ₁₄ (II), Rb _{2.5-x} Pb _{2x} Bi _{8.5-x} Se ₁₄ (III), Rb _{2.5-x} Sn _{2x} Bi _{8.5-x} Se ₁₄ (IV) and Rb _{2.5-x} Eu _{2x} Bi _{8.5-x} S ₁₄ (V)	417
Rb ₁₁ Bi ₁₅ Se ₂₈ (VI) and Rb ₄ EuBi ₆ Se ₁₂ (VII).....	425
Cs _{6-3x} Bi _{8+x} Se ₁₅ (VIII) and Rb _x Sn _{1+x} Bi _{6-x} Se ₁₀ (IX).....	434

Ba ₂ B ₁₀ O ₂₂ ·xH ₂ O	1
(XII).....	1
K ₂ Ph ₂ As ₂ O ₇	1
Rb ₂ P ₂ B ₁₀ O ₂₂ ·8H ₂ O	1
Ba ₂ U ₂ B ₁₀ O ₂₂ ·8H ₂ O	1
Ba ₂ U ₂ B ₁₀ O ₂₂ ·8H ₂ O	1
Ba ₂ U ₂ B ₁₀ O ₂₂ ·8H ₂ O	1
Charge transfer	1
5 Concluding Remarks	1

$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ (X), $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ (XI) and $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ (XII)	441
$\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ (XIII) and $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ (XIV)	457
$\text{RbPbBi}_3\text{S}_6$ (XV) and $\text{CsPbBi}_3\text{S}_6$ (XVI).....	467
$\text{BaLaBi}_2\text{S}_6$ (XVII), $\text{BaCeBi}_2\text{S}_6$ (XVIII), $\text{BaPrBi}_2\text{Se}_6$ (XIX) and $\text{BaLaBi}_2\text{Se}_6$ (XX).....	469
$\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$ (XXI).....	474
Charge transport properties and thermal conductivity	479
5. Concluding Remarks.....	483

Dec 21 Cross
BLS

Dec 22 At n
Para

Dec 23 At n
Para

Dec 24 At n
Para

Dec 25 At n
Para

Dec 26 BLS

Dec 27 Sele

Dec 28 BLS

Dec 29 BLS

Dec 30 Cross

Dec 31 At n
Para

Dec 32 At n
Para

Dec 33 Cross

Dec 34 At n
Para

Dec 35 Cross

LIST OF TABLES

		<u>Page</u>
Table 2-1.	Crystallographic Data for $A_2Bi_8Se_{13}$ ($A = Rb, Cs$), $CsBi_{3.67}Se_6$ and $BaBi_2Se_4$	37
Table 2-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $Rb_2Bi_8Se_{13}$	39
Table 2-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $Cs_2Bi_8Se_{13}$	40
Table 2-4.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $CsBi_{3.67}Se_6$	41
Table 2-5.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $BaBi_2Se_4$	42
Table 2-6.	Bond Distances ($\text{\AA}$) for $A_2Bi_8Se_{13}$ ($A = Rb, Cs$).....	48
Table 2-7.	Selected Angles (deg) for $A_2Bi_8Se_{13}$ ($A = Rb, Cs$).....	50
Table 2-8.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $CsBi_{3.67}Se_6$	55
Table 2-9.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $BaBi_2Se_4$	58
Table 3-1.	Crystallographic Data for $\gamma\text{-RbBi}_3S_5$ and $\alpha\text{-RbBi}_3Se_5$	96
Table 3-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-RbBi}_3S_5$	97
Table 3-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\alpha\text{-RbBi}_3Se_5$	98
Table 3-4.	Crystallographic Data for $\beta\text{-RbBi}_3Se_5$ and $CsBi_3Se_5$	99
Table 3-5.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-RbBi}_3Se_5$	100
Table 3-6.	Crystallographic Data for $\gamma\text{-RbBi}_3Se_5$ and $\beta\text{-RbBi}_3Se_5Te$	101

Table 3-7

Table 3-8

Table 3-9

Table 3-10

Table 3-11

Table 3-12

Table 3-13

Table 3-14

Table 4-1

Table 4-2

Table 4-3

Table 4-4

Table 4-5

Table 4-6

Table 4-7

Table 4-8

Table 4-9

Table 3-7.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-RbBi}_3\text{Se}_5$	102
Table 3-8.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for CsBi_3Se_5	103
Table 3-9.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbBi}_3\text{Se}_4\text{Te}$	104
Table 3-10.	Bond distances ($\text{\AA}$) and Selected Angles (deg) for $\gamma\text{-RbBi}_3\text{S}_5$	112
Table 3-11.	Bond distances ($\text{\AA}$) and Selected Angles (deg) for $\alpha\text{-RbBi}_3\text{Se}_5$	116
Table 3-12.	Bond distances ($\text{\AA}$) and Selected Angles (deg) for CsBi_3Se_5 and $\beta\text{-RbBi}_3\text{Se}_5$	121
Table 3-13.	Bond distances ($\text{\AA}$) and Selected Angles (deg) for $\gamma\text{-RbBi}_3\text{Se}_5$ and $\text{RbBi}_3\text{Se}_4\text{Te}$	127
Table 3-14.	Cell Parameters and Volumes for Several AM_3Q_5 structures.....	130
Table 4-1.	Crystallographic Data for $\text{Rb}_2\text{Bi}_4\text{Se}_7$ and RbBi_4Se_7	156
Table 4-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_4\text{Se}_7$	158
Table 4-3.	Crystallographic Data for $\text{Cs}_2\text{Bi}_4\text{Se}_7$ and CsBi_4Se_7	159
Table 4-4.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{Bi}_4\text{Se}_7$	160
Table 4-5.	Crystallographic Data for $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$, $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$ and $\text{CsBi}_7\text{Se}_{12}$	161
Table 4-6.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$	163
Table 4-7.	Crystallographic Data for $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$ and $\text{Rb}_2\text{Bi}_7\text{Se}_{12}$	164
Table 4-8.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$	165
Table 4-9.	Crystallographic Data for $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ and $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$	166

Table 4-10. A
Part

Table 4-11. A
Part

Table 4-12. A
Part

Table 4-13. A
Part

Table 4-14. A
Part

Table 4-15. A
Part

Table 4-16. A
Part

Table 4-17. O

Table 4-18. B
A

Table 4-19. B
C

Table 4-20. B

Table 4-21. B
R

Table 5-1. C
K

Table 5-2. C

Table 5-3. A
P

Table 5-4. A

Table 4-10.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$	167
Table 4-11.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for RbBi_4Se_7	168
Table 4-12.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for CsBi_4Se_7	169
Table 4-13.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$	170
Table 4-14.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_7\text{Se}_{12}$	171
Table 4-15.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{CsBi}_7\text{Se}_{12}$	172
Table 4-16.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$	173
Table 4-17.	Optical Band Gap and Melting Point Data.....	176
Table 4-18.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{A}_2\text{Bi}_4\text{Se}_7$ and ABi_4Se_7 (A = Rb, Cs).....	184
Table 4-19.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{A}_3\text{Bi}_7\text{Se}_{12}$ (A = Rb, Cs) and $\text{CsBi}_7\text{Se}_{12}$	192
Table 4-20.	Bond Distances ($\text{\AA}$) for $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$ and $\text{Rb}_2\text{Bi}_7\text{Se}_{12}$	196
Table 4-21.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ and $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$	203
Table 5-1.	Calculated and Observed X-ray Powder Diffraction Patterns for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and $\text{RbLa}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$	232
Table 5-2.	Crystallographic Data for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	234
Table 5-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$	236
Table 5-4.	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$..	237

Table 5-5

Table 5-6

Table 5-7

Table 5-8

Table 5-9

Table 5-10

Table 6-1

Table 6-2

Table 6-3

Table 6-4

Table 6-5

Table 6-6

Table 6-7

Table 7-1

Table 7-2

Table 7-

Table -

Table 5-5.	Bond Distances (Å) and Angles (deg) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$	238
Table 5-6.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	240
Table 5-7.	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	241
Table 5-8.	Bond Distances (Å) and Angles (deg) for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	243
Table 5-9.	Optical Band Gap and Melting Point Data for $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$	245
Table 5-10.	Single Crystal Unit Cells of $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$	245
Table 6-1.	Crystallographic Data for $\text{M}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ (M = Pb, Sr), and $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$	272
Table 6-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$	274
Table 6-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$	276
Table 6-4.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$	278
Table 6-5.	Bond Distances (Å) and Selected Angles (deg) for $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$	289
Table 6-6.	Bond Distances (Å) and Selected Angles (deg) for $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$	296
Table 6-7.	Bond Distances (Å) and Selected Angles (deg) for $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$	300
Table 7-1.	Crystallographic Data for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	322
Table 7-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	323
Table 7-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	324
Table 7-4.	Crystallographic Data for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$, $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	325

Table 7-0

Table 7-1

Table 7-2

Table 7-3

Table 7-4

Table 7-5

Table 7-6

Table 7-7

Table 7-8

Table 7-9

Table 7-10

Table 7-11

Table 8-1

Table 8-2

Table 8-3

Table 8-4

Table 8-5

Table 7-5.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	327
Table 7-6.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	328
Table 7-7.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	329
Table 7-8.	Bond Distances ($\text{\AA}$) and selected angles (deg) for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	338
Table 7-9.	Selected Bond-Valence Sums for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	340
Table 7-10.	Selected Bond-Valence Sums for $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$	341
Table 7-11.	Bond Distances ($\text{\AA}$) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	346
Table 7-12.	Selected Angles (deg) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	347
Table 7-13.	Selected Bond-Valence Sums for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	348
Table 7-14.	Selected Bond-Valence Sums for $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	349
Table 7-15.	Selected Bond-Valence Sums for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	354
Table 7-16.	Bond Distances ($\text{\AA}$) for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	355
Table 7-17.	Selected Angles (deg) for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	357
Table 8-1.	Crystallographic Data for $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ and $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$	394
Table 8-2.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$	395
Table 8-3.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$	396
Table 8-4.	Crystallographic Data for $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ and $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$	397
Table 8-5.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$	398

Table 8-6. A
Part

Table 8-7. C

Table 8-8. A
Part

Table 8-9. A
Part

Table 8-10. C

Table 8-11. A
Part

Table 8-12. A
Part

Table 8-13. C

Table 8-14. A
Part

Table 8-15. C
Part

Table 8-16. A
Part

Table 8-17. A
Part

Table 8-18. C

Table 8-19. A
Part

Table 8-20. C

Table 8-21. A
Part

Table 8-6.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$	399
Table 8-7.	Crystallographic Data for $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ and $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$	400
Table 8-8.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$	401
Table 8-9.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$	402
Table 8-10.	Crystallographic Data for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	403
Table 8-11.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$	404
Table 8-12.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	405
Table 8-13.	Crystallographic Data for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$	406
Table 8-14.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$	407
Table 8-15.	Crystallographic Data for $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ and $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	408
Table 8-16.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	409
Table 8-17.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	410
Table 8-18.	Crystallographic Data for $\text{CsPbBi}_3\text{S}_6$	411
Table 8-19.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{CsPbBi}_3\text{S}_6$	411
Table 8-20.	Crystallographic Data for $\text{BaLaBi}_2\text{S}_6$ and $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$	412
Table 8-21.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaLaBi}_2\text{S}_6$	413

File 8-22. A
Par.

File 8-23. O

File 8-24. B

File 8-25. S

File 8-26. B

File 8-27. B

File 8-28. B

File 8-29. B

File 8-30. B

File 8-31. S

File 8-32. B
S

File 8-33. B

File 8-34. B

File 8-35. B
S

File 8-36. B
S

File 8-37. S

File 8-38. S

File 8-39. B

File 8-40. B

Table 8-22.	Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$	414
Table 8-23.	Optical Band-Gaps and Melting Points for (I) through (XXI).....	416
Table 8-24.	Bond Distances ($\text{\AA}$) for $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ and $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$	422
Table 8-25.	Selected Angles (deg) for $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ and $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$	424
Table 8-26.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$	430
Table 8-27.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$	432
Table 8-28.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$	438
Table 8-29.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$..	439
Table 8-30.	Bond Distances ($\text{\AA}$) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	449
Table 8-31.	Selected Angles (deg) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	452
Table 8-32.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$	453
Table 8-33.	Bond-Valence Sums for $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	455
Table 8-34.	Bond-Valence Sums for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$	456
Table 8-35.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	462
Table 8-36.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	463
Table 8-37.	Selected Bond-Valence Sums for $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	465
Table 8-38.	Selected Bond-Valence Sums for $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	466
Table 8-39.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{CsPbBi}_3\text{S}_6$	469
Table 8-40.	Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{BaLaBi}_2\text{S}_6$	473

Table 8-41.	Bond Distances (Å) and Selected Angles (deg) for $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$	477
Table 8-42.	Selected Bond-Valence Sums for $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$	478

Figure 1-1

Figure 1-2

Figure 1-3

Figure 1-4

Figure 1-5

Figure 1-6

Figure 1-7

Figure 2-1

LIST OF FIGURES

	Page
Figure 1-1. The different coordination geometries that Bi atoms adopt in bismuth chalcogenides: (a) trigonal pyramid in β -CsBiS ₂ , (b) square pyramidal in Rb ₂ Bi ₈ Se ₁₃ , (c) perfect octahedral in RbBiS ₂ , (d) and (e) distorted octahedral in γ -RbBi ₃ S ₅ and CsBi ₃ Se ₅ respectively, (f) and (e) trigonal prismatic in KLa _{1±x} Bi _{4±x} S ₈ and Cs ₂ La _x Bi _{10-x} S ₁₆ respectively (black circles bismuth atoms, white circles chalcogen atoms)	5
Figure 1-2. The different building blocks that are found in multinary bismuth chalcogenides: (a) NaCl-type (b) Bi ₂ Te ₃ -type (c) CdI ₂ -type and (d) Sb ₂ Se ₃ -type (black circles bismuth atoms, white circles chalcogen atoms)	6
Figure 1-3. View of the structure of NaCl down the [110] plane. The shaded areas represent the different building blocks found in bismuth chalcogenides. All these blocks are essentially different cuts of the NaCl-type structure (black circles bismuth atoms, white circles chalcogen atoms)	7
Figure 1-4. Variations of the NaCl-type blocks encountered in multinary bismuth chalcogenides: (a) 3x2 NaCl-type blocks in Rb ₂ Bi ₈ Se ₁₃ , (b) 2x2 NaCl-type blocks in CsBi _{3,67} Se ₆ , (c) 1x3 NaCl-type blocks in BaBi ₂ Se ₄ and (d) NaCl-type block found in Eu _x Pb _{4-x-3y} Bi _{4+2y} Se ₁₀ , see text for more detailed explanation (black circles bismuth atoms, white circles chalcogen atoms).....	8
Figure 1-5. Two different building blocks that are found in multinary bismuth chalcogenides when lanthanide atoms are incorporated into the structures: (a) Gd ₂ S ₃ -type (b) EuBi ₂ S ₄ -type (black circles bismuth and lanthanide atoms, white circles chalcogen atoms).....	10
Figure 1-6. Schematic representation of (a) the Peltier and (b) Seebeck effects. a and b correspond to the two different conductors	12
Figure 1-7. The structure of Bi ₂ Te ₃ looking down the b-axis (black circles bismuth atoms, white circles tellurium atoms).....	14
Figure 2-1. Projection of the structure of A ₂ Bi ₈ Se ₁₃ down the b-axis. The shaded areas indicate the NaCl-, Sb ₂ Se ₃ - and CdI ₂ -type building blocks	46

Figure 2-2. Pr
b

Figure 2-3. Pr
sh

Figure 2-4. Pr
st

Figure 2-5. In
R

Figure 2-6. V
st

Figure 2-7. V
o

Figure 2-8. V
F

Figure 2-9. V
o

Figure 2-10. V
s
b

Figure 2-11. V
d

Figure 2-12. V
S
d

Figure 2-13. V
C

Figure 2-14. V
a

Figure 2-15. V
G

Figure 2-2.	Projection of the structures of (a) α - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ down the c-axis and (b) β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ down the b-axis	51
Figure 2-3.	Projection of the structure of $\text{CsBi}_{3.67}\text{Se}_6$ down the b-axis. The shaded areas indicate the NaCl-type building blocks.....	53
Figure 2-4.	Projection of the structure of BaBi_2Se_4 down the c-axis. The shaded areas indicate the NaCl-and CdI_2 -type building blocks.....	57
Figure 2-5.	Infrared absorption spectra showing band gap transitions for (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, (b) $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$, (c) $\text{CsBi}_{3.67}\text{Se}_6$, and (d) BaBi_2Se_4	62
Figure 2-6.	Variable temperature electrical conductivity and thermopower for single crystals of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$	67
Figure 2-7.	Variable temperature electrical conductivity and thermopower for oriented polycrystalline samples of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$	68
Figure 2-8.	Variable temperature electrical conductivity and thermopower for polycrystalline samples of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$	69
Figure 2-9.	Variable temperature electrical conductivity for single crystals and oriented polycrystalline samples of $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$	70
Figure 2-10.	Variable temperature thermopower for oriented polycrystalline samples of $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ showing both the n-type and p-type behavior.....	71
Figure 2-11.	Variable temperature power factor ($\sigma \cdot S^2$) for (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and (b) β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$	72
Figure 2-12.	Variable temperature electrical conductivity for (a) doped with SbBr_3 and (b) undoped single crystals of $\text{CsBi}_{3.67}\text{Se}_6$ prepared by the quenching technique	73
Figure 2-13.	Variable temperature thermopower for polycrystalline samples of $\text{CsBi}_{3.67}\text{Se}_6$ prepared by the quenching technique.....	74
Figure 2-14.	Variable temperature electrical conductivity and thermopower for an oriented polycrystalline ingot of BaBi_2Se_4	75
Figure 2-15.	Variable temperature thermal conductivity for an oriented ingot of (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and (b) BaBi_2Se_4	77

Figure 3-1. Solenoid
gap
and

Figure 3-2. Proj
shad

Figure 3-3. Proj

Figure 3-4. Proj
shad
bloo
the

Figure 3-5. Proj
bea

Figure 3-6. Proj
the
bloo
R&E

Figure 3-7. Proj
R&E

Figure 3-8. Proj

Figure 3-9. Proj

Figure 3-10. Proj

Figure 4-1. Typ
The

Figure 4-2. Typ
the
oth

Figure 4-3. Ran
rest

Figure 4-4. Proj
shad

Figure 3-1.	Solid-state UV/Vis and infrared absorption spectra showing band gap transitions for (a) γ -RbBi ₃ S ₅ (b) γ -RbBi ₃ Se ₅ , (c) β -RbBi ₃ Se ₅ and (d) α -RbBi ₃ Se ₅	108
Figure 3-2.	Projection of the structure of γ -RbBi ₃ S ₅ down the b-axis. The shaded area indicates Bi ₂ Te ₃ -type building block	111
Figure 3-3.	Projection of the structure of α -RbBi ₃ S ₅ down the a-axis	113
Figure 3-4.	Projection of the structure of α -RbBi ₃ Se ₅ down the b-axis. The shaded areas indicate the NaCl-, Bi ₂ Te ₃ -, and CdI ₂ -type building blocks. Part of the Bi ₂ Te ₃ -type rods have been removed to show the square-like tunnels.....	115
Figure 3-5.	Projection of the structure of CsBi ₃ Se ₅ and β -RbBi ₃ Se ₅ down the b-axis. The shaded areas indicate the NaCl-type building blocks	120
Figure 3-6.	Projection of the structure of γ -RbBi ₃ Se ₅ and RbBi ₃ Se ₄ Te down the b-axis. The shaded area indicates the Bi ₂ Te ₃ -type building block and the (*) indicate the Te containing chalcogen sites in RbBi ₃ Se ₄ Te.....	124
Figure 3-7.	Polyhedral representation of the structures of RbPbBi ₃ Se ₆ and γ -RbBi ₃ Se ₅	125
Figure 3-8.	Projection of the structure of KBi ₃ S ₅ down the b-axis.....	132
Figure 3-9.	Projection of the structure of CsEr ₃ Se ₅ down the b-axis.....	133
Figure 3-10.	Projection of the structure of TlIn ₃ S ₅ down the b-axis	134
Figure 4-1.	Typical DTA diagram of Cs ₃ Bi ₇ Se ₁₂ (top) and RbBi ₄ Se ₇ (bottom). The rest of the phases give similar diagrams.....	177
Figure 4-2.	Typical optical band-gaps of Rb ₂ Bi ₄ Se ₇ (top) and RbBi ₄ Se ₇ (bottom). The peak at RbBi ₄ Se ₇ is probably due to water. The other phases give similar spectra.....	178
Figure 4-3.	Raman spectrum of RbBi ₄ Se ₇ (top) and Cs ₂ Bi ₇ Se ₁₂ (bottom). The rest of the transformed phases give similar spectra	179
Figure 4-4.	Projection of the structure of Rb ₂ Bi ₄ Se ₇ down the b-axis. The shaded areas indicate the Bi ₂ Te ₃ - and CdI ₂ -type building blocks.	

Figure 4.5

Figure 4.6

Figure 4.7

Figure 4.8

Figure 4.9

Figure 4.10

Figure 4.11

Figure 4.12

	The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. Rb(2) and Rb(3) are partially occupied	182
Figure 4-5.	(a)View of the Se(5) rows looking down the c-axis in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. (b) View of the bonded Se(4) rows looking down the c-axis RbBi_4Se_7	183
Figure 4-6.	Projection of the structure of RbBi_4Se_7 down the b-axis. The same layers exist as in $\text{Rb}_2\text{Bi}_4\text{Se}_7$ but now are connected by Se-Se bonds. The Se-Se bonds are shown by the oval shaded areas. The inset shows the atom labeling.....	188
Figure 4-7.	Projection of the structure of $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ down the b-axis. The shaded areas indicate the Bi_2Te_3 - and CdI_2 -type building blocks. The CdI_2 -type block is smaller than that found in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. Cs(2) is partially occupied.....	191
Figure 4-8.	Projection of the structure of $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$ down the b-axis. The same layers exist as in $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ but now they form bilayers connected by Se-Se bonds. The bilayers are indicated with brackets. The inset shows the atom labeling	195
Figure 4-9.	Projection of the structure of $\text{CsBi}_7\text{Se}_{12}$ down the b-axis. The same layers exist as in $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ but now they are connected by Se-Se bonds. The inset shows the atom labeling. The Se-Se bonds are shown by the oval shaded areas.....	198
Figure 4-10.	Projection of the structure of $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ down the b-axis. The shaded areas indicate the Bi_2Te_3 - and CdI_2 -type building blocks. The Bi_2Te_3 -type block is longer than that found in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. All the Rb atoms are partially occupied	200
Figure 4-11.	Projection of the structure of $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ down the b-axis. The same layers exist as in $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ but now they are connected by Se-Se bonds. The inset shows the atom labeling. The Se-Se bonds are shown by the oval shaded areas	202
Figure 4-12.	Transformation of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ to RbBi_4Se_7 monitored by X-ray powder diffraction. A pure sample of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ was exposed to air and X-ray powder diffraction patterns were recorded at certain time points using the same sample. It can be seen that after only ~15 min of exposure to air the $\text{Rb}_2\text{Bi}_4\text{Se}_7$ starts to transform to RbBi_4Se_7 as evidenced from the splitting of the peak ~12°. The	

transf
diffract
RbBiS₃

Fig. 4-13. Project
Se cont

Fig. 4-14. Project
contact
uncap

Fig. 4-15. Project

Fig. 4-16. Schema
zipper-
adjacent
Single s
framework
layers

Fig. 5-1. Project
axis. The
building

Fig. 5-2. (A) One
columns
columns
lines sh
of the p
areas in

Fig. 5-3. The str
Gd₂S₃-t

Fig. 5-4. Variable
KLa₂Al

Fig. 5-5. Solid-s
RbCe₂

Fig. 5-6. (Top)
tempera
moment

Fig. 6-1. Solid-st
transition

	transformation is almost complete after ~18 h. The X-ray powder diffraction pattern at that point corresponds to that of pure RbBi_4Se_7	208
Figure 4-13.	Projection of the structure of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ down the b-axis. The Se-Se contacts are indicated with the arrow (square shaded areas).....	211
Figure 4-14.	Projection of the structure of CsBi_3Se_5 down the b-axis. The Se-Se contacts are indicated with the arrow (square shaded areas). The tricapped trigonal prismatic site is also shown.....	212
Figure 4-15.	Projection of the structure of $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ down the b-axis.....	213
Figure 4-16.	Schematic diagram showing the two different steps in the oxidative zipper-like action of two rows of Se atoms belonging to two adjacent $[\text{Bi}_7\text{Se}_{12}]^{3-}$ layers into a single row of diselenide groups. Single slabs join to double slabs, which finally couple to a full 3D-framework. The circles indicate the Cs atoms in the uncoupled layers.....	219
Figure 5-1.	Projection of the structure of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ viewed down the b-axis. The shaded areas indicate the NaCl-type and Gd_2S_3 -type building blocks.....	247
Figure 5-2.	(A) Orientation of the Gd_2S_3 -type infinite rod consisting of two columns of monocapped (coordination number 7) and two columns of bicapped (coordination number 8) prisms. The grey lines show the two different kinds of prisms. (B) Polyhedral view of the prisms as they stack along the b-axis. The solid colored areas indicate the prisms while the shaded areas show the caps.....	249
Figure 5-3.	The structures of La_2S_3 (A) and Bi_2S_3 (B) showing the same Gd_2S_3 -type infinite rod found in $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$	251
Figure 5-4.	Variable temperature electrical conductivity for pressed pellets of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and $\text{RbLa}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$	255
Figure 5-5.	Solid-state UV/Vis spectra of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ (I) and $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	256
Figure 5-6.	(Top) Inverse magnetic susceptibility $1/\chi_m$ plotted against temperature for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$. (Bottom) Effective magnetic moment vs temperature for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$	258
Figure 6-1.	Solid-state UV/Vis absorption spectra showing band gap transitions for $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$, $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ and $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$	281

Figure 6-2. Project
(OR)
the cr
sites...

Figure 6-3. Comp
struct
atom
occup
beams
gray
index
index
circul
prism
La,B
betw
CdL
then

Figure 6-4. Proj
prism
Pb-L
prism

Figure 6-5. Proj
(OR)
split
cross
plat
clar

Figure 6-6. The
5 (t
(A)
refe

Figure 6-7. Pro
shad
The
of t
atom
occ

Figure 6-8. Pro

Figure 6-2.	Projection of the structure of $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis (ORTEP view). The shaded crossed ellipsoids represent Bi atoms, the crossed S atoms and the plain represent the mixed occupancy sites	283
Figure 6-3.	Comparison of two related structures (a) Projection of the structure $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis. The black circles are Bi atoms, the white S atoms and the gray circles represent the mixed occupancy sites. (b) Projection of the structure $\text{La}_4\text{Bi}_2\text{S}_9$ down the b-axis. The black circles are Bi atoms, the white S atoms and the gray circles represent the La sites. The shaded rectangular areas indicate the Bi_2Te_3 - and Gd_2S_3 -type building blocks. The arrows indicate the direction of the NaCl-type walls whereas the shaded circular area shows the triangular fragment made of three trigonal prismatic sites. The same walls exist in the both structures but $\text{La}_4\text{Bi}_2\text{S}_9$ contains only a CdI_2 -type fragment in the space formed between the ribbons. For clarity reasons some of the Bi_2Te_3 - and CdI_2 -type have been removed to show the framework walls and rhombus-like tunnels.....	284
Figure 6-4.	Projection of the triangular fragment (a) made of three trigonal prismatic sites and the Gd_2S_3 -type (b) building blocks in $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis. The different kinds of trigonal prisms are also shown.....	287
Figure 6-5.	Projection of the structure of $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis (ORTEP view). Due to the better quality diffraction data, the splitting of the high coordinate sites can be seen. The shaded crossed ellipsoids represent Bi atoms, the crossed S atoms and the plain represent the mixed occupancy sites. For these sites for clarity reasons, only the La atoms are shown.....	292
Figure 6-6.	The coordination environments of cation site 9 (a) and cation site 5 (b) in $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$. The splitting in every site is also shown, (A) refers to the position located in the center of the site while (B) refers to site shifted away from the center to the side.....	293
Figure 6-7.	Projection of the structure of $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ down the b-axis. The shaded areas indicate the NaCl-, and CdI_2 -type building blocks. The shaded circular area shows the EuBi_2S_4 -type fragment made of three bicapped trigonal prismatic sites. The black circles are Bi atoms, the white S atoms and the gray circles represent the mixed occupancy (La and Bi) sites.....	295
Figure 6-8.	Projection of the EuBi_2S_4 -type fragment found in $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$	

down 10
made 10
La1001

Figure 6-9. Comput
kobellin
the ex
comm
an extr

Figure 6-10. Comput
M. Sa
axis with

Figure 7-1. Typical
(Vigil)

Figure 7-2. Project
down th
type bu
there is

Figure 7-3. Project
the bea
building
disorde

Figure 7-4. Project
The sh
blocks

Figure 7-5. The co
Ba10
while
site 11

Figure 7-6. Infrared
Eu, Pb
simila

Figure 7-7. Variab
two d
differe
differe

Figure 7-8. Variab

	down the b-axis. The fragment has a pseudo C_3 symmetry and is made up of three bicapped trigonal prismatic sites (La8, La9 and La10) that display mixed La/Bi occupancy.....	299
Figure 6-9.	Comparison of the structures of (a) $Cs_2La_xBi_{10-x}S_{16}$ and (b) kobellite $Pb_{12}(Cu,Fe)_2(Bi,Sb)_{14}S_{35}$ viewed down the b-axis. With the exception of the shaded area, the rest of the structure is common for the two compounds. The mineral kobellite contains an extra M_4S_3 block (see text) in the shaded area.....	303
Figure 6-10.	Comparison of the (a) M_6S_2 -block in $Cs_2La_xBi_{10-x}S_{16}$ and (b) $M_{10}S_5$ in kobellite $Pb_{12}(Cu,Fe)_2(Bi,Sb)_{14}S_{35}$ viewed down the b-axis with atom labeling	304
Figure 7-1.	Typical DTA diagram of $Eu_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$. (II), (III), (IV) and (V) give similar diagrams	332
Figure 7-2.	Projection of the structure of $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ($A = Eu, Sr$) down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks. The gray circles indicate the sites where there is disorder with Eu	334
Figure 7-3.	Projection of the structure of $A_xPb_{4-x}Bi_6Se_{13}$ ($A = Eu, Sr$) down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks. The gray circles indicate the sites where there is disorder with Eu.....	343
Figure 7-4.	Projection of the structure of $Ba_xPb_{6-x}Bi_6Se_{15}$ down the b-axis. The shaded areas indicate the NaCl- and Bi_2Te_3 -type building blocks	352
Figure 7-5.	The coordination environment of site 10 in $Ba_xPb_{6-x}Bi_6Se_{15}$. The Ba10 atom is sitting the center (A) of the trigonal prismatic site while the M10 is shifted to the side (B). The same is observed in site 11	353
Figure 7-6.	Infrared absorption spectra for (a) $Eu_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ (b) $Eu_xPb_{4-x}Bi_6Se_{13}$ and (c) $Ba_xPb_{6-x}Bi_6Se_{15}$. The Sr analogs behave similar to the Eu compounds.....	359
Figure 7-7.	Variable temperature electrical conductivity and thermopower for two different sets of single crystals of $Eu_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$. The differences in the properties of the two sets are attributed to different doping levels.....	362
Figure 7-8.	Variable temperature electrical conductivity for single crystals of	

Figure 7-9. Variable
Ba, Pb

Figure 7-10. Variable
a single

Figure 7-11. Variable
Ba, Pb

Figure 8-1. Project
shaded
blocks

Figure 8-2. Project
circular
atom lat

Figure 8-3. Project
corruga
layer

Figure 8-4. Project
corruga
compa

Figure 8-5. Project
shaded
blocks

Figure 8-6. Project
The s
buildi

Figure 8-7. Project
shade

Figure 8-8. Project
The s

Figure 8-9. Project
axis,
block

Figure 8-10. Project

	$\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ doped with various amounts of SbBr_3	363
Figure 7-9.	Variable temperature thermopower for single crystals of $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ doped with SbBr_3	364
Figure 7-10.	Variable temperature electrical conductivity and thermopower for a single crystal of $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$	365
Figure 7-11.	Variable temperature electrical conductivity for a single crystal of $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$	367
Figure 8-1.	Projection of the structure of $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ down the b-axis. The shaded areas indicate the NaCl-, Bi_2Te_3 - and CdI_2 -type building blocks	420
Figure 8-2.	Projection of the unit cell of $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ down the b-axis. The circular shaded area shows the splitting in site 9. The rest of the atom labeling is the same as in $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$	421
Figure 8-3.	Projection of the structure of $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ down the b-axis. The corrugated CdI_2 -type layers connect to form tunnels every other layer.....	428
Figure 8-4.	Projection of the structure of $\text{Rb}_4\text{EuBi}_6\text{S}_{12}$ down the b-axis. The corrugated CdI_2 -type layers connect to form smaller tunnels compared to $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$	429
Figure 8-5.	Projection of the structure of $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ down the b-axis. The shaded areas indicate the NaCl-, Bi_2Te_3 - and CdI_2 -type building blocks	436
Figure 8-6.	Projection of the structure of $\text{Rb}_x\text{Sn}_{1-x}\text{Bi}_{6-x}\text{Se}_{10}$ down the b-axis. The shaded areas indicate the NaCl-, Bi_2Te_3 - and CdI_2 -type building blocks.....	437
Figure 8-7.	Projection of the structure of $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.....	446
Figure 8-8.	Projection of the structure of $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks..	447
Figure 8-9.	Projection of the structure of $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks	448
Figure 8-10.	Projection of the structure of $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4-x+2y}\text{Se}_{10}$ down the b-	

axis 1
blocks

Figure 8-11. Project
axis 1
blocks
K, E, U

Figure 8-12. Project
atoms

Figure 8-13. Project
The sam

Figure 8-14. The do
in Bal
sharing
shown

Figure 8-15. (a) Pro
axis of

Figure 8-16. Variat
single

Figure 8-17. (a) V
for an
therm

	axis. The shaded areas indicate the NaCl- and CdI ₂ -type building blocks	460
Figure 8-11.	Projection of the structure of $K_xEu_{4-2x-3y}Bi_{4-x+2y}Se_{10}$ down the b-axis. The shaded areas indicate the NaCl- and CdI ₂ -type building blocks. Site 7 is split in three different positions compared to $K_xEu_{4-2x-3y}Bi_{4-x+2y}Se_{10}$	461
Figure 8-12.	Projection of the structure of CsPbBi ₃ S ₆ down the b-axis. The Cs atoms are disordered between the Bi ₂ Te ₃ -type layers.....	468
Figure 8-13.	Projection of the structure of BaLaBi ₂ S ₆ down the a-axis (top). The same projection after removing the La-S bonds (bottom).....	471
Figure 8-14.	The double columns of La atoms running along the [100] direction in BaLaBi ₂ S ₆ . Each single column is composed of LaS ₆ prisms sharing opposite triangular faces. The capped S atoms are also shown.....	472
Figure 8-15.	(a) Projection of the structure of $Ba_{3-x}U_{x-y}Bi_{3-y}Se_{9-z}$ down the b-axis. (b) The Se(9)-Se(9) zigzag chains running along the c-axis	476
Figure 8-16.	Variable temperature electrical conductivity and thermopower for single crystals of $Ba_{4-x}Bi_{6+2/3x}Se_{13}$	481
Figure 8-17.	(a) Variable temperature electrical conductivity and thermopower for an ingot (hot pressed) of BaLaBi ₂ Se ₆ . (b) Variable temperature thermal conductivity for an ingot (hot pressed) of BaLaBi ₂ Se ₆	482

LIST OF ABBREVIATIONS

CCD	Charge Coupled Device
DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectroscopy
IR	Infrared Spectroscopy
SEM	Scanning Electron Microscopy
SQUID	Superconducting Quantum Interference Device
TEM	Transmission Electron Microscopy
UV/Vis	Ultraviolet/Visible Spectroscopy

1. Introduction

Multinary borates

$MM_2B_2Q_4$, where

combination of metal

compositional and

these compounds

materials.

1.1. Multinary Borates

From a

important because

CHAPTER 1

Multinary Bismuth Chalcogenides and Thermoelectric Concepts

1. Introduction

Multinary bismuth chalcogenides are compounds of the general formula $M_xM'_yBi_zQ_w$ where Q is a chalcogen (S, Se or Te) and M, M' could be any metal or combination of metals. They are a fascinating class of compounds with a staggering compositional and structural complexity. Recently there has been renewed interest in these compounds due to the potential applications that they have as thermoelectric materials.

1-1. Multinary Bismuth Chalcogenides

From a solid state chemistry perspective, bismuth chalcogenides are very important because they exhibit a rich compositional and structural diversity¹. These

characteristics are sp

compounds are well

ions are often four

them contain -some

octahedral sites in

Although nat

primary bismuth ch

early 1990's very little

chalcogenides. Out of

compounds, the only

GB_2S_2 , RnB_2Se_2

SbTe_2 , $\text{Ti}_2\text{B}_2\text{S}_2$

$=\text{S}_2\text{Se}_2$, $\text{Pb}_2\text{In}_2\text{B}_2$

$\text{Q}=\text{S}_2\text{Se}_2$ solid sol

Bi_2Q_2 . However

and often the structu

Structurally tr

the bismuth chain

characteristics are spectacularly expressed in the natural occurring sulfosalts where Bi compounds are well represented and constitute ~20% of them. In these compounds, Bi atoms are often found to be disordered with Sb and/or Pb atoms. Furthermore several of them contain –sometimes at trace amounts- transition metals such as Cu, Fe or Ag sitting in tetrahedral sites in the Bi-Q (Q = S, Se) framework.

Although nature was very prolific in synthesizing such a large number of multinary bismuth chalcogenides careful examination of the literature reveals that up to early 1990's very little exploratory synthesis has been done in the area of ternary bismuth chalcogenides. Outside the well-known NaCl type ABiQ_2 (A = Li, Na, K; Q = S, Se)², compounds, the only other phases that had been reported were RbBiS_2 ³, RbBi_3S_5 ⁴, CsBi_3S_5 ⁵, RbBiSe_2 ³, $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ ⁶, SrBiSe_3 ⁷, $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ ⁸, α -, β - BaBi_2S_4 ⁹, BaBiSe_3 ¹⁰, SrBiTe_3 ¹¹, $\text{Tl}_4\text{Bi}_2\text{S}_5$ ¹², EuBi_2S_4 ¹³, Eu_2BiS_4 ¹⁴, $\text{La}_4\text{Bi}_2\text{S}_9$ ¹⁵, $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ ¹⁶, $\text{Eu}_3\text{Bi}_4\text{Q}_9$ (Q = S, Se)¹⁷, $\text{Pb}_2\text{In}_2\text{Bi}_4\text{S}_{13}$ ¹⁸ and $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ ¹⁹. In addition, mixed Bi/transition metal/Q (Q=S, Se) solid solutions have been investigated including $\text{Cu}_{1+3x}\text{Bi}_{5-x}\text{Q}_8$ ²⁰ and $\text{Mn}_{1-x}\text{Bi}_{2+y}\text{Q}_4$ ²¹. However, most of these compounds very lacking physical characterization and often the structural characterization was troublesome.

Structurally there are several reasons for this unparalleled diversity and complexity that bismuth chalcogenides compounds possess. Bismuth atoms can adopt several

different coordination

axial isometries

pyridine Respons

nitrogen lone pa

using the bismuth

energetically adjuste

Ammonia intermedi

expression and becom

observed. This pro

coordination geome

behavior of Bi^{3+} an

Several diffe

pyramidal in $\beta\text{-C}$

ReB_2S_7 distort

$\text{KLa}_{1-x}\text{Bi}_{x-1}\text{S}_7$ a

for (a) and (b) the

completely suppr

consequently we h

different coordination environments, from trigonal pyramidal, to square pyramidal, to octahedral (sometimes distorted), to trigonal prismatic and even 7, 8 and 9 coordination polyhedra. Responsible for such a rich repertoire of coordination environments is the bismuth $6s^2$ lone pair of electrons that can be stereochemically expressed to locally distort the bismuth coordination geometry, or suppressed by hybridizing with energetically adjacent p and d orbitals to produce a regular octahedral Bi^{3+} center. Almost any intermediate stage in the continuum which exists between full stereochemical expression and complete suppression of the $6s^2$ lone pair via sp^3d^2 hybridization is observed. This property gives rise to what may very well be the most malleable coordination geometry in the periodic table. Therefore, it is interesting to observe the behavior of Bi^{3+} and its role in stabilizing various structure types.

Several different coordination environments for Bi atoms such as trigonal pyramidal in $\beta\text{-CsBiS}_2$ ²², square pyramidal in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ ²³, perfect octahedral in RbBiS_2 ³, distorted octahedral in $\gamma\text{-RbBi}_3\text{S}_5$ ²⁴ and CsBi_3Se_5 ²⁴, trigonal prismatic in $\text{KLa}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ ²⁵ and $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ ²⁶, are shown in Figure 1-1. In the same Figure 1-1, for (a) and (b) the lone pair being is completely expressed while in (c) the lone pair is completely suppressed. For (d) and (e) the lone pair is only partially expressed, consequently we have short bonds (solid lines) trans to longer bonds (dashed lines). In

general, as we move

the resulting

Second, the E

edges forming a v

Bi_2Te_3 and CdTe

the first three fragm

atoms in a square p

NaCl-type fragment

Figure 1-3. Further

making even more

$\text{Bi}_2\text{Bi}_2\text{Se}_3^{22}$, CsB

block is 2x3 prism

tin atoms, lan

ation, these NaCl

$\text{E}_1\text{Pb}_{4-3}\text{Bi}_{4-3}\text{Se}_3$

general, as we move from the bismuth sulfides to the bismuth selenides to the bismuth tellurides the resulting octahedra are more regular due to size effects.

Second, the BiQ_6 ($Q = \text{S, Se, Te}$) octahedra combine with each other by sharing edges forming a variety of building blocks, the most common ones being the NaCl-, Bi_2Te_3 - and CdI_2 - type and occasionally the Sb_2Se_3 -type fragment, see Figure 1-2. While the first three fragments contain octahedral Bi atoms, the Sb_2Se_3 -type fragment has Bi atoms in a square pyramidal coordination. All these different building blocks are in effect NaCl-type fragments, but they just represent different cuts of the NaCl-type structure, see Figure 1-3. Furthermore each of the above mentioned blocks comes in different sizes creating even more structural possibilities, e.g. NaCl-type building blocks are found in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ ²³, $\text{CsBi}_{3.67}\text{Se}_6$ ²³ and BaBi_2Se_4 ²³, but in the first compound the NaCl-type block is 2x3 bismuth atoms (or bismuth octahedra) large while in the second is 2x2 bismuth atoms large and in last one is 3x1 bismuth atoms large, see Figure 1-4. In addition, these NaCl-type blocks can have irregular shapes as shown in Figure 1-4(d) in $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ ²⁷.

(a)

(c)



(f)



Figure 1-1. The 3
halogenides: (a) t
perfect octahedral
respectively. (f) a
respectively (black).

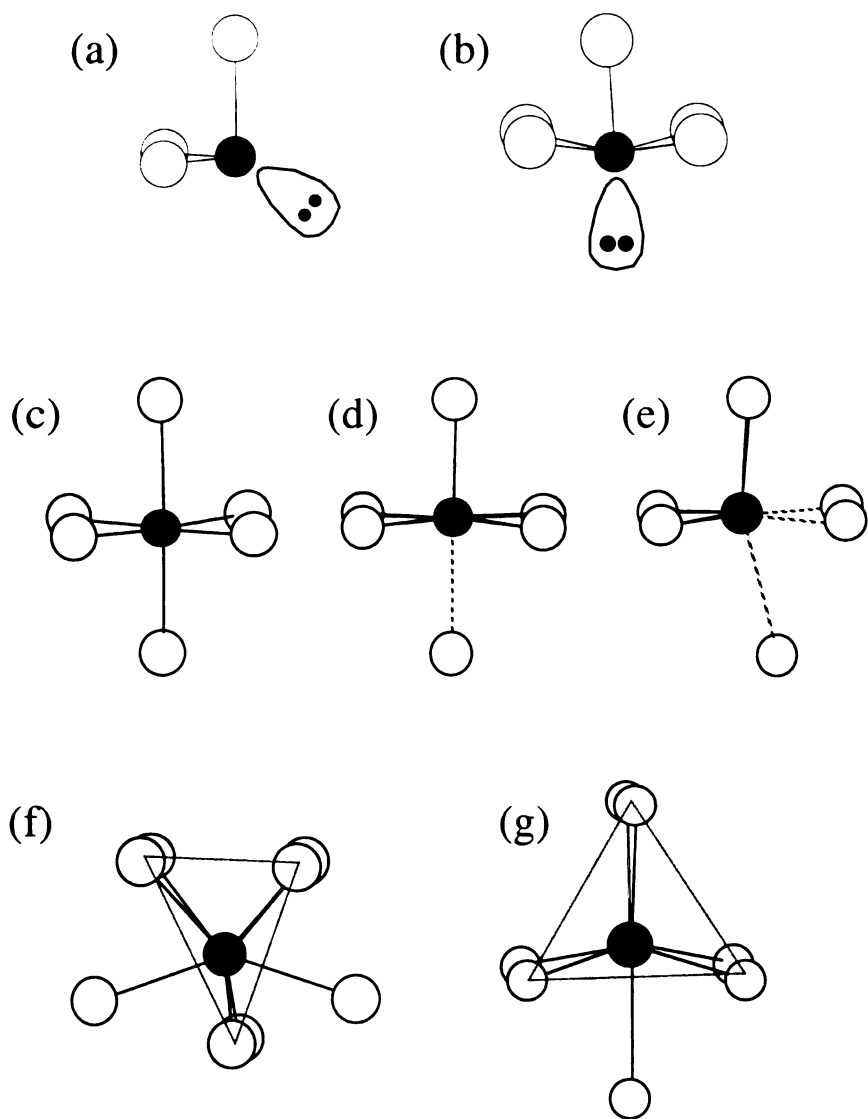


Figure 1-1. The different coordination geometries that Bi atoms adopt in bismuth chalcogenides: (a) trigonal pyramid in β -CsBiS₂, (b) square pyramidal in Rb₂Bi₈Se₁₃, (c) perfect octahedral in RbBiS₂, (d) and (e) distorted octahedral in γ -RbBi₃S₅ and CsBi₃Se₅ respectively, (f) and (g) trigonal prismatic in KLa_{1±x}Bi_{4±x}S₈ and Cs₂La_xBi_{10-x}S₁₆ respectively (black circles bismuth atoms, white circles chalcogen atoms).

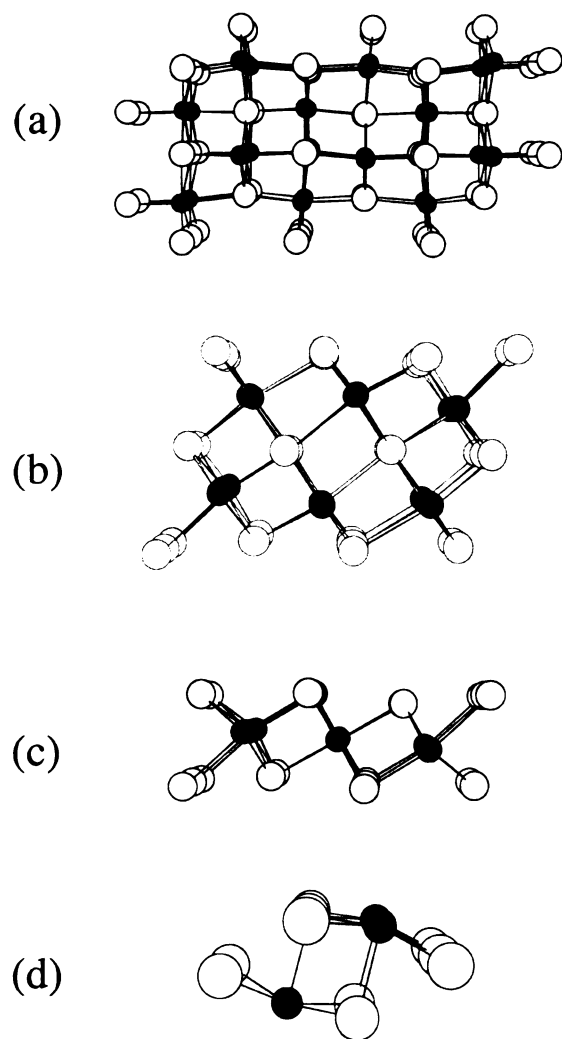


Figure 1-2. The different building blocks that are found in multinary bismuth chalcogenides: (a) NaCl-type (b) Bi_2Te_3 -type (c) CdI_2 -type and (d) Sb_2Se_3 -type (black circles bismuth atoms, white circles chalcogen atoms).

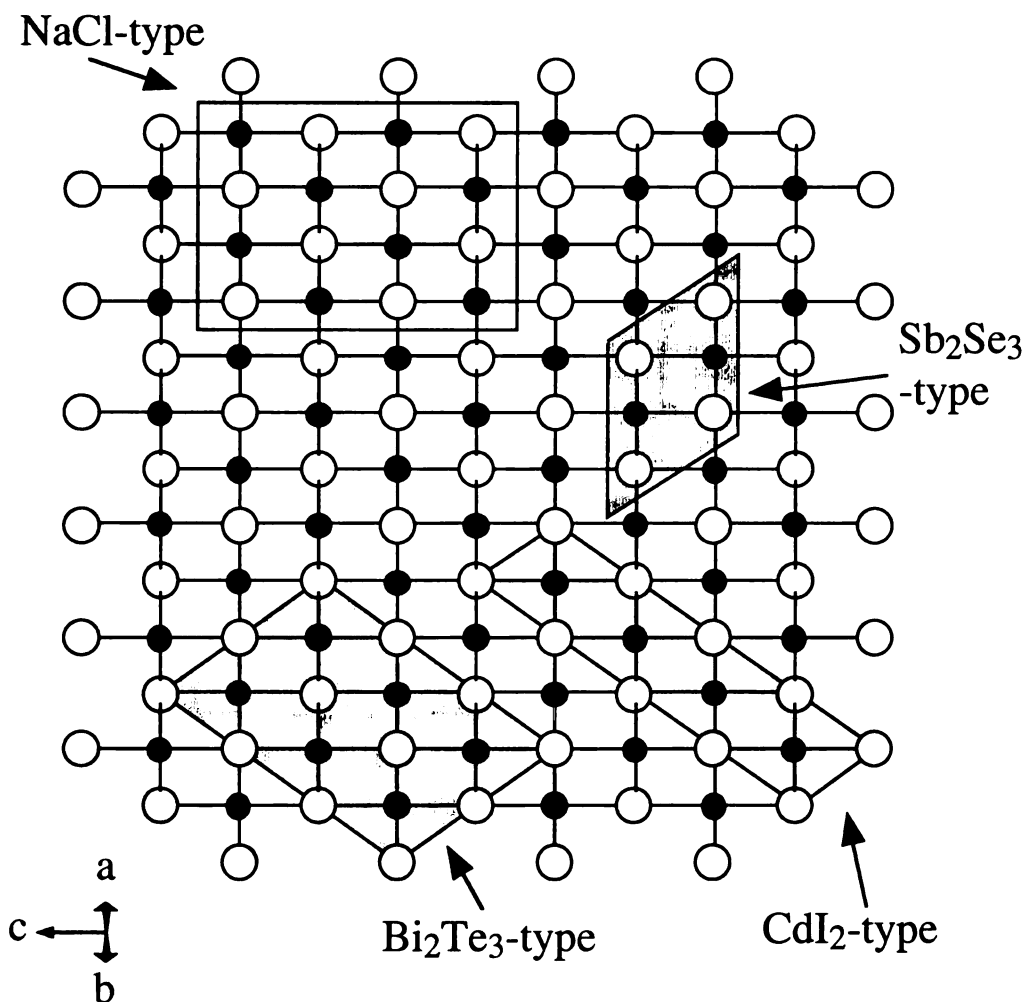


Figure 1-3. View of the structure of NaCl down the [110] plane. The shaded areas represent the different building blocks found in bismuth chalcogenides. All these blocks are essentially different cuts of the NaCl-type structure (black circles bismuth atoms, white circles chalcogen atoms).

$$2 \left[\begin{array}{c} \vdots \\ \vdots \end{array} \right]$$

(b)

$$2 \left[\begin{array}{c} \vdots \\ \vdots \end{array} \right]$$

(a)

Figure 1-

Intelligent

GB₁₋₂-Se

Elpe₁₋₂-A

GB₁₋₂-A

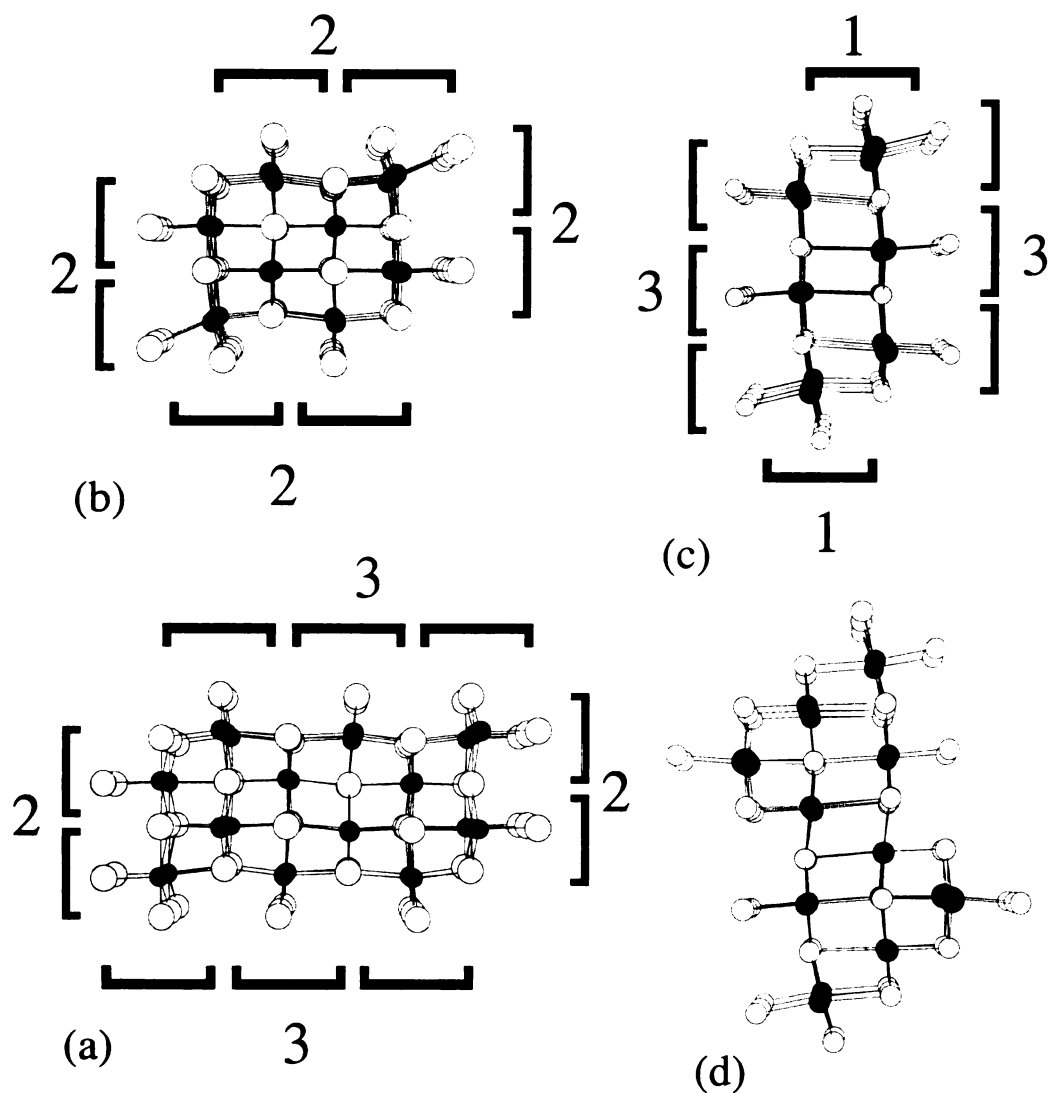


Figure 1-4. Variations of the NaCl-type blocks encountered in multinary bismuth chalcogenides: (a) 3x2 NaCl-type blocks in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, (b) 2x2 NaCl-type blocks in $\text{CsBi}_{3.67}\text{Se}_6$, (c) 1x3 NaCl-type blocks in BaBi_2Se_4 and (d) NaCl-type block found in $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$, see text for more detailed explanation (black circles bismuth atoms, white circles chalcogen atoms).

Third bismuth

on such alkali or s

s found in the tr

ngener, see Fig

formation of new s

time this mixed occ

will be described in

prefer to adopt, ho

phlogenic frame

encountered in the

base blocks are sh

and heaped trig

seemingly countless

This lack of

compounds posse

systems because m

structurally comp

Third bismuth atoms can display mixed occupancy with a variety of similar sized ions such alkali or alkaline earth metals, Pb Sn or rare earth metals. Usually the disorder is found in the trigonal prismatic sites that connect the blocks of BiSe_6 octahedra together, see Figure 1-1(f) and 1-1(g). The mixed occupancy often results in the formation of new structure types that do not exist in the simpler systems. At the same time, this mixed occupancy creates several problems in the solution of the structures as will be described in detail in the next chapters. In addition, since the rare earth atoms prefer to adopt high (>6) coordination sites their incorporation in the ternary chalcogenide framework results in the formation of new building blocks that are not encountered in the simple binary and ternary bismuth compounds. In Figure 1-5 two of these blocks are shown, the Gd_2S_3 ²⁸-type and EuBi_2S_4 ¹³-type that consist of monocapped and bicapped trigonal prisms. In summary, all the above characteristics point to a seemingly countless number of novel phases that can potentially form.

This lack of exploratory synthesis and the rich structural variety that these compounds possess led us to the investigation of multinary bismuth chalcogenides systems because much remains to be learnt about the chemistry and properties of these structurally complicated systems.

(a)

(b)

Figure 1-5. T

collegendes v

EuB₂S₂-typ

2005.

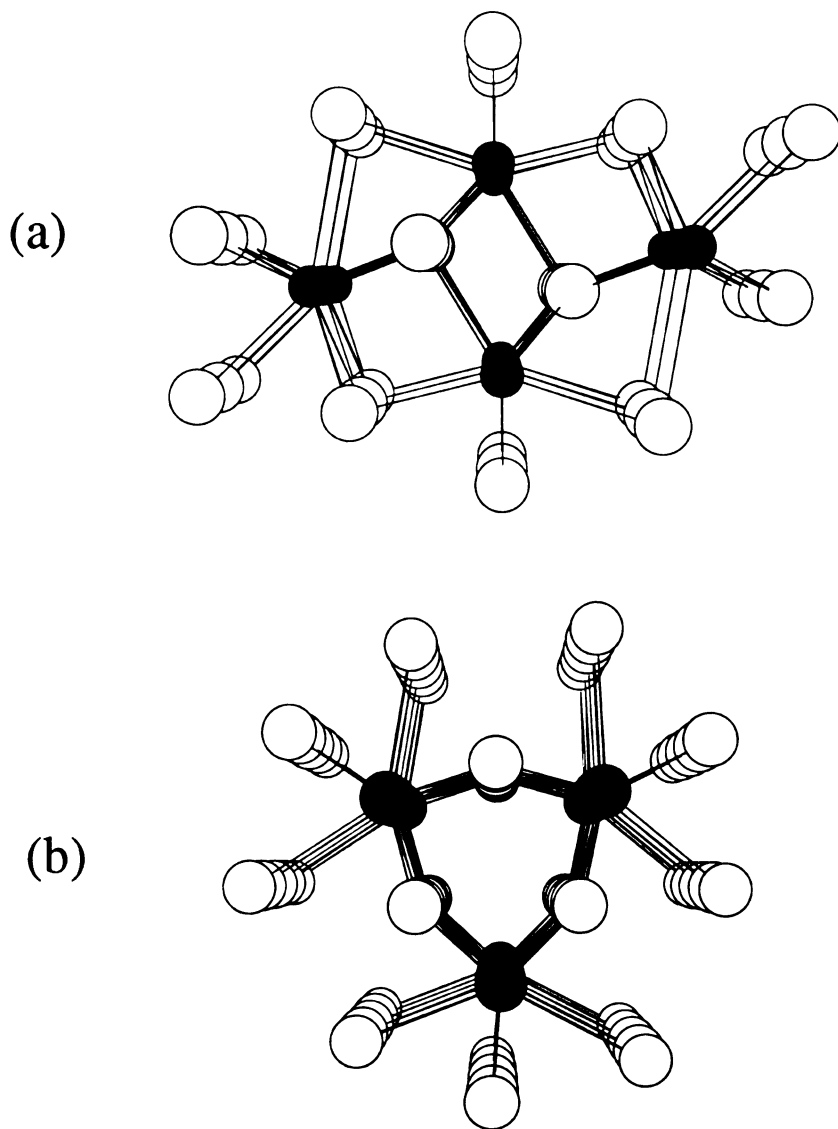


Figure 1-5. Two different building blocks that are found in multinary bismuth chalcogenides when lanthanide atoms are incorporated into the structures: (a) Gd_2S_3 -type (b) EuBi_2S_4 -type (black circles bismuth and lanthanide atoms, white circles chalcogen atoms).

1.2 Thermoelect

At a junction

electronically g

temperature. If a

generated whose

effects are called

Thompson, Pelt

refrigeration dev

In the T

conductor gives

refrigeration or

current through

in absorption re

64 The basic f

be thought as a c

Seebeck effect.

when the junction

1-2. Thermoelectric concepts

At a junction between two dissimilar conductors, a voltage gradient is automatically generated whose values depend on the conductors used and the temperature. If a temperature gradient exists along a conductor, a voltage difference is generated whose value depends on the conductor and the temperature gradient. These effects are called thermoelectric effects and three types may be distinguished, the Thompson, Peltier and Seebeck. Their main applications are in thermocouples, refrigeration devices and power generation.

In the Thompson effect a temperature gradient, ΔT , across a homogeneous conductor gives rise to a potential gradient, ΔV . The thermoelectric effect utilized for refrigeration or cooling is the Peltier effect. In the Peltier effect the flow of a electric current through two dissimilar semiconductors results in the liberation of heat (heating) or absorption (cooling) in the junction between the two semiconductors, see Figure 1-6(a). The basis for the generation of electricity from heat is the Seebeck effect. This can be thought as a combination of the two previous effects, the Thompson and Peltier. In the Seebeck effect, a voltage is produced across the junctions of two different conductors when the junctions are kept at different temperatures, see Figure 1-6(b).

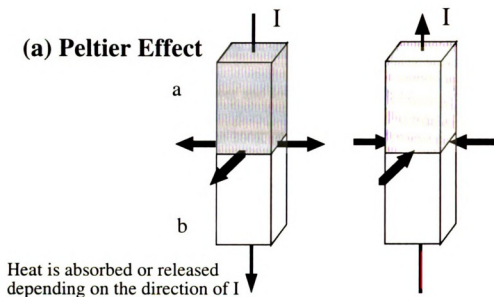
(a) Pelti

Heat is absor
depending on

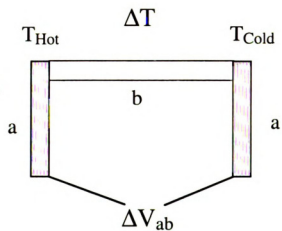
(b) Seeb

Figure 1-6. Schem
correspond to the t

(a) Peltier Effect



(b) Seebeck Effect



Seebeck coefficient $S = \Delta V / \Delta T$

Figure 1-6. Schematic representation of (a) the Peltier and (b) Seebeck effects. a and b correspond to the two different conductors.

The best m

solutions of Bi₂Te₃

conductivity and t

the highest figure

Bi₂Te₃ is a s

of Bi₂Te₃ consists o

These slabs are run

Wals gap.

To date, m

mainly focused on

M₂Q₃ (M = Bi, Sb)

However only sm

Therefore, it is no

potential performa

because for a ther

The challenge in

electrical conduct

The best materials currently used for thermoelectric cooling applications are solid solutions of Bi_2Te_3 , $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ ²⁹. These compounds possess high electrical conductivity and thermoelectric power and low thermal conductivity. Such alloys have the highest figure of merit, $ZT \sim 1.0$ at 300K (the definition of ZT will be given later).

Bi_2Te_3 is a semiconductor with an energy band-gap, $E_g = 0.15$ eV. The structure of Bi_2Te_3 consists of infinite slabs five atomic layers thick and is shown in Figure 1-7. These slabs are running in the ab-plane and are separated from each other by a van-der-Waals gap.

To date, most investigations in improving thermoelectric performance were mainly focused on tuning the composition of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ solid solutions,³⁰ doping M_2Q_3 ($\text{M} = \text{Bi, Sb}$; $\text{Q} = \text{S, Se}$) with other heavy metals³¹ and optimizing device design. However only small increases in ZT have been achieved in the last two decades. Therefore, it is now believed that the Bi_2Te_3 compounds may be nearing the limit of their potential performance.³² As a result, the discovery of new improved materials is essential because for a thermoelectric material to be commercially useful it must have a $ZT \geq 1.5$. The challenge in finding materials with high ZT lies in achieving simultaneously high electrical conductivity, high thermoelectric power and low thermal conductivity.

Figure 1-7.

2025 white

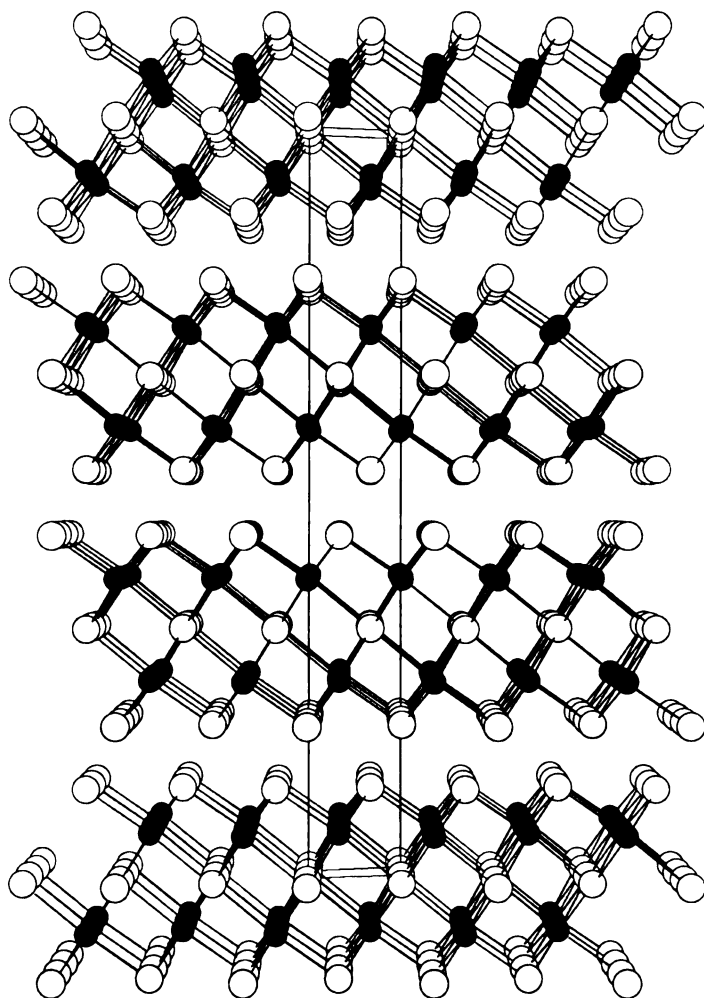


Figure 1-7. The structure of Bi_2Te_3 looking down the b-axis (black circles bismuth atoms, white circles tellurium atoms).

These properties are

where S is the thermal

thermal conductivity

determined by the

electrons or holes

difficult to improve

or simultaneous

electrical conductivity

Metals are

efficients are small

few carriers of

hundreds to thousands

concentration, it is

increasing carrier

The total

conductivity of the

thermal conductivity

These properties define the dimensionless thermoelectric figure of merit:

$$ZT = \frac{S^2 \cdot \sigma}{\kappa}$$

where S is the thermopower or Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity and T is the temperature. All three of these properties are determined by the details of the electronic structure and scattering of charge carriers (electrons or holes) and thus are not independently controllable parameters. Therefore is difficult to improve ZT , e.g. an increase in the thermoelectric power S usually also leads to a simultaneous decrease in the electrical conductivity, σ . In addition, an increase in the electrical conductivity leads to a comparable increase in the thermal conductivity, κ .

Metals are generally not useful for thermoelectric devices because the Seebeck coefficients are small (on the order of a few $\mu\text{V/K}$). Semiconductors, which contain much fewer carriers of electricity, exhibit much larger Seebeck coefficients, in the range of hundreds to thousands of $\mu\text{V/K}$. Since thermoelectric power S is a function of the carrier concentration, it will be large for low densities of electrons and holes and decrease with increasing carrier concentration or doping.

The total thermal conductivity κ_T of a material is the sum of the thermal conductivity of the electrical carriers κ_e and the atomic vibrations (phonons), or lattice thermal conductivity κ_l , thus $\kappa = \kappa_e + \kappa_l$. The lattice thermal conductivity is generally the

dominant mecha

zons, low sym

mer hand at m

σ . So one way

conductivity pr

In conc

good thermoe

theoretical fram

We ha

smooth chole

thermoelectro

complex com

give rise to h

some time po

where σ E,

electronic co

scanning is

dominant mechanism for thermal conductivity in semiconductors. The presence of heavy atoms, low symmetry and atomic disorder leads to lower thermal conductivities. On the other hand atomic disorder could lead to low carrier mobilities and consequently to lower σ . So one way of increasing the figure of merit, ZT , would be to decrease the thermal conductivity provided that the electrical conductivity and thermopower remain high.

In conclusion, a lot of opposing factors need to be fine-tuned in order to obtain a good thermoelectric material. Furthermore, all this must be done in the absence of a theoretical framework for the design of a thermoelectric material.

We have initiated an exploratory synthesis program to identify new multinary bismuth chalcogenides compounds with narrow band-gaps which may be suitable as thermoelectric materials. This work is based on the proposition that materials with more complex compositions and structures may have complex electronic structures which may give rise to high thermoelectric powers according to the Mott formula³³ below, and at the same time possess low thermal conductivities. The thermopower S is given by:

$$S = \frac{\pi^2}{3} \cdot \frac{k^2 T}{e} \cdot \left. \frac{d \ln \sigma(E)}{dE} \right|_{E=E_f}$$

where $\sigma(E)$ is the electrical conductivity determined as a function of band filling. The electronic conductivity $\sigma = \sigma(E) | E = E_f$ where E_f is the Fermi energy. If the carrier scattering is independent of energy, then $\sigma(E)$ is just proportional to the density of states

μE in the gene

Fermi surface -

re equation ab

simultaneously

A desired

structural comp

complexes in

symmetry in σ

conductivity co

elements as con

normally make

red in thermoe

complex semic

A sign

electricity like

crystal" conce

thermoelectro

lower the the

production, th

at E . In the general case, S is a measure of the difference in $\sigma(E)$ above and below the Fermi surface - specifically through the logarithmic derivative of with respect to E , see the equation above. So by manipulating the energy dependence of $\sigma(E)$ one can control simultaneously σ and S .

A desirable feature for new thermoelectric materials is a higher compositional and structural complexity than Bi_2Te_3 . These characteristics can result in corresponding complexities in the electronic structure which in their turn can produce the required asymmetry in $\sigma(E)$ to obtain large thermopowers. The phonon contribution to the thermal conductivity can also be lowered by such structural complexity, by choosing heavy elements as components of the material, and by choosing combinations of elements that normally make moderate to weak chemical bonds. Since the known materials that are used in thermoelectric devices are chalcogenide compounds, we are searching for more complex semiconducting compounds of this type.

A significant development is the concept and realization of materials that conduct electricity like a crystalline solid but heat like a glass. This “electron glass phonon crystal” concept was introduced by Slack as the limiting characteristic for a superior thermoelectric. In these materials a weakly bound atom or molecule 'rattler' is used to lower the thermal conductivity of the solid without severely affecting electronic conduction, thus leading to improved thermoelectric efficiency.^{34,35} A material which is

in electron glasses
certain atoms with
which results in
some orbitals of
Fermi level, the
essentially anti
thermopower

The clas
description beca
two-dimensional
atoms which
antropositive
in the structure
feature is very
These rattlers c
thus, reduce t
conductivity in
and mass fluctu

an “electron glass phonon crystal” features cages (or tunnels) in its crystal structure that contain atoms small enough to “rattle”. This situation produces a phonon damping effect which results in dramatic reduction of the solid’s lattice thermal conductivity. If the atomic orbitals of the “rattling” ions do not participate in the electronic structure near the Fermi level, the mobility of carriers throughout the rest of the structure may not be substantially affected, potentially giving rise to high electrical conductivity as well as thermopower.

The class of chalcogenide materials described in this thesis fall under this description because, as it will become apparent, they are made of three-dimensional or two-dimensional bismuth-chalcogenide frameworks, stabilized by weakly bonded alkali atoms which reside in cavities, tunnels or galleries of the framework. These electropositive atoms almost always possess the highest thermal displacement parameters in the structure, evidence that a certain degree of “rattling” motion is occurring. This feature is very important in the low observed thermal conductivities of these materials. These rattlers create low frequency vibrational modes that scatter acoustic phonons and thus, reduce the thermal conductivity. Other factors contributing to low thermal conductivity in materials are the presence of heavy atoms (e.g. Bi, Pb), large unit cells, and mass fluctuation disorder in the crystal lattice.

The

$K_2S_2O_8$

remoted

quaternary

of having

electropos

primary A

ketonoid

comp out

physico

thermoel

N

AB_2Q_3

polymer

structure

malonate

demonstr

malonate

from a

The compounds BaBiTe_3 ,³⁶ $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$,³⁷ $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$,³⁷ CsBi_4Te_6 ,³⁸ $\text{K}_2\text{Bi}_8\text{S}_{13}$,³⁹ and $\text{KBi}_{6.33}\text{S}_{10}$ ³⁹ discovered early on in our work exhibit promising thermoelectric properties, encouraging us to extend our work to even more complicated quaternary systems. Based on the ideas presented above on increasing the thermopower S by having complex structures and reducing the thermal conductivity κ by incorporating electropositive elements such as alkali, alkaline earth or rare earth we investigated the ternary A/Bi/Q and quaternary A/M/Bi/Q (A = K, Rb, Cs, Sr, Ba, Eu; M = Pb, Sn, lanthanide; Q = S, Se) systems. In the next seven chapters we will describe the compounds found during these synthetic investigations and present their physicochemical, spectroscopic and for the most promising compounds their thermoelectric properties .

More specifically, in Chapter 3 we will describe the structural complexity in the ABi_3Q_5 (A = Rb, Cs; Q = S, Se, Te) systems where we found a number of different polymorphs. In Chapters 5 and 6 we will present the complex three-dimensional structures that are formed by the incorporation of lanthanides into the bismuth chalcogenide framework. Chapter 8 will present numerous other examples which further demonstrate the amazing features and remarkable structural flexibility in the bismuth chalcogenides systems. Several new compounds with interesting structures that have shown promising thermoelectric properties will be presented in Chapters 2 and 7.

1000

1000

1000

Furthermore, in Chapter 4 we will present a unprecedented solid state topotactic two-dimensional to three dimensional transformation that is found in ternary bismuth selenides.

References

1. (a) Makovick
Fortschr.
23. (d) Makovick
Makovick
2. (a) Glem
G. Zema
S. L. Lu
Y. Golov
3. Voroshil
4. Schmitz
438-439
5. Kanishe
Naak SS
6. Cordier
7. Cook, R
8. Cordier
9. Aunvill
10. Volk, K
Chem.
11. Cook, I
12. Julien-
1313-1
13. Lemon
14. Lemon

References

1. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, 59, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, 63, 45-89. (c) Makovicky, E. *Z. Kristallogr.* **1985**, 173, 1-23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, 160, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, 5, 545-591.
2. (a) Glemser, O.; Filcek, M. *Z. Anorg. Allg. Chem.* **1955**, 279, 321-323. (b) Gattow, G.; Zemmann, J. *Z. Anorg. Allg. Chem.* **1955**, 279, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, 6, 961-964. (d) Peresh, E. Y.; Golovei, M. I.; Berul, S. I. *Inorg. Mater.* **1971**, 7, 27-30.
3. Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, 8, 677-678.
4. Schmitz, D.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, 29, 438-439.
5. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, 252, 96-99.
6. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 676-683.
7. Cook, R.; Schäfer, H. *Rev. Chim. Miner.* **1982**, 19, 19-27.
8. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 631-638.
9. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, A37, 399-407.
10. Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, 35, 136-140.
11. Cook, R.; Schäfer, H. *Stud. Inorg. Chem.* **1983**, 3, 757-760.
12. Julien-Pouzol, M.; Jaulmes, S.; Laruelle, P. *Acta Crystallogr., Sect. B* **1979**, B35, 1313-1315.
13. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, C42, 259-261.
14. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. B* **1982**, B38, 727-729.

15. Ecrepont, C.

16. Ceolin, R.

B33, 2804-2

17. Ahev, O. M.

P. G. *Inorg*

18. Kramer, V.

19. Kramer, V.

20. Liautard, B.

Inorg. Chem.

21. Lee, S., Fisch

5.

22. McCarthy, T.

C. R.; Kanat

23. See Chapter

24. See Chapter

25. Jordanidis, I.

Chem. 1999

26. See Chapter

27. See Chapter

28. Prewitt, C. T.

29. *CRC Handb.*

1995 and re

30. (a) Yim, W.

W. M.; Fitz

Przyłuska, J.

-
15. Ecrepont, C.; Guittard, M.; Flahaut, J. *Mater. Res. Bull.* **1988**, *23*, 37-42.
 16. Ceolin, R.; Toffoli, P.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2804-2806.
 17. Aliev, O. M.; Maksudova, T. F.; Samsonova, N. D.; Finkel'shtein, L. D.; Rustamov, P. G. *Inorg. Mater.* **1986**, *22*, 23-27.
 18. Krämer, V. *Acta Crystallogr., Sect. C* **1986**, *C42*, 1089-1091.
 19. Krämer, V.; Reis, I. *Acta Crystallogr., Sect. C* **1986**, *C42*, 249-251.
 20. Liautard, B.; Garcia, J. C.; Brun, G.; Tedenac, J. C.; Maurin, M. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 819-830.
 21. Lee, S.; Fischer, E.; Czerniak, J.; Nagasundaram, N. *J. Alloys Compd.* **1993**, *197*, 1-5.
 22. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
 23. See Chapter 2.
 24. See Chapter 3.
 25. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162. See also Chapter 5.
 26. See Chapter 6.
 27. See Chapter 7.
 28. Prewitt, C. T.; Sleight, A. W. *Inorg. Chem.* **1968**, *7*, 1090-1093.
 29. *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995 and references there in.
 30. (a) Yim, W. M.; Fitzke, E. V. *J. Electrochem. Soc.*, **1968**, *115*, 556-560 (b) Yim, W. M.; Fitzke, E. V.; Rosi, F. D. *J. Mater. Sci.*, **1966**, *1*, 52-65 (c) Borkowski, K.; Przyluski, J. *Mater. Res. Bull.*, **1987**, *22*, 381-387

31. (a) Chizhe-

Horak, J. C.

Lestak, P. A.

32. Goldsmid, H.

33. Mott, N. F.

Publications

34. Sales, B. C.

35. (a) Nolas, G.

73, 178-180

C. J. Appl. P.

36. Chung, D.-Y.

Kanatzidis, N.

37. Chung, D.-Y.

C. R.: Chen.

3071.

38. Chang, D.-Y.

Uher, C.: Ka

39. (a) Kanatzidis

Hogan, T.: B

(b) Chen, B.

1655-1658.

-
31. (a) Chizhevskaya, S. N.; Shelimova, L. E. *Inorg. Mater.* **1995**, *31*, 1083-1095. (b) Horak, J.; Cermak, K.; Koudelka, L. *J. Phys. Chem. Solids* **1986**, *47*, 805-809. (c) Lostak, P.; Horak, J.; Koudelka, L. *Phys. Status Solidi A* **1983**, *76*, K71-K75.
32. Goldsmid, H. J. *Electronic Refrigeration*, Pion: London, **1986**.
33. Mott, N. F.; Jones, H. *The theory of the Properties of Metals and Alloys*, Dover Publications: New York, NY.
34. Sales, B. C. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 284-289.
35. (a) Nolas, G. S.; Cohn, J. L.; Slack, G. A.; Schujman, S. B. *Appl. Phys. Lett.* **1998**, *73*, 178-180. (b) Nolas, G. S.; Slack, G. A.; Morelli, D. T.; Tritt, T. M.; Ehrlich, A. *C. J. Appl. Phys.* **1996**, *79*, 4002-4008.
36. Chung, D.-Y.; Jobic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
37. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
38. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science (Washington, D. C.)* **2000**, *287*, 1024-1027.
39. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474. (b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.

A₂Bi

New

1. Introduction

During the

quaternary bismut

that of the compo

chalcogenides ha

quaternary comp

$K_2B_4S_3$, α - β -

$Al_{1-x}Bi_{1-x}S_3$

$APbBi_3Se_6$, A

Rb, M = Sn, P

$CdBi_3S_3$, Cd₂

CHAPTER 2

$A_2Bi_8Se_{13}$ ($A = Rb, Cs$), $CsBi_{3.67}Se_6$ and $BaBi_2Se_4$:

New Ternary Semiconducting Bismuth Selenides

1. Introduction

During the last decade a fascinating chemistry associated with ternary and quaternary bismuth chalcogenides has emerged that rivals in diversity and attractiveness that of the complex mineral bismuth sulfosalts. This revival in the chemistry of bismuth chalcogenides has resulted in the discovery of several new interesting ternary and quaternary compounds. Our group has contributed: β -, γ - $CsBiS_2$ ¹, KBi_3S_5 ², $KBi_{6.33}S_{10}$ ³, $K_2Bi_8S_{13}$ ³, α -, β - $K_2Bi_8Se_{13}$ ^{1,4}, $K_{2.5}Bi_{8.5}Se_{14}$ ⁴, $A_xBi_4Se_7$ ⁵ ($x = 1, 2$), $BaBiTe_3$ ⁶, $CsBi_4Te_6$ ⁷, $ALn_{1\pm x}Bi_{4\pm x}S_8$ ⁸ ($A = K, Rb$; $Ln = La, Ce, Pr, Nd$), $BaLaBi_2Q_6$ ⁹ ($Q = S, Se$), α -, β - $APbBi_3Se_6$ ¹⁰ ($A = K, Rb, Cs$), $K_{1-x}Sn_{5-x}Bi_{11+x}Se_{22}$ ¹¹ and $A_{1+x}M'_{4-2x}Bi_{7+x}Se_{15}$ ¹² ($A = K, Rb$; $M' = Sn, Pb$). Other groups have described: $Sn_4Bi_2Se_7$ ¹³, $SnBi_4Se_7$ ¹⁴, $CdBi_2S_4$ ¹⁵, $CdBi_4S_7$ ¹⁵, $Cd_{2.8}Bi_{8.1}S_{15}$ ¹⁵, $Cd_2Bi_6S_{11}$ ¹⁵, $Ba_3Bi_{6.67}Se_{13}$ ¹⁶, $Ba_3MBi_6Se_{13}$ ¹⁶ ($M = Sn, Pb$).

Prior to these

ABQ_2 (A = alk.

$B.B_2S_2^{2-}$, SeB_2N

Substantia

thermoelectric ma

low thermal conc

reaching in the c

those of the best E

From a sol

clats with stagger

spectacularly exp

represented. The

several different

is suppressed by

adopt a normal

around 90° . This

distorted octahed

coordination en

Prior to these developments only a few bismuth chalcogenides were known such as ABiQ_2 (A = alkali metal; Q = chalcogen)¹⁷, CsBi_3S_5 ¹⁸, RbBi_3S_5 ¹⁹, $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ ²⁰, α -, β - BaBi_2S_4 ²¹, SrBiSe_3 ²², $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ ²³ and BaBiSe_3 ²⁴.

Substantial interest in this class of compounds derives from their potential as thermoelectric materials. Our work has shown that these types of compounds can possess low thermal conductivity, high thermopower and often high electrical conductivity²⁵, reaching in the case of CsBi_4Te_6 , a ZT ²⁶ of 0.8 at 225K. This value is comparable to those of the best $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ ²⁷ alloys currently used in thermoelectric applications.

From a solid state chemistry perspective, bismuth chalcogenides are a fascinating class with staggering compositional and structural complexity²⁸. These characteristics are spectacularly expressed in the natural occurring sulfosalts where Bi compounds are well represented. The stereochemical activity of the $6s^2$ lone pair causes bismuth to adopt several different coordination geometries depending on composition. When the lone pair is suppressed by hybridizing with energetically adjacent p and d orbitals, bismuth atoms adopt a normal octahedral geometry with six almost equidistant Bi-Q bonds and angles around 90° . This is not observed very often however and usually the bismuth atoms adopt distorted octahedral geometries having short bonds *trans* to long bonds and resulting in coordination environments that resemble a trigonal pyramid, a square pyramid, or a

regional bipyram

into occupy sites

in mixed site occ

or alkaline earth

When com

arise from the N

come in different

ether or through

seemingly counte

The above-

are desirable in

complexities in e

$3\text{-K}_2\text{Bi}_4\text{Se}_{13}$ sho

conductivity and

shown that its Z'

We report

characterization

$\text{Bi}_2\text{Bi}_2\text{Se}_4$. The

trigonal bipyramid. Furthermore, this astonishing bonding flexibility of bismuth enables it to occupy sites with coordination numbers up to nine and, when possible, to participate in mixed site occupation with similarly sized atoms e.g. Pb, Sn, lanthanide, alkali metal or alkaline earth metal atoms.

When combined together by sharing edges, the Bi-Q octahedra form blocks that derive from the NaCl-, Bi_2Te_3 -, CdI_2 - and Sb_2Se_3 -type structure. These octahedral blocks come in different shapes and sizes and are usually connected either directly with each other or through metal atoms of high (>6) coordination. These characteristics point to a seemingly countless number of novel phases that can potentially form.

The above-mentioned features can generate complexity, diversity and disorder that are desirable in good thermoelectric materials because they can lead to corresponding complexities in electronic structure as well as low thermal conductivity.^{29,30} For example, $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ shows promising thermoelectric properties by virtue of its very low thermal conductivity and relatively high power factor.^{4,26} Doping studies on this system have shown that its ZT can be improved to interestingly high values.^{4,31,44}

We report here the synthesis, physicochemical, spectroscopic, and structural characterization of four new compounds, $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$, $\text{CsBi}_{3.67}\text{Se}_6$ and BaBi_2Se_4 . The $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) feature a novel structure type. Electrical

conductivity, the

are also reported

2 Experimental

Reagents

mesh, Cerac, Mi

powder (99.95 %

Noranda, Canada

Milwaukee), rubi

(99.98% purity, A

mesh, Cerac Inc.

reaction of the con

Synthesis

a Vacuum Atmos

methanol and etha

almost quantitati

comparing the

crystallographica

conductivity, thermopower and thermal conductivity measurements on selected systems are also reported.

2. Experimental section

Reagents. Chemicals were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999% Noranda, Canada), selenium powder (99.95 % purity, -200 mesh, Cerac Inc., Milwaukee), selenium shots (99.999% Noranda, Canada), bismuth selenide powder (99.999% purity, -325 mesh, Cerac Inc., Milwaukee), rubidium metal (99.8% purity, Alfa Aesar, Ward Hill, MA), cesium metal (99.98% purity, Alfa Aesar, Ward Hill, MA), barium selenide powder (99.5 % purity, -20 mesh, Cerac Inc., Milwaukee). A_2Se ($A = Rb, Cs$) was prepared by a stoichiometric reaction of the corresponding alkali metal and selenium in liquid ammonia.

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All products were washed with degassed methanol and ether to remove any traces of excess flux. For all compounds the yield was almost quantitative and the purity and homogeneity of the products was verified by comparing the X-ray powder diffraction patterns to those calculated by the crystallographically determined atomic coordinates.

Bi_2S_3

transferred to

to 600°C in

product was

Rb_2I

mmol Bi_2S_3

vacuum. The

product con

dispersive a

needles gave

Cs_2E

mmol Bi_2S_3

vacuum. The

silvery-gray

storage com

CsBi

mixture of (j)

Bi₂Se₃. A mixture of 9.407 g (0.045 mol) of Bi and 5.331 g (0.068 mol) of Se was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 600 °C in 12 h, held at 600 °C for 2 d and then cooled down to 50 °C in 6 h. The product was pulverized and used for further reactions.

Rb₂Bi₈Se₁₃ (I). A mixture of 0.065 g (0.260 mmol) Rb₂Se and 0.568 g (0.867 mmol) Bi₂Se₃ was transferred to a carbon-coated silica tube and was flame-sealed under vacuum. The tube was heated for 2.5 d at 750 °C, then cooled to 50 °C in 12 h. The product consisted of silvery-gray thin needle-like crystals. Semiquantitative energy dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of Rb_{2.6}Bi_{7.9}Se₁₃.

Cs₂Bi₈Se₁₃ (II). A mixture of 0.065 g (0.188 mmol) Cs₂Se and 0.412 g (0.629 mmol) Bi₂Se₃ was transferred to a carbon-coated silica tube and was flame-sealed under vacuum. The tube was heated the same as for the case of (I). The product was obtained as silvery-gray thin needle-like crystals. SEM/EDS analysis on several crystals gave an average composition of Cs_{2.2}Bi_{7.9}Se₁₃.

CsBi_{3.67}Se₆ (III). *Method I.* Initially CsBi_{3.67}Se₆ was synthesized as follows: a mixture of 0.065 g (0.189 mmol) Cs₂Se, 0.242 g (0.904 mmol) Bi and 0.138 g (1.747

mmol) Se was 1

vacuum. The t

product consiste

Method 1

Bi₂Se₃ was trans

was placed unde

then the tube was

two more times t

reaches growing

average composit

BaBi₂Se₄

mmol) Bi₂Se₃ wa

under vacuum. Th

further cooled to

SEM/EDS analysi

3. Physical measu

mmol) Se was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 6 d at 750 °C, then cooled to 50 °C at 10 °C/h. The product consisted of silvery-gray polycrystalline rods.

Method II. A mixture of 0.130 g (0.337 mmol) Cs₂Se and 0.824 g (1.258 mmol) g Bi₂Se₃ was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a natural gas-oxygen torch until the mixture melted and then the tube was removed from the flame and let to solidify. The procedure was repeated two more times to ensure homogeneity. The product consisted of a silvery chunk with needles growing across its surface. SEM/EDS analysis on several crystals gave an average composition of Cs_{1.2}Bi_{3.7}Se₆.

BaBi₂Se₄ (IV). A mixture of 0.050 g (0.231 mmol) BaSe and 0.151 g (0.231 mmol) Bi₂Se₃ was transferred to a carbon-coated silica tube, which was flame-sealed under vacuum. The tube was heated for 3 d at 750 °C, cooled to 450 °C at 30 °C/h and further cooled to 50 °C in 6h. The product consisted of polycrystalline silvery chunks. SEM/EDS analysis on several crystals gave an average composition of Ba_{1.2}Bi_{1.9}Se₄.

3. Physical measurements

Electron

performed with

a Noran TN-55

were collected for

Differen

performed with

single crystals

ampoule contain

the detector. T

isothermed for 5

peak temperatur

ray diffraction.

Infrared

reflectance mea

spectra were rec

IR 750 Spectro

the Absorption

Mark function²

Electron microscopy. Quantitative microprobe analyses of the compounds were performed with a JEOL JSM-6400V Scanning Electron Microscope equipped with either a Noran TN-5500 or a Noran Vantage Energy Dispersive Spectroscopy detector. Data were collected for 45 s using an accelerating voltage of 25 kV.

Differential thermal analysis. Differential Thermal Analysis (DTA) was performed with a computer-controlled thermal analyzer (Shimadzu DTA-50). Ground single crystals (20-50 mg) were sealed in silica ampoules under vacuum. A silica ampoule containing alumina of equal mass was sealed and placed on the reference side of the detector. The samples were heated to the desired temperature at 10 °C/min, isothermed for 5 min and then cooled at 10 °C/min. The reported DTA temperature is the peak temperature upon heating. After DTA, the samples were examined with powder X-ray diffraction.

Infrared spectroscopy. Optical band-gaps were determined from diffuse reflectance measurements made on the finely ground sample at room temperature. The spectra were recorded in the infrared region (6000 - 400 cm⁻¹) with a Nicolet MAGNA-IR 750 Spectrometer equipped with a diffuse reflectance attachment from Spectra-Tech. Inc. Absorption (α/S) data were calculated from the reflectance data using the Kubelka-Munk function³². The band gap was defined as the intersection point between energy axis

at the absorption

edge in a GeS vs

Charge-

University DC

single crystals

measurements

gold wires used

pellet cross-sect

binocular micr

system describ

a slow ac techn

sample, as well

temperature g

samples with a

or thermopow

reversibility, r

Typically, the

sample to en

was within ± 5

at the absorption offset and the line extrapolated from the linear portion of the absorption edge in a α/S vs. E (eV) plot.

Charge-transport and thermal conductivity measurements. At Northwestern University DC electric conductivity and thermopower measurements were made on single crystals and polycrystalline compactions of the compound. Conductivity measurements were performed in the usual four-probe geometry with 60- and 25- μm gold wires used for the current and voltage electrodes, respectively. Measurements of the pellet cross-sectional area and voltage probe separation were made with a calibrated binocular microscope. Conductivity data were obtained with the computer-automated system described elsewhere^{33a}. Thermoelectric power measurements were made by using a slow ac technique^{33b} with 60 μm gold wires serving to support and conduct heat to the sample, as well as to measure the voltage across the sample resulting from the applied temperature gradient. In both measurements, the gold electrodes were attached on the samples with a conductive gold paste. For a variable-temperature run, data (conductivity or thermopower) were acquired during both sample cooling and warming to check reversibility. The temperature drift rate during an experiment was kept below 1 K/min. Typically, three to four separate variable-temperature runs were carried out for each sample to ensure reproducibility and stability. At a given temperature, reproducibility was within ± 5 %.

Research

of field

longitudi

samples

the conc

straining

the sun

Seebeck

calibrat

measur

fully ch

the sel

alternat

has use

stud. to

pressur

standar

At the University of Michigan electrical resistivity was measured using a Linear Research AC bridge with 16 Hz excitation in a cryostat equipped with a magnet capable of fields up to 5.5 T. Thermal conductivity and thermopower were determined using a longitudinal steady-state method over the temperature range 4-300 K. In this case samples were attached (using either a low melting point solder or silver-loaded epoxy) to the cold tip of the cryostat, while the other end of the sample is provided with a small strain gauge resistor (thin film) which serves as a heater. Temperature difference across the sample is measured using a differential chromel-constantan thermocouple. The Seebeck voltage was measured with thin copper wire the thermopower of which was calibrated against a high T_c superconductor up to 134 K.

At Michigan State University a four sample measurement system was used to measure electrical conductivity, thermoelectric power, and thermal conductivity³⁴. To fully characterize the figure of merit, the properties were measured for each sample over the selective temperature range of interest (system capability is 4.2 K to 475 K). To alleviate offset error voltages and increase the density of data points, a slow ac-technique was used with a heater pulse period of 720 seconds³⁵. The pulse shape was monitored, in-situ, to determine temperature stabilization, and the sample chamber was maintained at a pressure less than 10^{-5} Torr for the entire measurement run. Samples were mounted in the standard four probe configuration for the thermal conductivity, and the heater current was

adjusted

shield we

uniform

to monitor

system w

P

diffraction

using a

CPS 120

The pur

diffraction

S

diffraction

random

sample

SAINT

the stru

crystal

were re

adjusted for an average temperature gradient of 1 K. The sample stage and radiation shield were gold coated copper to minimize radiation effects and maintain temperature uniformity. All electrical leads were 25 μm in diameter with lengths greater than 10 cm to minimize thermal conduction losses. Data acquisition and computer control of the system was maintained under the LabVIEW³⁶ software environment.

Powder X-ray diffraction. The compounds were examined by X-ray powder diffraction to assess phase purity and for identification. Powder patterns were obtained using a Rigaku-Denki/Rw400F2 (Rotaflex) rotating-anode powder diffractometer and a CPS 120 INEL X-ray powder diffractometer equipped with a position-sensitive detector. The purity and homogeneity of all phases was confirmed by comparison of X-ray powder diffraction to those calculated from single crystal data using the CERIUS² software³⁷.

Single crystal X-ray crystallography. A Bruker SMART Platform CCD diffractometer was used for data collection. Several different sets of frames covering a random area of the reciprocal space were collected using 0.3° steps in ω at a detector-to-sample distance of ~5 cm. The SMART software was used for data acquisition and SAINT³⁸ for data extraction. The absorption correction was done with SADABS³⁸ and the structure solution and refinement was done with the SHELXTL³⁸ package of crystallographic programs. All structures were solved with direct methods. All atoms were refined anisotropically.

Rb_2Bi_8

exposure time

reflections sele

0.74 Å. Eight

on a crystallog

fractional ato

shown in Tabl

Cs_2Bi_8

exposure time

[58010] sele

0.81 Å. Becau

from (I) were

11.23%. The

parameters are

CsBi_3

an exposure tr

[58010] sele

0.80 Å. Four

crystallograph

Rb₂Bi₈Se₁₃ (I). Almost a full sphere of data were collected (1730 frames) with an exposure time of 35 sec per frame. The final cell was calculated from 1550 [$I > 10\sigma(I)$] reflections selected from the entire data set (Table 2-1). The resolution of the data set was 0.74 Å. Eight bismuth atoms, two rubidium and thirteen selenium atoms were found to sit on a crystallographic mirror plane. Final R values, R1 = 5.77% and wR2 = 11.59%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2-2.

Cs₂Bi₈Se₁₃ (II). A hemisphere of data was collected (1324 frames) with an exposure time of 55 sec per frame. The final cell was calculated from 4524 reflections [$I > 8\sigma(I)$] selected from the entire data set (Table 2-1). The resolution of the data set was 0.81 Å. Because the compound is isostructural with (I), the fractional atomic coordinates from (I) were used to refine the structure. Final R values, R1 = 4.97% and wR2 = 11.23%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2-3.

CsBi_{3.67}Se₆ (III). Almost a full sphere of data were collected (2047 frames) with an exposure time of 30 sec per frame. The final cell was calculated from 2888 reflections [$I > 8\sigma(I)$] selected from the entire data set (Table 2-1). The resolution of the data set was 0.80 Å. Four bismuth atoms, one cesium and six selenium atoms were found to sit on a crystallographic mirror plane. After refinement, the R1 and wR2 values were 11.2% and

29.2% respect.

other three Bi

in the structure

temperature 14.

This occupancy

electroneutrality

coordinates and

BaBi₂Se₂

exposure time of

Table 2-1). The

were found to st

values were 7.8%

was sitting in th

between 3.083(2

Therefore this at

*R2 = 16.8%.

016667). Final R

of Se(7) were co

29.2% respectively. At this point the U_{iso} of Bi(4) was $0.051 \text{ \AA}^2$, high compared to the other three Bi atoms (average $U_{\text{iso}} \sim 0.017 \text{ \AA}^2$) and there was not enough negative charge in the structure $\text{Cs}^{+1}[\text{Bi}_4\text{Se}_6]^0$. When the occupancy of Bi(4) was let to refine, it and the temperature factor dropped to $0.34/0.026 \text{ \AA}^2$ respectively ($R1 = 9.7\%$, $wR2 = 22.4\%$). This occupancy value corresponds to 66% occupation, exactly what is needed for electroneutrality. Final R values, $R1 = 6.11\%$ and $wR2 = 13.84\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2-4.

BaBi₂Se₄ (IV). A full sphere of data were collected (2140 frames) with an exposure time of 60 sec per frame. The final cell was calculated from 10191 reflections (Table 2-1). The resolution of the data set was $0.70 \text{ \AA}$. Four Bi, two Ba and nine Se atoms were found to sit on a crystallographic mirror plane. After refinement, the $R1$ and $wR2$ values were 7.8% and 19.8% respectively. At this point one of the nine selenium atoms was sitting in the center of a channel having distances to the neighboring Se atoms between $3.083(2)$ - $3.776(2) \text{ \AA}$ and generating a symmetry equivalent atom $2.16 \text{ \AA}$ away. Therefore this atom was assigned as Ba(3) and its occupancy was refined ($R1 = 5.8\%$, $wR2 = 16.8\%$). The occupancy of Ba(3) was refined to 0.07266 (full occupancy 0.16667). Final R values, $R1 = 3.71\%$ and $wR2 = 8.17\%$. The U_{33} of Ba(3) and the U_{11} of Se(7) were considerably higher than those of the other atoms and the formula was

Be₂-Bi₂-S

refine the

we believ

substance

to detect t

P₂ and P

having la

having las

Data were

coordinate

$\text{Ba}_{1.07}\text{Bi}_2\text{Se}_4$ indicating that there was 0.14 net positive charge per formula. Attempts to refine the occupancy of the other metal sites did not reveal any vacancies. Nevertheless, we believe that the extra charge must be distributed as vacancies throughout the metal sublattice and the very small fraction corresponding to each atom makes it very difficult to detect them by X-ray crystallography. Several other space groups were tried including P-3 and P1 but the behavior of the Ba(3) and Se(7) was unchanged, with the Ba(3) atoms having large temperature factors in the direction of the tunnels and the Se(7) atoms having large temperature factors perpendicular to the tunnels towards the Ba(3) atom. Data were collected from a second crystal with identical results. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2-5.

Table 2-1

BaBi₂Se₄

Empirical

Formula

Temperat

Crystal s

Space gr

Unit cell

Z, Volum

Density

Absorpti

F (000)

Crystal s

#range

Index ran

Reflecti

Indepen

Refineme

Data res

Goodnes

Final R

R index

Extincti

Largest

Table 2-1. Crystallographic Data for $A_2Bi_8Se_{13}$ ($A = Rb, Cs$), $CsBi_{3.67}Se_6$ and $BaBi_2Se_4$.

Empirical formula	$Rb_2Bi_8Se_{13}$ (I)	$Cs_2Bi_8Se_{13}$ (II)
Formula weight	2869.26	2964.14
Temperature, K	173.1(1)	173.1(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$
Unit cell dimensions, Å	$a = 13.4931(4)$ $b = 4.1558(3)$ $c = 24.876(2)$ $\beta = 96.571(4)^\circ$	$a = 13.704(1)$ $b = 4.1532(4)$ $c = 25.008(2)$ $\beta = 96.848(2)^\circ$
Z, Volume, Å ³	2, 1385.78(1)	2, 1413.2(2)
Density (calc.), g/cm ³	6.876	6.966
Absorption coeff., mm ⁻¹	71.156	68.892
F(000)	2360	2432
Crystal size, mm ³	0.40 x 0.03 x 0.02	0.02 x 0.02 x 0.30
θ range	1.52 to 28.75°	1.62 to 25.99°
Index ranges	$-17 \leq h \leq 17$ $-5 \leq k \leq 5$ $-32 \leq l \leq 32$	$-16 \leq h \leq 16$ $-5 \leq k \leq 4$ $-30 \leq l \leq 19$
Reflections collected	10652	8004
Independent reflections	3680 [$R_{(int)} = 0.1065$]	3155 [$R_{(int)} = 0.0541$]
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3680 / 0 / 140	3155 / 0 / 140
Goodness-of-fit on F^2	0.914	0.969
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0577$, $wR2 = 0.1159$	$R1 = 0.0497$, $wR2 = 0.1123$
R indices (all data)	$R1 = 0.1164$, $wR2 = 0.1244$	$R1 = 0.0668$, $wR2 = 0.1167$
Extinction	0.000144(18)	0.00037(3)
Largest peak and hole, e ⁻ Å ⁻³	4.825 and -4.801	4.775 and -3.600

Table 2-1. (cont'd).

Empirical formula	CsBi _{3.67} Se ₆ (III)	BaBi ₂ Se ₄ (IV)
Formula weight	1372.58	880.98
Temperature, K	296(2)	173.1(1)
Crystal system	Orthorhombic	Hexagonal
Space group	<i>Pnma</i>	<i>P6₃/m</i>
Unit cell dimensions, Å	<i>a</i> = 23.421(4) <i>b</i> = 4.1877(8) <i>c</i> = 13.710(3) -	<i>a</i> = 26.157(1) <i>b</i> = 26.157(1) <i>c</i> = 4.3245(3) γ = 120°
Z, Volume, Å ³	4, 1344.7(4)	12, 2562.4(3)
Density (calc.), g/cm ³	6.780	6.851
Absorption coeff., mm ⁻¹	66.680	62.932
F(000)	2253	4334
Crystal size, mm ³	0.03 x 0.03 x 0.44	0.02 x 0.03 x 0.30
θ range	1.72 to 26.37°	3.60 to 30.68°
Index ranges	-29 ≤ <i>h</i> ≤ 28 -5 ≤ <i>k</i> ≤ 5 -16 ≤ <i>l</i> ≤ 17	-35 ≤ <i>h</i> ≤ 37 -35 ≤ <i>k</i> ≤ 36 -6 ≤ <i>l</i> ≤ 6
Reflections collected	10914	29993
Independent reflections	1565 [<i>R</i> _(int) = 0.1027]	2857 [<i>R</i> _(int) = 0.0989]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	1565 / 0 / 68	2857 / 0 / 89
Goodness-of-fit on <i>F</i> ²	1.053	1.088
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0611, <i>wR</i> 2 = 0.1384	<i>R</i> 1 = 0.0371, <i>wR</i> 2 = 0.0817
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0737, <i>wR</i> 2 = 0.1421	<i>R</i> 1 = 0.0494, <i>wR</i> 2 = 0.0850
Extinction	0.00196(18)	0.00033(3)
Largest peak and hole, e Å ⁻³	3.889 and -3.310	4.424 and -2.573

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 2
($\times 10^3$)

B: 1)
B: 2)
B: 3)
B: 4)
B: 5)
B: 6)
B: 7)
B: 8)
R: 1)
R: 2)
Se: 1)
Se: 2)
Se: 3)
Se: 4)
Se: 5)
Se: 6)
Se: 7)
Se: 8)
Se: 9)
Se: 10)
Se: 11)
Se: 12)
Se: 13)

C_{eq} is

Table 2-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	0.0520(1)	-0.7500	0.4411(1)	13(1)
Bi(2)	-0.1280(1)	-0.7500	0.2130(1)	10(1)
Bi(3)	0.2802(1)	-0.2500	0.0320(1)	11(1)
Bi(4)	0.4387(1)	-0.2500	0.2674(1)	10(1)
Bi(5)	0.1158(1)	-0.2500	0.3084(1)	12(1)
Bi(6)	-0.0488(1)	-0.2500	0.0708(1)	12(1)
Bi(7)	0.1943(1)	0.2500	0.1708(1)	12(1)
Bi(8)	0.4249(1)	-0.7500	0.4357(1)	15(1)
Rb(1)	-0.2750(3)	-0.7500	0.3618(1)	19(1)
Rb(2)	0.5829(3)	-0.2500	0.1187(1)	21(1)
Se(1)	-0.1027(3)	-0.2500	0.4489(1)	13(1)
Se(2)	0.1965(3)	-0.2500	0.4154(1)	13(1)
Se(3)	-0.0304(3)	-0.7500	0.3208(1)	12(1)
Se(4)	0.0370(3)	-0.2500	0.1832(1)	9(1)
Se(5)	-0.2517(3)	-0.2500	0.2369(1)	14(1)
Se(6)	-0.1930(3)	-0.7500	0.0891(1)	13(1)
Se(7)	0.1037(3)	0.2500	0.0494(1)	9(1)
Se(8)	0.4126(3)	-0.7500	0.0216(1)	11(1)
Se(9)	0.3297(3)	-0.2500	0.1461(1)	10(1)
Se(10)	0.2616(3)	0.2500	0.2828(1)	11(1)
Se(11)	0.5582(3)	-0.7500	0.2385(1)	10(1)
Se(12)	0.5188(3)	-0.2500	0.3725(1)	12(1)
Se(13)	0.6129(3)	-0.7500	0.4864(1)	10(1)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table

(A.1)

B: 1.

B: 2.

B: 3.

B: 4.

B: 5.

B: 6.

B: 7.

B: 8.

Cs: 1.

Cs: 2.

Se: 1.

Se: 2.

Se: 3.

Se: 4.

Se: 5.

Se: 6.

Se: 7.

Se: 8.

Se: 9.

Se: 10.

Se: 11.

Se: 12.

Se: 13.

U

Table 2-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	0.0528(1)	-0.7500	0.4410(1)	15(1)
Bi(2)	-0.0251(1)	-0.7500	0.2132(1)	13(1)
Bi(3)	0.2764(1)	-0.2500	0.0329(1)	13(1)
Bi(4)	0.4357(1)	-0.2500	0.2673(1)	13(1)
Bi(5)	0.1178(1)	-0.2500	0.3087(1)	14(1)
Bi(6)	-0.0477(1)	-0.2500	0.0706(1)	14(1)
Bi(7)	0.1915(1)	0.2500	0.1706(1)	14(1)
Bi(8)	0.4238(1)	-0.7500	0.4363(1)	17(1)
Cs(1)	-0.2739(1)	-0.7500	0.3621(1)	18(1)
Cs(2)	0.5824(1)	-0.2500	0.1183(1)	20(1)
Se(1)	-0.0993(2)	-0.2500	0.4496(1)	15(1)
Se(2)	0.1953(2)	-0.2500	0.4154(1)	15(1)
Se(3)	-0.0269(2)	-0.7500	0.3201(1)	13(1)
Se(4)	0.0366(2)	-0.2500	0.1833(1)	13(1)
Se(5)	-0.2464(2)	-0.2500	0.2369(1)	14(1)
Se(6)	-0.1885(2)	-0.7500	0.0885(1)	14(1)
Se(7)	0.1031(2)	0.2500	0.0491(1)	13(1)
Se(8)	0.4072(2)	-0.7500	0.0233(1)	14(1)
Se(9)	0.3245(2)	-0.2500	0.1464(1)	13(1)
Se(10)	0.2606(2)	0.2500	0.2819(1)	13(1)
Se(11)	0.5540(2)	-0.7500	0.2396(1)	14(1)
Se(12)	0.5111(2)	-0.2500	0.3724(1)	14(1)
Se(13)	0.6100(2)	-0.7500	0.4857(1)	14(1)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2-4

($\text{\AA}^3 \times 10^3$)

B: 1)

B: 2)

B: 3)

B: 4)

C:

Se: 1)

Se: 2)

Se: 3)

Se: 4)

Se: 5)

Se: 6)

U_{eq} is d

Table 2-4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{CsBi}_{3.67}\text{Se}_6$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.0763(1)	0.2500	0.5468(1)	20(1)	
Bi(2)	0.3253(1)	-0.7500	0.8336(1)	27(1)	
Bi(3)	0.0242(1)	-0.7500	0.2261(1)	24(1)	
Bi(4)	0.2162(1)	-0.2500	0.6558(1)	28(1)	0.67
Cs	0.1334(1)	-0.2500	-0.0370(1)	32(1)	
Se(1)	0.0461(1)	-0.2500	0.3985(2)	16(1)	
Se(2)	0.0010(1)	-0.7500	-0.1001(2)	21(1)	
Se(3)	0.0962(1)	-0.2500	0.6900(2)	18(1)	
Se(4)	0.3504(1)	-0.2500	0.6866(2)	23(1)	
Se(5)	0.1966(1)	0.2500	0.4858(2)	21(1)	
Se(6)	0.2120(1)	-0.7500	0.7875(2)	29(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2-5. At

($\lambda^2 \times 10^3$) for

Br 1)

Br 2)

Br 3)

Br 4)

Br 1)

Br 2)

Br 3)

Se 1)

Se 2)

Se 3)

Se 4)

Se 5)

Se 6)

Se 7)

Se 8)

U_{ij} is defined

Table 2-5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for BaBi_2Se_4 .

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.4115(1)	0.4603(1)	0.2500	11(1)	
Bi(2)	0.5048(1)	0.6494(1)	-0.7500	10(1)	
Bi(3)	0.3333(1)	0.2743(1)	-0.7500	10(1)	
Bi(4)	0.1810(1)	0.1552(1)	-0.2500	14(1)	
Ba(1)	0.3243(1)	0.5552(1)	-0.2500	9(1)	
Ba(2)	0.2304(1)	0.3496(1)	-0.2500	9(1)	
Ba(3)	0.0000	0.0000	-0.2500	50(2)	0.436(9)
Se(1)	0.3048(1)	0.4533(1)	0.2500	9(1)	
Se(2)	0.3691(1)	0.3653(1)	-0.2500	10(1)	
Se(3)	0.4577(1)	0.5466(1)	-0.2500	11(1)	
Se(4)	0.4075(1)	0.6579(1)	-0.7500	9(1)	
Se(5)	0.5517(1)	0.7294(1)	-0.2500	9(1)	
Se(6)	0.3074(1)	0.1895(1)	-0.2500	10(1)	
Se(7)	0.1360(1)	0.0726(1)	-0.7500	34(1)	
Se(8)	0.2158(1)	0.2477(1)	-0.7500	11(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4. Results and

Synthe

almost stoich

Bi_2Se_3 at 750

loss occurring

not be synthe

reactions the p

$\text{CsBi}_{1/6}\text{Se}_6$ co

composition. I

$\text{Cs}_2\text{Bi}_3\text{Se}_{13}$ c

quenching a

$\text{CsBi}_{1/6}\text{Se}_6$ a

reactions in

Bi_2Se_3 when

and ABi_3Se_5

4. Results and discussion

Synthesis and thermal behavior. $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ form by reacting almost stoichiometric ($\text{A}_2\text{Se} : \text{Bi}_2\text{Se}_3$ 1.2 : 4) combinations of A_2Se ($\text{A} = \text{Rb}, \text{Cs}$) and Bi_2Se_3 at 750°C for 2 days. The slight excess of A_2Se is needed to compensate for any loss occurring due to reaction with the silica tube. The Rb analog of $\text{CsBi}_{3.67}\text{Se}_6$ could not be synthesized. Although $\text{CsBi}_{3.67}\text{Se}_6$ can be prepared from direct combination reactions the product contains several impurities with $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ being the major one. $\text{CsBi}_{3.67}\text{Se}_6$ could only be synthesized pure by quenching a melt of the corresponding composition. $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ can be also prepared by stoichiometric melt quenching whereas $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ could only be synthesized by slow cooling in a furnace. Interestingly, quenching a mixture of nominal stoichiometry " $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ " yielded a mixture of $\text{CsBi}_{3.67}\text{Se}_6$ and a new phase that is currently under investigation. Direct combination reactions in the furnace with lower $\text{A}_2\text{Se}/\text{Bi}_2\text{Se}_3$ ratios gave mixtures of $\text{A}_2\text{Bi}_8\text{Se}_{13}$ and Bi_2Se_3 , whereas higher $\text{A}_2\text{Se}/\text{Bi}_2\text{Se}_3$ ($\text{A} = \text{Rb}, \text{Cs}$) ratios gave $\text{A}_2\text{Bi}_4\text{Se}_7$ ⁵, $\text{A}_3\text{Bi}_7\text{Se}_{12}$ ^{39(a)}, and ABi_3Se_5 ^{39(a)}.

GB:

by d

C H

B:

B.B:

K.B:

comp

has a

does

with

think

type

$\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ melt congruently at 673 °C and 664 °C respectively.

$\text{CsBi}_{3.67}\text{Se}_6$ melts at 686 °C but it transforms to $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ as evidenced by powder X-ray diffraction.

Pure BaBi_2Se_4 was synthesized by reacting BaSe and Bi_2Se_3 at 1:1 ratio at 750 °C. Higher ratios in BaSe still give BaBi_2Se_4 while ratios rich in Bi_2Se_3 give $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ ³⁹. BaBi_2Se_4 can be also synthesized by quenching a melt with excess BaSe.

BaBi_2Se_4 melts congruently at 846 °C.

Structure description

$\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ (I) and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ (II). $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ are analogs of $\text{K}_2\text{Bi}_8\text{Se}_{13}$ however they adopt a different structure, see Figure 2-1. Since the Rb and Cs compounds are isomorphous we will describe in detail only $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$. The structure has a three-dimensional framework consisting of infinitely long rectangular NaCl-type rods running parallel to the b-axis. Similar building blocks with the same thickness but with different width are found in CsBi_4Te_6 ⁷. These rectangular rods are two Bi octahedra thick and three Bi octahedra wide (2x3). The blocks are connected through small CdI_2 -type fragments and two Bi atoms in a square pyramidal coordination (Sb_2Se_3 -type). The

same feature

different struc

filled with ro

The B

coordinate, w

between 2.7(0)

3.704(3) Å wh

octahedral env

center of the N

between 2.90(0)

other octahedr

octahedron to c

between 2.9-3.

the shorter on

opposite to thr

distorted towa

Å. one be

same feature with square pyramidal Bi atoms exists in $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ¹, which adopts a different structure type. As these rods are linked side by side they form parallel tunnels filled with rows of Rb^+ ions.

The Bi(8) atoms that exist in the Sb_2Se_3 -type fragment mentioned above are five-coordinate, with a square pyramidal environment and Bi(8)-Se bond distances varying between 2.700(4)-2.974(3) Å. There are also two other long Bi(8)-Se distances at 3.704(3) Å which are not considered bonding. All other Bi atoms in the structure have octahedral environments with varying degrees of distortion. Atom Bi(6), located in the center of the NaCl-type (2x3) block is the least distorted atom with Bi(6)-Se distances between 2.900(3)-3.014(3) Å, and Se-Bi(6)-Se angles between 85.38(9)°-93.57(9)°. The other octahedral Bi atoms exhibit two different kinds of distortion. The first causes the octahedron to distort towards a square pyramid having four bonds, almost equal in length between 2.9-3.0 Å, one shorter one between 2.7-2.8 Å, and a longer one ≥ 3.1 Å trans to the shorter one. The second creates a trigonal pyramid with three short Bi-Se bonds opposite to three longer ones, see Table 2-6. The Bi(1), Bi(5) and Bi(7) octahedra are distorted towards a square pyramid e.g. Bi(5) has four bonds between 2.907(3)-2.980(3) Å, one bond at 2.758(4) Å and one bond at 3.174(3) Å.

Sb₂Se₃-type

↓
NaCl-type

Figure 2-1.

indicate the

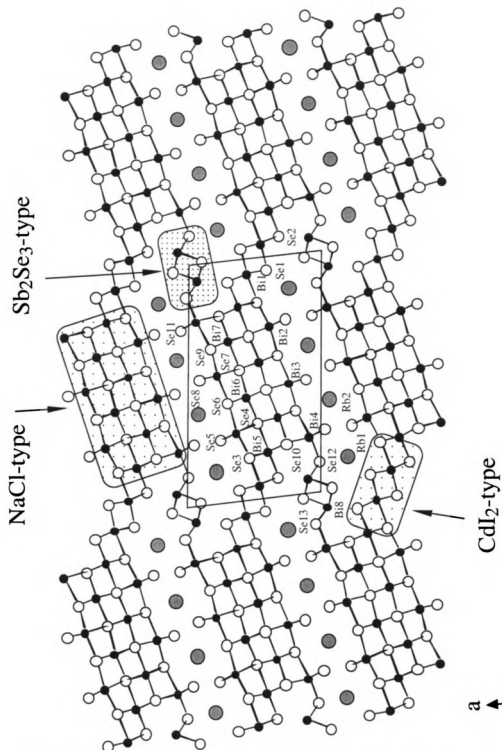


Figure 2-1. Projection of the structure of $A_2Bi_8Se_{13}$ down the b -axis. The shaded areas indicate the NaCl-, Sb_2Se_3 - and CdI_2 -type building blocks.

The B.

has the

33024

between

Selected

those of

structure

NaCl-2

fragmen

type blo

of the bi

meas re

The Bi(2), Bi(3) and Bi(4) octahedra are distorted toward a trigonal pyramid, e.g. Bi(4) has three short Bi-Se bonds between 2.714(4)-2.775(3) Å and three longer ones between 3.202(4)-3.222(3) Å.

The Rb^+ ions have a tricapped trigonal prismatic coordination with distances between 3.507(4)-3.782(4) Å for Rb(1) and 3.481(5)-3.810(4) Å for Rb(2).

$\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ has very similar characteristics and will not be discussed further.

Selected bond distances and angles are shown on Tables 6 and 7.

As mentioned earlier, the structure of $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) is different from those of α -, β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ although it has some similar features with α - $\text{K}_2\text{Bi}_8\text{Se}_{13}$. The structures of α -, β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ are shown in Figure 2-2. β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ consists of CdI_2 -, NaCl - and Bi_2Te_3 -type fragments. $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) do not contain Bi_2Te_3 -type fragments and its NaCl -type block is elongated in one direction compared with the NaCl -type block in β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ which has a neatly square-like cross section. The connectivity of the blocks in the two structures is different and as a result, the cavities where the alkali metals reside are of different size.

Table 2-6. B

Rb-

B:1-Set 1)
B:1-Set 1)
B:1-Set 2)
B:1-Set 3)
B:2-Set 5)
B:2-Set 3)
B:2-Set 6)
B:2-Set 4)
B:3-Set 8)
B:3-Set 9)
B:3-Set 6)
B:3-Set 7)
B:4-Set 12)
B:4-Set 11)
B:4-Set 9)
B:4-Set 10)
B:5-Set 2)
B:5-Set 3)
B:5-Set 10)
B:5-Set 4)
B:6-Set 4)
B:6-Set 6)
B:6-Set 7)
B:6-Set 7)
B:7-Set 10)
B:7-Set 9)
B:7-Set 4)
B:7-Set 7)

Table 2-6. Bond Distances (Å) for $A_2Bi_8Se_{13}$ (A = Rb, Cs).

Rb₂Bi₈Se₁₃		Cs₂Bi₈Se₁₃	
Bi(1)-Se(1)	2.745(4)	Bi(1)-Se(1)	2.736(3)
Bi(1)-Se(1)	2.968(3)x2	Bi(1)-Se(1)	2.969(2)x2
Bi(1)-Se(2)	2.968(3)x2	Bi(1)-Se(2)	2.972(2)x2
Bi(1)-Se(3)	3.070(4)	Bi(1)-Se(3)	3.088(3)
Bi(2)-Se(5)	2.771(3)x2	Bi(2)-Se(5)	2.768(2)x2
Bi(2)-Se(3)	2.849(4)	Bi(2)-Se(3)	2.848(3)
Bi(2)-Se(6)	3.108(4)	Bi(2)-Se(6)	3.134(3)
Bi(2)-Se(4)	3.195(3)x2	Bi(2)-Se(4)	3.189(2)x2
Bi(3)-Se(8)	2.772(3)x2	Bi(3)-Se(8)	2.772(2)x2
Bi(3)-Se(9)	2.840(4)	Bi(3)-Se(9)	2.837(3)
Bi(3)-Se(6)	3.106(4)	Bi(3)-Se(6)	3.131(3)
Bi(3)-Se(7)	3.226(3)x2	Bi(3)-Se(7)	3.217(2)x2
Bi(4)-Se(12)	2.714(4)	Bi(4)-Se(12)	2.706(3)
Bi(4)-Se(11)	2.775(3)x2	Bi(4)-Se(11)	2.773(2)x2
Bi(4)-Se(9)	3.202(4)	Bi(4)-Se(9)	3.220(3)
Bi(4)-Se(10)	3.222(3)x2	Bi(4)-Se(10)	3.227(2)x2
Bi(5)-Se(2)	2.758(4)	Bi(5)-Se(2)	2.753(3)
Bi(5)-Se(3)	2.907(3)x2	Bi(5)-Se(3)	2.909(2)x2
Bi(5)-Se(10)	2.980(3)x2	Bi(5)-Se(10)	2.984(2)x2
Bi(5)-Se(4)	3.174(3)	Bi(5)-Se(4)	3.198(3)
Bi(6)-Se(4)	2.900(3)	Bi(6)-Se(4)	2.917(3)
Bi(6)-Se(6)	2.918(3)x2	Bi(6)-Se(6)	2.906(2)x2
Bi(6)-Se(7)	2.997(3)	Bi(6)-Se(7)	2.999(3)
Bi(6)-Se(7)	3.014(3)x2	Bi(6)-Se(7)	3.023(2)x2
Bi(7)-Se(10)	2.830(4)	Bi(7)-Se(10)	2.830(3)
Bi(7)-Se(9)	2.879(3)x2	Bi(7)-Se(9)	2.875(2)x2
Bi(7)-Se(4)	3.012(3)x2	Bi(7)-Se(4)	3.014(2)x2
Bi(7)-Se(7)	3.125(4)	Bi(7)-Se(7)	3.133(3)

Table 2

B0-S-S

B0-S-S

B0-S-S

B0-S-S

R0-1-S

R0-1-S

R0-1-S

R0-1-S

R0-1-S

R0-1-S

R0-2-S

R0-2-S

R0-2-S

R0-2-S

R0-2-S

R0-2-S

Table 2-6. (cont'd).

Bi(8)-Se(13)	2.700(4)	Bi(8)-Se(13)	2.700(3)
Bi(8)-Se(13)	2.927(2)x2	Bi(8)-Se(13)	2.923(2)x2
Bi(8)-Se(12)	2.974(3)x2	Bi(8)-Se(12)	2.960(2)x2
Bi(8)-Se(2)	3.704(3)x2	Bi(8)-Se(2)	3.741(3)x2
Rb(1)-Se(12)	3.507(4)x2	Cs(1)-Se(12)	3.638(3)x2
Rb(1)-Se(3)	3.563(5)	Cs(1)-Se(3)	3.661(3)
Rb(1)-Se(11)	3.592(5)	Cs(1)-Se(11)	3.636(4)
Rb(1)-Se(13)	3.600(5)	Cs(1)-Se(13)	3.641(3)
Rb(1)-Se(1)	3.641(4)x2	Cs(1)-Se(1)	3.685(3)x2
Rb(1)-Se(5)	3.782(4)x2	Cs(1)-Se(5)	3.812(3)x2
Rb(2)-Se(5)	3.481(5)	Cs(2)-Se(5)	3.556(4)
Rb(2)-Se(8)	3.499(5)	Cs(2)-Se(8)	3.561(3)
Rb(2)-Se(9)	3.559(5)	Cs(2)-Se(9)	3.685(3)
Rb(2)-Se(11)	3.678(4)x2	Cs(2)-Se(11)	3.735(3)x2
Rb(2)-Se(8)	3.764(4)x2	Cs(2)-Se(8)	3.790(3)x2
Rb(2)-Se(6)	3.810(4)x2	Cs(2)-Se(6)	3.909(3)x2

Se 1

Se 1

Se 1

Se 2

Se 4

Se 5

Se 5

Se 5

Se 7

Se 8

Se 8

Se 8

Se 1

Se 1

Se 1

Se 1

Se 1

Se 1

Se 2

Se 2

Se 2

Se 7

Se 6

Se 6

Se 6

Se 4

Se 9

Se 1

Se 1

Se 1

Se 1

Se 1

Se 1

Table 2-7. Selected Angles (deg) for $A_2Bi_8Se_{13}$ ($A = Rb, Cs$).

Rb₂Bi₈Se₁₃		Cs₂Bi₈Se₁₃	
Se(1)-Bi(1)-Se(3)	83.35(9)	Se(1)-Bi(1)-Se(3)	84.33(7)
Se(1)-Bi(1)-Se(2)	90.46(7)	Se(1)-Bi(1)-Se(2)	90.69(5)
Se(1)-Bi(1)-Se(2)	96.92(9)	Se(1)-Bi(1)-Se(2)	97.74(7)
Se(1)-Bi(1)-Se(3)	173.2(1)	Se(1)-Bi(1)-Se(3)	172.78(8)
Se(4)-Bi(2)-Se(4)	81.14(8)	Se(4)-Bi(2)-Se(4)	81.26(6)
Se(5)-Bi(2)-Se(4)	90.85(7)	Se(5)-Bi(2)-Se(4)	90.76(5)
Se(5)-Bi(2)-Se(5)	97.1(1)	Se(5)-Bi(2)-Se(5)	97.20(8)
Se(5)-Bi(2)-Se(4)	171.96(8)	Se(5)-Bi(2)-Se(4)	172.00(5)
Se(7)-Bi(3)-Se(7)	80.18(9)	Se(7)-Bi(3)-Se(7)	80.42(6)
Se(8)-Bi(3)-Se(9)	90.73(9)	Se(8)-Bi(3)-Se(9)	90.64(7)
Se(8)-Bi(3)-Se(8)	97.1(1)	Se(8)-Bi(3)-Se(8)	97.04(9)
Se(8)-Bi(3)-Se(7)	171.41(8)	Se(8)-Bi(3)-Se(7)	171.57(6)
Se(10)-Bi(4)-Se(10)	80.32(9)	Se(10)-Bi(4)-Se(10)	80.12(6)
Se(11)-Bi(4)-Se(10)	90.50(7)	Se(11)-Bi(4)-Se(10)	90.63(5)
Se(11)-Bi(4)-Se(11)	97.0(1)	Se(11)-Bi(4)-Se(11)	96.97(8)
Se(12)-Bi(4)-Se(9)	176.1(1)	Se(12)-Bi(4)-Se(9)	174.28(8)
Se(10)-Bi(5)-Se(4)	86.88(9)	Se(10)-Bi(5)-Se(4)	86.62(7)
Se(2)-Bi(5)-Se(10)	90.51(9)	Se(2)-Bi(5)-Se(10)	91.73(7)
Se(2)-Bi(5)-Se(3)	95.43(9)	Se(2)-Bi(5)-Se(3)	95.34(7)
Se(2)-Bi(5)-Se(4)	176.4(1)	Se(2)-Bi(5)-Se(4)	177.69(8)
Se(7)-Bi(6)-Se(7)	85.38(9)	Se(7)-Bi(6)-Se(7)	85.40(7)
Se(6)-Bi(6)-Se(6)	90.8(1)	Se(6)-Bi(6)-Se(6)	91.24(8)
Se(6)-Bi(6)-Se(7)	93.57(9)	Se(6)-Bi(6)-Se(7)	93.46(7)
Se(6)-Bi(6)-Se(7)	177.94(9)	Se(6)-Bi(6)-Se(7)	177.56(6)
Se(4)-Bi(7)-Se(7)	84.07(8)	Se(4)-Bi(7)-Se(7)	84.66(7)
Se(9)-Bi(7)-Se(4)	89.76(7)	Se(9)-Bi(7)-Se(4)	89.83(5)
Se(10)-Bi(7)-Se(9)	94.03(9)	Se(10)-Bi(7)-Se(9)	93.46(7)
Se(10)-Bi(7)-Se(7)	175.7(1)	Se(10)-Bi(7)-Se(7)	176.85(8)
Se(13)-Bi(8)-Se(12)	79.19(9)	Se(13)-Bi(8)-Se(12)	79.95(7)
Se(13)-Bi(8)-Se(13)	85.19(9)	Se(13)-Bi(8)-Se(13)	84.93(7)
Se(13)-Bi(8)-Se(13)	90.47(9)	Se(13)-Bi(8)-Se(13)	90.54(8)
Se(13)-Bi(8)-Se(12)	164.4(1)	Se(13)-Bi(8)-Se(12)	164.88(9)

CdI₂-type

CdI₂-type

Figure 2-2. P

K₂B₄Se₁₃ do

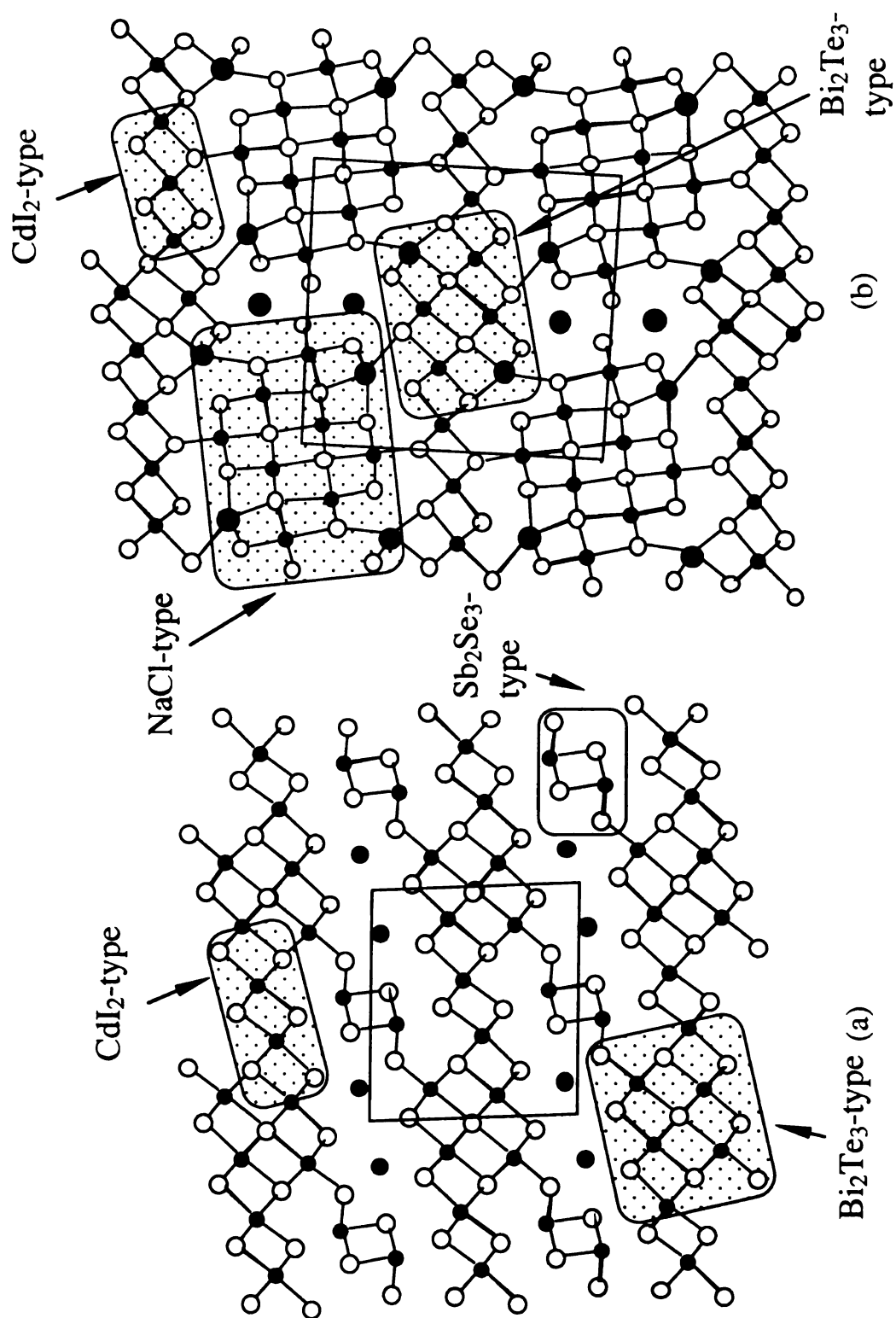


Figure 2-2. Projection of the structures of (a) $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$ down the c-axis and (b) $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ down the b-axis.

Also, due to

the alkali ions

several sites

K and Bi atoms

stability of the

electrical properties

thermoelectric

is not found in

building block

not have NaCl

CsBi₃

consists of b

(12), see Fig

b-axis and s

degrees.

Also, due to the larger size of the Rb^+ and Cs^+ ions there is no mixed occupancy between the alkali metals and the Bi atoms in $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$), whereas in $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ several sites exhibit mixed $\text{K}^+/\text{Bi}^{3+}$ occupancy. It is therefore apparent that the ability of K and Bi atoms to occupy the same crystallographic sites is probably the origin of stability of the $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ structure. It may also be a crucial factor in determining the electrical properties of the K-analog, which has been shown to be a promising thermoelectric material.⁴ $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) contains an Sb_2Se_3 -type fragment that is not found in $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ but exists in $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$. Although the arrangement of the building blocks in $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) and $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$ is similar, $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$ does not have NaCl-type blocks, it consists only of Sb_2Se_3 -, CdI_2 -, and Bi_2Te_3 -type fragments.

$\text{CsBi}_{3.67}\text{Se}_6$ (III). $\text{CsBi}_{3.67}\text{Se}_6$ adopts the structure of $\alpha\text{-CsPbBi}_3\text{Se}_6$ ¹⁰, which consists of building blocks of NaCl-type as those found in $\text{A}_2\text{Bi}_8\text{Se}_{13}$ but more narrow (2x2), see Figure 2-3. These blocks have the shape of infinite rods that run parallel to the b-axis and share edges as each rod is rotated with respect to its neighbors, by ~13 degrees.

NaCl-type

2/3 occupied



Figure 2-3.

indicate the

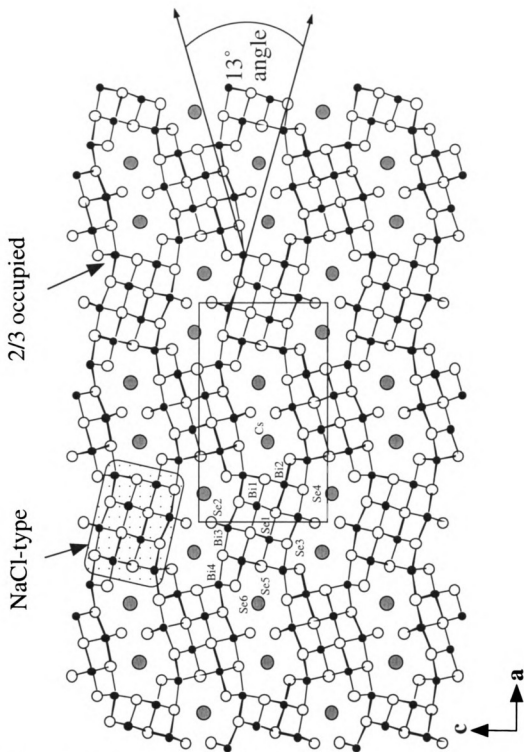


Figure 2-3. Projection of the structure of $\text{CsBi}_{3.67}\text{Se}_6$ down the b -axis. The shaded areas indicate the NaCl-type building blocks.

This rotation results

The Cs^+ ions reside

3.997(4) Å (Table 2-3)

All bismuth

distortion, as observed

NaCl-type block is

between 86.74(6)°

with four bonds to

3.141(3) Å. The

octahedron has two

and two long

environment. The

and is responsible

has three short

3.172(4) Å, and

charge neutral

occupied. By

charge balance

This rotation results in a corrugated arrangement of the NaCl-type rods in the ab-plane. The Cs^+ ions reside in tricapped trigonal prismatic sites with Cs-Se distances 3.672(4)-3.997(4) Å (Table 2-8).

All bismuth atoms are in octahedral coordination, again with varying degrees of distortion, as observed in $\text{A}_2\text{Bi}_8\text{Se}_{13}$. The Bi(1) atom that is situated in the center of the NaCl-type block is the least distorted with distances of 2.908(2)-3.003(2) Å and angles between 86.74(6)-92.23(7)°. The Bi(2) octahedron is distorted towards a square pyramid with four bonds between 2.964(2)-3.001(2) Å, one short at 2.728(3) Å and one long at 3.141(3) Å. The Bi(3) and Bi(4) octahedra exhibit different kinds of distortion. The Bi(3) octahedron has two short bonds at 2.778(2) Å, two bonds between 2.985(3)-3.045(3) Å and two long bonds at 3.199(2) Å resulting in a distortion towards a see-saw environment. The Bi(4) octahedron is the most distorted approaching a trigonal pyramid and is responsible for the zigzag arrangement of the NaCl-type blocks in the structure. It has three short bonds between 2.767(2)-2.850(3) Å, three long ones between 3.166(2)-3.172(4) Å, and Se-Bi-Se angles varying between 81.80(8)°-103.98(8)°. To maintain charge neutrality, the Bi(4) sites, which connect the NaCl-type rods, are only 2/3 occupied. By comparison, in $\alpha\text{-CsPbBi}_3\text{Se}_6$, these positions are fully occupied and the charge balance is maintained by Pb^{2+} .⁴⁰

Table 2-8. Bond Di

Bi(1)-Se(3)

Bi(1)-Se(5)

Bi(1)-Se(1)

Bi(1)-Se(1)

Bi(2)-Se(6)

Bi(2)-Se(4)

Bi(2)-Se(5)

Bi(2)-Se(1)

Bi(3)-Se(2)

Bi(3)-Se(4)

Bi(3)-Se(3)

Bi(3)-Se(1)

Bi(4)-Se(6)

Bi(4)-Se(3)

Bi(4)-Se(5)

Bi(4)-Se(4)

Cs-Se(2)

Cs-Se(6)

Cs-Se(4)

Cs-Se(2)

Cs-Se(3)

Cs-Se(5)

Table 2-8. Bond Distances (Å) and Selected Angles (deg) for CsBi_{3.67}Se₆.

Bi(1)-Se(3)	2.908(1)x2	Se(1)-Bi(1)-Se(1)	86.74(6)
Bi(1)-Se(5)	2.939(3)	Se(3)-Bi(1)-Se(5)	92.23(7)
Bi(1)-Se(1)	2.965(3)	Se(5)-Bi(1)-Se(1)	178.13(8)
Bi(1)-Se(1)	3.003(2)x2		
Bi(2)-Se(6)	2.728(3)	Se(5)-Bi(2)-Se(1)	88.10(7)
Bi(2)-Se(4)	2.964(2)x2	Se(6)-Bi(2)-Se(4)	92.06(8)
Bi(2)-Se(5)	3.001(2)x2	Se(4)-Bi(2)-Se(5)	178.12(9)
Bi(2)-Se(1)	3.141(3)		
Bi(3)-Se(2)	2.778(2)x2	Se(1)-Bi(3)-Se(1)	81.77(6)
Bi(3)-Se(4)	2.985(3)	Se(2)-Bi(3)-Se(2)	97.82(9)
Bi(3)-Se(3)	3.045(3)	Se(2)-Bi(3)-Se(1)	170.71(7)
Bi(3)-Se(1)	3.199(2)x2		
Bi(4)-Se(6)	2.767(2)x2	Se(6)-Bi(4)-Se(3)	81.80(8)
Bi(4)-Se(3)	2.850(3)	Se(5)-Bi(4)-Se(4)	103.98(8)
Bi(4)-Se(5)	3.166(2)x2	Se(6)-Bi(4)-Se(5)	167.4(1)
Bi(4)-Se(4)	3.172(4)		
Cs-Se(2)	3.666(4)		
Cs-Se(6)	3.682(3)x2		
Cs-Se(4)	3.732(3)x2		
Cs-Se(2)	3.841(3)x2		
Cs-Se(3)	3.843(3)		
Cs-Se(5)	3.993(4)		

BaBi_2Se_4 (IV)

and consists of CdI_2

$\text{BaBi}_2\text{S}_4^{21}$ has a sim

NaCl -type blocks w

$\text{SrBi}_2\text{Se}_3^{22}$ and BaBi_2Q

$\text{EuBi}_2\text{S}_4^{41}$ adopt the

tunnels that are parti

cell edges parallel to

wide) CdI_2 -type one

through them. This

discussed earlier.

BaBi₂Se₄ (IV). This compound adopts the hexagonal β -BaBi₂S₄²¹ structure type and consists of CdI₂-type and NaCl-type infinite rods, as shown in Figure 2-4. α -BaBi₂S₄²¹ has a similar structure but the NaCl-type part is shorter in length. Similar NaCl-type blocks with the same thickness but different lengths are also found in SrBiSe₃²² and BaBiQ₃^{6,24} (Q = Se, Te). Several other compounds such as SrBi₂S₄²¹ and EuBi₂S₄⁴¹ adopt the same structure type whose main characteristic is the existence of tunnels that are partially occupied by the divalent atoms. These tunnels are located at the cell edges parallel to the c-axis and form by connecting together six narrow (2 Bi atom wide) CdI₂-type one-dimensional infinite rods. The tunnels have 6₃ screw axes running through them. This structure type presents some intricate features, which have not been discussed earlier.

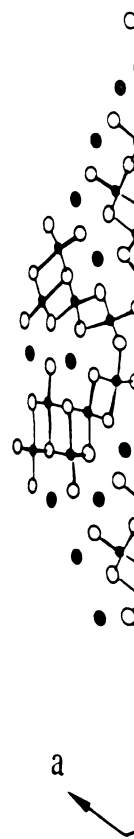


Figure 2-4. Proj
indicate the NaCl

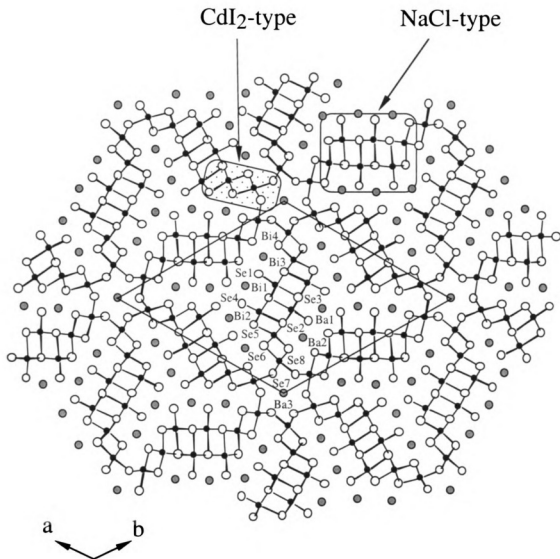


Figure 2-4. Projection of the structure of BaBi_2Se_4 down the c -axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.

Table 2-9. Bond D

Ba(1)-Se(1)	2
Ba(1)-Se(3)	2
Ba(1)-Se(2)	3
Ba(1)-Se(3)	3
Ba(2)-Se(4)	2
Ba(2)-Se(5)	2
Ba(2)-Se(3)	3
Ba(2)-Se(2)	3
Ba(3)-Se(8)	
Ba(3)-Se(6)	
Ba(3)-Se(2)	
Ba(3)-Se(5)	
Ba(4)-Se(7)	
Ba(4)-Se(7)	
Ba(4)-Se(6)	
Ba(4)-Se(8)	
Ba(1)-Se(1)	
Ba(1)-Se(4)	
Ba(1)-Se(4)	
Ba(1)-Se(5)	
Ba(1)-Se(3)	
Ba(2)-Se(1)	
Ba(2)-Se(8)	
Ba(2)-Se(6)	
Ba(2)-Se(2)	
Ba(2)-Se(5)	
Ba(3)-Se(7)	
Ba(3)-Se(7)	
Ba(3)-Ba(3)	

Table 2-9. Bond Distances (Å) and Selected Angles (deg) for BaBi₂Se₄.

Bi(1)-Se(1)	2.703(1)	Se(2)-Bi(1)-Se(3)	85.68(3)
Bi(1)-Se(3)	2.917(1)x2	Se(3)-Bi(1)-Se(3)	95.70(4)
Bi(1)-Se(2)	3.054(1)x2	Se(3)-Bi(1)-Se(2)	175.07(4)
Bi(1)-Se(3)	3.516(2)		
Bi(2)-Se(4)	2.664(1)	Se(3)-Bi(2)-Se(2)	84.02(3)
Bi(2)-Se(5)	2.8278(9)x2	Se(4)-Bi(2)-Se(3)	95.05(3)
Bi(2)-Se(3)	3.179(1)x2	Se(4)-Bi(2)-Se(2)	178.72(4)
Bi(2)-Se(2)	3.505(1)		
Bi(3)-Se(8)	2.791(1)	Se(6)-Bi(3)-Se(5)	80.46(3)
Bi(3)-Se(6)	2.9246(9)x2	Se(6)-Bi(3)-Se(6)	95.35(4)
Bi(3)-Se(2)	2.997(1)x2	Se(6)-Bi(3)-Se(2)	175.89(4)
Bi(3)-Se(5)	3.057(1)		
Bi(4)-Se(7)	2.858(2)	Se(7)-Bi(4)-Se(7)	82.38(8)
Bi(4)-Se(7)	2.861(1)x2	Se(7)-Bi(4)-Se(7)	98.20(6)
Bi(4)-Se(6)	2.963(1)	Se(7)-Bi(4)-Se(6)	173.54(6)
Bi(4)-Se(8)	3.026(10)x2		
Ba(1)-Se(1)	3.268(1)x2		
Ba(1)-Se(4)	3.285(1)x2		
Ba(1)-Se(4)	3.354(1)x2		
Ba(1)-Se(5)	3.435(2)		
Ba(1)-Se(3)	3.607(2)		
Ba(2)-Se(1)	3.246(1)x2		
Ba(2)-Se(8)	3.303(1)x2		
Ba(2)-Se(6)	3.363(1)x2		
Ba(2)-Se(2)	3.441(2)		
Ba(2)-Se(5)	3.480(2)		
Ba(3)-Se(7)	3.083(2)x3		
Ba(3)-Se(7)	3.766(2)x6		
Ba(3)-Ba(3)	2.1623(2)x2		

All Br a

the compounds

fragment have

bond at 2.703(1

at 3.516(2) Å.

2.8278(9)-3.17

distorted with

respectively.

The Ba

prismatic coord

3.246(1)-3.480

(and its symm

3.766(2) Å. ac

Both Ba(3) an

and U11 for

symmetry equ

site is 0.1666

maximum all

which corres

All Bi atoms have distorted octahedral coordination, similar to what is found in the compounds described above. Bi(1) and Bi(2) that are in the interior of the NaCl-type fragment have a similar distortion towards a square pyramid. Bi(1) has one short Bi-Se bond at 2.703(1) Å, four bonds between 2.917(1)-3.054(1) Å and one long Bi-Se distance at 3.516(2) Å. Similarly, Bi(2) has a short bond at 2.664(1) Å, four bonds between 2.8278(9)-3.179(1) Å and a long Bi-Se distance at 3.505(1) Å. Bi(3) and Bi(4) are less distorted with Bi-Se distances of 2.791(1)-3.057(1) Å and 2.858(2)-3.026(1) Å respectively.

The Ba atoms that reside between the NaCl-type blocks have a bicapped trigonal prismatic coordination with Ba-Se distances between 3.268(1)-3.607(2) Å for Ba(1) and 3.246(1)-3.480(2) Å for Ba(2). The Ba(3) atom situated in the tunnels interacts with Se(7) (and its symmetry equivalents) and has three distances at 3.083(2) Å and six distances at 3.766(2) Å, adopting essentially a tricapped trigonal prismatic coordination (Table 2-9). Both Ba(3) and Se(7) have one large anisotropic displacement parameter, U₂₂ for Ba(3) and U₁₁ for Se(7). This is because the Ba(3) is partially occupied and generates a symmetry equivalent at 2.1623(2) Å away. The full theoretical occupancy for the Ba(3) site is 0.16667 but since this creates symmetry equivalent atoms at a close distance, the maximum allowed occupancy is 0.08333 (50%). The observed occupancy was 0.07266, which corresponds to 44% of the full occupancy of this site. The final formula of the

compound is $\text{Ba}_{1.07}\text{Bi}_2\text{Se}_4$, resulting in an excess of 0.07 Ba^{2+} or 0.14 positive charge per formula. This excess of Ba (0.07) corresponds to the Ba atoms found inside the tunnels. If we assume that the atomic sites elsewhere in the structure are fully occupied then the charge is balanced (i.e. BaBi_2Se_4) and the Ba atoms in the tunnels are not needed. The same degree of excess metal cations was also found in EuBi_2S_4 and $\beta\text{-BaBi}_2\text{S}_4$, which actually have crystallographically refined formulas $\text{Eu}_{1.1}\text{Bi}_2\text{S}_4$ and $\text{Ba}_{1.07}\text{Bi}_2\text{S}_4$ respectively. Attempts to refine the occupancy of the other metal positions in the BaBi_2Se_4 structure did not reveal any specific atomic sites to have vacancies. However if the vacancies needed to neutralize the 0.07 Ba^{2+} charge were distributed over all metal sites, their effect on the diffraction properties would be almost negligible making it extremely difficult to detect them by X-ray crystallography. If we accept for a moment that $\text{Ba}_{1.07}\text{Bi}_2\text{Se}_4$ is the correct formula then the $[\text{Bi}_2\text{Se}_4]$ framework is partially reduced and this should lead to a metallic material. This not the case, however, as the material exhibits an energy band-gap and its electrical conductivity is only moderate in the range of semiconductors. Based on these observations we believe the existence of these partially occupied channels is important for the stabilization of the structure.

Energy gaps. All compounds described here are semiconductors as indicated by the presence of energy gaps detected directly by infrared spectroscopy. Both $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$

and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ have a clear band gap of ~ 0.45 eV whereas the gap is greater for $\text{CsBi}_{3.67}\text{Se}_6$, at ~ 0.53 eV and smaller for BaBi_2Se_4 at ~ 0.32 eV, see Figure 2-5. The origin of these electronic transitions is thought to be similar to that in Bi_2Se_3 , which involves charge transfer from Se p-levels in the valence band to low lying empty Bi^{3+} p-orbitals in the conduction band. $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ have lower band gaps compared to α and β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$, which at room temperature have gaps of ~ 0.76 eV and ~ 0.59 eV respectively.

$\text{CsBi}_{3.67}\text{Se}_6$ has a very similar size band gap to the isostructural α - $\text{CsPbBi}_3\text{Se}_6$, which has a band gap of ~ 0.55 eV. Interestingly, the band gap of BaBi_2Se_4 is very close to that of Bi_2Se_3 (0.26 eV). The size of the band gap in $\text{CsBi}_{3.67}\text{Se}_6$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ seems to correlate with the $\text{Cs}_2\text{Se}/\text{Bi}_2\text{Se}_3$ ratio in their formula so that as the ratio decreases the band gap also decreases. This relationship has been discussed more extensively in the $\text{A}_2\text{Q}/\text{CdQ}$ systems.⁴²

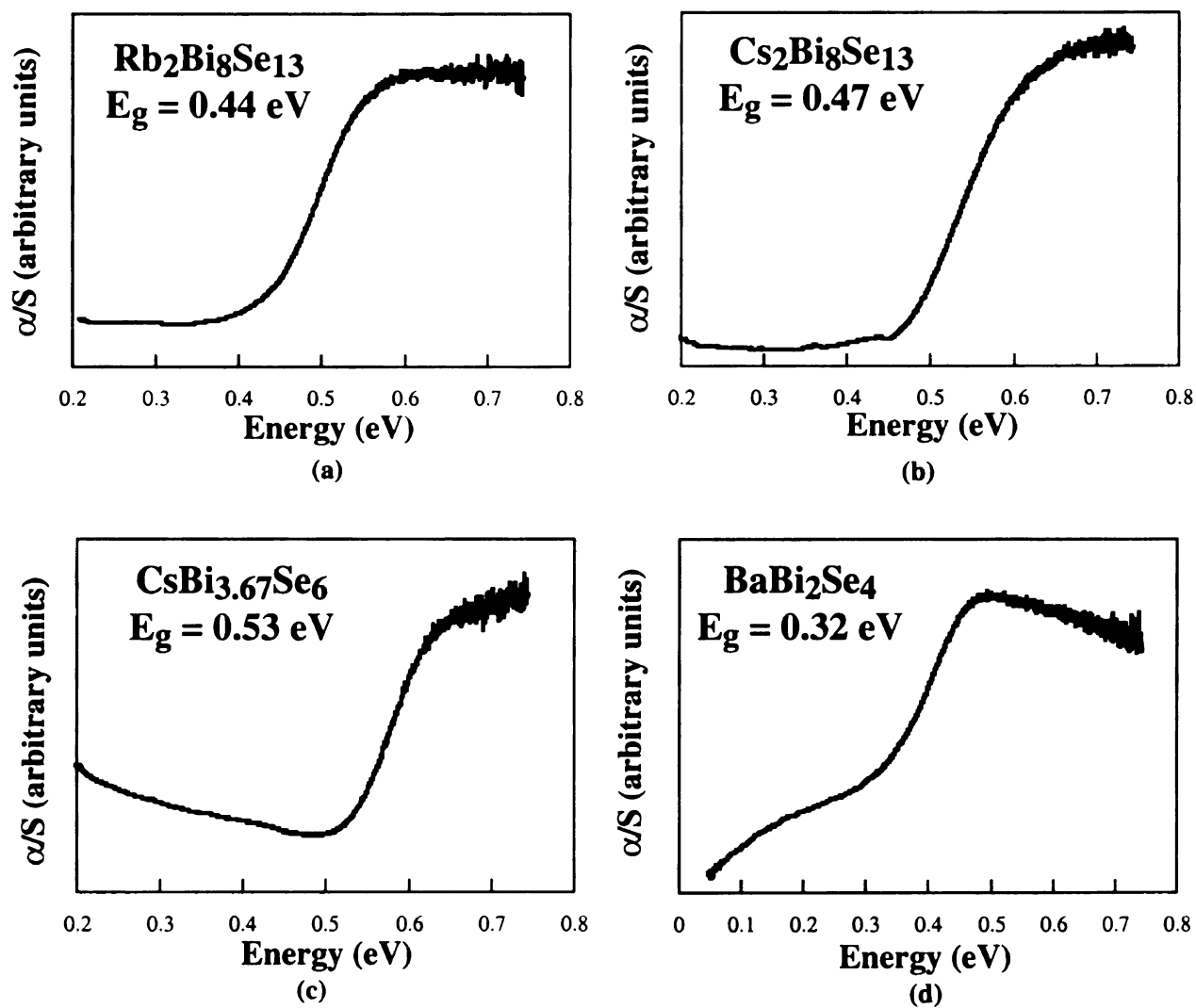


Figure 2-5. Infrared absorption spectra showing band gap transitions for (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, (b) $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$, (c) $\text{CsBi}_{3.67}\text{Se}_6$, and (d) BaBi_2Se_4 .

Charge transport properties. Temperature dependent electrical conductivity and thermoelectric power measurements were carried out on single crystals and polycrystalline oriented ingots (grown by the Bridgman technique)⁴³ of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$. The measurements were taken along the needle axis. The conductivity of single crystals of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ is generally low with room temperature values of ~ 10 S/cm, see Figure 2-6. However, the conductivity tended to vary somewhat from specimen to specimen reflecting differences in the doping state, which may arise from inadvertent inhomogeneities in the reaction mixture from which the crystals form. That these differences in conductivity are real and do not represent fluctuations in the experimental procedure are evident from the corresponding changes in thermopower. The conductivity of an oriented ingot of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ was slightly greater with a room temperature value of ~ 30 S/cm, see Figure 2-7. For the samples with low conductivity, the thermopower showed both very high positive and sometimes high negative values, even for samples from the same batch. The room temperature values were ~ 650 $\mu\text{V/K}$ for the p-type sample and -200 $\mu\text{V/K}$ for the n-type sample, see Figures 6 and 7. When higher values of conductivity ~ 80 S/cm were observed in different batches of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ the thermopower was lower, ~ 65 $\mu\text{V/K}$, see Figure 2-8. Nevertheless, all the conductivity plots have the same features having a slope change around 100 K and reaching a

maximum at low temperatures below 50 K. Although the values of electrical conductivity and thermopower are characteristic of semiconductors the temperature dependence of electrical conductivity and thermopower of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ show a metal-like behavior, similar to what is observed in narrow band gap semiconductors.

The electrical conductivity of single crystals of $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ was found to be even lower than the Rb analog with room temperature values of ~ 0.5 S/cm, see Figure 2-9. As with $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, samples with both high positive and high negative thermopower were observed. The room temperature values were ~ 200 $\mu\text{V/K}$ for the p-type sample and ~ -300 $\mu\text{V/K}$ for n-type sample, see Figure 2-10. The temperature dependence of the electrical conductivity and thermopower are consistent with semiconducting behavior.

The values of electrical conductivity and thermopower for $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) are similar to those of $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$.¹ Compared to $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ the $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) compounds exhibit equal or greater thermopower but their conductivities are considerably lower. At room temperature the thermopower of $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ⁴⁴ is ~ -220 $\mu\text{V/K}$ and its electrical conductivity ~ 250 S/cm. Consequently, the power factor of $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ (undoped) at 300K is 12 $\mu\text{W/cm}^2\text{K}$ and increasing at higher temperatures, whereas $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ exhibits a maximum at 150-200 of only 3.3 $\mu\text{W/cm}^2\text{K}$, Figure 2-

11. Summarizing, β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ outperforms $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ in thermoelectric performance mainly because of its higher electrical conductivity. Initial attempts to dope $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ with Sn and Sb did not drastically change the electrical behavior of the material and were not pursued. If we can improve the electrical conductivity of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ through appropriate doping without significant loss in the thermopower then this could be a promising thermoelectric material. An advantage of $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ($\text{A} = \text{Rb}, \text{Cs}$) over β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ is that these materials exhibit both an n- and p-type behavior, something that is important since a thermoelectric device requires both the n- and p-type form of the material to operate.

Crystals of $\text{CsBi}_{3.67}\text{Se}_6$ also exhibited a very low room temperature electrical conductivity similar to those of $\text{A}_2\text{Bi}_8\text{Se}_{13}$ at ~ 1 S/cm, see Figure 2-12. The temperature dependence of the conductivity shows signs of thermally activated transport typical of non-degenerate semiconductor. The room temperature thermopower was ~ -160 $\mu\text{V/K}$, see Figure 2-13. Some attempts were made to dope $\text{CsBi}_{3.67}\text{Se}_6$ in order to increase its electrical conductivity. Samples with 0.005 mol% SbBr_3 added, resulted in an increase of the conductivity to ~ 20 S/cm at room temperature, see Figure 2-12. These measurements were done on single crystals of the material prepared by the quenching technique

described above. By comparison the isostructural compound α -CsPbBi₃Se₆¹⁰ also has a low room temperature conductivity of 0.6 S/cm and a room temperature thermopower of $-730 \mu\text{V/K}$. While the conductivity of quenched CsBi_{3.67}Se₆ samples is very similar to that of α -CsPbBi₃Se₆ their thermopower values are considerably smaller.

For BaBi₂Se₄ temperature dependent electrical conductivity and thermoelectric power measurements were carried out on polycrystalline oriented ingots grown by the Bridgman technique.⁴³ Again, the measurements were done along the needle (c-) axis. The conductivity was higher than those of the previous compounds with a room temperature value of $\sim 130 \text{ S/cm}$, Figure 2-14. The thermopower is lower with a room temperature value of $-95 \mu\text{V/K}$, Figure 2-14. An interesting feature of the thermopower is that it increases as the temperature decreases reaching a maximum of $-150 \mu\text{V/K}$ at 100 K. The temperature dependence of the electrical conductivity and thermopower indicates that BaBi₂Se₄ is an n-type narrow gap semiconductor.

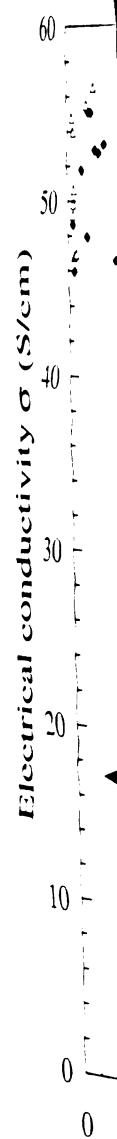


Figure 2-6. V
crystals of Rb_2

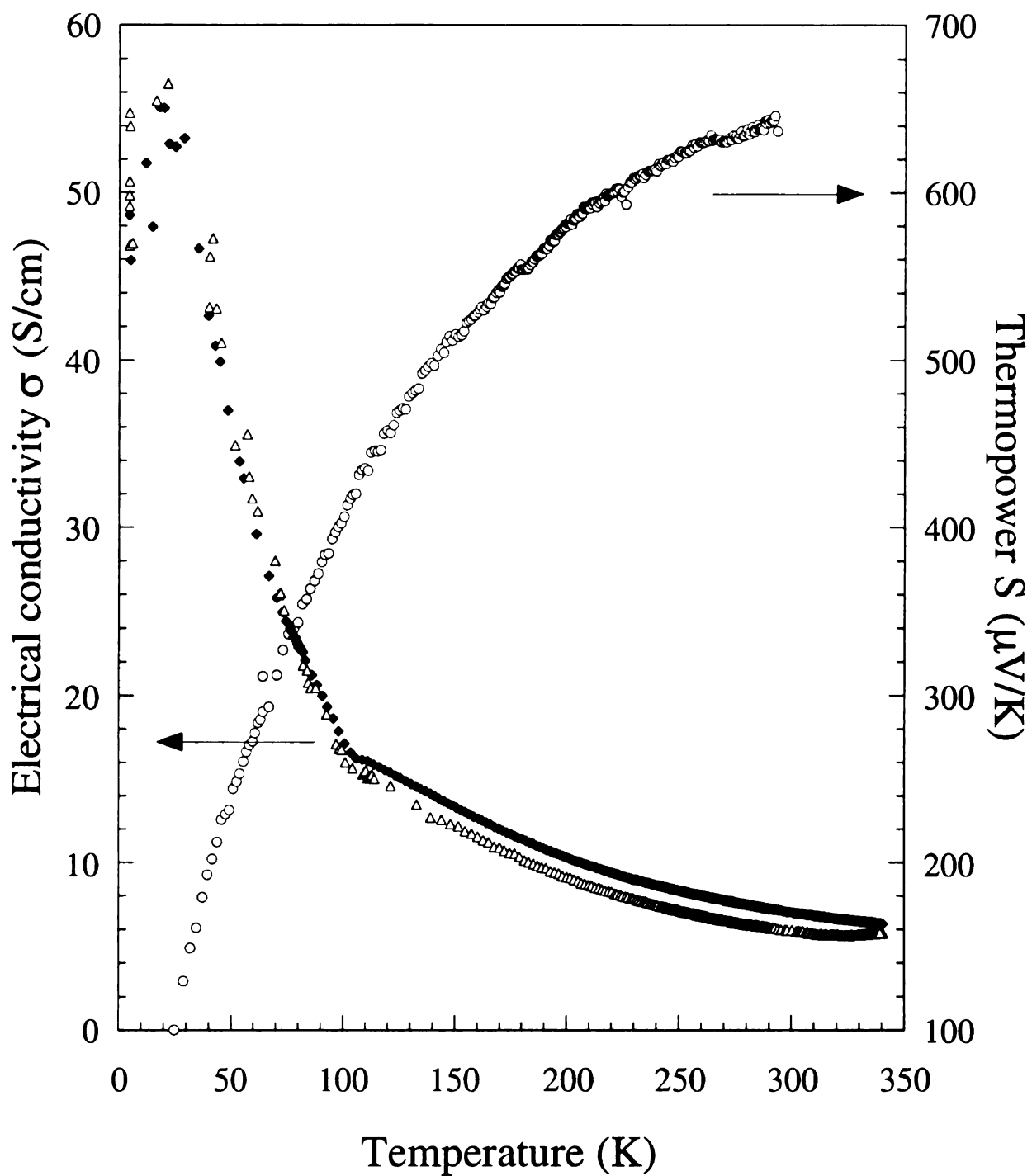


Figure 2-6. Variable temperature electrical conductivity and thermopower for single crystals of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$.

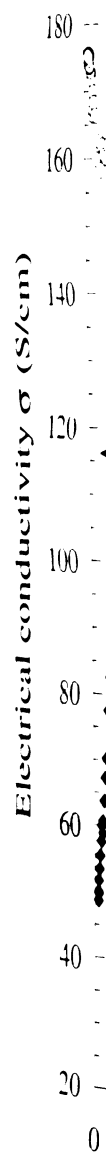


Figure 2-7. Va

Polycrystalline

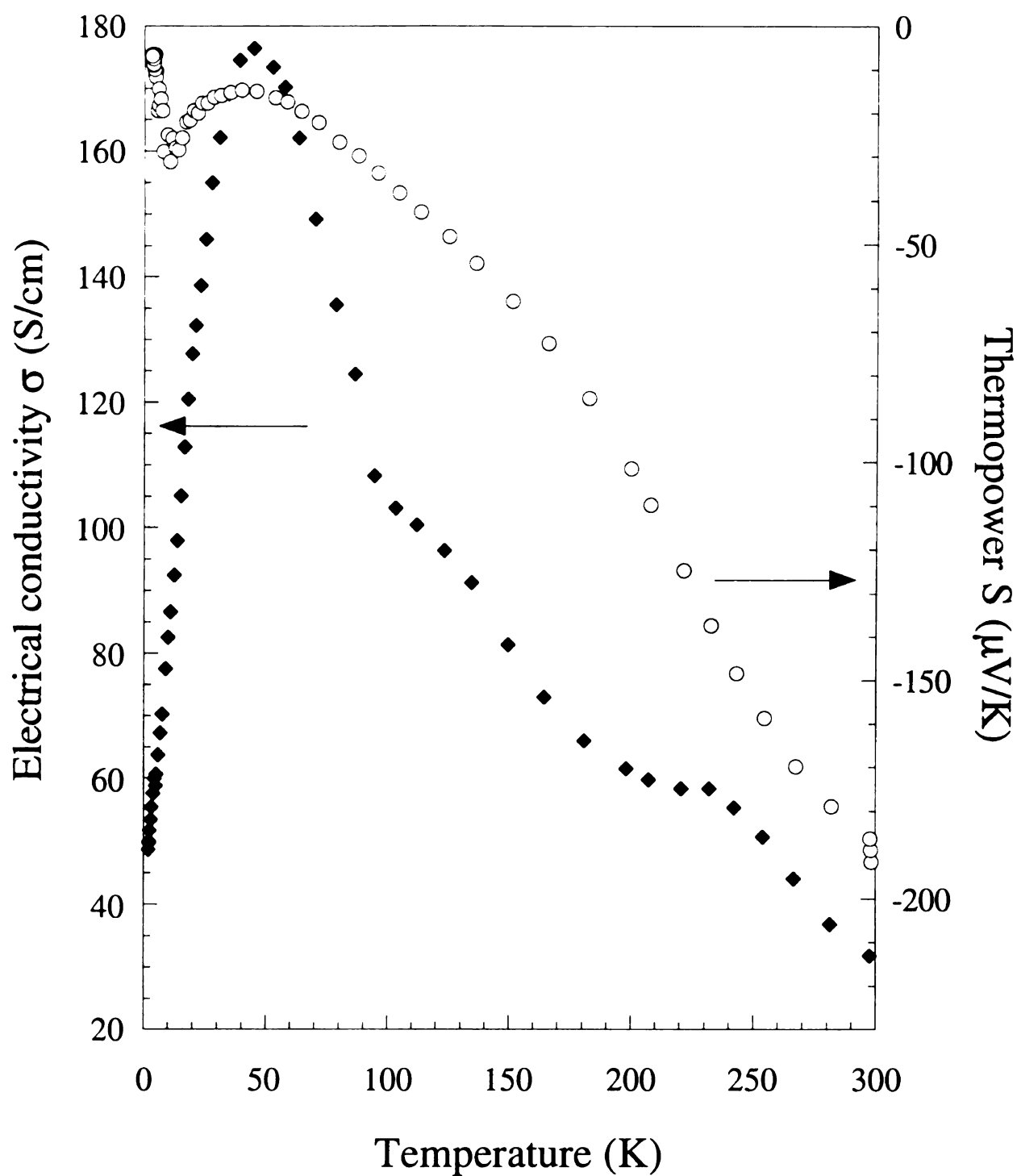


Figure 2-7. Variable temperature electrical conductivity and thermopower for oriented polycrystalline samples of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$.

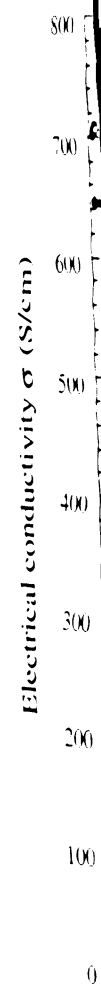


Figure 2-8. V
polycrystalline s

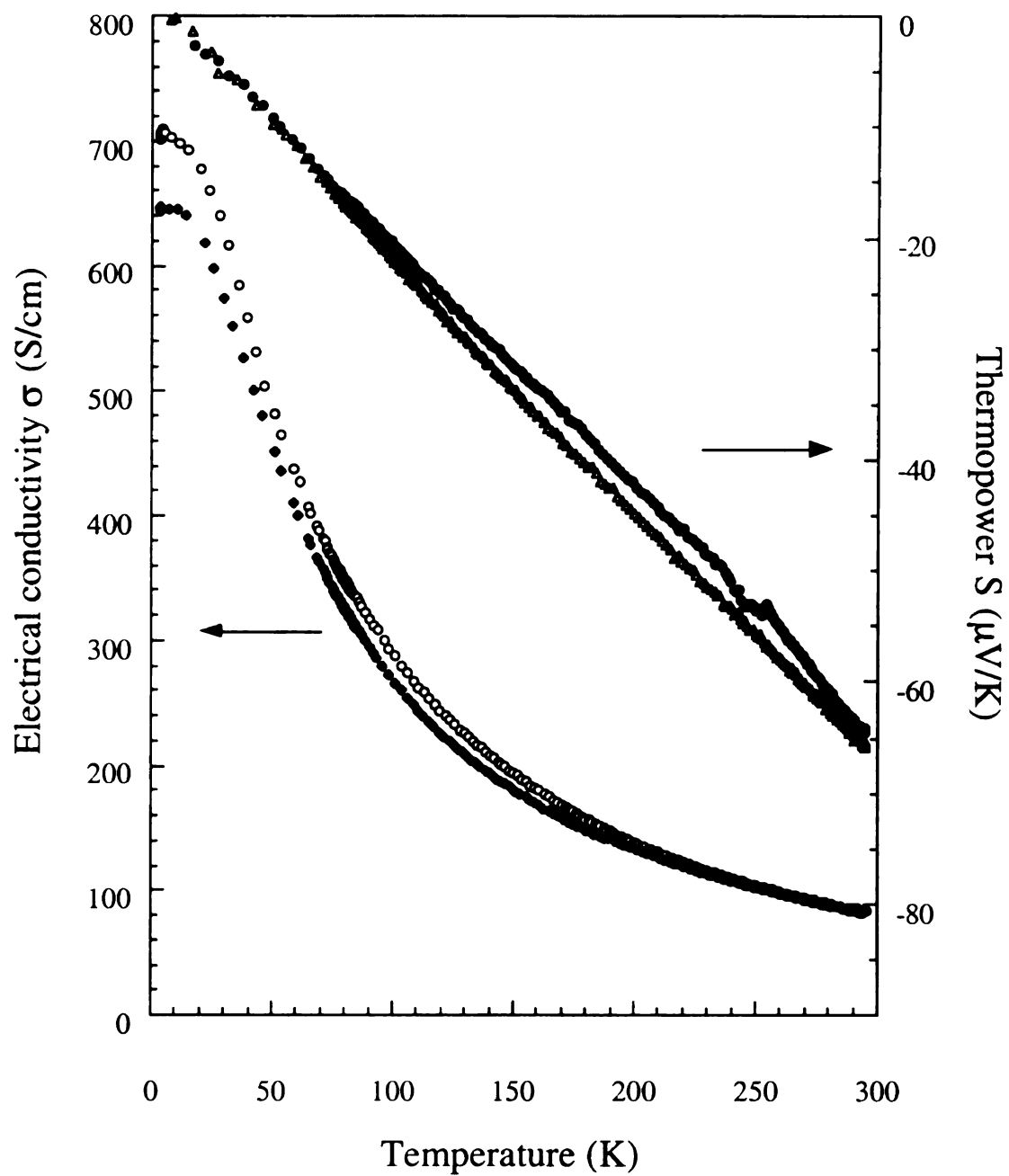


Figure 2-8. Variable temperature electrical conductivity and thermopower for polycrystalline samples of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$.

Electrical conductivity σ (S/cm)

1

0.01

10^{-4}

10^{-6}

10^{-8}

10^{-10}

10^{-12}

0

Figure 2-9. Variation of electrical conductivity with temperature for polycrystalline

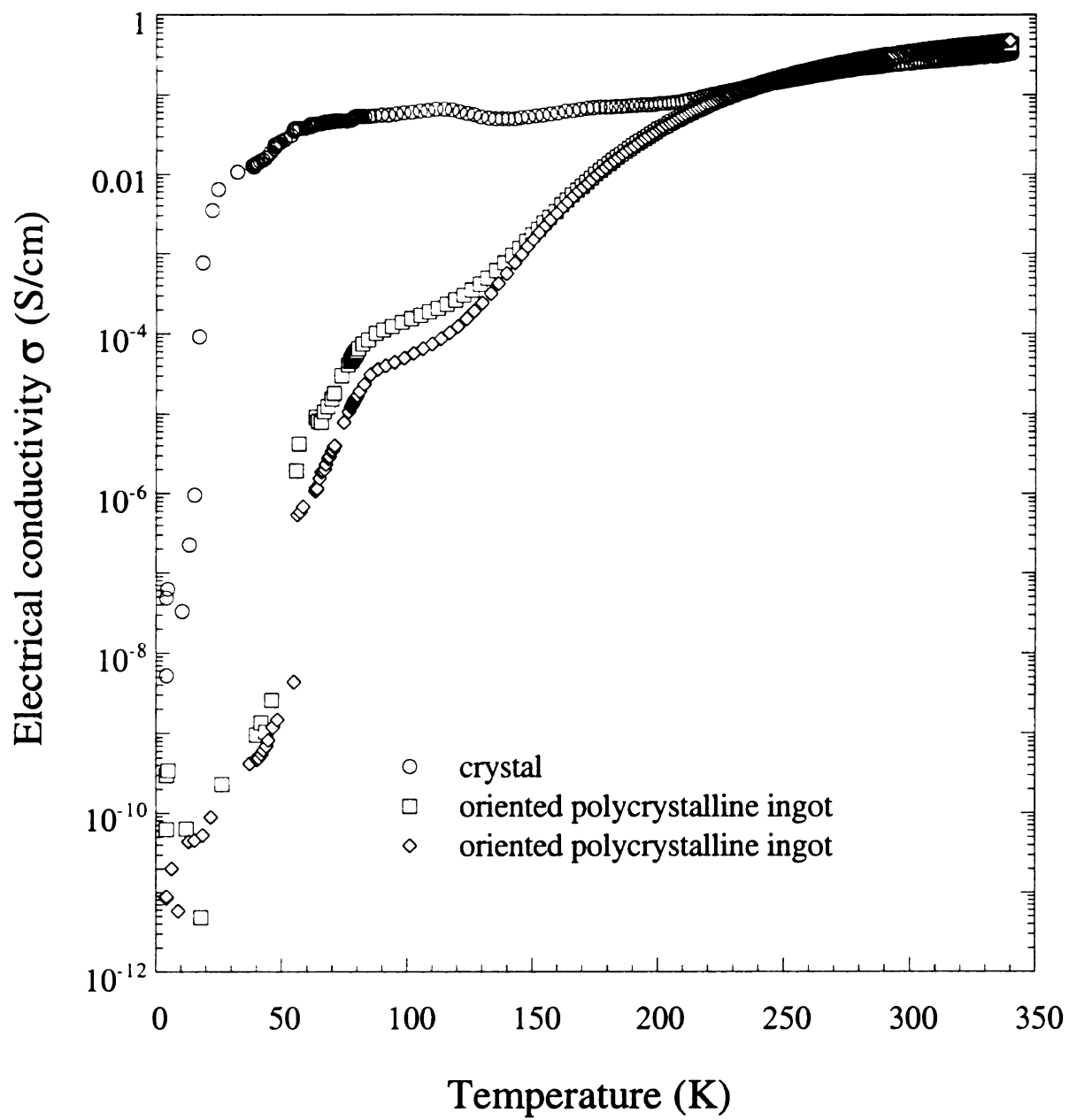


Figure 2-9. Variable temperature electrical conductivity for single crystals and oriented polycrystalline samples of $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$.

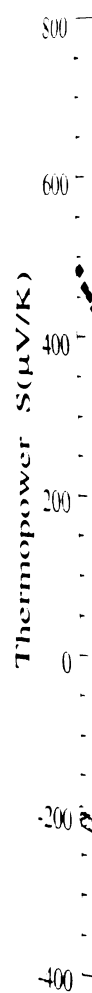


Figure 2-10. S vs T for

$\text{Cs}_3\text{Bi}_4\text{Se}_{13}$ showing

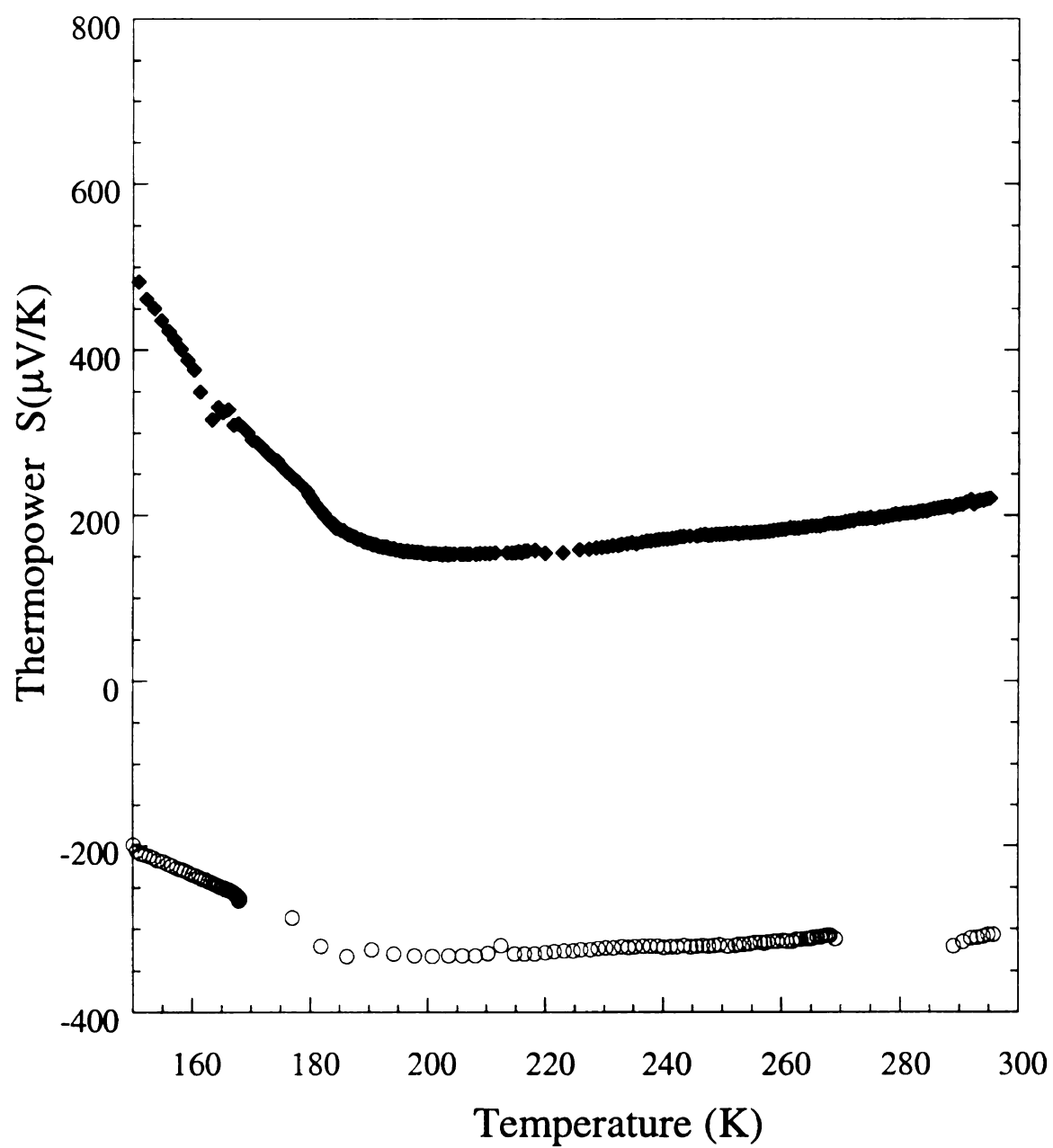


Figure 2-10. Variable temperature thermopower for oriented polycrystalline samples of $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$ showing both the n-type and p-type behavior.

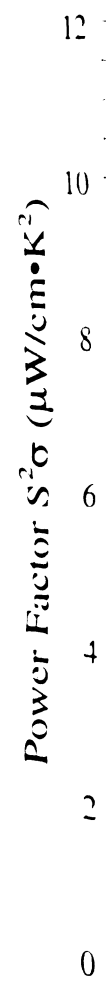
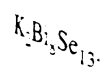


Figure 2-11. V



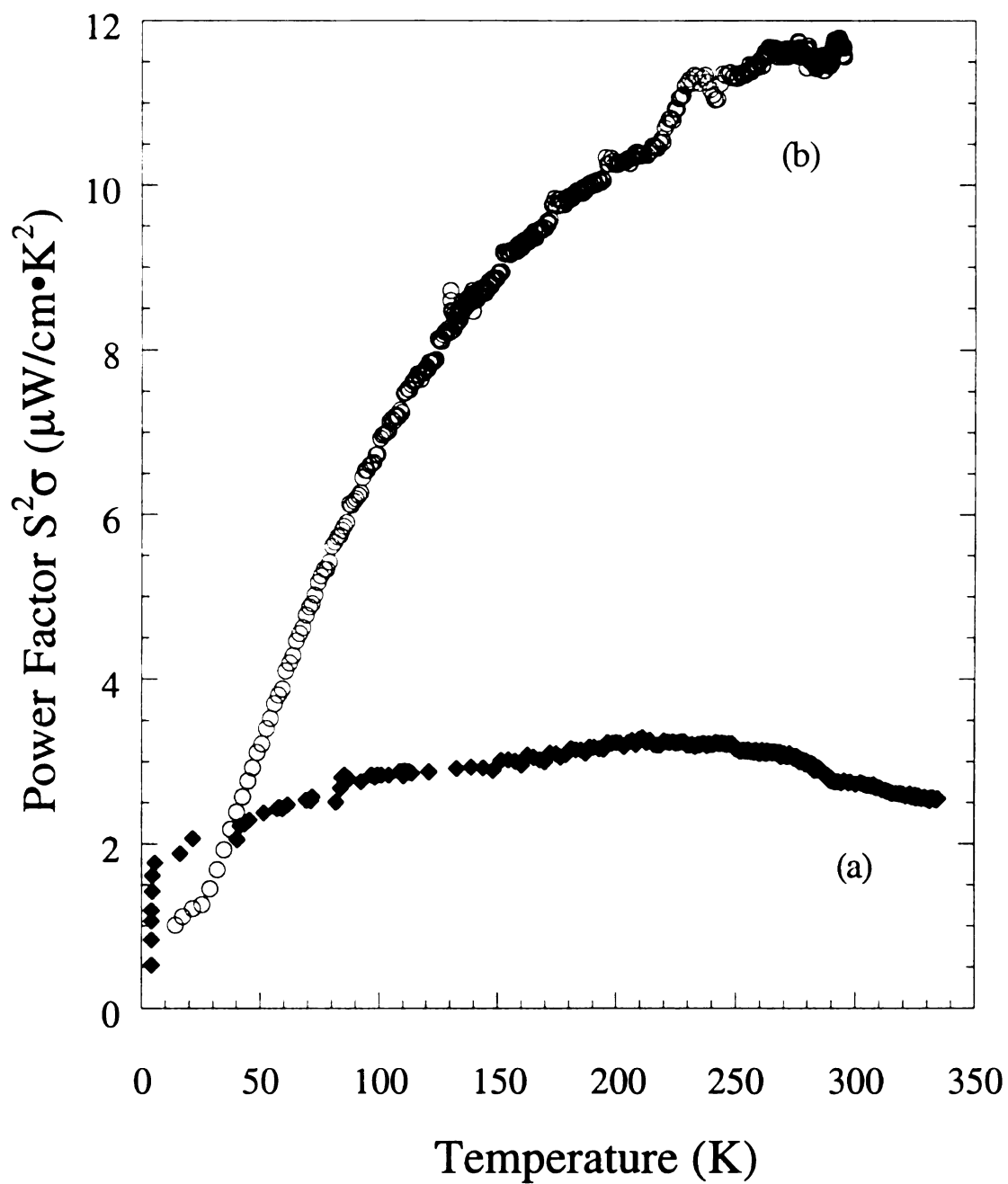


Figure 2-11. Variable temperature power factor ($\sigma \cdot S^2$) for (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and (b) $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$.

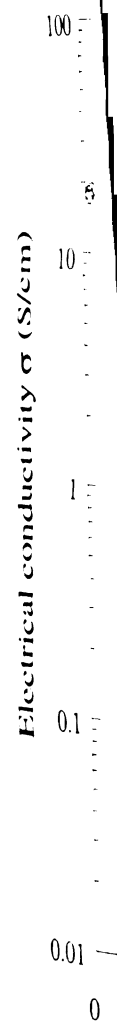


Figure 2-12. Var

undoped singl

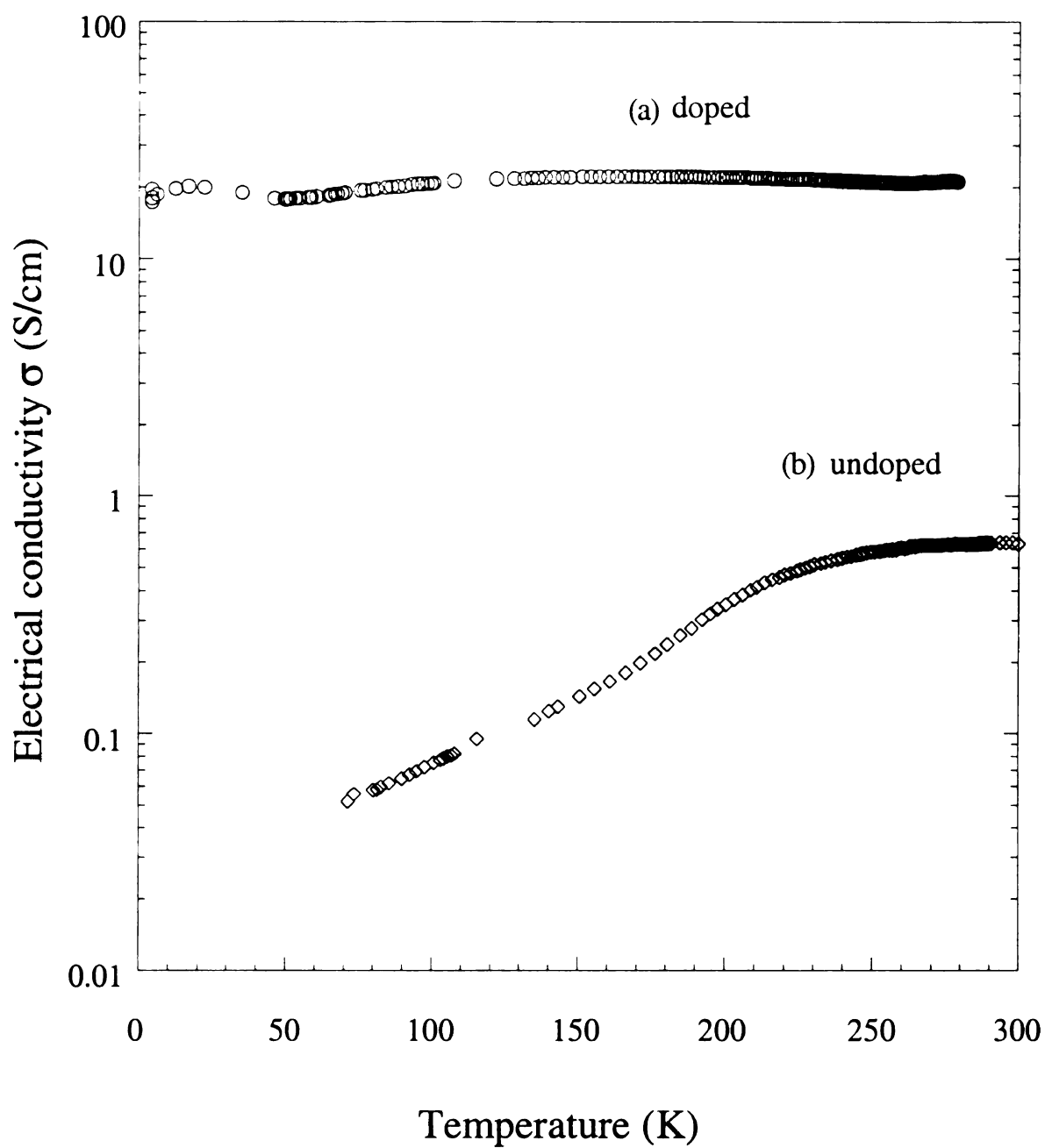


Figure 2-12. Variable temperature electrical conductivity for (a) doped with SbBr_3 and (b) undoped single crystals of $\text{CsBi}_{3.67}\text{Se}_6$ prepared by the quenching technique.

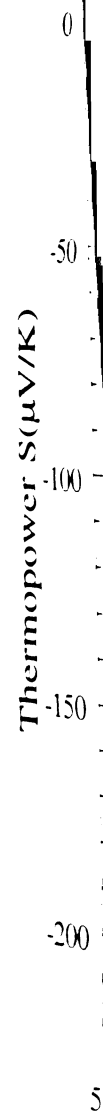


Figure 2-13. V_a

$\text{CsBi}_{1/6}\text{Se}_6$ prepared

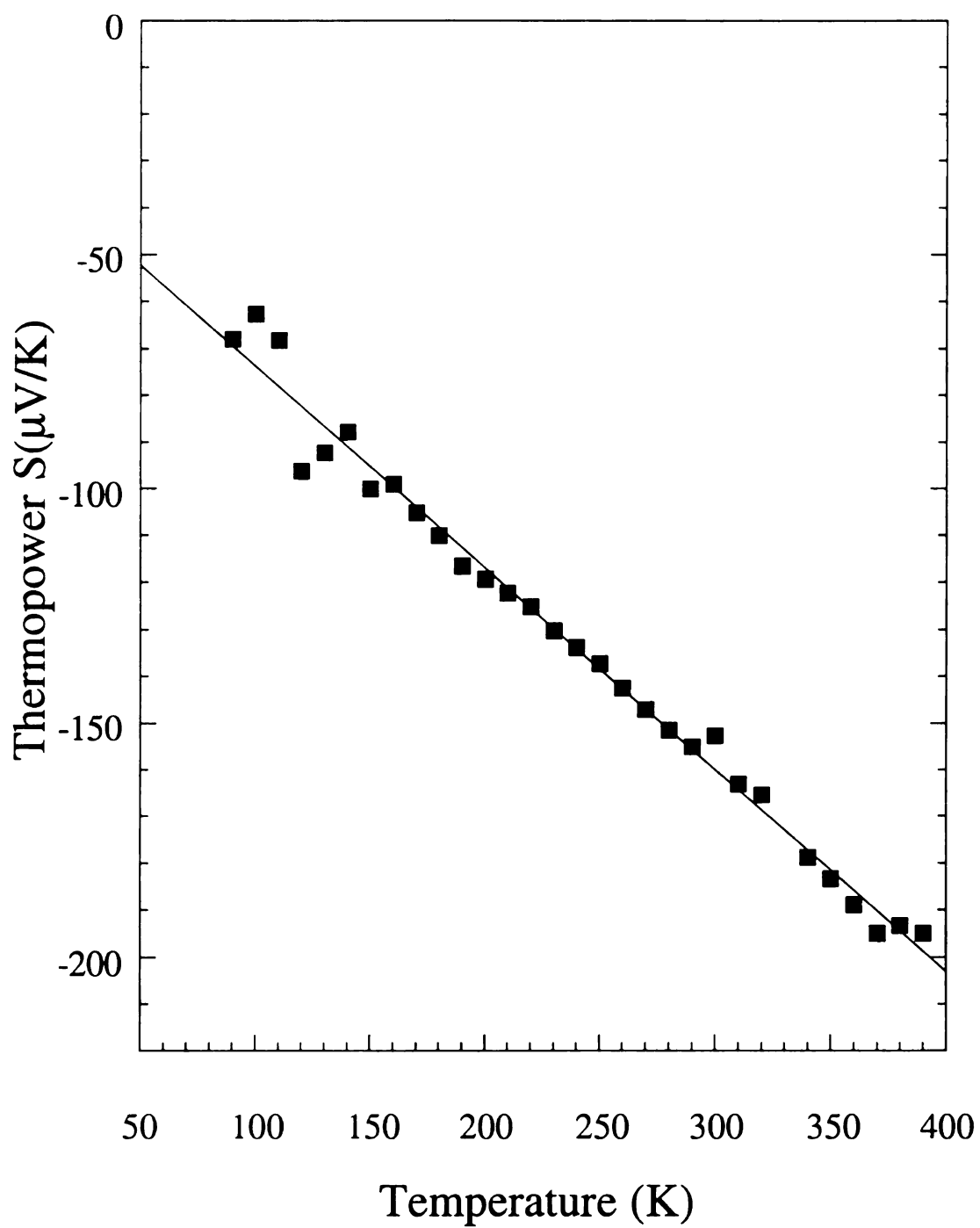


Figure 2-13. Variable temperature thermopower for polycrystalline samples of $\text{CsBi}_{3.67}\text{Se}_6$ prepared by the quenching technique.

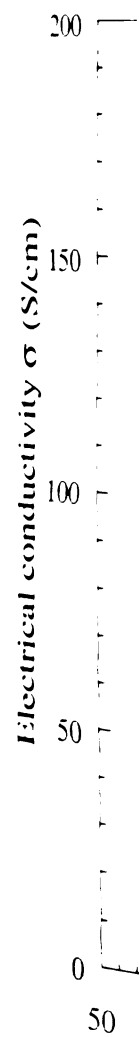


Figure 2-14. V
mented polycry

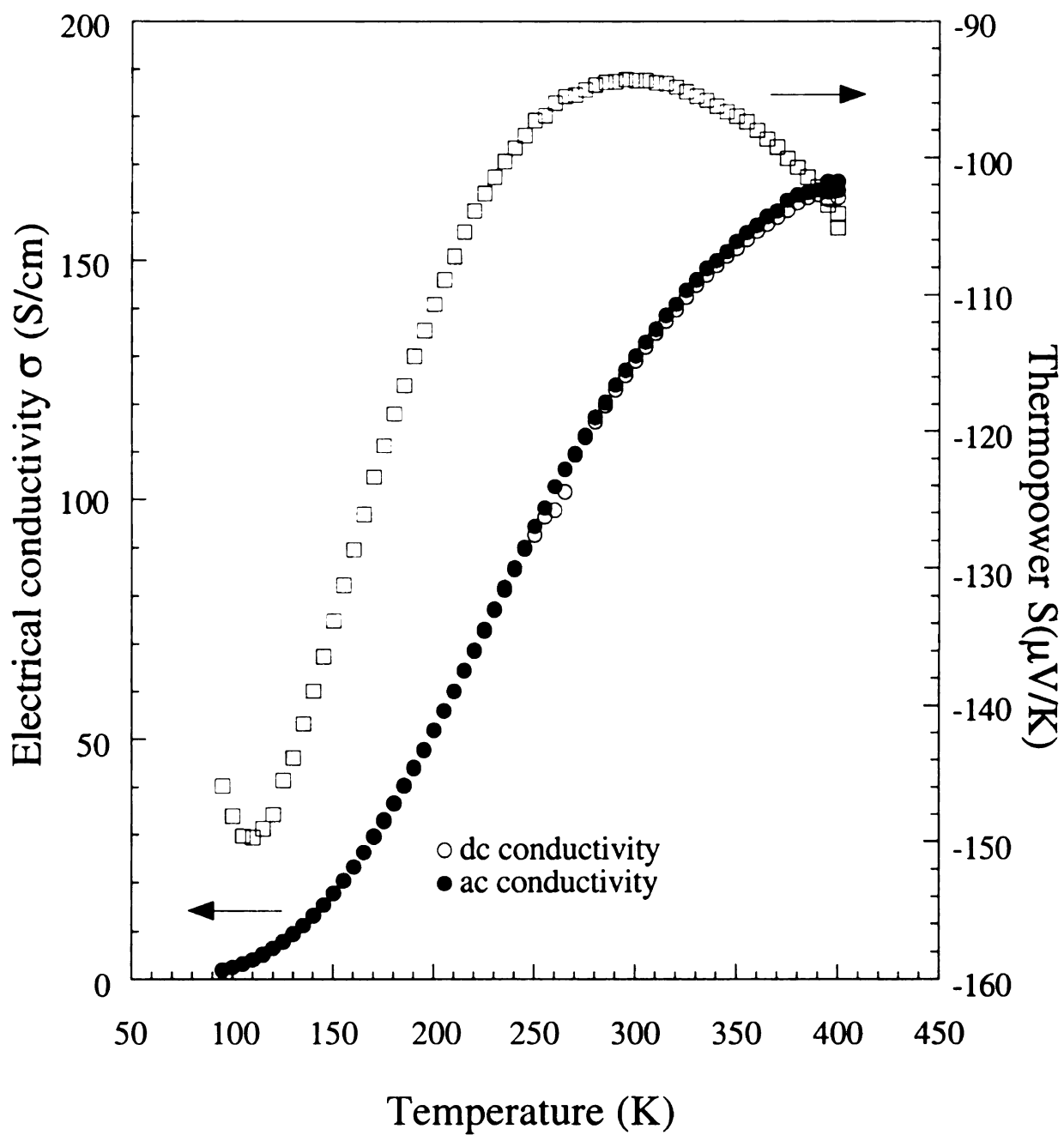


Figure 2-14. Variable temperature electrical conductivity and thermopower for an oriented polycrystalline ingot of BaBi_2Se_4 .

Thermal

along the growth

are displayed

temperature the

Good crystal

temperature.

phonon-phonon

that of optimum

quaternary b

thermal conduct

1.3-1.4 W/m

contribution

BaB

of ~1.2 W/m

Thermal conductivity. The thermal conductivity of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ was measured along the growth direction (b-axis) on a specimen cut from an oriented ingot. The data are displayed in Figure 15 as a function of temperature from 5 K to 300 K. At room temperature the thermal conductivity of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ is low with a value of 1.6 W/m·K. Good crystalline character of the material is revealed by a pronounced peak at low temperature. It arises as a consequence of interplay between the boundary scattering and phonon-phonon Umklapp process.⁴⁵ The value of thermal conductivity is very close to that of optimized Bi_2Te_3 alloy (1.5 W/m·K)⁴⁶ and reaffirms the fact that the ternary and quaternary bismuth chalcogenides^{3,12,25} can possess very low thermal conductivities. Its thermal conductivity is only slightly higher of that of $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ which has a value of 1.3-1.4 W/m·K at room temperature. The thermal conductivity is dominated by its lattice contribution with the electronic term representing not more than 1% of the total value.

BaBi_2Se_4 exhibits a very low thermal conductivity with a room value temperature of ~1.2 W/m·K, Figure 2-15.



Figure 2-15

$\text{Rb}_2\text{Bi}_3\text{Se}_{13}$

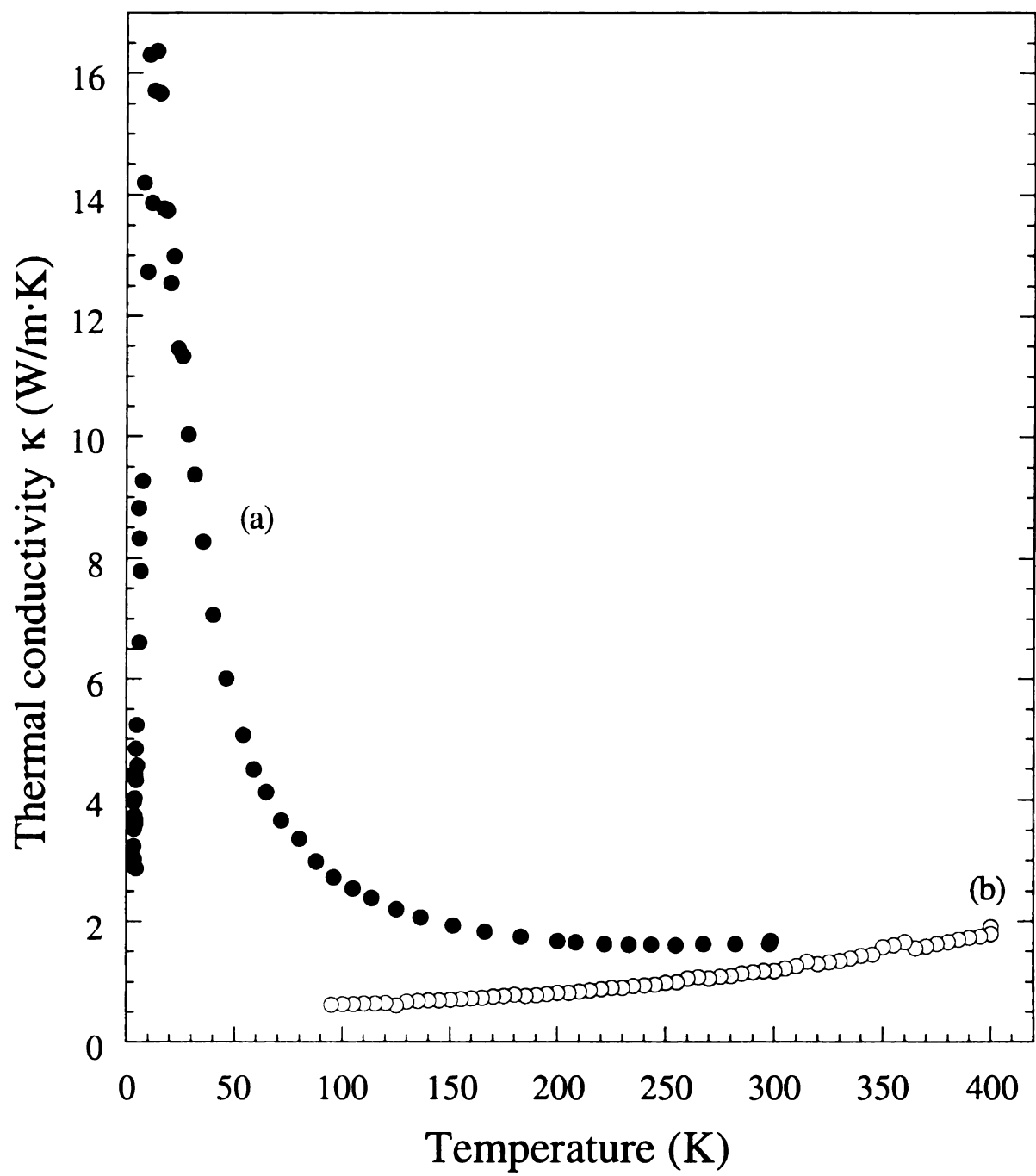


Figure 2-15. Variable temperature thermal conductivity for an oriented ingot of (a) $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ and (b) BaBi_2Se_4 .

5. Concluding

Four n

$\text{Cs}_2\text{Bi}_3\text{Se}_{13}$, C

gaps between

and very high

electrical co

thermopowe

exhibit n-type

for thermoe

CsB

electrical c

conductivity

current prop

BaB

very low th

thermopow

improved

5. Concluding Remarks

Four new ternary bismuth chalcogenides have been synthesized $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$, $\text{Cs}_2\text{Bi}_8\text{Se}_{13}$, $\text{CsBi}_{3.67}\text{Se}_6$ and BaBi_2Se_4 . All compounds are semiconductors with band gaps between 0.3-0.6 eV. $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ has a very low thermal conductivity of 1.6 W/m·K and very high thermopower, however, its electrical conductivity is very low. Clearly its electrical conductivity will have to be improved without a significant loss in thermopower and this may be achievable through appropriate doping. Both compounds exhibit n-type and p-type behavior an important property if a material is to be developed for thermoelectric applications.

$\text{CsBi}_{3.67}\text{Se}_6$ exhibits an n-type semiconducting behavior and has very low electrical conductivity. Doping experiments with SbBr_3 increased the electrical conductivity but not to the extent that is needed for thermoelectric applications. With its current properties, $\text{CsBi}_{3.67}\text{Se}_6$ is not a suitable candidate for thermoelectric purposes.

BaBi_2Se_4 can be described as an n-type narrow band gap semiconductor and has a very low thermal conductivity of 1.2 W/m·K, lower than that of optimized Bi_2Te_3 . Its thermopower and electrical conductivity values are promising but have to be further improved for thermoelectric applications. The structure type of this compound is

attractive because it is very stable and forms with a variety of other metals such Sr and some lanthanides. In addition, the fact that both the S and Se analogs are stable should lead to solid solutions with even lower thermal conductivities.

References

1. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
2. McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301.
3. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474.
(b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.
4. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
5. Iordanidis, L.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1928-1930.
6. Chung, D.-Y.; Jobic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
7. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science (Washington, D. C.)* **2000**, *287*, 1024-1027.
8. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162.
9. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805.
10. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
11. Mrotzek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.

-
12. Choi, K.-S.; Chung, D.-Y.; Mrozek, A.; Brazis, W.; Kannewurf, C. R.; Kanatzidis, M. G. *submitted for publication*.
 13. Adouby, K.; Perez Vicente, C.; Jumas, J. C.; Fourcade, R.; Abba Touré, A. Z. *Kristallogr.* **1998**, *213*, 343-349.
 14. Perez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Abba Touré, A.; Kra, G. *Inorg. Chem.* **1999**, *38*, 2131-2135.
 15. Choe, W.; Lee, S.; O'Connell, P.; Covey A. *Chem. Mater.* **1997**, *9*, 2025-2030.
 16. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011-1017.
 17. (a) Glemser, O.; Filcek, M. Z. *Anorg. Allg. Chem.* **1955**, *279*, 321-323. (b) Gattow, G.; Zemmann, J. Z. *Anorg. Allg. Chem.* **1955**, *279*, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, *6*, 961-964. (d) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, *8*, 677-678. (e) Peresh, E. Y.; Golovei, M. I.; Berul, S. I. *Inorg. Mater.* **1971**, *7*, 27-30.
 18. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, *252*, 96-99.
 19. Schmitz, D.; Bronger, W. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29*, 438-439.
 20. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 676-683.
 21. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 399-407.
 22. Cook, R.; Schäfer, H. *Rev. Chim. Miner.* **1982**, *19*, 19-27.
 23. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 631-638.
 24. Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 136-140.
 25. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Hogan, T.; Kannewurf, C. R.; Iordanidis, L. *Mater. Res. Soc. Symp. Proc.* **1996**, *410*, 37-43. (b)

-
- Chung, D.-Y.; Hogan, T.; Schindler, J.; Iordanidis, L.; Brazis, P.; Kannewurf, C. R.; Chen, B.; Uher, C.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **1997**, 478, 333-344. (c) Iordanidis, L.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **1999**, 545, 189-196. (d) Kanatzidis, M. G.; Chung, D.-Y.; Iordanidis, L.; Choi, K.-S.; Brazis, P.; Rocci, M.; Hogan, T.; Kannewurf, C. *Mater. Res. Soc. Symp. Proc.* **1999**, 545, 233-246.
26. The thermoelectric figure of merit is defined as: $ZT = (S^2\sigma/\kappa)T$; where S is the thermopower, σ the electrical conductivity, κ the thermal conductivity and T is the temperature. The numerator $S^2\sigma$ is called the power factor. All three of these properties are determined by the details of the electronic structure and scattering of charge carriers (electrons or holes) and thus are not independently controllable parameters. κ also has a contribution from lattice vibrations, κ_l , the phonon thermal conductivity. Thus $\kappa = \kappa_e + \kappa_l$, where κ_e is the carrier thermal conductivity.
27. *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995 and references there in.
28. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, 59, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, 63, 45-89. (c) Makovicky, E. *Z. Kristallogr.* **1985**, 173, 1-23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, 160, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, 5, 545-591.
29. (a) Chung, D.-Y.; Iordanidis, L.; Choi, K.-S.; Kanatzidis, M. G. *Bull. Korean Chem. Soc.* **1998**, 19, 1283-1293. (b) Kanatzidis, M. G, *Semicond. Semimet.* **2000**, in press.
30. (a) Slack, G. A. "New Materials and Performance Limits for Thermoelectric Cooling" in *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995, pp. 407-440. (b) Slack, G. A. *Solid State Physics*; Ehrenreich, H.;

-
- Seitz, F.; Turnbull, D., Ed.; Academic Press: New York, **1997**, 34, 1.
31. Brazis, P. W.; Ireland, J. R.; Lane, A.; Kyratsi, T.; M.; Chung, D.-Y; Kanatzidis, M. G.; Kannewurf, C. R. *Mat. Res. Soc. Symp Proc.* **2000**, in press.
32. (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Kotüm, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969. (c) Tandon, S. P.; Gupta, J. P. *Phys. Status Solidi.* **1970**, 38, 363-367.
33. (a) Lyding, J. W.; Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instrum. Meas.* **1988**, 37, 76-80. (b) Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instrum. Meas.* **1990**, 39, 756-760.
34. Hogan, T.; Ghelani, N.; Loo, S.; Sportouch, S.; Kim, S.-J.; Chung, D.-Y; Kanatzidis, M. G. *Proc. Int. Conf. Thermoelectr.* **1999**, 18th, 671-674.
35. Maldonado, O. *Cryogenics* **1992**, 32, 908-912.
36. LabVIEW, Version 5.0, National Instruments, Austin, TX, 1999.
37. CERIU², Version 3.8., Molecular Simulations Inc, Cambridge, England, 1999.
38. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.
39. (a) Iordanidis, L.; Kanatzidis, M. G., Work in progress. (b) A compound with the formula $\text{Ba}_3\text{Bi}_{6.67}\text{Se}_{13}$ having the same structure type was reported recently, see reference 16.
- 40 This suggests that in $\alpha\text{-CsPbBi}_3\text{Se}_6$, the Bi(4) site is more likely to be a Pb atom with the rest of the sites being Bi atoms. However, a disorder of Pb/Bi atoms over all metal sites in the structure cannot be ruled out since Pb and Bi due to their close chemical resemblance and similar X-ray scattering properties cannot be crystallographically distinguished.

-
41. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, *C42*, 259-261.
 42. (a) Axtell, E. A.; Liao, J.-H.; Pikramenou, Z.; Park, Y.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12191-12192. (b) Axtell, E. A.; Liao, J.-H.; Pikramenou, Z.; Park, Y.; Kanatzidis, M. G. *Chem. Eur. J.* **1996**, *2*, 656-666.
 43. Kyratsi, T.; Chung, D.-Y.; Choi, K.-S.; Dick, J. S.; Chen, W.; Uher, C.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **2000**, in press.
 44. Brazis, P. W.; Rocci-Lane, A. M.; Ireland, J. R.; Chung, D.-Y.; Kanatzidis, M. G.; Kannewurf, C. R. *Proc. Int. Conf. Thermoelectr.* **1999**, *18th*, 619-622.
 45. The lattice thermal conductivity follows a T^3 law at very low temperatures, and a T^{-1} law at higher temperatures. These different dependencies reflect the contributions of boundary scattering and phonon/phonon Umklapp scattering mechanisms respectively.
 46. Encyclopedia of Materials Science and Engineering; Thermoelectric Semiconductors; MIT Press: Cambridge, MA; Pergamon Press: Oxford, 1986; p 4968.

CHAPTER 3

Structural Complexity in the ABi_3Q_5

(A = Rb, Cs; Q = S, Se, Te) Systems

1. Introduction

In the past decade extensive investigations in the ternary and quaternary bismuth chalcogenide systems uncovered a large number of new compounds¹⁻¹⁶ expanding significantly this previously limited class of materials.¹⁷ One of the important motivations for this work is the potential of complex bismuth chalcogenides as useful thermoelectric materials.¹⁸ These compounds however are also interesting because of the great structural and compositional diversity that they exhibit¹⁹. These characteristics are found in the natural occurring sulfosalts, which include many bismuth chalcogenides. There are several reasons for this unparalleled diversity and complexity. One main reason is the different coordination environments that bismuth can adopt which is affected by the stereochemical expression or suppression of the so-called bismuth $6s^2$ lone pair.

Although bismuth atoms usually exhibit a distorted octahedral geometry they also adopt a variety of other coordination polyhedra ranging from trigonal pyramidal e.g. in β - CsBiS_2 ¹, to square pyramidal e.g. in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ ¹³, to trigonal prismatic e.g. in $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ ⁸ (A = K, Rb; Ln = La, Ce, Pr, Nd). A second reason has to do with the propensity of the BiQ_6 (Q = S, Se, Te) octahedra to combine with each other by sharing edges forming a variety of building blocks, the most common ones being the NaCl-, Bi_2Te_3 -²⁰ and CdI_2 -²⁰ type and occasionally the Sb_2Se_3 -type fragment. Furthermore each of the above mentioned blocks comes in different sizes creating even more structural possibilities, e.g. NaCl-type building blocks are found both in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ ¹³ and BaBi_2Se_4 ¹³, but in the former the NaCl-type block is 2x3 bismuth atoms large while in the latter is 3x1 bismuth atoms large. A third reason for the structural diversity is the mixed occupancy bismuth atoms can display with a variety of similar sized ions such as alkali^{3,4} or alkaline earth¹⁶ metals, Pb^{10,12,16,19}, Sn^{11,12,16,19} or lanthanides⁸. Usually the mixed occupancy and consequently disorder is found in the high coordination capped trigonal prismatic sites that connect the blocks of BiSe_6 octahedra together. These characteristics enable the formation of a seemingly "countless" number of phases.

An example of the above mentioned structural diversity and complexity is found in the six new compounds with the general formula ABi_3Q_5 ($\text{A} = \text{Rb}, \text{Cs}$; $\text{Q} = \text{chalcogen}$) reported in this work. Another member of this family, KBi_3S_5 with excellent ion-exchange properties was reported earlier.² We present here the synthesis, physicochemical, spectroscopic, and structural characterization of $\gamma\text{-RbBi}_3\text{S}_5$, $\alpha\text{-RbBi}_3\text{Se}_5$, $\beta\text{-RbBi}_3\text{Se}_5$, $\gamma\text{-RbBi}_3\text{Se}_5$, CsBi_3Se_5 and $\text{RbBi}_3\text{Se}_4\text{Te}$. These compounds crystallize in four different structure types.

2. Experimental section

Reagents. Chemicals were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999% Noranda, Canada), sulfur powder, sublimed, (Spectrum Chemical Mfg. Corp., Gardena, CA), selenium powder (99.95 % purity, -200 mesh, Cerac Inc., Milwaukee), selenium shots (99.999% Noranda, Canada), bismuth selenide powder (99.999% purity, -325 mesh, Cerac Inc., Milwaukee), bismuth telluride powder (99.999% purity, -325 mesh, Cerac Inc., Milwaukee), rubidium metal (99.8% purity, Alfa Aesar, Ward Hill, MA), cesium metal (99.98% purity, Alfa

Aesar, Ward Hill, MA). A_2Q ($A = \text{Rb, Cs}$; $Q = \text{S, Se}$) was prepared by a stoichiometric reaction of the corresponding alkali metal and chalcogen in liquid ammonia.

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All the products were washed with degassed methanol and ether to remove any traces of excess flux. For all compounds the yield was quantitative and the purity and homogeneity of the samples was verified by comparing the X-ray powder diffraction patterns to those calculated by X-ray single crystal diffraction.

Bi_2S_3 . A mixture of 11.633 g (0.056 mol) of Bi and 2.677 g (0.083 mol) of S was transferred into a quartz tube, which was flame-sealed under vacuum. The tube was heated to 650 °C in 48 h, stayed at 650 °C for 2 days and then cooled down to 50 °C in 10 h. The product was ground into powder and used for further reactions.

Bi_2Se_3 . A mixture of 9.407 g (0.045 mol) of Bi and 5.331 g (0.068 mol) of Se was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 600 °C in 12 h, stayed at 600 °C for 2 days and then cooled down to 50 °C in 6 h. The product was ground into powder and used for further reactions.

$\gamma\text{-RbBi}_3\text{S}_5$ (I). A mixture of 0.050 g (0.246 mmol) Rb_2S and 0.380 g (0.739 mmol) Bi_2S_3 was transferred to a carbon-coated silica tube which was flame-sealed under

vacuum. The

furthermore c

like crystals.

electron micr

$\text{Rb}_{1.04}\text{Bi}_{2.93}\text{S}_3$

$\alpha\text{-RbBi}$

mmol) g Bi_2Se_3

The tube was se

and then further

made of hair-li

several needles

$\beta\text{-RbBi}_2$

mmol) g Bi_2Se_3

The tube was p

then the tube w

of a silvery ingo

ratio) as evidence

vacuum. The tube was heated for 1 day at 800 °C, then cooled to 500 °C in 30 h and furthermore cooled to 50 °C in 10 h. The product consisted of silvery-gray thin needle-like crystals. Semiquantitative energy dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of $\text{Rb}_{1.04}\text{Bi}_{2.93}\text{S}_5$.

$\alpha\text{-RbBi}_3\text{Se}_5$ (II). A mixture of 0.060 g (0.240 mmol) Rb_2Se and 0.456 g (0.696 mmol) Bi_2Se_3 was transferred to a carbon crucible which was inserted into a silica tube. The tube was sealed under vacuum, heated at 780 °C for 72 h, cooled to 475 °C in 60 h and then further cooled to 50 °C in 8 h. The product consisted of a silvery-black chunk made of hair-like thin needles. SEM/EDS using a scanning electron microscope on several needles gave an average composition of $\text{Rb}_{1.16}\text{Bi}_{3.19}\text{Se}_5$.

$\beta\text{-RbBi}_3\text{Se}_5$ (III). A mixture of 0.060 g (0.240 mmol) Rb_2Se and 0.393 g (0.600 mmol) Bi_2Se_3 was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a gas-oxygen torch until the sample melted and then the tube was removed from the flame and was let to solidify. The product consisted of a silvery ingot. The above synthesis produces a mixture with $\gamma\text{-RbBi}_3\text{Se}_5$ (approx. 1:1 ratio) as evidenced from X-ray powder diffraction.

γ -RbB

mmol) g Bi₂S

The tube was

then the tube

procedure was

a silvery ingot

electron micros

CsBi₃Se

mmol) g Bi₂Se₃

consisted of a s

needles gave an

RbBi₃Se

mmol) Bi₂Se₃ an

tube which was

cooled to 400 °C

silvery-gray thin

microscope on se

γ -RbBi₃Se₅ (IV). A mixture of 0.122 g (0.488 mmol) Rb₂Se and 0.700 g (1.069 mmol) g Bi₂Se₃ was transferred to a silica tube which was flame-sealed under vacuum. The tube was place under the flame of a gas-oxygen torch until the sample melted and then the tube was removed from the flame and was let to solidify (i.e. quench). The procedure was repeated two more times to ensure homogeneity. The product consisted of a silvery ingot with needle morphology across its surface. SEM/EDS using a scanning electron microscope on several needles gave an average composition of Rb_{1.21}Bi_{3.05}Se₅.

CsBi₃Se₅ (V). A mixture of 0.040 g (0.116 mmol) Cs₂Se and 0.227 g (0.347 mmol) g Bi₂Se₃ was prepared and heated the same way as in the case of (II). The product consisted of a silvery chunk. SEM/EDS using a scanning electron microscope on several needles gave an average composition of Cs_{0.86}Bi_{3.04}Se₅.

RbBi₃Se₄Te (VI). A mixture of 0.050 g (0.200 mmol) Rb₂Se, 0.305 g (0.466 mmol) Bi₂Se₃ and 0.107 g (0.134 mmol) Bi₂Te₃ was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 3 days at 700 °C, cooled to 400 °C in 45 h and then cooled to 50 °C in 11 h. The product consisted of silvery-gray thin needle-like crystals. SEM/EDS analysis using a scanning electron microscope on several needles gave an average composition of Rb_{1.20}Bi₃Se_{4.05}Te_{1.02}.

RbBi₃

mmol) Bi₂Se₃

tube which w

cooled to 440

silvery-gray to

microscope on

3. Physical Me

The inst

Thermal Analy

that in Chapter

Solid-S

were made at r

monochromator

was equipped w

powder was used

the reflectance da

Single cry

RbBi₃Se₃Te₂ (VII). A mixture of 0.040 g (0.160 mmol) Rb₂Se, 0.175 g (0.267 mmol) Bi₂Se₃ and 0.171 g (0.212 mmol) Bi₂Te₃ was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 3 days at 740 °C, cooled to 440 °C in 45 h and then cooled to 50 °C in 11 h. The product consisted of silvery-gray thin needle-like crystals. SEM/EDS analysis using a scanning electron microscope on several needles gave an average composition of Rb_{0.99}Bi₃Se_{3.17}Te_{1.97}.

3. Physical Measurements

The instrument and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis*, *Infrared Spectroscopy* and *Powder X-ray diffraction* are the same as that in Chapter 2 (Section 3).

Solid-State UV/Vis Spectroscopy. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer operating in the 200-2500 nm region. The instrument was equipped with an integrating sphere and controlled by a personal computer. BaSO₄ powder was used as reference (100 % reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function²¹.

Single crystal X-ray crystallography. A Bruker (formerly Siemens) SMART

Platform CC

frames cover

to at a detect

acquisition an

SADABS²² an

SHELX97/SH

γ -RbBi

exposure time

reflections from

0.74 Å. Three b

crystallographic

8.1% respective

The fractional at

shown in Table 3

α -RbBi₃S

exposure time of

reflections (Table

three rubidium an

Platform CCD diffractometer was used for data collection. Several different sets of frames covering a random area of the reciprocal space were collected using 0.3° steps in ω at a detector-to-sample distance of ~ 5 cm. The SMART²² software was used for data acquisition and SAINT²² for data extraction. The absorption correction was done with SADABS²² and the structure solution (direct methods) and refinement was done with the SHELX97/SHELXTL²² package of crystallographic programs.

γ -RbBi₃S₅ (I). A hemisphere of data were collected (1282 frames) with an exposure time of 40 sec per frame. The final cell was calculated from 2343 [$I > 8\sigma(I)$] reflections from the actual data collection (Table 3-1). The resolution of the data set was 0.74 Å. Three bismuth atoms, one rubidium and five sulfur atoms were found to sit on a crystallographic mirror plane. After refinement, the R1 and wR2 values were 3.7% and 8.1% respectively. All the atoms were refined anisotropically (R1 = 2.9%, wR2 = 6.3%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-2.

α -RbBi₃Se₅ (II). Over a hemisphere of data were collected (1397 frames) with an exposure time of 35 sec per frame. The final cell was calculated from 2540 [$I > 10\sigma(I)$] reflections (Table 3-1). The resolution of the data set was 0.74 Å. Ten bismuth atoms, three rubidium and fifteen selenium atoms were found to sit on a crystallographic mirror

plane. After

the atoms were

coordinates at

β -RbBi

exposure time

reflections (T)

is isostructura

sites from (V)

and wR^2 value

peaks appear

assigned as R

atoms were r

crystallograph

formula of R

occupancies o

atomic coordin

3-5.

γ -RbBi

exposure time

plane. After refinement, the R1 and wR2 values were 5.7% and 12.3% respectively. All the atoms were refined anisotropically (R1 = 4.9%, wR2 = 9.9%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-3.

β -RbBi₃Se₅ (III). A full hemisphere of data were collected (2229 frames) with an exposure time of 50 sec per frame. The final cell was calculated from 3510 [I>8 σ (I)] reflections (Table 3-4). The resolution of the data set was 0.76 Å. Because the compound is isostructural with (V), (see below) the fractional atomic coordinates for the Bi and Se sites from (V) were used for initial refinement of the structure. After refinement, the R1 and wR2 values were 9.6% and 28.9% respectively. At this stage of the refinement, six peaks appear in the electron density map sitting between the layers. These peaks were assigned as Rb and their occupancy was refined (R1 = 7.7%, wR2 = 11.9%). All the atoms were refined anisotropically (R1 = 4.9%, wR2 = 11.0%). At this point, the crystallographically refined formula was Rb_{1.05}Bi₃Se₅, extremely close to the ideal formula of RbBi₃Se₅. When a general constraint was used to bring the sum of the occupancies of the Rb atoms to 1 there was no change in the R values. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-5.

γ -RbBi₃Se₅ (IV). A hemisphere of data were collected (1288 frames) with an exposure time of 80 sec per frame. The final cell was calculated from 959 [I>8 σ (I)]

reflections (

one rubidium

plane. After

the atoms we

coordinates a

CsBi_3Se_5

exposure time

reflections (Ta

the structure in

was solved suc

stage using a m

Bi and Se atom

the R1 and wR

electron density

and their occup

refined anisotro

$\text{Cs}_{1.02}\text{Bi}_3\text{Se}_5$ ver

the Cs atoms to

reflections (Table 3-6). The resolution of the data set was 0.78 Å. Three bismuth atoms, one rubidium and five selenium atoms were found to sit on a crystallographic mirror plane. After refinement, the R1 and wR2 values were 7.5% and 20.5% respectively. All the atoms were refined anisotropically (R1 = 6.2%, wR2 = 13.7%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-7.

CsBi₃Se₅ (V). A full sphere of data were collected (2060 frames) with an exposure time of 30 sec per frame. The final cell was calculated from 4679 [$I > 10\sigma(I)$] reflections (Table 3-4). The resolution of the data set was 0.74 Å. Initial attempts to solve the structure in $P2_1/m$ were not successful. The symmetry was lowered and the structure was solved successfully in Pm (only the Bi-Se framework was located). At a subsequent stage using a missing center utility in teXsan²³ a center of symmetry was found, the extra Bi and Se atoms were deleted and the structure was refined in $P2_1/m$. After refinement, the R1 and wR2 values were 18.1% and 41.1% respectively. Six peaks appear in the electron density map sitting in the space between the layers, these were assigned as Cs, and their occupancy was refined. (R1 = 10.9%, wR2 = 30.7%). All the atoms were refined anisotropically (R1 = 6.1%, wR2 = 13.4%). The formula at this point was Cs_{1.04}Bi₃Se₅ very close to the ideal CsBi₃Se₅. Constraints were used to bring the sum of the Cs atoms to the ideal amount with no significant change in the R values. The

fractional a

shown in Ta

RbBi

exposure tim

reflections (T

one rubidium

plane. After re

of the seleniu

$0.005 \text{ \AA}^2$ com

$0.014 \text{ \AA}^2$. The

the atoms were

the other three

the occupancy

did not change

change in the

occupied by Se.

parameters are s

fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-8.

RbBi₃Se₄Te (VI). A hemisphere of data were collected (1289 frames) with an exposure time of 45 sec per frame. The final cell was calculated from 1110 [$I > 10\sigma(I)$] reflections (Table 3-6). The resolution of the data set was 0.75 Å. Three bismuth atoms, one rubidium and five "selenium" atoms were found to sit on a crystallographic mirror plane. After refinement, the R1 and wR2 values were 8.6% and 16.8% respectively. Two of the selenium atoms had very small isotropic displacement parameters, $U_{\text{iso}} \sim 0.002$ - 0.005 Å^2 compared to the other three Se atoms which their U_{iso} varied between 0.011 - 0.014 Å^2 . These two Se atoms were disordered with Te (R1 = 7.7%, wR2 = 14.4%). All the atoms were refined anisotropically (R1 = 6.2%, wR2 = 10.3%). In order to check if the other three Se sites contain Te the Se occupancies were refined. For two of the sites the occupancy increased slightly to 0.52 (0.500 for full occupancy) and for the third atom did not changed at all (remained at 0.5). At the same time, there was no significant change in the R values therefore the remaining three chalcogen sites were left fully occupied by Se. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 3-9.

Table 3-1. C

Empirical formula
Formula weight
Temperature
Crystal system
Space group
Unit cell dimensions

Z, Volume, Å³

Density (calculated)

Absorption coefficient

F(000)

Crystal size, mm

θ range for data

Index ranges

Reflections collected

Independent reflections

Refinement method

Data / restraints

Goodness-of-fit

Final R indices

R indices (all data)

Extinction

Largest peak and

$$R1 = \sum |F_o| - |F_c|$$

Table 3-1. Crystallographic Data for γ -RbBi₃S₅ and α -RbBi₃Se₅.

	γ -RbBi ₃ S ₅ (I)	α -RbBi ₃ Se ₅ (II)
Empirical formula	γ -RbBi ₃ S ₅ (I)	α -RbBi ₃ Se ₅ (II)
Formula weight	872.71	1107.21
Temperature, K	173.1(1)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	Pnma	C2/m
Unit cell dimensions, Å	$a = 11.744(2)$ $b = 4.0519(5)$ $c = 21.081(3)$ -	$a = 36.779(4)$ $b = 4.1480(5)$ $c = 25.363(3)$ $\beta = 120.403(2)^\circ$
Z, Volume, Å ³	4, 1003.1(2)	12, 3337.3(7)
Density (calculated), g/cm ³	5.779	6.611
Absorption coefficient, mm ⁻¹	58.281	67.977
F(000)	1464	5472
Crystal size, mm ³	0.50 x 0.02 x 0.01	0.50 x 0.02 x 0.02
θ range for data collection	1.93 to 28.79°	1.64 to 28.77°
Index ranges	$-15 \leq h \leq 11$ $-5 \leq k \leq 5$ $-28 \leq l \leq 27$	$-46 \leq h \leq 47$ $-5 \leq k \leq 5$ $-34 \leq l \leq 22$
Reflections collected	5867	11280
Independent reflections	1383 [$R_{\text{int}} = 0.0376$]	4492 [$R_{\text{int}} = 0.0575$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1383 / 0 / 56	4492 / 0 / 165
Goodness-of-fit on F^2	1.095	0.954
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0289, wR2 = 0.0633	R1 = 0.0488, wR2 = 0.0988
R indices (all data)	R1 = 0.0428, wR2 = 0.0655	R1 = 0.0853, wR2 = 0.1070
Extinction	0.00064(6)	-
Largest peak and hole, e Å ⁻³	2.383 and -1.906	4.971 and -3.296

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 3-2.

($\text{\AA}^2 \times 10^3$) for

Bi(1)

Bi(2)

Bi(3)

Rb(1)

S(1)

S(2)

S(3)

S(4)

S(5)

U_{eq} is defined

Table 3-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-RbBi}_3\text{S}_5$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	-0.1324(1)	0.2500	0.1432(1)	11(1)
Bi(2)	0.1798(1)	0.2500	0.0260(1)	12(1)
Bi(3)	0.1470(1)	-0.2500	0.1914(1)	12(1)
Rb(1)	0.5040(1)	-0.2500	0.1080(1)	23(1)
S(1)	0.3053(3)	-0.2500	-0.0242(2)	15(1)
S(2)	0.2850(3)	0.2500	0.1330(2)	12(1)
S(3)	0.0083(3)	0.2500	0.2400(2)	12(1)
S(4)	0.0173(3)	-0.2500	0.0810(2)	12(1)
S(5)	0.2432(3)	-0.2500	0.3122(2)	13(1)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\alpha\text{-RbBi}_3\text{Se}_5$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	0.6558(1)	0	0.3389(1)	13(1)
Bi(2)	0.6118(1)	-0.5000	0.4375(1)	14(1)
Bi(3)	0.7771(1)	-0.5000	0.4443(1)	13(1)
Bi(4)	0.5000	-0.5000	0	15(1)
Bi(5)	0.4117(1)	0	0.0156(1)	14(1)
Bi(6)	0.2250(1)	0	-0.1587(1)	12(1)
Bi(7)	0.3058(1)	0.5000	0.0078(1)	13(1)
Bi(8)	0.3888(1)	0	0.1765(1)	13(1)
Bi(9)	0.4573(1)	-0.5000	0.3409(1)	13(1)
Bi(10)	0.5000	0	0.5000	16(1)
Rb(1)	0.1621(1)	0	-0.3469(1)	15(1)
Rb(2)	0.3267(1)	0	-0.1915(1)	20(1)
Rb(3)	0.5219(1)	-0.5000	0.2103(1)	20(1)
Se(1)	0.6280(1)	-0.5000	0.2525(1)	14(1)
Se(2)	0.5812(1)	0	0.3438(1)	14(1)
Se(3)	0.8578(1)	-0.5000	0.4652(1)	14(1)
Se(4)	0.6912(1)	-0.5000	0.4481(1)	12(1)
Se(5)	0.7470(1)	0	0.3567(1)	14(1)
Se(6)	0.5340(1)	-0.5000	0.4548(1)	16(1)
Se(7)	0.4075(1)	-0.5000	-0.0651(1)	12(1)
Se(8)	0.4999(1)	0	0.0824(1)	13(1)
Se(9)	0.3143(1)	0	-0.0638(1)	11(1)
Se(10)	0.1330(1)	0	-0.2340(1)	11(1)
Se(11)	0.2364(1)	-0.5000	-0.2237(1)	12(1)
Se(12)	0.3983(1)	0.5000	0.0942(1)	14(1)
Se(13)	0.2874(1)	0	0.0775(1)	11(1)
Se(14)	0.4708(1)	0	0.2638(1)	14(1)
Se(15)	0.4232(1)	0	0.3813(1)	12(1)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-4.

Empirical
Formula w
Temperatu
Crystal sys
Space grou
Unit cell di

Z, Volume,

Density (ca

Absorption

$F(000)$

Crystal size

θ range for

Index range

Reflections

Independent

Refinement

Data / restr

Goodness-c

Final R ind

R indices (a

Extinction

Largest pea

$$R1 = \sum F_o$$

Table 3-4. Crystallographic Data for β -RbBi₃Se₅ and CsBi₃Se₅.

Empirical formula	β -RbBi ₃ Se ₅ (III)	CsBi ₃ Se ₅ (V)
Formula weight	1107.21	1154.65
Temperature, K	298(2)	299(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$
Unit cell dimensions, Å	$a = 13.537(2)$ $b = 4.1431(6)$ $c = 21.545(3)$ $\beta = 91.297(3)^\circ$	$a = 13.603(3)$ $b = 4.1502(8)$ $c = 21.639(4)$ $\beta = 92.435(3)^\circ$
Z, Volume, Å ³	4, 1208.0(3)	4, 1221.2(4)
Density (calculated), g/cm ³	6.088	6.280
Absorption coefficient, mm ⁻¹	62.597	60.900
F(000)	1824	1896
Crystal size, mm ³	0.40 x 0.05 x 0.01	0.41x 0.03 x 0.01
θ range for data collection	1.50 to 27.91°	1.50 to 28.55°
Index ranges	$-17 \leq h \leq 17$ $-5 \leq k \leq 7$ $-28 \leq l \leq 28$	$-18 \leq h \leq 17$ $-5 \leq k \leq 5$ $-28 \leq l \leq 27$
Reflections collected	12148	11430
Independent reflections	3245 [$R_{\text{int}} = 0.0638$]	3254 [$R_{\text{int}} = 0.0713$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3245 / 1 / 140	3254 / 1 / 138
Goodness-of-fit on F^2	0.985	1.158
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0490$, $wR2 = 0.1099$	$R1 = 0.0607$, $wR2 = 0.1337$
R indices (all data)	$R1 = 0.0928$, $wR2 = 0.1221$	$R1 = 0.0820$, $wR2 = 0.1428$
Extinction	0.00003(2)	0.00007(2)
Largest peak and hole, e Å ⁻³	2.975 and -3.556	2.625and -3.117

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 3-5.

($\text{\AA}^2 \times 10^3$) for

Bit(1)	0
Bit(2)	0
Bit(3)	0
Bit(4)	0
Bit(5)	0
Bit(6)	0
Se(1)	0
Se(2)	0
Se(3)	0
Se(4)	0
Se(5)	0
Se(6)	0
Se(7)	0
Se(8)	0
Se(9)	0
Se(10)	0
Rbt(1)	0
Rbt(2)	0
Rbt(3)	0
Rbt(4)	0
Rbt(5)	0
Rbt(6)	0

U_{eq} is defined as

Table 3-5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-RbBi}_3\text{Se}_5$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.5957(1)	-0.7500	-0.4460(1)	19(1)	
Bi(2)	0.7908(1)	-0.2500	-0.3310(1)	19(1)	
Bi(3)	0.0027(1)	0.2500	-0.2223(1)	16(1)	
Bi(4)	0.2173(1)	-0.2500	-0.1095(1)	18(1)	
Bi(5)	0.3258(1)	-0.2500	0.1710(1)	20(1)	
Bi(6)	0.1120(1)	-0.7500	0.0542(1)	17(1)	
Se(1)	0.5584(2)	-0.7500	-0.5716(1)	20(1)	
Se(2)	0.7488(2)	-0.2500	-0.4577(1)	20(1)	
Se(3)	0.9457(2)	0.2500	-0.3456(1)	17(1)	
Se(4)	0.1489(2)	-0.2500	-0.2361(1)	16(1)	
Se(5)	0.3498(2)	-0.7500	-0.1273(1)	25(1)	
Se(6)	0.6426(2)	-0.7500	-0.3029(1)	20(1)	
Se(7)	0.8497(2)	-0.2500	-0.1894(1)	15(1)	
Se(8)	0.0469(2)	0.2500	-0.0762(1)	15(1)	
Se(9)	0.7443(2)	-0.7500	-0.0340(1)	14(1)	
Se(10)	0.4572(2)	-0.7500	0.1499(1)	36(1)	
Rb(1)	0.4957(9)	-0.7500	0.0019(6)	207(19)	0.384(8)
Rb(2)	0.3733(17)	-0.7500	-0.2864(8)	190(20)	0.40(3)
Rb(3)	0.8611(17)	-0.7500	-0.5820(10)	68(9)	0.223(17)
Rb(4)	0.4030(14)	-0.2500	-0.2751(7)	300(70)	0.31(3)
Rb(5)	0.7731(12)	-0.2500	-0.6261(7)	144(9)	0.366(11)
Rb(6)	0.9490(30)	0.2500	-0.5273(16)	200(30)	0.325(18)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-6.

Empirical formula
Formula weight
Temperature
Crystal system
Space group
Unit cell dimensions

Z, Volume, V

Density (calc)

Absorption coefficient

F(000)

Crystal size, s θ range for data

Index ranges

Reflections collected

Independent reflections

Refinement method

Data / restraints

Goodness-of-fit

Final R indices

R indices (all data)

Extinction

Largest peak and hole

$$R1 = \sum |F_o| -$$

Table 3-6. Crystallographic Data for γ -RbBi₃Se₅ and β -RbBi₃Se₅Te .

Empirical formula	γ -RbBi ₃ Se ₅ (IV)	RbBi ₃ Se ₄ Te (VI)
Formula weight	1107.21	1155.85
Temperature, K	297(2)	173.1(1)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions, Å	$a = 21.956(7)$ $b = 4.136(1)$ $c = 12.357(4)$	$a = 22.018(3)$ $b = 4.2217(6)$ $c = 12.614(2)$
Z, Volume, Å ³	4, 1122.0(6)	4, 1172.5(3)
Density (calculated), g/cm ³	6.555	6.548
Absorption coefficient, mm ⁻¹	67.398	63.830
F(000)	1824	1896
Crystal size, mm ³	0.13 x 0.01 x 0.01	0.64x 0.01 x 0.01
θ range for data collection	1.86 to 27.11°	1.85 to 26.99°
Index ranges	-26 ≤ h ≤ 28 -2 ≤ k ≤ 5 -13 ≤ l ≤ 15	-26 ≤ h ≤ 28 -5 ≤ k ≤ 5 -16 ≤ l ≤ 12
Reflections collected	6433	6225
Independent reflections	1417 [R _(int) = 0.1239]	1453[R _(int) = 0.1088]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1417 / 0 / 56	1453 / 0 / 58
Goodness-of-fit on F ²	0.993	1.056
Final R indices [I>2σ(I)]	R1 = 0.0617, wR2 = 0.1353	R1 = 0.0623, wR2 = 0.1030
R indices (all data)	R1 = 0.1372, wR2 = 0.1554	R1 = 0.1276, wR2 = 0.1191
Extinction	0.00051(9)	0.00005(4)
Largest peak and hole, e Å ⁻³	4.733 and -2.721	2.985and -2.606

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 3-7.

($\text{\AA}^3 \times 10^3$) fo

Bi(1)

Bi(2)

Bi(3)

Rb(1)

Se(1)

Se(2)

Se(3)

Se(4)

Se(5)

U_{eq} is defin

Table 3-7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-RbBi}_3\text{Se}_5$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	0.0248(1)	0.2500	0.1361(1)	22(1)
Bi(2)	0.0765(1)	-0.2500	0.4056(1)	21(1)
Bi(3)	0.1284(1)	-0.7500	0.6944(1)	22(1)
Rb(1)	0.2120(2)	-0.7500	0.0106(4)	36(1)
Se(1)	0.0659(2)	0.2500	-0.0838(3)	21(1)
Se(2)	0.1159(2)	-0.2500	0.1925(3)	24(1)
Se(3)	0.1613(2)	-0.7500	0.4722(4)	20(1)
Se(4)	0.2066(2)	-0.2500	0.7532(4)	31(1)
Se(5)	-0.0201(2)	0.2500	0.3616(3)	19(1)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-8.
($\text{\AA}^2 \times 10^3$) for

Bi(1)

Bi(2)

Bi(3)

Bi(4)

Bi(5)

Bi(6)

Se(1)

Se(2)

Se(3)

Se(4)

Se(5)

Se(6)

Se(7)

Se(8)

Se(9)

Se(10)

Cs(1)

Cs(2)

Cs(3)

Cs(4)

Cs(5)

Cs(6)

U_{eq} is defined

Table 3-8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for CsBi_3Se_5 .

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.5970(1)	-0.7500	-0.4464(1)	27(1)	
Bi(2)	0.7940(1)	-0.2500	-0.3308(1)	24(1)	
Bi(3)	0.0036(1)	0.2500	-0.2213(1)	21(1)	
Bi(4)	0.2178(1)	-0.2500	-0.1089(1)	18(1)	
Bi(5)	0.3250(1)	-0.2500	0.1718(1)	22(1)	
Bi(6)	0.1105(1)	-0.7500	0.0545(1)	21(1)	
Se(1)	0.5569(2)	-0.7500	-0.5717(1)	26(1)	
Se(2)	0.7487(2)	-0.2500	-0.4576(1)	26(1)	
Se(3)	0.9491(2)	0.2500	-0.3455(1)	22(1)	
Se(4)	0.1502(2)	-0.2500	-0.2351(1)	20(1)	
Se(5)	0.3487(2)	-0.7500	-0.1259(1)	26(1)	
Se(6)	0.6477(2)	-0.7500	-0.3047(1)	22(1)	
Se(7)	0.8515(2)	-0.2500	-0.1905(1)	14(1)	
Se(8)	0.0469(2)	0.2500	-0.0756(1)	18(1)	
Se(9)	0.7462(2)	-0.7500	-0.0354(1)	20(1)	
Se(10)	0.4558(2)	-0.7500	0.1543(2)	56(1)	
Cs(1)	0.4959(3)	-0.7500	0.0040(2)	33(1)	0.50
Cs(2)	0.3846(4)	-0.7500	-0.2836(2)	117(4)	0.550(6)
Cs(3)	0.8510(10)	-0.7500	-0.5859(6)	62(4)	0.200(6)
Cs(4)	0.4094(10)	-0.2500	-0.2713(5)	73(7)	0.168(8)
Cs(5)	0.7770(7)	-0.2500	-0.6251(4)	81(4)	0.285(8)
Cs(6)	0.9593(8)	0.2500	-0.5207(5)	81(4)	0.301(8)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3-9.

(Å² × 10³) for

Bi(1)

Bi(2)

Bi(3)

Rb(1)

Se(1)

Se(2)

Te(2)

Se(3)

Se(4)

Te(4)

Se(5)

U_{eq} is defined

Table 3-9. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbBi}_3\text{Se}_4\text{Te}$.

	x	y	z	U(eq)	occ.
Bi(1)	0.0260(1)	0.2500	0.1335(1)	15(1)	
Bi(2)	0.0741(1)	-0.2500	0.4081(1)	16(1)	
Bi(3)	0.1273(1)	-0.7500	0.6930(1)	14(1)	
Rb(1)	0.2131(2)	-0.7500	0.9992(4)	33(1)	
Se(1)	0.0647(2)	0.2500	-0.0829(3)	13(1)	
Se(2)	0.1218(1)	-0.2500	0.1928(2)	18(1)	0.52(2)
Te(2)	0.1218(1)	-0.2500	0.1928(2)	18(1)	0.48(2)
Se(3)	0.1599(1)	-0.7500	0.4738(3)	11(1)	
Se(4)	0.2127(1)	-0.2500	0.7503(3)	22(1)	0.48(3)
Te(4)	0.2127(1)	-0.2500	0.7503(3)	22(1)	0.52(3)
Se(5)	-0.0200(2)	0.2500	0.3603(3)	10(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4. Results

Sy

and Bi_2S_3

During c

system w

RbBi_3S_5

made via

$\text{Rb}_3\text{Bi-S}$

would f

reacting

an 1:3 r

atoms i

was for

RbBi_3S_5

4. Results and Discussion

Synthesis and thermal behavior. γ - RbBi_3S_5 was synthesized by reacting Rb_2S and Bi_2S_3 in a 1:3 molar ratio. This phase however forms from a wide range of ratios. During our investigations, the only other phase that we encountered in the Rb/Bi/S system was RbBiS_2 ^{17(d)}. After repeated attempts we could not synthesize the α - form of RbBi_3S_5 ^{17(f)} for which no synthesis is published. Furthermore, β - RbBi_3S_5 can only be made via an ion exchange reaction² using KBi_3S_5 and RbCl .

α - RbBi_3Se_5 was discovered initially as a byproduct in the synthesis of $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$. We noticed that prolonged heating periods (> 60 h at 750 °C) of $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$ would form well-shaped rods on its surface. Later a rational synthesis was developed by reacting Rb_2Se and Bi_2Se_3 in 1:2.9 molar ratio at 780 °C. CsBi_3Se_5 was synthesized from an 1:3 molar ratio of $\text{Cs}_2\text{Se}/\text{Bi}_2\text{Se}_3$ at 780 °C.

$\text{RbBi}_3\text{Se}_4\text{Te}$ was initially synthesized in an attempt to replace some of the Se atoms in $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ ¹³ with Te. The replacement did not occur and instead a new phase was formed with mixed Se/Te occupancy. A rational synthesis was used to obtain pure $\text{RbBi}_3\text{Se}_4\text{Te}$ by reacting Rb_2Se with Bi_2Se_3 and Bi_2Te_3 in a 3:7:2 molar ratio.

Sim

system wh

possible to

RbBi_3Se_5

formula A

the most s

Th

technique

quenchin

from X-

$\beta\text{-RbBi}_3$

investig

that the

evidenc

spacing

increase

which is

Since the above compounds have the same general formula, we looked for a system where all three different structures exist as different polymorphs. This was only possible for the Rb/Bi/Se system. In Cs/Bi/Se only CsBi_3Se_5 (isostructural with $\beta\text{-RbBi}_3\text{Se}_5$) could be obtained. In the A/Bi/Te systems ($A = \text{Rb}, \text{Cs}$) no compound with the formula ABi_3Te_5 ($A = \text{Rb}, \text{Cs}$) was found, instead $\text{Rb}_{0.5}\text{Bi}_{1.83}\text{Te}_5$ ²⁴ and CsBi_4Te_6 ⁷ were the most stable products.

The "all Se" analog of $\text{RbBi}_3\text{Se}_4\text{Te}$, $\gamma\text{-RbBi}_3\text{Se}_5$ was prepared with the quenching technique described in the synthesis section. $\beta\text{-RbBi}_3\text{Se}_5$ was synthesized also with the quenching technique but only as a mixture with $\gamma\text{-RbBi}_3\text{Se}_5$ (~1:1 ratio) as evidenced from X-ray powder diffraction. Although we tried a number of ways to synthesize pure $\beta\text{-RbBi}_3\text{Se}_5$ we were not successful probably due to its metastable character. We also investigated the amount of Te that the $\text{RbBi}_3\text{Se}_4\text{Te}$ structure can accommodate. We found that the structure remains stable up to two Te atoms per formula ($\text{RbBi}_3\text{Se}_3\text{Te}_2$) as evidenced by powder X-ray diffraction (shifting of the diffraction peaks to higher d-spacing) and EDS/SEM analysis ($\text{Rb}_{0.99}\text{Bi}_3\text{Se}_{3.17}\text{Te}_{1.97}$). When the amount of Te increases further the powder diffraction pattern changes indicating a different phase, which is under investigation.

Th.

congruent.

evidenced

to note that

congruently

$\text{Rb}_2\text{Bi}_3\text{Se}_{13}$

and we found

CsBi_3Se_5 m

performed to

polymorph.

480 °C and

summary, γ -

also finally c

Ener

energy gaps

As ex

~1.1 eV, see

The differential thermal analysis (DTA) studies indicate that γ -RbBi₃S₅ melts congruently at 697 °C. γ -RbBi₃Se₅ melts at 675 °C but transforms to Rb₂Bi₈Se₁₃ as evidenced by powder X-ray diffraction indicating its metastable character. It is interesting to note that the presence of Te atoms stabilizes the RbBi₃Se₄Te structure since it melts congruently at 642 °C. α -RbBi₃Se₅ melts at ~680 °C and converts to γ -RbBi₃Se₅ and Rb₂Bi₈Se₁₃. We also examined the thermal behavior of the β - and γ -RbBi₃Se₅ mixture and we found that at 678 °C it converts to a mixture of γ -RbBi₃Se₅ and Rb₂Bi₈Se₁₃. CsBi₃Se₅ melts at 686 °C converting to CsBi_{3.67}Se₆¹³. Annealing studies were also performed to check if any of the three phases α -, β -, γ - RbBi₃Se₅ transforms to another polymorph. The samples of α -, β -, β + γ -mixture, and CsBi₃Se₅ were annealed for 60 h at 480 °C and the results were identical to those of the differential thermal analysis. In summary, γ -RbBi₃Se₅ seems to be the most relatively stable of the three forms although it also finally converts to Rb₂Bi₈Se₁₃.

Energy gaps. All materials are semiconductors as indicated by the presence of energy gaps detected by optical absorption UV-Vis and infrared spectroscopy.

As expected the sulfide compound γ -RbBi₃S₅ exhibits the highest band gap at ~1.1 eV, see Figure 3-1.

a/S (arbitrary units)

0

Figure 3-1.
transitions for

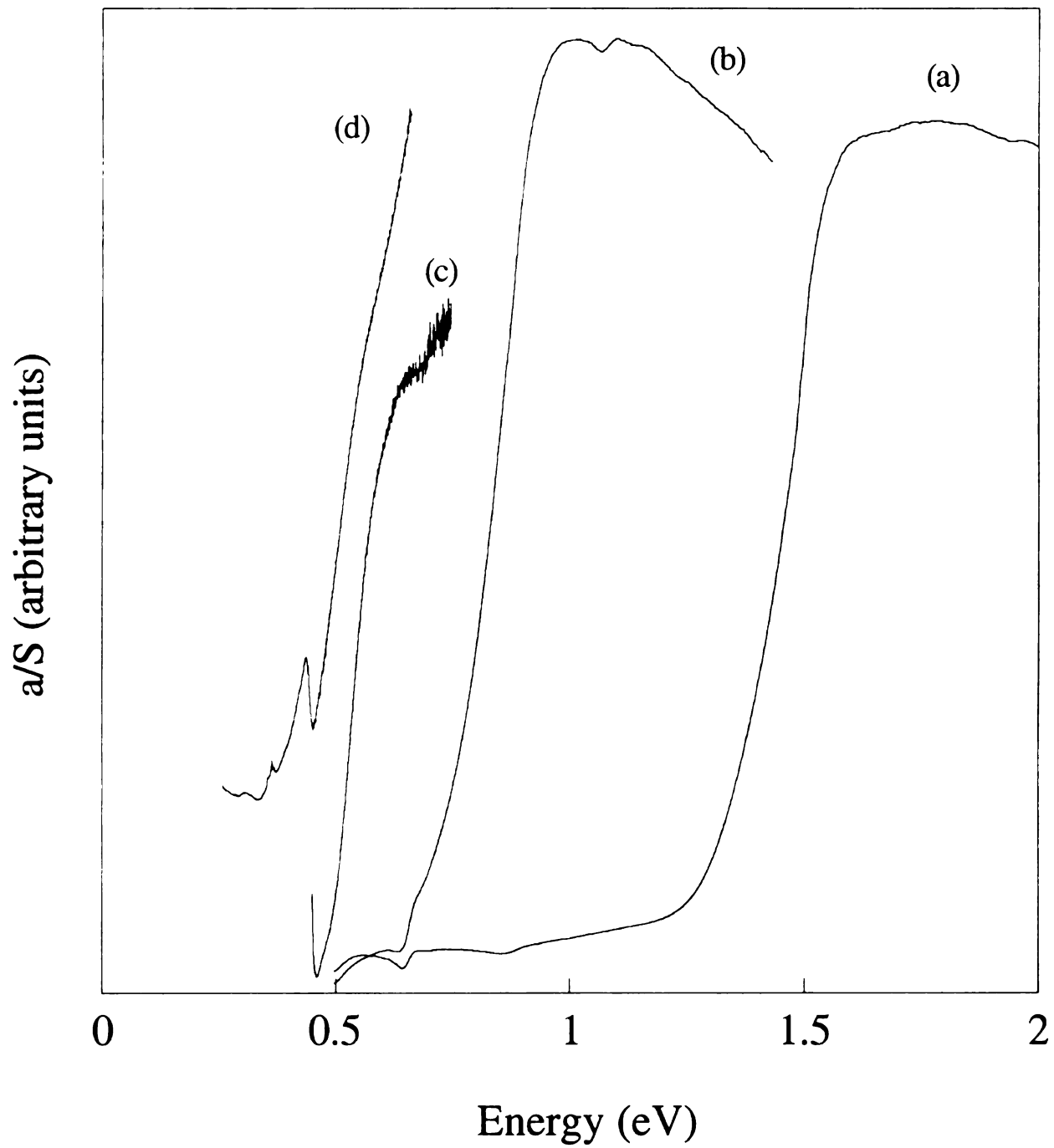


Figure 3-1. Solid-state UV/Vis and infrared absorption spectra showing band gap transitions for (a) γ -RbBi₃S₅ (b) γ -RbBi₃Se₅, (c) β -RbBi₃Se₅ and (d) α -RbBi₃Se₅.

γ -RbBi₃Se₅

gap of 0.5

atoms into

gap of 0.4 eV

RbBi₃Se₅ has

that γ -RbBi₃

thickness of

has thicker

structure and

reported K₂

of γ -RbBi₃

Str

γ -Rb

α -RbBi₃S

Rb⁺ ions

γ -RbBi₃Se₅ has a band gap of 0.8 eV while its isostructural RbBi₃Se₄Te has a lower band gap of 0.5 eV. This is in agreement with the fact that the incorporation of the larger Te atoms into a selenide compound is expected to lower the band gap. CsBi₃Se₅ has a band gap of 0.46 eV, its isostructural β -RbBi₃Se₅ has a similar band gap of 0.48 eV while α -RbBi₃Se₅ has a gap of 0.43 eV. If we compare the three forms of RbBi₃Se₅, we notice that γ -RbBi₃Se₅ has the highest gap and this is due to its low dimensionality and the small thickness of its [Bi₃Se₅]⁻ layers. β -RbBi₃Se₅ which also has a two-dimensional structure has thicker layers and consequently a lower gap. α -RbBi₃Se₅ has a three-dimensional structure and its band gap is very similar to that of the β -RbBi₃Se₅. The previously reported KBi₃S₅ and β -RbBi₃Se₅ have a band gap of ~1.2 eV, a value comparable to that of γ -RbBi₃S₅.

Structure description

γ -RbBi₃S₅ (I). The compound is isostructural with CsBi₃S₅^{17(e)} but different from α -RbBi₃S₅^{17(f)} and β -RbBi₃S₅. The β - form is formed by the ion-exchange of the K⁺ with Rb⁺ ions in KBi₃S₅². The structure of γ -RbBi₃S₅ consists of Bi₂Te₃-type infinite rods

three Br a

2. Each ro

zigzag fas

such as C

fashion. In

essentially

The

octahedral

pyramid hav

2.626(3) Å.

Å. Bi(3) is lo

between 84.3

The F

between 3.27

The st

Figure 3-3. Th

tunnel between

framework of

three Bi atoms wide that are connected with each other by sharing corners, see Figure 3-2. Each rod is connected with four other rods and the Bi_2Te_3 -type rods are arranged in a zigzag fashion. The zigzag arrangement is found also in other bismuth chalcogenides, such as $\text{CsBi}_{3.67}\text{Se}_6$ ¹³, where a different block, NaCl-type, is arranged in a similar fashion. In the space created between the Bi_2Te_3 -type rods the Rb atoms reside creating essentially tunnels filled by Rb metal ions.

The three Bi atoms that make up the Bi_2Te_3 -type block have a distorted octahedral coordination (Table 3-10). Bi(1) and Bi(2) are distorted towards a trigonal pyramid having three short bonds trans to three longer bonds e.g. Bi(1) has one bond at 2.626(3) Å, two bonds at 2.669(2) Å, two bonds at 2.986(2) Å and one bond at 3.227(4) Å. Bi(3) is less distorted with distances varying between 2.781(3)-2.872(3) Å and angles between 84.33(8)-99.38(8)°.

The Rb has a bicapped trigonal prismatic coordination with distances varying between 3.275(4)-3.792(3) Å.

The structure of $\gamma\text{-RbBi}_3\text{S}_5$ is different from the structure of $\alpha\text{-RbBi}_3\text{S}_5$ ^{17(f),25}, see Figure 3-3. The α -structure has the unusual characteristic of having a S^{2-} ion sitting in the tunnel between the Rb atoms. In a way this structure can be described as a neutral tunnel framework of " Bi_2S_3 " stuffed with Rb_2S .

Bi_2Te_3 -type



Figure 3-2

indicates B

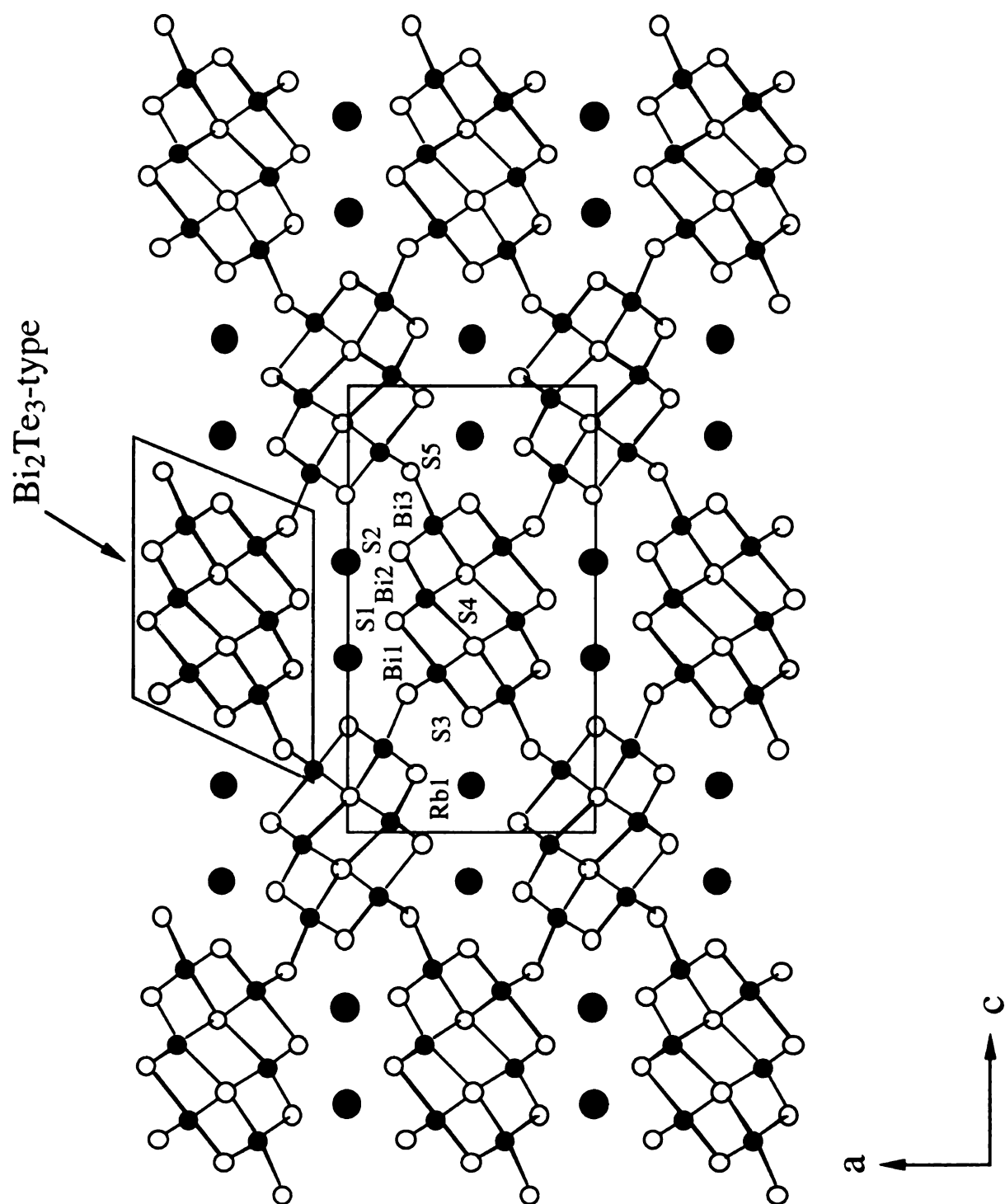


Figure 3-2. Projection of the structure of $\gamma\text{-RbBi}_3\text{S}_5$ down the b -axis. The shaded area indicates Bi_2Te_3 -type building block.

Table 3-1

B(1)-S(2)

B(1)-S(5)

B(1)-S(4)

B(1)-S(1)

B(2)-S(2)

B(2)-S(1)

B(2)-S(4)

B(2)-S(4)

B(3)-S(4)

B(3)-S(5)

B(3)-S(3)

B(3)-S(2)

Rb(1)-S(5)

Rb(1)-S(2)

Rb(1)-S(1)

Rb(1)-S(1)

Rb(1)-S(3)

Table 3-10. Bond Distances (Å) and Selected Angles (deg) for γ -RbBi₃S₅.

Bi(1)-S(3)	2.626(3)	S(5)-Bi(1)-S(1)	85.96(9)
Bi(1)-S(5)	2.669(2)x2	S(5)-Bi(1)-S(5)	98.8(1)
Bi(1)-S(4)	2.986(2)x2	S(3)-Bi(1)-S(1)	180.0(1)
Bi(1)-S(1)	3.227(4)		
Bi(2)-S(2)	2.572(3)	S(4)-Bi(2)-S(4)	79.34(8)
Bi(2)-S(1)	2.719(2)x2	S(1)-Bi(2)-S(4)	96.70(9)
Bi(2)-S(4)	3.015(3)x2	S(2)-Bi(2)-S(4)	163.0(1)
Bi(2)-S(4)	3.232(3)		
Bi(3)-S(4)	2.781(3)	S(5)-Bi(3)-S(3)	84.33(8)
Bi(3)-S(5)	2.786(3)	S(5)-Bi(3)-S(2)	99.38(9)
Bi(3)-S(3)	2.794(2)x2	S(4)-Bi(3)-S(5)	170.7(1)
Bi(3)-S(2)	2.872(3)x2		
Rb(1)-S(5)	3.275(4)		
Rb(1)-S(2)	3.316(3)x2		
Rb(1)-S(1)	3.498(3)x2		
Rb(1)-S(1)	3.635(4)		
Rb(1)-S(3)	3.792(3)x2		

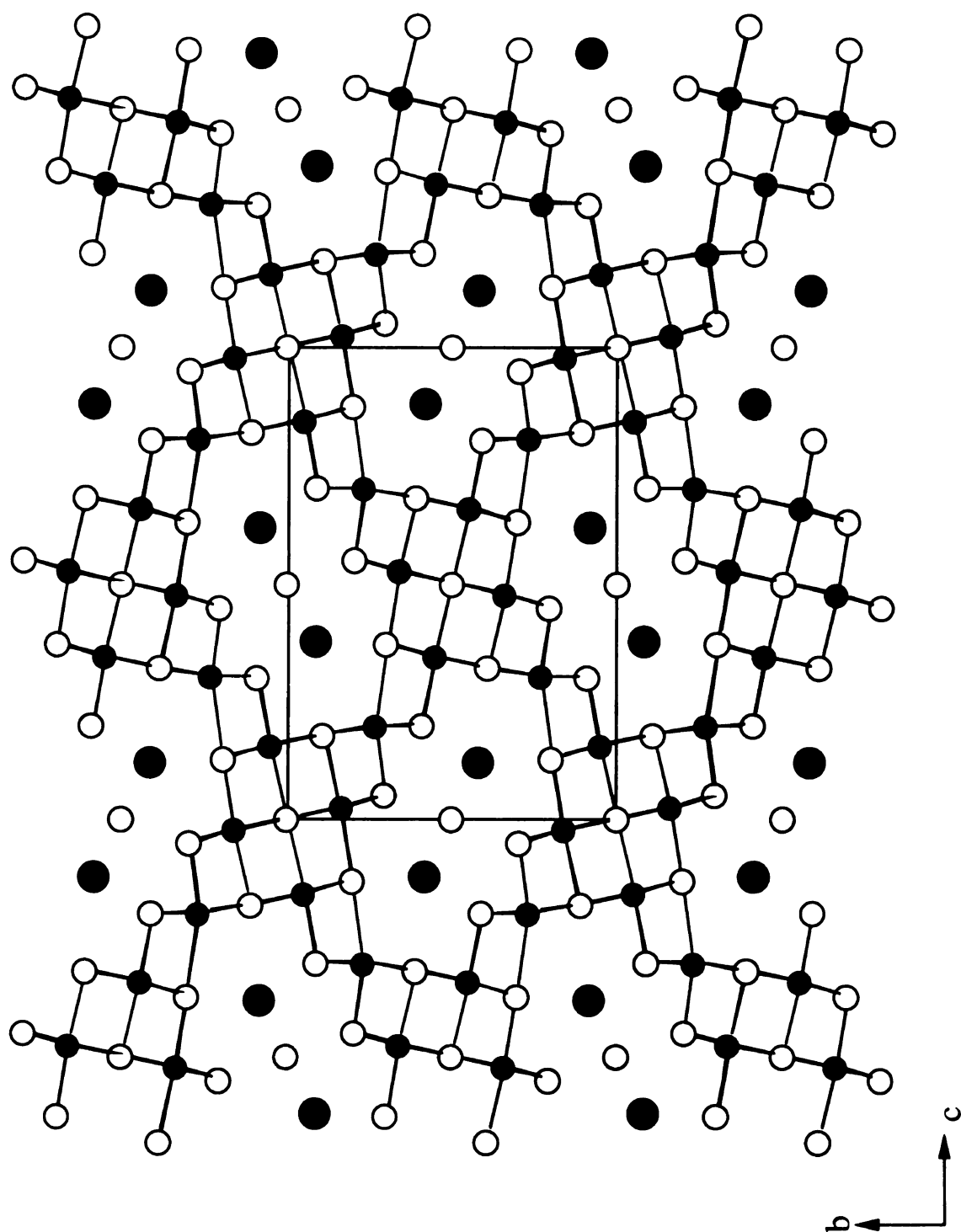


Figure 3-3. Projection of the structure of $\alpha\text{-RbBi}_3\text{S}_5$ down the a -axis.

Unfortun.

α -

consists of

CdI_2 -type

essentially

fragments

atoms wide

running along

infinite layers

CdI_2 -type fragments

All

(Table 3-1)

fragment width

88.95(6)-9

with Bi-Se

between 88

more distorted

at 3.015(2)

Unfortunately we were not able to reproduce the synthesis of this seemingly novel phase.

α -RbBi₃Se₅ (II). This compound adopts a new three-dimensional structure which consists of Bi₂Te₃-type, NaCl-type and CdI₂-type infinite fragments, see Figure 3-4. The CdI₂-type fragments are running in two directions, along and perpendicular to the a-axis, essentially forming square like tunnels. At the corners of the tunnels the NaCl-type fragments are found while the tunnels are filled with Bi₂Te₃-type infinite rods, three Bi atoms wide. Furthermore, each tunnel contains six Rb atoms. The CdI₂-type fragments running along the a-axis fuse with the NaCl-type fragments creating essentially an infinite layer running along the ab-plane while in other direction, in the ac-plane the CdI₂-type fragments alternate with the NaCl-type fragments creating stepped layers.

All the Bi atoms have octahedral coordination with varying degree of distortion. (Table 3-11). The least distorted is Bi(4) located at the cell corners in the CdI₂-type fragment with Bi-Se varying between 2.934(3)-2.945(2) Å and Se-Bi-Se angles between 88.95(6)-91.05(6)° and Bi(10) located in other CdI₂-type fragment at the center of the cell with Bi-Se distances varying between 2.904(3)-2.939(2) Å and Se-Bi-Se angles varying between 88.74(6)-91.26(6)°. Bi(7) sitting in the center of the NaCl-type block is slightly more distorted with two bonds at 2.878(2) Å, two between 2.971(3)-2.985(3) Å and two at 3.015(2) Å. One kind of common octahedral distortion is towards a trigonal pyramid.

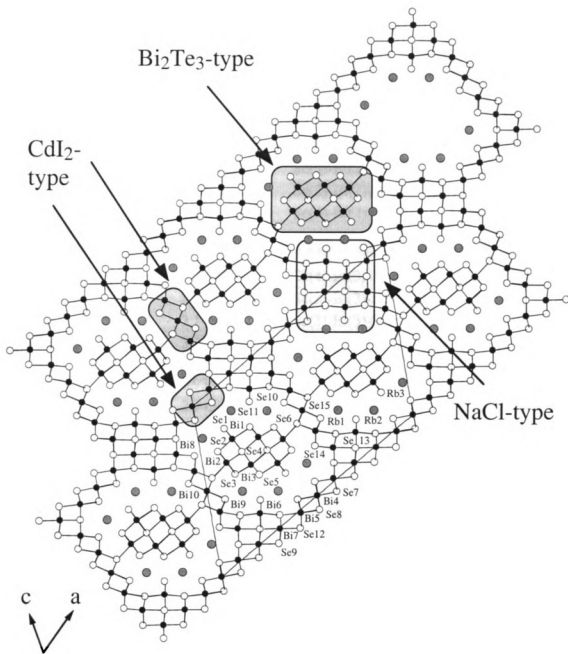


Figure 3-4. Projection of the structure of $\alpha\text{-RbBi}_3\text{Se}_5$ down the b -axis. The shaded areas indicate the NaCl-, Bi₂Te₃-, and CdI₂-type building blocks. Part of the Bi₂Te₃-type rods have been removed to show the square-like tunnels.

Table 3-11. Bond Distances (Å) and Selected Angles (deg) for α -RbBi₃Se₅.

Bi(1)-Se(1)	2.807(2)x2	Se(4)-Bi(1)-Se(4)	81.86(7)
Bi(1)-Se(2)	2.812(3)	Se(1)-Bi(1)-Se(1)	95.27(9)
Bi(1)-Se(5)	3.149(3)	Se(2)-Bi(1)-Se(5)	170.69(8)
Bi(1)-Se(4)	3.166(2)x2		
Bi(2)-Se(4)	2.794(3)	Se(3)-Bi(2)-Se(6)	82.50(7)
Bi(2)-Se(2)	2.916(2)x2	Se(2)-Bi(2)-Se(6)	96.42(7)
Bi(2)-Se(3)	2.975(2)x2	Se(4)-Bi(2)-Se(6)	168.20(8)
Bi(2)-Se(6)	3.104(3)		
Bi(3)-Se(3)	2.738(3)	Se(4)-Bi(3)-Se(4)	84.94(6)
Bi(3)-Se(5)	2.822(2)x2	Se(3)-Bi(3)-Se(5)	96.18(7)
Bi(3)-Se(4)	3.145(2)x2	Se(3)-Bi(3)-Se(4)	168.83(8)
Bi(3)-Se(4)	3.211(3)		
Bi(4)-Se(7)	2.934(3)x2	Se(7)-Bi(4)-Se(8)	88.95(6)
Bi(4)-Se(8)	2.945(2)x4	Se(7)-Bi(4)-Se(8)	91.05(6)
		Se(8)-Bi(4)-Se(8)	180.0
Bi(5)-Se(8)	2.798(3)	Se(7)-Bi(5)-Se(9)	84.77(6)
Bi(5)-Se(7)	2.862(2)x2	Se(8)-Bi(5)-Se(12)	97.15(7)
Bi(5)-Se(12)	3.084(2)x2	Se(7)-Bi(5)-Se(12)	168.76(8)
Bi(5)-Se(9)	3.095(3)		
Bi(6)-Se(11)	2.812(2)x2	Se(13)-Bi(6)-Se(13)	83.53(7)
Bi(6)-Se(10)	2.926(3)	Se(11)-Bi(6)-Se(11)	95.07(8)
Bi(6)-Se(9)	2.930(3)	Se(10)-Bi(6)-Se(9)	169.22(8)
Bi(6)-Se(13)	3.114(2)x2		
Bi(7)-Se(9)	2.878(2)x2	Se(13)-Bi(7)-Se(13)	84.77(6)
Bi(7)-Se(12)	2.971(3)	Se(12)-Bi(7)-Se(13)	94.66(6)
Bi(7)-Se(13)	2.985(3)	Se(9)-Bi(7)-Se(13)	173.95(7)
Bi(7)-Se(13)	3.015(2)x2		

Table 3-11. (cont'd).

Bi(8)-Se(14)	2.691(3)	Se(10)-Bi(8)-Se(13)	83.54(6)
Bi(8)-Se(10)	2.872(2)x2	Se(14)-Bi(8)-Se(12)	95.34(7)
Bi(8)-Se(12)	3.086(2)x2	Se(10)-Bi(8)-Se(12)	170.01(8)
Bi(8)-Se(13)	3.278(3)		
Bi(9)-Se(6)	2.838(3)	Se(10)-Bi(9)-Se(14)	83.52(6)
Bi(9)-Se(15)	2.866(2)x2	Se(6)-Bi(9)-Se(14)	104.51(7)
Bi(9)-Se(10)	3.044(3)	Se(15)-Bi(9)-Se(14)	163.88(8)
Bi(9)-Se(14)	3.061(2)x2		
Bi(10)-Se(15)	2.904(3)x2	Se(15)-Bi(10)-Se(6)	88.74(6)
Bi(10)-Se(6)	2.939(2)x4	Se(15)-Bi(10)-Se(6)	91.26(6)
		Se(15)-Bi(10)-Se(15)	179.998(1)
Rb(1)-Se(3)	3.409(3)x2		
Rb(1)-Se(5)	3.475(4)		
Rb(1)-Se(15)	3.485(3)x2		
Rb(1)-Se(10)	3.529(4)		
Rb(1)-Se(11)	3.590(3)x2		
Rb(2)-Se(1)	3.477(3)x2		
Rb(2)-Se(9)	3.489(4)		
Rb(2)-Se(11)	3.638(3)x2		
Rb(2)-Se(5)	3.663(4)		
Rb(2)-Se(7)	3.712(3)x2		
Rb(3)-Se(1)	3.487(4)		
Rb(3)-Se(14)	3.497(3)x2		
Rb(3)-Se(8)	3.583(3)x2		
Rb(3)-Se(2)	3.612(3)x2		
Rb(3)-Se(12)	3.973(4)		

In this distortion, there are three short bonds *trans* to three longer ones. Sometimes the three short bonds are almost equal, as a result the three longer bonds will be equal in distance while other times one of the three short bonds is shorter than the other two, as a result the corresponding long bond is longer than the other two. The coordination octahedra of Bi(1), Bi(3), Bi(5), Bi(8), Bi(9) belong to this category. For example Bi(1) has three short bonds between 2.807(2)-2.812(3) Å *trans* to three longer bonds between 3.149(3)-3.166(2) Å while Bi(3) has one short bond at 2.738(3) Å, two short bonds at 2.822(2) Å, two longer bonds at 3.145(2) Å and even longer one at 3.211(3) Å. The distortion of Bi(2) can be described as square pyramid with four almost equal basal bonds between 2.916(2)-2.975(2) Å and one short bond at 2.794(3) Å forming the apex *trans* to a longer one at 3.104(3). Bi(6) have three sets of equal distances, two at 2.812(2) Å, two at 2.926(3) and two longer at 3.114(2) and its distortion can be described as "seesaw".

The three Rb atoms are eight coordinate with a bicapped trigonal prismatic coordination. The Rb-Se distances for Rb(1) vary between 3.409(3)-3.590(3) Å for Rb(1), 3.477(3)-3.712(3) Å for Rb(2) and 3.487(4)-3.973(4) Å for Rb(3).

β -RbBi₃Se₅ (III) and CsBi₃Se₅ (V). These two compounds are isostructural, therefore only CsBi₃Se₅ will be described in detail. CsBi₃Se₅ is a layered structure with layers assembled NaCl-type fragments, see Figure 3-5. This fragment repeats creating stepped layers. In the space between the layers two different tunnels are formed, one

small that can accommodate only one Cs atom and a larger one where several Cs atoms are found and are disordered in several different trigonal prismatic sites.

In this compound also the Bi atoms have distorted octahedral coordination (Table 3-12). The Bi(6) atom at the center of the NaCl-type is the least distorted with Bi-Se bond distances varying between 2.884(2)-3.024(2) Å and Se-Bi-Se angles varying between 86.73(7)-92.34(7)°. This feature has been observed in other bismuth selenides where the atoms sitting in center of the NaCl-type exhibit the smallest distortion.¹³ Bi(1) has one Bi-Se bond at 2.752(3) Å, four bonds at 2.941(2)-2.980(2) Å and longer Bi-Se bond *trans* to the shorter bond at 3.125(3) Å, having a distortion toward a square pyramid. Similarly, the coordination environments of Bi(2) and Bi(3) have the same characteristics. Bi(4) and Bi(5) exhibit a different kind of distortion having three short bond *trans* to three longer ones. For example Bi(4) has two short bonds at 2.766(2) Å, one slightly longer bond at 2.859(3) Å and three longer bonds between 3.148(3)-3.211(2) Å.

The location and behavior of the alkali atoms deserves special mention here. All the Cs atoms residing in the tunnels between the layers are partially occupied since they are at a close distance to each other. Cs(1) that is located in the smaller tunnel between the layers having a tricapped trigonal prismatic coordination with Cs-Se distances varying between 3.311(6)-4.072(5) Å. The Cs(1) generates a symmetry equivalent 2.0856(8) Å away, as a result is only 50% occupied.

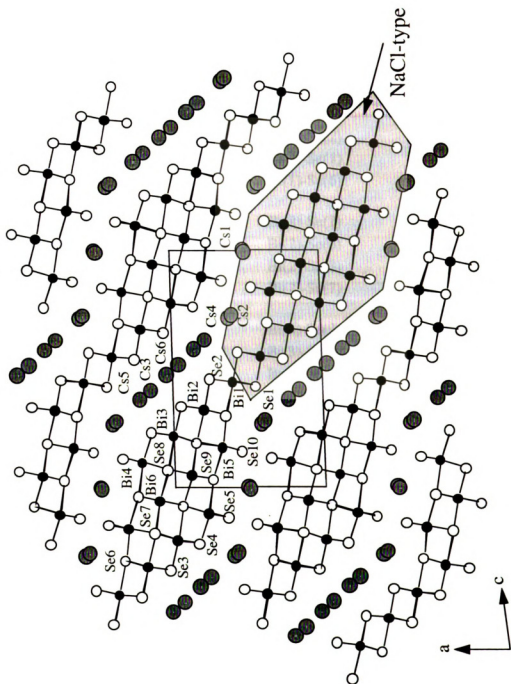


Figure 3-5. Projection of the structure of CsBi_3Se_5 and $\beta\text{-RbBi}_3\text{Se}_5$ down the b -axis. The

shaded areas indicate the NaCl-type building blocks.

Table 3-12. Bond Distances (Å) and Selected Angles (deg) for CsBi₃Se₅ and β -RbBi₃Se₅.

CsBi ₃ Se ₅		β -RbBi ₃ Se ₅	
Bi(1)-Se(1)	2.752(3)	Bi(1)-Se(1)	2.740(3)
Bi(1)-Se(2)	2.941(2)x2	Bi(1)-Se(2)	2.946(2)x2
Bi(1)-Se(1)	2.980(2)x2	Bi(1)-Se(1)	2.969(2)x2
Bi(1)-Se(6)	3.125(3)	Bi(1)-Se(6)	3.134(2)
Bi(2)-Se(2)	2.797(3)	Bi(2)-Se(2)	2.776(3)
Bi(2)-Se(6)	2.939(2)x2	Bi(2)-Se(6)	2.956(2)x2
Bi(2)-Se(3)	2.982(2)x2	Bi(2)-Se(3)	2.970(2)x2
Bi(2)-Se(7)	3.117(2)	Bi(2)-Se(7)	3.136(2)
Bi(3)-Se(3)	2.768(3)	Bi(3)-Se(3)	2.750(2)
Bi(3)-Se(4)	2.899(2)x2	Bi(3)-Se(4)	2.885(2)x2
Bi(3)-Se(7)	3.017(2)x2	Bi(3)-Se(7)	3.024(2)x2
Bi(3)-Se(8)	3.194(3)	Bi(3)-Se(8)	3.190(2)
Bi(4)-Se(5)	2.766(2)	Bi(4)-Se(5)	2.773(2)x2
Bi(4)-Se(4)	2.859(3)	Bi(4)-Se(4)	2.860(2)
Bi(4)-Se(9)	3.148(3)	Bi(4)-Se(9)	3.124(2)
Bi(4)-Se(8)	3.211(2)x2	Bi(4)-Se(8)	3.194(2)x2
Bi(5)-Se(10)	2.766(2)x2	Bi(5)-Se(10)	2.775(2)x2
Bi(5)-Se(6)	2.891(3)	Bi(5)-Se(6)	2.866(2)
Bi(5)-Se(9)	3.082(3)	Bi(5)-Se(9)	3.079(2)
Bi(5)-Se(7)	3.206(2)x2	Bi(5)-Se(7)	3.184(2)x2
Cs(1)-Se (9-coordinate)	3.311(6)-4.072(5)	Rb(1)-Se (9-coordinate)	3.24(1)-3.97(1)
Cs(2)-Se (8-coordinate)	3.460(5)-4.068(6)	Rb(2)-Se (8-coordinate)	3.45(2)-4.23(2)
Cs(3)-Se (6-coordinate)	3.756(9)-4.02(1)	Rb(3)-Se (6-coordinate)	3.71(1)-4.11(2)
Cs(4)-Se (7-coordinate)	3.09(1)-3.93(1)	Rb(4)-Se (7-coordinate)	3.26(2)-3.91(2)
Cs(5)-Se (6-coordinate)	3.655(9)-3.845(8)	Rb(5)-Se (6-coordinate)	3.65(1)-3.87(2)
Cs(6)-Se (6-coordinate)	3.798(8)-4.01(1)	Rb(6)-Se (6-coordinate)	3.74(2)-4.11(4)

Table 3-12. (cont'd).

Se(2)-Bi(1)-Se(6)	86.73(7)	Se(2)-Bi(1)-Se(6)	87.54(6)
Se(1)-Bi(1)-Se(2)	92.34(7)	Se(1)-Bi(1)-Se(2)	91.71(6)
Se(2)-Bi(1)-Se(1)	177.19(8)	Se(2)-Bi(1)-Se(1)	177.58(8)
Se(3)-Bi(2)-Se(7)	86.70(6)	Se(3)-Bi(2)-Se(7)	86.45(6)
Se(2)-Bi(2)-Se(6)	93.16(6)	Se(2)-Bi(2)-Se(6)	94.41(6)
Se(6)-Bi(2)-Se(3)	174.76(7)	Se(6)-Bi(2)-Se(3)	174.14(7)
Se(7)-Bi(3)-Se(8)	83.80(5)	Se(7)-Bi(3)-Se(8)	83.28(5)
Se(3)-Bi(3)-Se(4)	93.94(6)	Se(3)-Bi(3)-Se(4)	94.49(6)
Se(4)-Bi(3)-Se(7)	173.00(7)	Se(4)-Bi(3)-Se(7)	172.26(7)
Se(8)-Bi(4)-Se(8)	80.50(6)	Se(8)-Bi(4)-Se(8)	80.86(6)
Se(5)-Bi(4)-Se(5)	97.24(9)	Se(5)-Bi(4)-Se(5)	96.68(9)
Se(4)-Bi(4)-Se(9)	170.22(7)	Se(4)-Bi(4)-Se(9)	170.70(7)
Se(7)-Bi(5)-Se(7)	80.66(5)	Se(7)-Bi(5)-Se(7)	81.18(5)
Se(10)-Bi(5)-Se(10)	97.21(10)	Se(10)-Bi(5)-Se(10)	96.59(9)
Se(6)-Bi(5)-Se(9)	169.09(8)	Se(6)-Bi(5)-Se(9)	170.65(7)
Se(7)-Bi(5)-Se(7)	80.66(5)	Se(7)-Bi(5)-Se(7)	81.18(5)
Se(10)-Bi(5)-Se(10)	97.21(10)	Se(10)-Bi(5)-Se(10)	96.59(9)
Se(6)-Bi(5)-Se(9)	169.09(8)	Se(6)-Bi(5)-Se(9)	170.65(7)
Se(8)-Bi(6)-Se(8)	86.67(7)	Se(8)-Bi(6)-Se(8)	86.21(6)
Se(9)-Bi(6)-Se(8)	92.67(6)	Se(9)-Bi(6)-Se(8)	92.59(6)
Se(8)-Bi(6)-Se(7)	172.82(7)	Se(8)-Bi(6)-Se(7)	172.56(7)

Cs(2) and Cs(4) have bicapped and monocapped trigonal prismatic coordination respectively sitting in the edges of the large cavity area between the layers while Cs(3), Cs(5) and Cs(6) are six coordinate having a trigonal prismatic coordination. The equivalent isotropic displacement parameters of the Cs atoms with the exception of Cs(1) are large. This can be rationalized if we consider Cs(1) acting as a pillar between the Bi-Se layers. Thus the Cs(2)-Cs(6) are sitting in a tunnel which is slightly too large giving rise to a rattling motion and large displacement parameters. The same situation is also observed in KBi_3S_5 ² and it is believed to be responsible for its good ion-exchange properties. Based on these facts we anticipate that the Cs(2)-Cs(6) atoms could be ion-exchangeable.

The $\beta\text{-RbBi}_3\text{Se}_5$ exhibits the same characteristic with the only difference being the different occupancies of the alkali metal ions between the layers compared to the occupancies of the Cs analog. Selected distances and angles are shown on Table 3-12.

$\gamma\text{-RbBi}_3\text{Se}_5$ (IV) and $\text{RbBi}_3\text{Se}_4\text{Te}$ (VI). These two compounds are isostructural, therefore only $\gamma\text{-RbBi}_3\text{Se}_5$ will be described in detail and then compared to $\text{RbBi}_3\text{Se}_4\text{Te}$. This structure is layered and its layers consist of Bi_2Te_3 -type fragments, see Figure 3-6.

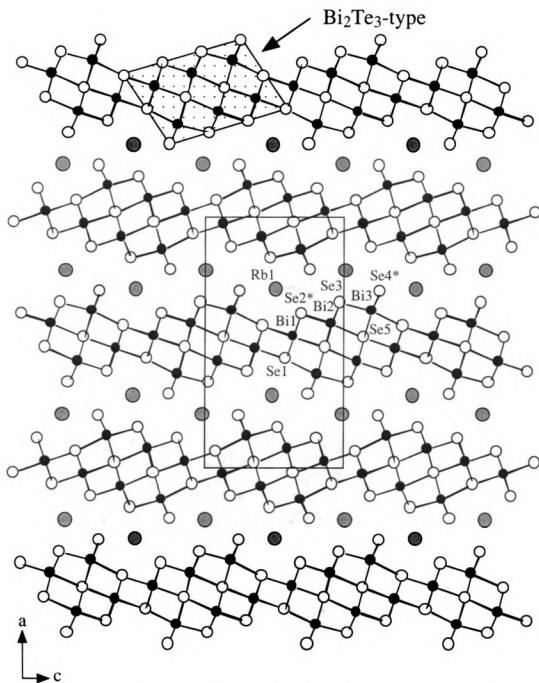


Figure 3-6. Projection of the structure of $\gamma\text{-RbBi}_3\text{Se}_5$ and $\text{RbBi}_3\text{Se}_4\text{Te}$ down the b -axis.

The shaded area indicates the Bi_2Te_3 -type building block and the (*) indicate the Te containing chalcogen sites in $\text{RbBi}_3\text{Se}_4\text{Te}$.



Figure 3-7. Polyhedral representation of the structures of $\text{RbPbBi}_3\text{Se}_6$ and $\gamma\text{-RbBi}_3\text{Se}_5$.

It is interesting to compare this structure with that of $\text{RbPbBi}_3\text{Se}_6$ ¹⁰ in which the layers are composed of infinite Bi_2Te_3 -type fragments. $\text{RbPbBi}_3\text{Se}_6$ can be thought essentially as Bi_2Te_3 with alkali metals residing between the layers. By comparison in $\gamma\text{-RbBi}_3\text{Se}_5$ these fragments are only three bismuth atoms long, see Figure 3-7, and are connected in a stepwise manner creating corrugated layers. Adjacent layers are running in opposite directions. The Rb atoms reside in the space formed between the layers.

The three Bi sites have distorted octahedral coordination (Table 3-13). Bi(1) that connects the Bi_2Te_3 -type blocks together is the least distorted with Bi(1)-Se bonds varying between 2.864(4)-2.961(4) Å and Se-Bi(1)-Se angles varying between 88.58(14)-91.05(8)°. Bi(3) is distorted towards a trigonal pyramid with three short distances trans to three longer ones while Bi(2) is distorted towards a square pyramid with one short bond at 2.773 Å, four bonds between 2.901(3)-3.012(4) Å and one long bond trans to the short bond at 3.131(4) Å.

The Rb atoms have a bicapped trigonal prismatic coordination with Rb-Se distances varying between 3.413(6)-3.796(6) Å.

Interestingly in $\text{RbBi}_3\text{Se}_4\text{Te}$ the Te atoms are not statistically disordered with the Se atoms but seem to preferentially occupy the chalcogen sites that are on the periphery ("surface") of the layers. Both sites are almost occupied by ~50% Te.

Table 3-13. Bond distances (Å) and Selected Angles (deg) for γ -RbBi₃Se₅ and RbBi₃Se₄Te.

γ -RbBi ₃ Se ₅		RbBi ₃ Se ₄ Te	
Bi(1)-Se(1)	2.864(4)	Bi(1)-Se(1)	2.859(4)
Bi(1)-Se(1)	2.942(3)x2	Bi(1)-Se(1)	2.975(3)x2
Bi(1)-Se(5)	2.955(5)	Bi(1)-Se(5)	3.035(4)
Bi(1)-Se(2)	2.961(4)x2	Bi(1)-Te(2)/Se(2)	3.076(2)x2
Bi(2)-Se(2)	2.773(5)	Bi(2)-Te(2)/Se(2)	2.912(3)
Bi(2)-Se(3)	2.901(3)x2	Bi(2)-Se(3)	2.951(2)x2
Bi(2)-Se(5)	3.012(4)x2	Bi(2)-Se(5)	3.018(3)x2
Bi(2)-Se(5)	3.131(5)	Bi(2)-Se(5)	3.154(4)
Bi(3)-Se(4)	2.784(4)x2	Bi(3)-Te(4)/Se(4)	2.918(2)x2
Bi(3)-Se(3)	2.840(5)	Bi(3)-Se(3)	2.855(4)
Bi(3)-Se(1)	3.064(4)	Bi(3)-Se(1)	3.146(4)
Bi(3)-Se(5)	3.227(4)x2	Bi(3)-Se(5)	3.240(3)x2
Rb(1)-Se(1)	3.413(6)	Rb(1)-Se(1)	3.429(5)
Rb(1)-Se(4)	3.490(7)	Rb(1)-Te(4)/Se(4)	3.563(5)
Rb(1)-Se(3)	3.499(5)x2	Rb(1)-Se(3)	3.519(4)x2
Rb(1)-Se(2)	3.711(6)x2	Rb(1)-Te(2)/Se(2)	3.803(4)x2
Rb(1)-Se(4)	3.796(6)x2	Rb(1)-Te(4)/Se(4)	3.783(4)x2
Se(2)-Bi(1)-Se(2)	88.6(1)	Te(2)/Se(2)-Bi(1)-Te(2)/Se(2)	86.66(9)
Se(1)-Bi(1)-Se(2)	91.05(8)	Se(1)-Bi(1)-Te(2)/Se(2)	91.62(8)
Se(1)-Bi(1)-Se(5)	178.9(1)	Se(1)-Bi(1)-Se(5)	177.8(1)
Se(5)-Bi(2)-Se(5)	83.5(1)	Se(5)-Bi(2)-Se(5)	88.8(1)
Se(2)-Bi(2)-Se(5)	92.8(1)	Te(2)/Se(2)-Bi(2)-Se(5)	93.54(9)
Se(3)-Bi(2)-Se(5)	173.0(1)	Se(3)-Bi(2)-Se(5)	174.6(1)
Se(5)-Bi(3)-Se(5)	79.7(1)	Se(5)-Bi(3)-Se(5)	81.32(8)
Se(4)-Bi(3)-Se(4)	95.9(2)	Te(4)/Se(4)-Bi(3)-Te(4)/Se(4)	92.7(1)
Se(3)-Bi(3)-Se(1)	168.1(1)	Se(3)-Bi(3)-Se(1)	168.5(1)

The rest of the structure is similar. Selected distances and angles are shown on Table 3-13. It is tempting to speculate that a lamellar structure is adopted in this case because the larger tellurium atoms need more space to be accommodated. A three-dimensional framework may not have much room to expand, upon replacement of Se with Te atoms, and at the same time achieve optimum packing. By placing the Te atoms on the "surface" of the $[\text{Bi}_3\text{Q}_5]$ slab some of the lattice expansion can be achieved by increasing the interlayer distance (i.e. a-axis).

Comparison of the AM_3Q_5 structures. It is remarkable and extraordinary that the general formula AM_3Q_5 where M is an octahedrally bonded metal atom and Q a chalcogen generates more than 7 structural architectures. It is also exceptional that with the same element i.e. Bi at least 5 different types are observed. The three structures of RbBi_3Se_5 have different asymmetric units. In the γ - form the asymmetric unit has the formula " RbBi_3Se_5 ", the β -form has the formula " $\text{Rb}_2\text{Bi}_6\text{Se}_{10}$ " and the α - form has the formula " $\text{Rb}_3\text{Bi}_9\text{Se}_{15}$ ". The three compounds can be regarded as members of a homologous series $(\text{ABi}_3\text{Se}_5)_n$ where $n = 1, 2, 3, \dots$. As the formula of the asymmetric unit increases, we have a gradual increase in the complexity of the structure. γ - RbBi_3Se_5 with the simplest formula contains only simple three atoms wide Bi_2Te_3 -type fragments, β - RbBi_3Se_5 although is also made of one block (NaCl-type) this block is more elaborate and

α -RbBi₃Se₅ is made up of three different building blocks (Bi₂Te₃-, NaCl- and CdI₂-type). This gradual increase in structural complexity is a unique example in the bismuth chalcogenide systems. Examining the densities α -RbBi₃Se₅ is the most dense ($d = 6.611 \text{ g/cm}^3$) followed by γ -RbBi₃Se₅ ($d = 6.555 \text{ g/cm}^3$) and β -RbBi₃Se₅ ($d = 6.088 \text{ g/cm}^3$). α -RbBi₃Se₅, which is three-dimensional, is expected to be denser than β - and γ -RbBi₃Se₅ which are two-dimensional. β -RbBi₃Se₅ is the least dense compound since it contains a great number of partially occupied Rb sites. If we compare the volumes of α -, γ - RbBi₃S₅ and KBi₃S₅ (β -RbBi₃S₅ has the same structure as KBi₃S₅) we notice that the α - form is more dense having the smaller volume followed by the γ - form. KBi₃S₅ is the least dense having the larger volume although it contains a smaller alkali metal ion.

There are several other chalcogenides with the formula AM₃Q₅ with similar unit cells, volumes, or both to the compounds presented in this paper. Most of these compounds adopt different structure types although the building blocks they contain are similar. Table 3-14 lists these compounds together with those presented here.

Table 3-14. Cell Parameters and Volumes for Several AM_3Q_5 structures.

Formula	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)	Space group
α -RbBi ₃ S ₅	4.16(1)	12.90(2)	18.47(8)	90	987.7	<i>Pmnn</i> (#58)
γ -RbBi ₃ S ₅ *	11.744(2)	4.0519(5)	21.081(3)	90	1003.1(2)	<i>Pnma</i> (#62)
CsBi ₃ S ₅	4.064(1)	12.098(3)	21.098(4)	90	1037.4	<i>Pmnb</i> (#62)
α -RbBi ₃ Se ₅ *	36.779(4)	4.1480(5)	25.363(3)	120.403(2)	3337.3(7)	<i>C2/m</i> (#12)
β -RbBi ₃ Se ₅ *	13.537(2)	4.1431(6)	21.545(3)	91.297(3)	1208.0(3)	<i>P2₁/m</i> (#14)
CsBi ₃ Se ₅ *	13.603(3)	4.1502(8)	21.639(4)	92.453(3)	1221.2(4)	<i>P2₁/m</i> (#14)
γ -RbBi ₃ Se ₅ *	21.956(7)	4.136(1)	12.357(4)	90	1122.0(6)	<i>Pnma</i> (#62)
RbBi ₃ Se ₄ Te*	22.018(3)	4.2217(6)	12.614(2)	90	1172.5(3)	<i>Pnma</i> (#62)
KBi ₃ S ₅ [§]	17.013(5)	4.076(2)	17.365(4)	90	1122.0(6)	<i>Pnma</i> (#62)
CsEr ₃ Se ₅	22.059(9)	4.095(2)	12.155(5)	90	1098.0	<i>Pnma</i> (#62)
TlIn ₃ S ₅ [#]	20.258(6)	3.826(1)	12.821(3)	121.4	848.3	<i>C2/m</i> (#12)

*this work

other compounds such as ACr₃S₅ (A= Rb, Tl) adopt the same structure type.[§] β -RbBi₃S₅ has the structure of KBi₃S₅ (ion exchange product).

Furthermore, if we consider the general formula $(AM_3Q_5)_n$ where $n = 1, 2, 3...$ mentioned above, the compounds found in the AM_3Q_5 systems have $n = 1$, meaning that the formula of the asymmetric unit is the same as the formula of the compound and they consist only from one type of building block. For example, KBi_3S_5 ², $CsEr_3Se_5$ ²⁶ and $TlIn_3S_5$ ²⁷ are only made of CdI_2 -type fragments while $\alpha\text{-RbBi}_3S_5$ ^{17(f)} has only NaCl-type blocks, see Figures 3-3, 3-8, 3-9 and 3-10. KBi_3S_5 , $CsEr_3Se_5$ and $TlIn_3S_5$ have CdI_2 -type running in two different directions and this is a characteristic that is also found in $\alpha\text{-RbBi}_3Se_5$.

5. Concluding Remarks

Six compounds with the general formula ABi_3Q_5 ($A = Rb, Cs$; $Q = S, Se, Te$) were synthesized. $\gamma\text{-RbBi}_3S_5$ and $RbBi_3Se_4Te$ are thermally stable whereas $\alpha\text{-}, \beta\text{-}, \gamma\text{-RbBi}_3Se_5$ and $CsBi_3Se_5$ transform to $Rb_2Bi_8Se_{13}$ and $CsBi_{3.67}Se_6$ respectively. The existence of these phases demonstrates the structural variety and complexity found in the bismuth chalcogenides systems.

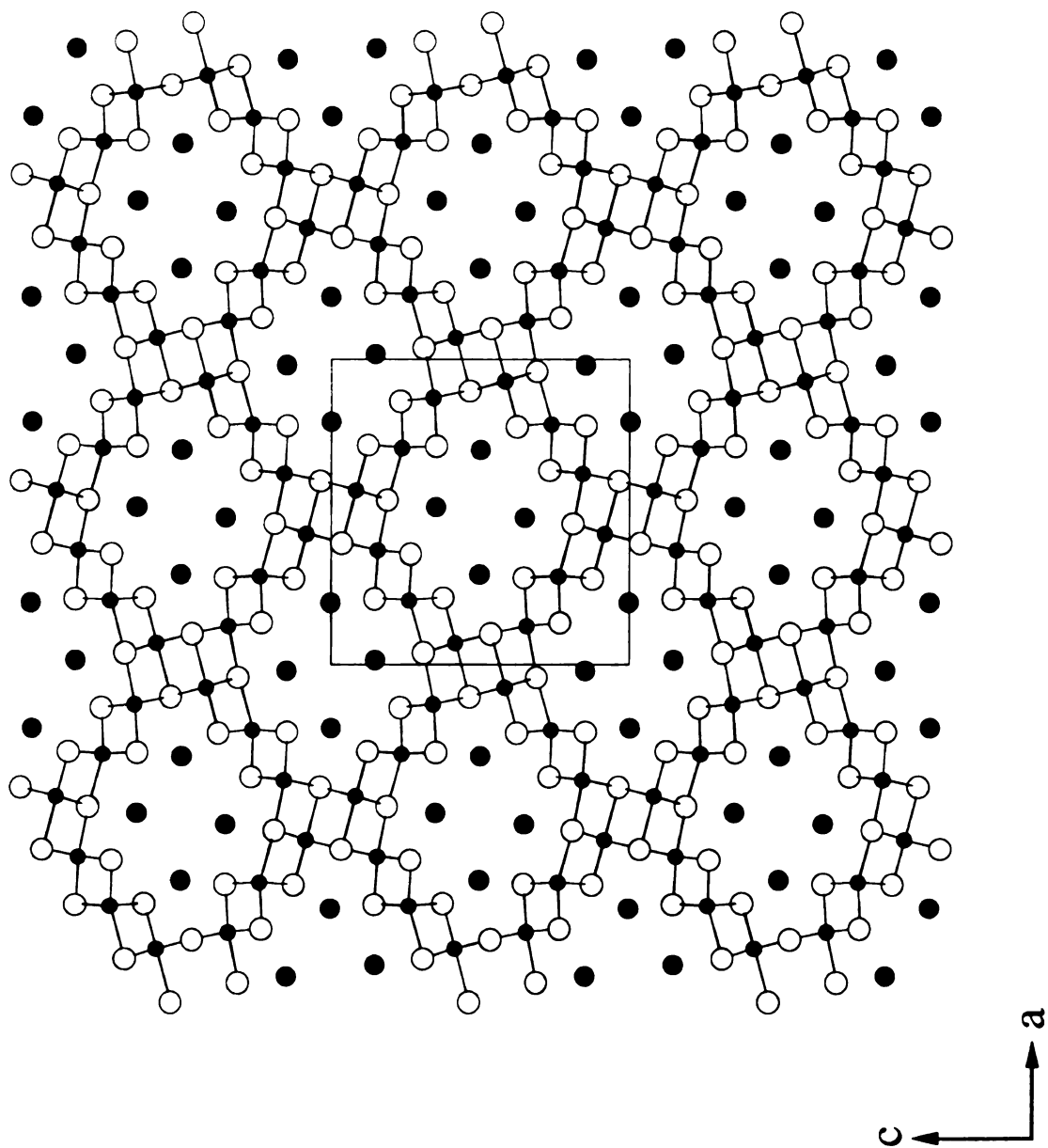


Figure 3-8. Projection of the structure of KBi_3S_5 down the b-axis.

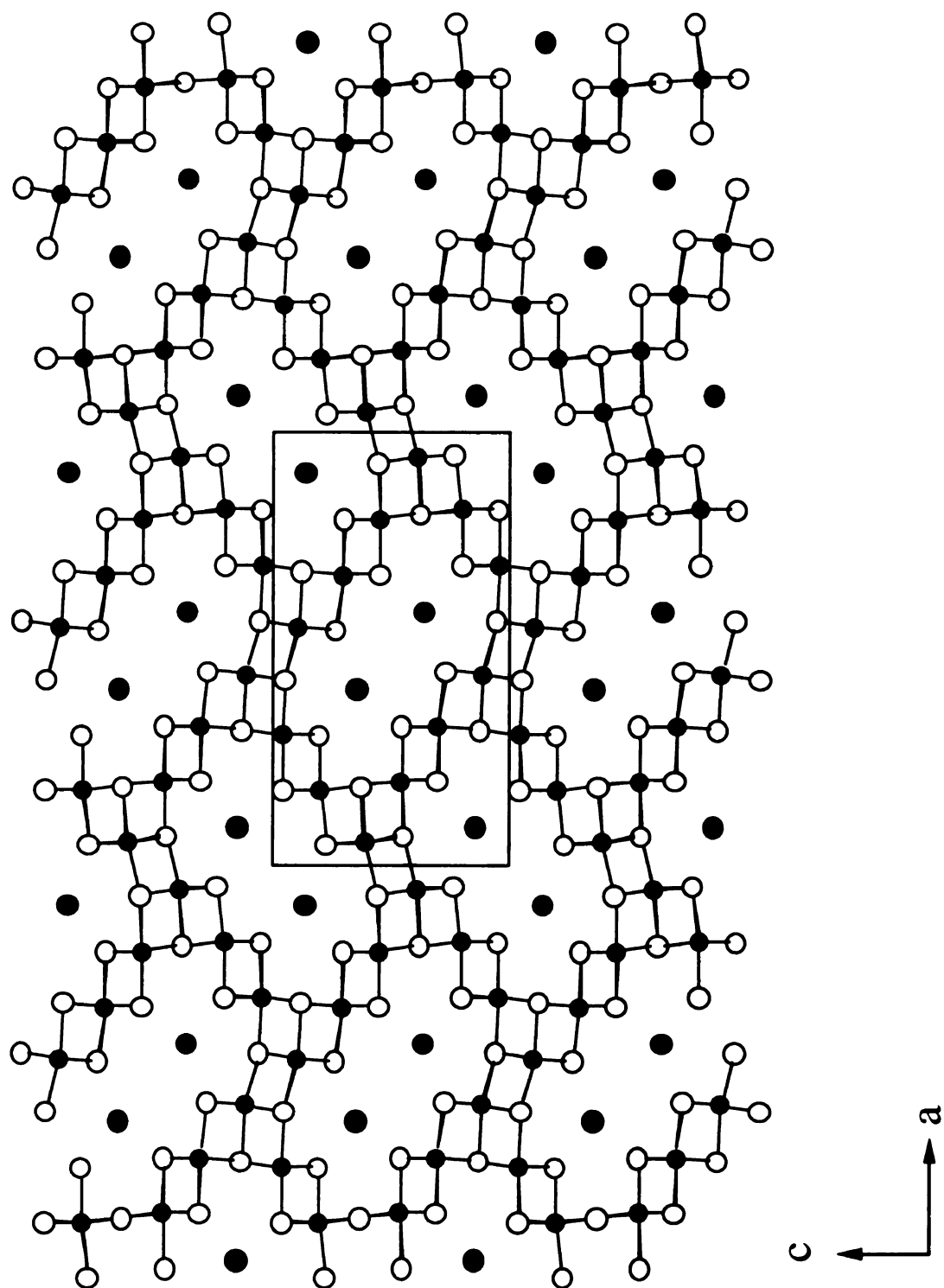


Figure 3-9. Projection of the structure of CsEr_3Se_5 down the b -axis.

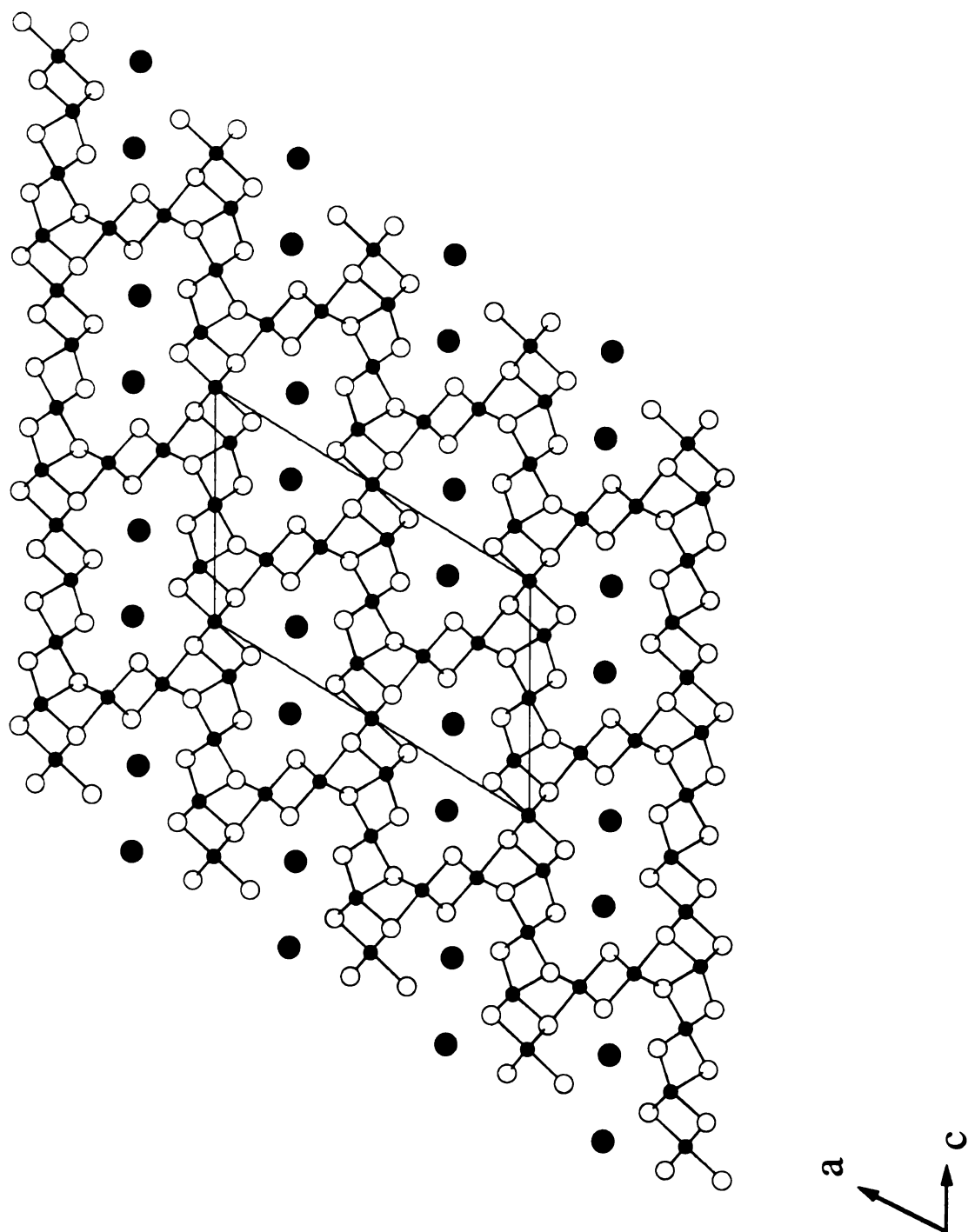


Figure 3-10. Projection of the structure of TlIn_3S_5 down the b -axis.

References

1. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
2. (a) McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301. (b) Chondroudis, K.; Kanatzidis, M. G. *J. Solid State Chem.* **1998**, *136*, 328-332.
3. Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474.
4. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
5. (a) Iordanidis, L.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1928-1930. (b) Iordanidis, L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 8319-8320.
6. Chung, D.-Y.; Jovic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
7. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science (Washington, D. C.)* **2000**, *287*, 1024-1027.
8. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162.
9. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805.
10. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
11. Mroczek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.

-
12. Choi, K.-S.; Chung, D.-Y.; Mrotzek, A.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Submitted for publication*.
 13. Iordanidis, L.; Brazis, P. W.; Kyratsi, T.; Ireland, J.; Lane, M.; Kannewurf, C. R.; Dyck, J. S.; Uher, C.; Ghelani, N. A.; Hogan, T.; Kanatzidis, M. G. *Chem. Mater.* **2000**, in press. See also Chapter 2.
 14. Choe, W.; Lee, S.; O'Connell, P.; Covey, A. *Chem. Mater.* **1997**, 9, 2025-2030.
 15. (a) Adouby, K.; Perez Vicente, C.; Jumas, J. C.; Fourcade, R.; Abba Touré, A. Z. *Kristallogr.* **1998**, 213, 343-349. (b) Perez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Abba Touré, A.; Kra, G. *Inorg. Chem.* **1999**, 38, 2131-2135.
 16. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, 12, 1011-1017.
 17. (a) Glemser, O.; Filcek, M. Z. *Anorg. Allg. Chem.* **1955**, 279, 321-323. (b) Gattow, G.; Zemann, J. Z. *Anorg. Allg. Chem.* **1955**, 279, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, 6, 961-964. (d) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, 8, 677-678. (e) Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, 252, 96-99. (f) Schmitz, D.; Bronger, W. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, 29, 438-439. (g) Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 676-683. (h) Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, A37, 399-407. (i) Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 631-638. (j) Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, 35, 136-140.
 18. Kanatzidis, M. G. *Semicond. Semimet.* **2000**, in press.
 19. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, 59, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, 63, 45-89. (c) Makovicky, E. Z. *Kristallogr.* **1985**, 173, 1-

-
23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, *160*, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, *5*, 545-591.
20. Bi₂Te₃- and CdI₂- type fragments derive of course from NaCl, however, we have used this notation to differentiate between the various "cuts" of the NaCl lattice.
21. (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Kotüm, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969. (c) Tandon, S. P.; Gupta, J. P. *Phys. Status Solidi.* **1970**, *38*, 363-367.
22. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.
23. teXsan v1.8, 1996 Molecular Structure Corporation, The Woodlands, Texas 77831 USA.
24. Chung, D.-Y.; Kanatzidis, M. G. work in progress.
25. The R values for α -RbBi₃S₅ are ~10% indicating most probably that the structural solution is not right.
26. Kim, S.-J.; Park, S.-J.; Yun H.; Do, J. *Inorg. Chem.* **1996**, *35*, 5283-5289.
27. Walther, R.; Deiseroth, H. J. *Z. Kristallogr.* **1996**, *211*, 49.

CHAPTER 4

Observation of Topotactic Two-Dimensional to Three-Dimensional Transformations in the Solid State. Redox-Induced “Zipper” Action in Ternary Bismuth Selenides

1. Introduction

Interest in multinary bismuth chalcogenide compounds has recently increased due to their potential relevance in thermoelectric applications.¹ Such compounds, however, are also interesting for other scientific reasons particularly with respect to their structural features, electronic properties and smooth interconversions which gives them the ability to form unusual homologous series. Exemplary are the bismuth compounds, occurring in natural sulfosalts which exhibit a staggering compositional complexity and structural diversity². Bismuth can adopt several different coordination environments, from trigonal pyramidal, to square pyramidal, to octahedral (sometimes distorted), to trigonal prismatic and even 7, 8 and 9 coordination polyhedra. Responsible for such a rich repertoire of coordination environments is the bismuth $6s^2$ lone pair of electrons that can be

stereochemically expressed to locally distort the bismuth coordination geometry, or suppressed by hybridizing with energetically adjacent p and d orbitals to produce a regular octahedral Bi^{3+} center. In the past twenty years, only a few bismuth compounds have been structurally characterized³⁻¹⁰. Recently, however, several new ternary and quaternary compounds have been synthesized expanding significantly this class of compounds¹¹⁻²⁶.

Our interest to explore new solid state chemistry in the Rb/Bi/Se and Cs/Bi/Se systems led us to the discovery of $\text{A}_2\text{Bi}_4\text{Se}_7$, $\text{A}_3\text{Bi}_7\text{Se}_{12}$ ($\text{A} = \text{Rb}, \text{Cs}$) and $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$. The behavior of these phases was very different from other A/Bi/Se phases we studied in several ways. First, moisture sensitivity was apparent which made polycrystalline powders of $\text{A}_2\text{Bi}_4\text{Se}_7$, $\text{A}_3\text{Bi}_7\text{Se}_{12}$ and $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ to become wet and clump together. Second single crystals gave diffraction patterns that could not be indexed to one unit cell and third X-ray powder diffraction patterns seemed to change with time. Careful diffraction and spectroscopic work on samples of $\text{Rb}_2\text{Bi}_4\text{Se}_7$, monitored over a period of 1-3 years, helped us to understand the puzzling behavior of these systems and discover an unprecedented and remarkable redox transformation in the solid state. This transformation, of which we know no other examples, involves the topotactic oxidative

coupling of entire rows of Se^{2-} ions to Se_2^{2-} groups in a cooperative way reminiscent of the closing action of a zipper.

The number of topotactic single-crystal to single-crystal solid state transformations is limited. Most of the cases involve the dimerization or polymerization of organic²⁷ or organometallic²⁷ molecules by heat or light, or loss of solvent molecules from coordination complexes²⁸ or rigid framework structures²⁹ without the collapse of the rest of the structure. However, these examples are quite different from ours because they involve mainly organic or organometallic compounds and possess a molecular structure. Our structures are not porous and there is no solvent to be lost. Some examples that bears some similarity with our systems is the topotactic oxidation of $\gamma\text{-MnO}_2$ to $\text{MnO}(\text{OH})$ with hydrazine³⁰ and the reduction of $\text{Mg}_3(\text{VO}_4)_2$ to $\text{Mg}_3\text{V}_2\text{O}_6$ by hydrogen.³¹

This amazing zipper process results in the daughter compounds ABi_4Se_7 ^{32a}, $\text{A}_2\text{Bi}_7\text{Se}_{12}$, $\text{ABi}_7\text{Se}_{12}$ ($\text{A} = \text{Rb}, \text{Cs}$ ^{32b}) and $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$. The facility with which the process transforms the starting compounds is attested by the clean conversion of whole single crystals from one phase to the next without loss of crystallinity.

2. Experimental Section

Reagents. Chemicals were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999% Noranda, Canada), selenium powder (99.95 % purity, -200 mesh, Cerac Inc., Milwaukee), selenium shots (99.999% Noranda, Canada), bismuth selenide powder (99.999% purity, -325 mesh, Cerac Inc., Milwaukee), rubidium metal (99.8% purity, Alfa Aesar, Ward Hill, MA), cesium metal (99.98% purity, Alfa Aesar, Ward Hill, MA). A_2Se ($A = Rb, Cs$) was prepared by a stoichiometric reaction of the corresponding alkali metal and selenium in liquid ammonia.

Synthesis.

Bi_2Se_3 . A mixture of 9.407 g (0.045 mol) of Bi and 5.331 g (0.068 mol) of Se was transferred into a silica tube which was flame-sealed under vacuum. The tube was heated to 600 °C in 12 h, stayed at 600 °C for 2 days and then cooled down to 50 °C in 6 h. The product was ground into powder and used for further reactions.

$Rb_2Bi_4Se_7$ (I). A mixture of 0.060 g (0.240 mmol) Rb_2Se and 0.314 g (0.480 mmol) Bi_2Se_3 was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 6 days at 810 °C, then cooled to 510 °C at 7 °C/h and further cooled to 50 °C in 10 h. The product consisted of silver-gray long laths.

Semiquantitative energy dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of $\text{Rb}_{2.2}\text{Bi}_{3.8}\text{Se}_7$.

$\text{Cs}_2\text{Bi}_4\text{Se}_7$ (II). A mixture of 0.060 g (0.174 mmol) Cs_2Se and 0.228 g (0.348 mmol) Bi_2Se_3 was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 1 day at 680 °C, then cooled to 480 °C at 7 °C/h and further cooled to 50 °C in 10 h. The product consisted of silver-gray long laths. SEM/EDS on several crystals gave an average composition of $\text{Cs}_{2.1}\text{Bi}_{3.5}\text{Se}_7$.

$\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ (III). A mixture of 0.100 g (0.290 mmol) Cs_2Se and 0.354 g (0.541 mmol) Bi_2Se_3 was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a gas-oxygen torch until the sample melted and then the tube was removed from the flame and was let to solidify. The procedure was repeated two more times. The product consisted of a silver chunk with blade-like crystals growing across its surface. SEM/EDS analysis on several crystals gave an average composition of $\text{Cs}_{3.1}\text{Bi}_{6.7}\text{Se}_{12}$.

$\text{Rb}_3\text{Bi}_7\text{Se}_{12}$ (IV). A mixture of 0.060 g (0.240 mmol) Rb_2Se and 0.367 g (0.559 mmol) Bi_2Se_3 was processed and heated using the same heating profile as for (II). The product consisted of silver-gray long laths. SEM/EDS on several crystals gave an average

composition of $\text{Rb}_{3.5}\text{Bi}_{6.8}\text{Se}_{12}$. It has to be noted that in the synthesis of $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$ there is a small impurity of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ as evidenced by X-ray powder diffraction.

$\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ (V). A mixture of 0.060 g (0.240 mmol) Rb_2Se and 0.367 g (0.559 mmol) Bi_2Se_3 was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated for 6 h at 700 °C, then cooled to 600 °C in 6 h and further cooled to 50 °C in 7 h. SEM/EDS on several crystals gave an average composition of $\text{Rb}_{3.5}\text{Bi}_{6.8}\text{Se}_{17}$.

ABi_4Se_7 (A = Rb, Cs) (VI and VII). An amount of 0.1 g $\text{A}_2\text{Bi}_4\text{Se}_7$ were ground into powder and were added into 100 ml of a 2.5 mM solution of I_2 in degassed wet CH_3CN at 23 °C. The mixture was continuously stirred under an N_2 atmosphere. The oxidation to ABi_4Se_7 is complete in less than 60 min. SEM/EDS on several crystals gave an average composition of $\text{Rb}_{1.3}\text{Bi}_{4.2}\text{Se}_7$ and $\text{Cs}_{1.0}\text{Bi}_{3.8}\text{Se}_7$.

$\text{A}_2\text{Bi}_7\text{Se}_{12}$ (A = Cs, Rb) (VIII and IX). An amount of 0.450g of $\text{A}_3\text{Bi}_7\text{Se}_{12}$ was ground into powder and added into 250 ml of H_2O . This suspension was under stirred and air was bubbled through it at very small flow. After six hours, the transformation of $\text{A}_3\text{Bi}_7\text{Se}_{12}$ to $\text{A}_2\text{Bi}_7\text{Se}_{12}$ was complete as judged from X-ray powder diffraction.

SEM/EDS on several crystals gave an average composition of $\text{Rb}_{2.3}\text{Bi}_{6.8}\text{Se}_{12}$ and $\text{Cs}_{1.8}\text{Bi}_{6.7}\text{Se}_{12}$.

$\text{ABi}_7\text{Se}_{12}$ (A = Cs, Rb) (X and XI) An amount of 0.100 g of $\text{A}_3\text{Bi}_7\text{Se}_{12}$ was ground into powder and added into 350 ml of a 2.25 mM I_2 in wet CH_3CN ($\text{H}_2\text{O}:\text{CH}_3\text{CN}$ 1:7 v/v). The mixture was continuously stirred and kept under an N_2 atmosphere. The solution was left overnight and the next day the transformation of $\text{A}_3\text{Bi}_7\text{Se}_{12}$ to $\text{ABi}_7\text{Se}_{12}$ was complete as judged from X-ray powder diffraction. SEM/EDS on several crystals gave an average composition of $\text{Rb}_{1.0}\text{Bi}_{6.9}\text{Se}_{12}$ and $\text{Cs}_{1.2}\text{Bi}_{6.5}\text{Se}_{12}$.

$\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ (XII). An amount of 1 g of $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ was ground into powder and added into 500 ml of H_2O . This suspension was under stirred and air was bubbled through it at very small flow. The reaction was left overnight and the transformation of $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ to $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ was complete as judged from X-ray powder diffraction. SEM/EDS on several crystals gave an average composition of $\text{Rb}_{2.3}\text{Bi}_{6.8}\text{Se}_{12}$.

3. Physical Measurements

The instruments and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis*, *Infrared Spectroscopy* and *Powder X-ray diffraction* are the same as that in Chapter 2 (Section 3).

Raman Spectroscopy. One or both of two different procedures were used for data collection:

(i) Raman spectra were recorded on a Holoprobe Raman Spectrograph equipped with a 633 nm HeNe laser and a CCD camera detector. The instrument was coupled to an Olympus BX60 microscope. For each sample, crystals were simply placed onto a small glass slide and a 50x objective lens was used to choose the area of the crystal specimens to be measured. The spot size of the laser beam when using the 50x objective lens was 10 μm .

(ii) Raman spectra ($600\text{--}175\text{ cm}^{-1}$, at 4 cm^{-1} resolution) were recorded on a BIO-RAD FT Raman spectrometer equipped with a Spectra-Physics Topaz T10-106c 1.064nm YAG laser and a GE detector. Single crystals were loaded into a glass tube.

Single crystal X-ray crystallography. A Bruker (formerly Siemens) SMART Platform CCD diffractometer, using graphite monochromatized Mo $K\alpha$ radiation, was used for data collection. Several different sets of frames, covering a random area of the

reciprocal space, were collected using 0.3° steps in ω [0.2° for (VIII)] at a detector-to-sample distance of ~5 cm. In addition, occasionally, for the purpose of a better absorption correction, ϕ scans were collected (0.3° steps in ϕ). The low temperature data were obtained on a CCD diffractometer equipped with an Oxford Cryosystems "Cryostream" low temperature system. The SMART³³ software was used for data acquisition and SAINT³³ for data extraction. The absorption correction was done with SADABS³³ and the structure solution and refinement were done with the SHELXTL³³ or/and SHELX97³⁴ package of crystallographic programs.

Rb₂Bi₄Se₇ (I). A region of 1.3 hemispheres of reciprocal space was surveyed to a resolution of 0.78 Å with an exposure time of 30 s per frame. Final cell constants were calculated from a set of 1252 strong reflections (Table 4-1). The structure was solved with direct methods. The first solution could not yield a reasonable refinement because it was shifted from the correct origin resulting in unreasonable symmetry equivalent atoms. Although the second best solution had a higher combined figure of merit (CFOM as defined in SHELXS), it contained the correct atoms with the right origin. Initially, four bismuth, seven sulfur, and two rubidium atoms were located (R1 = 19.4%, wR2 = 51.9%). The atoms were refined anisotropically (R1 = 9.5%, wR2 = 26.8%). At that point the isotropic displacement parameter, U_{iso} , of Rb(3) was high, 0.074 Å² compared to that

of Rb(1), $U_{\text{isi}} = 0.026 \text{ \AA}^2$. A significant peak of electron density ($\sim 20 \text{ e} \cdot \text{\AA}^{-3}$) also appeared 2.27 $\text{\AA}$ from Rb(3). This peak was assigned as Rb(2) and its occupancy was refined together with the occupancy of Rb(3) ($R1 = 6.8\%$, $wR2 = 17.6\%$). The occupancy of Rb(2) was 0.33678 while that of Rb(3) was 0.16006. Since Rb(3) is 2.69(1) $\text{\AA}$ away from its symmetry equivalent and 2.27(1) $\text{\AA}$ from Rb(2), statistically Rb(3) should be 33% occupied while Rb(2) should be 67% occupied (from a total occupancy of 0.500). The occupancy of Rb(2) was constrained to value of 0.3333 and Rb(3) to 0.1667 with no change in the R values. Rb(2) was refined anisotropically ($R1 = 6.6\%$, $wR2 = 16.0\%$). The final formula was $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-2.

$\text{Cs}_2\text{Bi}_4\text{Se}_7$ (II). More than a hemisphere of data was collected with an exposure time of 55 s per frame. The final cell was calculated from a set of 3423 reflections (Table 4-3). The resolution of the data set is 0.74 $\text{\AA}$. Because the compound is isostructural with (I), the coordinates from (I) were used as a starting point for subsequent refinements. The final R values were $R1 = 3.7\%$, $wR2 = 9.4\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-4.

$\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ (III). A full sphere of data was collected with an exposure time of 40 s per frame. The final cell was calculated from a set of 4292 reflections (Table 4-5). The resolution of the data set was 0.75 $\text{\AA}$. The structure was solved with direct methods in the

space group *C2/m*. Initially, seven bismuth, two cesium, and twelve selenium atoms were found. After refinement, the R1 and wR2 values were 9.0% and 26.6% respectively. The U_{iso} of Cs(2) was high compared ($U_{\text{iso}} = 0.070 \text{ \AA}^2$) to the U_{iso} of Cs(1) ($U_{\text{iso}} = 0.011 \text{ \AA}^2$), suggesting too much positive charge in the site. In addition, there was a symmetry equivalent atom generated 2.267(4) Å away from Cs(2). Therefore the occupancy of Cs(2) was let to refine and this resulted in occupancy/ U_{iso} for Cs(2) of 0.25180/0.018 Å² (R1 = 6.3%, wR2 = 14.2%). The occupancy was constrained to 0.25 with no change in the R values. All atoms were refined anisotropically (R1 = 3.5%, wR2 = 8.3%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-6.

The compound Cs₃Bi₇Se₁₂ has been described earlier in the *Cm* space group⁶. In *Cm* the Cs(2) instead of being disordered over two different sites, is located only on one site, while the other site is empty. According to the authors, the choice of *Cm* instead of *C2/m* was made because they wanted to avoid a disorder model. Since the two sites are in fact chemically equivalent, we believe a disorder model³⁵ is preferable for the Cs atoms since in *C2/m* the remaining part of the structure is described very well with only half the number of parameters.

Rb₃Bi₇Se₁₂ (IV). A full sphere of reciprocal space was surveyed to a resolution of 0.84 Å with an exposure time of 30 s per frame. Final cell constants were calculated from a set of 1852 strong reflections (Table 4-7). Because the compound is isostructural with (III), the coordinates from (III) were used as a starting point for subsequent refinements. The final R values were R1 = 7.4%, wR2 = 15.8%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-8.

Rb₄Bi₁₀Se₁₇ (V). A full sphere of reciprocal space was surveyed to a resolution of 0.69 Å with an exposure time of 45 s per frame. Final cell constants were calculated from a set of 818 strong reflections from the actual data collection (Table 4-9). The structure was solved with direct methods. Attempts to solve the structure in *C2/m* were unsuccessful but when the symmetry was dropped to *Cm*, the structure was solved. Initially all the Bi-Se framework was located. Subsequently the missing center of symmetry was found and the space group was changed to *C2/m* (R1 = 13%, wR2 = 37%). Six peaks appeared in the space between the layers and these peaks were assigned as Rb. Since the peaks were too close to each other their occupancies were also refined (R1 = 7.6%, wR2 = 21.8%). An constraint command was used to bring the amount of Rb to 4 without any significant change in the R values. All the atoms were refined anisotropically (R1 = 5.7%, wR2 = 14.0%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-10.

RbBi₄Se₇ (VI). Data on this compound were collected on two different crystals.

The second crystal used for data collection *was the same crystal (now transformed) used to determine the structure of compound (I).*

(i) The first crystal was selected from a converted batch of sample. A region of 1.3 hemispheres of reciprocal space was surveyed to a resolution of 0.84 Å with an exposure time of 90 s per frame (Table 4-1).

The structure was solved with direct methods. The best solution suggested by the direct methods program was, as in the case for (I), shifted from the correct origin resulting in unreal symmetry equivalent atoms. The second, best solution, with the same CFOM as the first, gave the correct atoms with the correct origin. Initially four bismuth, and seven sulfur atoms were found ($R1 = 26.4\%$, $wR2 = 61.1\%$). At this point all the Bi/Se framework was located leaving a large cavity where the Rb atoms should reside. Because there were many “ghost” peaks the Rb atoms could not be located at this stage; so we proceeded to refine the Bi/Se framework atoms anisotropically ($R1 = 16.1\%$, $wR2 = 45.6\%$). At this point, two peaks with electron densities of $13.9 \text{ e}\cdot\text{\AA}^{-3}$ and $13.5 \text{ e}\cdot\text{\AA}^{-3}$ appeared in the middle of the cavity and were assigned as Rb(1) and Rb(2) respectively ($R1 = 10.1\%$, $wR2 = 29.0\%$). The Rb atoms had large U_{iso} isotropic displacement parameters, of $0.21 \text{ \AA}^2$ and $0.23 \text{ \AA}^2$ respectively and there was too much Rb in the structure than what was needed to achieve electroneutrality. Therefore the occupancies

were refined ($R1 = 9.2\%$, $wR2 = 24.9\%$) and the occupancy/ U_{iso} for Rb(1) were 0.28/0.12 $\text{\AA}^2$ and for Rb(2) 0.24/0.11 $\text{\AA}^2$. The total occupancy of the Rb atoms was 0.52, very close to what is required for electroneutrality (0.500). Their occupancies were constrained to 0.25 each and the isotropic displacement parameters after refinement were 0.09960 $\text{\AA}^2$ for Rb(1) and 0.11160 $\text{\AA}^2$ for Rb(2) with no significant changes in the R values. The Rb atoms were finally refined anisotropically ($R1 = 8.2\%$, $wR2 = 20.9\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-11.

(ii) The same *crystal* used for the data collection of (I) was left to stand on the glass fiber undisturbed, exposed to air for a few weeks. Data were collected again almost one month after the initial data collection using a SMART Platform CCD diffractometer with the same technique as above and an exposure time of 25 s per frame. The initial cell, determined by 31 reflections was that of RbBi_4Se_7 (not $\text{Rb}_2\text{Bi}_4\text{Se}_7$) and final cell constants were calculated from a set of 717 strong reflections from the data collection. The solution of the previous data set was used for refinements and the results are presented in Table 4-1.

CsBi₄Se₇ (VII). A full sphere of reciprocal space was surveyed to a resolution of 0.74 Å with an exposure time of 35 s per frame. Final cell constants were calculated from a set of 1324 strong reflections from the actual data collection (Table 4-3).

Because the compound is isostructural with (VI), the coordinates from (VI) were used to refine the structure. The final R values were R1 = 5.3% and wR2 = 12.3%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-12.

Cs₂Bi₇Se₁₂ (VIII). The *same* crystal used for collection of Cs₃Bi₇Se₁₂ (III) was let to stand in air, still mounted on a fiber, undisturbed. In less than one week after the initial data collection, a cell re-determination had shown that the cell had already changed to that of (VIII). Data were collected after a few weeks but attempts to solve the structure were unsuccessful because of twinning, which resulted in splitting of the reflections. In an attempt to get better quality data, the crystal was cut in half and data were recollected on one of the fragments. This resulted in a single crystal and better data. A hemisphere of reciprocal space was surveyed to a resolution of 0.73 Å with an exposure time of 45 s per frame. Final cell constants were calculated from a set of 948 strong reflections ($I > 10\sigma(I)$) from the actual data collection (Table 4-5).

The structure was solved with direct methods. Attempts to solve the structure in *C2/m* were unsuccessful but when the symmetry was dropped to *Cm*, the structure was

solved. Initially all the Bi-Se framework was located. Subsequently the missing center of symmetry was found and the space group was changed to $C2/m$. The existing Bi and Se atoms were refined anisotropically because due to large number of “ghost” peaks the Cs atoms were difficult to locate. Careful examination of the electron density map revealed several peaks sitting in trigonal prismatic sites between the layers. The sites were assigned as Cs atoms and their occupancy was refined since several of these peaks were too close to each other to be occupied at the same time. The formula of the anionic Bi-Se framework taking into account the diselenides is $[(\text{Bi}^{3+})_7(\text{Se}^{2-})_{11}(\text{Se}^{-1})]^{2-}$. For electroneutrality reasons the total occupancy of the Cs atoms was constrained to two fully occupied Cs sites. The final R values ($I > 2\sigma(I)$) were $R1 = 7.5\%$ and $wR2 = 18.6\%$. The fractional coordinates and temperature factors are given in Table 4-13.

Rb₂Bi₇Se₁₂ (IX). A full sphere of reciprocal space was surveyed to a resolution of 0.84 Å with an exposure time of 55 s per frame. Final cell constants were calculated from a set of 2013 strong reflections (Table 4-7). Because the compound was isostructural with (VIII), the coordinates of (VIII) for the Bi and Se atoms were used as a starting point for subsequent refinements. The existing Bi and Se were refined anisotropically. The Rb atoms were found and treated similarly as in the case of (VIII). The final R values ($I > 2\sigma(I)$) are $R1 = 9.06\%$ and $wR2 = 21.36\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-14.

CsBi₇Se₁₂ (X). A full sphere of reciprocal space was surveyed to a resolution of 0.88 Å with an exposure time of 55 s per frame. Final cell constants were calculated from a set of 1340 strong reflections (Table 4-5). The structure was solved with direct methods (SIR97)³⁶. All the atoms were found and from the connectivity it was obvious that this was the all-the-way-transformed structure. The same [Bi₇Se₁₂] layers that exist in Cs₃Bi₇Se₁₂ remain intact but now all the layers are connected with each other by diselenide bonds. Unfortunately due to the broad shape of the peaks the integration and the subsequent absorption correction with SADABS were not successful, consequently there were residual peaks around the heavy atoms, high temperatures factors and considerably high R values. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-15.

RbBi₇Se₁₂ (XI). Only the cell was determined and was found to be $a = 22.403(1)$ Å, $b = 4.1862(1)$ Å, $c = 15.5303(7)$ Å, $\beta = 107.030(2)^\circ$.

Rb₂Bi₁₀Se₇ (XII). A full sphere of reciprocal space was surveyed to a resolution of 0.84 Å with an exposure time of 53 s per frame. Final cell constants were calculated from a set of 2793 strong reflections from the data collection (Table 4-9). The structure was solved with direct methods. All the atoms were found and from the connectivity it was obvious that this was the all-the-way-transformed structure. The same [Bi₁₀Se₁₇]

layers that exist in $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ remain intact but now all the layers are connected with each other by diselenide bonds. Final R values, $R1 = 7.0\%$, $wR2 = 18.2\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4-16.

Table 4-1. Crystallographic Data for Rb₂Bi₄Se₇ and RbBi₄Se₇.

Empirical formula	Rb ₂ Bi ₄ Se ₇ ^a (I)	RbBi ₄ Se ₇ ^a (VI)
Formula weight	1559.58	1474.11
Temperature, K	173(2)	123(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 13.062(2) <i>b</i> = 4.2072(5) <i>c</i> = 15.301(2) β = 93.137(2)°	<i>a</i> = 22.3519(8) <i>b</i> = 4.1728(3) <i>c</i> = 19.718(1) β = 116.506(3)°
Volume, Å ³	839.61(17)	1645.82(17)
Z	2	4
Density (calculated), g/cm ³	6.169	5.949
Absorption coefficient, mm ⁻¹	62.689	61.020
F(000)	1288	2428
Crystal size, mm ³	0.65 x 0.025 x 0.025	0.65 x 0.025 x 0.025
θ range for data collection	1.56 to 25.09°	1.84 to 25.09°
Index ranges	-15 ≤ <i>h</i> ≤ 8 -4 ≤ <i>k</i> ≤ 5 -18 ≤ <i>l</i> ≤ 17	-20 ≤ <i>h</i> ≤ 26 -4 ≤ <i>k</i> ≤ 4 -23 ≤ <i>l</i> ≤ 22
Reflections collected	3887	4041
Independent reflections	1689 [<i>R</i> _(int) = 0.0365]	1637 [<i>R</i> _(int) = 0.1218]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	1689 / 0 / 85	1637 / 0 / 80
Goodness-of-fit on <i>F</i> ²	1.066	1.065
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0658 <i>wR</i> 2 = 0.1602	<i>R</i> 1 = 0.0980 <i>wR</i> 2 = 0.2306
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0924 <i>wR</i> 2 = 0.1736	<i>R</i> 1 = 0.1677 <i>wR</i> 2 = 0.2559
Extinction	-	0.00025(6)
Largest peak and hole, e·Å ⁻³	6.605 and -3.151	6.426 and -4.016

Table 4-1.(cont'd).

Empirical formula	RbBi ₄ Se ₇ ^b (VI)
Formula weight	1474.11
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 22.286(5) <i>b</i> = 4.1760(8) <i>c</i> = 19.794(4) β = 116.89(3)°
Z, Volume, Å ³	4, 1642.9(6)
Density (calculated), g/cm ³	5.960
Absorption coefficient, mm ⁻¹	61.127
F(000)	2428
Crystal size, mm ³	0.35 x 0.025 x 0.025
θ range for data collection	1.84 to 25.22°
Index ranges	-23 ≤ <i>h</i> ≤ 26 -4 ≤ <i>k</i> ≤ 4 -23 ≤ <i>l</i> ≤ 23
Reflections collected	4127
Independent reflections	1651 [<i>R</i> _(int) = 0.0843]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1651 / 0 / 80
Goodness-of-fit on <i>F</i> ²	1.153
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0822, <i>wR</i> 2 = 0.2092
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1084, <i>wR</i> 2 = 0.2234
Extinction	0.00013(5)
Largest peak and hole, e·Å ⁻³	5.639 and -3.755

a. Both data sets were collected in the same crystal, the first before and the second has transformed.

b. The data was collected in a crystal selected from a converted batch of sample.

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 4-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_4\text{Se}_7$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3897(1)	-0.2500	0.4312(1)	20(1)	
Bi(2)	0.1668(1)	0.2500	0.2780(1)	19(1)	
Bi(3)	0.0591(1)	0.2500	-0.1240(1)	20(1)	
Bi(4)	0.2728(1)	-0.2500	0.0471(1)	18(1)	
Se(1)	0.5402(3)	-0.7500	0.3877(2)	18(1)	
Se(2)	0.2339(3)	0.2500	0.4593(2)	19(1)	
Se(3)	0.0043(3)	-0.2500	0.3023(2)	20(1)	
Se(4)	0.2155(3)	-0.2500	-0.1414(2)	20(1)	
Se(5)	0.4118(3)	-0.7500	0.0347(2)	21(1)	
Se(6)	0.3126(3)	-0.2500	0.2423(2)	18(1)	
Se(7)	0.0952(2)	0.2500	0.0842(2)	17(1)	
Rb(1)	0.4320(3)	-0.7500	-0.1889(2)	29(1)	1
Rb(2)	0.1878(4)	-0.2500	-0.3669(4)	32(1)	0.67
Rb(3)	0.0531(8)	-0.2500	-0.4667(7)	32(3)	0.33

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-3. Crystallographic Data for Cs₂Bi₄Se₇ and CsBi₄Se₇.

Empirical formula	Cs ₂ Bi ₄ Se ₇ (II)	CsBi ₄ Se ₇ ^a (VII)
Formula weight	1654.46	1521.55
Temperature, K	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 13.227(1) <i>b</i> = 4.1857(4) <i>c</i> = 15.556(2) <i>β</i> = 94.592(2)°	<i>a</i> = 22.224(7) <i>b</i> = 4.178(1) <i>c</i> = 19.742(6) <i>β</i> = 116.384(1)°
Z, Volume, Å ³	2, 858.5(1)	4, 1642.2(9)
Density (calculated), g/cm ³	6.400	6.154
Absorption coefficient, mm ⁻¹	59.856	60.395
F(000)	1360	2500
Crystal size, mm ³	0.01 x 0.02 x 0.5	0.42 x 0.02 x 0.02
θ range for data collection	2.11 to 28.46°	1.85 to 28.58°
Index ranges	-17 ≤ <i>h</i> ≤ 17 -5 ≤ <i>k</i> ≤ 5 -19 ≤ <i>l</i> ≤ 18	-28 ≤ <i>h</i> ≤ 28 -5 ≤ <i>k</i> ≤ 5 -26 ≤ <i>l</i> ≤ 25
Reflections collected	5978	7393
Independent reflections	2224 [R _(int) = 0.0394]	2154 [R _(int) = 0.0674]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2224 / 0 / 86	2154 / 0 / 80
Goodness-of-fit on F ²	1.084	0.933
Final R indices [I > 2σ(I)]	R1 = 0.0365 wR2 = 0.0944	R1 = 0.0526 wR2 = 0.1227
R indices (all data)	R1 = 0.0411 wR2 = 0.0966	R1 = 0.0988 wR2 = 0.1304
Extinction	0.00107(9)	0.000043(15)
Largest peak and hole, e·Å ⁻³	3.792 and -3032	6.112 and -3.589

a. The data was collected in a crystal selected from a converted batch of sample.

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 4-4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{Bi}_4\text{Se}_7$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3908(1)	-0.2500	0.4296(1)	12(1)	
Bi(2)	0.1707(1)	0.2500	0.2738(1)	1(1)	
Bi(3)	0.0540(1)	0.2500	-0.1196(1)	11(1)	
Bi(4)	0.2731(1)	-0.2500	0.0497(1)	10(1)	
Se(1)	0.5405(1)	-0.7500	0.3926(1)	11(1)	
Se(2)	0.2385(1)	0.2500	0.4526(1)	11(1)	
Se(3)	0.0124(1)	-0.2500	0.2945(1)	11(1)	
Se(4)	0.2066(1)	-0.2500	-0.1352(1)	9(1)	
Se(5)	0.4091(1)	-0.7500	0.0361(1)	10(1)	
Se(6)	0.3140(1)	-0.2500	0.2408(1)	10(1)	
Se(7)	0.0979(1)	0.2500	0.0827(1)	9(1)	
Cs(1)	0.4273(1)	-0.7500	-0.1910(1)	15(1)	1
Cs(2)	0.1852(1)	-0.2500	-0.3662(1)	26(1)	0.67
Cs(3)	0.0492(2)	-0.2500	-0.4687(2)	22(1)	0.33

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-5. Crystallographic Data for Cs₃Bi₇Se₁₂, Cs₂Bi₇Se₁₂ and CsBi₇Se₁₂

Empirical formula	Cs ₃ Bi ₇ Se ₁₂ (III)	Cs ₂ Bi ₇ Se ₁₂ ^a (VIII)
Formula weight	2809.11	2676.20
Temperature, K	173(2) K	173.1(2) K
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 27.4432(1) <i>b</i> = 4.1815(1) <i>c</i> = 13.2100(1) β = 107.363(1)°	<i>a</i> = 31.974(6) <i>b</i> = 4.1367(8) <i>c</i> = 22.045(4) β = 100.659(3)°
Z, Volume, Å ³	2, 1446.82(4)	4, 2865.6(9)
Density (calculated), g/cm ³	6.448	6.203
Absorption coefficient, mm ⁻¹	61.218	60.564
F(000)	2308	4396
Crystal size, mm ³	0.55 x 0.02 x 0.02	0.25 x 0.02 x 0.02
θ range for data collection	1.55 to 28.31°	1.74 to 25.05°
Index ranges	-35 ≤ <i>h</i> ≤ 35 -5 ≤ <i>k</i> ≤ 5 -17 ≤ <i>l</i> ≤ 17	-38 ≤ <i>h</i> ≤ 30 -4 ≤ <i>k</i> ≤ 4 -25 ≤ <i>l</i> ≤ 26
Reflections collected	8806	6023
Independent reflections	1978 [<i>R</i> _(int) = 0.0459]	2710 [<i>R</i> _(int) = 0.0500]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	1978 / 0 / 72	2710 / 1 / 143
Goodness-of-fit on <i>F</i> ²	1.005	1.019
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0354 <i>wR</i> 2 = 0.0825	<i>R</i> 1 = 0.0751 <i>wR</i> 2 = 0.1855
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0454 <i>wR</i> 2 = 0.0854	<i>R</i> 1 = 0.1497 <i>wR</i> 2 = 0.2122
Extinction	0.00038(3)	-
Largest peak and hole, e·Å ⁻³	3.311 and -3.950	5.336 and -3.442

Table 4-5. (cont'd).

Empirical formula	CsBi ₇ Se ₁₂ ^a (X)
Formula weight	2543.29
Temperature, K	293(2) K
Crystal system	Monoclinic
Space group	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 22.700(17) <i>b</i> = 4.179(3) <i>c</i> = 15.709(12) β = 108.968(12)°
Z, Volume, Å ³	2, 1409.49(18)
Density (calculated), g/cm ³	5.993
Absorption coefficient, mm ⁻¹	60.294
F(000)	2088
Crystal size, mm ³	0.26 x 0.05 x 0.02
θ range for data collection	3.59 to 23.74°
Index ranges	-25 ≤ <i>h</i> ≤ 25 -4 ≤ <i>k</i> ≤ 4 -17 ≤ <i>l</i> ≤ 15
Reflections collected	2698
Independent reflections	1176 [<i>R</i> _(int) = 0.0616]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1176 / 0 / 71
Goodness-of-fit on <i>F</i> ²	1.093
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1179, <i>wR</i> 2 = 0.3107
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1626, <i>wR</i> 2 = 0.3421
Largest peak and hole, e·Å ⁻³	5.888 and -3.560

a. The data was collected in a crystal selected from a converted batch of sample.

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 4-6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.0000	0.0000	0.0000	13(1)	
Bi(2)	0.0866(1)	-0.5000	0.2588(1)	12(1)	
Bi(3)	0.1795(1)	0.0000	0.5216(1)	11(1)	
Bi(4)	0.2232(1)	0.0000	0.2149(1)	10(1)	
Se(1)	-0.0194(1)	-0.5000	0.1427(1)	11(1)	
Se(2)	0.0757(1)	0.0000	0.4116(1)	10(1)	
Se(3)	0.1694(1)	-0.5000	0.6707(1)	10(1)	
Se(4)	0.2296(1)	-0.5000	0.0809(1)	10(1)	
Se(5)	0.1072(1)	-0.0000	0.1231(1)	10(1)	
Se(6)	0.2995(1)	0.0000	0.6207(1)	9(1)	
Cs(1)	0.3645(1)	-0.5000	0.1262(1)	16(1)	1
Cs(2)	0.0296(1)	-0.5000	-0.4191(1)	18(1)	0.5

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-7. Crystallographic Data for Rb₃Bi₇Se₁₂ and Rb₂Bi₇Se₁₂.

	Rb ₃ Bi ₇ Se ₁₂ (IV)	Rb ₂ Bi ₇ Se ₁₂ ^a (IX)
Empirical formula	Rb ₃ Bi ₇ Se ₁₂ (IV)	Rb ₂ Bi ₇ Se ₁₂ ^a (IX)
Formula weight	2666.79	2581.32
Temperature, K	173(2) K	173.1(2) K
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 26.886(5) <i>b</i> = 4.1749(8) <i>c</i> = 13.033(2) β = 106.223(3)°	<i>a</i> = 31.842(9) <i>b</i> = 4.122(3) <i>c</i> = 21.691(6) β = 100.279(4)°
Z, Volume, Å ³	2, 1404.6(5)	4, 2801(1)
Density (calculated), g/cm ³	6.305	6.120
Absorption coefficient, mm ⁻¹	64.390	62.842
F(000)	2200	4252
Crystal size, mm ³	0.5 x 0.07 x 0.07	0.26 x 0.05 x 0.02
θ range for data collection	1.58 to 25.05°	1.30 to 25.05°
Index ranges	-29 ≤ <i>h</i> ≤ 32 -4 ≤ <i>k</i> ≤ 4 -15 ≤ <i>l</i> ≤ 15	-37 ≤ <i>h</i> ≤ 37 -4 ≤ <i>k</i> ≤ 4 -25 ≤ <i>l</i> ≤ 25
Reflections collected	5225	10594
Independent reflections	1420 [R _(int) = 0.0680]	2843 [R _(int) = 0.1369]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1420 / 0 / 72	2843 / 1 / 144
Goodness-of-fit on F ²	0.963	1.062
Final R indices [I > 2σ(I)]	R1 = 0.0739 wR2 = 0.1578	R1 = 0.0906 wR2 = 0.2136
R indices (all data)	R1 = 0.0879 wR2 = 0.1621	R1 = 0.1883 wR2 = 0.2549
Extinction	0.000000(13)	0.0000247(11)
Largest peak and hole, e·Å ⁻³	5.991 and -2.652	4.374 and -5.826

a. The data was collected in a crystal selected from a converted batch of sample.

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 4-8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{Bi}_7\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.0000	0.0000	0.0000	24(1)	
Bi(2)	0.0857(1)	-0.5000	0.2600(1)	24(1)	
Bi(3)	0.1774(1)	0.0000	0.5239(1)	25(1)	
Bi(4)	0.2246(1)	0.0000	0.2152(1)	25(1)	
Se(1)	0.1076(2)	0.0000	0.1229(3)	21(1)	
Se(2)	0.0725(2)	0.0000	0.4137(4)	23(1)	
Se(3)	0.1665(2)	-0.5000	0.6760(4)	27(1)	
Se(4)	0.2309(2)	-0.5000	0.0798(4)	28(1)	
Se(5)	-0.0221(2)	-0.5000	0.1429(4)	22(1)	
Se(6)	0.3002(2)	0.0000	0.6184(4)	23(1)	
Rb(1)	0.3631(2)	-0.5000	0.1203(4)	38(1)	1
Rb(2)	0.0290(4)	-0.5000	-0.4205(9)	37(2)	0.5

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-9. Crystallographic Data for Rb₄Bi₁₀Se₁₇ and Rb₂Bi₁₀Se₁₇.

Empirical formula	Rb ₄ Bi ₁₀ Se ₁₇ (V)	Rb ₂ Bi ₁₀ Se ₁₇ ^a (XII)
Formula weight	3774	3603.06
Temperature, K	296(2)	297(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 32.443(5) <i>b</i> = 4.1690(6) <i>c</i> = 15.699(2) β = 93.947(3)°	<i>a</i> = 35.880(7) <i>b</i> = 4.1547(8) <i>c</i> = 13.796(3) β = 93.302(4)°
Z, Volume, Å ³	2, 2118.3(5)	2, 2053.2(7)
Density (calculated), g/cm ³	5.917	5.828
Absorption coefficient, mm ⁻¹	60.546	60.108
F(000)	2428	2964
Crystal size, mm ³	0.26 x 0.04 x 0.01	0.24 x 0.04 x 0.05
θ range for data collection	1.75 to 30.33°	1.48 to 25.05°
Index ranges	-44 ≤ <i>h</i> ≤ 42 -5 ≤ <i>k</i> ≤ 5 -21 ≤ <i>l</i> ≤ 20	-42 ≤ <i>h</i> ≤ 42 -4 ≤ <i>k</i> ≤ 4 -16 ≤ <i>l</i> ≤ 16
Reflections collected	11206	7985
Independent reflections	3212 [<i>R</i> _(int) = 0.0776]	2051 [<i>R</i> _(int) = 0.0464]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	3212 / 1 / 126	2051 / 1 / 95
Goodness-of-fit on <i>F</i> ²	0.947	1.200
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0571 <i>wR</i> 2 = 0.1401	<i>R</i> 1 = 0.0703 <i>wR</i> 2 = 0.1822
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0989 <i>wR</i> 2 = 0.1567	<i>R</i> 1 = 0.0944 <i>wR</i> 2 = 0.1921
Largest peak and hole, e·Å ⁻³	3.826 and -3.662	6.809 and -3.825

a. The data was collected in a crystal selected from a converted batch of sample.

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 4-10. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	-0.2073(1)	-0.5000	-0.0623(1)	21(1)	
Bi(2)	-0.1201(1)	0	-0.1907(1)	20(1)	
Bi(3)	-0.0263(1)	-0.5000	-0.3101(1)	18(1)	
Bi(4)	-0.0639(1)	0	-0.5599(1)	19(1)	
Bi(5)	-0.1566(1)	-0.5000	-0.4302(1)	24(1)	
Se(1)	-0.2702(1)	0	-0.1047(1)	19(1)	
Se(2)	-0.3556(1)	-0.5000	0.0232(1)	19(1)	
Se(3)	-0.4435(1)	0	0.1483(1)	20(1)	
Se(4)	-0.5351(1)	-0.5000	0.2716(1)	17(1)	
Se(5)	-0.1218(1)	-0.5000	-0.6010(1)	19(1)	
Se(6)	-0.2093(1)	0	-0.4809(2)	36(1)	
Se(7)	-0.1800(1)	-0.5000	-0.2490(1)	20(1)	
Se(8)	-0.0870(1)	0	-0.3738(1)	17(1)	
Se(9)	0	-0.5000	-0.5000	17(1)	
Rb(1)	-0.2701(2)	0	-0.3233(3)	43(2)	0.531(9)
Rb(2)	-0.1172(3)	-0.5000	-0.8339(6)	55(3)	0.315(9)
Rb(3)	-0.5265(3)	-0.5000	0.0391(5)	76(4)	0.383(9)
Rb(4)	-0.2874(4)	-0.5000	-0.3068(8)	114(8)	0.303(10)
Rb(5)	-0.1467(4)	0	-0.7948(7)	128(8)	0.315(10)
Rb(6)	-0.0628(9)	-0.5000	-0.9172(13)	100(11)	0.175(10)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-11. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for RbBi_4Se_7 .

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.2379(1)	0.0000	0.0805(1)	24(1)	
Bi(2)	0.2121(1)	0.5000	0.2467(1)	20(1)	
Bi(3)	0.1603(1)	0.0000	0.3987(1)	18(1)	
Bi(4)	0.1329(1)	0.5000	0.5723(1)	18(1)	
Se(1)	0.3296(2)	0.5000	0.0724(2)	23(1)	
Se(2)	0.1487(2)	0.5000	0.0881(2)	20(1)	
Se(3)	0.1172(2)	0.0000	0.2434(2)	20(1)	
Se(4)	0.0756(2)	0.5000	0.4002(2)	17(1)	
Se(5)	0.0369(2)	0.0000	0.5653(2)	19(1)	
Se(6)	0.3146(2)	0.0000	0.2652(2)	20(1)	
Se(7)	0.2706(2)	0.5000	0.4216(2)	12(1)	
Rb(1)	0.4761(7)	0.0000	0.1212(11)	104(6)	0.50
Rb(2)	0.4630(9)	0.0000	0.2050(11)	117(7)	0.50

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-12. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for CsBi_4Se_7 .

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.2382(1)	0.0000	0.0808(1)	16(1)	
Bi(2)	0.2120(1)	0.5000	0.2471(1)	15(1)	
Bi(3)	0.1599(1)	0.0000	0.3993(1)	12(1)	
Bi(4)	0.1333(1)	0.5000	0.5734(1)	12(1)	
Se(1)	0.3305(2)	0.5000	0.0716(2)	14(1)	
Se(2)	0.1496(2)	0.5000	0.0895(2)	13(1)	
Se(3)	0.1167(2)	0.0000	0.2443(2)	13(1)	
Se(4)	0.0758(2)	0.5000	0.4024(2)	12(1)	
Se(5)	0.0363(2)	0.0000	0.5654(2)	16(1)	
Se(6)	0.3144(2)	0.0000	0.2654(2)	12(1)	
Se(7)	0.2709(2)	0.5000	0.4222(2)	9(1)	
Cs(1)	0.4812(2)	0.0000	0.1032(3)	29(1)	0.50
Cs(2)	0.4605(2)	0.0000	0.2104(3)	33(1)	0.50

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-13. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3526(1)	0	0.2398(1)	20(1)	
Bi(2)	0.4619(1)	-0.5000	0.2729(1)	20(1)	
Bi(3)	0.5791(1)	0	0.3205(1)	17(1)	
Bi(4)	0.6981(1)	-0.5000	0.3623(1)	19(1)	
Bi(2')	0.7413(1)	0	0.2077(1)	20(1)	
Bi(3')	0.6284(1)	-0.5000	0.1649(1)	19(1)	
Bi(4')	0.9861(1)	-0.5000	0.8749(1)	22(1)	
Se(1)	0.3905(2)	-0.5000	0.3272(4)	31(2)	
Se(2)	0.5016(2)	0	0.3603(3)	16(2)	
Se(3)	0.6145(2)	-0.5000	0.4011(3)	18(2)	
Se(4)	0.7276(2)	0	0.4435(4)	35(2)	
Se(5)	0.2753(2)	0	0.2992(3)	15(1)	
Se(6)	0.6579(2)	0	0.2592(3)	24(2)	
Se(1')	0.6867(2)	-0.5000	0.8467(3)	16(1)	
Se(2')	0.7971(2)	0	0.8798(3)	23(2)	
Se(3')	0.9114(2)	-0.5000	0.9202(3)	19(2)	
Se(4')	0.0234(2)	0	0.9653(3)	28(2)	
Se(5')	0.4265(2)	0	0.1793(3)	30(2)	
Se(6')	0.5448(2)	-0.5000	0.2179(3)	16(2)	
Cs(1)	0.6572(6)	0	0.5498(9)	92(8)	0.390(17)
Cs(2)	0.6695(12)	-0.5000	0.5628(17)	190(20)	0.34(2)
Cs(3)	0.4344(7)	0	0.4784(10)	67(9)	0.262(15)
Cs(4)	0.5162(6)	-0.5000	0.5027(9)	23(6)	0.201(10)
Cs(5)	0.6323(6)	-0.5000	0.9658(9)	59(7)	0.277(14)
Cs(6)	0.6708(7)	0	0.9755(9)	43(7)	0.239(13)
Cs(7)	0.7839(5)	-0.5000	0.0120(7)	47(7)	0.298(15)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-14. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_7\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3519(1)	-0.0000	0.2398(2)	28(1)	
Bi(2)	0.4616(1)	-0.5000	0.2744(2)	27(1)	
Bi(3)	0.5781(1)	0.0000	0.3224(1)	26(1)	
Bi(4)	0.6965(1)	-0.5000	0.3621(2)	36(1)	
Bi(2')	0.7406(1)	-0.0000	0.2059(2)	30(1)	
Bi(3')	0.6276(1)	-0.5000	0.1642(2)	29(1)	
Bi(4')	0.9869(1)	-0.5000	0.8746(2)	33(1)	
Se(1)	0.3893(2)	-0.5000	0.3275(4)	32(2)	
Se(2)	0.5000(2)	0.0000	0.3634(4)	27(2)	
Se(3)	0.6143(2)	-0.5000	0.4043(4)	30(2)	
Se(4)	0.7266(2)	-0.0000	0.4443(4)	41(2)	
Se(5)	0.2748(2)	-0.0000	0.2983(4)	29(2)	
Se(6)	0.6580(2)	0.0000	0.2605(4)	29(2)	
Se(1')	0.6868(2)	-0.5000	0.8487(4)	30(2)	
Se(2')	0.7980(2)	0.0000	0.8822(4)	27(2)	
Se(3')	0.9113(2)	-0.5000	0.9214(4)	27(2)	
Se(4')	0.0225(3)	-0.0000	0.9649(4)	40(2)	
Se(5')	0.4273(2)	-0.0000	0.1805(4)	34(2)	
Se(6')	0.5449(2)	-0.5000	0.2197(4)	24(2)	
Rb(1)	0.6596(17)	-0.0000	0.5410(30)	220(30)	0.47(2)
Rb(2)	0.8102(8)	-0.0000	0.4031(13)	54(9)	0.35(2)
Rb(3)	0.4350(20)	-0.0000	0.4780(40)	70(30)	0.12(2)
Rb(4)	0.5170(7)	-0.5000	0.5015(12)	25(8)	0.248(19)
Rb(5)	0.6320(12)	-0.5000	0.9617(19)	76(15)	0.27(3)
Rb(6)	0.8374(9)	-0.5000	0.0237(14)	23(10)	0.20(2)
Rb(7)	0.7905(8)	-0.5000	0.0135(12)	52(9)	0.33(2)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-15. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{CsBi}_7\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0	0	0.5000	40(1)	
Bi(2)	-0.1295(2)	0.5000	0.3060(2)	45(1)	
Bi(3)	-0.2721(2)	0	0.1151(2)	42(1)	
Bi(4)	-0.4163(2)	0.5000	-0.0876(3)	53(1)	
Se(1)	-0.0951(3)	0.5000	0.4923(5)	24(2)	
Se(2)	-0.2210(4)	0	0.3016(8)	54(3)	
Se(3)	-0.3616(4)	0.5000	0.1081(7)	38(2)	
Se(4)	-0.5008(5)	0	-0.0764(10)	78(4)	
Se(5)	-0.0337(3)	0	0.2977(7)	39(2)	
Se(6)	-0.3212(4)	0	-0.0975(6)	39(2)	
Cs(1)	-0.3580(50)	0.5000	0.3470(50)	250(40)	0.25
Cs(2)	-0.2810(20)	-0.5000	0.4520(30)	105(13)	0.25

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4-16. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$.

	x	y	z	$U_{(\text{eq})}$	occ.
Bi(1)	-0.2148(1)	0.5000	0.9198(1)	31(1)	
Bi(2)	0.1462(1)	0	0.2580(1)	28(1)	
Bi(3)	0.0856(1)	0.5000	0.4634(1)	23(1)	
Bi(4)	-0.0211(1)	0	0.3434(1)	24(1)	
Bi(5)	-0.0479(1)	0.5000	0.8473(1)	27(1)	
Se(1)	-0.2102(1)	0	0.0745(3)	32(1)	
Se(2)	0.2213(1)	0	0.2300(3)	28(1)	
Se(3)	0.1582(1)	0.5000	0.4079(3)	26(1)	
Se(4)	-0.0978(1)	0	0.3965(2)	22(1)	
Se(5)	0.0332(1)	0.5000	0.7952(3)	24(1)	
Se(6)	0.0328(1)	0	0.0054(3)	29(1)	
Se(7)	0.1248(1)	0.5000	0.1076(3)	29(1)	
Se(8)	0.0615(1)	0	0.3069(2)	20(1)	
Se(9)	0	0.5000	0.5000	19(1)	
Rb(1)	-0.1656(5)	-0.5000	0.2629(12)	86(6)	0.368(13)
Rb(2)	0.1322(6)	-0.5000	0.8240(16)	144(10)	0.421(14)
Rb(3)	-0.2041(14)	0	0.3790(30)	160(20)	0.212(13)

$U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4. Results and discussion

Synthesis, thermal behavior and spectroscopy. $A_2Bi_4Se_7$, $A_3Bi_7Se_{12}$ ($A = Rb$, Cs) and $Rb_4Bi_{10}Se_{17}$ were synthesized at temperatures above $650^\circ C$ by direct combination of A_2Se and Bi_2Se_3 . $A_2Bi_4Se_7$ was made from a 1:2 molar ratio while $A_3Bi_7Se_{12}$ from a 1:2.33 ratio. The above synthesis for $A_3Bi_7Se_{12}$ always results to a small impurity of $A_2Bi_4Se_7$. The quenching technique described in the experimental section allowed in the case of $Cs_3Bi_7Se_{12}$ a pure product with no traces of $Cs_2Bi_4Se_7$, however the same procedure did not work for $Rb_3Bi_7Se_{12}$. $Rb_4Bi_{10}Se_{17}$ can be synthesized by reacting Rb_2Se and Bi_2Se_3 at 1:2.3 ratio. Usually a small excess of Rb_2Se is needed to compensate for any losses occurring due attack of the silica tube. The Cs analog of $Rb_4Bi_{10}Se_{17}$ could not be made. All these compounds can be described as members of the same family with the general formula $(Rb_2Se)(Bi_2Se_3)_m$. $Rb_4Bi_{10}Se_{17}$ can be rewritten as $(Rb_2Se)(Bi_2Se_3)_{2.5}$ whereas $Rb_2Bi_4Se_7$ can be rewritten as $(Rb_2Se)(Bi_2Se_3)_2$ and $Rb_3Bi_7Se_{12}$ as $(Rb_2Se)(Bi_2Se_3)_{2.33}$. Lower amounts of Bi_2Se_3 produce $ABiSe_2$ and $A_{11}Bi_{15}Se_{28}$ ³⁷ while higher ratios produce ABi_3Se_5 ³⁸ and $A_2Bi_8Se_{13}$ ²². ABi_4Se_7 , $A_xBi_7Se_{12}$ and $Rb_2Bi_{10}Se_{17}$ ($A = Rb, Cs$; $x = 1, 2$) are the products

of oxidative transformation (see below) of $A_2Bi_4Se_7$, $A_3Bi_7Se_{12}$ ($A = Rb, Cs$) and $Rb_4Bi_{10}Se_{17}$ respectively. Figure 4-1 (bottom) shows a typical DTA scan of a sample of $RbBi_4Se_7$. The data reveal a melting point at 651 °C and two crystallization peaks on cooling suggesting the presence of two phases. X-ray diffraction of the residue shows that $RbBi_4Se_7$ melts incongruently, decomposing to $Rb_2Bi_8Se_{13}$ ²² and Bi_2Se_3 and probably Se^0 . The rest of transformed phases behave similarly decomposing upon heating to $A_2Bi_8Se_{13}$ ($A = Rb, Cs$) and Bi_2Se_3 .

All the compounds are narrow band-gap semiconductors with band gaps between 0.3-0.6 eV as shown in Table 4-17. The band gap spectra of $Rb_2Bi_4Se_7$ and $RbBi_4Se_7$ is shown in Figure 4-2. These energy gaps are in agreement with those of other A/Bi/Se compounds such as α -, β - $K_2Bi_8Se_{13}$ ^{11,14}, $K_{2.5}Bi_{8.5}Se_{14}$ ¹⁴ and $A_2Bi_8Se_{13}$ ²² ($A = Rb, Cs$). As will be discussed below for the transformation process to take place electrons have to come out from the structure. The narrow band gaps observed here facilitate this oxidation process by allowing sufficient electron transport through the structure.

The formation of Se-Se bonds in the transformed samples was also confirmed by Raman spectroscopy. Samples of ABi_4Se_7 , ABi_7Se_{12} and $Rb_2Bi_{10}Se_{17}$ exhibit the characteristic shift due to the presence of the diselenide bond at 233 cm^{-1} , see Figure 4-3.

Table 4-17. Optical Band Gap and Melting Point Data.

Compound	E_g (eV)	m.p. (°C)	Comments
Rb ₂ Bi ₄ Se ₇	0.53	667	congruently
Cs ₂ Bi ₄ Se ₇	0.56	679	congruently
Rb ₃ Bi ₇ Se ₁₂	0.46	678	congruently
Cs ₃ Bi ₇ Se ₁₂	0.49	677	congruently
Rb ₄ Bi ₁₀ Se ₁₇	0.48	645	congruently
RbBi ₄ Se ₇	0.42	651	incongruently*
CsBi ₄ Se ₇	0.36	660	incongruently*
Rb ₂ Bi ₇ Se ₁₂	0.41	652	incongruently*
Cs ₂ Bi ₇ Se ₁₂	0.40	670	incongruently*
RbBi ₇ Se ₁₂	0.26	680	incongruently*
CsBi ₇ Se ₁₂	0.32	677	incongruently*
Rb ₂ Bi ₁₀ Se ₁₇	0.34	665	incongruently*

*decomposes to A₂Bi₈Se₁₃ (A = Rb, Cs) and Bi₂Se₃.

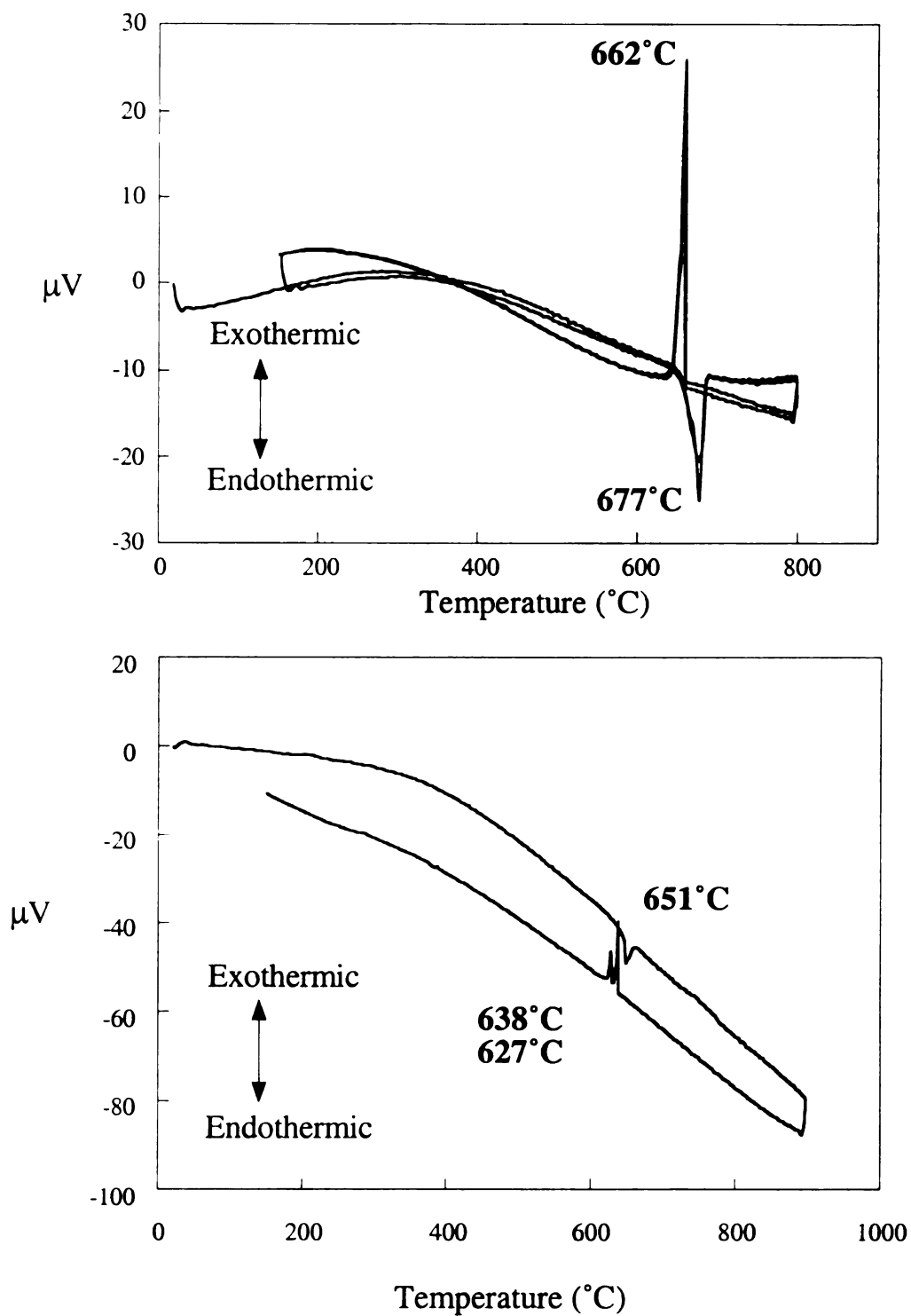


Figure 4-1. Typical DTA diagram of $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ (top) and RbBi_4Se_7 (bottom). The rest of the phases give similar diagrams.

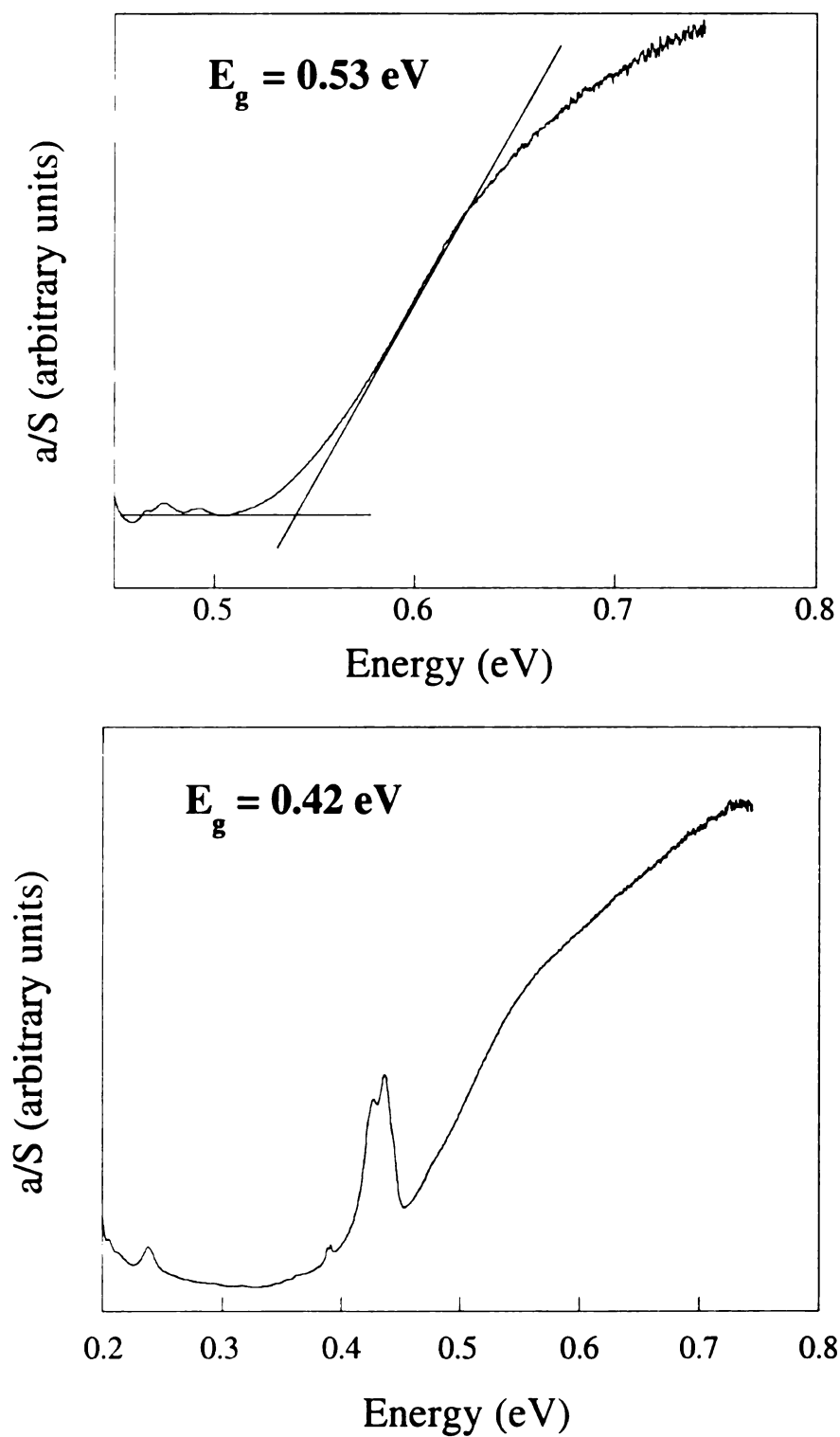


Figure 4-2. Typical optical band-gaps of Rb₂Bi₄Se₇ (top) and RbBi₄Se₇ (bottom). The peak at RbBi₄Se₇ is probably due to water. The other phases give similar spectra.

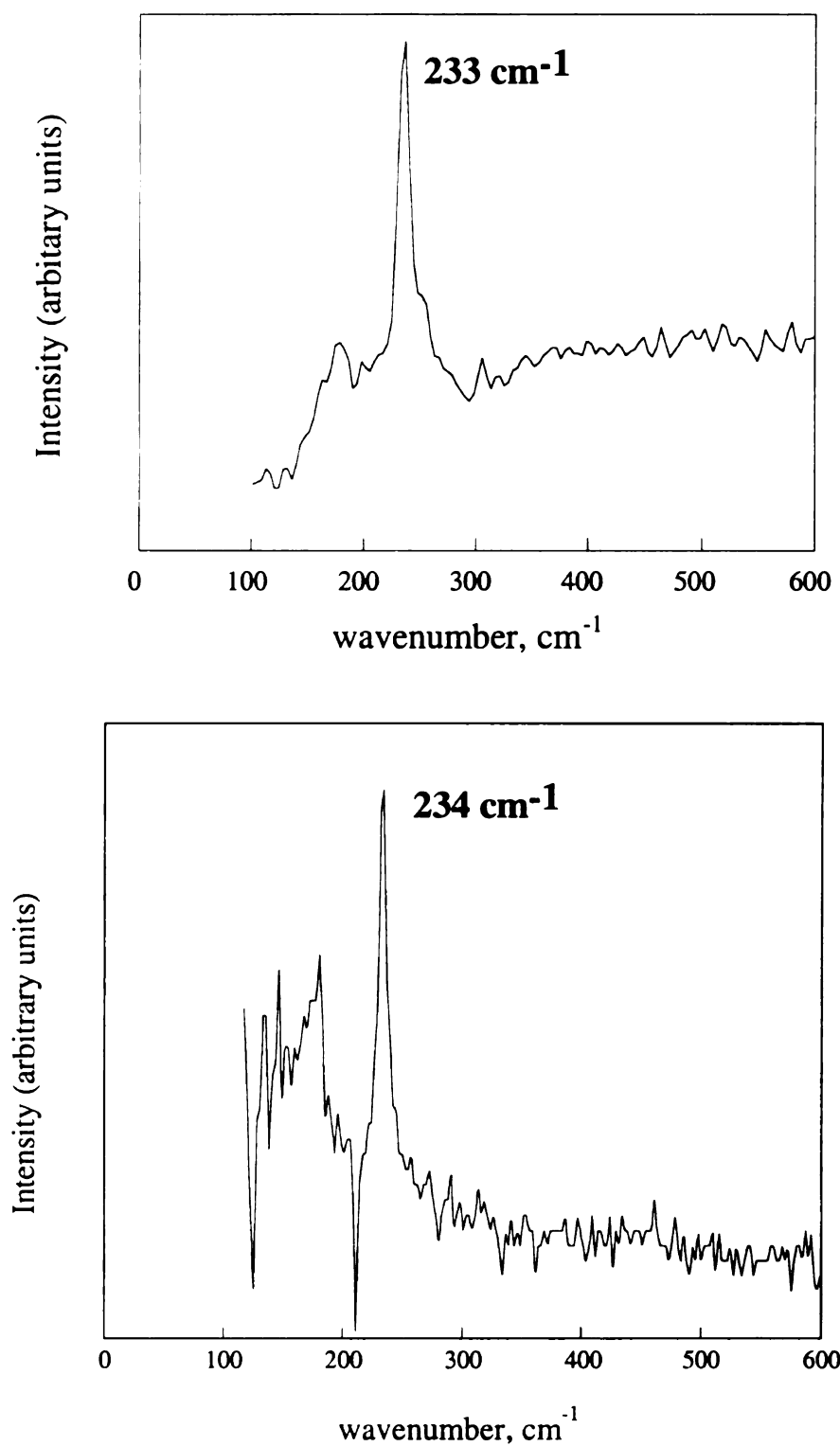


Figure 4-3. Raman spectrum of RbBi₄Se₇ (top) and Cs₂Bi₇Se₁₂ (bottom). The rest of the transformed phases give similar spectra.

Structure Description. Before a detailed account of the unique "zipper" like solid state transformation is given, it is important to present in detail the crystal structures of all of the compounds.

A₂Bi₄Se₇ (A = Rb, Cs) (I) and (II). Since the two compounds are isostructural only the Rb analog is going to be described. The compound is a two-dimensional layered structure made of Bi₂Te₃-type and CdI₂-type blocks, see Figure 4-4. The Rb atoms reside between the layers in trigonal prismatic sites. The [Bi₄Se₇]²⁻ framework consists of edge sharing BiSe₆ octahedra.

All Bi atoms possess a distorted octahedral coordination. Bi(1) and Bi(2) are slightly distorted with Bi-Se bond distances varying between 2.870(3)-3.009(3) Å for Bi(1) and 2.863(3)-3.061(3) Å for Bi(2) (Table 4-18). The octahedra around atoms Bi(3) and Bi(4) are more distorted with Bi-Se distances varying between 2.808(4)-3.194(3) Å for Bi(3) and 2.792(2)-3.205(3) Å for Bi(4). The structure exhibits a characteristic feature which is common in many bismuth chalcogenides: the existence of a short bond *trans* to a long bond. For example, in the Bi(4) octahedra there are two short Bi-Se bonds at 2.792(2) Å *trans* to two long bonds at 3.205(3) Å. The bond angles for Bi(1) and Bi(2) octahedra are more regular, varying between 86.74(8)°-92.58(9)° for Bi(1) and 86.55(8)°-93.47(9)° for Bi(2) while they are less regular in the Bi(3) and Bi(4) octahedra varying between 82.06(8)°-94.64(9)° and 82.05(8)°-97.8(1)° respectively. Bond distances and

selected angles are shown in Table 4-18.

A key characteristic of the structure is that adjacent layers come in close non-bonding contact through atoms Se(5) at 3.336(6) Å. As seen in Figure 4-5A, Se(5) atoms in each layer form rows which approach one another side by side to make pairs so that the Se atoms in one row are staggered with respect to those in the other row.

Rb(1) has a bicapped trigonal prismatic coordination with distances varying between 3.445(5)-3.733(4) Å. Rb(2) and Rb(3) have similar trigonal prismatic coordination. In Rb(2) the distances vary between 3.451(6)-3.584(6) Å while in Rb(3) the distances vary between 3.394(9)-3.76(1) Å. Rb(3) generates a symmetry equivalent atom at 2.69(1) while the distance between Rb(3) and Rb(2) is 2.27(1) Å. Since these distances are unreasonably close for Rb atoms, all these sites cannot be occupied at the same time. Statistically this is satisfied by Rb(3) being 33% occupied and Rb(2) 67% occupied. In the space between the layers, several similar trigonal prismatic sites exist and the Rb atoms can occupy any one of them. As a result, these atoms can be thought of as very mobile, a characteristic that is important for the transformation process.

$\text{Cs}_2\text{Bi}_4\text{Se}_7$ has very similar characteristics and will not be discussed further.

Selected bond distances and angles are shown on Table 4-18.

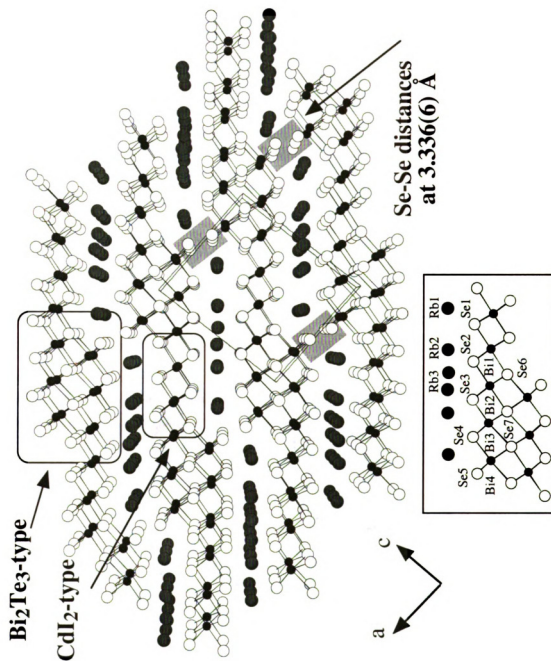


Figure 4-4. Projection of the structure of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ down the b -axis. The shaded areas indicate the Bi_2Te_3 - and CdI_2 -type building blocks. The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. Rb(2) and Rb(3) are partially occupied.

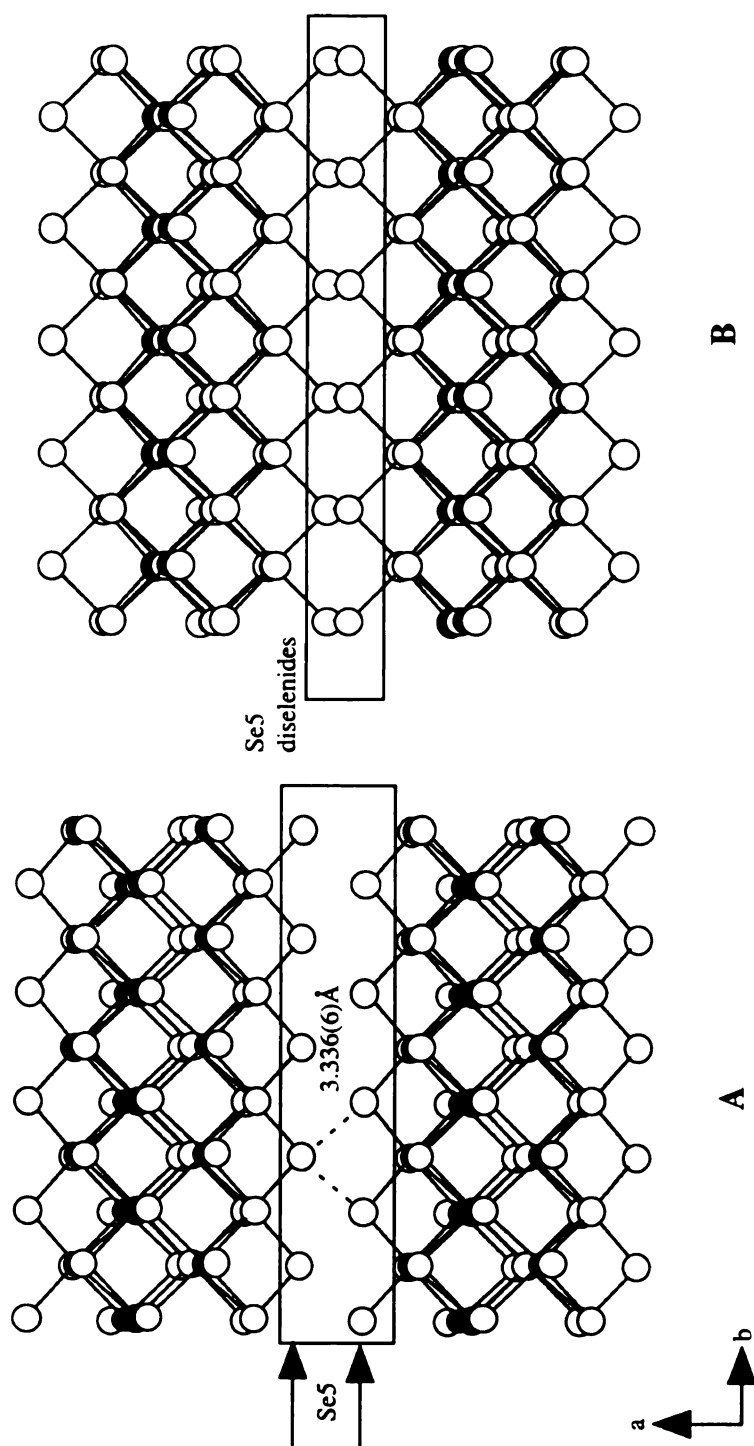


Figure 4-5. (a)View of the Se(5) rows looking down the c -axis in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. (b) View of the bonded Se(4) rows looking down the c -axis RbBi_4Se_7 .

Table 4-18. Bond Distances and Selected Angles for $A_2Bi_4Se_7$ and ABi_4Se_7 A = Rb, Cs.

	Rb₂Bi₄Se₇	Cs₂Bi₄Se₇	RbBi₄Se₇	CsBi₄Se₇
Bi(1)-Se(1)	2.870(3)	2.841(1)	2.703(5)	2.703(4)
Bi(1)-Se(2)	2.974(3)x2	2.9468(9)x2	2.933(3)x2	2.928(3)x2
Bi(1)-Se(1)	2.979(3)x2	2.969(1)x2	2.976(3)x2	2.990(3)x2
Bi(1)-Se(6)	3.009(3)	3.030(1)	3.260(5)	3.266(3)
Bi(2)-Se(2)	2.863(3)	2.854(1)	2.801(4)	2.787(3)
Bi(2)-Se(6)	2.909(3)x2	2.8961(9)x2	2.993(3)x2	2.990(2)x2
Bi(2)-Se(3)	3.026(3)x2	2.9961(9)x2	2.950(3)x2	2.957(2)x2
Bi(2)-Se(7)	3.061(3)	3.045(1)	3.097(4)	3.104(3)
Bi(3)-Se(3)	2.808(4)	2.791(1)	2.776(4)	2.771(3)
Bi(3)-Se(4)	2.955(3)x2	2.9309(8)x2	2.825(3)x2	2.822(2)x2
Bi(3)-Se(7)	2.999(2)x2	2.9887(9)x2	3.098(3)x2	3.110(3)x2
Bi(3)-Se(7)	3.194(3)	3.154(1)	3.173(4)	3.158(3)
Bi(4)-Se(5)	2.792(2)x2	2.7789(8)x2	2.947(3)x2	2.955(3)x2
Bi(4)-Se(4)	2.940(3)	2.940(1)	3.050(4)	3.031(3)
Bi(4)-Se(6)	3.003(4)	2.979(1)	2.883(4)	2.863(3)
Bi(4)-Se(7)	3.205(3)x2	3.194(1)x2	2.962(3)x2	2.956(2)x2
Se(5)-Se(5)	3.336(6)x2	3.443(2)x2	2.354(9)	2.359(7)

Table 4-18. (cont'd).

	Rb₂Bi₄Se₇	Cs₂Bi₄Se₇		RbBi₄Se₇	CsBi₄Se₇
A(1)-Se(5)	3.445(5)	3.560(2)	A(1)-A(2)	1.81(3)	2.358(7)
A(1)-Se(6)	3.478(5)	3.569(2)			
A(1)-Se(4)	3.630(4)x2	3.750(1)x2	A(1)-Se(1)	3.62(1)x2	3.757(5)x2
A(1)-Se(5)	3.692(4)x2	3.746(2)x2	A(1)-Se(3)	3.64(1)x2	3.706(5)x2
A(1)-Se(1)	3.733(4)x2	3.823(1)x2	A(1)-Se(2)	3.80(2)	3.620(6)
			A(1)-Se(2)	4.19(2)	3.870(5)
A(2)-A(3)	2.27(1)	2.307(3)			
			A(2)-Se(4)	3.53(2)	3.508(5)
A(2)-Se(4)	3.451(6)	3.581(2)	A(2)-Se(1)	3.61(2)x2	3.630(5)x2
A(2)-Se(3)	3.460(5)x2	3.595(2)x2	A(2)-Se(3)	3.79(2)x2	3.849(5)x2
A(2)-Se(2)	3.469(5)x2	3.625(2)x2	A(2)-Se(6)	3.99(2)	3.854(6)
A(2)-Se(1)	3.584(6)	3.684(2)			
A(3)-A(3)	2.69(1)	2.611(3)			
A(3)-Se(3)	3.394(9)x2	3.570(2)x2			
A(3)-Se(2)	3.403(9)x2	3.555(2)x2			
A(3)-Se(3)	3.56(1)	3.677(3)			
A(3)-Se(2)	3.76(1)	3.833(3)			

A = Rb or Cs.

Table 4-18. (cont'd).

	Rb₂Bi₄Se₇	Cs₂Bi₄Se₇
Se(2)-Bi(1)-Se(6)	86.74(8)	86.45(3)
Se(2)-Bi(1)-Se(2)	90.0(1)	90.51(4)
Se(1)-Bi(1)-Se(2)	92.58(9)	92.88(3)
Se(1)-Bi(1)-Se(6)	179.0(1)	179.05(3)
Se(3)-Bi(2)-Se(7)	86.55(8)	86.33(3)
Se(2)-Bi(2)-Se(6)	90.76(8)	90.78(3)
Se(2)-Bi(2)-Se(3)	93.47(9)	93.59(3)
Se(2)-Bi(2)-Se(7)	180.0(1)	179.90(3)
Se(7)-Bi(3)-Se(7)	82.06(8)	83.18(3)
Se(4)-Bi(3)-Se(4)	90.8(1)	91.13(3)
Se(3)-Bi(3)-Se(4)	94.64(9)	94.84(3)
Se(4)-Bi(3)-Se(7)	173.5(1)	173.70(3)
Se(7)-Bi(4)-Se(7)	82.05(8)	81.87(3)
Se(5)-Bi(4)-Se(7)	89.83(7)	90.07(2)
Se(5)-Bi(4)-Se(5)	97.8(1)	97.72(4)
Se(4)-Bi(4)-Se(6)	175.2(1)	173.07(4)
	RbBi₄Se₇	CsBi₄Se₇
Se(2)-Bi(1)-Se(6)	88.1(1)	87.88(7)
Se(1)-Bi(1)-Se(6)	92.0(1)	92.19(8)
Se(2)-Bi(1)-Se(1)	179.15(9)	178.79(7)
Se(3)-Bi(2)-Se(7)	87.2(1)	88.02(8)
Se(2)-Bi(2)-Se(6)	96.1(1)	96.29(7)
Se(2)-Bi(2)-Se(7)	175.3(1)	175.7(1)
Se(7)-Bi(3)-Se(7)	83.43(9)	82.91(8)
Se(3)-Bi(3)-Se(4)	96.5(1)	96.70(8)
Se(3)-Bi(3)-Se(7)	172.3(1)	172.2(1)
Se(6)-Bi(4)-Se(5)	88.4(1)	89.18(8)
Se(6)-Bi(4)-Se(7)	91.9(1)	92.02(8)
Se(5)-Bi(4)-Se(7)	179.6(1)	178.8(1)

ABi₄Se₇ (A = Rb, Cs) (VI) and (VII). Since the two compounds are isostructural only the Rb analog is going to be described. This compound is the oxidized form of **(I)** and is structurally related to it as shown in Figure 4-6. In fact, it is the close similarity of the structures between ABi₄Se₇ and A₂Bi₄Se₇, which proves that their redox interconversion (see below) is topotactic. The structure of ABi₄Se₇ contains the same [Bi₄Se₇] framework as in A₂Bi₄Se₇ but now the layers are connected through diselenide bonds to form a three-dimensional structure. Compared to **(I)** the layers have shifted with respect to each other but also moved in such way so that the Se(5) atoms in the two adjacent rows are eclipsed to each other in order to form bonds as shown in Figure 4-5B. The Se(5)-Se(5) bond is normal at 2.354(9) Å.

All Bi atoms have a distorted octahedral coordination. Bi(1) and Bi(4) have distances between 2.703(5)-3.260(5) Å and 2.883(4)-3.050(4) Å respectively while their angles are closer to that of a normal octahedron varying between 88.1(1)°-92.0(1)° for Bi(1) and between 88.4(1)°-91.9(1)° for Bi(4). In the case of Bi(2) and Bi(3) the Bi-Se distances vary between 2.801(4)-3.097(4) Å and 2.776(4)-3.173(4) Å respectively. The angles for Bi(2) and Bi(3) are between 87.2°(1)-96.1°(1) and 83.43(9)°-96.5(1)° respectively. Selected bond distances and angles are given in Table 4-18.

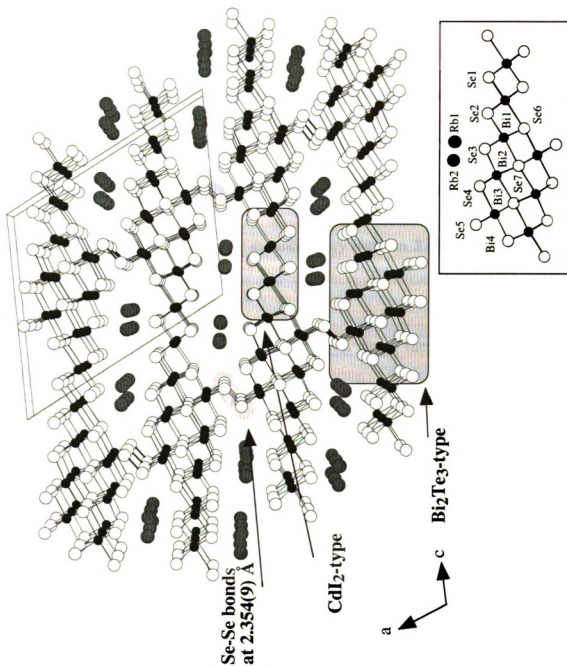


Figure 4-6. Projection of the structure of RbBi_4Se_7 down the b -axis. The same layers exist as in $\text{Rb}_2\text{Bi}_4\text{Se}_7$ but now are connected by Se-Se bonds. The Se-Se bonds are shown by the oval shaded areas. The inset shows the atom labeling.

The Rb atoms occupy similar trigonal prismatic sites but they show a diffuse character (high temperature factors) probably due to the transformation process. Rb(1) has distances between 3.62(1)-4.19(2) Å while in Rb(2) vary between 3.53(2)-3.99(2) Å. Rb(1) is 1.81(3) Å away from Rb(2), this distance is too close for Rb atoms so each site is 50% occupied. The Cs analog, CsBi₄Se₇ has very similar Bi-Se distances (Table 4-18) with the RbBi₄Se₇. The Cs-Se bond distances vary between 3.620(6)-3.869(5) Å for Cs(1) and 3.508(5)-3.854(6) Å for Cs(2).

A₃Bi₇Se₁₂ (A = Cs, Rb) (III) and (IV). Since the two compounds are isostructural only the Cs analog is going to be described. This structure is also layered and structurally related to that of A₂Bi₄Se₇. The Bi₂Te₃-type fragment is the same while the CdI₂-type fragment is shorter with only one Bi atom wide instead of two. As a result, the cavities formed between the layers are smaller accommodating fewer alkali metal atoms, i.e. only two atoms instead of three in Rb₂Bi₄Se₇, see Figure 4-7.

Similar to what is found in Rb₂Bi₄Se₇, in Cs₃Bi₇Se₁₂ the Bi atoms in the CdI₂-type fragment show a more regular octahedral coordination with distances varying between 2.907(1)-2.9682(9) Å for Bi(1) (Table 4-19). Bi(2) is slightly more distorted with Bi-Se distances varying between 2.857(1) to 3.055(1) Å while Bi(3) and Bi(4) show a more distorted octahedral coordination with distances varying between 2.784(1)-

3.159(1) Å and 2.7892(8)-3.206(1) Å respectively.

The angles for Bi(1) vary between 89.34(3)°-90.66(3)° showing its more regular octahedral coordination, while for the remaining three Bi atoms the angles have a larger range varying between 86.64(3)°-94.08(3)° for Bi(2), 83.54(3)°-93.63(3)° for Bi(3) and 81.42(3)°-97.57(4)° for Bi(4). Selected bond distances and angles are shown on Table 4-19.

In the structure of Cs₃Bi₇Se₁₂ also adjacent layers come in close non-bonding contact by rows of Se atoms [Se(4) atom] that are staggered in respect with each other. The Se(4)-Se(4) contact is 3.409(2) Å.

Cs(1) is fully occupied and has a bicapped trigonal prismatic coordination with Cs-Se distances varying between 3.569(2)-3.782(1)Å. Cs(2) has a trigonal prismatic coordination with Cs-Se distances varying between 3.559(2)-3.744(2) Å. The Cs(2) is only 50% occupied since it generates a symmetry equivalent atom at 2.267(4) Å away from itself.

The isostructural Rb₃Bi₇Se₁₂ exhibits the same characteristics, selected bond distances are shown in Table 4-19.

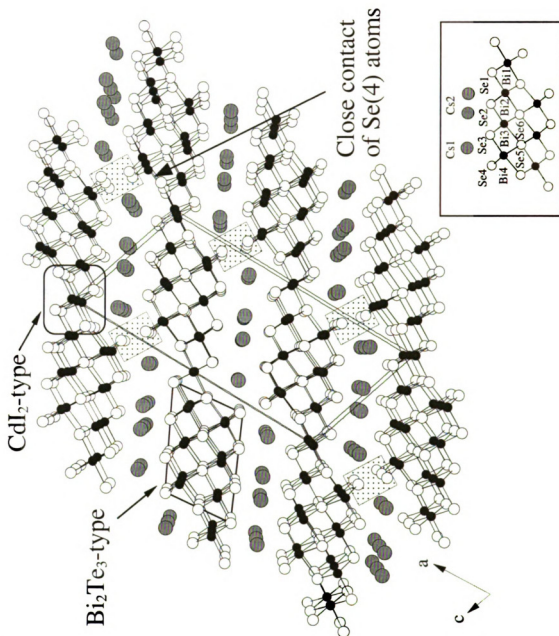


Figure 4-7. Projection of the structure of $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ down the b -axis. The shaded areas indicate the Bi_2Te_3 - and CdI_2 -type building blocks. The CdI_2 -type block is smaller than that found in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. Cs(2) is partially occupied.

Table 4-19. Bond Distances and Selected Angles for $A_3Bi_7Se_{12}$ (A = Rb, Cs) and $CsBi_7Se_{12}$.

	Rb₃Bi₇Se₁₂	Cs₃Bi₇Se₁₂	CsBi₇Se₁₂
Bi(1)-Se(5)	2.889(4)x2	2.907(1)x2	3.018(10)x2
Bi(1)-Se(1)	2.966(3)x4	2.9681(9)x4	2.979(5)x4
Bi(2)-Se(1)	2.872(5)	2.857(1)	2.773(8)
Bi(2)-Se(5)	2.913(3)x2	2.917(1)x2	3.049(5)x2
Bi(2)-Se(2)	2.982(3)x2	2.9825(9)x2	2.931(7)
Bi(2)-Se(6)	3.036(5)	3.055(1)	3.098(9)
Bi(3)-Se(2)	2.784(5)	2.784(1)	2.777(12)
Bi(3)-Se(3)	2.948(4)x2	2.9422(9)x2	2.891(6)x2
Bi(3)-Se(6)	2.964(4)x2	2.9808(9)x2	3.050(8)x2
Bi(3)-Se(6)	3.184(5)	3.159(1)	3.159(9)
Bi(4)-Se(4)	2.769(3)x2	2.7792(8)x2	2.881(9)x2
Bi(4)-Se(3)	2.875(5)	2.883(1)	2.917(11)
Bi(4)-Se(5)	3.036(5)	3.048(1)	3.122(11)
Bi(4)-Se(6)	3.211(4)x2	3.206(1)x2	3.045(8)x2
Se(4)-Se(4)	3.306(7)	3.409(2)	2.39(3)
Se(1)-Bi(1)-Se(1)	89.5(1)	89.56(4)	89.1(2)
Se(1)-Bi(1)-Se(1)	90.5(1)	90.44(4)	90.9(2)
Se(5)-Bi(1)-Se(5)	180.00(9)	180.0	180.0
Se(2)-Bi(2)-Se(6)	86.6(1)	86.64(3)	88.0(3)
Se(1)-Bi(2)-Se(2)	93.8(1)	94.08(3)	88.8(3)
Se(1)-Bi(2)-Se(6)	179.5(2)	178.98(4)	175.4(2)
Se(6)-Bi(3)-Se(6)	82.6(1)	83.54(3)	85.4(2)
Se(2)-Bi(3)-Se(3)	94.1(1)	93.63(3)	95.0(2)
Se(3)-Bi(3)-Se(6)	174.2(1)	174.50(4)	172.4(3)
Se(6)-Bi(4)-Se(6)	81.1(1)	81.42(3)	86.7(3)
Se(4)-Bi(4)-Se(4)	97.9(2)	97.57(4)	93.0(4)
Se(3)-Bi(4)-Se(5)	174.1(1)	172.33(4)	176.4(2)

Table 4-19. (cont'd).

	Rb₃Bi₇Se₁₂	Cs₃Bi₇Se₁₂	CsBi₇Se₁₂	
A(1)-Se(4)	3.446(7)	3.569(2)	Cs(1)-Cs(2)	1.98(11)
A(1)-Se(5)	3.472(7)	3.602(2)		
A(1)-Se(3)	3.637(6)x2	3.731(1)x2	Cs(1)-Se(1)	3.69(4)x2
A(1)-Se(1)	3.669(6)x2	3.762(1)x2	Cs(1)-Se(3)	3.72(6)
A(1)-Se(4)	3.724(6)x2	3.782(1)x2	Cs(1)-Se(5)	3.81(11)
			Cs(1)-Se(2)	3.99(7)x2
A(2)-Se(2)	3.438(8)x2	3.559(2)x2		
A(2)-Se(2)	3.457(8)x2	3.593(2)x2	Cs(2)-Cs(2)	2.69(6)
A(2)-Se(3)	3.56(1)	3.662(2)		
A(2)-Se(1)	3.67(1)	3.744(2)	Cs(2)-Se(2)	3.73(3)x2
			Cs(2)-Se(1)	3.82(3)x2
A(2)-A(2)	2.22(2)	2.267(4)	Cs(2)-Se(2)	3.86(4)
			Cs(2)-Se(1)	4.06(4)

A = Rb or Cs.

A₂Bi₇Se₁₂ (A = Cs, Rb) (VIII) and (IX). This structure-type is again related topotactically to that of (III) and (IV). The same [Bi₇Se₁₂] framework found in A₃Bi₇Se₁₂ exists but in A₂Bi₇Se₁₂ *contrary* to A₂Bi₄Se₇ (where the Se-Se bonds form in every layer resulting to a three-dimensional framework) the Se-Se bonds form in *every other* layer. Consequently, the structure remains two-dimensional but the old layers [Bi₇Se₁₂] have stitched together via Se-Se bond into pairs, see Figure 4-8.

In Cs₂Bi₇Se₁₂, Se(4)' has a bond with its symmetry equivalent at 2.35(1) Å creating the diselenide bridges while Se(4) is still 3.34(1) Å away from its symmetry equivalent in the adjacent layer.

In Cs₂Bi₇Se₁₂, as in Cs₃Bi₇Se₁₂, Bi(1) has the most regular octahedral coordination with distances Bi-Se distances varying between 2.921(8)-3.002(7) Å and angles varying between 89.7°(2)-91.7°(2) (Table 4-20). Due to the occurrence of the diselenide bonds every other layer, the unit cell has doubled along the layer stacking axis (*c* axis) compared to that of the corresponding parent compound. The site Bi(2) in Cs₃Bi₇Se₁₂ now separates into two symmetrically inequivalent atoms Bi(2) and Bi(2)' in Cs₂Bi₇Se₁₂.

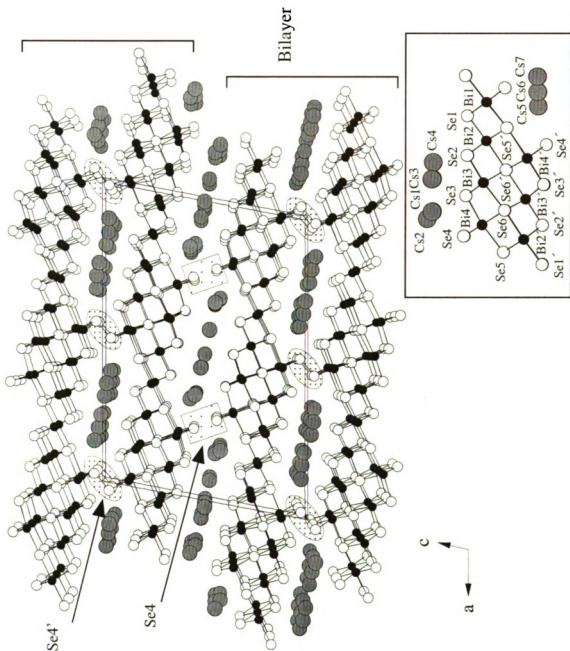


Figure 4-8. Projection of the structure of $\text{Cs}_2\text{Bi}_7\text{Se}_{12}$ down the b -axis. The same layers exist as in $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ but now they form bilayers connected by Se-Se bonds. The bilayers are indicated with brackets. The inset shows the atom labeling.

Table 4-20. Bond Distances for Cs₂Bi₇Se₁₂ and Rb₂Bi₇Se₁₂.

	Cs₂Bi₇Se₁₂	Rb₂Bi₇Se₁₂		Cs₂Bi₇Se₁₂	Rb₂Bi₇Se₁₂
Bi(1)-Se(1)	2.932(6)x2	2.911(7)x2			
Bi(1)-Se(5')	2.921(8)	2.918(8)			
Bi(1)-Se(1')	2.933(5)x2	2.934(6)x2			
Bi(1)-Se(5)	3.002(7)	2.958(8)			
Bi(2)-Se(1)	2.767(8)	2.752(8)	Bi(2')-Se(1')	2.784(7)	2.779(7)
Bi(2)-Se(2)	2.950(5)x2	2.937(6)x2	Bi(2')-Se(2')	2.938(5)x2	2.929(6)x2
Bi(2)-Se(5')	2.992(6)x2	2.966(7)x2	Bi(2')-Se(5)	2.953(5)x2	2.944(6)x2
Bi(2)-Se(6')	3.112(6)	3.091(6)	Bi(2')-Se(6)	3.085(7)	3.072(8)
Bi(3)-Se(2)	2.778(6)	2.786(7)	Bi(3')-Se(2')	2.741(7)	2.733(8)
Bi(3)-Se(3)	2.824(5)x2	2.829(7)x2	Bi(3')-Se(3')	2.923(5)x2	2.900(6)x2
Bi(3)-Se(6)	3.073(7)	3.081(8)	Bi(3')-Se(6)	2.960(6)x2	2.971(7)x2
Bi(3)-Se(6')	3.111(5)x2	3.080(6)x2	Bi(3')-Se(6')	3.111(6)	3.086(7)
Bi(4)-Se(4)	2.784(5)x2	2.781(6)x2	Bi(4')-Se(3')	2.753(7)	2.774(8)
Bi(4)-Se(3)	2.953(6)	2.924(8)	Bi(4')-Se(4')	2.949(5)x2	2.938(6)x2
Bi(4)-Se(5)	3.051(7)	3.059(8)	Bi(4')-Se(6')	2.965(5)x2	2.953(6)x2
Bi(4)-Se(6)	3.164(5)x2	3.106(6)x2	Bi(4')-Se(5')	3.236(8)	3.172(8)
Se(4)-Se(4)	3.35(1)	3.32(1)			
Se(4')-Se(4')	2.33(1)	2.32(2)			
	Cs₂Bi₇Se₁₂			Rb₂Bi₇Se₁₂	
Cs(1)-Se	3.54(2)-4.21(2)	Rb(1)-Se	3.25(5)-4.13(5)		
Cs(2)-Se	3.32(4)-4.06(3)	Rb(2)-Se	2.95(3)-4.24(3)		
Cs(3)-Se	3.67(2)-3.95(2)	Rb(3)-Se	3.51(8)-3.92(7)		
Cs(4)-Se	3.72(2)-4.38(2)	Rb(4)-Se	3.60(2)-4.05(3)		
Cs(5)-Se	3.41(2)-3.98(2)	Rb(5)-Se	3.25(4)-3.91(3)		
Cs(6)-Se	3.63(2)-4.17(2)	Rb(6)-Se	3.51(3)-4.04(3)		
Cs(7)-Se	3.66(1)-4.33(2)	Rb(7)-Se	3.56(2)-3.92(3)		

The two different atoms however still have very similar coordination environments e.g. The Bi-Se bond distances in Bi(2) vary between 2.767(8)-3.112(6) Å while for Bi(2)' the Bi-Se distances have similar values, varying between 2.784(7)-3.085(7) Å. The same relationship applies for Bi(3)-Bi(3)' and Bi(4)-Bi(4)'. Selected bond distances and angles are shown on Table 4-20.

The Rb analog $\text{Rb}_2\text{Bi}_7\text{Se}_{12}$ has the same characteristics (Table 4-20) and will not be discussed further.

$\text{ABi}_7\text{Se}_{12}$ (A = Cs, Rb) (X) and (XI). These two compounds are the fully oxidized forms of (III) and (IV) respectively, and they are structurally related to them as shown in Figure 4-9. The $[\text{Bi}_7\text{Se}_{12}]$ layer has remained intact but now the selenium atoms Se(4) on each side on the layer have formed diselenide bonds with the adjacent layers resulting to a three-dimensional structure. Similar to what we have seen before the layers shifted with result to each other in such a way so that the Se(4) atoms in the two adjacent rows are eclipsed to each other. The Se(4)-Se(4) bond is 2.39(3) Å. Bonds and selected angles are shown in Table 4-19.

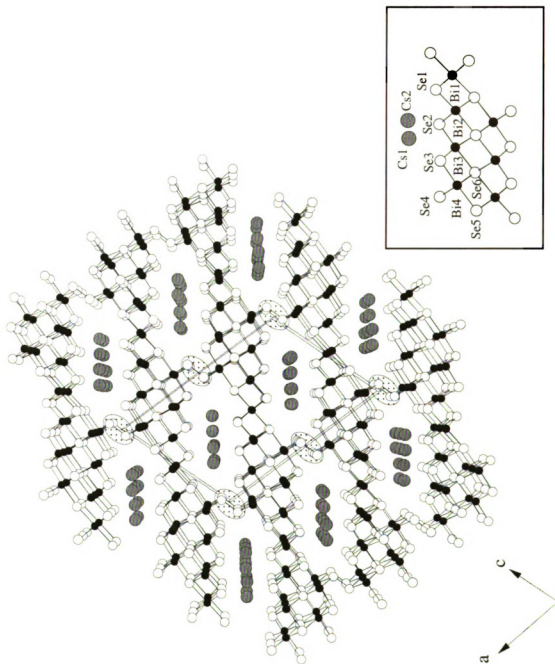


Figure 4-9. Projection of the structure of $\text{CsBi}_7\text{Se}_{12}$ down the b -axis. The same layers exist as in $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ but now they are connected by Se-Se bonds. The inset shows the atom labeling. The Se-Se bonds are shown by the oval shaded areas.

Rb₄Bi₁₀Se₁₇ (V). This compound is also layered and is structurally related with Rb₂Bi₄Se₇ and Rb₃Bi₇Se₁₂ since it consists also of Bi₂Te₃- and CdI₂-type fragments, see Figure 4-10. In Rb₄Bi₁₀Se₁₇, the Bi₂Te₃-type fragment is four bismuth atoms long compared to the others two structures where the same fragment is three bismuth atoms long. The Bi₂Te₃-type blocks in Rb₄Bi₁₀Se₁₇ are connected with a similar way as in Rb₂Bi₄Se₇, instead of the blocks being connected by a single bismuth atom as in the case of Rb₃Bi₇Se₁₂ there are two bismuth atoms forming an CdI₂-type fragment that connects the Bi₂Te₃-type blocks together.

As a result of the longer building blocks the cavity where the Rb atoms reside is wider compared to those of Rb₂Bi₄Se₇ and Rb₃Bi₇Se₁₂. The Rb atoms have trigonal prismatic coordination and exhibit a certain degree of disorder between the cavities. All the bismuth atoms that form the layers are in octahedral coordination with varying degrees of distortion. Bi(4) seems less distorted with Bi-Se distances and angles between 2.849(1)-3.065(2) Å and 84.90(3)-94.05(6)° respectively. The remaining Bi atoms are more distorted with Bi-Se distances between 2.75-3.15 Å. Similar to what is found in the other structures adjacent layers form close non-bonding contacts through rows of Se atoms [Se(6) atom] with Se(6)-Se(6) distances of 3.383(4) Å.

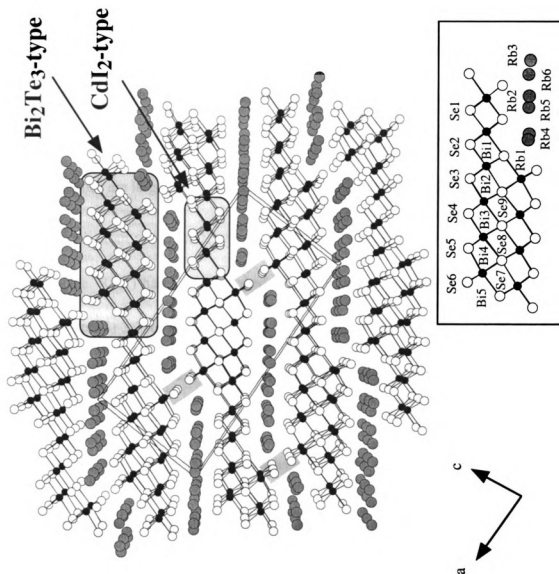


Figure 4-10. Projection of the structure of $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ down the b -axis. The shaded areas indicate the Bi_2Te_3 - and CdI_2 -type building blocks. The Bi_2Te_3 -type block is longer than that found in $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The Se-Se contacts are shown by the shaded square areas. The inset shows the atom labeling. All the Rb atoms are partially occupied.

As mentioned earlier all the Rb atoms are in trigonal prismatic coordination. There are several different trigonal prismatic sites between the Se atoms of two adjacent layers, not all of them can be occupied at the same time and there isn't any preference in the system as to which sites are going to be filled. This also could be related with the fact that the cavities are larger in $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ compared to the previous compounds. This fact makes the Rb atom very mobile, which is very important for the transformation process to take place. Rb(1) has a monocapped trigonal prismatic coordination with distances between 3.268(5)-3.736(4) Å while the other Rb are all trigonal prismatic (Table 4-21). All the Rb sites are partially occupied since each site has close distances ~2.1-2.7 Å with the neighboring Rb sites.

$\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ (XII). This compound is the fully oxidized form of (V) and it is structurally related as shown in Figure 4-11. The $[\text{Bi}_{10}\text{Se}_{17}]$ layer has remained intact but now the Se(6) atoms on each side on the layer have formed Se-Se bonds with the adjacent layers resulting in a three-dimensional structure. Similar to what we observed above, the layers in (VIII) have shifted with respect to those in (V) so that the Se(6) atoms in the two adjacent rows are eclipsed to each other. The Se(6)-Se(6) bond length is 2.349(8) Å. The remaining alkali metal atoms reside in tunnels which form after Se-Se coupling. These atoms spread over the entire tunnels which now provide considerably empty space. Distances and selected angles are shown in Table 4-21.

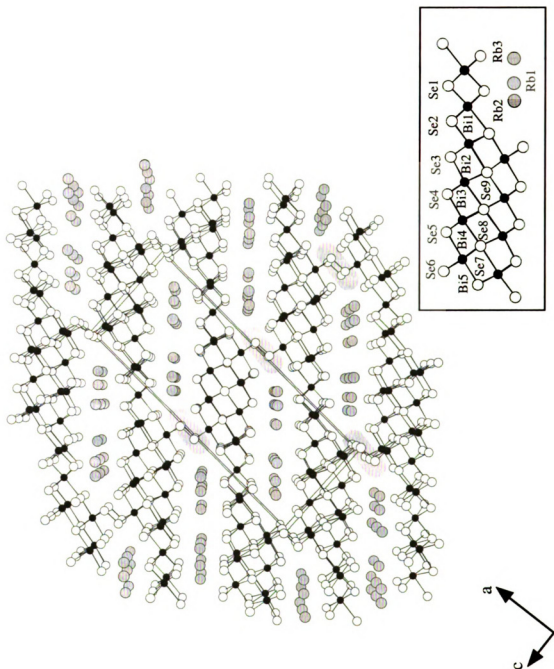


Figure 4-11. Projection of the structure of $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ down the b -axis. The same layers exist as in $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ but now they are connected by Se-Se bonds. The inset shows the atom labeling. The Se-Se bonds are shown by the oval shaded areas.

Table 4-21. Bond Distances and Selected Angles for Rb₄Bi₁₀Se₁₇ and Rb₂Bi₁₀Se₁₇.

	Rb₄Bi₁₀Se₁₇	Rb₂Bi₁₀Se₁₇		Rb₄Bi₁₀Se₁₇	Rb₂Bi₁₀Se₁₇
Bi(1)-Se(1)	2.769(2)	2.696(4)	Se(2)-Bi(1)-Se(7)	87.61(5)	87.59(9)
Bi(1)-Se(2)	2.954(2)x2	2.930(3)x2	Se(1)-Bi(1)-Se(2)	91.51(5)	88.9(1)
Bi(1)-Se(1)	2.960(2)x2	2.977(3)x2	Se(1)-Bi(1)-Se(7)	178.76(6)	175.0(1)
Bi(1)-Se(7)	3.119(2)	3.274(4)			
Bi(2)-Se(2)	2.797(2)	2.746(4)	Se(3)-Bi(2)-Se(8)	85.90(5)	87.37(8)
Bi(2)-Se(7)	2.952(2)x2	3.004(3)x2	Se(2)-Bi(2)-Se(7)	94.00(5)	96.72(9)
Bi(2)-Se(3)	2.977(2)	2.945(3)x2	Se(7)-Bi(2)-Se(3)	174.51(6)	173.7(1)
Bi(2)-Se(8)	3.138(2)	3.148(3)			
Bi(3)-Se(3)	2.785(2)	2.759(4)	Se(8)-Bi(3)-Se(9)	84.17(4)	82.89(7)
Bi(3)-Se(4)	2.917(2)x2	2.855(3)x2	Se(3)-Bi(3)-Se(4)	95.11(5)	94.44(9)
Bi(3)-Se(8)	2.992(2)x2	3.083(3)x2	Se(4)-Bi(3)-Se(8)	172.42(6)	172.10(9)
Bi(3)-Se(9)	3.1562(9)	3.140(1)			
Bi(4)-Se(5)	2.849(1)x2	2.840(3)x2	Se(9)-Bi(4)-Se(8)	84.90(3)	85.04(5)
Bi(4)-Se(4)	2.865(2)	2.889(4)x2	Se(5)-Bi(4)-Se(5)	94.05(6)	94.0(1)
Bi(4)-Se(9)	3.043(2)x2	3.060(1)	Se(5)-Bi(4)-Se(9)	174.49(4)	173.64(8)
Bi(4)-Se(8)	3.065(2)	3.035(4)			
Bi(5)-Se(6)	2.779(2)x2	2.935(3)x2	Se(8)-Bi(5)-Se(8)	82.70(5)	87.9(1)
Bi(5)-Se(5)	2.980(2)	3.034(4)	Se(6)-Bi(5)-Se(6)	97.21(8)	90.1(1)
Bi(5)-Se(7)	2.995(2)	2.863(4)	Se(6)-Bi(5)-Se(8)	172.28(5)	178.2(1)
Bi(5)-Se(8)	3.155(2)x2	2.993(3)x2			
Se(6)-Se(6)	3.383(4)x2	2.349(8)			

Table 4-21. (cont'd).

Rb₄Bi₁₀Se₁₇	
Rb(1)-Se (7 coordinate)	3.268(5)-3.736(4)
Rb(2)-Se (6 coordinate)	3.670(10)-3.714(9)
Rb(3)-Se (6 coordinate)	3.681(6)-3.880(10)
Rb(4)-Se (6 coordinate)	3.327(14)-3.814(10)
Rb(5)-Se (6 coordinate)	3.590(12)-3.731(9)
Rb(6)-Se (6 coordinate)	3.65(2)-3.93(3)
Rb(1)-Rb(4)	2.179(5)
Rb(2)-Rb(6)	2.27(3)
Rb(2)-Rb(5)	2.391(9)
Rb(3)-Rb(3)	2.18(2)
Rb(3)-Rb(6)	2.51(2)
Rb(4)-Rb(5)	2.76(2)
Rb₂Bi₁₀Se₁₇	
Rb(1)-Se (5 coordinate)	3.62(1)-4.06(2)
Rb(2)-Se (6 coordinate)	3.55(2)-3.94(2)
Rb(3)-Se (6 coordinate)	3.81(5)-4.19(5)
Rb(1)-Rb(2)	1.74(3)
Rb(1)-Rb(3)	3.00(4)

Topotactic solid state chemistry and "zipper" action. The first compound to be discovered in the series was $\text{Rb}_2\text{Bi}_4\text{Se}_7$ using a rubidium polyselenide flux. The sample looked homogeneous and its morphology was that of extremely thin long bladelike ribbons. A single crystal X-ray structure determination in a four-circle diffractometer could not be carried out due to the small size and quality of the crystals. We then attempted to solve the structure by X-ray powder crystallography but we quickly discovered that it was not possible to index the powder diffraction pattern to a single phase. We also noticed that fresh batches of the compound, which we always stored in air, tended to become 'wet' and stick to the vials walls, yet no obvious decomposition of the compound was evident. Furthermore, we observed, from X-ray powder diffraction, that the same phase could also be made from direct stoichiometric reactions involving Rb_2Se and Bi_2Se_3 . The appearance and behavior (e.g. tendency to get 'wet' in air) of these samples was identical to those obtained from the rubidium polyselenide flux.

After many attempts and with the help of a CCD area detector diffractometer we were able to collect sufficient data from a crystal to solve the structure. Surprisingly, we discovered the presence of diselenide (Se_2^{2-}) groups and the composition of RbBi_4Se_7 not $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The structure solution allowed us to index most peaks in the powder pattern diffraction, suggesting that the remaining peaks were due to another phase. At first we

rationalized the presence of this Se_2^{2-} group to the polyselenide flux medium of synthesis, although the existence of such groups among bismuth chalcogenides compounds (made by a polychalcogenide flux or otherwise) is quite rare³⁹. Although the flux synthesis could justify the formation of Se_2^{2-} in RbBi_4Se_7 there were problems justifying the synthesis of RbBi_4Se_7 from a direct stoichiometric reaction with a nominal composition of $\text{Rb}_2\text{Bi}_4\text{Se}_7$. If this were the case then a considerable amount of Rb could not be accounted for. In addition, several attempts to repeat both the flux and direct combination synthesis resulted in a product whose powder pattern was similar but not identical to that of RbBi_4Se_7 . In fact, its diffraction lines were the same as those left unindexed in the pattern of the sample from which the RbBi_4Se_7 crystal was selected.

We monitored the X-ray powder diffraction pattern of fresh samples obtained from direct combination reactions intended to give $\text{Rb}_2\text{Bi}_4\text{Se}_7$ and found them to be changing with time upon exposure of the sample in the ambient, and we concluded that an oxidative, probably topotactic, transformation was under way which converted $\text{Rb}_2\text{Bi}_4\text{Se}_7$ to RbBi_4Se_7 over a period of time. We decided to study carefully the structures of both compounds in order to understand what appeared to be an important and rare example of topotactic chemistry in the solid state.

As we will discuss later, the recognition and understanding of this process led us to predict other related systems which might be prone to the same kind of transformation. We identified thus three additional pairs namely $\text{Rb}_3\text{Bi}_7\text{Se}_{12}/\text{Rb}_2\text{Bi}_7\text{Se}_{12}/\text{RbBi}_7\text{Se}_{12}$, $\text{Cs}_3\text{Bi}_7\text{Se}_{12}/\text{Cs}_2\text{Bi}_7\text{Se}_{12}/\text{CsBi}_7\text{Se}_{12}$ and $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}/\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$ which undergo similar redox chemistry.

The phase transformation for both $\text{A}_2\text{Bi}_4\text{Se}_7$, $\text{A}_3\text{Bi}_7\text{Se}_{12}$ and $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$ was studied extensively by powder X-ray diffraction. These experiments demonstrated that the transformation can occur very rapidly beginning immediately upon exposure of the sample to air and can be complete within a few hours to a day depending on relative humidity, as shown in Figure 4-12. The experiment presented in Figure 4-12 was set the following way: A pure sample of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ was exposed to air at the time point “0” and its X-ray powder diffraction pattern was recorded. Several more X-ray powder diffraction pattern were taken at different time points (each scan is between 30 to 60 sec. and the results were normalized). The important thing to notice is that after only ~15 min. the $\text{Rb}_2\text{Bi}_4\text{Se}_7$ starts to convert to RbBi_4Se_7 as evidenced by the splitting of the peak $\sim 12^\circ$. The peak due to $\text{Rb}_2\text{Bi}_4\text{Se}_7$ gets smaller in intensity while the peak due to RbBi_4Se_7 grows in intensity as time passes. Furthermore, the strongest peak at $\sim 7^\circ$ shift to higher angles while the peak at $\sim 21^\circ$ shifts to lower angles.

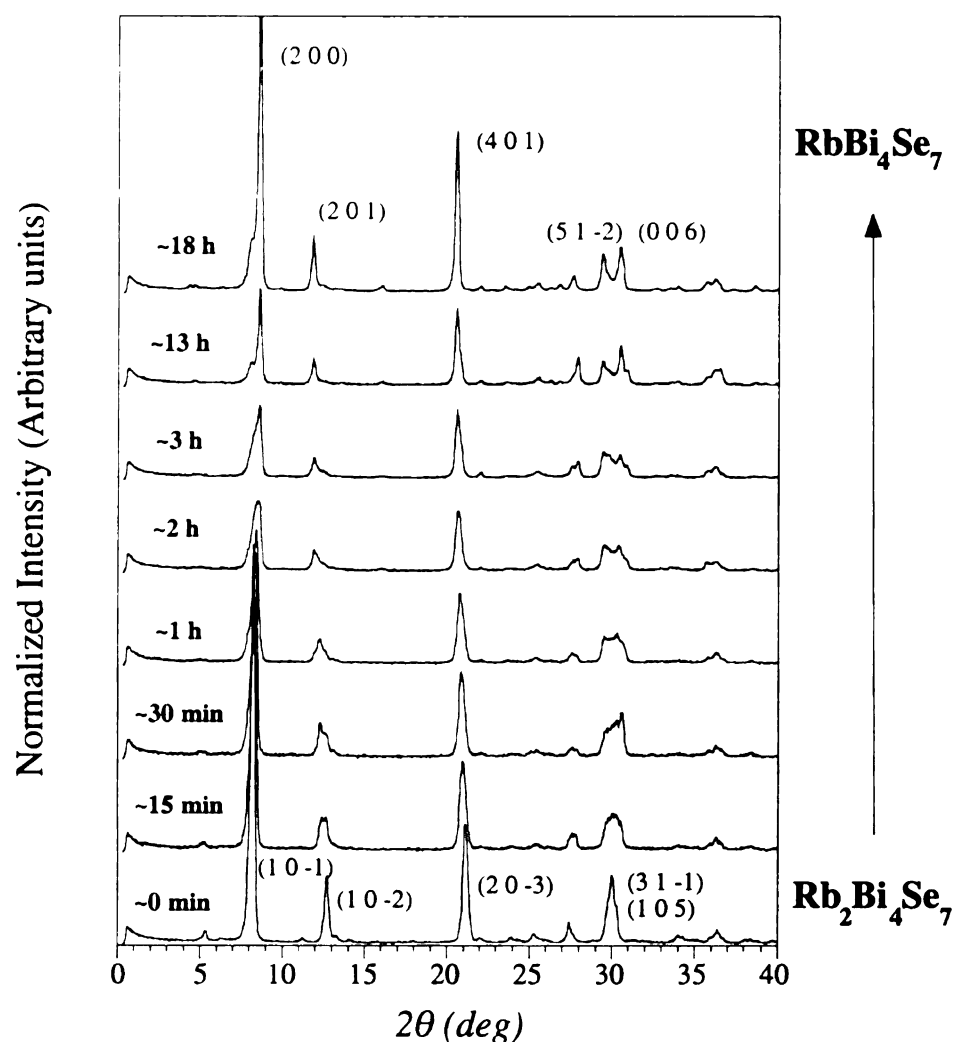


Figure 4-12. Transformation of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ to RbBi_4Se_7 monitored by X-ray powder diffraction. A pure sample of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ was exposed to air and X-ray powder diffraction patterns were recorded at certain time points using the same sample. It can be seen that after only ~15 min of exposure to air the $\text{Rb}_2\text{Bi}_4\text{Se}_7$ starts to transform to RbBi_4Se_7 as evidenced from the splitting of the peak $\sim 12^\circ$. The transformation is almost complete after ~18 h. The X-ray powder diffraction pattern at that point corresponds to that of pure RbBi_4Se_7 .

Also the peak at $\sim 30^\circ$ get broader and finally it splits to two peak after ~ 18 h of exposure to air. At that point, after ~ 18 h, the transformation of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ to RbBi_4Se_7 is almost complete and only a small residual of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ is left (as it can be seen from the small shoulder of strongest peak at $\sim 7^\circ$). Another feature that needs to be pointed out, except from the fact that this process is fast, is that the transformation is inhomogeneous (i.e. two phases) as opposed to homogeneous (one phase) since both phases can be seen at the powder diffraction patterns.

Both water and oxygen are needed for these transformations to occur. When the samples are stored under dry nitrogen or vacuum they remain unchanged. Samples exposed to dry air (e.g. inside a drying oven) or to oxygen free water did not transform. The oxidation of $\text{A}_3\text{Bi}_7\text{Se}_{12}$ to $\text{ABi}_7\text{Se}_{12}$ does not occur readily in air but it is possible with $\text{I}_2/\text{H}_2\text{O}-\text{CH}_3\text{CN}$ solutions.

Based on the work reported here there are several characteristics that a structure needs to have in order for a redox-induced “zipper” action process to take place. First the structure must contain the two aligned rows of Se atoms each in adjacent layers in a staggered fashion with Se-Se distances in the range of 3.3-3.4 Å. Second, the ability of the $[\text{Bi}_x\text{Se}_y]^{z-}$ layers to slide freely with respect to one another is also important. Third, the compound must have a high content of alkali ions that can move freely between the

layers and diffuse out of the structure. If any of these three characteristics is missing, the process does not seem to take place. For example, $A_2Bi_8Se_{13}$ ²², (A = Rb, Cs) shown in Figure 4-13, has the two rows of Se atoms at 3.44 Å yet it does not transform because the layers are locked and cannot slide freely with respect to each other due to several bismuth atoms that pin the layers together. Furthermore, ABi_3Se_5 ³⁸, shown in Figure 4-14, has independent layers with appropriate rows of Se atoms (3.44 Å apart). This structure does not transform due to the tricapped trigonal prismatic site of the alkali metal. The alkali metal residing in that site cannot move freely out of the structure, essentially locking the layers together and preventing them from sliding. A third example is $Rb_{11}Bi_{15}Se_{28}$ ³⁷, see Figure 4-15. This structure has a high content of alkali metal and the layers are able to slide with respect to each other. However the structure is missing the rows of Se atoms, therefore after a few days in air it decomposes to Se and Bi_2Se_3 .

The fact that the oxidative coupling occurs in the presence of water suggests that the process is electrochemical in nature. Given that these phases are dense, and not porous, and that all possible Se^{2-} atoms couple to Se_2^{2-} groups also supports the electrochemical nature of the reaction. The oxidant, be it oxygen, I_2 or otherwise, does not have direct access to all Se^{2-} atoms except perhaps those on the surface of the crystals.

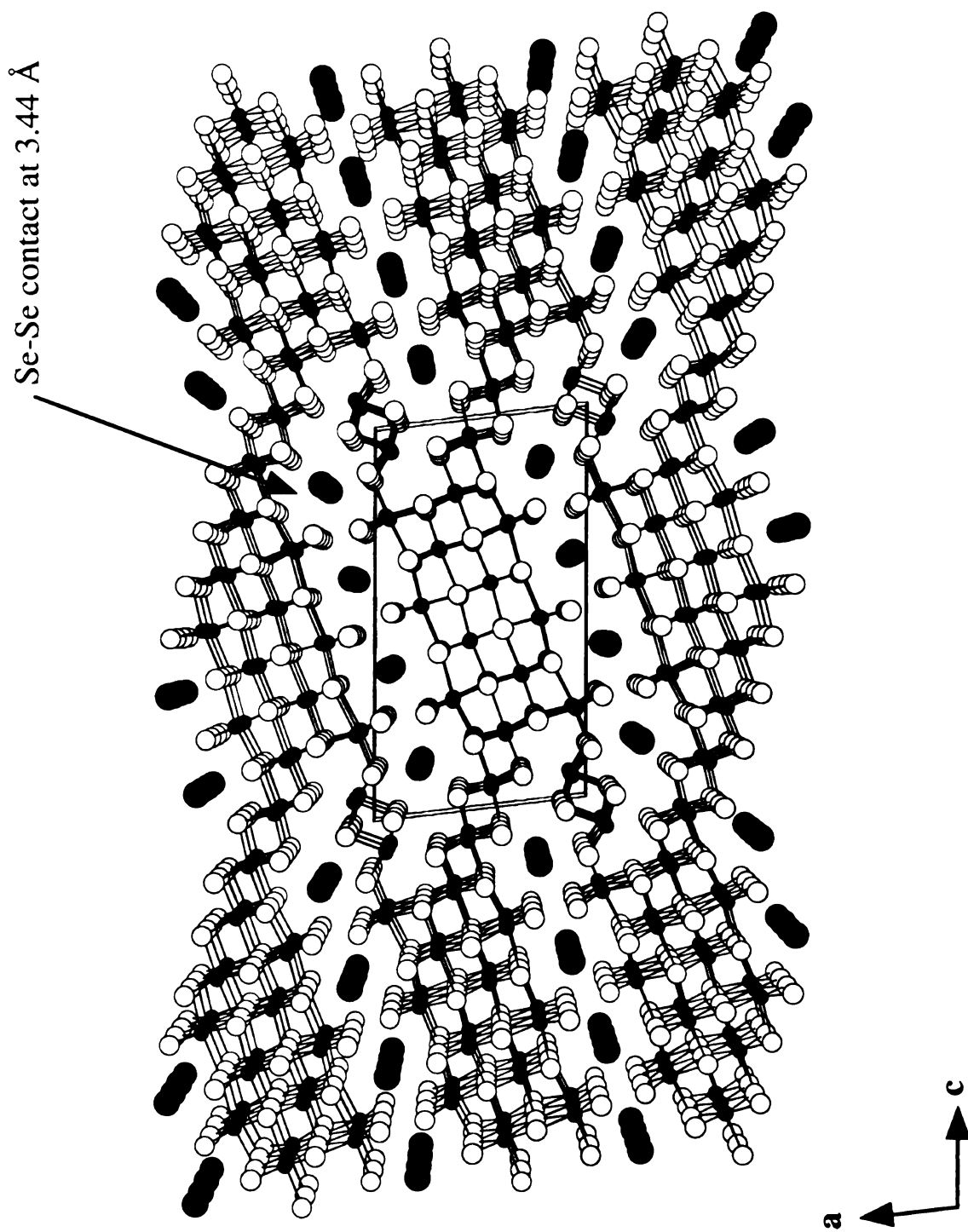


Figure 4-13. Projection of the structure of $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$ down the b-axis. The Se-Se contacts are indicated with the arrow (square shaded areas).

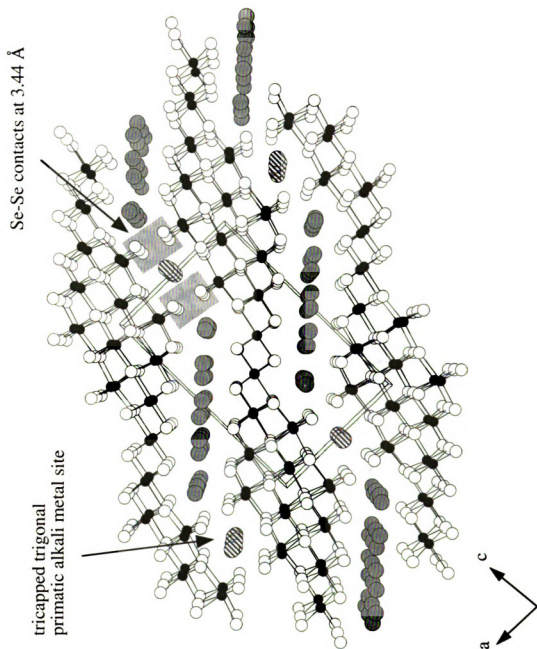


Figure 4-14. Projection of the structure of CsBi_3Se_5 down the b-axis. The Se-Se contacts are indicated with the arrow (square shaded areas). The tricapped trigonal prismatic site is also shown.

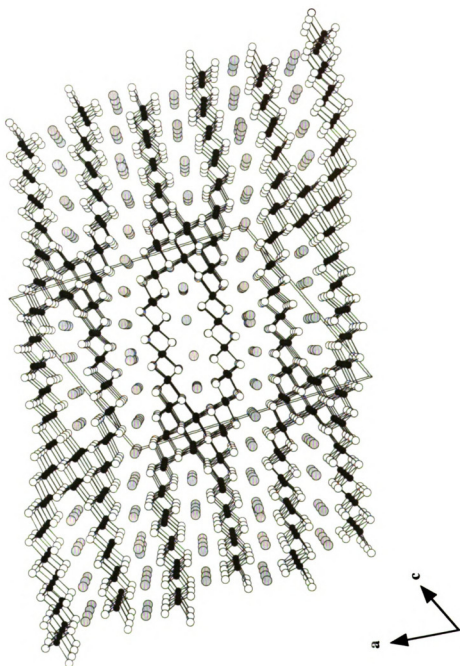


Figure 4-15. Projection of the structure of $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ down the b -axis.

Therefore, electrons must be removed through the conductive $[\text{Bi}_x\text{Se}_y]^{z-}$ framework generating holes, which end up on the Se^{2-} atoms thereby causing them to form Se-Se bonds across the layers. These bonds therefore represent a form of hole localization in these materials.

The $[\text{Bi}_x\text{Se}_y]^{z-}$ frameworks therefore serve as conduits for electron transport between the Se^{2-} atoms and the oxidizing molecules, which lie a long distance away. The narrow energy band gaps present in $\text{A}_x\text{Bi}_4\text{Se}_7$, $\text{A}_x\text{Bi}_7\text{Se}_{12}$ and $\text{Rb}_x\text{Bi}_{10}\text{Se}_{17}$ (i.e. < 0.55 eV) allow sufficient electron transport at room temperature to complete the transformation. To maintain electroneutrality alkali metal atoms are simultaneously de-intercalated, and in this sense the reaction is similar to other oxidative de-intercalation reactions such as those of LiTaS_2 , LiTiS_4 , KMoS_2 etc. The singular aspect, however of the process described in this paper is the topotactic Se-Se bond formation, that resembles a "zipper" like action, in key sites in the lattice, that raises the framework connectivity and dimensionality. We anticipate that the 'zipper' like action in these materials, will also be possible using electrochemical means.

It is interesting that the $\text{A}_3\text{Bi}_7\text{Se}_{12}$ ($\text{A} = \text{Rb}, \text{Cs}$) phases behave differently from the $\text{A}_2\text{Bi}_4\text{Se}_7$ ($\text{A} = \text{Rb}, \text{Cs}$) and $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$. Instead of oxidatively coupling all possible Se...Se pairs into Se-Se bonds, to form a three-dimensional framework, we have

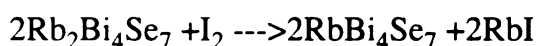
formation of Se-Se bonds in *alternate* layers. As a result every layer on one side makes Se-Se bonds with the adjacent layer while on the other side it retains the configuration it had in the parent structure. This alternation results in "doubling" of the unit cell. We investigated if the rest of compounds presented here behave the same way. When freshly prepared samples of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ react with $\text{I}_2/\text{dry-CH}_3\text{CN}$ solution a new phase formed whose X-ray powder diffraction pattern did not match that of either $\text{Rb}_2\text{Bi}_4\text{Se}_7$ or RbBi_4Se_7 . More specifically its diffraction peaks were between those of $\text{Rb}_2\text{Bi}_4\text{Se}_7$ and RbBi_4Se_7 . Upon exposure to air the phase quickly changed to RbBi_4Se_7 . We mounted one of these crystals under nitrogen and we found a new cell of $a = 42.542(7) \text{ \AA}$, $b = 4.1611(7) \text{ \AA}$, $c = 19.683(3) \text{ \AA}$, $\beta = 107.395(3)^\circ$. We solved the structure in $C2/m$ ($V = 3325.0(9) \text{ \AA}^3$, $Z = 8$) and we got an arrangement that resembles a half transformed product with Se-Se bonds *every other layer* with the layers being identical to those found in $\text{A}_2\text{Bi}_4\text{Se}_7$. The same crystal after it was let to sit in air after a few days gave the unit cell of $\text{Rb}_2\text{Bi}_4\text{Se}_7$. The same exact feature was observed for $\text{Rb}_4\text{Bi}_{10}\text{Se}_{17}$. Initially we got a cell of $a = 46.30(1) \text{ \AA}$, $b = 4.147(1) \text{ \AA}$, $c = 21.869(6) \text{ \AA}$, $\beta = 96.386(9)^\circ$. Again when we solved the structure in $C2/m$ we got the pattern of a "half transformed" structure forming Se-Se bonds every other layer. When the same crystal was left to sit in air it gave the cell of the fully transformed $\text{Rb}_2\text{Bi}_{10}\text{Se}_{17}$. For both cases the refinements were not good and it

seems that these phases are very unstable since they convert to the fully transformed products as soon as they are exposed to air. Nevertheless it is apparent that the transformation of $A_2Bi_4Se_7$ to ABi_4Se_7 and $Rb_4Bi_{10}Se_{17}$ to $Rb_2Bi_{10}Se_{17}$ happens through an intermediate product in which Se-Se bonds form in alternate layers. Therefore, the intermediate products have the formulas $A_{1.5}Bi_4Se_7$ and $Rb_3Bi_{10}Se_{17}$. This difference in behavior in the stability of the intermediate product is hard to explain, although it could stem from the capacity of each structure to expel alkali metals. This ultimately could rest on the charge density of the framework and its ability to transport electrons.

If we examine the volume of the asymmetric units (V/Z where V = volume of the cell and Z the number of asymmetric units in the cell) in the initial and the transformed products we notice that there is a gradual decrease which is in agreement with the fact that the structure has to contract since it is losing alkali metal ions. For example the volume of the asymmetric units for $Rb_2Bi_4Se_7$, " $Rb_{1.5}Bi_4Se_7$ " and $RbBi_4Se_7$ are $\sim 420 \text{ \AA}^3$, $415 \text{ \AA}^3$ and $\sim 411 \text{ \AA}^3$, respectively. Furthermore, going from $Cs_3Bi_7Se_{12}$ to $Cs_2Bi_7Se_{12}$ to $CsBi_7Se_{12}$ the volume decreases from $\sim 723 \text{ \AA}^3$ to $\sim 716 \text{ \AA}^3$ to $\sim 705 \text{ \AA}^3$, respectively.

Oxidation (closing the zipper)/reduction (opening the zipper) chemistry. The interconversion of the pairs $Rb_2Bi_4Se_7/RbBi_4Se_7$ and $Rb_3Bi_7Se_{12}/RbBi_7Se_{12}$ (and their Cs analogs) can be readily effected by proper oxidants and reductants.

Reaction of the $A_2Bi_4Se_7$ samples with I_2/H_2O-CH_3CN solution under a nitrogen atmosphere also results in the transformation of the samples, usually within a few hours. The same experiment performed without I_2 left the samples remained unchanged verifying the fact that I_2 is the oxidizing agent.

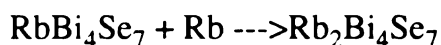


When an $I_2/dry-CH_3CN$ solution under nitrogen was used a different phase was obtained which powder diffraction peaks between $Rb_2Bi_4Se_7$ and $RbBi_4Se_7$. Although this phase by exposure to air converts very fast to $RbBi_4Se_7$ we believe that this is the half transformed product (see above).

The oxidation of $A_3Bi_7Se_{12}$ with $I_2/dry-CH_3CN$ solution is not possible. When I_2/H_2O-CH_3CN solutions are used instead, the oxidation occurs very rapidly and results in the final products ABi_7Se_{12} . In the case where excess of I_2 is used the all-transformed phase ABi_7Se_{12} is formed while when less than stoichiometric amount of I_2 is used a mixture of $A_2Bi_7Se_{12}$ and ABi_7Se_{12} is observed. The half oxidized product can be made

by bubbling air through a suspension of the material in H₂O. The two step oxidation process is shown in Figure 4-16. The same way can be used to convert Rb₄Bi₁₀Se₁₇ to Rb₂Bi₁₀Se₁₇. When possible we avoid long reaction times with I₂ solutions because the I₂ starts attacking the Bi-Se framework. Qualitatively both the structure and alkali metal seems to affect the rate of the redox transformation. The transformation of A₂Bi₄Se₇ is faster while the transformation of A₃Bi₇Se₁₂ is considerably slower. Between the two analogs A₃Bi₇Se₁₂ the Cs seems to transform slower than Rb. The rate of transformation of Rb₄Bi₁₀Se₁₇ seems to be comparable to that of A₃Bi₇Se₁₂.

In addition, when transformed samples of RbBi₄Se₇ are heated at moderate temperatures with stoichiometric amounts of the corresponding alkali metal they absorb it and they give back the parent phases.



This was not possible for the case of ABi₇Se₁₂ (A = Rb, Cs) systems. Instead we only got decomposition products.

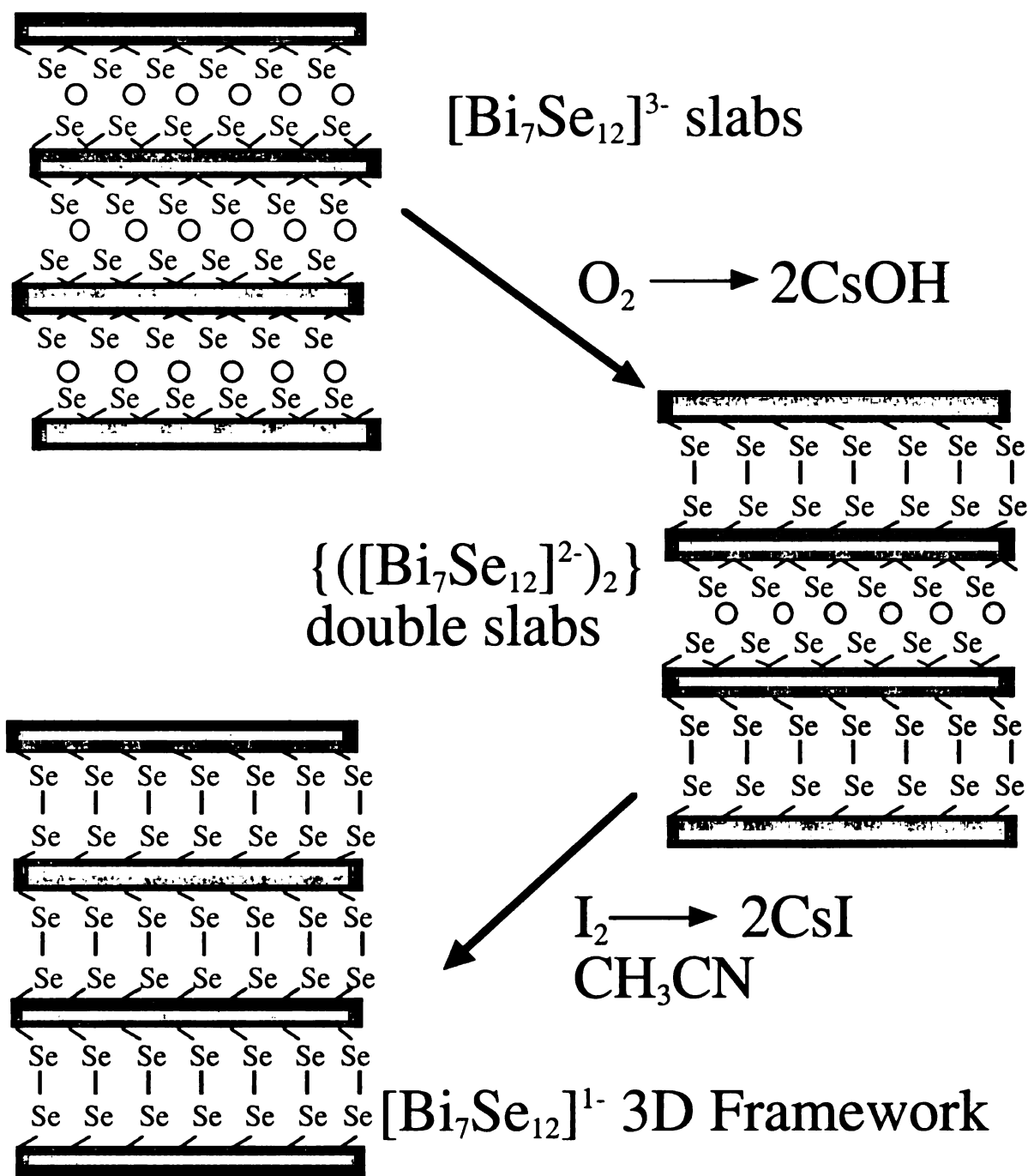


Figure 4-16. Schematic diagram showing the two different steps in the oxidative zipper-like action of two rows of Se atoms belonging to two adjacent $[\text{Bi}_7\text{Se}_{12}]^{3-}$ layers into a single row of diselenide groups. Single slabs join to double slabs, which finally couple to a full 3D-framework. The circles indicate the Cs atoms in the uncoupled layers.

5. Concluding Remarks

An unprecedented all solid state, topotactic oxidative coupling has been discovered which generates rows of Se-Se bonds, a process resembling the closing action of a zipper. $A_2Bi_4Se_7$, $A_3Bi_7Se_{12}$ and $Rb_4Bi_{10}Se_{17}$ have the unique characteristic of oxidatively transforming to produce ABi_4Se_7 , $A_xBi_7Se_{12}$ ($x = 1, 2$) and $Rb_4Bi_{10}Se_{17}$ without loss of crystallinity. The transformation takes place in the presence of an oxidant such as atmospheric oxygen or iodine. In the transformed products, the layers remain intact but they shift with respect to each other to make diselenide bonds. In the case of ABi_4Se_7 and ABi_7Se_{12} these diselenide bonds produce a three-dimensional framework while in the case of $A_2Bi_7Se_{12}$ the diselenide bonds form every other layer resulting to a two-dimensional framework with a thicker layer. We believe that the transformation follows the same path in the other compounds but the intermediate are too unstable to isolate. We expect that both the initial layered and final fully transformed products could be good ion exchange materials.

References

1. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Hogan, T.; Kannewurf, C. R.; Iordanidis, L. *Mater. Res. Soc. Symp. Proc.* **1996**, *410*, 37-43. (b) Chung, D.-Y.; Hogan, T.; Schindler, J.; Iordanidis, L.; Brazis, P.; Kannewurf, C. R.; Chen, B.; Uher, C.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **1997**, *478*, 333-344. (c) Iordanidis, L.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **1999**, *545*, 189-196. (d) Kanatzidis, M. G.; Chung, D.-Y.; Iordanidis, L.; Choi, K.-S.; Brazis, P.; Rocci, M.; Hogan, T.; Kannewurf, C. *Mater. Res. Soc. Symp. Proc.* **1999**, *545*, 233-246.
2. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, *59*, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, *63*, 45-89. (c) Makovicky, E. *Z. Kristallogr.* **1985**, *173*, 1-23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, *160*, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, *5*, 545-591.
3. (a) Glemser, O.; Filcek, M. *Z. Anorg. Allg. Chem.* **1955**, *279*, 321-323. (b) Gattow, G.; Zemmann, J. *Z. Anorg. Allg. Chem.* **1955**, *279*, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, *6*, 961-964. (d) Peresh, E. Y.; Golovei, M. I.; Berul, S. I. *Inorg. Mater.* **1971**, *7*, 27-30. (e) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, *8*, 677-678.
4. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, *252*, 96-99.
5. Schmitz, D.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29*, 438-439.
6. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 676-683.
7. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 399-407.
8. Cook, R.; Schäfer, H. *Rev. Chim. Miner.* **1982**, *19*, 19-27.

-
9. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 631-638.
 10. Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 136-140.
 11. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
 12. (a) McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301. (b) Chondroudis, K.; Kanatzidis, M. G. *J. Solid State Chem.* **1998**, *136*, 328-332.
 13. Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474.
 14. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
 15. Chung, D.-Y.; Jobic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
 16. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science (Washington, D. C.)* **2000**, *287*, 1024-1027.
 17. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162.
 18. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805.
 19. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
 20. Mrotzek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.

-
21. Choi, K.-S.; Chung, D.-Y.; Mroczek, A.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Submitted for publication*.
 22. Iordanidis, L.; Brazis, P. W.; Kyratsi, T.; Ireland, J.; Lane, M.; Kannewurf, C. R.; Dyck, J. S.; Uher, C; Ghelani, N. A.; Hogan, T.; Kanatzidis, M. G. *Chem. Mater.* **2000**, in press. See also Chapter 2.
 23. Choe, W.; Lee, S.; O'Connell, P.; Covey, A. *Chem. Mater.* **1997**, *9*, 2025-2030.
 24. Adouby, K.; Perez Vicente, C.; Jumas, J. C.; Fourcade, R.; Abba Touré, A. Z. *Kristallogr.* **1998**, *213*, 343-349.
 25. Perez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Abba Touré, A.; Kra, G. *Inorg. Chem.* **1999**, *38*, 2131-2135.
 26. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011-1017.
 27. (a) Honda, K.; Nakanishi, F.; Feeder, N. *J. Am. Chem. Soc.* **1999**, *121*, 8246-8250. (b) Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1998**, *120*, 12755-12769 and references therein. (c) Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1997**, *119*, 1462-1463. (d) Suzuki, T.; *Pure Appl. Chem.* **1996**, *68*, 281-284.
 28. (a) Rabe, S.; Muller, U. *Z. Anorg. Allg. Chem.* **1999**, *625*(8), 1367-1370. (b) Englert, U.; Ganter, B.; Wagnet, T.; Klaui, W. *Z. Anorg. Allg. Chem.* **1998**, *624*(6), 970-974.
 29. Kepert, C. J.; Rosseinsky, M. J. *Chem. Comm.* **1999**, 375-376.
 30. Feitknect, W.; Oswald, H. R.; Feitknect-Steinmann, U. *Helv. Chim. Acta* **1960**, *43*, 1947-1950.
 31. Wang, X.; Zhang, H.; Sinkler, W.; Poeppelmeier, K. R.; Marks, L. D. *J. Alloys Comp.* **1998**, *270*, 88-94.

-
32. (a) Iordanidis, L.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1928-1930.
(b) Iordanidis, L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 8319-8320.
33. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.
34. Sheldrick, G. M. University of Göttingen, Germany.
35. (a) Marsh, R. E. *Acta Crystallogr., Sect. B* **1986**, *B42*, 193-198. (b) Marsh, R. E. *Acta Crystallogr., Sect. A* **1994**, *A50*, 450-455. (c) Marsh, R. E. *Acta Crystallogr., Sect. B* **1995**, *B51*, 897-907. (d) Herbstein, F. H.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1998**, *B54*, 677-686.
36. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.
37. See Chapter 8.
38. See Chapter 3.
39. A diselenide bond exists also in $\text{BaLaBi}_2\text{Q}_6^{18b}$ (Q = S, Se).



THESIS

6

2001

LIBRARY Michigan State University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

INVESTIGATIONS IN THE MULTINARY BISMUTH CHALCOGENIDES
SYSTEMS: SYNTHESIS, CHARACTERIZATION AND THERMOELECTRIC
PROPERTIES OF BISMUTH CHALCOGENIDES

VOLUME II

By

Lykourgos Iordanidis

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

2000

$\text{Aln}_{1-x}\text{Bi}_{4-x}\text{S}_6$

Semicon

1. Introduction

Bismuth compounds

These minerals exhibit a

due to the Bi 6s² 6p³

distorted local coordinat

structurally inactive

intermediate stage in the c

complete suppressi

which gives rise to w

the periodic table. T

respective, it is inter

CHAPTER 5

$ALn_{1\pm x}Bi_{4\pm x}S_8$ (A = K, Rb; Ln = La, Ce, Pr, Nd) : New

Semiconducting Quaternary Bismuth Sulfides

1. Introduction

Bismuth compounds constitute a great part of the naturally occurring sulfosalts. These minerals exhibit a staggering compositional complexity and structural diversity¹, partly due to the Bi $6s^2$ lone pair which can be stereochemically expressed leading to a distorted local coordination for the Bi atom. Alternatively the lone pair can be totally stereochemically inactive to produce a regular octahedral Bi^{3+} center. Almost any intermediate stage in the continuum which exists between full stereochemical expression and complete suppression of the $6s^2$ lone pair via sp^3d^2 hybridization is observed. This property gives rise to what may very well be the most malleable coordination geometry in the periodic table. Therefore, from a coordination as well as solid state chemistry perspective, it is interesting to observe the behavior of Bi^{3+} and its role in stabilizing

crystal structure types. It

is growing due to their

despite the fact that $\text{Bi}_2(\text{Sb}_2\text{I})$

intermediate compounds

In the last twenty

structurally characterized

$2\text{Bi}_2\text{S}_3 \cdot \text{Cs}_2\text{Bi}_2\text{Se}_{12}$ or

secondary compounds

$\text{Bi}_{12}\text{S}_{10}^{13}$, $\text{K}_2\text{Bi}_4\text{S}_{13}^{14}$

$2\text{Bi}_2\text{S}_3 \cdot \text{Cd}_2\text{Bi}_3\text{S}_{15}^{15}$

thermochemical properties

stability and properties of

The incorporation of

transition chalcogenide frame

stability due to the high

strong Ln-Q bonds

that such as $\text{EuBi}_2\text{S}_2^{16}$, La

various structure types. Furthermore, interest in multinary Bi chalcogenides compounds is growing due to their potential relevance in thermoelectric applications². It is noteworthy that $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ alloys are currently the best thermoelectric materials³ for room temperature cooling applications.

In the last twenty years several synthetic Bi ternary compounds have been structurally characterized: ABiQ_2 (A = alkali metal; Q = chalcogen)⁴, $\text{CsBi}_3\text{S}_{55}$, RbBi_3S_5 ⁶, $\text{Cs}_3\text{Bi}_7\text{Se}_{12}$ ⁷, α -, β - BaBi_2S_4 ⁸, $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ ⁹, BaBiSe_3 ¹⁰. Only recently several new ternary compounds have been synthesized such as β -, γ - CsBiS_2 ¹¹, KBi_3S_5 ¹², $\text{KBi}_{6.33}\text{S}_{10}$ ¹³, $\text{K}_2\text{Bi}_8\text{S}_{13}$ ¹³, α -, β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$, $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ ¹⁴, BaBiTe_3 ¹⁵, CdBi_2S_4 ¹⁶, CdBi_4S_7 ¹⁶, $\text{Cd}_{2.8}\text{Bi}_{8.1}\text{S}_{15}$ ¹⁶, $\text{Cd}_2\text{Bi}_6\text{S}_{11}$ ¹⁶ some of which seem to possess interesting thermoelectric properties^{2,14,15,17}. Much remains to be learnt however about the chemistry and properties of these structurally complicated systems.

The incorporation of large electropositive ions such as lanthanides (Ln) into bismuth chalcogenide frameworks is expected to lead to materials with low thermal conductivity, due to the high coordination sites they adopt and the ionic character of the surrounding Ln-Q bonds¹⁷. Only a limited number of ternary lanthanide compounds is known such as EuBi_2S_4 ¹⁸, Eu_2BiS_4 ¹⁹, $\text{La}_4\text{Bi}_2\text{S}_9$ ²⁰, $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ ²¹, $\text{Eu}_3\text{Bi}_4\text{Q}_9$ (Q = S,

Q²⁺ and these compounds

antibond bismuth chalc

occupies an octahedral

coordination sites. Given

as the similarity of the

observed in Bi³⁺Ln³⁺ systems

where orbital energies be

into a Bi-Q framework

network. For these reasons

Bi-Bi-Q systems (A = alkali

metals) have already reported on

utilized by Q²⁺ groups

optoelectronic, structural

$\text{Bi}_{1-x}\text{Bi}_{1-x}\text{S}_3$ (A = K, Rb)

$\text{Bi}_{1-x}\text{Bi}_{1-x}\text{S}_3$ is examined

the

Se)²² and these compounds are little studied. Even less is known about quaternary lanthanide bismuth chalcogenides. In the ternary compounds the Bi atom most often occupies an octahedral (often distorted) coordination but it can also occupy higher coordination sites. Given the high effective ionic radius in these high coordination sites and the similarity of the size of Bi³⁺ to the sizes of several Ln³⁺ ions, we became interested in Bi³⁺/Ln³⁺ substitution chemistry in such sites. Because of the very different valence orbital energies between Ln³⁺ and Bi³⁺ centers, the incorporation of lanthanide ions into a Bi-Q framework could dramatically affect the electronic properties of that framework. For these reasons we decided to explore the solid state chemistry of the A-Ln-Bi-Q systems (A = alkali or alkaline earth metal, M = lanthanide metal, Q = S, Se). We have already reported on BaLaBi₂Q₆²³ (Q = S, Se) which possesses a tunnel structure stabilized by Q₂²⁻ groups. Here we report on the synthesis, physicochemical, spectroscopic, structural and electrical characterization of the new compounds ALn_{1±x}Bi_{4±x}S₈ (A = K, Rb; Ln = La, Ce, Pr, Nd). The relationship of these phases with Ce_{1.25}Bi_{3.75}S₈²¹ is examined and it is proposed that the latter is in fact a KCe_{1±x}Bi_{4±x}S₈ phase.

Experimental section

Reagents. Chem

99.999% purity, -1000 m

250 micron. Alfa Aes

Chemical Mfg. Corp., G

Acet Chemical Co., I

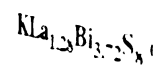
Woburn, MA overlan

As_2S_3 and Re_2S_7 were pre

red and sulfur in liquid

Synthesis. All m

ing a vacuum atmosph



mol Bi_2S_3 and 0.092 g

ex which was flame-se

for 6 days at 820 °C and

product consisted of silic

in water, methanol and

2. Experimental section

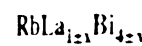
Reagents. Chemicals in this work were used as obtained: (i) bismuth powder 99.999+% purity, -100 mesh, Cerac, Milwaukee, WI (ii) cerium powder 99.9% purity, <250 micron, Alfa Aesar, Ward Hill, MA (iii) sulfur powder, sublimed, Spectrum Chemical Mfg. Corp., Gardena, CA (iv) potassium metal granules, 99%, purity, <6 mm, Aldrich Chemical Co., Inc., Milwaukee, WI (v) rubidium metal 99.8% purity, Alfa Aesar, Ward Hill, MA (vi) lanthanum sulfide 99.9% purity, -200 mesh, Cerac, Milwaukee, WI. K_2S and Rb_2S were prepared by a stoichiometric reaction of the corresponding alkali metal and sulfur in liquid ammonia as described earlier.¹³

Synthesis. All manipulations were performed under a atmosphere of dry nitrogen using a vacuum atmosphere DriLab glovebox.

$KL_{1.28}Bi_{3.72}S_8$ (I). A mixture of 0.027 g (0.245 mmol) K_2S , 0.500 g (0.972 mmol) Bi_2S_3 and 0.092 g (0.246 mmol) La_2S_3 was transferred to a carbon coated quartz tube which was flame-sealed under high vacuum (10^{-4} – 10^{-5} mbar). The tube was heated for 6 days at 820 °C and was cooled to 420 °C at 10 °C/h and then to 50 °C in 10 h. The product consisted of silver-gray needles, several mm long, and was isolated by washing with water, methanol and ether. Semiquantitative energy dispersive analysis (EDS) using

scanning electron

composition of $K_{0.1}La_{0.9}$



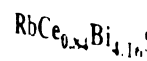
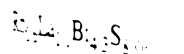
mmol Bi_2S_3 and 0.00

the which was flame

at was cooled to 450

energy needles

fieldless SEM E



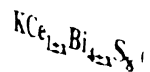
mmol Bi_2S_3 , 0.0068 g

is transferred into a

for 6 days and cool

consisted of a metal

SEEDS analysis gave



0.01 g (0.272 mmol) K

a scanning electron microscope (SEM) on a number of needles gave an average composition of $\text{K}_{0.9}\text{La}_{1.3}\text{Bi}_{4.0}\text{S}_{8.0}$.

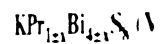
$\text{RbLa}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ (II). A mixture of 0.030 g (0.148 mmol) Rb_2S , 0.304 g (0.591 mmol) Bi_2S_3 and 0.055 g (0.147 mmol) La_2S_3 was transferred to a carbon coated quartz tube which was flame-sealed under vacuum. The tube was heated for 6 days at 850 °C and was cooled to 450 °C at 10 °C/h and then to 50 °C in 10 h. The product consisted of silver-gray needles and was isolated by washing with water, methanol and ether. Standardless SEM/EDS on a number of needles gave an average composition of $\text{Rb}_{0.6}\text{La}_{1.1}\text{Bi}_{4.3}\text{S}_{8.0}$.

$\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$ (III). A mixture of 0.050 g (0.246 mmol) Rb_2S , 0.500 g (0.972 mmol) Bi_2S_3 , 0.068 g (0.485 mmol) Ce metal and 0.024 g (0.748 mmol) of elemental S was transferred into a carbon coated quartz tube, sealed under vacuum and heated at 850 °C for 6 days and cooled to 450 °C at 10 °C/h and then to 50 °C in 10 h. The product consisted of a metallic-gray chunk with needles growing on its top. Standardless SEM/EDS analysis gave all four elements with the following ratio: $\text{Rb}_{0.6}\text{Ce}_{0.9}\text{Bi}_{4.6}\text{S}_{8.0}$.

$\text{KCe}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ (IV). The procedure was similar to the ones above. A mixture of 0.030 g (0.272 mmol) K_2S , 0.559 g (1.087 mmol) Bi_2S_3 , 0.076 g (0.542 mmol) Ce metal

±0.026 g, ±0.811 mmol

the all four elements with



res above. A mixture of

g for 2r or 0.041 g for Na

3 were used. Their elem

respectively. All compoun

Physical Measurements

The instrument and

Thermal Analysis and Characterization

Section 3). The instrument

the same as that in Chapter

Magnetic measurements

measured over the range

magnetometer. Samples were

film and loaded into PV

omagnetism. Magnetization

It was investigated to

and 0.026 g (0.811 mmol) of elemental S were used. Standardless SEM/EDS analysis gave all four elements with the following ratio: $\text{K}_{0.9}\text{Ce}_{1.1}\text{Bi}_{4.2}\text{S}_{8.0}$.

$\text{KPr}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ (V) and $\text{KNd}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ (VI). The procedure was similar to the ones above. A mixture of 0.016 g (0.145 mmol) K_2S , 0.292 g (0.568 mmol) Bi_2S_3 , 0.040 g for Pr (or 0.041 g for Nd) (0.277 mmol) metal and 0.014 g (0.437 mmol) of elemental S were used. Their elemental compositions were $\text{K}_{0.9}\text{Pr}_{1.6}\text{Bi}_{3.9}\text{S}_8$ and $\text{K}_{1.7}\text{Nd}_{1.4}\text{Bi}_{4.2}\text{S}_8$ respectively. All compounds are stable in air and water.

3. Physical Measurements

The instrument and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis* and *Charge-transport measurement* are the same as that in Chapter 2 (Section 3). The instrument and experimental setup for *Solid-State UV/Vis Spectroscopy* is the same as that in Chapter 4 (Section 3).

Magnetic measurements. The magnetic response of the Ce compounds was measured over the range 2-300 K using a MPMS Quantum Design SQUID magnetometer. Samples were ground to a fine powder to minimize possible anisotropic effects and loaded into PVC containers. The results were corrected for core atom diamagnetism. Magnetization as a function of field strength (at a constant temperature of 5 K) was investigated to determine if the samples experienced saturation of their

magnetic signal. For

ged over the range

performed at moder

Powder X-

power diffraction t

showed that all pha

Debye RW400F2 R

Key powder diffra

homogeneity of all

the calculated tr

contains the d_{calc} d

III

Single-Crys

$\text{KLa}_{1.23}\text{Bi}_{3.77}$

for data collection

indexed from thre

94 orthogonal we

main determined

554 strong ref

magnetic signal. For both compounds magnetization increased linearly with increasing field over the range 100-10000 G. The subsequent temperature-dependent studies were performed at moderate field strengths (1000-2000 G).

Powder X-ray crystallography. The compounds were examined by X-ray powder diffraction to check for phase purity and for identification. These powder patterns showed that all phases are isostructural. Powder patterns were obtained using a Rigaku-Denki/Rw400F2 (Rotaflex) rotating-anode powder diffractometer and a CPS 120 INEL Xray powder diffractometer equipped with a position-sensitive detector. The purity and homogeneity of all phases was confirmed by comparison of X-ray powder diffraction to those calculated from single crystal data using the CERIUS² software²⁴. Table 5-1 contains the d_{calc} , d_{obs} and I/I_{max} (obs) for (I) together with the d_{obs} and I/I_{max} (obs) for (II).

Single-Crystal X-ray crystallography.

KL_{1.28}Bi_{3.72}S₈ (I). A Siemens SMART Platform CCD diffractometer was used for data collection. An initial set of cell constants was calculated from reflections harvested from three sets of 15 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an orientation matrix determined from 80 reflections. Final cell constants were calculated from a set of 5334 strong reflections obtained from the data collection (Table 5-2).

Table 5-1. Calculat

 $\text{KLa}_{123}\text{Bi}_{3-7}\text{S}_8$ and R

λ	d_{calc}
10.1	13.1
10.2	10.7
10.0	8.3
10.1	7.7
10.2	6.57
10.3	5.42
10.1	5.36
10.4	5.11
10.3	4.38
10.5	4.16
11.1	3.87
11.2	3.69
10.3	3.59
11.1	3.59
11.6	3.58
11.3	3.52
11.2	3.45
11.5	3.39
11.6	3.29
10.1	3.25
11.1	3.23
11.4	3.17
10.2	3.17
11.2	3.12
11.4	3.01
10.3	3.01
11.5	2.99
11.0	2.90
11.4	2.82

Table 5-1. Calculated and Observed X-ray Powder Diffraction Patterns for

KLa_{1.28}Bi_{3.72}S₈ and RbLa_{1±x}Bi_{4±x}S₈.

<i>h k l</i>	KLa _{1.28} Bi _{3.72} S ₈			RbLa _{1±x} Bi _{4±x} S ₈	
	<i>d_{calc}</i> , Å	<i>d_{obs}</i> , Å	<i>I/I_{max}</i> (obs)	<i>d_{obs}</i> , Å	<i>I/I_{max}</i> (obs)
1 0 1	13.148	13.123	4	13.301	3
0 0 2	10.755	10.735	5	10.893	2
2 0 0	8.306	8.300	19	8.379	13
2 0 1	7.749	7.742	7	7.810	6
2 0 2	6.574	6.563	22	6.632	9
2 0 3	5.428	5.427	4	5.484	2
3 0 1	5.363	5.359	13	5.397	11
1 0 4	5.116	5.107	3	5.160	1
3 0 3	4.383	4.377	12	4.416	8
1 0 5	4.165	4.160	5	4.205	4
1 1 1	3.874	3.870	2	3.899	3
1 1 2	3.698	3.697	3	3.720	1
4 0 3	3.594	3.589	100	3.619	100
2 1 1	3.592				
0 0 6	3.585				
0 1 3	3.529	3.528	7	3.541	6
2 1 2	3.451	3.446	5	3.473	3
3 0 5	3.397	3.394	13	3.426	9
2 0 6	3.292	3.284	26	3.311	14
5 0 1	3.284				
3 1 1	3.234	3.233	8	3.252	5
1 1 4	3.177	3.174	16	3.193	13
5 0 2	3.174				
3 1 2	3.129	3.125	2	3.148	2
2 1 4	3.016	3.014	16	3.035	13
5 0 3	3.015				
1 1 5	2.905	2.903	9	2.926	7
4 1 0	2.901				
5 0 4	2.826	2.824	3	2.846	3

Table 5-1. (cont'd).

314	2.79
215	2.78
305	2.63
603	2.58
316	2.43
605	2.32
317	2.24
612	2.23
309	2.19
613	2.17
318	2.07
409	2.07
2012	1.75

Table 5-1. (cont'd).

3 1 4	2.795	2.779	10	2.801	8
2 1 5	2.780				
5 0 5	2.630	2.629	5	2.648	4
6 0 3	2.583	2.582	16	2.598	13
3 1 6	2.416	2.416	6	2.434	3
6 0 5	2.328	2.323	3	2.344	3
3 1 7	2.240	2.237	6	2.254	3
6 1 2	2.236			2.241	2
3 0 9	2.194	2.193	8	2.214	4
6 1 3	2.178	2.176	4	2.188	3
3 1 8	2.077	2.071	13	2.090	12
4 0 9	2.072				
2 0 12	1.752	1.747	8	1.756	6

Table 5.2. Crystallography

Empirical formula

Formula weight

Temperature, K

Crystal system

Space group, Å

Z Volume, Å³Density (calc.), g/cm³Absorption coeff., mm⁻¹

F(00)

Crystal size, mm³

Wavelength, Å

Frag(s)

Index ranges

Reflections collected

Independent reflections

Refinement method

Max. and min. transmission

Data/restraints/parameters

Goodness-of-fit on F^2 Final R indices [$I > 2\sigma(I)$]

R indices (all data)

Extinction coefficient

Largest peak and hole, e/Å³

$$R_1 = \sum |F_o| - F_c / \sum |F_o|$$

Table 5-2. Crystallographic Data for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$.

Empirical formula	$\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$	$\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$
Formula weight	1250.79	1329.36
Temperature, K	293 (2)	293 (2)
Crystal system	Orthorhombic	Orthorhombic
Space group, Å	<i>Pnma</i> (#62)	<i>Pnma</i> (#62)
	$a = 16.6524(9)$	$a = 16.7469(2)$
	$b = 4.0712(2)$	$b = 4.0528(1)$
	$c = 21.589(1)$	$c = 21.753(1)$
Z, Volume, Å ³	4, 1463.6(1)	4, 1476.42(4)
Density (calc.), g/cm ³	5.676	5.981
Absorption coeff., mm ⁻¹	49.617	56.366
F(000)	2115	2237
Crystal size, mm ³	0.80 x 0.05 x 0.05	0.50 x 0.09 x 0.15
Wavelength, Å	0.71073	0.71073
θ range	1.54 to 27.14°	1.53 to 25.03°
Index ranges	-18 ≤ h ≤ 20 -5 ≤ k ≤ 4 -26 ≤ l ≤ 25	-19 ≤ h ≤ 19 -4 ≤ k ≤ 4 -25 ≤ l ≤ 25
Reflections collected	7609	12291
Independent reflections	1734 [$R_{\text{int}} = 0.0507$]	1504 [$R_{\text{int}} = 0.0497$]
Refinement method	Full-matrix least-squares on F^2	
Max. and min transmission	1.000 and 0.321	1.000 and 0.268
Data/restraints/parameters	1733 / 0 / 88	1504 / 0 / 88
Goodness-of-fit on F^2	1.068	1.111
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0313$ $wR2 = 0.0677$	$R1 = 0.0292$ $wR2 = 0.0597$
R indices (all data)	$R1 = 0.0397$ $wR2 = 0.0743$	$R1 = 0.0345$, $wR2 = 0.0613$
Extinction coefficient	0.00123(7)	0.00059(5)
Largest peak and hole, eÅ ⁻³	3.077 and -2.077	2.058 and -1.635

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

The data collection

region of reciprocal space

0.075 Å Three measurements

exposure time of 10 s

acquisition and SAIL

The absorption

was using the SHELX

relaxation and energy

in 4.0 x 10⁻⁴ eV (Table 1)

16.7 eV² and the thermal

for bismuth atoms is

for both sites. The electron

site occupancies were

atoms in this site were

distances with the shortest

coordination with distances

square pyramidal coordination

The data collection technique used is known as hemisphere collection. Here a region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.75 Å. Three major swaths of frames were collected with 0.30° steps in ω and an exposure time of 10 sec per frame. The SMART^{25a} software was used for data acquisition and SAINT^{25b} for data extraction.

The absorption correction was done using SADABS^{25c} and all refinements were done using the SHELXTL^{25d} package of crystallographic programs. Four bismuth atoms, one lanthanum and eight sulfur atoms were found to sit on crystallographic mirror planes (site 4c, x 1/4 z) (Table 5-3). Next to the La(2) site significant electron density was found (18.17 eÅ⁻³) and the thermal parameter U of Bi(4) was higher (0.025 Å²) compared to the other bismuth atoms (~0.012 Å², $R1=7.1\%$ $wR2=17.0\%$). A disorder model was applied for both sites. The electron density close to La(2) site was assigned as Bi(5) and the sum of the occupancies was constrained equal to 0.500 (fully occupied). The assignment of atoms in this site was done according to the coordination environments and bond distances with the surrounding sulfur atoms. La(2) has a bicapped trigonal prism coordination with distances varying between 2.940(2)–3.246(4) Å while Bi(5) has a square pyramid coordination with distances varying between 2.723(8)–2.979(4) Å (Table 5-5).

Table 5-3. Atomic Coordi

 $\bar{A}^2 \times 10^3$ for $\text{KLa}_{1.25}\text{Bi}_3$

	λ
Bi(1)	0.54
Bi(2)	0.65
Bi(3)	0.42
Bi(4)	0.47
La(1)	0.47
La(2)	0.70
Bi(5)	0.72
K(1)	0.80
S(1)	0.606
S(2)	0.416
S(3)	0.685
S(4)	0.475
S(5)	0.709
S(6)	0.616
S(7)	0.284
S(8)	0.573

 $\bar{A}$ is defined as one third

Table 5-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters**($\text{\AA}^2 \times 10^3$) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$.**

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.5432(1)	0.2500	0.7426(1)	13(1)	
Bi(2)	0.6510(1)	0.7500	0.8968(1)	12(1)	
Bi(3)	0.4278(1)	0.2500	0.9158(1)	14(1)	
Bi(4)	0.4669(1)	0.7500	0.5928(1)	16(1)	0.550(8)
La(1)	0.4669(1)	0.7500	0.5928(1)	16(1)	0.450(8)
La(2)	0.7066(1)	0.7500	0.5464(1)	8(1)	0.831(6)
Bi(5)	0.7266(4)	0.7500	0.5339(3)	17(2)	0.169(6)
K(1)	0.8017(2)	0.7500	0.7418(1)	18(1)	
S(1)	0.6066(2)	0.7500	0.6755(2)	12(1)	
S(2)	0.4105(2)	0.2500	0.6725(2)	12(1)	
S(3)	0.6886(2)	0.2500	0.8205(2)	13(1)	
S(4)	0.4746(2)	0.7500	0.8317(2)	16(1)	
S(5)	0.7908(2)	0.7500	0.9465(2)	11(1)	
S(6)	0.6165(2)	0.2500	0.9983(2)	13(1)	
S(7)	0.2842(2)	0.2500	0.8757(2)	11(1)	
S(8)	0.5732(2)	0.2500	0.5441(1)	10(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S-4. Anisotropic P

	U
B(1)	14
B(2)	11
B(3)	11
B(4)	10
La(1)	10
K(1)	21
S(1)	17
S(2)	13
S(3)	14
S(4)	8.2
S(5)	9.2
S(6)	7.2
S(7)	12.2
S(8)	12.2

Transisotropic displacement

$$2k^2(a^2U_{11} + k^2b^2U_{22})$$

$$-2k^2b^2c^2U_{33}]$$

Table 5-4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	14(1)	15(1)	9(1)	0	0(1)	0
Bi(2)	11(1)	18(1)	12(1)	0	0(1)	0
Bi(3)	11(1)	17(1)	8(1)	0	-1(1)	0
Bi(4)	19(1)	15(1)	16(1)	0	2(1)	0
La(1)	19(1)	15(1)	16(1)	0	2(1)	0
K(1)	21(2)	22(2)	13(2)	0	3(1)	0
S(1)	17(2)	17(2)	13(2)	0	5(1)	0
S(2)	13(2)	14(2)	7(2)	0	2(1)	0
S(3)	14(2)	16(2)	7(2)	0	2(1)	0
S(4)	8(2)	19(2)	6(2)	0	-1(1)	0
S(5)	9(2)	17(2)	5(2)	0	2(1)	0
S(6)	7(2)	20(2)	7(2)	0	1(1)	0
S(7)	12(2)	17(2)	7(2)	0	2(1)	0
S(8)	12(2)	20(2)	7(2)	0	2(1)	0

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2 h k a^* b^* U_{12} + 2 h l a^* c^* U_{13} + 2 k l b^* c^* U_{23}].$$

Table S-5. Bond Distances

B(1)-S(1)	2.1
B(1)-S(2)	2.1
B(1)-S(3)	2.1
B(1)-S(4)	3.1
B(2)-S(3)	2.1
B(2)-S(4)	3.1
B(2)-S(5)	2.1
B(2)-S(6)	3.1
B(3)-S(4)	2.1
B(3)-S(6)	2.1
B(3)-S(6)	3.1
B(3)-S(7)	2.1
M(1)-S(1)	2.1
M(1)-S(2)	2.1
M(1)-S(3)	2.1
M(1)-S(5)	3.1
M(1)-S(5)	3.1
B(5)-La(2)	0.1
B(5)-S(1)	3.1
B(5)-S(5)	2.1
B(5)-S(6)	2.1
B(5)-S(7)	2.1
B(5)-S(5)	3.1
La(2)-S(1)	3.1
La(2)-S(5)	2.1
La(2)-S(6)	3.1
La(2)-S(7)	2.1
La(2)-S(5)	3.1

Table 5-5. Bond Distances (Å) and Angles (deg) for $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$.

Bi(1)-S(1)	2.713(2) x 2	S(2)-Bi(1)-S(1)	91.11(8)
Bi(1)-S(2)	2.679(3)	S(2)-Bi(1)-S(3)	179.60(9)
Bi(1)-S(3)	2.948(3)	S(4)-Bi(1)-S(4)	84.62(9)
Bi(1)-S(4)	3.024(2) x 2		
Bi(2)-S(3)	2.693(2) x 2	S(5)-Bi(2)-S(3)	92.58(9)
Bi(2)-S(4)	3.257(4)	S(3)-Bi(2)-S(6)	171.65(8)
Bi(2)-S(5)	2.563(3)	S(5)-Bi(2)-S(6)	82.54(8)
Bi(2)-S(6)	3.046(2) x 2	S(6)-Bi(2)-S(4)	98.09(8)
Bi(3)-S(4)	2.837(2) x 2	S(7)-Bi(3)-S(4)	92.32(9)
Bi(3)-S(6)	2.850(2) x 2	S(4)-Bi(3)-S(6)	88.57(7)
Bi(3)-S(6)	3.612(3)	S(7)-Bi(3)-S(6)	170.33(9)
Bi(3)-S(7)	2.542(3)	S(6)-Bi(3)-S(6)	84.49(8)
M(1)-S(1)	2.932(3)		
M(1)-S(2)	2.827(2) x 2		
M(1)-S(8)	2.895(2) x 2		
M(1)-S(5)	3.053(3)		
M(1)-S(8)	3.029(3)		
Bi(5)-La(2)	0.429(6)		
Bi(5)-S(1)	3.652(8)		
Bi(5)-S(5)	2.790(4) x 2		
Bi(5)-S(6)	2.723(8)		
Bi(5)-S(7)	2.979(4) x 2		
Bi(5)-S(8)	3.274(6) x 2		
La(2)-S(1)	3.246(4)	K-S(1)	3.551(5)
La(2)-S(5)	2.966(3) x 2	K-S(2)	3.293(4) x 2
La(2)-S(6)	3.124(4)	K-S(3)	3.252(3) x 2
La(2)-S(7)	2.940(2) x 2	K-S(4)	3.288(5)
La(2)-S(8)	3.013(3) x 2	K-S(7)	3.266(4) x 2

La₂O₃ was introduced

sum of the occupied

and R^2 values of

by 63.7 Br and 1

except La₂O₃ and

of the compound

RbCe_{0.94}I₃

used for data collection

exposure time was

and the final cell

collection (Table

used for data acquisition

After absorption

programs, as in the

were found to show

Significant electro

thermal parameter

4017 Å², $R_1=0.017$

La(1) was introduced also in Bi(4) site (i.e. a mixed occupancy model was used) and the sum of the occupancies was set equal to 0.500 (fully occupied). After refinement the R1 and wR2 values dropped to 4.8% and 11.3% respectively. The split La(2) site is occupied by 83% Bi and 17% La while the Bi(4) site contains 55% Bi and 45% La. All the atoms except La(2) and Bi(5) were refined anisotropically (R1=4.0%, wR2=7.4%). The formula of the compound refined to $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$.

RbCe_{0.84}Bi_{4.16}S₈ (III). A Siemens SMART Platform CCD diffractometer was used for data collection. This same technique as above was used for data collection. The exposure time was 30 sec per frame. The initial cell was determined from 69 reflections and the final cell was calculated from a set of 8013 reflections from the actual data collection (Table 5-2). The resolution of the data set is 0.84 Å. The SMART software was used for data acquisition and SAINT for data extraction.

After absorption correction with SADABS and refinement with the SHELXTL programs, as in the previous case, four bismuth atoms, one cerium and eight sulfur atoms were found to sit on a crystallographic mirror plane (site 4c, x 1/4 z) (Table 5-6). Significant electron density (21.04 eÅ⁻³) was found close to the Ce(2) site and also the thermal parameter U of Bi(4) was higher (0.029 Å²) compared to the other bismuth atoms (~0.017 Å², R1=8.0% wR2=19.8%). A disorder model was applied for both sites.

Table 5-6. Atomic Coord

(Å $\times 10^3$) for RbCe₆Si₆I₆

	λ
B(1)	0.5
B(2)	0.1
B(3)	0.4
B(4)	0.4
Ce(1)	0.4
B(5)	0.22
Ce(2)	0.2
Rb	0.28
S(1)	0.6
S(2)	0.42
S(3)	0.68
S(4)	0.4
S(5)	0.28
S(6)	0.11
S(7)	0.28
S(8)	0.5

^a λ is defined as one third

Table 5-6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.5396(1)	0.2500	0.2598(1)	18(1)	
Bi(2)	0.1465(1)	0.7500	0.3972(1)	17(1)	
Bi(3)	0.4272(1)	0.2500	0.0849(1)	19(1)	
Bi(4)	0.4728(1)	0.7500	0.4100(1)	23(1)	0.702(9)
Ce(1)	0.4728(1)	0.7500	0.4100(1)	23(1)	0.298(9)
Bi(5)	0.2255(4)	0.7500	0.0307(3)	29(1)	0.460(8)
Ce(2)	0.2075(4)	0.7500	0.0433(3)	15(1)	0.540(8)
Rb	0.2984(1)	0.7500	0.2427(1)	21(1)	
S(1)	0.6051(2)	0.7500	0.3251(1)	16(1)	
S(2)	0.4115(2)	0.2500	0.3326(1)	16(1)	
S(3)	0.6819(2)	0.2500	0.1784(1)	18(1)	
S(4)	0.4726(2)	0.7500	0.1682(1)	20(1)	
S(5)	0.2881(2)	0.7500	0.4440(1)	16(1)	
S(6)	0.1156(2)	0.2500	0.4980(1)	18(1)	
S(7)	0.2823(2)	0.2500	0.1190(1)	16(1)	
S(8)	0.5758(2)	0.2500	0.4579(1)	17(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5-7. Anisotrop

B: 1)
B: 2)
B: 3)
B: 4)
C: 1)
Rb
S: 1)
S: 2)
S: 3)
S: 4)
S: 5)
S: 6)
S: 7)
S: 8)

The anisotropic displa

$$\frac{1}{2} \hbar^2 a^2 U_{11} + k^2 U_{11}$$

2010-01-23

Table 5-7. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	19(1)	17(1)	17(1)	0	0(1)	0
Bi(2)	18(1)	17(1)	16(1)	0	1(1)	0
Bi(3)	18(1)	19(1)	19(1)	0	0(1)	0
Bi(4)	28(1)	17(1)	24(1)	0	-2(1)	0
Ce(1)	28(1)	17(1)	24(1)	0	-2(1)	0
Rb	22(1)	22(1)	21(1)	0	3(1)	0
S(1)	17(2)	17(2)	16(2)	0	0(1)	0
S(2)	11(2)	20(2)	17(2)	0	-1(1)	0
S(3)	24(2)	17(2)	12(2)	0	1(1)	0
S(4)	23(2)	20(2)	17(2)	0	-3(1)	0
S(5)	15(2)	18(2)	15(2)	0	0(1)	0
S(6)	21(2)	18(2)	15(2)	0	2(1)	0
S(7)	16(2)	17(2)	16(2)	0	-2(1)	0
S(8)	13(2)	23(2)	15(2)	0	-1(1)	0

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2 h k a^* b^* U_{12} + 2 h l a^* c^* U_{13} + 2 k l b^* c^* U_{23}].$$

The electron density map

occupancies was constant

atoms in this site was

sources with the sum

ordination with distan

square pyramid coordin

55. Ce11 was introduced

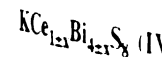
4.2 to 0.500 (fully occu

219.1% respectively. Th

304 site contains 70%

efined anisotropically. R

the refinement was R_wCe



mounted on a glass fiber a

single-crystal monochrom

the cell was calculated

centrally centered reflectio

the compound and the stru

The electron density near the Ce(2) site, was assigned as Bi(5) and the sum of the occupancies was constrained to be equal to 0.500 (fully occupied). The assignment of atoms in this site was done according to the coordination environments and bond distances with the surrounding sulfur atoms. Ce(2) has a bicapped trigonal prism coordination with distances varying between 2.897(6)–3.338(6) Å while Bi(5) has a square pyramid coordination with distances varying between 2.754(7)–2.954(5) Å (Table 5-8). Ce(1) was introduced also in the Bi(4) site and the sum of the occupancies was set equal to 0.500 (fully occupied). After refinement the R1 and wR2 values dropped to 4.1% and 9.1% respectively. The split Ce(2) site is occupied by 54% Bi and 46% Ce while the Bi(4) site contains 70% Bi and 30% Ce. All the atoms except Ce(2) and Bi(5) were refined anisotropically (R1=3.5%, wR2=6.1%). The formula of the compound based on this refinement was $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$.

$\text{KCe}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ (IV). A crystal with dimensions 0.65 × 0.05 × 0.05 mm was mounted on a glass fiber and a Rigaku AFC6S four circle diffractometer equipped with a graphite-crystal monochromator was used for data collection at room temperature. The final cell was calculated from a least-squares refinement using the 2θ angles of 15 carefully centered reflections in the $20 \leq 2\theta \leq 30^\circ$ range. Although data were collected for this compound and the structure solved, its refinement had several problems.

Table 5-8. Bond Distances

B(1)-S(1)	2.1
B(1)-S(2)	2.1
B(1)-S(3)	2.1
B(1)-S(4)	2.1
B(2)-S(3)	2.1
B(2)-S(4)	2.1
B(2)-S(5)	2.1
B(2)-S(6)	2.1
B(3)-S(4)	2.1
B(3)-S(6)	2.1
B(3)-S(7)	2.1
M(1)-S(1)	2.1
M(1)-S(2)	2.1
M(1)-S(3)	2.1
M(1)-S(5)	2.1
M(1)-S(8)	2.1
B(5)-Ce(2)	0.4
B(5)-S(1)	3.7
B(5)-S(5)	2.7
B(5)-S(6)	2.7
B(5)-S(7)	2.9
B(5)-S(8)	3.2
Ce(2)-S(1)	3.3
Ce(2)-S(5)	2.9
Ce(2)-S(6)	3.1
Ce(2)-S(7)	2.8
Ce(2)-S(8)	2.9

Table 5-8. Bond Distances (Å) and Angles (deg) for RbCe_{0.84}Bi_{4.16}S₈.

Bi(1)-S(1)	2.707(2) x 2	S(2)-Bi(1)-S(1)	90.80(8)
Bi(1)-S(2)	2.667(3)	S(2)-Bi(1)-S(3)	179.89(9)
Bi(1)-S(3)	2.969(3)	S(4)-Bi(1)-S(4)	83.12(8)
Bi(1)-S(4)	3.055(2) x 2		
Bi(2)-S(3)	2.676(2) x 2	S(5)-Bi(2)-S(3)	92.22(9)
Bi(2)-S(4)	3.242(3)	S(3)-Bi(2)-S(6)	171.40(7)
Bi(2)-S(5)	2.580(3)	S(5)-Bi(2)-S(6)	82.60(8)
Bi(2)-S(6)	3.032(2) x 2	S(6)-Bi(2)-S(4)	99.46(8)
Bi(3)-S(4)	2.823(2) x 2	S(7)-Bi(3)-S(4)	94.00(8)
Bi(3)-S(6)	2.862(2) x 2	S(4)-Bi(3)-S(6)	89.03(6)
Bi(3)-S(6)	3.636(3)	S(7)-Bi(3)-S(6)	167.25(8)
Bi(3)-S(7)	2.537(3)	S(6)-Bi(3)-S(6)	83.66(8)
M(1)-S(1)	2.883(3)		
M(1)-S(2)	2.827(2) x 2		
M(1)-S(8)	2.858(2) x 2		
M(1)-S(5)	3.181(3)		
M(1)-S(8)	2.987(3)		
Bi(5)-Ce(2)	0.407(7)		
Bi(5)-S(1)	3.729(6)		
Bi(5)-S(5)	2.778(5) x 2		
Bi(5)-S(6)	2.754(7)		
Bi(5)-S(7)	2.951(5) x 2		
Bi(5)-S(8)	3.233(5) x 2		
Ce(2)-S(1)	3.338(6)	Rb-S(1)	3.558(4)
Ce(2)-S(5)	2.963(5) x 2	Rb-S(2)	3.395(3) x 2
Ce(2)-S(6)	3.121(6)	Rb-S(3)	3.295(3) x 2
Ce(2)-S(7)	2.897(6) x 2	Rb-S(4)	3.336(4)
Ce(2)-S(8)	2.996(5) x 2	Rb-S(7)	3.378(3) x 2

The results were similar.

presented the same kind

in positive definite. De

and (III). The fina

$1045.3 \text{ \AA}$, $b = 4048.2$

4 Results and Discussion

Synthesis and th

ating the correspond

temperatures above 500°

ating the corresponding

compounds melt incongru

XRD studies (Table 5-9).

K_2S or Rb_2S , a different

Probably, due to the larger

in the atoms rearrange to

The results were similar to those described above, that is both high coordinate sites presented the same kind of disorder as in (I) and (III) however many sulfur atoms were non-positive definite. Despite this there is no doubt that this compound is isomorphous to (I) and (III). The final cell, determined from a single crystal, was found to be $a = 16.645(3) \text{ \AA}$, $b = 4.048(2) \text{ \AA}$, $c = 21.577(1) \text{ \AA}$ and the space group orthorhombic *Pnma*.

4. Results and Discussion

Synthesis and thermal behavior. Compounds **I** and **II** were synthesized by reacting the corresponding alkali metal sulfide, Bi_2S_3 and La_2S_3 in 1:4:1 ratio at temperatures above 800°C . Compounds **III** and **IV** were synthesized similarly by reacting the corresponding alkali metal sulfide, Bi_2S_3 , Ce and S in a 1:4:2:3 ratio. All compounds melt incongruently between $770\text{--}880^\circ\text{C}$ as determined by DTA and powder XRD studies (Table 5-9). When similar reactions were performed with Cs_2S , instead of K_2S or Rb_2S , a different phase with the composition $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ ²⁶ is formed. Probably, due to the larger ionic radius of Cs^+ , the $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ structure is not favored and the atoms rearrange to give a different product.

Table 5-9. Optical B

Compound
$\text{KLa}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{RbLa}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{RbCe}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KCe}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KPr}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KNd}_{0.25}\text{Bi}_{0.75}\text{S}_3$

Table 5-10. Single C

Compound
$\text{KLa}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KCe}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KPr}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{KNd}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{RbLa}_{0.25}\text{Bi}_{0.75}\text{S}_3$
$\text{RbCe}_{0.25}\text{Bi}_{0.75}\text{S}_3$

Table 5-9. Optical Band Gap and Melting Point Data for $ALn_{1\pm x}Bi_{4\pm x}S_8$.

Compound	E_g (eV)	m.p.(°C)	Comments
$KLa_{1.28}Bi_{3.72}S_8$	1.0	801	incongruently
$RbLa_{1\pm x}Bi_{4\pm x}S_8$	1.2	778	incongruently
$RbCe_{0.84}Bi_{4.16}S_8$	1.1	786	incongruently
$KCe_{1\pm x}Bi_{4\pm x}S_8$	1.1	772	incongruently
$KPr_{1\pm x}Bi_{4\pm x}S_8$	1.1	780	incongruently
$KNd_{1\pm x}Bi_{4\pm x}S_8$	1.1	778	incongruently

Table 5-10. Single Crystal Unit Cells of $ALn_{1\pm x}Bi_{4\pm x}S_8$

Compound	a (Å)	b (Å)	c (Å)	V (Å ³)
$KLa_{1.28}Bi_{3.72}S_8$	16.6524(9)	4.0712(2)	21.589(1)	1463.6(1)
$KCe_{1\pm x}Bi_{4\pm x}S_8$	16.645(3)	4.048(2)	21.577(1)	1437.7(7)
$KPr_{1\pm x}Bi_{4\pm x}S_8$	16.502(2)	4.0391(5)	21.511(3)	1433.8(4)
$KNd_{1\pm x}Bi_{4\pm x}S_8$	16.462(4)	4.0316(5)	21.503(4)	1427.0(5)
$RbLa_{1\pm x}Bi_{4\pm x}S_8$	16.700(3)	4.078(1)	21.698(5)	1477.6(6)
$RbCe_{0.84}Bi_{4.16}S_8$	16.7469(2)	4.0528(1)	21.753(1)	1476.42(4)

Although pure P

Rn reagents in 1:4:1 rat

forms from ratios such

$\text{Al}_{1/2}\text{Bi}_{1/2}\text{S}_2$ phase is

peaks which they could

Bi_2S_3 are used, such as

and a mixture of product

between ternary A-Bi-S

is structural with RbBiS_2

The Pr and Nd. A

was as described for L

measured their X-ray powd

Structure descri

and is made up of NaCl -

tunnels filled with alkali

types of metal positions.

numbers.

Although pure products can be obtained by reacting the $A_2S/Bi_2S_3/La_2S_3$ ($A=K, Rb$) reagents in 1:4:1 ratio (1:4:2:3 when $A_2S/Bi_2S_3/Ce/S$ is used) this structure type also forms from ratios such as 1:3:1 and 1:3:2. In these cases the XRD shows that the $ALn_{1\pm x}Bi_{4\pm x}S_8$ phase is the main product with the presence of some impurity (5-10%) peaks which they could not be attributed to any known phases. When ratios lower in Bi_2S_3 are used, such as 1:2:1 and 1:1:1, then the $ALn_{1\pm x}Bi_{4\pm x}S_8$ phase is no longer stable and a mixture of products is obtained with the main characteristic being the separation between ternary A-Bi-S phases and binary Ln-S phases. The A-Bi-S phases are β - $KBiS_2$ (isostructural with $RbBiS_2$) and $RbBiS_2^{4d}$.

The Pr and Nd, $ALn_{1\pm x}Bi_{4\pm x}S_8$ analogs can also be prepared from similar reagent ratios as described for La and Ce above. Although they were not crystallographically refined, their X-ray powder diagrams indicate that they are isostructural.

Structure description. The structure type adopted by all compounds is unusual and is made up of NaCl-type and Gd_2S_3 -type²¹ building blocks which connect to form tunnels filled with alkali metals ions as shown in Figure 5-1. This structure type has three types of metal positions, a six coordinate type and two with higher (>6) coordination numbers.

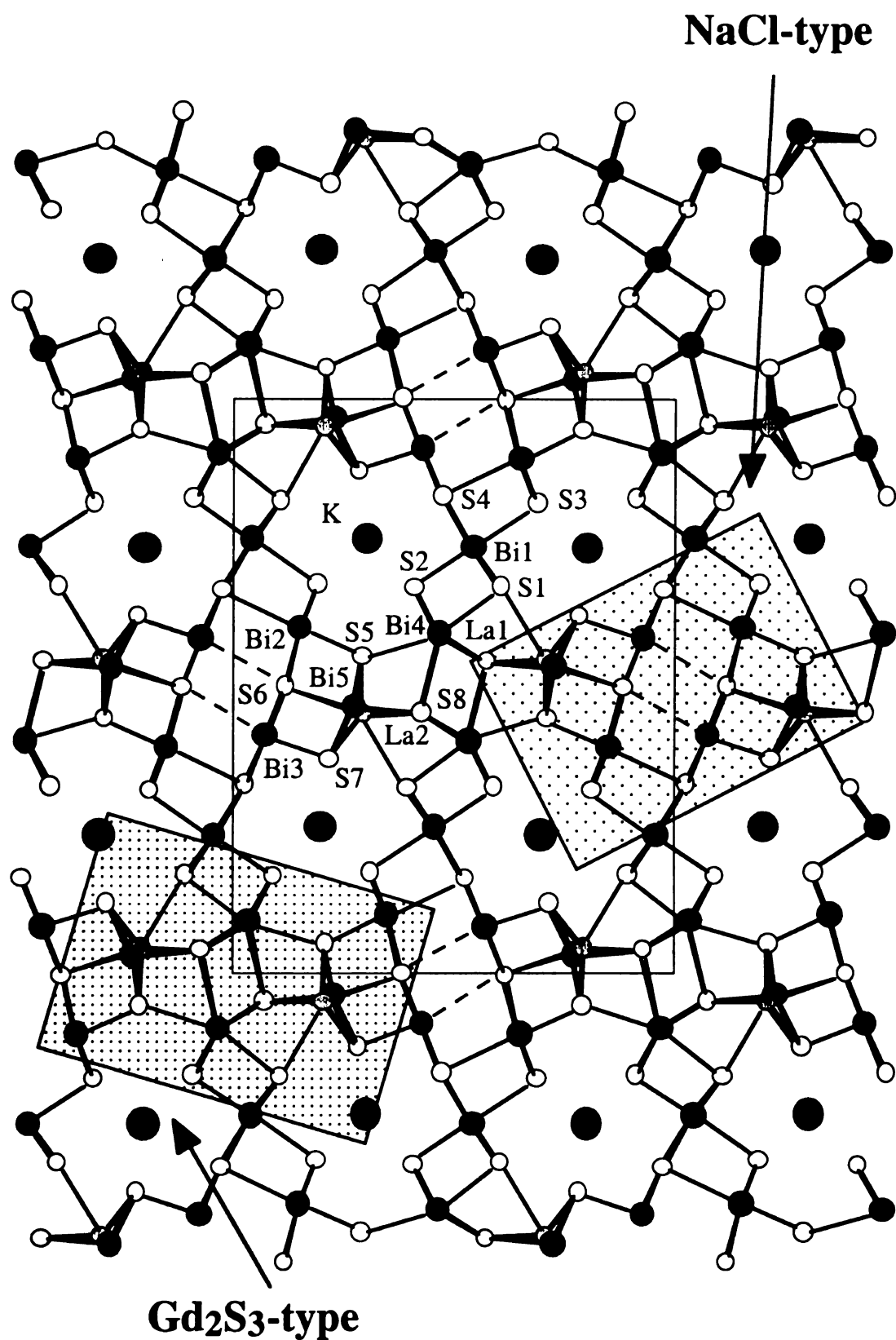


Figure 5-1. Projection of the structure of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ viewed down the b -axis. The

shaded areas indicate the NaCl-type and Gd_2S_3 -type building blocks.

The NaCl-type fragments

occupied by Bi atoms

coordinate positions. The

fragments, where Bi has

may Bi chalcogenides

A second character

subsection consisting

columns of biocapped oct

unoccupied prisms, stac

ed by sharing trigonal

are disposed perpendicu

cluding Gd_2S_3 , $CeTeS_3$

In $KLa_{1-2}Bi_{1-2}S_3$

positions M1 and M2, se

coordination (7) and cons

trapped trigonal prismatic

electron density at a distan

position into two sites, in w

is occupied by Bi in M2

The NaCl-type fragment contains the six-coordinate positions which are exclusively occupied by Bi atoms, while the Gd_2S_3 -type fragment contains the seven and eight-coordinate positions which display mixed occupancy. The presence of NaCl-type fragments, where Bi has a distorted octahedral coordination, is a common feature in many Bi chalcogenides¹¹.

A second characteristic of the structure is an infinite rod with a lozenge-like cross-section consisting of two columns of monocapped (coordination number 7) and two columns of bicapped (coordination number 8) prisms, see Figure 5-2A & 5-2B. The monocapped prisms stack into a column by sharing edges while the bicapped prisms stack by sharing trigonal faces. This arrangement causes the two different kind of prisms to be disposed perpendicular to each other. This feature occurs in a variety of compounds including Gd_2S_3 ²⁷, CeTmS_3 ²⁸, $\text{La}_{10}\text{Er}_9\text{S}_{27}$ ²⁹, PbBi_2S_4 ³⁰, $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ ³¹ and $\text{La}_4\text{Bi}_2\text{S}_9$ ²⁰.

In $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$, there is a disorder between Bi and La in the high coordinate positions M1 and M2, see Figure 5-2A. Site M1 has a monocapped trigonal prismatic coordination (7) and consists of ~55% Bi (Bi4) and ~45% La (La1). M2 position has a bicapped trigonal prismatic coordination (8). The existence of a considerable amount of electron density at a distance of 0.429(6) Å from M2 leads to the resolved splitting of this position into two sites, in which one is ~83% occupied by La (M2, La2) while the other is ~17% occupied by Bi (M2', Bi5).

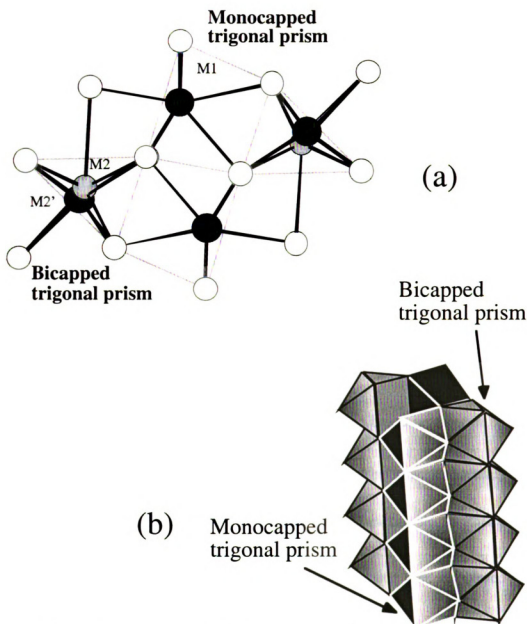


Figure 5-2. (A) Orientation of the Gd_2S_3 -type infinite rod consisting of two columns of mon capped (coordination number 7) and two columns of bicapped (coordination number 8) prisms. The grey lines show the two different kinds of prisms. (B) Polyhedral view of the prisms as they stack along the b-axis. The solid colored areas indicate the prisms while the shaded areas show the caps.

The coordination
sites (La-S_2) and b
characteristics. As m
unoccupied ($\text{La}1 - 7$) c
as in Bi_2S_3 , one Bi at
Bi-S interaction resem
the Bi (Bi_2) has a se
392-403 Å) resemb
between Bi and La in K
arrangements of Bi
halogenides. Bi atoms
each atom occupies a
ns. These high coordina
are to connect the vari
bonds. Large ions suc
increasing substitution ch
compounds.

The coordination environments of La^{3+} and Bi^{3+} in the corresponding binary sulfides (La_2S_3 and Bi_2S_3 respectively), as shown in Figure 5-3, have common characteristics. As mentioned before in La_2S_3 (Gd_2S_3 -type), La atoms exist in monocapped (La1 -7 coordinate) and bicapped (La2 -8 coordinate) trigonal prismatic sites. In Bi_2S_3 , one Bi atom (Bi1) has a distorted octahedral coordination and a extra long Bi-S interaction resembling a monocapped trigonal prismatic coordination, while the other Bi (Bi2) has a square pyramidal coordination with three long Bi-S distances (3.32–4.03 Å) resembling a bicapped trigonal prismatic coordination. The disorder between Bi and La in $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ can be rationalized based on the similar size and atom arrangements of Bi and La in their binary sulfides. Also in several ternary bismuth chalcogenides, Bi atoms occupy high coordinate sites. For example, in $\text{K}_2\text{Bi}_8\text{S}_{13}$ ¹³ one bismuth atom occupies a distorted bicapped trigonal prismatic site, disordered with K^+ ions. These high coordinate sites (which usually are occupied by Bi and other large ions) serve to connect the various structural blocks formed from the octahedrally coordinated Bi atoms. Large ions such as lanthanides can occupy these positions allowing for some interesting substitution chemistry and enabling the tuning of the electronic properties of the compounds.

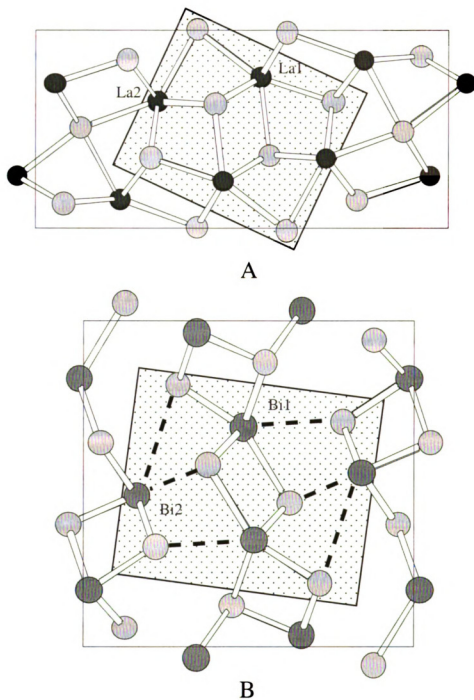


Figure 5-3. The structures of La_2S_3 (A) and Bi_2S_3 (B) showing the same Gd_2S_3 -type infinite rod found in $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$.

In site M1, the

the values of La^{III} are

common for Bi-S bonds

2.40(2)–3.24(4) Å.

1.91–3.18 Å). Regard

different. Now there are

A three long distances (1

are of a square pyrami

M2 and M2' as Bi (Bi5

shared. Characteristic

bond. This type of coord

results from the influen

sation is more prone

2.40(2) Å trans to 3.25

–3.29 Å.

$\text{ReCe}_{0.92}\text{Bi}_{1.08}\text{S}_8$

shared, with a long bond

the metal-sulfur bonds vary

at 0.9% Ce. The other in

In site M1, the metal-sulfur bonds vary between 2.827(2)–3.053(3) Å, very close to the values of La(7 coordinate)-S bonds in La₂S₃ (2.94–3.05 Å). These values are also common for Bi-S bonds. In site M2, the metal-sulfur bonds are in the range 2.940(2)–3.246(4) Å, again very close to the La(8 coordinate)-S bonds in La₂S₃ (2.91–3.18 Å). Regarding the M2' site where the splitting took place the situation is different. Now there are three short bonds [2.723(8)–2.790(4) Å], one bond at 2.979(4) Å, three long distances [3.274(6)–3.652(8) Å] and the coordination of the atom resembles more of a square pyramid. Based on the metal-sulfur distances M2 was assigned as La (La2) and M2' as Bi (Bi5). The coordination of the three octahedral bismuth atoms is also distorted. Characteristic of all Bi atoms is the existence of a long bond *trans* to a short bond. This type of coordination environment is prevalent in bismuth chalcogenides and results from the influence of the stereochemically active 6s² electron lone pair. This distortion is more pronounced for atoms Bi(3) [2.542(3) Å *trans* to 3.612(3) Å] and Bi(2) [2.563(3) Å *trans* to 3.257(4) Å]. For all three Bi atoms the bond angles range between ~82–98°.

RbCe_{0.84}Bi_{4.16}S₈ has the same characteristics. The octahedral Bi atoms are distorted, with a long bond *trans* to a short bond. In site M1 (monocapped trigonal prism) the metal-sulfur bonds vary between 2.827(2)–3.181(3) Å and this site consists of 70% Bi and 30% Ce. The other high coordinate (bicapped trigonal prism) position is disordered

in the same way as in

M. B. 51.

The stoichiometry

parent phases of the for

pure compositional form

the lanthanide whole in

mentioned before the

coordination preference

coordinate sites and pro

stoichiometry. In fact, w

Bi_2S_3 to be accessible u

Remarkably, the

structural characteristics

$\text{Ca}_{1-x}\text{Bi}_x\text{S}_3$ crystallize

single unit cell of $a = 10$

synthesized from a mixture

days under a bath of KCl

in the same way as in $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and consists of 46% Ce (M2, Ce2) and 54% Bi (M2', Bi5).

The stoichiometry of these compounds is intermediate between two isostructural parent phases of the formula $\text{ALn}_2\text{Bi}_3\text{S}_8$ and ABi_5S_8 , none of which has been reported in pure compositional form. In $\text{ALn}_2\text{Bi}_3\text{S}_8$ the high coordinate sites are fully occupied by the lanthanide while in ABi_5S_8 the same sites are occupied by bismuth atoms. As it was mentioned before the similar sizes of Bi^{3+} with La^{3+} and Ce^{3+} and the similar coordination preferences of Bi and Ln result in occupational disorder in the high coordinate sites and produce substantial, entropically favored, deviations from the ideal stoichiometry. In fact, we expect the entire composition range between $\text{ALn}_2\text{Bi}_3\text{S}_8$ and ABi_5S_8 to be accessible under proper experimental conditions.

Remarkably, the compound $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ ²¹ was reported to have very similar structural characteristics with those of the $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ compounds presented here. $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ crystallizes in the same orthorhombic space group *Pnma* with a very similar unit cell of $a = 16.55(1) \text{ \AA}$, $b = 4.053(2) \text{ \AA}$, $c = 21.52(1) \text{ \AA}$. The compound was synthesized from a mixture of nominal composition CeBiS_3 which was maintained for 15 days under a bath of KCl and KI melted at around 750 °C as described by the authors²¹

The published structure

structures presented

is occupied by Ce with

the M2 is occupied

$(\text{Ce}_{0.25}\text{□}_{0.75})\text{Ce}(\text{B}_{1.5})$

described as $(\text{K}+\text{Bi})$

Bi:Ce ratio, were re-

needs the Ce atoms

charge balancing with

halogenide compo-

ners, it is also unpre-

with S-S bonds in the

likely a $\text{KCe}_{0.25}\text{Bi}_{0.75}$

Charge tran

conductivity for pre-

semiconductors with

S cm at 75 K

The published fractional atomic positions in the ternary $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ and the quaternary structures presented in this work are the same. The difference is that the alkali metal site is occupied by Ce which is 1/4 occupied, the M1 site is occupied by 0.78 Bi atoms and the M2 is occupied fully by Ce. Thus, $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ can be described as $(\text{Ce}_{0.25}\square_{0.75})(\text{Ce})(\text{Bi}_{0.78}\square_{0.22})\text{Bi}_3\text{S}_8$ while for comparison $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ can be described as $(\text{K})(\text{Bi}_{0.17}\text{La}_{0.83})(\text{Bi}_{0.55}\text{La}_{0.45})\text{Bi}_3\text{S}_8$. No other analytical data, except for the Bi/Ce ratio, were reported. Furthermore, in order to charge balance $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ one needs the Ce atoms to have a mixed valency of 3+ and 4+, however, the problem of charge balancing was not addressed by the authors. The occurrence of Ce^{4+} in a chalcogenide compound is not only unlikely, given that Ce^{4+} is too oxidizing for sulfide ions, it is also unprecedented. Simple compounds such as CeS_2 are in fact Ce^{3+} systems with S-S bonds in the structure. From the above we conclude that $\text{Ce}_{1.25}\text{Bi}_{3.78}\text{S}_8$ is most likely a $\text{KCe}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ phase, with the K atoms originating from the KCl/KI flux.

Charge transport properties and energy gaps. Figure 5-4 shows the electrical conductivity for pressed pellets of the (I) and (II) compounds. Both compounds are semiconductors with a room temperature conductivity $\sigma \sim 10^{-4}$ S/cm which drops to 10^{-9} S/cm at 75 K.

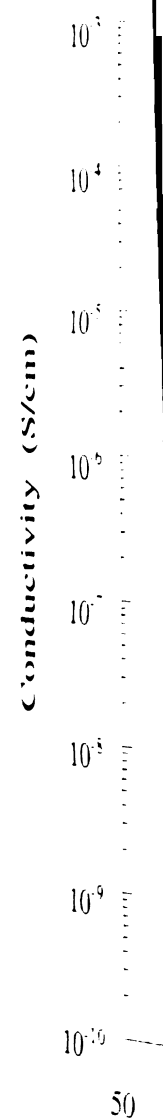


Figure 5-4. Variation of Conductivity with Temperature for $\text{K}_{2-x}\text{Bi}_x\text{S}_3$ and $\text{R}_{2-x}\text{Bi}_x\text{S}_3$ (R = Na, K, Ag, Tl).

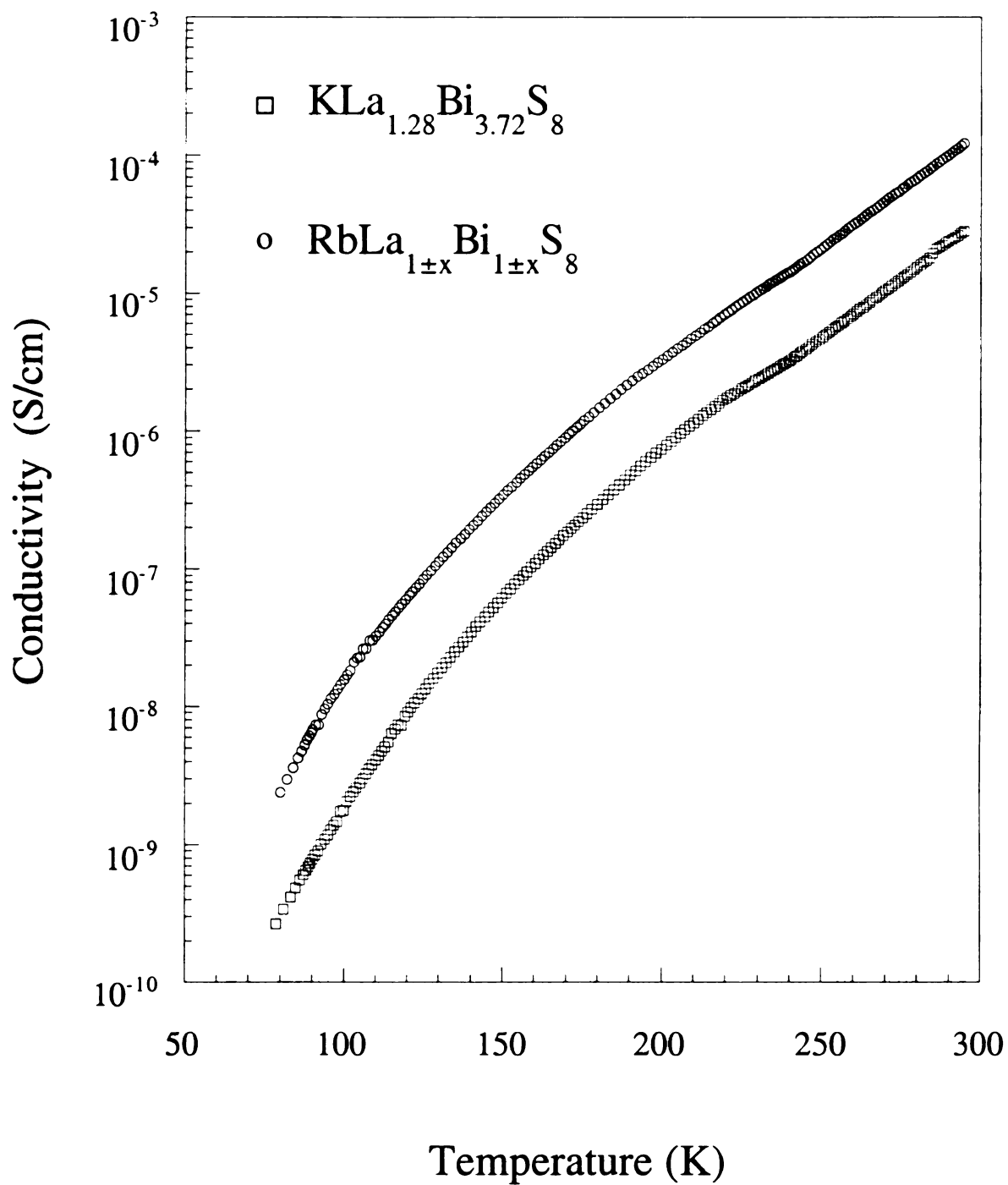


Figure 5-4. Variable temperature electrical conductivity for pressed pellets of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ and $\text{RbLa}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$.

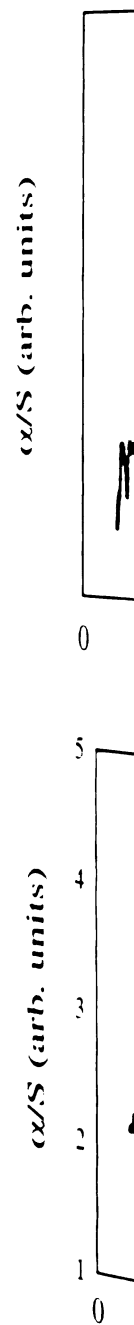


Figure 3-5. Solid-state

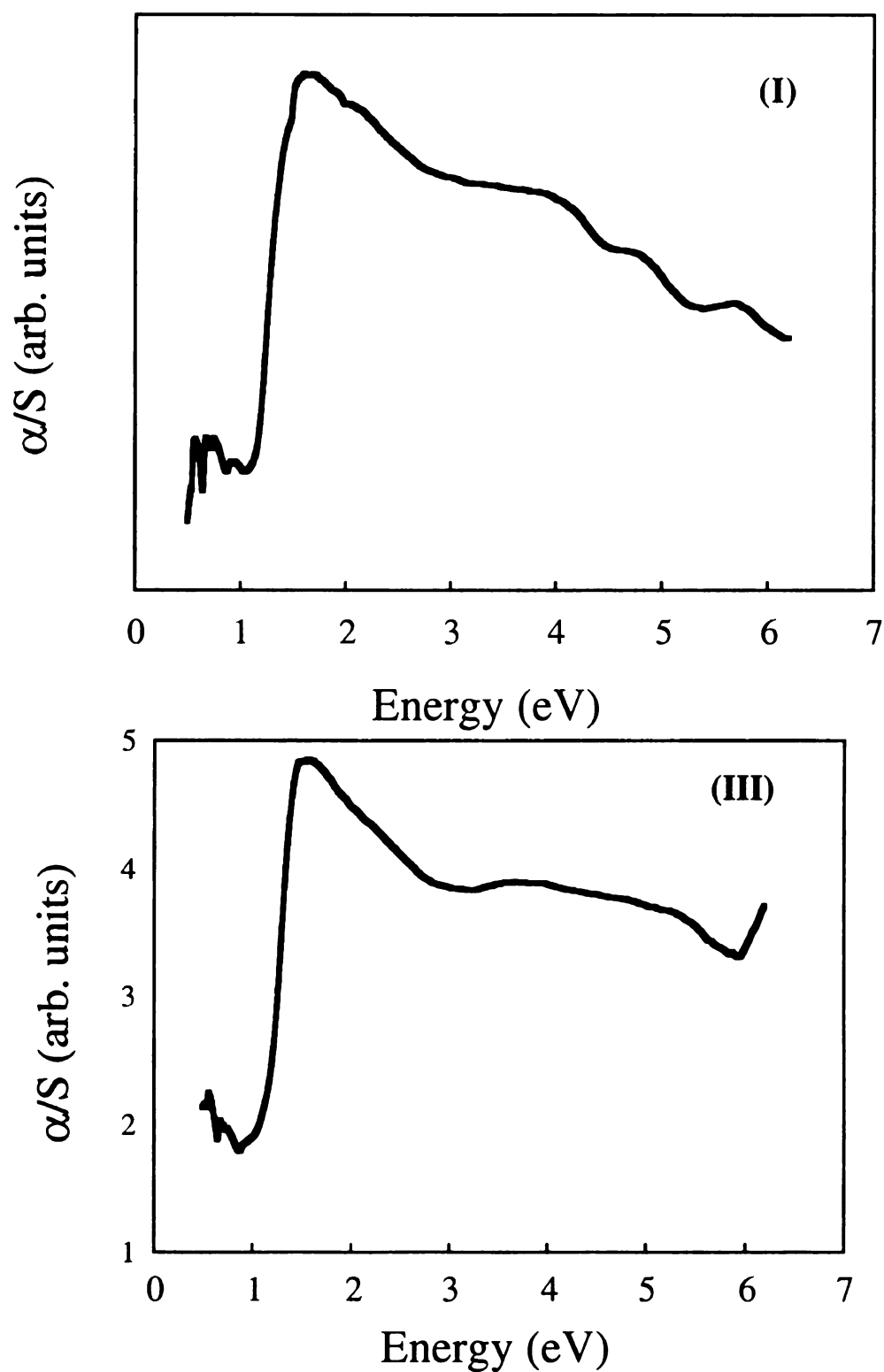


Figure 5-5. Solid-state UV/Vis spectra of $\text{KLa}_{1.28}\text{Bi}_{3.72}\text{S}_8$ (I) and $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$ (III).

These values suggest

with the optical data

5)

Magnetic pr

response of (III) is

paramagnet at high tem

optical field splitting

were estimated by using

1.9 Ce^{3+} per formula

(IV) behaves in a simil

60-61 K. The magne

at 4 K and is expe

were not studied.

These values suggest the presence of a relatively wide band-gap and are in agreement with the optical data which show band gaps between 1.0-1.2 eV (Table 5-9 and Figure 5-5).

Magnetic properties. The temperature-dependent magnetic susceptibility response of (III) is shown in Figure 5-6. The compound behaves as a Curie-Weiss paramagnet at high temperature with deviations at low temperatures (< 50 K), caused by crystal field splitting. Above the onset of deviation, an μ_{eff} of $2.31 \mu_B$ and a Θ of -43 K were estimated by fitting a straight line to the data. If we take into account that there are 0.84 Ce^{3+} per formula the μ_{eff} is very close to that calculated $2.13 \mu_B$ for the free ion³². (IV) behaves in a similar way (Curie-Weiss paramagnet) with an μ_{eff} of $2.34 \mu_B$ and a Θ of -61 K. The magnetic response of the (I) and (II) was not investigated, since La^{3+} is an f^0 cation and is expected to be diamagnetic. The magnetic properties of (V) and (VI) were not studied.



Figure 5-6. (Top) Inver

$\text{Rb}_{0.92}\text{CaB}_{14.5}\text{S}_3$ (Bottom)

$\text{Rb}_{0.92}\text{CaB}_{14.5}\text{S}_3$

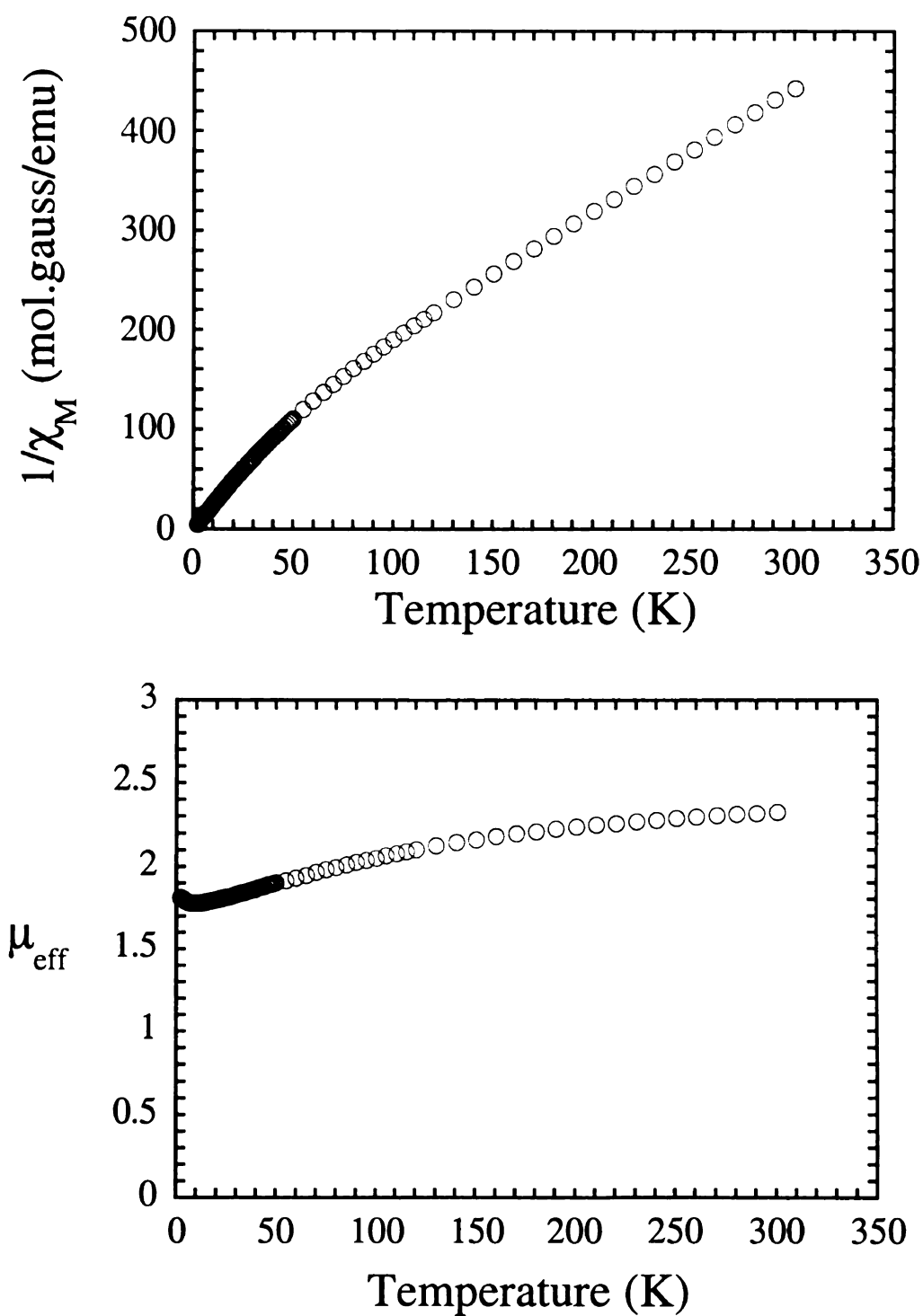


Figure 5-6. (Top) Inverse magnetic susceptibility $1/\chi_m$ plotted against temperature for $\text{RbCe}_{0.84}\text{Bi}_{4.16}\text{S}_8$. (Bottom) Effective magnetic moment vs temperature for $\text{Rb}_{0.84}\text{CeBi}_{4.16}\text{S}_8$.

5. Concluding Remarks

The family of

structure type consists

channels in which the

there is a mixed occu

from the similar size

around 1.0 eV and

electrical conductivity

in order to increase the

sampled by working

5. Concluding Remarks

The family of phases of the type $ALn_{1\pm x}Bi_{4\pm x}S_8$ with La, Ce, Pr and Nd adopts a structure type consisting of Gd_2S_3 -type and NaCl-type fragments which connect to form channels in which the alkali metals reside. In the 7 and 8- coordinate sites in the structure there is a mixed occupancy between the lanthanide and the bismuth atoms which derives from the similar size of these atoms. All compounds are semiconductors with band gaps around 1.0 eV and the La-compounds show a room conductivity of 10^{-4} S/cm. The electrical conductivities are too small for room temperature thermoelectric applications. In order to increase the conductivity, the band gaps should be decreased and this could be attempted by working with the corresponding Se systems.

References

1. (a) Makovicky, E. L. *Fortschr. Miner.* 1978, 34, 1-10.
(b) Makovicky, E. L. *Am. Mineral.* 1979, 64, 1-10.
(c) Makovicky, E. L. *Am. Mineral.* 1980, 65, 1-10.
2. (a) Kanatzidis, N. G. *Chem. Rev.* 1980, 80, 1-10.
(b) Kanatzidis, N. G. *Chem. Rev.* 1981, 81, 1-10.
(c) Kanatzidis, N. G. *Chem. Rev.* 1982, 82, 1-10.
3. *CRC Handbook of Chemistry and Physics*, 1995 and references therein.
4. (a) Glemser, O.; Zemann, J. Z. *Naturwissenschaften* 1978, 65, 1-10.
(b) Glemser, O.; Zemann, J. Z. *Naturwissenschaften* 1979, 66, 1-10.
(c) Glemser, O.; Zemann, J. Z. *Naturwissenschaften* 1980, 67, 1-10.
5. Kanisheva, A. S. *Sov. Chem. Rev.* 1980, 49, 1-10.
6. Schmitz, D.; Bron, H. *Chem. Ber.* 1980, 113, 1-10.
7. Cordier, G.; Schaefer, B. *Chem. Ber.* 1980, 113, 1-10.
8. Aurivillius, B. *Chem. Ber.* 1980, 113, 1-10.
9. Cordier, G.; Schaefer, B. *Chem. Ber.* 1980, 113, 1-10.
10. Volk, K.; Cordier, G. *Chem. Ber.* 1980, 113, 1-10.

References

1. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, 59, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, 63, 45-89. (c) Makovicky, E. *Z. Kristallogr.* **1985**, 173, 1-23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, 160, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, 5, 545-591.
2. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Hogan, T.; Kannewurf, C. R.; Iordanidis, L. *Mater. Res. Soc. Symp. Proc.* **1996**, 410, 37-43. (b) Chung, D.-Y.; Hogan, T.; Schindler, J.; Iordanidis, L.; Brazis, P.; Kannewurf, C. R.; Chen, B.; Uher, C.; Kanatzidis, M. G. *Mater. Res. Soc. Symp. Proc.* **1997**, 478, 333-344.
3. *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995 and references there in.
4. (a) Glemser, O.; Filcek, M. *Z. Anorg. Allg. Chem.* **1955**, 279, 321-323. (b) Gattow, G.; Zemann, J. *Z. Anorg. Allg. Chem.* **1955**, 279, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, 6, 961-964. (d) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, 8, 677-678. (e) Peresh, E. Y.; Golovei, M. I.; Berul, S. I. *Inorg. Mater.* **1971**, 7, 27-30.
5. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, 252, 96-99.
6. Schmitz, D.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, 29, 438-439.
7. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 676-683.
8. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, A37, 399-407.
9. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 631-638.
10. Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, 35B, 136-140.

11. McCarthy, T. J.,
C. R. Kanatzidis
12. McCarthy, T. J.,
1294-1301.
13. (a) Kanatzidis, M.
Hogan, T., Kanno,
(b) Chen, B., Uchida,
1655-1658.
14. Chung, D.-Y., C.
Kannewurf, C. R.,
9, 3060-3071.
15. Chung, D.-Y., J.
Kanatzidis, M. G.
16. Choe, W., Lee, S.
17. Kanatzidis, M. G.
18. Lemoine, P., Carre,
19. Lemoine, P., Carre,
20. Escepont, C., Guerin,
21. Ceolin, R., Toffoli,
B33, 2804-2806.
22. Alev, O. M., Makris,
P. G. *Inorg. Mater.*
23. Choi, K.-S., Jordan,
36, 3804-3805. See
24. CERICS², Version 3

-
11. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
 12. McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301.
 13. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474.
(b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.
 14. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
 15. Chung, D.-Y.; Jovic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
 16. Choe, W.; Lee, S.; O'Connell, P.; Covey A. *Chem. Mater.* **1997**, *9*, 2025-2030.
 17. Kanatzidis, M. G.; DiSalvo, F. J. *Nav. Res. Rev.* **1996**, *4*, 14-22.
 18. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, *C42*, 259-261.
 19. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 727-729.
 20. Ecrepont, C.; Guittard, M.; Flahaut, J. *Mater. Res. Bull.* **1988**, *23*, 37-42.
 21. Ceolin, R.; Toffoli, P.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2804-2806.
 22. Aliev, O. M.; Maksudova, T. F.; Samsonova, N. D.; Finkel'shtein, L. D.; Rustamov, P. G. *Inorg. Mater.* **1986**, *22*, 23-27.
 23. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805. See also Chapter 8.
 24. CERIU², Version 1.6, Molecular Simulations Inc, Cambridge, England, 1994.

25. (a) SMART, 19

53719 USA (b)

Madison, Wis.

Germany, to be

Inc. Madison, W

26. See Chapter 6.

27. Prewitt, C. T., S

28. Rodier, N. *Bull.* 2

29. Carre, D.; Larue

30. Iizuka, Y.; Nowa

31. Kramer, V.; Reiss

32. Greenwood, N. N

York, 1984; p 144

-
25. (a) SMART, 1996, Siemens Analytical Xray Systems Inc. Madison, Winsconsin 53719 USA. (b) SAINT V-4, 1994-1996, Siemens Analytical Xray Systems Inc. Madison, Winsconsin 53719 USA. (c) Sheldrick, G. M. University of Göttingen, Germany, to be published. (d) SHELXTL V-5, Siemens Analytical Xray Systems Inc. Madison, Winsconsin 53719 USA.
- 26 . See Chapter 6.
27. Prewitt, C. T.; Sleight, A. W. *Inorg. Chem.* **1968**, 7, 1090-1093.
28. Rodier, N. *Bull. Soc. Fr. Mineral. Cristallogr.* **1973**, 96, 350-355.
29. Carre, D.; Laruelle, P. *Acta Crystallogr., Sect. B* **1973**, 29, 70-73.
30. Iitaka, Y.; Nowacki, W. *Acta Crystallogr.* **1962**, 15, 691-698.
31. Krämer, V.; Reis, I. *Acta Crystallogr., Sect. C* **1986**, C42, 249-251.
32. Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 1443.

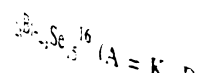
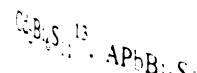
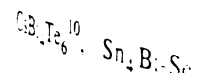
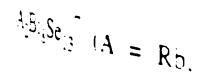
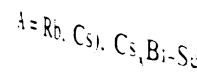
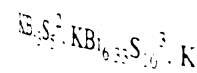
Novel Quaternary

$\text{Pb}_2\text{La}_2\text{B}_2$

1. Introduction

Synthetic investigations

have contributed



CHAPTER 6

Novel Quaternary Lanthanum Bismuth Sulfides



with Complex Structures

1. Introduction

Synthetic investigations in multinary bismuth chalcogenides systems in the last decade have contributed a great number of new compounds such as β -, γ - CsBiS_2 ¹, KBi_3S_5 ², $\text{KBi}_{6.33}\text{S}_{10}$ ³, $\text{K}_2\text{Bi}_8\text{S}_{13}$ ³, α -, β - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ ^{1,4}, $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ ⁴, $\text{A}_x\text{Bi}_4\text{Se}_7$ ⁵ ($x = 1, 2$; $\text{A} = \text{Rb}, \text{Cs}$), $\text{Cs}_x\text{Bi}_7\text{Se}_{12}$ ⁵ ($x = 1, 2$ or 3), ABi_3Q_5 ⁶ ($\text{A} = \text{Rb}, \text{Cs}$; $\text{Q} = \text{S}, \text{Se}, \text{Te}$), $\text{A}_2\text{Bi}_8\text{Se}_{13}$ ⁷ ($\text{A} = \text{Rb}, \text{Cs}$), $\text{CsBi}_{3.67}\text{Se}_6$ ⁷, BaBi_2Se_4 ⁷, $\text{Ba}_3\text{Bi}_{6.67}\text{Se}_{13}$ ⁸, BaBiTe_3 ⁹, CsBi_4Te_6 ¹⁰, $\text{Sn}_4\text{Bi}_2\text{Se}_7$ ¹¹, SnBi_4Se_7 ¹², CdBi_2S_4 ¹³, CdBi_4S_7 ¹³, $\text{Cd}_{2.8}\text{Bi}_{8.1}\text{S}_{15}$ ¹³, $\text{Cd}_2\text{Bi}_6\text{S}_{11}$ ¹³, $\text{APbBi}_3\text{Se}_6$ ¹⁴ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), $\text{K}_{1-x}\text{Sn}_{5-x}\text{Bi}_{11+x}\text{Se}_{22}$ ¹⁵, $\text{A}_{1+x}\text{M}'_4$ _{2x} $\text{Bi}_{7+x}\text{Se}_{15}$ ¹⁶ ($\text{A} = \text{K}, \text{Rb}$; $\text{M}' = \text{Sn}, \text{Pb}$) and $\text{Ba}_3\text{MBi}_6\text{Se}_{13}$ ⁸ ($\text{M} = \text{Sn}, \text{Pb}$). The great

majority of these phases

feature novel structural

salts. Small chalcogen

phases in contrast to the

phases. The rich com

adaptable and versatile

In addition, bism

salts exhibit an a

numbers from six (octa

coordination number gr

Cd_2 - and Sb_2Se_3 -type

combined together by

occupation with similar

each metal atoms. Due

the occupation of Bi^{3+} a

Furthermore, lan

Only a limited number of

$\text{E}_2\text{B}_2\text{Q}_6$ ($\text{Q} = \text{S}, \text{Se}$)²²

majority of these phases, often not found in the corresponding published phase diagrams, feature novel structure types reminiscent of, but distinct from, those of the mineral sulfosalts. Small changes in the synthetic conditions and elemental ratio can result in new phases in contrast to many other multinary systems which tend to give mixtures of known phases. The rich compositional and structural variety makes them some of the most adaptable and versatile systems in solid state chemistry.

In addition, bismuth atoms both in the compounds mentioned above and the natural sulfosalts exhibit an astonishing bonding flexibility occupying sites with coordination numbers from six (octahedral, most of the times distorted) up to nine¹⁻¹⁷. These sites with coordination number greater than six connect with each other the several NaCl-, Bi₂Te₃-, CdI₂- and Sb₂Se₃-type blocks, formed by the BiQ₆ (Q = chalcogen) octahedra when combined together by sharing edges. Often bismuth atoms participate in mixed site occupation with similarly sized atoms e.g. Pb, Sn, lanthanide, alkali metal or alkaline earth metal atoms. Due to the size similarity of Bi³⁺ to several Ln³⁺ ions, possible mixed site occupation of Bi³⁺ and Ln³⁺ could enable the formation of novel structural types.

Furthermore, lanthanide-bismuth chalcogenide systems are relatively unexplored. Only a limited number is known e.g. EuBi₂S₄¹⁸, Eu₂BiS₄¹⁹, La₄Bi₂S₉²⁰, Ce_{1.25}Bi_{3.78}S₈²¹, Eu₃Bi₄Q₉ (Q = S, Se)²² and they are little studied. Even less is known about quaternary

granule bismuth chloride

chemistry of the A-L

metal Q = S, Se, W

Ce, Pr, Nd) and Bi

physicochemical, spec

$(\text{Sr}_2\text{La}_2\text{Bi}_{3.4}\text{S}_{12})$

previously reported co

2 Experimental section

Reagents. Chem

99.999% Cr, -100 mesh

Canadian lead granule

99.95% Cerac, Milwaukee

Corp., Gardena, CA), >

99% lanthanum sulfide

prepared by a stoichiomet

described earlier.¹

lanthanide bismuth chalcogenides. For these reasons we decided to explore the solid state chemistry of the A-Ln-Bi-Q systems (A = alkali or alkaline earth metal, M = lanthanide metal, Q = S, Se). We have already reported on $ALn_{1\pm x}Bi_{4\pm x}S_8$ ²³ (A = K, Rb; Ln = La, Ce, Pr, Nd) and $BaLaBi_2Q_6$ ²⁴ (Q = S, Se). We describe here the synthesis, physicochemical, spectroscopic characterization and novel structures types of $Pb_2La_xBi_{8-x}S_{14}$, $Sr_2La_xBi_{8-x}S_{14}$, and $Cs_2La_xBi_{10-x}S_{16}$ and examine their relationships with other previously reported compounds.

2. Experimental section

Reagents. Chemicals in this work were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999% Noranda, Canada), lead granules (99.999%, -20 mesh, Cerac, Milwaukee, WI), cesium metal (99.98%, Cerac, Milwaukee, WI), sulfur powder (sublimed, Spectrum Chemical Mfg. Corp., Gardena, CA), strontium sulfide (99.9% purity, -200 mesh, Cerac, Milwaukee, WI), lanthanum sulfide (99.9% purity, -200 mesh, Cerac, Milwaukee, WI). Cs_2S was prepared by a stoichiometric reaction of the cesium metal and sulfur in liquid ammonia as described earlier.¹

Synthesis

a Vacuum Atmos

water, methanol, a

was almost quant

comparing the χ

crystallographically

Bi_2S_3 . A m

transferred into a sil

to 650 °C in 48 h. A

product was ground

$\text{Pb}_2\text{La}_1\text{Bi}_{8-x}\text{S}_{14}$

Bi_2O_3 0.66 g (2.058 mmol)

coated silica tube wh

650 °C and was cool

consisted of long silve

composition of $\text{Pb}_{2-x}\text{La}_x$

$\text{Sr}_2\text{La}_1\text{Bi}_{8-x}\text{S}_{14}$

mmol La_2S_3 and 0.580

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All products were washed with degassed water, methanol and ether to remove traces of excess flux. For all compounds the yield was almost quantitative and the purity and homogeneity of the samples was verified by comparing the X-ray powder diffraction patterns to those calculated by the crystallographically determined fractional atomic coordinates.

Bi₂S₃. A mixture of 11.633 g (0.056 mol) Bi and 2.677 g (0.083 mol) S was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 650 °C in 48 h, kept at 650 °C for 2 days and then cooled down to 50 °C in 10 h. The product was ground into powder and used for further reactions.

Pb₂La_xBi_{8-x}S₁₄ (I). A mixture of 0.078 g (0.376 mmol) Pb, 0.234 g (1.120 mmol) Bi, 0.066 g (2.058 mmol) S and 0.140 g (0.374 mmol) La₂S₃ was transferred to a carbon coated silica tube which was flame-sealed under vacuum. The tube was heated for 99 h at 950 °C and was cooled to 550 °C at 10 °C/h and then to 50 °C in 10 h. The product consisted of long silver-gray needles. SEM/EDS on a number of needles gave an average composition of Pb_{2.3}La_{2.0}Bi_{6.3}S₁₄.

Sr₂La_xBi_{8-x}S₁₄ (II). A mixture of 0.090 g (0.752 mmol) SrS, 0.281 g (0.751 mmol) La₂S₃ and 0.580 g (1.128 mmol) Bi₂S₃ was transferred to a carbon coated silica

tube which was fitted

was cooled to 650

silver-gray needles.

$\text{Sr}_{1.9}\text{La}_{2.2}\text{Bi}_{6.1}\text{S}_{15.6}$

$\text{Cs}_2\text{La}_4\text{Bi}_{10}$

mmol) La_2S_3 and (

tube which was fitted

and was cooled to 4

silver-gray needles.

$\text{Cs}_2\text{La}_{1.1}\text{Bi}_{1.5}\text{S}_{1.6}$

3. Physical Measure

The instrumen

Thermal Analysis and

Section 3). The instru

is the same as that in C

Single-Crystal

Platform CCD diffract

tube which was flame-sealed under vacuum. The tube was heated for 1 day at 950 °C and was cooled to 650 °C in one day and then to 50 °C in 11 h. The product consisted of long silver-gray needles. SEM/EDS on a number of needles gave an average composition of $\text{Sr}_{1.9}\text{La}_{2.2}\text{Bi}_{6.1}\text{S}_{15.6}$.

$\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ (III). A mixture of 0.040 g (0.134 mmol) Cs_2S , 0.050 g (0.134 mmol) La_2S_3 and 0.276 g (0.536 mmol) Bi_2S_3 was transferred to a carbon coated silica tube which was flame-sealed under vacuum. The tube was heated for 6 days at 900 °C and was cooled to 400 °C in 75 h and then to 50 °C in 10 h. The product consisted of long silver-gray needles. SEM/EDS on a number of needles gave an average composition of $\text{Cs}_{2.3}\text{La}_{1.1}\text{Bi}_{7.8}\text{S}_{16}$.

3. Physical Measurements

The instrument and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis* and *Powder X-ray Diffraction* are the same as that in Chapter 2 (Section 3). The instrument and experimental setup for *Solid-State UV/Vis Spectroscopy* is the same as that in Chapter 4 (Section 3).

Single-Crystal X-ray Crystallography. A Bruker (formerly Siemens) SMART Platform CCD diffractometer was used for data collection. Several different sets of

frames covering a full

at a detector-to-sam

The SMART software

The absorption corre

methods and refinement

programs. A analytical

Pb₂La₁Bi₈S₁₄

exposure time of 35 s

from 5289 ($I > 10\sigma(I)$)

M and fourteen sulfur

structure has the gener

initially all ten metal

30.67% Pb and Bi due

properties cannot be c

previous results²³ and r

edge; similar coordinat

ship the occupancy of th

For four sites with octah

frames covering a random area of the reciprocal space were collected using 0.3° steps in ω at a detector-to-sample distance between 4-5 cm depending on the desired resolution. The SMART software was used for data acquisition and SAINT²⁵ for data extraction. The absorption correction was done with SADABS²⁵ and the structure solution (direct methods) and refinement was done with the SHELXTL²⁵ package of crystallographic programs. A analytical absorption correction was applied before SABABS for (II).

Pb₂La_xBi_{8-x}S₁₄ (I): A hemisphere of data were collected (1271 frames) with an exposure time of 35 sec per frame to a resolution of 0.75 Å. The final cell was calculated from 5289 [$I > 10\sigma(I)$] reflections chosen from the data set (Table 6-1). Ten metal atoms *MI* and fourteen sulfurs atoms were located on a crystallographic mirror plane and the structure has the general formula $MI_{10}S_{14}$ where *MI* is any combination of Bi, Pb or La. Initially all ten metal positions were assigned and refined as Bi ($R1 = 9.7\%$, $wR2 = 20.6\%$). Pb and Bi due to their close chemical resemblance and similar X-ray scattering properties cannot be crystallographically distinguished. Furthermore we know from previous results²³ and from Cs₂La_xBi_{10-x}S₁₆ (see below) that Bi and La atoms tend to adopt similar coordination environments and present mixed occupancy. In a subsequent step the occupancy of the ten "bismuth" atoms was refined ($R1 = 8.8\%$, $wR2 = 17.5\%$). For four sites with octahedral coordination the occupancy did not change while for the

remaining six sites

dropped to less than

in the refinement

balancing purpose

$\text{Pb}_2\text{La}_2\text{Bi}_{10}\text{S}_{14}$ T

presence of all four

anisotropically (R

equivalent isotropic

$\text{Sr}_2\text{La}_4\text{Bi}_{10}\text{S}_{14}$

in exposure time of

calculated from 100

assigned as Bi and

Similar to what was

the four octahedral

141 Table 6-3). The

numbers greater than

than 0.5 (theoretical

exhibit any splitting a

remaining six sites, with coordination numbers higher than six (7 or 8), the occupancy dropped to less than 0.5 (full theoretical occupancy). In these six sites, La was introduced in the refinement. The formula at that point was $\text{La}_{2.1}\text{Bi}_{7.9}\text{S}_{14}$, however for charge balancing purposes the compound should have the general formula $\text{Pb}_2(\text{La,Bi})_8\text{S}_{14}$ or $\text{Pb}_2\text{La}_{2.1}\text{Bi}_{5.9}\text{S}_{14}$. This is agreement with the EDS/SEM data, which confirmed the presence of all four elements with $\text{Pb}_{2.3}\text{La}_{2.0}\text{Bi}_{6.3}\text{S}_{14}$ ratio. All atoms were refined anisotropically ($R1 = 4.7\%$, $wR2 = 7.9\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 6-2.

$\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ (II): Over a hemisphere of data were collected (1685 frames) with an exposure time of 45 sec per frame to a resolution of 0.66 Å. The final cell was calculated from 10670 [$I > 8\sigma(I)$] reflections (Table 6-1). Initially all ten metal sites were assigned as Bi and their occupancies was let to refine ($R1 = 9.8\%$, $wR2 = 30.4\%$). Similar to what was found in the Pb compound above the occupancies did not change in the four octahedral metal sites indicating that they are occupied exclusively by Bi (sites 1-4) (Table 6-3). The occupancy of the remaining six sites (sites 5-10), with coordination numbers greater than six (monocapped or bicapped trigonal prismatic), refined to be less than 0.5 (theoretical full occupancy). One of the high coordinate sites, site 7 did not exhibit any splitting and was disordered between Sr and La only. A significant difference

compared to (1) is the

exhibit a splitting. In

the site (A) and the

octahedral or square

while the first (A) was

It also consists of two

assumption. Initially,

suggesting that site 5

B³⁺(B⁵⁺) and posit

$\text{Sr}_{0.5}\text{La}_{2.5}\text{Bi}_{0.5}\text{S}_{4.5}$

crystals of $\text{Sr}_2\text{La}_3\text{Bi}_{0.5}$

was identical. Individu

(1500) and a general co

electroneutrality (R1

B³⁺(B⁵⁺) and the four

The final formula was S

in the other data sets

displacement parameters

compared to (I) is that in (II) the remaining five of these six sites (sites 5, 6, 8, 9 and 10) exhibit a splitting. In sites 6, 8, 9 and 10, one of the split atoms is sitting in the center of the site (A) and the other is shifted ($\sim 0.4\text{-}0.5\text{ \AA}$) to the side (B) having a distorted octahedral or square pyramidal environment. That second position (B) was assigned as Bi while the first (A) was disordered between La and Sr. The fifth high coordinate site (site 5) also consists of two positions, (A) and (B) but the splitting is different (see structure description). Initially both positions were refined as Bi and the total occupancy was 98% suggesting that site 5 was mainly occupied by Bi. In the end, position (B) was assigned as Bi [Bi(5')] and position (A) as Bi and Sr [Bi(5)/Sr(5)]. The formula at that time was $\text{Sr}_{1.92}\text{La}_{2.51}\text{Bi}_{5.49}\text{S}_{14}$. In order to verify this result data were collected on three more crystals of $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ from different synthetic batches but the behavior of the site 5 was identical. Individual constraints were used in each site to sum the total occupancy to 0.5000 and a general constrain was used to set the Sr amount to what was necessary for electroneutrality ($R1 = 4.43\%$, $wR2 = 8.90\%$). The four Bi atoms, La(7)/Sr(7), Bi(5)/Sr(5) and the fourteen S were refined anisotropically ($R1 = 3.34\%$, $wR2 = 6.33\%$). The final formula was $\text{Sr}_{2.00(5)}\text{La}_{2.58(5)}\text{Bi}_{5.42(3)}\text{S}_{14}$. The value of x varied between 2.4-2.7 in the other data sets. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 6-3.

$\text{Cs}_2\text{La}_x\text{Bi}_{10-x}$

exposure time of 62 s

553 ($>10\sigma(I)$) ref

"bismuth" atoms were

1416. Three of the

relatively high isotropy

other octahedral bismuth

used for these three

anisotropically ($R1 = 5$

The fractional atomic

shown in Table 6-4.

Cs₂La_xBi_{10-x}S₁₆ (III): A full sphere of data were collected (2082 frames) with an exposure time of 62 sec per frame to 0.74 Å resolution. The final cell was calculated from 3553 [I>10σ(I)] reflections (Table 6-1). Initially two cesium, sixteen sulfur and ten "bismuth" atoms were found. After refinement the R values were R1 = 8.2% and wR2 = 14.1%. Three of the "bismuth" atoms with bicapped trigonal prismatic coordination had a relatively high isotropic displacement parameter, U_{iso} ~ 0.050 Å² compared to that of the other octahedral bismuth atoms U_{iso} ~ 0.015 Å². A disorder model with La and Bi was used for these three sites (R1 = 7.7%, wR2 = 12.5%). All the atoms were refined anisotropically (R1 = 5.0%, wR2 = 6.6%). The final formula was Cs₂La_{1.19(4)}Bi_{8.81(4)}S₁₆. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 6-4.

Table 6-1. Crystallon

Su

Empirical formula

Formula weight

Temperature, K

Crystal system

Space group

Unit cell dimensions,

Z Volume, Å³Density (calc.), g cm⁻³Absorption coeff., mm⁻¹

F(000)

Crystal size, mm³

#range

Index ranges

Reflections collected

Independent reflections

Refinement method

Data / restraints / par.

Goodness-of-fit on F²

Final R indices [I > 2σ]

R indices (all data)

Extinction

Largest peak and hole

Table 6-1. Crystallographic Data for $M_2La_xBi_{8-x}S_{14}$ ($M = Pb, Sr$), and $Cs_2La_xBi_{10-x}S_{16}$

Empirical formula	$Pb_2La_{2.10(6)}Bi_{5.90(6)}S_{14}$ (I)	$Sr_{2.00(5)}La_{2.58(5)}Bi_{5.42(3)}S_{14}$ (II)
Formula weight	2388.26	2113.23
Temperature, K	296(2)	298(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions, Å	$a = 21.2592(4)$ $b = 4.0418(1)$ $c = 28.1718(3)$	$a = 21.190(1)$ $b = 4.0417(2)$ $c = 28.285(2)$
Z, Volume, Å ³	4, 2420.67(8)	4, 2422.4(2)
Density (calc.), g/cm ³	6.553	5.794
Absorption coeff., mm ⁻¹	61.417	49.208
F(000)	3990	2432
Crystal size, mm ³	0.26 x 0.03 x 0.03	0.02 x 0.02 x 0.30
θ range	1.45 to 28.29°	1.44 to 32.53°
Index ranges	$-28 \leq h \leq 28$ $-5 \leq k \leq 5$ $-36 \leq l \leq 29$	$-31 \leq h \leq 30$ $-6 \leq k \leq 6$ $-42 \leq l \leq 41$
Reflections collected	16057	27443
Independent reflections	3334 [$R_{(int)} = 0.0748$]	4676 [$R_{(int)} = 0.0535$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3334 / 0 / 152	4676 / 7 / 167
Goodness-of-fit on F^2	1.036	1.092
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0465$, $wR2 = 0.0785$	$R1 = 0.0334$, $wR2 = 0.0633$
R indices (all data)	$R1 = 0.0786$, $wR2 = 0.0864$	$R1 = 0.0456$, $wR2 = 0.0668$
Extinction	0.000205(13)	0.000148(12)
Largest peak and hole, e.Å ⁻³	4.322 and -3.722	3.891 and -3.280

Table 6-1 (cont'd).

Empirical formula
Formula weight
Temperature, K
Crystal system
Space group
Unit cell dimensions

Z Volume, Å³

Density (calc.), g/cm³

Absorption coeff., mm⁻¹

F(000)

Crystal size, mm³

θ range

Index ranges

Reflections collected

Independent reflections

Refinement method

Data / restraints / parameters

Goodness-of-fit on F²

Final R indices [I > 2σ(I)]

R indices (all data)

Extinction

Largest peak and hole

$$R_I = \frac{\sum |F_o| - F_c}{\sum |F_o|}$$

Table 6-1 (cont'd).

Empirical formula	Cs ₂ La _{1.19(4)} Bi _{8.81(4)} S ₁₆ (III)
Formula weight	2785.55
Temperature, K	296(2)
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions, Å	<i>a</i> = 34.893(4) <i>b</i> = 4.0697(4) <i>c</i> = 21.508(2)
Z, Volume, Å ³	4, 3054.2(6)
Density (calc.), g/cm ³	6.058
Absorption coeff., mm ⁻¹	55.648
F(000)	2253
Crystal size, mm ³	0.01 x 0.01 x 0.23
θ range	1.50 to 28.78°
Index ranges	-45 ≤ <i>h</i> ≤ 42 -5 ≤ <i>k</i> ≤ 5 -27 ≤ <i>l</i> ≤ 27
Reflections collected	26767
Independent reflections	4213 [<i>R</i> _(int) = 0.1473]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4213 / 0 / 172
Goodness-of-fit on <i>F</i> ²	0.872
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.0664
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1226, <i>wR</i> 2 = 0.0782
Extinction	-
Largest peak and hole, e.Å ⁻³	2.408 and -2.863

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 6-2. Atomic

 $(\text{\AA}^3 \times 10^3)$ for Pb_2La_3

Cation site

1 Bi(1)*

2 Bi(2)

3 Bi(3)

4 Bi(4)

5 Mi(5)*

La(5)

6 Mi(6)

La(6)

7 Mi(7)

La(7)

8 Mi(8)

La(8)

9 Mi(9)

La(9)

10 Mi(10)

La(10)

S(1)

S(2)

S(3)

Table 6-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$.

Cation site		x	y	z	U(eq)	occ.
1	Bi(1) [#]	-0.4416(1)	-0.7500	0.4443(1)	18(1)	1
2	Bi(2)	-0.6432(1)	-0.7500	0.4414(1)	14(1)	1
3	Bi(3)	-0.3090(1)	-0.7500	0.3059(1)	17(1)	1
4	Bi(4)	0.0637(1)	0.2500	0.3020(1)	15(1)	1
5	M(5) [*]	-0.0556(1)	-0.2500	0.4457(1)	18(1)	0.898(10)
	La(5)	-0.0556(1)	-0.2500	0.4457(1)	18(1)	0.102(10)
6	M(6)	0.1376(1)	-0.2500	0.4294(1)	24(1)	0.578(10)
	La(6)	0.1376(1)	-0.2500	0.4294(1)	24(1)	0.422(10)
7	M(7)	0.2611(1)	-0.2500	0.3226(1)	25(1)	0.469(10)
	La(7)	0.2611(1)	-0.2500	0.3226(1)	25(1)	0.531(10)
8	M(8)	-0.0330(1)	-0.2500	0.1680(1)	33(1)	0.691(11)
	La(8)	-0.0330(1)	-0.2500	0.1680(1)	33(1)	0.309(11)
9	M(9)	-0.2337(1)	-0.7500	0.4349(1)	36(1)	0.772(11)
	La(9)	-0.2337(1)	-0.7500	0.4349(1)	36(1)	0.228(11)
10	M(10)	-0.1243(1)	-0.2500	0.3097(1)	30(1)	0.496(10)
	La(10)	-0.1243(1)	-0.2500	0.3097(1)	30(1)	0.504(10)
	S(1)	-0.3528(2)	-0.2500	0.4523(2)	21(1)	
	S(2)	-0.4423(2)	-0.7500	0.3525(2)	17(1)	
	S(3)	-0.5397(2)	-0.2500	0.4386(2)	19(1)	

Table 6-2. (cont)

Si(4)
Si(5)
Si(6)
Si(7)
Si(8)
Si(9)
Si(10)
Si(11)
Si(12)
Si(13)
Si(14)

* See reference 20

* The positions w
real atoms indic

U_{eq} is defined

Table 6-2. (cont'd).

S(4)	0.2746(2)	-0.2500	0.4376(2)	26(1)
S(5)	-0.6358(2)	-0.7500	0.3475(2)	16(1)
S(6)	-0.0445(2)	0.2500	0.2526(2)	19(1)
S(7)	-0.2059(2)	-0.7500	0.2565(2)	14(1)
S(8)	-0.2454(2)	-0.2500	0.3593(2)	15(1)
S(9)	0.1472(2)	-0.2500	0.2533(2)	20(1)
S(10)	0.1760(2)	0.2500	0.3629(2)	13(1)
S(11)	0.0209(2)	-0.2500	0.3550(2)	17(1)
S(12)	0.0369(2)	-0.7500	0.4562(2)	14(1)
S(13)	-0.1186(2)	-0.7500	0.3877(2)	13(1)
S(14)	0.1741(2)	-0.7500	0.5107(2)	16(1)

See reference 29.

* The positions with M(number) are occupied by Bi, Pb, or both. The number next to the metal atoms indicates the sites they belong e.g. La(5) and M(5) all belong to cation site 5.

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6-3. Atomic

 $(A \times 10^3)$ for Sr_2La

Cation site

1 B(1)

2 B(2)

3 B(3)

4 B(4)

A B(5)

5 A Sr(5)

B B(5)

A La(6)

6 A Sr(6)

B B(6)

7 La(7)

Sr(7)

A La(8)

8 A Sr(8)

B B(8)

A La(9)

9 A Sr(9)

B B(9)

Table 6-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$.

Cation site		x	y	z	U(eq)	occ.
<i>1</i>	Bi(1) [§]	-0.4427(1)	-0.7500	0.4438(1)	18(1)	1
<i>2</i>	Bi(2)	-0.6425(1)	-0.7500	0.4402(1)	14(1)	1
<i>3</i>	Bi(3)	-0.3083(1)	-0.7500	0.3054(1)	16(1)	1
<i>4</i>	Bi(4)	0.0661(1)	0.2500	0.3033(1)	14(1)	1
<i>A</i>	Bi(5)	-0.0579(1)	-0.2500	0.4444(1)	17(1)	0.683(5)
<i>5 A</i>	Sr(5)	-0.0579(1)	-0.2500	0.4444(1)	17(1)	0.234(5)
<i>B</i>	Bi(5')	-0.0663(4)	-0.132(3)	0.4566(3)	18(2)	0.042(2)
<i>A</i>	La(6)	0.1364(1)	-0.2500	0.4320(1)	12(1)	0.674(9)
<i>6 A</i>	Sr(6)	0.1364(1)	-0.2500	0.4320(1)	12(1)	0.293(8)
<i>B</i>	Bi(6)	0.1240(9)	-0.2500	0.4167(9)	27(5)	0.033(4)
<i>7</i>	La(7)	0.2624(1)	-0.2500	0.3220(1)	13(1)	0.556(7)
	Sr(7)	0.2624(1)	-0.2500	0.3220(1)	13(1)	0.444(7)
<i>A</i>	La(8)	-0.0311(1)	-0.2500	0.1717(1)	17(1)	0.538(14)
<i>8 A</i>	Sr(8)	-0.0311(1)	-0.2500	0.1717(1)	17(1)	0.325(10)
<i>B</i>	Bi(8)	-0.0283(2)	-0.2500	0.1581(3)	19(1)	0.137(6)
<i>A</i>	La(9)	-0.2469(1)	-0.7500	0.4405(1)	13(1)	0.407(10)
<i>9 A</i>	Sr(9)	-0.2469(1)	-0.7500	0.4405(1)	13(1)	0.188(8)
<i>B</i>	Bi(9)	-0.2293(1)	-0.7500	0.4291(1)	25(1)	0.404(4)

Table 6-3. (cont)

A La(10)

10 A Sr(10)

B Bi(10)

Si(1)

Si(2)

Si(3)

Si(4)

Si(5)

Si(6)

Si(7)

Si(8)

Si(9)

Si(10)

Si(11)

Si(12)

Si(13)

Si(14)

The number next

B, Si all belong to

position in center of

side. U_{eq} is defn

Table 6-3. (cont'd).

10	<i>A</i>	La(10)	-0.1194(1)	-0.2500	0.3088(1)	12(1)	0.401(10)
	<i>A</i>	Sr(10)	-0.1194(1)	-0.2500	0.3088(1)	12(1)	0.516(9)
	<i>B</i>	Bi(10)	-0.1401(5)	-0.2500	0.3160(3)	27(2)	0.083(4)
		S(1)	-0.3519(1)	-0.2500	0.4548(1)	18(1)	
		S(2)	-0.4387(1)	-0.7500	0.3536(1)	17(1)	
		S(3)	-0.5379(1)	-0.2500	0.4380(1)	18(1)	
		S(4)	0.2763(1)	-0.2500	0.4374(1)	25(1)	
		S(5)	-0.6349(1)	-0.7500	0.3467(1)	14(1)	
		S(6)	-0.0429(1)	0.2500	0.2529(1)	16(1)	
		S(7)	-0.2051(1)	-0.7500	0.2560(1)	14(1)	
		S(8)	-0.2463(1)	-0.2500	0.3600(1)	15(1)	
		S(9)	0.1466(1)	-0.2500	0.2530(1)	18(1)	
		S(10)	0.1771(1)	0.2500	0.3637(1)	11(1)	
		S(11)	0.0222(1)	0.2500	0.3554(1)	15(1)	
		S(12)	0.0387(1)	-0.7500	0.4559(1)	14(1)	
		S(13)	-0.1186(1)	-0.7500	0.3879(1)	14(1)	
		S(14)	0.1760(1)	-0.7500	0.5095(1)	17(1)	

[§]The number next to the metal atoms indicates the sites they belong e.g. La(8), Sr(8) and Bi(8) all belong to cation site 8. For the sites that exhibit splitting (*A*) refers to the position in center of the site and (*B*) to the position shifted away from the center to the side. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6-4. Atomic

 $(A \times 10^3)$ for Cs_2La

	λ
B: 1)	0.2309
B: 2)	0.2433
B: 3)	0.1311
B: 4)	0.3456
B: 5)	0.0513
B: 6)	0.0472
B: 7)	0.0452
B: 8)	0.1384
La: 8)	0.1384
B: 9)	0.2472
La: 9)	0.2472
B: 10)	0.1228
La: 10)	0.1228
Cs: 1)	-0.0115
Cs: 2)	0.3598
S: 1)	0.2726
S: 2)	0.1926
S: 3)	0.1998
S: 4)	0.1729
S: 5)	0.2029

Table 6-4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$.

	x	y	z	U(eq)	occ.
Bi(1)	0.2309(1)	0.2500	0.2582(1)	15(1)	1
Bi(2)	0.2433(1)	-0.7500	-0.0936(1)	18(1)	1
Bi(3)	0.1311(1)	-0.7500	0.3543(1)	18(1)	1
Bi(4)	0.3456(1)	-0.7500	0.0143(1)	20(1)	1
Bi(5)	0.0513(1)	-0.7500	-0.4981(1)	19(1)	1
Bi(6)	0.0472(1)	-0.7500	-0.1366(1)	17(1)	1
Bi(7)	0.0452(1)	-0.7500	0.0607(1)	17(1)	1
Bi(8)	0.1384(1)	-0.2500	-0.0456(1)	39(1)	0.632(12)
La(8)	0.1384(1)	-0.2500	-0.0456(1)	39(1)	0.368(12)
Bi(9)	0.2472(1)	-0.2500	0.0870(1)	41(1)	0.685(13)
La(9)	0.2472(1)	-0.2500	0.0870(1)	41(1)	0.315(13)
Bi(10)	0.1228(1)	-0.2500	0.1788(1)	37(1)	0.498(12)
La(10)	0.1228(1)	-0.2500	0.1788(1)	37(1)	0.502(12)
Cs(1)	-0.0115(1)	-0.7500	-0.3063(1)	21(1)	1
Cs(2)	0.3598(1)	0.2500	0.2288(1)	38(1)	1
S(1)	0.2726(2)	-0.2500	0.2163(3)	14(1)	
S(2)	0.1926(2)	0.2500	0.1568(3)	15(1)	
S(3)	0.1998(2)	-0.2500	-0.1377(3)	16(2)	
S(4)	0.1729(2)	-0.2500	0.2993(3)	22(2)	
S(5)	0.2029(2)	-0.7500	0.0035(3)	18(2)	

Table 6-4. (cont'd).

S(6)	0.2942
S(7)	0.0896
S(8)	0.2984
S(9)	0.1158
S(10)	0.0860
S(11)	-0.0217
S(12)	0.0483
S(13)	0.1225
S(14)	0.0435
S(15)	0.0543
S(16)	0.1177

U_{eff} is defined as one
to the metal atoms in
cation site.

Table 6-4. (cont'd).

S(6)	0.2942(2)	-0.2500	-0.0369(4)	27(2)
S(7)	0.0896(2)	-0.7500	0.2548(3)	16(1)
S(8)	0.2984(2)	-0.7500	0.1065(3)	18(2)
S(9)	0.1158(2)	-0.7500	-0.4242(3)	20(2)
S(10)	0.0860(2)	-0.2500	-0.5839(3)	22(2)
S(11)	-0.0217(2)	-0.7500	-0.5700(3)	16(1)
S(12)	0.0483(2)	-0.2500	-0.2171(3)	17(1)
S(13)	0.1225(2)	-0.7500	-0.1282(3)	16(1)
S(14)	0.0435(2)	-0.2500	0.1470(3)	19(2)
S(15)	0.0543(2)	-0.2500	-0.0341(3)	17(1)
S(16)	0.1177(2)	-0.7500	0.0706(3)	16(2)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The number next to the metal atoms indicates the sites they belong e.g. La(8) and Bi(8) belong to the same cation site.

Synthesis

synthesized by re

to be the most s

reactants resulted

lower amount of

true for $\text{Sr}_2\text{La}_3\text{B}$

1:1:5 ratio also

was found in m

$\text{Ce}_2\text{S}_3\text{La}_2\text{S}_3\text{Bi}_2\text{S}_3$

main product wa

to be a narrow ra

the X-ray powd

congruently betw

III, at $\sim 746^\circ\text{C}$.

Figure 6-1. These

(Ce, Pr, Nd) and E

4. Results and Discussion

Synthesis, thermal behavior and energy gaps. $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ ($x \sim 2.1$) was synthesized by reacting $\text{Pb/Bi/La}_2\text{S}_3/\text{S}$ in an 1:3:1:5.5 ratio at 950 °C. This phase seems to be the most stable in this system and attempts to vary the amount of any of the reactants resulted in a mixture of (I) with the corresponding binary compounds. When a lower amount of La_2S_3 was used, Pb/Bi/S ternary phases were found. The same was also true for $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ ($x \sim 2.6$) that was synthesized by reacting $\text{SrS/La}_2\text{S}_3/\text{Bi}_2\text{S}_3$ in 1:1:1.5 ratio also at 950 °C. Again when a lower amount of La_2S_3 was used, SrBi_2S_4 ²⁶ was found in mixture with (II). $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ ($x \sim 1.2$) was synthesized by reacting $\text{Cs}_2\text{S/La}_2\text{S}_3/\text{Bi}_2\text{S}_3$ in 1:1:4 ratio at 900 °C. When the amount of Bi_2S_3 was increased the main product was CsBi_3S_5 ²⁷ with (III) as a minor phase. For all three compounds there is to be a narrow range of x under which they can be obtained in a pure form. The DTA and the X-ray powder diffraction results after DTA indicate that all compounds melt congruently between 740 °C and 860 °C, namely (I) melts at ~800 °C, (II) at ~850 °C and (III) at ~746 °C. All compounds are semiconductors with well-defined gaps of ~1 eV, see Figure 6-1. These values are very similar to those of $\text{ALn}_{1\pm x}\text{Bi}_{4\pm x}\text{S}_8$ ($A = \text{K, Rb}$; $\text{Ln} = \text{La, Ce, Pr, Nd}$) and $\text{BaLaBi}_2\text{S}_6$.

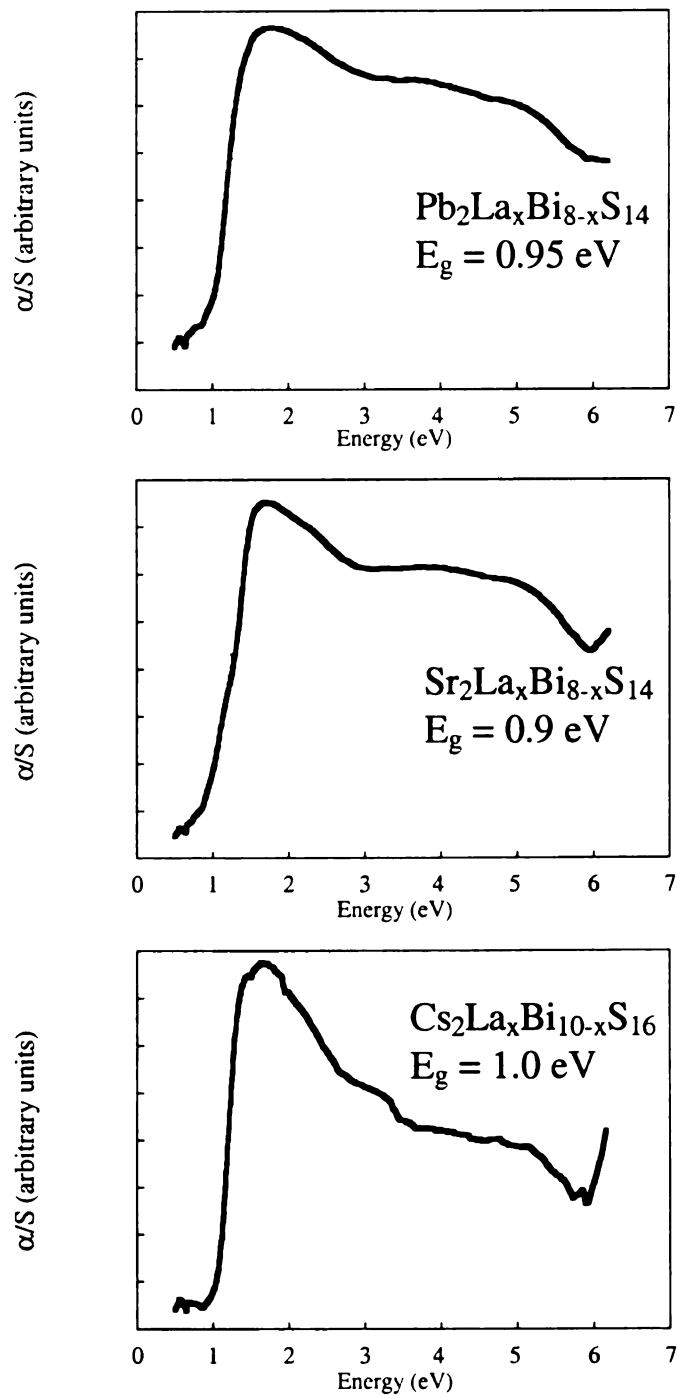


Figure 6-1. Solid-state UV/Vis absorption spectra showing band gap transitions for

$\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$, $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ and $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$.

Structure 1

$Pb_2La_xBi_{8-x}$

three-dimensional

structures, one

consisting of infinite

the infinite walls re

Figures 6-2 and 6-3

thick. The angle de

infinite Gd_2S_7 -typ

sections that are th

have been remove

to an extensive co

common in the lea

$Al_{1-x}Bi_{4-x}S_8^{23}$

The unit c

after display ma

the remainin

Structure Description.

Pb₂La_xBi_{8-x}S₁₄ (x ~ 2.1) (I): Although this structure has a dense complicated three-dimensional framework, it can be well understood if it is separated into two substructures, one comprising of a porous framework with parallel tunnels and one consisting of infinitely long rods filling those tunnels. The porous substructure consists of thin infinite walls running diagonally along the ac-plane in two different directions, see Figures 6-2 and 6-3a. The walls consist of distorted NaCl-type fragments two-metal-atom thick. The angle defined by the walls is ~70°. At the intersection point the walls form infinite Gd₂S₃-type rods. This arrangement creates tunnels with rhombus-like cross sections that are filled with infinite Bi₂Te₃-type rods. In Figure 6-3a some of these rods have been removed to show the tunnels. The similar sizes²⁸ of Pb²⁺, Bi³⁺ and La³⁺ result to an extensive occupancy disorder in the structure. The Pb²⁺ and Bi³⁺ disorder is very common in the lead bismuth sulfosalts¹⁷ while the Bi³⁺ and La³⁺ disorder is also found in A₂Ln_{1±x}Bi_{4±x}S₈²³ (A = K, Rb; Ln = La, Ce, Pr, Nd).

The unit cell has ten metal atom positions and several of them, as mentioned earlier, display mixed occupancy. Four of these metal positions contain no La atoms at all while the remaining six contain a significant fraction.

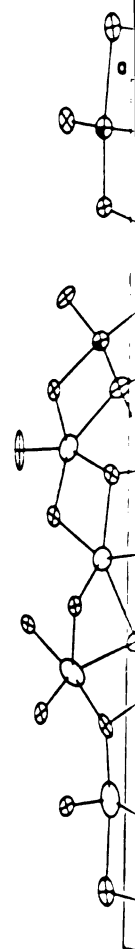


Figure 6-2. Projecta

The shaded crossed
represent the mixed

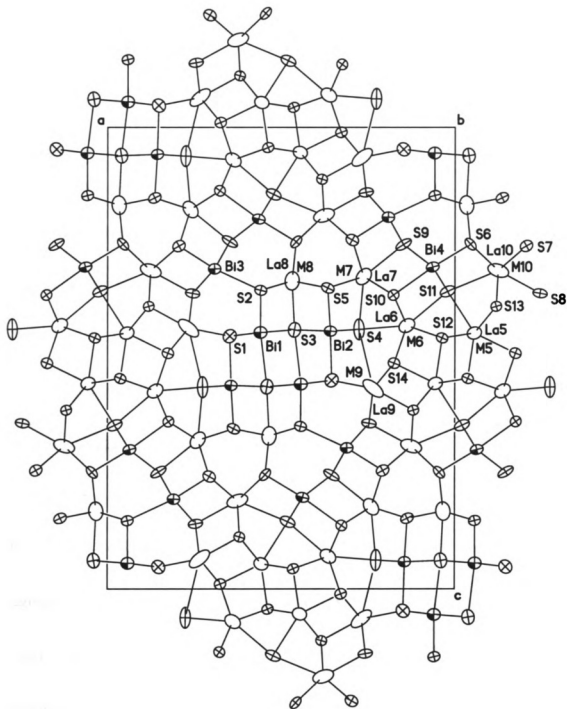


Figure 6-2. Projection of the structure of $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis (ORTEP view).

The shaded crossed ellipsoids represent Bi atoms, the crossed S atoms and the plain represent the mixed occupancy sites.

Figure 6-3. Comparison

$\text{Bi}_{1-x}\text{Sb}_x$ down the

gray circles represent

Sb down the b-axis

to represent the La site

type building blocks

near the shaded circular

sites. The same w

type fragment in the sp

Bi_2Te_3 and CdI_2 -typ

channel-like tunnels.

Figure 6-3. Comparison of two related structures (a) Projection of the structure $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b-axis. The black circles are Bi atoms, the white S atoms and the gray circles represent the mixed occupancy sites. (b) Projection of the structure $\text{La}_4\text{Bi}_2\text{S}_9$ down the b-axis. The black circles are Bi atoms, the white S atoms and the gray circles represent the La sites. The shaded rectangular areas indicate the Bi_2Te_3 - and Gd_2S_3 -type building blocks. The arrows indicate the direction of the NaCl-type walls whereas the shaded circular area shows the triangular fragment made of three trigonal prismatic sites. The same walls exist in the both structures but $\text{La}_4\text{Bi}_2\text{S}_9$ contains only a CdI_2 -type fragment in the space formed between the ribbons. For clarity reasons some of the Bi_2Te_3 - and CdI_2 -type have been removed to show the framework walls and rhombus-like tunnels.

NaCl type ribbons
two metal atoms thick

NaCl type ribbons

Figure 6-3.

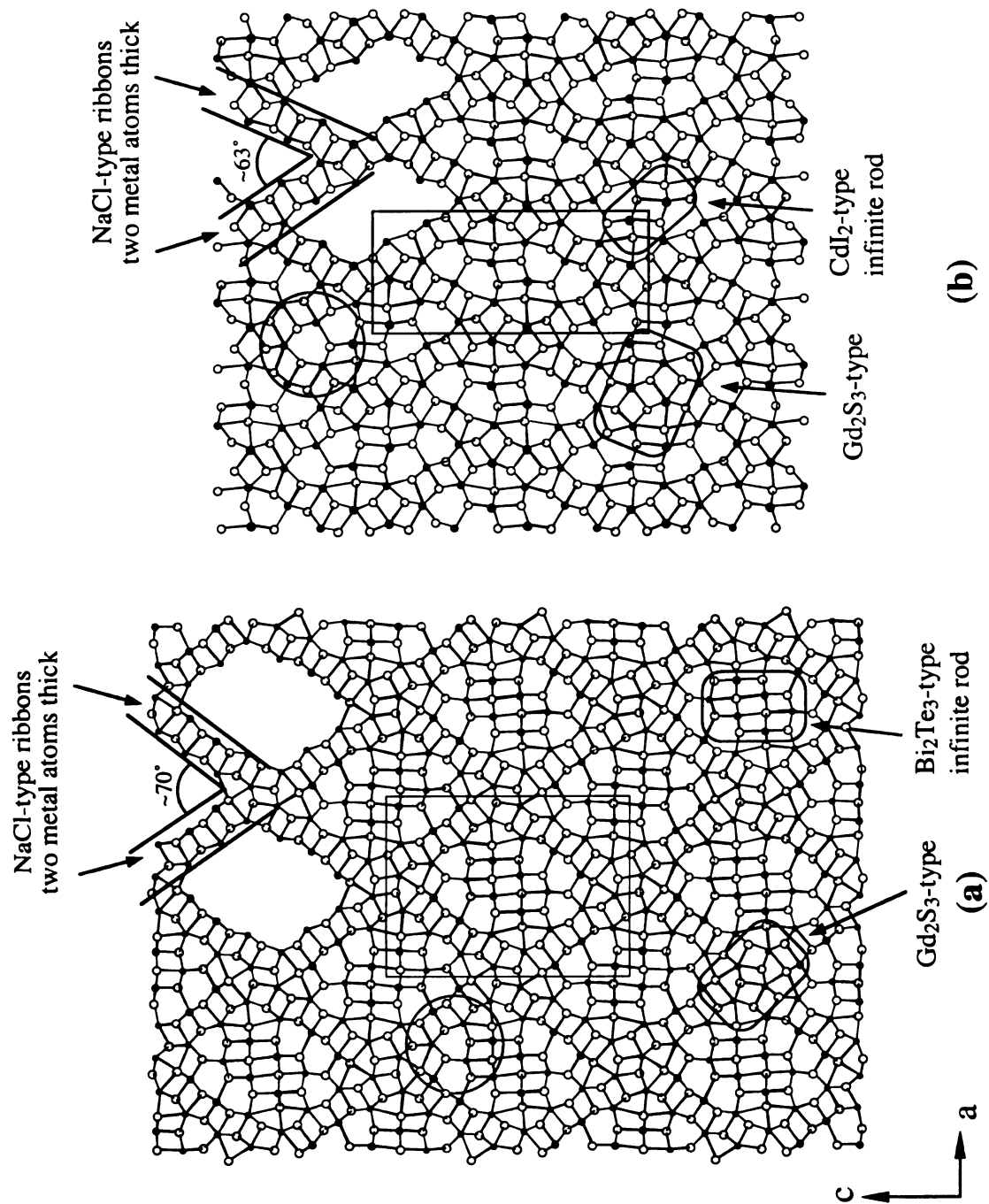


Figure 6-3.

The La-fre

shorter Bi-S bond

bonds at 2.674(3)

Bi(2) belong to the

type framework w

The Gd₂S₃

Figure 6-4a. The

coordination and d

is eight coordinate

varying between 2.8

A = K, Rb; Ln =

Pb₂Ln₂Bi-S₁₈³³ and

prisms form an int

sharing trigonal face

disposed perpendicu

The La-free sites, Bi(1), Bi(2), Bi(3) and Bi(4)²⁹ are octahedral, having three shorter Bi-S bonds trans to three longer bonds e.g. Bi(2) has one bond at 2.650(5) Å, two bonds at 2.674(3) Å, two bonds at 2.988(4) Å and one bond at 2.998(5) Å. Bi(1) and Bi(2) belong to the Bi₂Te₃-type rod fragment while Bi(3) and Bi(4) belong to the NaCl-type framework walls, see Figure 6-2.

The Gd₂S₃-type fragment is made up of sites M(5)/La(5) and M(6)/La(6), see Figure 6-4a. The M(5)/La(5) site is seven coordinate with a monocapped trigonal coordination and distances varying between 2.795(5)-3.029(5) Å, while site M(6)/La(6) is eight coordinate having a bicapped trigonal prismatic coordination with distances varying between 2.875(3)-3.248(5) Å. This fragment is also observed in ALn_{1±x}Bi_{4±x}S₈²³ (A = K, Rb; Ln = La, Ce, Pr, Nd), Gd₂S₃³⁰, CeTmS₃³¹, La₁₀Er₉S₂₇³², PbBi₂S₄^{17a}, Pb₄In₃Bi₇S₁₈³³ and La₄Bi₂S₉²⁰. One characteristic of this fragment is the monocapped prisms form an infinite column by sharing edges while the bicapped prisms stack by sharing trigonal faces. This arrangement causes the two different kind of prisms to be disposed perpendicular to each other.

Monoclinic
trigonal

S4

(a) S10

(b)

Monocapped
trigonal prism



Figure 6-4. Proje.

ties and the Gd_2S_3

different kinds of tri

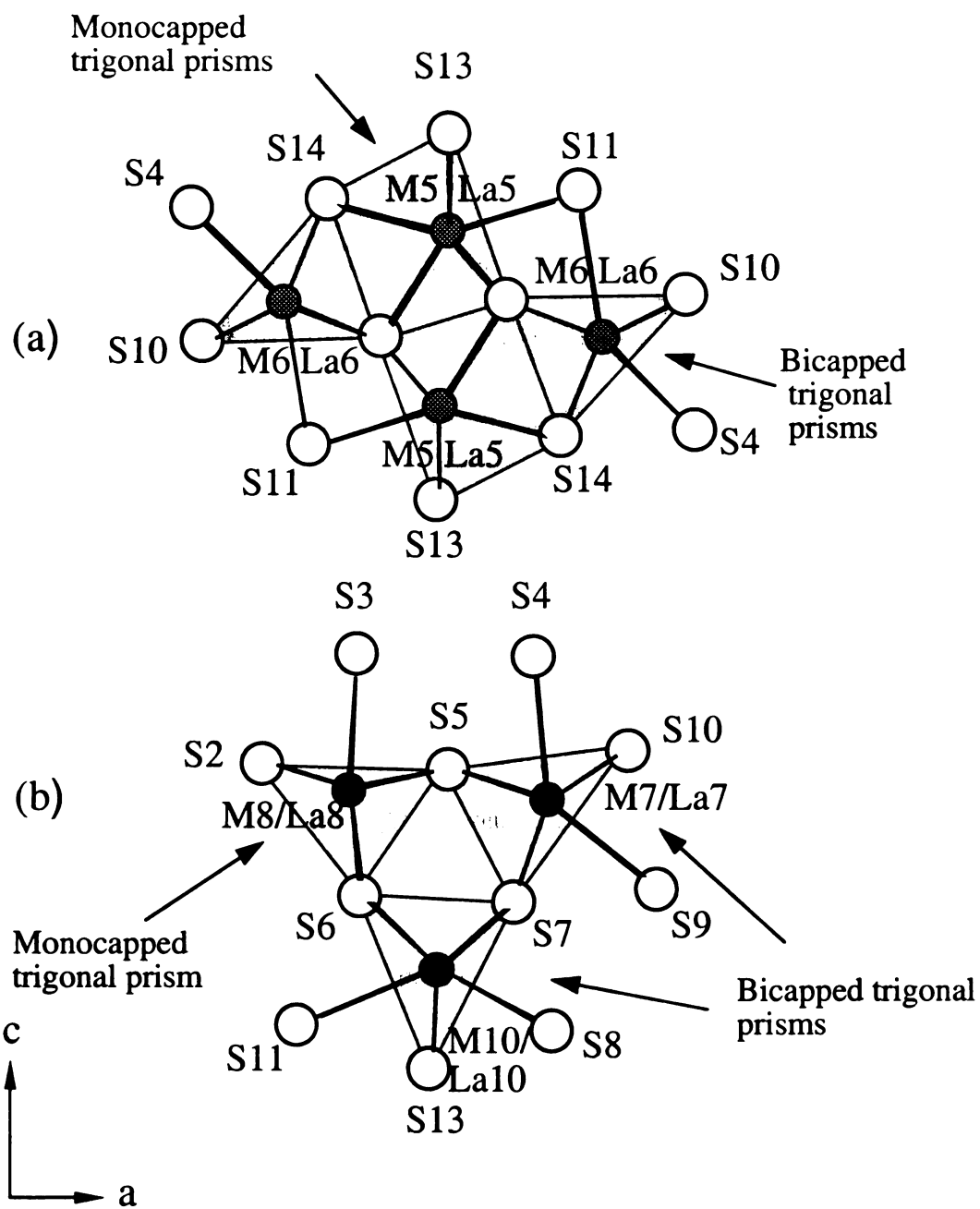


Figure 6-4. Projection of the triangular fragment (a) made of three trigonal prismatic sites and the Gd_2S_3 -type (b) building blocks in $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b -axis. The different kinds of trigonal prisms are also shown.

The infin:

B(1) and B(2) a

distances varying

The NaCl-

the sites Mi^{7+} La

numbers. Site M

coordination with

M9(La9) is sev

with M9(La9)-S

is eight-coordinate

Se distances betwe

on Table 6-5.

As can be s

least one large am

occupancy in these

the modeling of the

(see below).

The infinite Bi_2Te_3 -type rod fragment is made up from the two octahedral sites Bi(1) and Bi(2) and site M(8)/La(8) which is seven coordinate, with M(8)/La(8)-Se distances varying between 2.852(3)-3.134(4) Å, see Figure 6-2.

The NaCl-type walls are made up from the octahedral sites Bi(3) and Bi(4) and the sites M(7)/La(7), M(9)/La(9) and M(10)/La(10) which have higher (>6) coordination numbers. Site M(7)/La(7) is eight-coordinate having a bicapped trigonal prismatic coordination with M(7)/La(7)-Se distances varying between 2.941(3)-3.254(6) Å. Site M(9)/La(9) is seven-coordinate having a monocapped trigonal prismatic coordination with M(9)/La(9)-Se distances varying between 2.786(5)-3.276(4) Å while M(10)/La(10) is eight-coordinate having a bicapped trigonal prismatic coordination with M(10)/La(10)-Se distances between 2.929(5)-3.341(5) Å. Bond distances and selected angles are shown on Table 6-5.

As can be seen in Figure 6-2 the high (>6) coordinate disordered sites have at least one large anisotropic temperature factor. This feature derives from the mixed occupancy in these sites. The resolution of the diffraction data was not sufficient to allow the modeling of these sites as split positions although this was possible in the case of (II) (see below).

Table 6-5. Bond

B(1)-Si(2)
B(1)-Si(1)
B(1)-Si(3)
B(1)-Si(3)
B(2)-Si(5)
B(2)-Si(4)
B(2)-Si(3)
B(2)-Si(1)
B(3)-Si(7)
B(3)-Si(9)
B(3)-Si(8)
B(3)-Si(2)
B(4)-Si(11)
B(4)-Si(6)
B(4)-Si(10)
B(4)-Si(9)
M(5)-La(5)-Si(12)
M(5)-La(5)-Si(14)
M(5)-La(5)-Si(12)
M(5)-La(5)-Si(13)
M(5)-La(5)-Si(11)
M(6)-La(6)-Si(16)
M(6)-La(6)-Si(4)
M(6)-La(6)-Si(12)
M(6)-La(6)-Si(14)
M(6)-La(6)-Si(11)
M(7)-La(7)-Si(10)
M(7)-La(7)-Si(5)
M(7)-La(7)-Si(7)
M(7)-La(7)-Si(9)
M(7)-La(7)-Si(4)

Table 6-5. Bond Distances (Å) and Selected Angles (deg) for $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$

Bi(1)-S(2)	2.584(5)	S(2)-Bi(1)-S(3)	86.63(12)
Bi(1)-S(1)	2.775(4)x2	S(2)-Bi(1)-S(1)	94.86(13)
Bi(1)-S(3)	2.908(4)x2	S(2)-Bi(1)-S(3)	172.85(13)
Bi(1)-S(3)	3.323(5)		
Bi(2)-S(5)	2.650(5)	S(3)-Bi(2)-S(3)	85.10(13)
Bi(2)-S(4)	2.674(3)x2	S(4)-Bi(2)-S(4)	98.19(16)
Bi(2)-S(3)	2.988(4)x2	S(4)-Bi(2)-S(3)	172.44(12)
Bi(2)-S(1)	2.998(5)		
Bi(3)-S(7)	2.596(5)	S(7)-Bi(3)-S(8)	83.24(12)
Bi(3)-S(9)	2.781(3)x2	S(8)-Bi(3)-S(2)	102.01(11)
Bi(3)-S(8)	2.858(3)x2	S(9)-Bi(3)-S(8)	170.93(15)
Bi(3)-S(2)	3.123(5)		
Bi(4)-S(11)	2.673(3)x2	S(10)-Bi(4)-S(9)	77.75(12)
Bi(4)-S(6)	2.688(4)	S(6)-Bi(4)-S(9)	105.55(12)
Bi(4)-S(10)	2.940(5)	S(11)-Bi(4)-S(9)	163.76(14)
Bi(4)-S(9)	3.019(4)x2		
M(5)/La(5)-S(12)	2.795(5)	M(8)/La(8)-S(2)	2.852(3)x2
M(5)/La(5)-S(14)	2.802(5)	M(8)/La(8)-S(3)	3.007(5)
M(5)/La(5)-S(12)	2.835(3)x2	M(8)/La(8)-S(5)	3.008(4)x2
M(5)/La(5)-S(13)	2.923(3)x2	M(8)/La(8)-S(6)	3.134(4)x2
M(5)/La(5)-S(11)	3.029(5)		
M(6)/La(6)-S(10)	2.875(3)x2	M(9)/La(9)-S(13)	2.786(5)
M(6)/La(6)-S(4)	2.922(5)	M(9)/La(9)-S(14)	2.836(3)x2
M(6)/La(6)-S(12)	3.039(4)x2	M(9)/La(9)-S(8)	2.947(3)x2
M(6)/La(6)-S(14)	3.152(4)x2	M(9)/La(9)-S(1)	3.276(4)x2
M(6)/La(6)-S(11)	3.248(5)		
M(7)/La(7)-S(10)	2.941(3)x2	M(10)/La(10)-S(8)	2.929(5)
M(7)/La(7)-S(5)	3.063(4)x2	M(10)/La(10)-S(13)	2.988(3)x2
M(7)/La(7)-S(7)	3.090(4)x2	M(10)/La(10)-S(7)	3.055(4)x2
M(7)/La(7)-S(9)	3.111(5)	M(10)/La(10)-S(6)	3.090(4)x2
M(7)/La(7)-S(4)	3.254(6)	M(10)/La(10)-S(11)	3.341(5)

Another

running along the

angular prisms situated

the ac-plane, see Fig.

prismatic sites. No

M(Si)La(Si). The

being that the three

almost a three fold

$\text{Pb}_2\text{La}_4\text{Bi}_8$

Both structures have

fragments in the po

is formed between

fragment. CdI_2 -typ

Furthermore, the

relationship between

homologous series of

walls forming tunne

Another characteristic of the structure is the existence of small infinite rods running along the b-axis made up from three trigonal prisms. Along the b-axis the trigonal prisms stack on top of each other, sharing trigonal faces, while they share edge in the ac-plane, see Figures 6-3a and 6-4b. These rods are made up of two bicapped trigonal prismatic sites, M(7)/La(7) and M(10)/La(10) and one monocapped trigonal prismatic M(8)/La(8). The same motif is found also in $\text{Cs}_2\text{La}_{1+x}\text{Bi}_{9-x}\text{S}_{16}$ with the only difference being that the three sites are bicapped trigonal prismatic and the whole fragment exhibits almost a three fold local symmetry (see below).

$\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ shares some structures features with $\text{La}_4\text{Bi}_2\text{S}_9$ ²⁰, see Figure 6-3. Both structures have the NaCl-type walls running along the ac-plane forming Gd_2S_3 -type fragments in the point they intercept. In the case of $\text{La}_4\text{Bi}_2\text{S}_9$ the rhombus-like tunnel that is formed between opposite running walls is significantly narrower and contain a thinner fragment, CdI_2 -type, compared to the Bi_2Te_3 -type fragment found in $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$. Furthermore, the angle defined by the walls in $\text{La}_4\text{Bi}_2\text{S}_9$ is smaller ($\sim 63^\circ$). This relationship between the two compounds is very interesting since it hints of a possible homologous series of compounds that feature porous substructures made up of NaCl-type walls forming tunnels of larger cross section.

$\text{Sr}_2\text{La}_4\text{Bi}_4$

S_{14} . It is not un-

similar size.²⁸ The

splitting of five m

for Bi(1) through

distances in (II) v

distances vary bet

splitting, the dist.

between 2.941(2)-

2.957(2)-3.278(3)

splitting in (II). Fo

3.276(4) Å while m

Bi with Bi(9)-S dis

prismatic position c

3.507(4) Å, see Fig

occurs for sites 6.

made based on the h

A significant

Sr₂La_xBi_{8-x}S₁₄ (x ~ 2.6): This compound adopts the same structure as Pb₂La_xBi_{8-x}S₁₄. It is not unusual for the Sr and Pb analogs to adopt the same structure given their similar size.²⁸ The quality of the diffraction data of (II) enabled us to better resolve the splitting of five metal sites, see Figure 6-5. The coordination environments and distances for Bi(1) through Bi(4) are very similar in the two compounds e.g. for Bi(4) the Bi-S distances in (II) vary between 2.669(2)-3.003(2) Å while for the same atom in (I) the distances vary between 2.673(3)-3.019(4) Å. Also for site 7, which does not exhibit a splitting, the distances are very similar e.g. in (I) the M(7)/La(7)-S distances vary between 2.941(3)-3.254(6) Å while in (II) the La(7)/Sr(7)-S distances vary between 2.957(2)-3.278(3) Å. The difference in distances is greater in the sites that exhibit splitting in (II). For example, site 9 in Pb₂La_{2+x}Bi_{6-x}S₁₄ has distances between 2.786(5)-3.276(4) Å while in (II) site 9 contains two positions, one square pyramidal, occupied by Bi with Bi(9)-S distances varying between 2.618(3)-2.895(2) Å, and a bicapped trigonal prismatic position occupied by La and Sr with distances La(9)/Sr(9)-S between 2.888(2)-3.507(4) Å, see Figure 6-6a. The two positions are 0.495(1) Å apart. The same situation occurs for sites 6, 8 and 10. The assignment of the atoms in these split positions was made based on the bond distances.

A significant difference between the two compounds is the behavior of site 5.

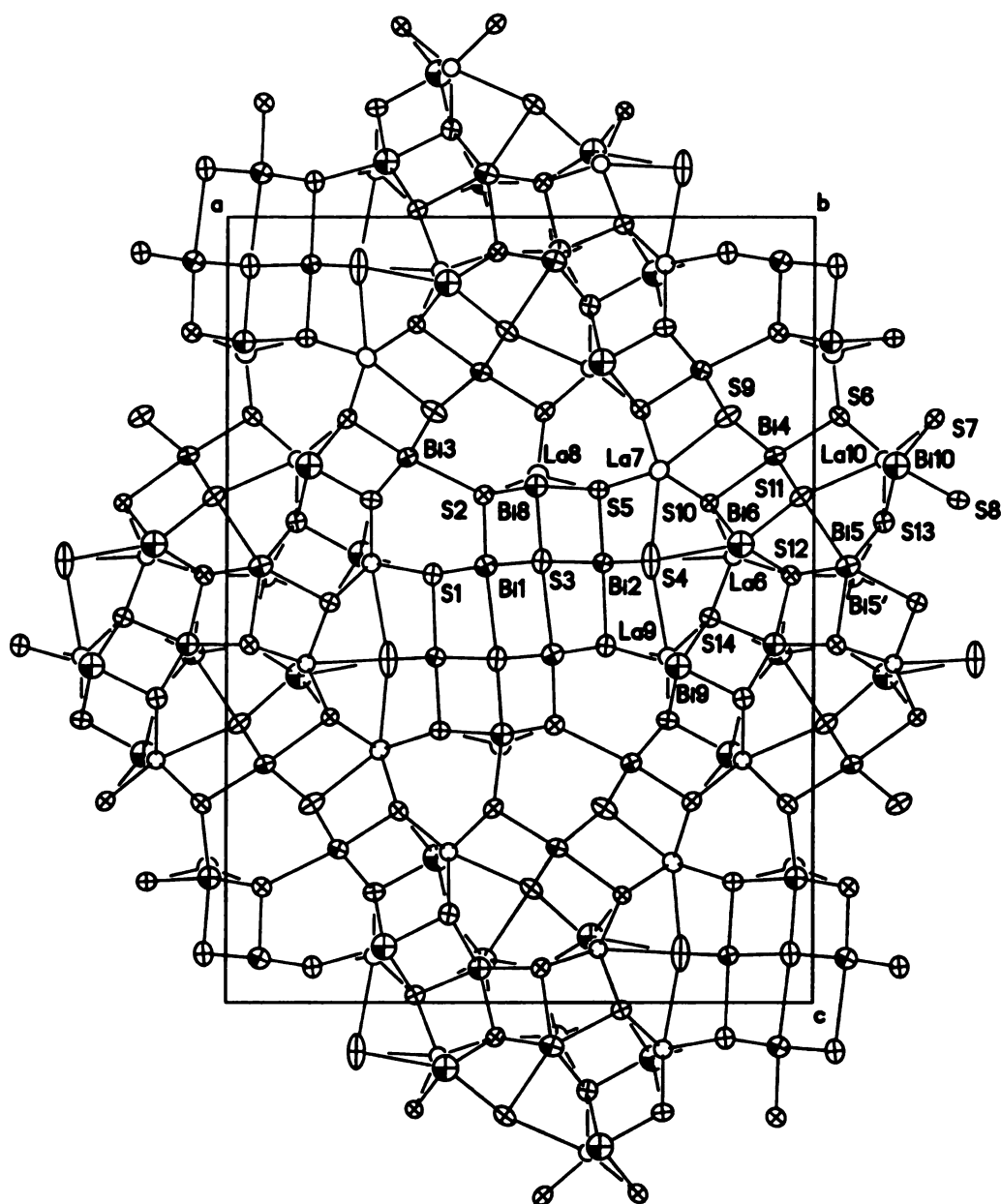


Figure 6-5. Projection of the structure of $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ down the b -axis (ORTEP view).

Due to the better quality diffraction data, the splitting of the high coordinate sites can be seen. The shaded crossed ellipsoids represent Bi atoms, the crossed S atoms and the plain represent the mixed occupancy sites. For these sites for clarity reasons, only the La atoms are shown.

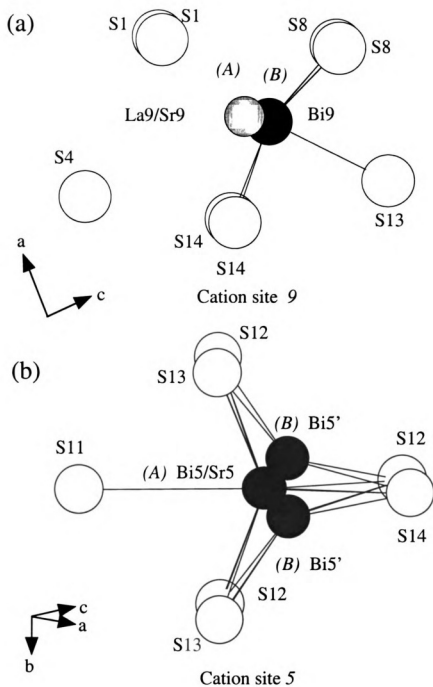


Figure 6-6. The coordination environments of cation site 9 (a) and cation site 5 (b) in $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$. The splitting in every site is also shown, (A) refers to the position located in the center of the site while (B) refers to site shifted away from the center to the side.

In (I) the site is

we have an un-

$\text{Bi}^{5+}\text{Sn}^{5+}$ is st

while Bi^{5+} is s

prism having fo

between 3.34(1) Å

to be assigned ma

together with site

feature of (II) be

characteristics. T

distances and sele

$\text{Cs}_2\text{La}_2\text{Bi}$

$\text{E}(\text{Bi}_2\text{S}_4)^{18}$ -type m

kobellite³⁴ $\text{Pb}_{12}(\text{O})$

There are two dif

The NaCl-type b

$\text{E}(\text{Bi}_2\text{S}_4)$ -type blo

in these blocks di

In (I) the site is disordered between M(5) (Pb or Bi) and La(5), whereas in (II) for site 5 we have an unusual splitting perpendicular to the ac-plane. As seen on Figure 6-6b, Bi(5)/Sr(5) is sitting on the mirror plane with distances between 2.821(3)-3.037(2) Å while Bi(5') is shifted up and below the mirror plane towards the faces of the trigonal prism having four short distances between 2.559(9)-2.710(8) Å and three long ones between 3.34(1)-3.45(1) Å. This is an unusual coordination for Bi, yet both positions had to be assigned mainly as Bi since they refined freely to a total occupancy of 98%. Site 5 together with site 6 belongs to the Gd₂S₃-type fragment. This splitting is a real structural feature of (II) because all four data sets that we collected exhibited the same exact characteristics. There seems to be no indication for such kind of splitting in (I). Bond distances and selected angles are shown on Table 6-6.

Cs₂La_xBi_{10-x}S₁₆ (x ~ 1.2): This compound consists of CdI₂-, NaCl- and EuBi₂S₄¹⁸-type infinite blocks, see Figure 6-7, and is structurally related with the mineral kobellite³⁴ Pb₁₂(Cu,Fe)₂(Bi,Sb)₁₄S₃₅. These blocks create tunnels filled by Cs atoms. There are two different NaCl-type blocks where the BiS₆ octahedra are severely distorted. The NaCl-type blocks are connected with each other with the EuBi₂S₄-type blocks. The EuBi₂S₄-type blocks consist of three bicapped trigonal prisms that share edges. The sites in these blocks display mixed Bi-La occupancy.

NaCl-type



Figure 6-

areas indi

the EuBi-

circles are

occupancy

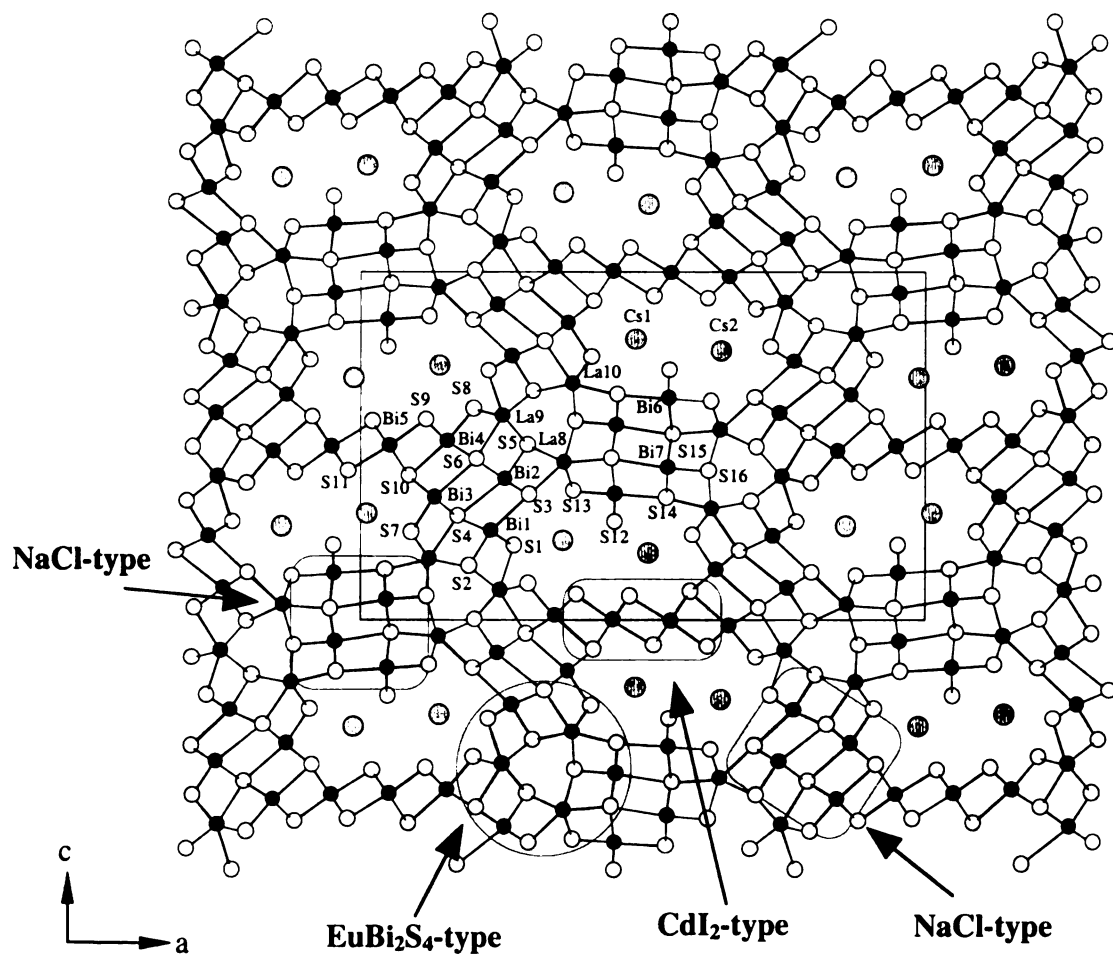


Figure 6-7. Projection of the structure of $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ down the b -axis. The shaded areas indicate the NaCl-, and CdI_2 -type building blocks. The shaded circular area shows the EuBi_2S_4 -type fragment made of three bicapped trigonal prismatic sites. The black circles are Bi atoms, the white S atoms and the gray circles represent the mixed occupancy (La and Bi) sites.

Table 6-6. Bond

B(1)-S(2)

B(1)-S(1)

B(1)-S(3)

B(1)-S(3)

B(2)-S(5)

B(2)-S(4)

B(2)-S(1)

B(2)-S(3)

B(3)-S(7)

B(3)-S(9)

B(3)-S(8)

B(3)-S(2)

B(4)-S(11)

B(4)-S(6)

B(4)-S(10)

B(4)-S(9)

B(5)-S(5)-S(14)

B(5)-S(5)-S(12)

B(5)-S(5)-S(13)

B(5)-S(5)-S(12)

B(5)-S(5)-S(11)

B(5)-S(5)-B(5')

B(5')-B(5')=8

B(5')-B(5')=10

L(6)-S(6)-B(6)

L(6)-S(6)-S(10)

L(6)-S(6)-S(4)

L(6)-S(6)-S(12)

L(6)-S(6)-S(14)

L(6)-S(6)-S(11)

Table 6-6. Bond Distances (Å) and Selected Angles (deg) for $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$

Bi(1)-S(2)	2.553(2)	S(2)-Bi(1)-S(3)	88.08(6)
Bi(1)-S(1)	2.808(2)x2	S(2)-Bi(1)-S(1)	95.04(6)
Bi(1)-S(3)	2.860(2)x2	S(2)-Bi(1)-S(3)	174.94(7)
Bi(1)-S(3)	3.368(3)		
Bi(2)-S(5)	2.650(2)	S(3)-Bi(2)-S(3)	84.73(6)
Bi(2)-S(4)	2.656(2)x2	S(4)-Bi(2)-S(4)	99.07(9)
Bi(2)-S(1)	2.971(3)	S(4)-Bi(2)-S(3)	172.25(6)
Bi(2)-S(3)	2.999(2)x2		
Bi(3)-S(7)	2.594(2)	S(7)-Bi(3)-S(8)	84.47(6)
Bi(3)-S(9)	2.779(2)x2	S(8)-Bi(3)-S(2)	99.94(6)
Bi(3)-S(8)	2.862(2)x2	S(9)-Bi(3)-S(8)	172.60(8)
Bi(3)-S(2)	3.082(2)		
Bi(4)-S(11)	2.669(2)x2	S(10)-Bi(4)-S(9)	79.57(6)
Bi(4)-S(6)	2.715(2)	S(6)-Bi(4)-S(9)	103.58(6)
Bi(4)-S(10)	2.907(2)	S(11)-Bi(4)-S(9)	165.79(7)
Bi(4)-S(9)	3.003(2)x2		
Bi(5)/Sr(5)-S(14)	2.821(3)	Bi(5')-S(14)	2.559(9)
Bi(5)/Sr(5)-S(12)	2.849(2)	Bi(5')-S(12)	2.590(8)
Bi(5)/Sr(5)-S(13)	2.881(2)x2	Bi(5')-S(12)	2.710(8)x2
Bi(5)/Sr(5)-S(12)	2.895(2)x2	Bi(5')-Bi(5')	3.09(2)
Bi(5)/Sr(5)-S(11)	3.037(2)	Bi(5')-S(12)	3.344(12)
		Bi(5')-S(13)	3.351(12)
Bi(5)/Sr(5)-Bi(5')	0.61(1)	Bi(5')-S(11)	3.453(12)
Bi(5')-Bi(5')#8	0.95(2)		
Bi(5')-Bi(5')#10	3.09(2)	Bi(5')-Bi(5)/Sr(5)-Bi(5')	101.9(14)
La(6)/Sr(6)-Bi(6)	0.51(3)		
La(6)/Sr(6)-S(10)	2.925(2)x2	Bi(6)-S(10)	2.75(1)x2
La(6)/Sr(6)-S(4)	2.967(3)	Bi(6)-S(11)	2.76(3)
La(6)/Sr(6)-S(12)	2.971(2)x2	Bi(6)-S(12)	2.93(1)x2
La(6)/Sr(6)-S(14)	3.098(2)x2	Bi(6)-S(4)	3.28(2)
La(6)/Sr(6)-S(11)	3.249(3)	Bi(6)-S(14)	3.50(2)x2

Table 6-6

[illegible]

Table 6-6. (cont'd)

La(7)/Sr(7)-S(10)	2.957(2)x2		
La(7)/Sr(7)-S(5)#13	3.051(2)x2		
La(7)/Sr(7)-S(7)#15	3.071(2)x2		
La(7)/Sr(7)-S(9)	3.135(3)		
La(7)/Sr(7)-S(4)	3.278(3)		
La(8)/Sr(8)-Bi(8)	0.386(7)		
La(8)/Sr(8)-S(2)	2.903(2)x2	Bi(8)-S(3)	2.728(9)
La(8)/Sr(8)-S(5)	3.031(2)x2	Bi(8)-S(2)	2.793(3)x2
La(8)/Sr(8)-S(6)	3.070(3)x2	Bi(8)-S(5)	3.034(3)x2
La(8)/Sr(8)-S(3)	3.105(4)	Bi(8)-S(6)	3.370(7)x2
La(9)/Sr(9)-Bi(9)	0.495(1)		
La(9)/Sr(9)-S(14)	2.888(2)x2	Bi(9)-S(13)	2.618(3)
La(9)/Sr(9)-S(1)	3.033(2)x2	Bi(9)-S(8)	2.834(2)x2
La(9)/Sr(9)-S(8)	3.046(2)x2	Bi(9)-S(14)	2.895(2)x2
La(9)/Sr(9)-S(13)	3.100(3)	Bi(9)-S(1)	3.371(3)x2
La(9)/Sr(9)-S(4)#9	3.507(4)		
La(10)/Sr(10)-Bi(10)	0.49(1)		
La(10)/Sr(10)-S(13)	3.015(2)x2	Bi(10)-S(8)	2.57(1)
La(10)/Sr(10)-S(6)	3.035(2)x2	Bi(10)-S(13)	2.901(5)x2
La(10)/Sr(10)-S(8)	3.055(3)	Bi(10)-S(7)	2.977(5)x2
La(10)/Sr(10)-S(7)	3.100(2)x2	Bi(10)-S(6)	3.39(1)x2
La(10)/Sr(10)-S(11)	3.276(3)	Bi(10)-S(11)	3.61(1)

The E_g

are four

Both the

varying

octahedra

255616

octahedra

an extra

bonds at

interaction

In

ax displa

C₃ symm

trigonal pr

trigonal an

that the ser

The EuBi_2S_4 -type fragment in $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ is shown in Figure 6-8. Similar fragments are found also in EuBi_2S_4 , $\text{Eu}_3\text{Sb}_4\text{S}_9$ ³⁵ and kobellite.

As mentioned above the BiS_6 octahedra have distorted coordination geometries. Bi(5) that belongs to the CdI_2 fragment has the least distorted coordination with distances varying between 2.712(4)-3.002(5) Å and angles between 85.4(2)°-97.3(2)°. The BiS_6 octahedra of Bi(1), Bi(4) and Bi(6) are more distorted with distances varying between 2.556(6)-3.295(6) Å, 2.578(6)-3.187(7) Å and 2.635(6)-3.173(6) Å respectively. The octahedral distortion in Bi(2), Bi(3) and Bi(7) can be described as square pyramidal with an extra Bi-S interaction above 3.5 Å, e.g. Bi(2) has one short bond at 2.520(6) Å, two bonds at 2.710(4) Å which are trans to longer bonds at 2.962(5) Å and a long Bi-S interaction at 3.720(7) Å. Selected distances and angles are shown on Table 6-7.

In the EuBi_2S_4 -type block, the three sites with coordination numbers greater than six display mixed occupancy and form a arrangement that seems to have locally a pseudo C_3 symmetry, see Figures 6-7 and 6-8. All three sites are eight-coordinate (bicapped trigonal prisms) in contrast with what is found in (I) and (II) where we have two bicapped trigonal and one monocapped trigonal prismatic sites, see Figure 6-4a. It has to be noted that the same fragment in EuBi_2S_4 has a true C_3 symmetry.

S10



Figure 6-8. Project

basis. The fragm

ingonal prismatic

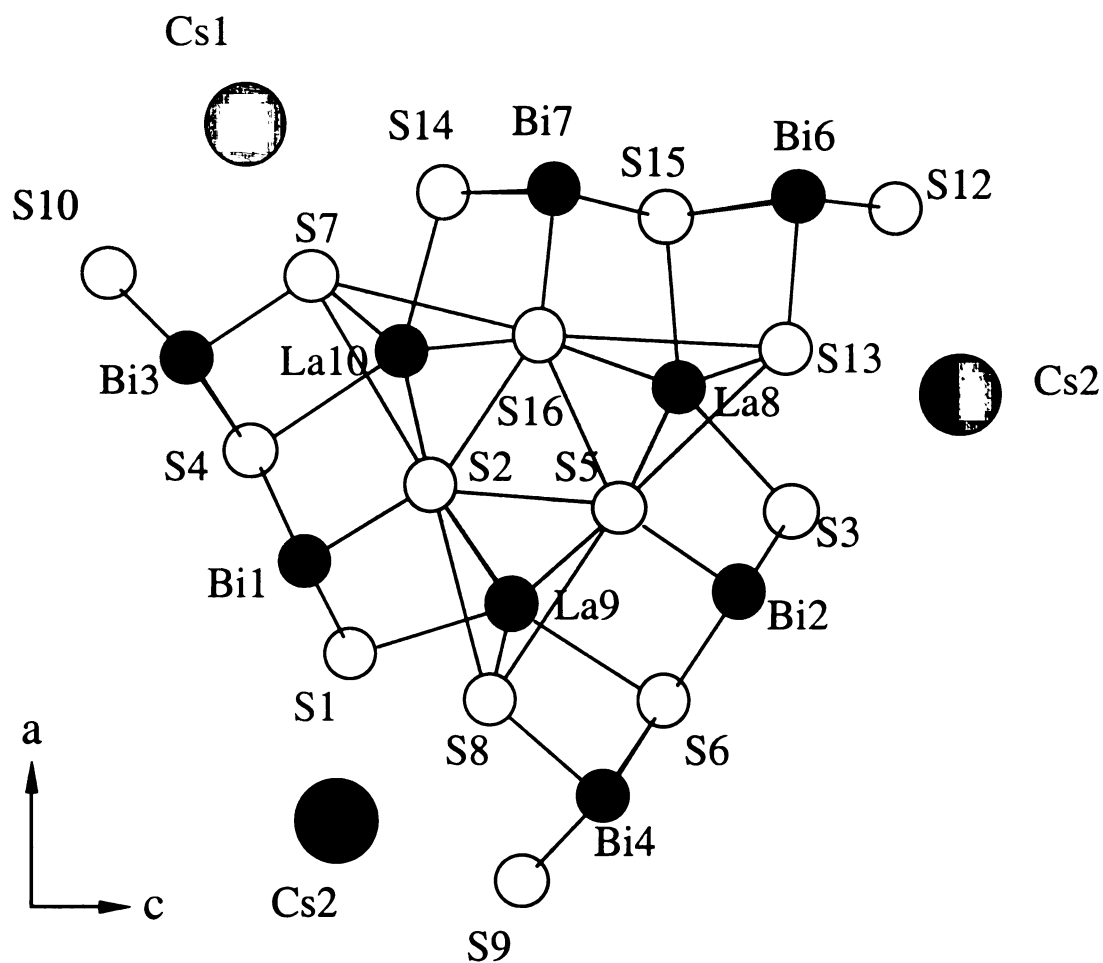


Figure 6-8. Projection of the EuBi_2S_4 -type fragment found in $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ down the b-axis. The fragment has a pseudo C_3 symmetry and is made up of three bicapped trigonal prismatic sites (La8, La9 and La10) that display mixed La/Bi occupancy.

Table 6-7. Bon

B: 1-S: 2)

B: 1-S: 1)

B: 1-S: 4)

B: 1-S: 3)

B: 2-S: 5)

B: 2-S: 3)

B: 2-S: 6)

B: 2-S: 4)

B: 3-S: 7)

B: 3-S: 4)

B: 3-S: 10)

B: 3-S: 6)

B: 4-S: 8)

B: 4-S: 9)

B: 4-S: 6)

B: 4-S: 10)

B: 5-S: 11)

B: 5-S: 9)

B: 5-S: 11)

B: 5-S: 10)

B: 6-S: 13)

B: 6-S: 12)

B: 6-S: 15)

B: 6-S: 14)

B: 7-S: 16)

B: 7-S: 14)

B: 7-S: 15)

B: 7-S: 15)

Table 6-7. Bond Distances (Å) and Selected Angles (deg) for Cs₂La_xBi_{10-x}S₁₆.

Bi(1)-S(2)	2.556(6)	S(1)-Bi(1)-S(3)	80.11(15)
Bi(1)-S(1)	2.659(4)x2	S(4)-Bi(1)-S(3)	107.10(15)
Bi(1)-S(4)	3.002(5)x2	S(2)-Bi(1)-S(3)	164.30(18)
Bi(1)-S(3)	3.295(6)		
Bi(2)-S(5)	2.520(6)	S(6)-Bi(2)-S(4)	77.59(17)
Bi(2)-S(3)	2.710(4)x2	S(3)-Bi(2)-S(4)	102.90(15)
Bi(2)-S(6)	2.962(5)x2	S(5)-Bi(2)-S(4)	162.26(18)
Bi(2)-S(4)	3.720(7)		
Bi(3)-S(7)	2.583(6)	S(4)-Bi(3)-S(6)	83.86(16)
Bi(3)-S(4)	2.769(4)x2	S(10)-Bi(3)-S(6)	95.62(15)
Bi(3)-S(10)	2.896(5)x2	S(7)-Bi(3)-S(6)	166.00(18)
Bi(3)-S(6)	3.505(8)		
Bi(4)-S(8)	2.578(6)	S(8)-Bi(4)-S(6)	84.11(19)
Bi(4)-S(9)	2.775(4)x2	S(6)-Bi(4)-S(10)	102.14(18)
Bi(4)-S(6)	2.928(5)x2	S(9)-Bi(4)-S(6)	170.3(2)
Bi(4)-S(10)	3.187(7)		
Bi(5)-S(11)	2.712(4)x2	S(10)-Bi(5)-S(10)	85.35(18)
Bi(5)-S(9)	2.756(7)	S(11)-Bi(5)-S(11)	97.3(2)
Bi(5)-S(11)	2.981(6)	S(11)-Bi(5)-S(10)	173.88(14)
Bi(5)-S(10)	3.002(5)2		
Bi(6)-S(13)	2.635(6)	S(13)-Bi(6)-S(15)	82.43(15)
Bi(6)-S(12)	2.673(4)x2	S(12)-Bi(6)-S(12)	99.2(2)
Bi(6)-S(15)	3.010(5)x2	S(12)-Bi(6)-S(15)	171.18(15)
Bi(6)-S(14)	3.173(6)		
Bi(7)-S(16)	2.541(6)	S(16)-Bi(7)-S(15)	87.13(16)
Bi(7)-S(14)	2.755(4)x2	S(14)-Bi(7)-S(14)	95.2(2)
Bi(7)-S(15)	2.898(5)x2	S(14)-Bi(7)-S(15)	174.26(17)
Bi(7)-S(15)	3.516(6)		

Table 6-7. (con-

$B_1S_1La_1S_1S_1$
 $B_1S_1La_1S_1S_1$
 $B_1S_1La_1S_1S_1$
 $B_1S_1La_1S_1S_1$
 $B_1S_1La_1S_1S_1$

 $B_19_1La_19_1S_1$
 $B_19_1La_19_1S_1$
 $B_19_1La_19_1S_1$
 $B_19_1La_19_1S_1$
 $B_19_1La_19_1S_1$

 $B_110_1La_110_1S_1$
 $B_110_1La_110_1S_1$
 $B_110_1La_110_1S_1$
 $B_110_1La_110_1S_1$
 $B_110_1La_110_1S_1$

Table 6-7. (cont'd).

Bi(8)/La(8)-S(13)	2.758(4)x2	Cs(1)-S(12)	3.491(5)x2
Bi(8)/La(8)-S(3)	2.920(6)	Cs(1)-S(10)	3.510(7)
Bi(8)/La(8)-S(15)	2.946(6)	Cs(1)-S(11)	3.545(5)x2
Bi(8)/La(8)-S(5)	3.213(5)x2	Cs(1)-S(7)	3.577(5)x2
Bi(8)/La(8)-S(16)	3.302(5)x2	Cs(1)-S(14)	3.604(7)
Bi(9)/La(9)-S(8)	2.742(4)x2	Cs(2)-S(8)	3.392(7)
Bi(9)/La(9)-S(1)	2.920(6)	Cs(2)-S(12)	3.409(7)
Bi(9)/La(9)-S(5)	3.122(5)x2	Cs(2)-S(3)	3.547(6)
Bi(9)/La(9)-S(6)	3.128(8)	Cs(2)-S(1)	3.671(5)x2
Bi(9)/La(9)-S(2)	3.166(5)x2	Cs(2)-S(13)	3.739(5)x2
		Cs(2)-S(9)	3.960(6)x2
Bi(10)/La(10)-S(14)	2.849(6)		
Bi(10)/La(10)-S(7)	2.855(4)x2		
Bi(10)/La(10)-S(16)	3.096(5)		
Bi(10)/La(10)-S(4)	3.128(7)x2		
Bi(10)/La(10)-S(2)	3.209(5)x2		

As men

CdI₂-type frag

distances vary

prismatic coord

The stru

kobellite Pb₁₂(C

group with very

4.035(6) Å. Figu

blocks in kobelli

contains CdI₂-typ

are compared, k

general formula M

9 and 6-10, the sh

S atoms, or a M₆S₂

Bi (or Sb) atoms ar

same space kobelli

As mentioned above the Cs atoms reside in tunnels formed by the NaCl-type and CdI₂-type fragments. Cs(1) has a bicapped trigonal prismatic coordination with Cs-S distances varying between 3.491(5)-3.604(7) Å while Cs(2) has a tricapped trigonal prismatic coordination with Cs-S distances varying between 3.392(7)-3.960(2) Å.

The structure of (III) contains several similar building blocks with the mineral kobellite Pb₁₂(Cu,Fe)₂(Bi,Sb)₁₄S₃₅. This mineral crystallizes in the Pnnm (#58) space group with very similar cell parameters of $a = 22.575(3)$ Å, $b = 34.104(4)$ Å and $c = 4.038(6)$ Å. Figure 6-9b shows the structure of kobellite for comparison. The EuBi₂S₄-blocks in kobellite contain Pb atoms. A significant difference is that Cs₂La_{1+x}Bi_{9-x}S₁₆ contains CdI₂-type fragments, whereas this is not the case for kobellite. If the formulas are compared, kobellite has the general formula M₂₈S₃₅ while Cs₂La_xBi_{10-x}S₁₆ has the general formula M₁₂S₁₆ or M₂₄S₃₂ so kobellite has an extra M₄S₃ fragment. In Figures 6-9 and 6-10, the shaded area in Cs₂La_xBi_{10-x}S₁₆ has four Cs atoms, two Bi atoms and two S atoms, or a M₆S₂ block, whereas kobellite has two Cu (or Fe) atoms, six Pb atoms, two Bi (or Sb) atoms and five sulfur atoms or a M₁₀S₅ block. As a result, in the approximately same space kobellite packs an extra M₄S₃ block.

(a)

(b)

Figure 6-9. Com

$Pb_{1-x}Cu_xFe_{1-x}Bi_xS$

the rest of the sta

contains an extra N

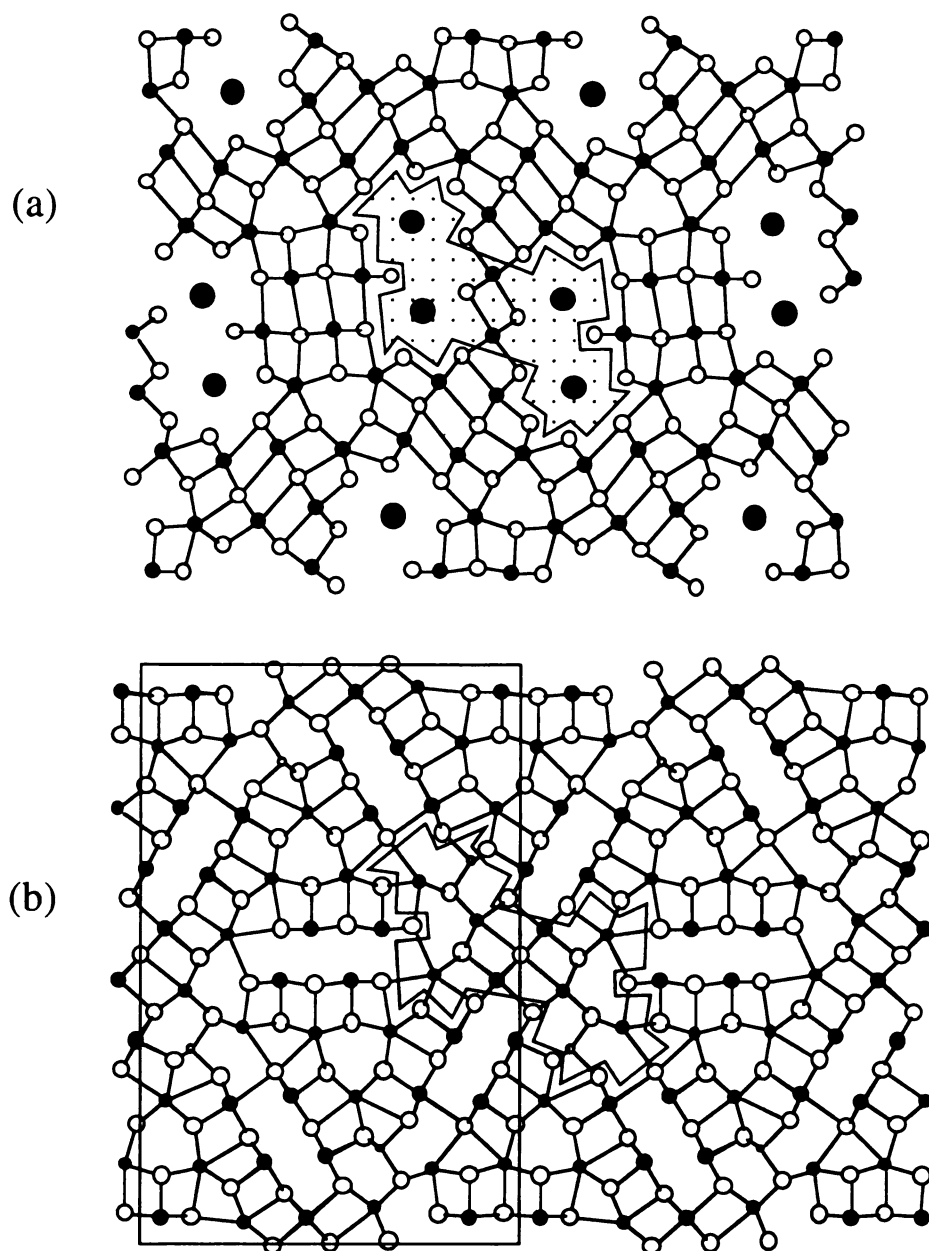


Figure 6-9. Comparison of the structures of (a) $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ and (b) kobellite

$\text{Pb}_{12}(\text{Cu,Fe})_2(\text{Bi,Sb})_{14}\text{S}_{35}$ viewed down the b-axis. With the exception of the shaded area,

the rest of the structure is common for the two compounds. The mineral kobellite

contains an extra M_4S_3 block (see text) in the shaded area.

(a)

M_6S_2 -b



(b)

$M_{10}S_5$

Figure 6-10. Cor.

Kobe, Ite $Pb_{1/2}(Cu, F$

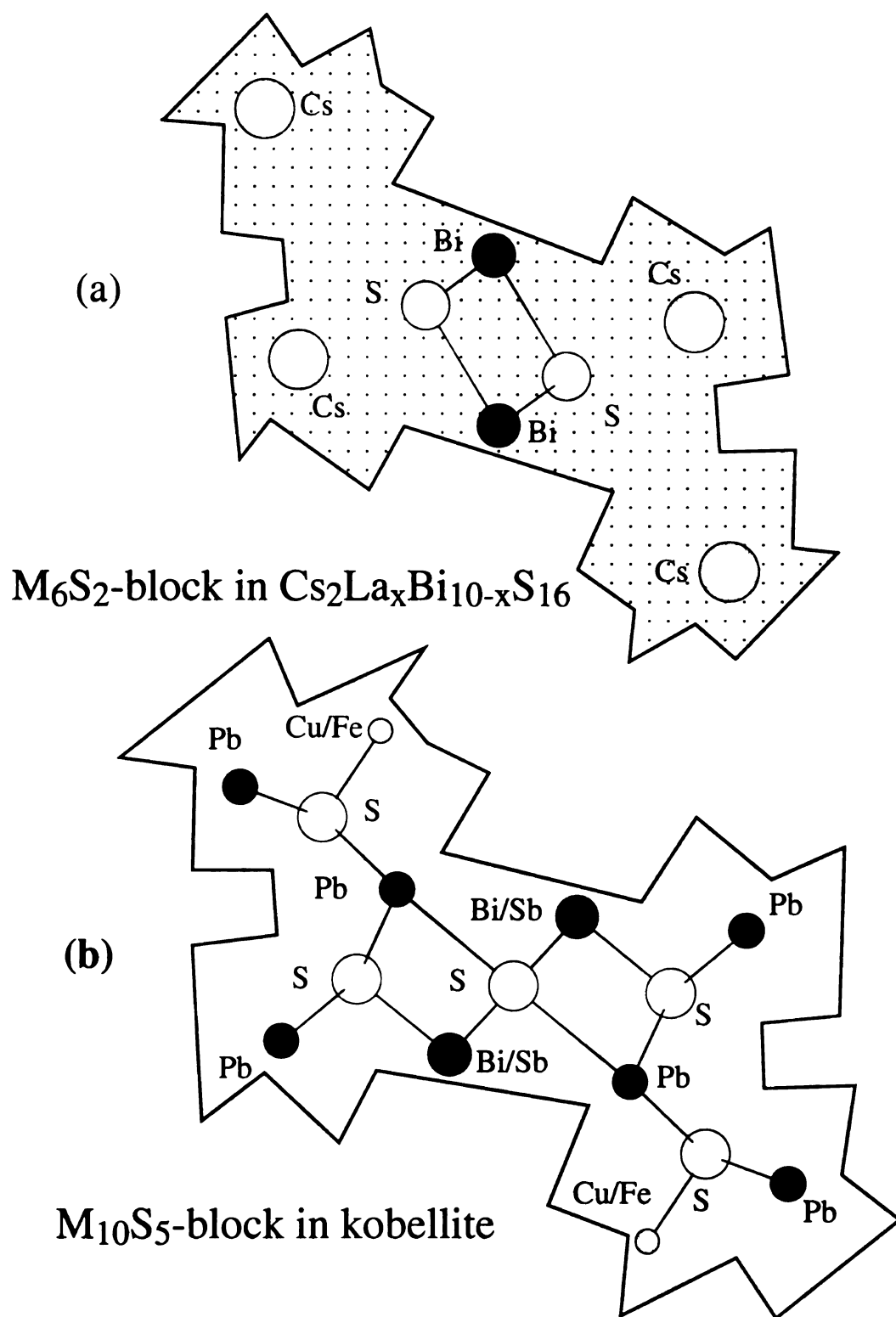


Figure 6-10. Comparison of the (a) M_6S_2 -block in $Cs_2La_xBi_{10-x}S_{16}$ and (b) $M_{10}S_5$ in kobellite $Pb_{12}(Cu,Fe)_2(Bi,Sb)_{14}S_{35}$ viewed down the b-axis with atom labeling.

5. Concluding

The in-

(A = Sr, Cs or

$\text{Sr}_2\text{La}_x\text{Bi}_{3-x}\text{S}_{14}$

and possess bu

compounds A B

type and the Eu

diversity and pos

example, La_2Bi_2

members of a ser

to fill the tunnel

kobellite present

replaced by a stru

all these systems

the bismuth atom

size of these cat

5. Concluding Remarks

The incorporation of La_2S_3 into the ternary bismuth chalcogenide systems A/Bi/S (A = Sr, Cs or Pb) resulted in the formation of the new compounds $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$, $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ and $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$. The complex three-dimensional structures are new and possess building blocks that are not encountered in the simpler ternary bismuth compounds A/Bi/Q (A = alkali or alkaline earth; Q = chalcogenide), such as the Gd_2S_3 -type and the EuBi_2S_4 -type fragments described above. This leads to greater complexity, diversity and possibilities in a system that already presents a large structural variety. For example, $\text{La}_4\text{Bi}_2\text{S}_9$ and $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ could be regarded as the first and second members of a series of compounds that have similar framework walls but different blocks to fill the tunnels formed between the walls. $\text{Cs}_2\text{La}_x\text{Bi}_{10-x}\text{S}_{16}$ and its relationship with kobellite present a example how the same structure is preserved while one fragment is replaced by a structurally different one but with the same dimensions. A characteristic of all these systems is the extensive disorder that is encountered between the lanthanide and the bismuth atoms and sometimes the alkaline earth or Pb and this is due to the similar size of these cations. In fact it may well be the case that the mixed occupancy is

responsible for

of compounds

responsible for the stability of these compounds as has been determined in another class of compounds in the Nb/Ta/S, Hf/Ta/S and Zr/Ta/Ge systems.³⁶

References

1. McCarthy, C. R., K.
2. McCarthy, 1294-130
3. (a) Kanatzidis, Hogan, T.
(b) Chen, 1655-1658
4. Chung, D. Kannew, 1997, 9, 36
5. (a) Jordan, (b) Jordan
6. See Chapter
7. Jordanidis, Dyck, J. S. 2000, in p
8. Wang, Y.
9. Chung, D. Kanatzidis
10. Chung, D. Kanatzidis
11. Adouby, I. *Kristallog*

References

1. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
2. McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301.
3. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474.
(b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.
4. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
5. (a) Iordanidis, L.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1928-1930.
(b) Iordanidis, L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 8319-8320.
6. See Chapter 3.
7. Iordanidis, L.; Brazis, P. W.; Kyratsi, T.; Ireland, J.; Lane, M.; Kannewurf, C. R.; Dyck, J. S.; Uher, C.; Ghelani, N. A.; Hogan, T.; Kanatzidis, M. G. *Chem. Mater.* **2000**, in press. See also Chapter 2.
8. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011-1017.
9. Chung, D.-Y.; Jovic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, R.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, **1997**, *119*, 2505-2515.
10. Chung, D.-Y.; Jovic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
11. Adouby, K.; Perez Vicente, C.; Jumas, J. C.; Fourcade, R.; Abba Touré, A. Z. *Kristallogr.* **1998**, *213*, 343-349.

12. Perez Vis.

Inorg. Ch.

13. Choe, W.

14. Chung, D.

Kanatzidis.

15. Mroczek, A.

10. 1667-16

16. Choi, K.-S.

Kanatzidis, N.

17. (a) Iitaka, Y.

Takagi, J. *P.*

Yamanaka, T.

Takagi, J. Z. *A.*

Mineral., Abh.

Kristallgeom.,

Wright, A. C.

Acta Crystallog.

B 1979, *B*35, 1

79.

1. Lemoine, P.; Ca

2. Lemoine, P.; Ca

3. Ecrepont, C.; Gu

4. Ceolin, R.; Toff

*B*33, 2804-2806.

-
12. Perez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Abba Touré, A.; Kra, G. *Inorg. Chem.* **1999**, *38*, 2131-2135.
 13. Choe, W.; Lee, S.; O'Connell, P.; Covey A. *Chem. Mater.* **1997**, *9*, 2025-2030.
 14. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
 15. Mroczek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.
 16. Choi, K.-S.; Chung, D.-Y.; Mroczek, A.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Submitted for publication*.
 17. (a) Iitaka, Y.; Nowacki, W. *Acta Crystallogr.* **1962**, *15*, 691-698. (b) Takeuchi, Y.; Takagi, J. *Proc. Jap. Acad.* **1974**, *50*, 222-225. (c) Takeuchi, Y.; Takagi, J.; Yamanaka, T. *Proc. Jap. Acad.* **1974**, *50*, 317-321. (d) Takeuchi, Y.; Ozawa, T.; Takagi, J. *Z. Kristallogr.* **1979**, *150*, 75-84. (e) Otto, H. H.; Strunz, H. *Neues Jahrb. Mineral., Abh.* **1968**, *108*, 1-19. (f) Srikrishnan, T.; Nowacki, W. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1974**, *140*, 114-136. (g) Tilley, R. J. D.; Wright, A. C. *J. Solid State Chem.* **1986**, *65*, 45-62. (h) Takagi, J.; Takeuchi, Y. *Acta Crystallogr., Sect. B* **1972**, *28*, 649-651. (i) Matzat, E. *Acta Crystallogr., Sect. B* **1979**, *B35*, 133-136. (j) Takeuchi, Y.; Takagi, J. *Proc. Jap. Acad.* **1974**, *50*, 76-79.
 18. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, *C42*, 259-261.
 19. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 727-729.
 20. Ecrepont, C.; Guittard, M.; Flahaut, J. *Mater. Res. Bull.* **1988**, *23*, 37-42.
 21. Ceolin, R.; Toffoli, P.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2804-2806.

22. Aliev, O.

P. G. *Inorg.*

23. Iordanidis

Chem. 19

24. Choi, K.

36, 3804

25. SMART

SHELXT

USA.

26. Aurvillier

27. Kanishev

Nauk SSSR

28. Shannon,

29. (a) We b

This is s

identity c

that these

sites, tha

is alway

$\text{Pb}_2\text{La}_4\text{B}_6$

$\text{Bi}(4) \cdot \text{R}_2$

$\text{Sr}_2\text{La}_4\text{B}_6$

$\text{Bi}(4)$, (b

Research

-
22. Aliev, O. M.; Maksudova, T. F.; Samsonova, N. D.; Finkel'shtein, L. D.; Rustamov, P. G. *Inorg. Mater.* **1986**, *22*, 23-27.
23. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162.
24. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805. See also Chapter 8.
25. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, SHELXTL V-5.1, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.
26. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 399-407.
27. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, *252*, 96-99.
28. Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751-767.
29. (a) We believe that the octahedral sites 1-4 are occupied exclusively by Bi atoms. This is supported by the structure of the Sr analog where there is no doubt for the identity of these sites. Also bond-valence calculations in $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ indicate that these four octahedral sites should be occupied by Bi. For the remaining six sites, that contain La, the bond-valence results are harder to evaluate because there is always the possibility of a triple Pb/La/Bi disorder. Bond-valence sums in $\text{Pb}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ are: 2.897 for Bi(1), 3.117 for Bi(2), 3.050 for Bi(3) and 3.048 for Bi(4) ($R_0 = 2.552$, $B = 0.370$). Using the same parameters the bond-valence sums in $\text{Sr}_2\text{La}_x\text{Bi}_{8-x}\text{S}_{14}$ are: 2.976 for Bi(1), 3.193 for Bi(2), 3.076 for Bi(3) and 3.072 for Bi(4). (b) VALENCE v2.00, distributed by I. D. Brown, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

30. Prewitt.

31. Rodier.

32. Carre, D.

33. Krämer.

34. Miehe, C.

35. Lemoine.

36. (a) Yao.

Franzen.

H. F. J. J.

J. Am. C.

State Che

Chem. 20

-
30. Prewitt, C. T.; Sleight, A. W. *Inorg. Chem.* **1968**, *7*, 1090-1093.
31. Rodier, N. *Bull. Soc. Fr. Mineral. Cristallogr.* **1973**, *96*, 350-355.
32. Carre, D.; Laruelle, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 70-73.
33. Krämer, V.; Reis, I. *Acta Crystallogr., Sect. C* **1986**, *C42*, 249-251.
34. Mieke, G. *Nature (London), Phys. Sci.* **1971**, *231*, 133-134.
35. Lemoine, P.; Carre, D.; Guittard, M. *Acta Cryst.*, **1982**, *B37*, 1281-1284.
36. (a) Yao, X. Q.; Franzen, H. F. *J. Solid State Chem.* **1990**, *86*, 88-93. (b) Yao, X. Q.; Franzen, H. F. *Z. Anorg. Allg. Chem.* **1991**, *598*, 353-362. (c) Yao, X. Q.; Franzen, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 1426-1427. (d) Marking, G. A.; Franzen, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 6126-6130. (e) Cheng, J.; Franzen, H. F. *J. Solid State Chem.* **1996**, *121*, 362-371. (f) Richter, K. W.; Franzen, H. F. *J. Solid State Chem.* **2000**, *150*, 347-355.

A_xP

1. Introduction

Bismuth

structural dive

occurring bism

if bismuth cha

this area of ch

chalcogenides

A large d

is the potentia

CHAPTER 7

Synthesis and Characterization of the New Quaternary Bismuth Selenides:

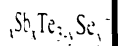
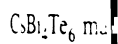


1. Introduction

Bismuth chalcogenides consist a family of compounds that presents a remarkable structural diversity and complexity. These characteristics are not only found in natural occurring bismuth sulfosalts¹ but also in the great number of ternary²⁻¹² and quaternary¹²⁻¹⁷ bismuth chalcogenides synthesized during the last decade. Prior to these developments this area of chemistry was relatively unexplored with only a few bismuth ternary¹⁸⁻²⁵ chalcogenides known.

A large driving force behind the great interest in multinary bismuth chalcogenides is the potential that these compounds have as thermoelectric materials. Several

compounds



Our wo

chalcogenide

similar proper

incorporation

Furthermore t

quaternary sys

reported on α -

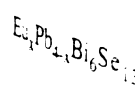
have also perfo

Sr and Ba as w

alkaline earth m

We repor

characterization



thermopower me

compounds such as $\text{KBi}_{6.33}\text{S}_{10}$ ⁴, $\text{K}_2\text{Bi}_8\text{S}_{13}$ ⁴, $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ⁵, $\text{K}_{1+x}\text{Pb}_{4-2x}\text{Bi}_{7+x}\text{Se}_{15}$ ¹⁷ and CsBi_4Te_6 ⁸ are promising candidates for thermoelectric applications. For example CsBi_4Te_6 may achieve a ZT ²⁶ of 0.8 at 225 K, a value superior to that of the best $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ ²⁷ alloys at the same temperature.

Our work in ternary bismuth systems A/Bi/Q (A = alkali or alkaline earth; Q = chalcogenide) has been expanded to include the quaternary A/Pb/Bi/Q . Pb has many similar properties with Bi and since it has different charge balancing requirements its incorporation in the ternary systems could lead to the formation of new structure types. Furthermore the great number of known Pb/Bi/S ²⁸ compounds suggests that the quaternary systems would also present a rich structural chemistry. We have already reported on $\alpha\text{-}\beta\text{-APbBi}_3\text{Q}_6$ ¹⁵ ($\text{A} = \text{K, Rb, Cs}$; $\text{Q} = \text{S, Se}$) and $\text{K}_{1+x}\text{Pb}_{4-2x}\text{Bi}_{7+x}\text{Se}_{15}$ ¹⁷. We have also performed corresponding investigations with the alkaline earth metals such as Sr and Ba as well as Eu which due to its similarity in size and chemical reactivity to the alkaline earth metals can be considered a pseudo alkaline earth element.²⁹

We report here the synthesis, physicochemical, spectroscopic, and structural characterization of five new compounds, $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$, $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$, $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$, $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$. Electrical conductivity and thermopower measurements on selected systems are also reported.

2. Experiment

Reagents

mesh, Cerac.

Quebec, Cana.

powder (99.95

Advanced Ma

City, MI), lead

(99.9%, <250

Chinese Rare

powder (99.99

(99.5%, -20 me

Cerac, Milwauk

Synthesis

a Vacuum Atmo

methanol and eth

almost quantitat

comparing the

2. Experimental section

Reagents. Chemicals were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999%, Noranda Advanced Materials, Quebec, Canada), bismuth chunks (99.999%, Tellurex, Traverse City, MI), selenium powder (99.95%, -200 mesh, Cerac, Milwaukee, WI), selenium shots (99.999%, Noranda Advanced Materials, Quebec, Canada), selenium shots (99.999%, Tellurex, Traverse City, MI), lead powder (99.999%, -20 mesh, Cerac, Milwaukee, WI), europium powder (99.9%, <250 mm, Alfa Aesar, Ward Hill, MA), europium metal chunk³⁰ (99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), bismuth selenide powder (99.999%, -325 mesh, Cerac Inc., Milwaukee), strontium selenide powder (99.5%, -20 mesh, Cerac, Milwaukee, WI), barium selenide powder (99.5%, -20 mesh, Cerac, Milwaukee, WI).

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All products were washed with degassed methanol and ether to remove any traces of excess flux. For all compounds the yield was almost quantitative and the purity and homogeneity of the products was verified by comparing the X-ray powder diffraction patterns to those calculated by the

crystallography

Bi₂Se₃

transferred in

to 600 °C in

product was g

PbSe.

transferred int

tube was heated

in 10 h. The pr

EuSe.

was transferred

The tube was h

then to 800 °C

The product w

Eu₂Pb₃

mmol) Pb, 0.2

carbon coated

for 72 h at 900

product consis

crystallographically determined atomic coordinates.

Bi₂Se₃. A mixture of 9.407 g (0.045 mol) of Bi and 5.331 g (0.068 mol) of Se was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 600 °C in 12 h, kept at 600 °C for 2 days and then cooled down to 50 °C in 6 h. The product was ground into a fine powder and used for further reactions.

PbSe. A mixture of 6.114 g (0.030 mol) of Pb and 2.330 g (0.030 mol) of Se was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 650 °C in 12 h, kept at 650 °C for 72 h and then cooled down to 50 °C in 10 h. The product was ground into a fine powder and used for further reactions.

EuSe. A mixture of 0.900 g (5.900 mmol) of Eu and 0.465 g (5.900 mmol) of Se was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 300 °C in 24 h, kept at 300 °C for 24 h, heated to 400 °C in 24 h, then to 800 °C to 24 h, kept at 800 °C for 48 h and then cooled down to 50 °C in 10 h. The product was ground into a fine powder (dark red) and used for further reactions.

Eu_xPb_{4-x-3y}Bi_{4+2y}Se₁₀ (I). A mixture of 0.080 g (0.526 mmol) Eu, 0.109 g (0.526 mmol) Pb, 0.220 g (1.053 mmol) Bi and 0.208 g (2.634 mmol) Se was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated for 72 h at 900 °C, cooled to 500 °C in 12 h and then further cooled to 50 °C in 10 h. The product consisted of an ingot made of rod shaped needles. Semiquantitative energy

dispersive

needles gave

Sr_4Pb

(0.360 mm)

coated silica

at 900 °C, con

ingot made of

composition of

Eu_4Pb

mmol) Bi_2Se_3

which was ins

heated for 24

temperature for

consisted of an

gave an average

$\text{Sr}_x\text{Pb}_{4-x}$

mmol) Bi_2Se_3 and

dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of $\text{Eu}_{2.21}\text{Pb}_{1.70}\text{Bi}_{3.91}\text{Se}_{10}$.

$\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (II). A mixture of 0.060 g (0.360 mmol) SrSe, 0.236 g (0.360 mmol) Bi_2Se_3 and 0.103 g (0.360 mmol) PbSe was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated for 99 h at 900 °C, cooled to 600 °C in 30 h and then to 50 °C in 10 h. The product consisted of an ingot made of rod shaped needles. EDS/SEM analysis on several needles gave an average composition of $\text{Sr}_{2.06}\text{Pb}_{1.87}\text{Bi}_{3.96}\text{Se}_{10}$.

$\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (III). A mixture of 0.090 g (0.390 mmol) EuSe, 0.343 g (0.524 mmol) Bi_2Se_3 and 0.100 g (0.349 mmol) PbSe was transferred into a carbon crucible which was inserted into a silica tube. The tube was flame-sealed under vacuum and heated for 24 h at 650 °C, further heated to 950 °C in 3h which remained at that temperature for 12 h, cooled to 500 °C in 30 h and then to 50 °C in 10 h. The product consisted of an ingot made of rod shaped needles. EDS/SEM analysis on several needles gave an average composition of $\text{Eu}_{1.79}\text{Pb}_{2.08}\text{Bi}_{5.91}\text{Se}_{13}$.

$\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (IV). A mixture of 0.072 g (0.432 mmol) SrSe, 0.340 g (0.520 mmol) Bi_2Se_3 and 0.074 g (0.259 mmol) PbSe was transferred into a carbon coated silica

tube, which

cooled to 5°

made of rock

composition

Ba₁Pb

mmol Bi₂Se

tube, which w

as in the case

analysis on se

3. Physical Me

The ins

Thermal Analys

and Powder X-r

Single-C

Platform CCD

frames covering

tube, which was flame-sealed under vacuum. The tube was heated for 48 h at 880 °C, cooled to 580 °C in 30 h and then to 50 °C in 10 h. The product consisted of an ingot made of rod shaped needles. EDS/SEM analysis on several needles gave an average composition of $\text{Sr}_{1.79}\text{Pb}_{2.08}\text{Bi}_{5.91}\text{Se}_{13}$.

$\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ (V). A mixture of 0.075 g (0.347 mmol) BaSe, 0.272 g (0.415 mmol) Bi_2Se_3 and 0.139 g (0.486 mmol) EuSe was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated using the same profile as in the case of (II). The product consisted of an ingot made of needles. EDS/SEM analysis on several needles gave an average composition of $\text{Ba}_{2.36}\text{Pb}_{3.66}\text{Bi}_{5.88}\text{Se}_{15}$.

3. Physical Measurements

The instrument and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis*, *Infrared Spectroscopy*, *Charge-transport conductivity measurements*, and *Powder X-ray diffraction* is the same as that in Chapter 2 (Section 3).

Single-Crystal X-ray Crystallography. A Bruker (formerly Siemens) SMART Platform CCD diffractometer was used for data collection. Several different sets of frames covering a random area of the reciprocal space were collected using 0.3° steps in

e

a

S

Si

Er

ce

me

Pa

B

Sc

d

as

St

Ac

B

0.5

me

ω at a detector-to-sample distance of ~5 cm. The SMART³¹ software was used for data acquisition and SAINT³¹ for data extraction. The absorption correction was done with SADABS³¹ and the structure solution (direct methods) and refinement was done with the SHELXTL³¹ package of crystallographic programs.

Eu_xPb_{4-x-3y}Bi_{4+2y}Se₁₀ (I). A hemisphere of data was collected (1271 frames) with an exposure time of 20 sec per frame. The resolution of the data set was 0.78 Å. The final cell was calculated from 4842 [$I > 10\sigma(I)$] reflections in the data set (Table 7-1). Eight metal atoms *Ml* and ten selenium atoms were found to sit on a crystallographic mirror plane and the structure has the general formula Ml_8S_{10} where *Ml* is any combination of Bi, Pb or Eu. Pb and Bi due to their close chemical resemblance and similar X-ray scattering properties cannot be crystallographically distinguished. We expected to have disorder between the different metal atoms so initially all the metal positions were refined as Bi together with the occupancy of all metal positions (R1 = 9.4%, wR2 = 19.1%). The structure contains five octahedral and three high (>6) coordinate sites. For four of the octahedral sites the occupancy did not change indicating that these sites are occupied by Bi or/and Pb. For the three high (>6) coordinate sites the occupancy dropped to less than 0.5 (theoretical full occupancy). In these three sites, Eu was introduced in the refinement since the coordination environments and bond distances are consistent with other

compounds³² that contain Eu and Se. The remaining octahedral site also showed a small decrease in occupancy (95% occupied). We chose not to introduce Eu in this site since the shortest bonds are at ~ 2.77 Å which are too short for Eu-Se distances e.g., in EuSe^{33} , Eu has an octahedral coordination with Eu-Se at ~ 3.00 Å. Instead, this site was modeled with partial occupation. The formula at that point was $\text{Eu}_{2.07}\square_{0.08}\text{Bi}_{5.85}\text{Se}_{10}$. In order for the compound to charge balance it needs to have the general formula $\text{Eu}_x\square_y\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ where x and y are the crystallographically refined amounts of the Eu and the vacancies respectively. This rationale gave $\text{Eu}_{2.07}\square_{0.08}\text{Pb}_{1.69}\text{Bi}_{4.16}\text{Se}_{10}$ as the final formula. The formula agrees well the EDS ratio that gives an average composition of $\text{Eu}_{2.21}\text{Pb}_{1.70}\text{Bi}_{3.91}\text{Se}_{10}$. All the atoms were refined anisotropically ($R1 = 5.3\%$, $wR2 = 11.2\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 7-2.

$\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (II). A full sphere of data was collected (2082 frames) with an exposure time of 30 sec per frame. The final cell was calculated from 3079 [$I > 20\sigma(I)$] reflections (Table 7-1). The resolution of the data set was 0.75 Å. Because the compound is isostructural with (I), the fractional atomic coordinates from (I) were used for initial refinement of the structure after replacing the Eu with Sr. Final R values, $R1 = 5.6\%$,



wR2 = 11.3%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 7-3.

Eu_xPb_{4-x}Bi₆Se₁₃ (III). A hemisphere of data was collected (1271 frames) with an exposure time of 12 sec per frame. The final cell was calculated from 1284 [$I > 10\sigma(I)$] reflections (Table 7-4). The resolution of the data set was 0.78 Å. Similar to (I), ten metal atoms *Ml* and thirteen selenium atoms were found to sit on a crystallographic mirror plane and the structure has the general formula $Ml_{10}S_{13}$ where *Ml* is any combination of Bi, Pb or Eu. Initially all the ten metal sites were modeled as bismuth and their occupancies were refined ($R1 = 7.1\%$, $wR2 = 15.5\%$). Only four sites had an occupancy less than 0.5 (full occupancy) and in these sites (M7-M10) Eu was introduced. Site M7 is octahedral while M8-M10 have higher (>6) coordination numbers. The remaining octahedral sites M1-M6 were fully occupied with Bi/Pb. All atoms were refined anisotropically ($R1 = 6.1\%$, $wR2 = 11.8\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 7-5.

Sr_xPb_{4-x}Bi₆Se₁₃ (IV). Over a hemisphere of data was collected (1567 frames) with an exposure time of 45 sec per frame. The final cell was calculated from 4856 [$I > 10\sigma(I)$] reflections (Table 7-4). The resolution of the data set was 0.70 Å. Because the compound is isostructural with (III), the fractional atomic coordinates from (III) were used for initial refinement of the structure after replacing the Eu with Sr. Final R values

$R1 = 4.4\%$, $wR2 = 10.9\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 7-6.

Ba_xPb_{6-x}Bi₆Se₁₅ (V). A full sphere of data was collected (2132 frames) with an exposure time of 30 sec per frame. The final cell was calculated from 8452 [$I > 10\sigma(I)$] reflections (Table 7-4). The resolution of the data set was 0.69 Å. Nine metal atoms *MI*, three barium and ten selenium atoms were found to sit on a crystallographic mirror plane and the structure has the general formula Ba₃*MI*₉Se₁₅ where *MI* is a combination of Bi and Pb. The nine metal sites were refined as Bi together with the occupancies of all twelve metal sites ($R1 = 4.8\%$, $wR2 = 12.0\%$). Only two Ba sites had occupancies more than 0.5 and at the same time two peaks ($\sim 10 \text{ e} \cdot \text{\AA}^{-3}$) appeared close ($\sim 0.4\text{-}0.6 \text{ \AA}$) to these Ba atoms. Whereas, the Ba atoms are sitting in the center of the trigonal prismatic site (*A*) those peaks were shifted to the side (*B*) having three short bonds ($\sim 3.0 \text{ \AA}$) trans to three ($> 3.4 \text{ \AA}$) longer bonds. The two peaks were assigned as Bi (Pb) and after refinement the R values were $R1 = 4.0\%$ and $wR2 = 9.9\%$. The formula at this stage was Ba_{2.62}Bi_{9.38}Se₁₅ but for electroneutrality reasons the final formula should be (Ba,Pb)₆Bi₆Se₁₅ or Ba_{2.62}Pb_{3.38}Bi₆Se₁₅. The formula agrees well the EDS ratio that gives an average composition of Ba_{2.36}Pb_{3.66}Bi_{5.88}Se₁₅. Constrains were used to set the occupancy of the two split sites *10* and *11* to 0.5 (fully occupied) with no significant

change in the R-values. All atoms were refined anisotropically ($R1 = 2.9\%$, $wR2 = 6.2\%$). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 7-7.

Bond Valence Calculations. The program VaList³⁴ was used for the calculation of bond valence sums. The following parameters, taken from the program were used for the calculations; $R_0 = 2.70$, $B = 0.35$ for Bi^{3+} ; $R_0 = 2.69$, $B = 0.37$ for Pb^{2+} ; $R_0 = 2.72$, $B = 0.37$ for Sr^{2+} ; $R_0 = 2.66$, $B = 0.37$ for Eu^{2+} and $R_0 = 2.88$, $B = 0.37$ for Ba^{2+} . The CIF files generated by SHELXL were used as input.

Table 7-1. Crystallographic Data for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$.

Empirical formula	$\text{Eu}_{2.07}\text{Pb}_{1.69}\text{Bi}_{4.16}\text{Se}_{10}$ (I)	$\text{Sr}_{1.94}\text{Pb}_{1.92}\text{Bi}_{4.09}\text{Se}_{10}$ (II)
Formula weight	2323.80	2213.15
Temperature, K	293(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions, Å	$a = 24.6321(1)$ $b = 4.2232(1)$ $c = 19.8927(4)$	$a = 24.708(2)$ $b = 4.2374(4)$ $c = 20.017(2)$
Z, Volume, Å ³	4, 2069.36(6)	4, 2095.8(3)
Density (calculated), g/cm ³	7.459	7.014
Absorption coefficient, mm ⁻¹	72.692	71.681
F(000)	3817	3644
Crystal size, mm ³	0.60 x 0.04 x 0.04	0.41 x 0.04 x 0.04
θ range for data collection	1.32 to 27.09°	1.65 to 28.44°
Index ranges	$-31 \leq h \leq 30$ $-5 \leq k \leq 5$ $-25 \leq l \leq 16$	$-32 \leq h \leq 32$ $-5 \leq k \leq 5$ $-26 \leq l \leq 26$
Reflections collected	10792	15456
Independent reflections	2492 [$R_{\text{int}} = 0.1164$]	2821 [$R_{\text{int}} = 0.0741$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2492 / 0 / 114	2821 / 0 / 113
Goodness-of-fit on F^2	0.959	1.104
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0525$, $wR2 = 0.1117$	$R1 = 0.0556$, $wR2 = 0.1133$
R indices (all data)	$R1 = 0.0723$, $wR2 = 0.1169$	$R1 = 0.0709$, $wR2 = 0.1184$
Extinction	0.00066(4)	-
Largest peak and hole, e.Å ⁻³	4.938 and -2.975	3.659 and -3.116

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 7-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.0655(1)	-0.2500	-0.0390(1)	22(1)	
M(2)	0.2004(1)	-0.7500	-0.0924(1)	19(1)	
M(3)	0.6731(1)	-0.7500	0.1865(1)	18(1)	
M(4)	0.3487(1)	0.2500	0.0186(1)	19(1)	
M(5)	0.5113(1)	-0.7500	0.0936(1)	21(1)	0.921(5)
M(6)	0.5418(1)	-0.2500	0.2694(1)	23(1)	0.51(2)
Eu(6)	0.5418(1)	-0.2500	0.2694(1)	23(1)	0.49(2)
M(7)	0.2041(1)	-0.2500	0.1142(1)	19(1)	0.14(2)
Eu(7)	0.2041(1)	-0.2500	0.1142(1)	19(1)	0.86(2)
M(8)	0.3697(1)	-0.2500	0.2103(1)	26(1)	0.28(2)
Eu(8)	0.3697(1)	-0.2500	0.2103(1)	26(1)	0.72(2)
Se(1)	0.0022(1)	-0.2500	0.0877(2)	21(1)	
Se(2)	0.1387(1)	-0.7500	0.0235(1)	18(1)	
Se(3)	0.1374(1)	-0.2500	-0.1568(1)	19(1)	
Se(4)	0.2716(1)	-0.2500	-0.0303(1)	19(1)	
Se(5)	0.7408(1)	-0.2500	0.2296(1)	17(1)	
Se(6)	0.6258(1)	-0.7500	0.3094(1)	17(1)	
Se(7)	0.5902(1)	-0.2500	0.1288(1)	19(1)	
Se(8)	0.2964(1)	0.2500	0.1396(1)	15(1)	
Se(9)	0.4220(1)	-0.2500	0.0618(2)	20(1)	
Se(10)	0.4641(1)	-0.7500	0.2199(1)	19(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 7-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.0655(1)	-0.2500	-0.0386(1)	19(1)	
M(2)	0.2002(1)	-0.7500	-0.0926(1)	13(1)	
M(3)	0.6731(1)	-0.7500	0.1869(1)	13(1)	
M(4)	0.3488(1)	0.2500	0.0176(1)	14(1)	
M(5)	0.5113(1)	-0.7500	0.0939(1)	17(1)	0.955(5)
M(6)	0.5419(1)	-0.2500	0.2699(1)	18(1)	0.601(9)
Sr(6)	0.5419(1)	-0.2500	0.2699(1)	18(1)	0.399(9)
M(7)	0.2050(1)	-0.2500	0.1144(1)	18(1)	0.173(9)
Sr(7)	0.2050(1)	-0.2500	0.1144(1)	18(1)	0.827(9)
M(8)	0.3709(1)	-0.2500	0.2071(1)	26(1)	0.287(9)
Sr(8)	0.3709(1)	-0.2500	0.2071(1)	26(1)	0.713(9)
Se(1)	0.0021(1)	-0.2500	0.0872(2)	18(1)	
Se(2)	0.1386(1)	-0.7500	0.0229(1)	12(1)	
Se(3)	0.1374(1)	-0.2500	-0.1558(1)	14(1)	
Se(4)	0.2721(1)	-0.2500	-0.0312(1)	14(1)	
Se(5)	0.7407(1)	-0.2500	0.2290(1)	11(1)	
Se(6)	0.6260(1)	-0.7500	0.3091(1)	12(1)	
Se(7)	0.5899(1)	-0.2500	0.1295(1)	13(1)	
Se(8)	0.2974(1)	0.2500	0.1385(1)	10(1)	
Se(9)	0.4226(1)	-0.2500	0.0605(2)	15(1)	
Se(10)	0.4645(1)	-0.7500	0.2200(1)	13(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 7-4. Crystallographic Data for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$, $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

Empirical formula	$\text{Eu}_{2.29}\text{Pb}_{1.72}\text{Bi}_6\text{Se}_{13}$ (III)	$\text{Sr}_{2.08}\text{Pb}_{1.92}\text{Bi}_6\text{Se}_{13}$ (IV)
Formula weight	2982.92	2860.41
Temperature, K	293(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$
Unit cell dimensions, Å	$a = 16.975(2)$ $b = 4.2106(5)$ $c = 18.260(2)$ $\beta = 90.646(2)^\circ$	$a = 17.064(2)$ $b = 4.2157(6)$ $c = 18.359(3)$ $\beta = 90.623(2)^\circ$
Z, Volume, Å ³	2, 1305.1(3)	2, 1320.7(3)
Density (calculated), g/cm ³	7.591	7.193
Absorption coefficient, mm ⁻¹	74.828	74.075
F(000)	2449	2353
Crystal size, mm ³	0.13 x 0.03 x 0.03	0.65 x 0.026 x 0.26
θ range for data collection	1.12 to 25.03°	3.52 to 30.31°
Index ranges	$-20 \leq h \leq 19$ $-3 \leq k \leq 5$ $-21 \leq l \leq 21$	$-20 \leq h \leq 23$ $-5 \leq k \leq 5$ $-24 \leq l \leq 24$
Reflections collected	6282	10812
Independent reflections	2586 [$R_{\text{(int)}} = 0.0958$]	3964 [$R_{\text{(int)}} = 0.0493$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2586 / 0 / 144	3964 / 0 / 144
Goodness-of-fit on F^2	0.963	1.028
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0608$, $wR2 = 0.1183$	$R1 = 0.0436$, $wR2 = 0.1087$
R indices (all data)	$R1 = 0.1116$, $wR2 = 0.1361$	$R1 = 0.0531$, $wR2 = 0.1127$
Extinction	0.00109(7)	0.00073(6)
Largest peak and hole, e.Å ⁻³	3.412 and -3.839	3.673 and -3.680

Table 7-4. (cont'd).

Empirical formula	Ba _{2.62} Pb _{3.38} Bi ₆ Se ₁₅ (V)
Formula weight	3498.41
Temperature, K	295(2)
Crystal system	Monoclinic
Space group	<i>P2₁/m</i>
Unit cell dimensions, Å	<i>a</i> = 17.335(2) <i>b</i> = 4.2900(5) <i>c</i> = 21.823(3) <i>β</i> = 98.619(2)°
Z, Volume, Å ³	2, 1604.6(43)
Density (calculated), g/cm ³	7.241
Absorption coefficient, mm ⁻¹	70.593
F(000)	2864
Crystal size, mm ³	0.50 x 0.02 x 0.02
<i>θ</i> range for data collection	1.62 to 30.92°
Index ranges	-24 ≤ <i>h</i> ≤ 24 -5 ≤ <i>k</i> ≤ 5 -27 ≤ <i>l</i> ≤ 30
Reflections collected	17923
Independent reflections	5095 [<i>R</i> _(int) = 0.0338]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5095 / 0 / 166
Goodness-of-fit on <i>F</i> ²	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0286, <i>wR</i> 2 = 0.0615
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0382, <i>wR</i> 2 = 0.0645
Extinction	0.000255(18)
Largest peak and hole, e.Å ⁻³	2.685 and -2.207

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 7-5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.0070(1)	-0.2500	0.6202(1)	14(1)	
M(2)	0.1881(1)	-0.2500	0.4568(1)	15(1)	
M(3)	0.3930(1)	-0.7500	0.4771(1)	18(1)	
M(4)	0.6743(1)	-0.7500	0.1213(1)	14(1)	
M(5)	0.4167(1)	0.2500	0.0788(1)	14(1)	
M(6)	0.1709(1)	-0.7500	0.0193(1)	13(1)	
M(7)	0.5132(1)	-0.2500	0.2518(1)	18(1)	0.78(3)
Eu(7)	0.5132(1)	-0.2500	0.2518(1)	18(1)	0.22(3)
M(8)	0.2237(1)	-0.7500	0.6796(1)	21(1)	0.46(3)
Eu(8)	0.2237(1)	-0.7500	0.6796(1)	21(1)	0.54(3)
M(9)	0.2437(2)	-0.2500	0.2279(1)	24(1)	0.17(3)
Eu(9)	0.2437(2)	-0.2500	0.2279(1)	24(1)	0.83(3)
M(10)	0.0107(2)	-0.7500	0.8413(1)	32(1)	0.30(4)
Eu(10)	0.0107(2)	-0.7500	0.8413(1)	32(1)	0.70(4)
Se(1)	0.1068(3)	-0.2500	0.7368(2)	14(1)	
Se(2)	-0.0784(3)	-0.7500	0.6855(2)	15(1)	
Se(3)	0.2646(3)	-0.7500	0.3711(2)	15(1)	
Se(4)	0.4807(3)	-0.2500	0.4086(2)	18(1)	
Se(5)	0.3049(3)	-0.2500	0.5616(2)	17(1)	
Se(6)	0.1049(3)	-0.7500	0.5411(3)	14(1)	
Se(7)	0.7820(3)	-0.2500	0.1461(2)	15(1)	
Se(8)	0.6394(3)	-0.7500	0.2662(2)	13(1)	
Se(9)	0.5418(3)	-0.2500	0.0906(2)	13(1)	
Se(10)	0.3871(3)	0.2500	0.2257(2)	16(1)	
Se(11)	0.3002(3)	-0.2500	0.0601(2)	14(1)	
Se(12)	0.1249(3)	-0.7500	0.1643(2)	15(1)	
Se(13)	0.0685(3)	-0.2500	-0.0163(2)	14(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 7-6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.0073(1)	-0.2500	0.6195(1)	16(1)	
M(2)	0.1888(1)	-0.2500	0.4569(1)	17(1)	
M(3)	0.3937(1)	-0.7500	0.4777(1)	22(1)	
M(4)	0.6745(1)	-0.7500	0.1213(1)	15(1)	
M(5)	0.4167(1)	0.2500	0.0787(1)	15(1)	
M(6)	0.1709(1)	-0.7500	0.0200(1)	14(1)	
M(7)	0.5130(1)	-0.2500	0.2520(1)	19(1)	0.866(5)
Sr(7)	0.5130(1)	-0.2500	0.2520(1)	19(1)	0.134(5)
M(8)	0.2229(1)	-0.7500	0.6806(1)	26(1)	0.470(6)
Sr(8)	0.2229(1)	-0.7500	0.6806(1)	26(1)	0.530(6)
M(9)	0.2432(1)	-0.2500	0.2268(1)	30(1)	0.295(6)
Sr(9)	0.2432(1)	-0.2500	0.2268(1)	30(1)	0.705(6)
M(10)	0.0083(1)	-0.7500	0.8387(1)	43(1)	0.289(6)
Sr(10)	0.0083(1)	-0.7500	0.8387(1)	43(1)	0.711(6)
Se(1)	0.1063(1)	-0.2500	0.7357(1)	14(1)	
Se(2)	-0.0785(1)	-0.7500	0.6834(1)	14(1)	
Se(3)	0.2649(1)	-0.7500	0.3718(1)	16(1)	
Se(4)	0.4798(1)	-0.2500	0.4090(1)	20(1)	
Se(5)	0.3052(1)	-0.2500	0.5618(1)	17(1)	
Se(6)	0.1055(1)	-0.7500	0.5400(1)	16(1)	
Se(7)	0.7814(1)	-0.2500	0.1447(1)	14(1)	
Se(8)	0.6401(1)	-0.7500	0.2650(1)	16(1)	
Se(9)	0.5412(1)	-0.2500	0.0904(1)	13(1)	
Se(10)	0.3870(1)	0.2500	0.2250(1)	16(1)	
Se(11)	0.3003(1)	-0.2500	0.0595(1)	15(1)	
Se(12)	0.1255(1)	-0.7500	0.1640(1)	14(1)	
Se(13)	0.0696(1)	-0.2500	-0.0159(1)	15(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 7-7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.4555(1)	-0.7500	0.6714(1)	18(1)	
M(2)	0.2483(1)	-0.2500	0.6133(1)	19(1)	
M(3)	-0.0339(1)	-0.2500	0.4069(1)	22(1)	
M(4)	0.1830(1)	0.2500	0.4435(1)	21(1)	
M(5)	0.3969(1)	-0.2500	0.4707(1)	21(1)	
M(6)	0.1905(1)	-0.2500	0.1025(1)	17(1)	
M(7)	-0.0699(1)	-0.2500	0.0659(1)	18(1)	
M(8)	0.3223(1)	-0.7500	-0.0212(1)	15(1)	
M(9)	0.0504(1)	0.2500	0.2146(1)	20(1)	
M(10) [§]	0.6737(2)	-0.2500	0.7344(2)	31(1)	0.202(6)
Ba(10) [§]	0.6842(1)	-0.2500	0.7215(1)	14(1)	0.798(6)
M(11) [§]	0.2303(3)	-0.2500	0.8148(3)	32(1)	0.156(6)
Ba(11) [§]	0.2163(1)	-0.2500	0.7997(1)	15(1)	0.844(6)
Ba(12)	0.5041(1)	-0.7500	0.1313(1)	16(1)	
Se(1)	0.5667(1)	-0.7500	0.7728(1)	15(1)	
Se(2)	0.3740(1)	-0.2500	0.7208(1)	16(1)	
Se(3)	-0.1788(1)	-0.2500	0.3211(1)	18(1)	
Se(4)	0.0403(1)	0.2500	0.3491(1)	26(1)	
Se(5)	0.2631(1)	-0.2500	0.3822(1)	18(1)	

Table 7-7. (cont'd).

Se(6)	0.4634(1)	-0.7500	0.3985(1)	21(1)
Se(7)	0.3270(1)	0.2500	0.5438(1)	18(1)
Se(8)	0.1061(1)	-0.2500	0.5146(1)	18(1)
Se(9)	0.2982(1)	-0.7500	0.1209(1)	16(1)
Se(10)	0.1751(1)	-0.2500	0.2257(1)	17(1)
Se(11)	0.0546(1)	0.2500	0.0779(1)	16(1)
Se(12)	-0.0725(1)	-0.2500	0.1925(1)	17(1)
Se(13)	0.1893(1)	-0.2500	-0.0493(1)	17(1)
Se(14)	0.3493(1)	-0.7500	-0.1417(1)	14(1)
Se(15)	0.4280(1)	-0.2500	0.0113(1)	15(1)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both. [§]Ba10 and Ba11 are sitting in the center (A) of the trigonal prismatic site while M10 and M11 are shifted to the side (B).

4. Results and Discussion

Synthesis and thermal behavior. $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ($A = Eu, Sr$) was synthesized by reacting ASe ($A = Eu, Sr$), $PbSe$ and Bi_2Se_3 at $\sim 1:1:1$ molar ratio. Increasing the amount of Bi_2Se_3 gives rise to the $A_xPb_{4-x}Bi_6Se_{13}$ phase ($A = Eu, Sr$) which forms along with $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ($A = Eu, Sr$). Pure $A_xPb_{4-x}Bi_6Se_{13}$ ($A = Eu, Sr$) is obtained from the reaction of ASe ($A = Eu, Sr$), $PbSe$ and Bi_2Se_3 in $\sim 1:1:2$ molar ratio. When the amount of Bi_2Se_3 is increased a mixture of Bi_2Se_3 with $A_xPb_{4-x}Bi_6Se_{13}$ ($A = Eu, Sr$) is obtained.

Interestingly, the all-Pb analog $Pb_2Bi_2Se_5$, (or $Pb_4Bi_4Se_{10}$) of $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ($A = Eu, Sr$) could not be prepared although the $Pb_4Sb_4Se_{10}$ ³⁵ compound is known. Instead $Pb_5Bi_6Se_{14}$ ³⁶ is formed which adopts the structure of cannizarite²⁸⁽ⁱ⁾.

$Ba_xPb_{6-x}Bi_6Se_{15}$ forms by reacting with $BaSe$, $PbSe$ and Bi_2Se_3 in a 2.6:3.4:3 molar ratio. For all compounds there seems to be a narrow range of x under which they are obtained in a pure form.

The DTA of $Eu_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ is shown in Figure 7-1.

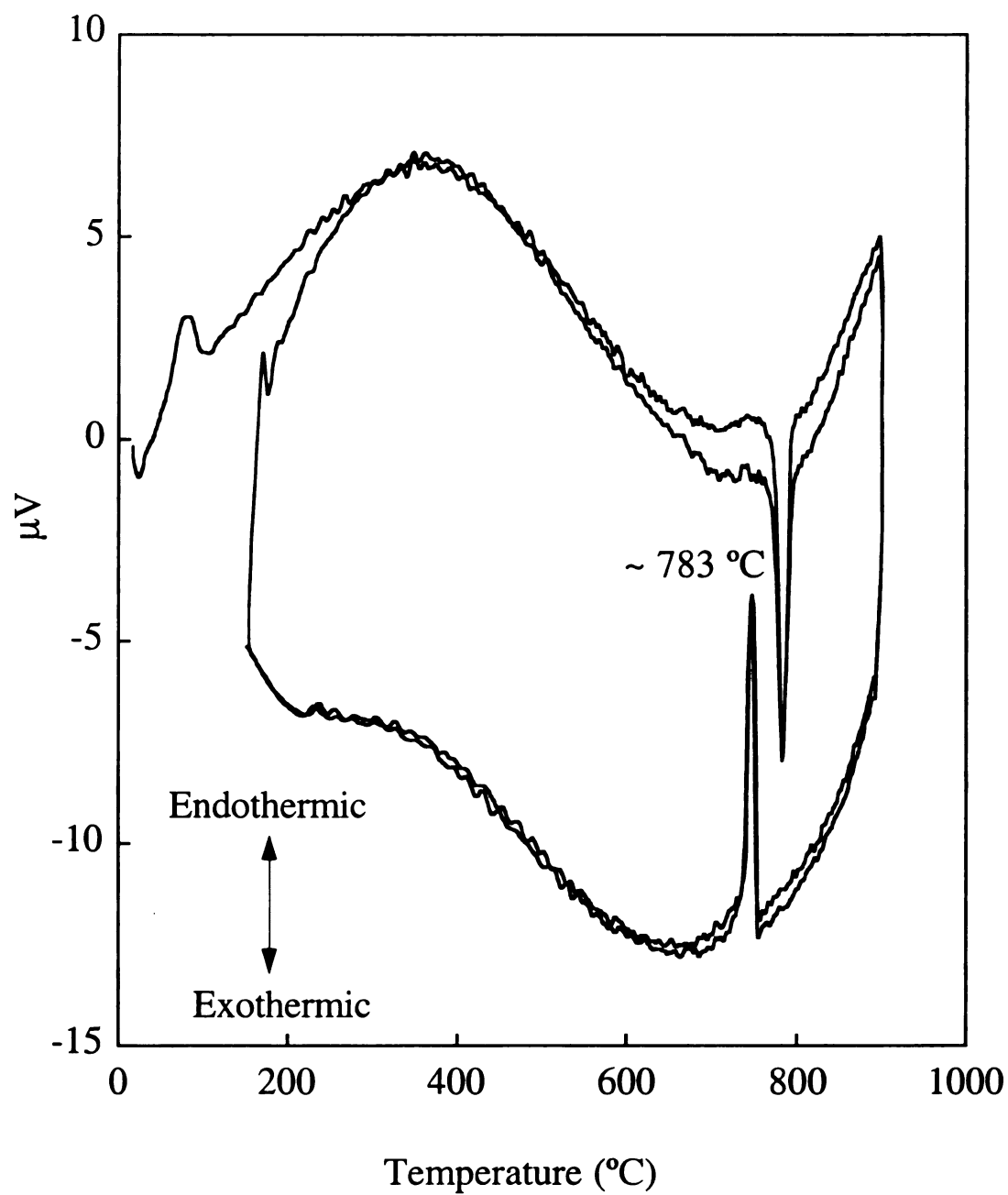


Figure 7-1. Typical DTA diagram of $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (II), (III), (IV) and (V) give

similar diagrams.

(I), (II) and (IV) compounds melt congruently between 780 °C and 820 °C, namely (I) melts at ~784 °C, (II) at ~780 °C and (V) at ~814 °C. (II) and (IV) melt with decomposition around ~780 °C. The X-ray powder diffraction pattern after DTA resembles that of $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$.

Structure description

$\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (I) and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (II). The two compounds adopt the cosalite $\text{Pb}_2\text{Bi}_2\text{S}_5$ ^{28(f)} structure, see Figure 7-2. Since they are isostructural only (I) will be described in detail. Because of the very similar sizes^{29(b)} of Eu^{2+} and Sr^{2+} often Eu and Sr analogs adopt the same structure such as in ABi_2S_4 ^{22,37} and $\text{A}_4\text{Sb}_3\text{S}_9$ (A = Eu, Sr)³⁸.

This structure type is very stable and several compounds such as $\text{Pb}_4\text{Sb}_4\text{Se}_{10}$ ³⁵, $\text{KBi}_{6.33}\text{S}_{10}$ ⁴, $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ ³⁹ and TlBi_3Se_5 ³⁶ belong to it. The structure consists of elongated NaCl-type infinite blocks that are arranged in a zigzag fashion. The space that between the NaCl-type blocks is filled up with CdI_2 -type fragments. There are several sites, mainly located on the outside (surface) of the NaCl-type block that exhibit mixed occupancy between the Eu or Sr and the Bi/Pb atoms.

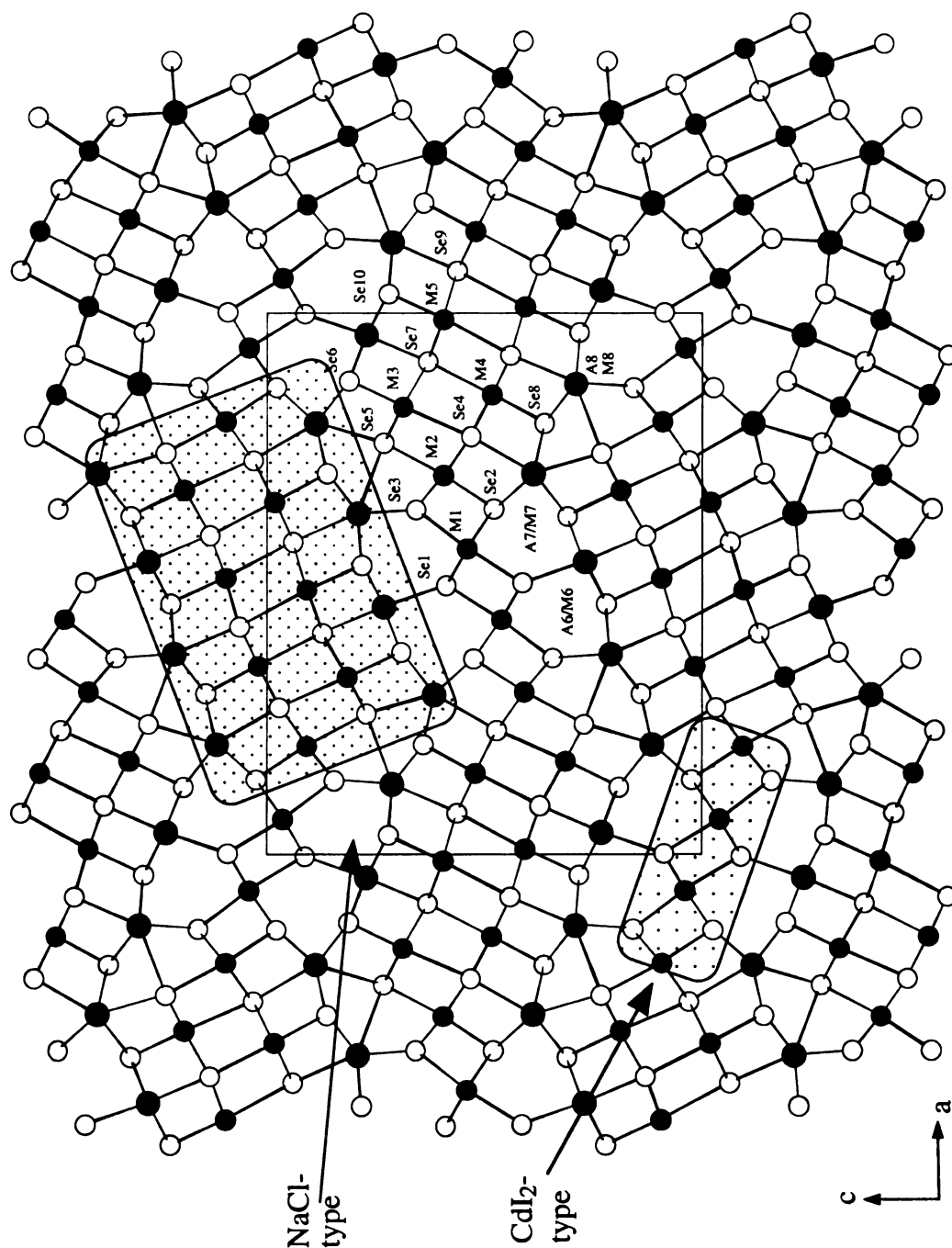


Figure 7-2. Projection of the structure of $A_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ ($A = \text{Eu}, \text{Sr}$) down the b -axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks. The gray circles indicate the sites where there is disorder with Eu.

Sites M1-M6 have a octahedral coordination while M7 and M8 are eight coordinate having a bicapped trigonal prismatic coordination. Sites M1-M4 are fully occupied by Bi/Pb with no contribution from Eu. Site M5 is partially occupied with Bi/Pb while sites M6, M7 and M8 display mixed occupancy and contain Eu.

All the octahedral sites exhibit varying degrees of distortion (Table 7-8). M1 is slightly distorted with M1-Se distances varying between 2.860(2)-3.042(2) Å and Se-M1-Se angles varying between 87.92(7)-95.19(9)°. M2 and M4 are distorted towards a square pyramid having a short M-Se bond ~2.7 Å trans to a longer one (>3.0 Å) and four almost equal M-Se bonds (2.9-3.0 Å). For example M4 has a short bond at 2.730(3) Å, four bonds between 2.908(2)-3.000(2) and a long bond trans to the short one at 3.296(3) Å. M3 and M5 are distorted towards a trigonal pyramid having three short bonds to Se atoms trans to three longer ones e.g. M3 has a short bond at 2.709(3) Å trans to a long one at 3.394(3) and two bonds at 2.825(2) Å trans to two bonds at 3.152(2) Å. M6/Eu6 is the least distorted atom approaching the ideal octahedral coordination with six equidistant bonds and all angles at 90°. M6/Eu6 has six bonds varying between 3.005(3)-3.062(2) Å and angles varying between 87.20(8)-95.95(7)°. This site contain ~50 % Eu. Sites M7/Eu7 and M8/Eu8 have bicapped trigonal prismatic coordination with distances varying between 3.144(2)-3.321(3) Å and 3.113(2)-3.392(3) Å respectively. These two trigonal prismatic sites are mainly occupied by Eu.

The Sr analog has many similar characteristics with (I). As shown in Table 7-8 the distances are very similar in both compounds. Furthermore the occupancies in the disordered sites are very similar e.g. in (I) site M8 contains ~72 % Eu while the same site in (II) contains ~71% Sr.

If we compare $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ with other compounds that adopt the same structure type we notice that the trigonal prismatic sites exhibit mixed occupancy e.g. in $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ ³⁹ the sites M7 and M8 display K/Bi mixed occupancy. Also M5 is partially occupied in other compounds e.g. 81% in $\text{KBi}_{6.33}\text{S}_{10}$ ⁴ and 93% in $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ ³⁹.

Pb and Bi are crystallographically indistinguishable and in an attempt to evaluate the distribution of Pb and Bi in two structures the bond valence sums for all metal sites were calculated. Tables 7-9 and 7-10 summarize these calculations. As it can be seen, in both (I) and (II), sites M1-M4 (octahedral sites with full occupancy) have bond valence sums around ~3 suggesting that most probably are exclusively occupied by Bi. Site M5 has a bond valence sum ~2.5 indicating a mixture of 3+ ion (Bi) and a 2+ ion (Pb or Eu). Since this site has bonds around 2.77 Å which are short for Eu^{2+} -Se bonds we think that M5 is partially occupied, containing only Bi and Pb. The partial occupancy in that site as mentioned above is something encountered in other compounds adopting the same structure type. Site M6 has also a bond valence sum less than 3, ~2.3 indicating a mixture

of 3+ and 2+ ions. As mentioned above this site is the least distorted with six almost equal M-Se bonds between 3.005(3)-3.062(2) Å. These kind of distances are both found in PbSe and ASe (A = Eu, Sr), therefore we believe that site M6 is occupied by all three Bi, Pb and Eu (Sr). The two remaining trigonal prismatic sites have bond valence sums slightly less than 2. This indicates that most probably these two sites are mainly occupied by Pb and Eu (Sr).

The use of bond-valence sums seems to be a reasonably reliable and convenient way to assign metal sites in these compounds. In a recent paper⁴⁰ synchrotron radiation was used to distinguish between Pb and Bi in certain sulfosalts, taking advantage the anomalous dispersion effects near the corresponding absorption edges. One of the compounds studied was cosalite $\text{Pb}_2\text{Bi}_2\text{S}_5$. Atom assignments, made using the bond-valence sums, agree well with the atom assignment in this paper, thus validating the practice. Using the same atom naming as in (I) and (II), it was found that sites M1-M4 are occupied by Bi whereas sites M5-M8 are occupied by Pb.

Table 7-8. Bond Distances (Å) and selected angles (deg) for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (I) and $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (II).

	(I)	(II)		(I)	(II)
M(1)-Se(1)	2.860(2) x2	2.869(2) x2	M(2)-Se(2)	2.762(3)	2.766(3)
M(1)-Se(3)	2.938(3)	2.943(3)	M(2)-Se(3)	2.917(2) x2	2.915(2) x2
M(1)-Se(1)	2.962(3)	2.965(3)	M(2)-Se(4)	3.012(2) x2	3.025(2) x2
M(1)-Se(2)	3.042(2) x2	3.044(2) x2	M(2)-Se(5)	3.091(3)	3.098(3)
M(3)-Se(6)	2.709(3)	2.708(3)	M(4)-Se(8)	2.730(3)	2.733(3)
M(3)-Se(5)	2.825(2) x2	2.827(2) x2	M(4)-Se(9)	2.908(2) x2	2.925(2) x2
M(3)-Se(7)	3.152(2) x2	3.166(2) x2	M(4)-Se(4)	3.000(2) x2	3.006(2) x2
M(3)-Se(4)	3.394(3)	3.399(3)	M(4)-Se(7)	3.296(3)	3.312(3)
	(I)	(II)			
M(6)/A(6)-Se(1)	3.005(3)	3.023(3)			
M(6)/A(6)-Se(10)	3.015(2) x2	3.025(3) 2			
M(6)/A(6)-Se(7)	3.041(3)	3.050(3)			
M(6)/A(6)-Se(6)	3.062(2) x2	3.071(2) x2			
M(7)/A(7)-Se(8)	3.144(2) x2	3.152(2) x2			
M(7)/A(7)-Se(2)	3.212(2) x2	3.246(2) x2			
M(7)/A(7)-Se(5)	3.234(3)	3.256(3)			
M(7)/A(7)-Se(6)	3.238(2) x2	3.263(2) x2			
M(7)/A(7)-Se(4)	3.321(3)	3.351(3)			
M(8)/A(8)-Se(8)	3.113(2) x2	3.109(2) x2			
M(8)/A(8)-Se(10)	3.147(2) x2	3.148(2) x2			
M(8)/A(8)-Se(9)	3.223(3)	3.202(3)			
M(8)/A(8)-Se(3)	3.388(3) x2	3.472(3) x2			
M(8)/A(8)-Se(5)	3.392(3)	3.461(3)			

Table 7-8. (cont'd).

	(I)	(II)
Se(1)-M(1)-Se(2)	87.92(7)	88.31(6)
Se(3)-M(1)-Se(2)	88.21(7)	87.94(6)
Se(1)-M(1)-Se(1)	95.19(9)	95.23(8)
Se(1)-M(1)-Se(2)	175.21(8)	175.50(7)
Se(3)-M(2)-Se(5)	82.01(7)	82.41(6)
Se(4)-M(2)-Se(5)	95.12(7)	94.66(6)
Se(2)-M(2)-Se(5)	174.57(8)	174.77(8)
Se(7)-M(3)-Se(4)	85.78(6)	85.80(6)
Se(5)-M(3)-Se(5)	96.74(9)	96.07(8)
Se(5)-M(3)-Se(7)	173.51(6)	173.25(5)
Se(9)-M(4)-Se(4)	88.69(5)	88.74(5)
Se(9)-M(4)-Se(7)	88.80(7)	88.60(6)
Se(9)-M(4)-Se(9)	93.13(9)	92.84(7)
Se(9)-M(4)-Se(4)	177.82(7)	177.86(6)
Se(10)-M(5)-Se(9)	83.58(7)	84.42(6)
Se(7)-M(5)-Se(9)	91.64(5)	91.52(5)
Se(7)-M(5)-Se(9)	176.05(8)	176.30(6)
Se(6)-M(6)-Se(6)	87.20(8)	87.25(7)
Se(1)-M(6)-Se(10)	95.95(7)	96.17(7)
Se(10)-M(6)-Se(6)	175.46(9)	174.93(8)

M = Pb, Bi or both for (I) and (II), A = Eu for (I) and Sr for (II)

Table 7-9. Selected Bond-Valence Sums for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$.

Site Number	Atom type	Oxidn. state assumed	Bond Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	2.998	0
	Pb	(2)	3.027	51
	Eu	(2)	2.790	40
2	Bi	(3)	3.061	2
	Pb	(2)	3.081	54
	Eu	(2)	2.841	42
3	Bi	(3)	3.063	2
	Pb	(2)	3.061	53
	Eu	(2)	2.824	41
4	Bi	(3)	3.052	2
	Pb	(2)	3.068	53
	Eu	(2)	2.829	41
5	Bi	(3)	2.502	17
	Pb	(2)	2.536	27
	Eu	(2)	2.338	17
6	Bi	(3)	2.319	23
	Pb	(2)	2.376	19
	Eu	(2)	2.191	10
7	Bi	(3)	1.843	39
	Pb	(2)	1.940	3
	Eu	(2)	1.790	10
8	Bi8	(3)	1.814	40
	Pb	(2)	1.911	4
	Eu	(2)	1.760	12

The atoms in bold indicate the most probable metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Table 7-10. Selected Bond-Valence Sums for $\text{Sr}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$.

Site Number	Atom type	Oxidn. state assumed	Bond Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	2.954	2
	Pb	(2)	2.985	49
	Sr	(2)	3.237	62
2	Bi	(3)	3.021	1
	Pb	(2)	3.042	52
	Sr	(2)	3.301	65
3	Bi	(3)	3.033	1
	Pb	(2)	3.034	52
	Sr	(2)	3.291	65
4	Bi	(3)	2.970	1
	Pb	(2)	2.988	49
	Sr	(2)	3.241	62
5	Bi	(3)	2.456	18
	Pb	(2)	2.491	25
	Sr	(2)	2.701	35
6	Bi	(3)	2.249	25
	Pb	(2)	2.310	16
	Sr	(2)	2.505	25
7	Bi	(3)	1.730	42
	Pb	(2)	1.831	8
	Sr	(2)	1.981	1
8	Bi	(3)	1.750	42
	Pb	(2)	1.841	8
	Sr	(2)	1.997	0

The atoms in bold indicate the most probable metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Eu_xPb_{4-x}Bi₆Se₁₃ (III) and Sr_xPb_{4-x}Bi₆Se₁₃ (IV). The two compounds are isostructural and adopt the Sr₄Bi₆Se₁₃²⁴ structure type, as shown in Figure 7-3. This structure is also very stable and is one of the most commonly encountered in the A/Bi/Q systems having several members such as K₂Bi₈S₁₃⁴, β-K₂Bi₈Se₁₃⁵, Ba₃Bi_{6.67}Se₁₃¹², Ba₃MBi₆Se₁₃¹² (M = Sn, Pb). The main characteristic is that the [Bi₆Se₁₃]⁸⁻ part of the structure remains intact while the Sr²⁺ positions can be substituted with a variety of similarly sized ions such as Ba²⁺, K⁺, Bi³⁺, Pb²⁺ etc. Often these substitutions result in mixed occupancy between the alkali or alkaline earth metal and the bismuth atoms.

Since the two compounds are isostructural, only (III) will be described in detail. The structure consists of NaCl-, and CdI₂-type infinite rods which connect with each other to form a three-dimensional network. The CdI₂-type rods alternate with NaCl-type fragments forming layers with steps perpendicular to the c-axis. The different kinds of blocks are connected with each other with high (>6) coordinate sites which exhibit mixed occupancy between the Eu (Sr) and the Bi/Pb atoms.

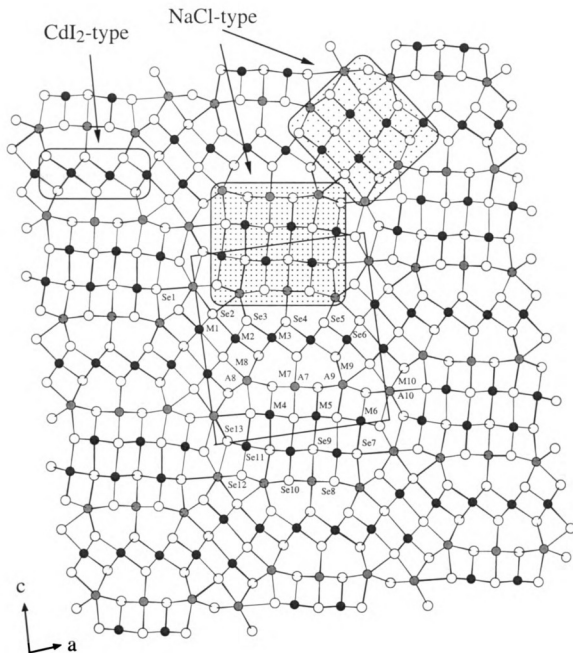


Figure 7-3. Projection of the structure of $A_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ ($A = \text{Eu}, \text{Sr}$) down the b -axis.

The shaded areas indicate the NaCl- and CdI_2 -type building blocks. The gray circles indicate the sites where there is disorder with Eu.

The structure contains 10 metal sites, seven of them M1-M7 are six coordinate having distorted octahedral coordination while the remaining three, M8-M10 have higher coordination residing in bicapped or tricapped trigonal prismatic environments. These three sites, M8, M9 and M10 together with an octahedral one, M7, display an mixed occupancy with Eu. The rest of the octahedral sites M1-M6 are fully occupied by Bi/Pb.

From the six octahedral sites occupied by Bi/Pb, the M(3) site is the least distorted with M(3)-Se distances varying between 2.873(3)-3.018(4) and Se-M(3)-Se angles between 88.2(1)-95.7(1)° (Tables 7-11 and 7-12). The remaining five sites can be divided into two categories, those that are distorted towards a square pyramid and those that are distorted towards a trigonal pyramid. Sites M1, M2 and M5 belong to first category having a short bond trans to longer one for example, M1 has a bond at 2.707(5) Å trans to one at 3.486(5) Å. M4 and M6 have a distortion towards a trigonal pyramid with three short bond trans to three longer ones e.g. M6 has one bond at 2.768(5) Å, two bonds at 2.802(3) Å, two bonds at 3.125(4) Å and one bond at 3.133(5) Å.

From the four sites that display mixed occupancy, the M7/Eu7 approaches the ideal octahedral coordination with six bonds between 2.923(5)-3.036(4) Å and angles between 87.8(1)-93.2(1)°. The same exact characteristic is found also in the previous structure of (I) and (II) where the least distorted octahedral site displays mixed occupancy. This of course could be an artifact of the distance averaging occurring due to mixed atom occupancy.

M8/Eu8 and M9/Eu9 are bicapped trigonal prismatic with M-Se distances varying between 3.084(4)-3.323(4) Å for M8/Eu8 and 3.131(4)-3.372(4) Å for M9/Eu9. M10/Eu10 is tricapped trigonal prismatic with distances varying between 3.120(4)-3.524(6) Å.

The Sr analog presents many similar characteristics with (III) and will not be described further (Tables 7-11 and 7-12).

Again for the purpose of evaluating the distribution of Pb and Bi in the metal sites bond valence calculations were performed for (III) and (IV). The results are summarized in Tables 7-13 and 7-14. The octahedral sites M1-M6 exhibit bond valence sums ≥ 3 , therefore they are assigned as Bi. M7 which is the least distorted octahedral site and M8-M10 with trigonal prismatic coordination have bond valence sums ≤ 2 and should be occupied by Pb and Eu (Sr).

Table 7-11. Bond Distances (Å) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (III) and $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (IV).

	(III)	(IV)		(III)	(IV)
M(1)-Se(1)	2.707(5)	2.707(2)	M(4)-Se(8)	2.718(5)	2.710(2)
M(1)-Se(2)	2.828(3)x2	2.828(1)	M(4)-Se(7)	2.821(3)x2	2.818(1)
M(1)-Se(6)	3.055(4)x2	3.072(1)	M(4)-Se(9)	3.127(4)x2	3.147(1)
M(1)-Se(6)	3.486(5)	3.487(2)	M(4)-Se(11)	3.345(5)	3.351(2)
M(2)-Se(5)	2.740(5)	2.752(2)	M(5)-Se(10)	2.735(5)	2.738(2)
M(2)-Se(3)	2.935(3)x2	2.935(1)	M(5)-Se(11)	2.906(4)x2	2.915(1)
M(2)-Se(6)	2.974(3)x2	2.973(1)	M(5)-Se(9)	2.996(4)x2	2.998(1)
M(2)-Se(2)	3.179(5)	3.175(2)	M(5)-Se(9)	3.179(5)	3.195(2)
M(3)-Se(4)	2.873(3)x2	2.869(1)	M(6)-Se(12)	2.768(5)	2.762(2)
M(3)-Se(3)	2.898(5)	2.918(2)	M(6)-Se(13)	2.802(3)x2	2.800(1)
M(3)-Se(4)	2.975(5)	2.982(2)	M(6)-Se(11)	3.125(4)x2	3.133(1)
M(3)-Se(5)	3.018(4)x2	3.026(1)	M(6)-Se(7)	3.133(5)	3.141(2)
	(III)	(IV)			
M(7)/A(7)-Se(4)	2.923(5)	2.944(2)			
M(7)/A(7)-Se(9)	2.988(5)	3.010(2)			
M(7)/A(7)-Se(8)	3.013(4)x2	3.031(1)			
M(7)/A(7)-Se(10)	3.036(4)x2	3.049(1)			
M(9)/A(9)-Se(12)	3.131(4)x2	3.123(2)x2			
M(9)/A(9)-Se(10)	3.218(4)x2	3.235(2)x2			
M(9)/A(9)-Se(11)	3.221(5)	3.233(2)			
M(9)/A(9)-Se(2)	3.236(5)	3.273(2)			
M(9)/A(9)-Se(3)	3.372(4)x2	3.413(3)x2			
M(10)/A(10)-Se(12)	3.120(4)x2	3.107(2)x2			
M(10)/A(10)-Se(2)	3.207(5)	3.197(2)			
M(10)/A(10)-Se(1)	3.287(4)x2	3.298(2)x2			
M(10)/A(10)-Se(13)	3.479(5)	3.528(2)			
M(10)/A(10)-Se(13)	3.479(4)x2	3.551(2)x2			
M(10)/A(10)-Se(7)	3.524(6)	3.599(2)			

M = Pb, Bi or both for (I) and (II), A = Eu for (I) and Sr for (II)

Table 7-12. Selected Angles (deg) for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (III) and $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ (IV).

	(III)	(IV)
Se(6)-M(1)-Se(6)	83.99(12)	84.24(4)
Se(2)-M(1)-Se(6)	94.56(12)	93.73(4)
Se(2)-M(1)-Se(6)	175.35(10)	174.88(4)
Se(3)-M(2)-Se(2)	79.78(12)	80.20(4)
Se(6)-M(2)-Se(2)	98.42(12)	97.69(4)
Se(3)-M(2)-Se(6)	177.90(14)	177.63(5)
Se(3)-M(3)-Se(5)	88.15(12)	87.93(4)
Se(4)-M(3)-Se(3)	95.71(12)	95.31(4)
Se(3)-M(3)-Se(4)	177.29(15)	177.55(5)
Se(9)-M(4)-Se(11)	85.60(11)	85.54(3)
Se(7)-M(4)-Se(7)	96.52(16)	96.84(5)
Se(8)-M(4)-Se(11)	174.84(15)	174.87(5)
Se(9)-M(5)-Se(9)	84.57(11)	84.45(4)
Se(10)-M(5)-Se(9)	93.86(12)	93.94(4)
Se(10)-M(5)-Se(9)	177.79(15)	177.73(5)
Se(11)-M(6)-Se(11)	84.71(13)	84.58(4)
Se(13)-M(6)-Se(13)	97.42(15)	97.68(5)
Se(12)-M(6)-Se(7)	178.38(15)	178.74(5)
Se(10)-M(7)/A(7)-Se(10)	87.80(14)	87.48(5)
Se(4)-M(7)/A(7)-Se(8)	93.20(12)	93.90(4)
Se(8)-M(7)/A(7)-Se(10)	176.02(14)	175.16(5)

M = Pb, Bi or both for (I) and (II), A = Eu for (I) and Sr for (II)

Table 7-13. Selected Bond-Valence Sums for $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

Site Number	Atom type	Oxidn. state assumed	Bond Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	3.200	7
	Pb	(2)	3.195	60
	Eu	(2)	2.946	47
2	Bi	(3)	3.082	3
	Pb	(2)	3.101	55
	Eu	(2)	2.860	43
3	Bi	(3)	3.050	2
	Pb	(2)	3.077	54
	Eu	(2)	2.837	42
4	Bi	(3)	3.114	4
	Pb	(2)	3.115	56
	Eu	(2)	2.872	44
5	Bi	(3)	3.127	4
	Pb	(2)	2.875	44
	Eu	(2)	2.651	33
6	Bi	(3)	3.201	7
	Pb	(2)	3.208	60
	Eu	(2)	2.957	48
7	Bi	(3)	2.552	15
	Pb	(2)	2.209	10
	Eu	(2)	2.035	2
8	Bi	(3)	1.866	38
	Pb	(2)	1.780	11
	Eu	(2)	1.641	18
9	Bi	(3)	1.776	41
	Pb	(2)	1.713	14
	Eu	(2)	1.579	21
10	Bi1	(3)	1.630	46
	Pb1	(2)	1.628	19
	Eu1	(2)	1.499	25

The atoms in bold indicate the most probable metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Table 7-14. Selected Bond-Valence Sums for $\text{Sr}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

Site Number	Atom type	Oxidn. state assumed	Bond Valence Sum	% Deviation from assumed oxid. state
1	Bi1	(3)	3.164	5
	Pb1	(2)	3.161	58
	Sr1	(2)	3.428	71
2	Bi2	(3)	3.057	2
	Pb2	(2)	2.808	40
	Sr2	(2)	3.045	52
3	Bi3	(3)	3.005	0
	Pb3	(2)	3.032	52
	Sr3	(2)	3.291	65
4	Bi4	(3)	3.114	4
	Pb4	(2)	2.945	47
	Sr4	(2)	3.191	60
5	Bi5	(3)	3.076	3
	Pb5	(2)	2.836	42
	Sr5	(2)	3.077	54
6	Bi6	(3)	3.204	7
	Pb6	(2)	2.913	46
	Sr6	(2)	3.161	58
7	Bi7	(3)	2.424	19
	Pb7	(2)	2.099	5
	Sr7	(2)	2.276	14
8	Bi8	(3)	1.799	40
	Pb8	(2)	1.726	14
	Sr8	(2)	1.870	6
9	Bi9	(3)	1.705	43
	Pb9	(2)	1.657	17
	Sr9	(2)	1.798	10
10	Bi10	(3)	1.577	47
	Pb10	(2)	1.588	21
	Sr10	(2)	1.722	14

The atoms in bold indicate the most probable metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Ba_xPb_{6-x}Bi₆Se₁₅ (V). This structure is related to that of (III) and (IV). It consists of the same NaCl-type building block but the CdI₂-block is thicker, essentially forming a Bi₂Te₃-type block, see Figure 7-4. Other compounds such as A_{1+x}M_{4-2x}M'_{7+x}Se₁₅¹⁷ (A = K, Rb; M = Pb, Sn; M' = Bi, Sb) adopt the same structure. In this structure, there are two bicapped trigonal prismatic sites that display mixed occupancy between Ba and Bi/Pb.

There are twelve metal sites, nine of them are octahedral (M1-M9) and three of them have higher coordination numbers (M10/Ba10, M11/Ba11 and Ba12). The octahedral sites M1-M9 are occupied from Bi/Pb. The bond-valence sum calculations shown in Table 7-15 suggest that only sites 1, 8 and possibly 6 can be regarded as occupied by Bi while all others octahedral sites are probably occupied by both Bi and Pb in different percentages. From the three trigonal prismatic sites only Ba12 is occupied exclusively by Ba whereas the other two (M10/Ba10, M11/Ba11) exhibit a splitting. The Ba atoms reside in the center of the sites (A) while the Bi/Pb is found towards one side (B) of the pocket, see Figure 7-5. Similar to what is found in the two previous systems the octahedral sites exhibit varying degrees of distortion. Sites M2 and M9 are the least distorted with distances varying between 2.9354(8)-3.0637(9) Å and 2.967(1)-3.0292(8) Å respectively (Tables 7-16 and 7-17). Sites M1, M3, M6, and M8 distort towards a trigonal pyramid having three short distances trans to three longer ones e.g. M6 has a bond of 2.740(1) Å trans to a long bond of 3.311(1) Å and two bonds at 2.8324(7) Å

trans to bonds at 3.1718(8) Å. M5 and M7 adopt a distortion towards a square pyramid having only a short bond trans to a longer one e.g. M5 had a short bond at 2.787(1) Å trans to a longer one at 3.455(1) while the remaining four bonds vary between 2.9924(9)-3.0312(9) Å.

Ba10 and Ba11 reside in bicapped trigonal prismatic sites with Ba-Se distances varying between 3.269(2)-3.407(2) Å and 3.266(1)-3.440(1) Å respectively. Both sites also display an splitting, while the Ba atoms are sitting in the center (A) of the trigonal prismatic sites shifted to one side (B) there is an second atom M10, 0.356(5) Å far away from Ba10 and M11, 0.380(6) Å far away from Ba11, see Figure 7-5. This kind of splitting has been in other bismuth chalcogenides such as $ALn_{1\pm x}Bi_{4\pm x}S_8$ ¹³ (A = K, Rb; Ln = La, Ce, Pr, Nd) and $Sr_2La_xBi_{8-x}S_{14}$ ³⁹. Both M10 and M11 have trigonal pyramidal environments having three distances between 3.035(4)-3.123(5) Å for M10 and between 3.028(5)-3.151(6) Å for M11, see Figure 7-5. Ba12 has a tricapped trigonal prismatic coordination with Ba-Se distances varying between 3.3078(9)-3.583(1) Å. That site is fully occupied by Ba and there is no splitting as to what is found in Ba10 and Ba11. Mixed occupancy in the bicapped trigonal sites is also encountered in $A_{1+x}M_4$ _{2x}M'_{7+x}Se₁₅¹⁷ (A = K, Rb; M = Pb, Sn; M' = Bi, Sb) between the alkali metal and Bi (Sb) and or Pb (Sn).

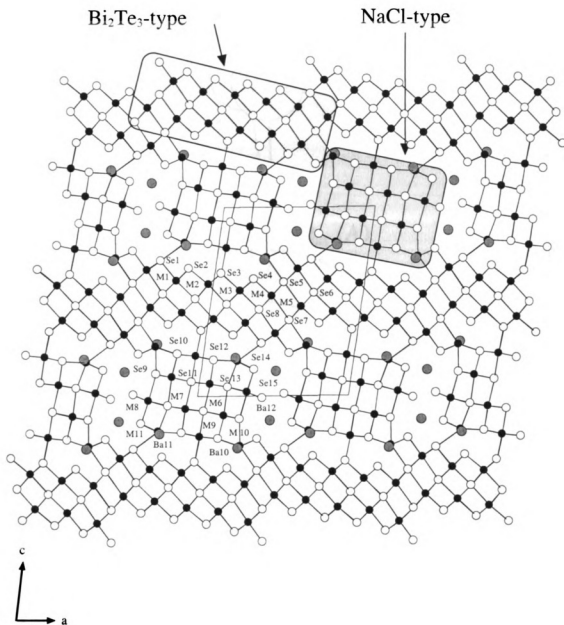


Figure 7-4. Projection of the structure of $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ down the b -axis. The shaded areas indicate the NaCl- and Bi_2Te_3 -type building blocks.

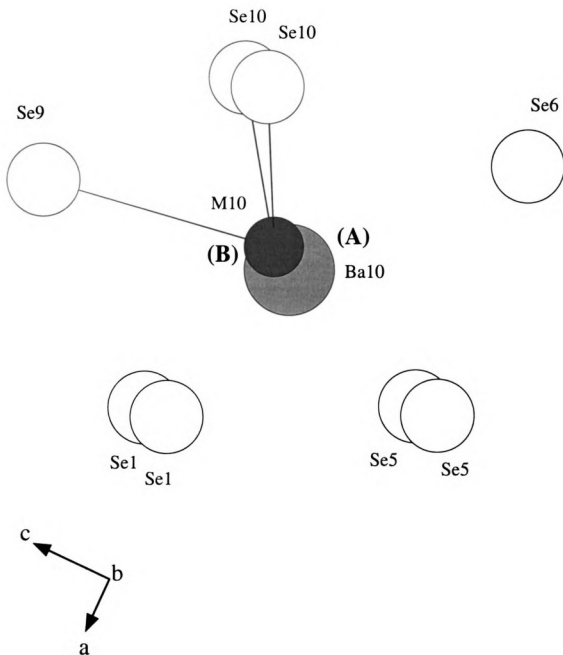


Figure 7-5. The coordination environment of site 10 in $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$. The Ba10 atom is sitting the center (A) of the trigonal prismatic site while the M10 is shifted to the side (B). The same is observed in site 11.

Table 7-15. Selected Bond-Valence Sums for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$.

Site Number	Atom type	Oxidn. state assumed	Bond Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	3.056	2
	Pb	(2)	3.063	53
2	Bi	(3)	2.614	13
	Pb	(2)	2.661	33
3	Bi	(3)	2.644	12
	Pb	(2)	2.683	34
4	Bi	(3)	2.412	20
	Pb	(2)	2.466	23
5	Bi	(3)	2.542	15
	Pb	(2)	2.577	29
6	Bi	(3)	2.959	1
	Pb	(2)	2.967	48
7	Bi	(3)	2.790	7
	Pb	(2)	2.821	41
8	Bi	(3)	3.050	2
	Pb	(2)	3.061	53
9	Bi	(3)	2.504	17
	Pb	(2)	2.555	28
10A	Ba	(2)	2.379	19
	Pb	(2)	1.279	36
10B	Bi	(3)	1.452	52
	Pb	(2)	1.518	24
11A	Ba	(2)	2.301	15
	Pb	(2)	1.248	38
11B	Bi	(3)	1.404	53
	Pb	(2)	1.464	27
12	Ba	(2)	2.079	4
	Pb	(2)	1.155	42

(A) refers to the position in the center of the trigonal prismatic site while (B) to the side. The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Table 7-16. Bond Distances (Å) for Ba_xPb_{6-x}Bi₆Se₁₅.

M(1)-Se(1)	2.709(1)	M(6)-Se(10)	2.740(1)
M(1)-Se(2)	2.8673(8)x2	M(6)-Se(9)	2.8324(7)x2
M(1)-Se(6)	3.0905(9)x2	M(6)-Se(11)	3.1718(8)x2
M(1)-Se(7)	3.294(1)	M(6)-Se(13)	3.311(1)
M(2)-Se(3)	2.9354(8)x2	M(7)-Se(12)	2.771(1)
M(2)-Se(2)	2.952(1)	M(7)-Se(13)	2.9647(8)x2
M(2)-Se(8)	3.022(1)	M(7)-Se(11)	3.0260(8)x2
M(2)-Se(7)	3.0636(9)x2	M(7)-Se(11)	3.188(1)
M(3)-Se(4)	2.8867(9)x2	M(8)-Se(14)	2.739(1)
M(3)-Se(3)	2.899(1)	M(8)-Se(15)	2.8404(7)x2
M(3)-Se(8)	3.115(1)	M(8)-Se(13)	3.1423(8)x2
M(3)-Se(8)	3.1212(9)x2	M(8)-Se(9)	3.190(1)
M(4)-Se(4)	2.972(1)	M(9)-Se(4)	2.967(1)
M(4)-Se(5)	2.9793(9)x2	M(9)-Se(11)	2.994(1)
M(4)-Se(7)	3.065(1)	M(9)-Se(12)	3.0105(8)x2
M(4)-Se(8)	3.0678(9)x2	M(9)-Se(10)	3.0291(8)x2
M(5)-Se(5)	2.787(1)		
M(5)-Se(6)	2.9924(9)x2		
M(5)-Se(7)	3.0313(9)x2		
M(5)-Se(6)	3.455(1)		

Table 7-16. (cont'd).

M(10)-Se(1)	3.035(4)x2	M(11)-Se(14)	3.028(5)x2
M(10)-Se(9)	3.123(5)	M(11)-Se(13)	3.151(6)
M(10)-Se(10)	3.398(3)x2	M(11)-Se(2)	3.455(4)
M(10)-Se(6)	3.463(4)	M(11)-Se(12)	3.461(4)x2
Ba(10)-Se(1)	3.269(2)x2	Ba(11)-Se(14)	3.266(1)x2
Ba(10)-Se(10)	3.322(1)x2	Ba(11)-Se(12)	3.313(1)x2
Ba(10)-Se(5)	3.343(2)x2	Ba(11)-Se(3)	3.385(1)x2
Ba(10)-Se(6)	3.376(2)	Ba(11)-Se(13)	3.398(2)
Ba(10)-Se(9)	3.407(2)	Ba(11)-Se(2)	3.440(1)
Ba(10)-M(10)	0.356(5)	Ba(11)-M(11)	0.380(6)
Ba(12)-Se(14)	3.3078(9)x2		
Ba(12)-Se(1)	3.355(1)x2		
Ba(12)-Se(15)	3.4875(9)x2		
Ba(12)-Se(15)	3.490(1)		
Ba(12)-Se(9)	3.542(1)		
Ba(12)-Se(2)	3.583(1)		

M = Pb, Bi or both.

Table 7-17. Selected Angles (deg) for $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$.

Se(6)-M(1)-Se(7)	83.28(3)	Se(11)-M(6)-Se(13)	86.41(2)
Se(2)-M(1)-Se(2)	96.85(3)	Se(9)-M(6)-Se(9)	98.46(3)
Se(1)-M(1)-Se(7)	177.21(3)	Se(10)-M(6)-Se(13)	174.10(3)
Se(3)-M(2)-Se(2)	85.45(3)	Se(11)-M(7)-Se(11)	85.54(2)
Se(3)-M(2)-Se(3)	93.90(3)	Se(13)-M(7)-Se(13)	92.69(3)
Se(3)-M(2)-Se(7)	177.27(3)	Se(13)-M(7)-Se(11)	177.56(3)
Se(8)-M(3)-Se(8)	85.22(3)	Se(15)-M(8)-Se(9)	86.02(3)
Se(4)-M(3)-Se(3)	96.73(3)	Se(15)-M(8)-Se(15)	98.08(3)
Se(4)-M(3)-Se(8)	172.74(3)	Se(14)-M(8)-Se(9)	177.74(3)
Se(5)-M(4)-Se(7)	86.31(3)	Se(11)-M(9)-Se(10)	87.48(3)
Se(4)-M(4)-Se(5)	94.86(3)	Se(4)-M(9)-Se(10)	93.91(3)
Se(4)-M(4)-Se(7)	178.30(4)	Se(4)-M(9)-Se(11)	178.02(4)
Se(7)-M(5)-Se(6)	81.46(3)		
Se(6)-M(5)-Se(6)	99.03(3)		
Se(6)-M(5)-Se(7)	179.03(3)		

M = Pb, Bi or both.

The same 2x3 structural block of NaCl-type found in $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ and $\text{A}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ ($\text{A} = \text{Eu}, \text{Sr}$) is also found in $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ ⁵ and $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ ³⁹. The only difference between these different types is the thickness of the stepped layers that connect together the NaCl-type blocks.

Energy gaps. The $\text{A}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ compounds ($\text{A} = \text{Eu}, \text{Sr}$) absorb all light in the UV-visible-near-IR range of the spectrum (0.5-6.2eV). The compounds exhibit very broad transitions in the IR range close to the detection limit of the instrument. Figure 7-6a shows a characteristic spectrum for $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$. Compound (II) behaves in a similar way. This lack of a well defined gap transition indicates that these compounds may be heavily doped or possess a large number of defects. Similar optical behavior was found in $\text{KBi}_{6.33}\text{S}_{10}$ ⁴ which adopts the same structure as (I). In contrast, $\text{A}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ ($\text{A} = \text{Eu}, \text{Sr}$) and $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ have well defined band gaps of 0.5 eV and 0.57eV respectively, see Figure 7-6b and 7-6c. By comparison $\text{K}_{1+x}\text{Pb}_{4-2x}\text{Bi}_{7+x}\text{Se}_{15}$ which is isostructural with (V) and $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ which is isostructural with (III) and (IV) have band gaps of 0.53 eV and 0.59 eV, respectively.

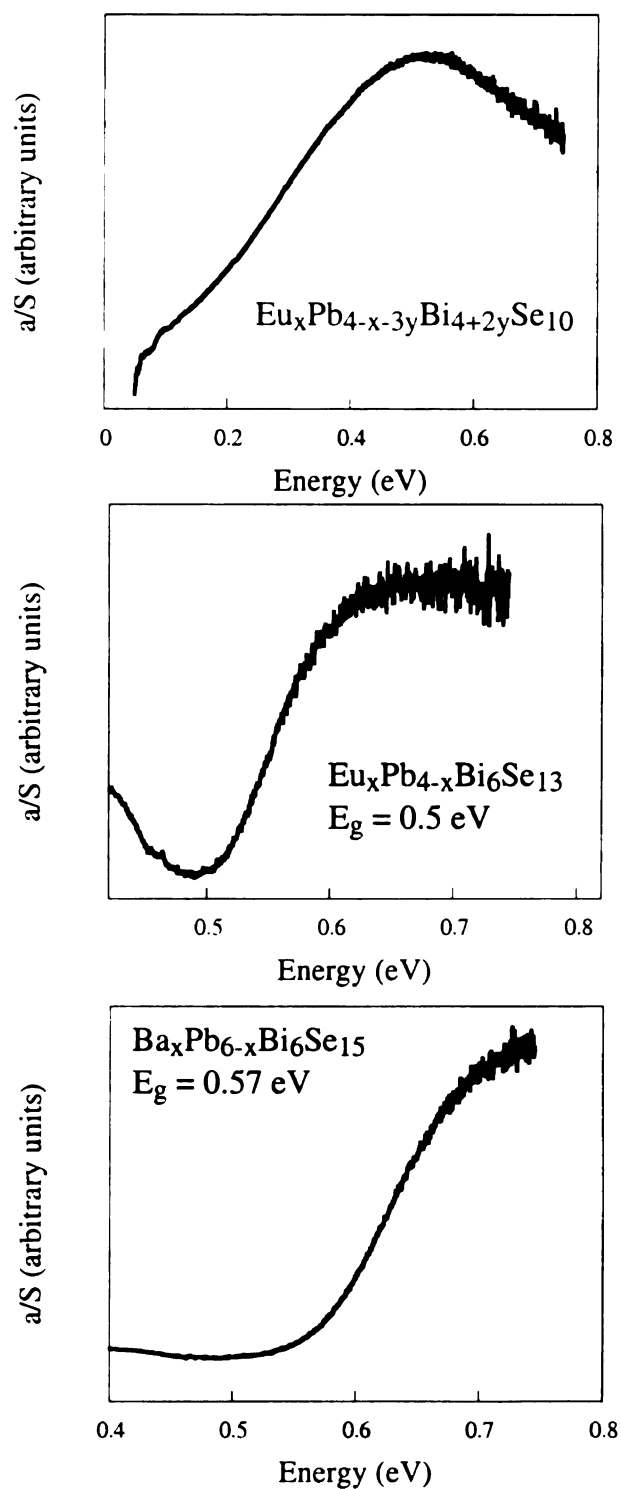


Figure 7-6. Infrared absorption spectra for (a) $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ (b) $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ and (c) $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$. The Sr analogs behave similar to the Eu compounds.

Charge transport properties. Temperature dependent electrical conductivity and thermoelectric power measurements were carried out on needle-shaped single crystals of $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$. Data were obtained from two different crystals that exhibited different levels of doping, see Figure 7-7. One crystal with lower carrier density exhibited room temperature conductivity between 300-500 S/cm and thermopower values of ~ -140 $\mu\text{V/K}$. The temperature dependence of the conductivity of this sample is very weak down to ~ 100 K. At lower temperatures it decreases significantly suggesting a type of carrier localization. The other crystal was more highly doped and had higher electrical conductivity values (>2800 S/cm) and lower thermopower values ~ -25 $\mu\text{V/K}$. The temperature dependence of this sample is metallic like as it is typically found in highly doped narrow gap semiconductors. The thermopower of the lower doped sample increases linearly with the temperature pointing to higher values at higher temperatures.

In an attempt to modify the properties of $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$ we used SbBr_3 as a dopant in several concentrations (0.3%, 0.15%, 0.07% and 0.015% molar). Due to the fragile nature of the crystals, which tended to shatter during cooling, thermopower data were obtained only for two out of four doping concentrations and conductivity data for only three samples. For the fourth sample only partial conductivity data were obtained and they were extrapolated. Figures 7-8 and 7-9 show the conductivity and thermopower data for the different doping ratios. It can be seen that the charge transport behavior of the

doped samples can be varied substantially with respect to the undoped material. All samples exhibit n-type metallic behavior with the thermopower increasing as the temperature increases. The conductivity also increases reaching a maximum and after that exhibits a slow decrease. The conductivity has higher values for the intermediate doping ratios (0.07% and 0.15% molar SbBr_3) with a room temperature value $\sim 1500 \text{ S/cm}$. Examining the values of thermopower we notice that the 0.15% ratio has the highest thermopower with a room temperature value of $\sim -140 \mu\text{V/K}$. The power factor, $S^2 \cdot \sigma$ at room temperature of the 0.15% sample the value is $\sim 29 \mu\text{W/cmK}^2$ which makes it a very promising material for thermoelectric applications. Therefore more work needs to be done to consistently reproduce these results and the thermal conductivity needs to be measured in order to better evaluate the potential of this material.

The electrical conductivity and thermoelectric power were also measured for single crystal of $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$. Figure 7-10 shows the temperature dependence of the electrical conductivity and thermopower. This compound has very similar properties with $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_4\text{Se}_{10}$. No measurements were done on the Sr analogs.

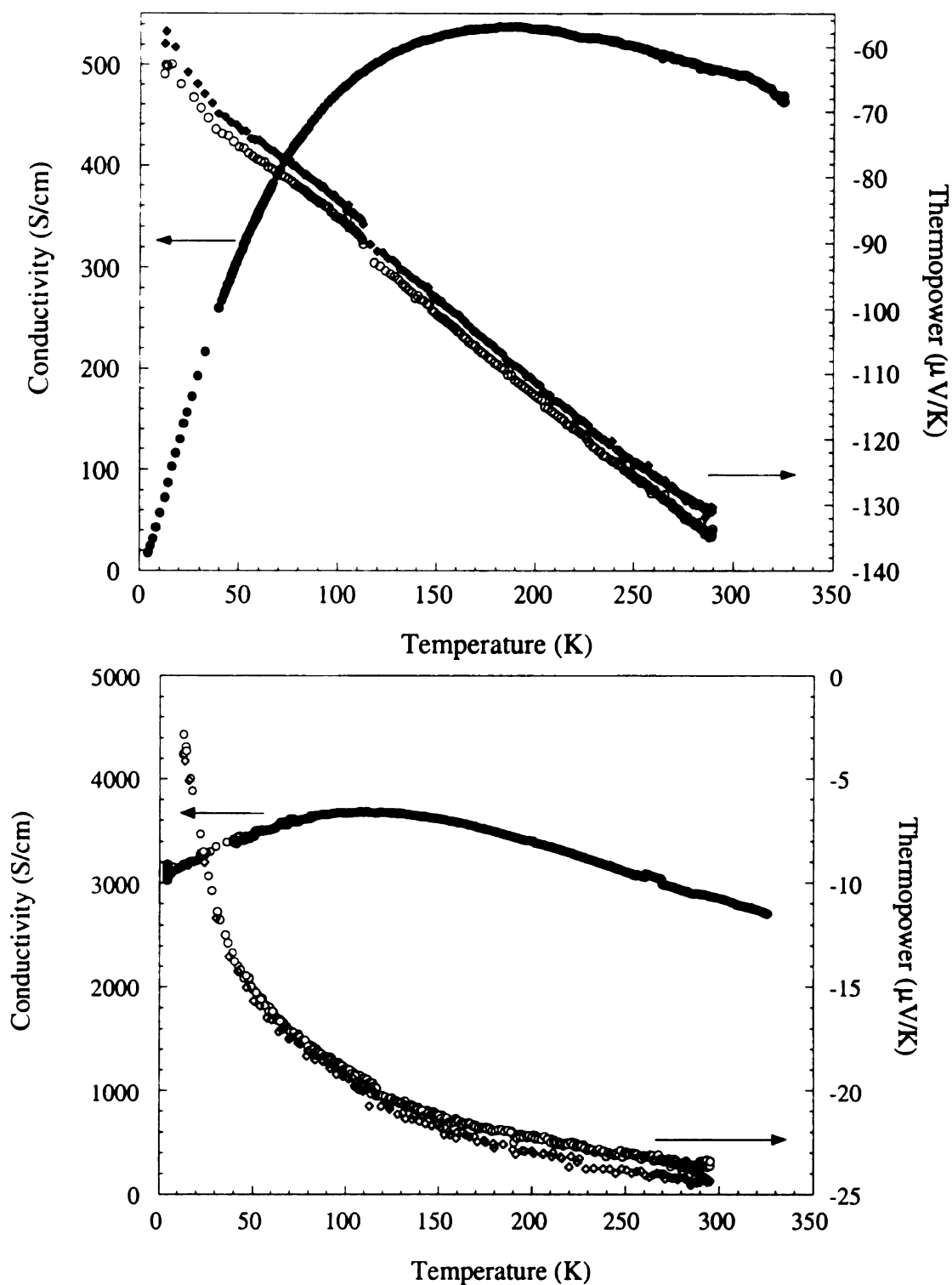


Figure 7-7. Variable temperature electrical conductivity and thermopower for two different sets of single crystals of $\text{Eu}_x\text{Pb}_{4-x-3y}\text{Bi}_{4+2y}\text{Se}_{10}$. The differences in the properties of the two sets are attributed to different doping levels.

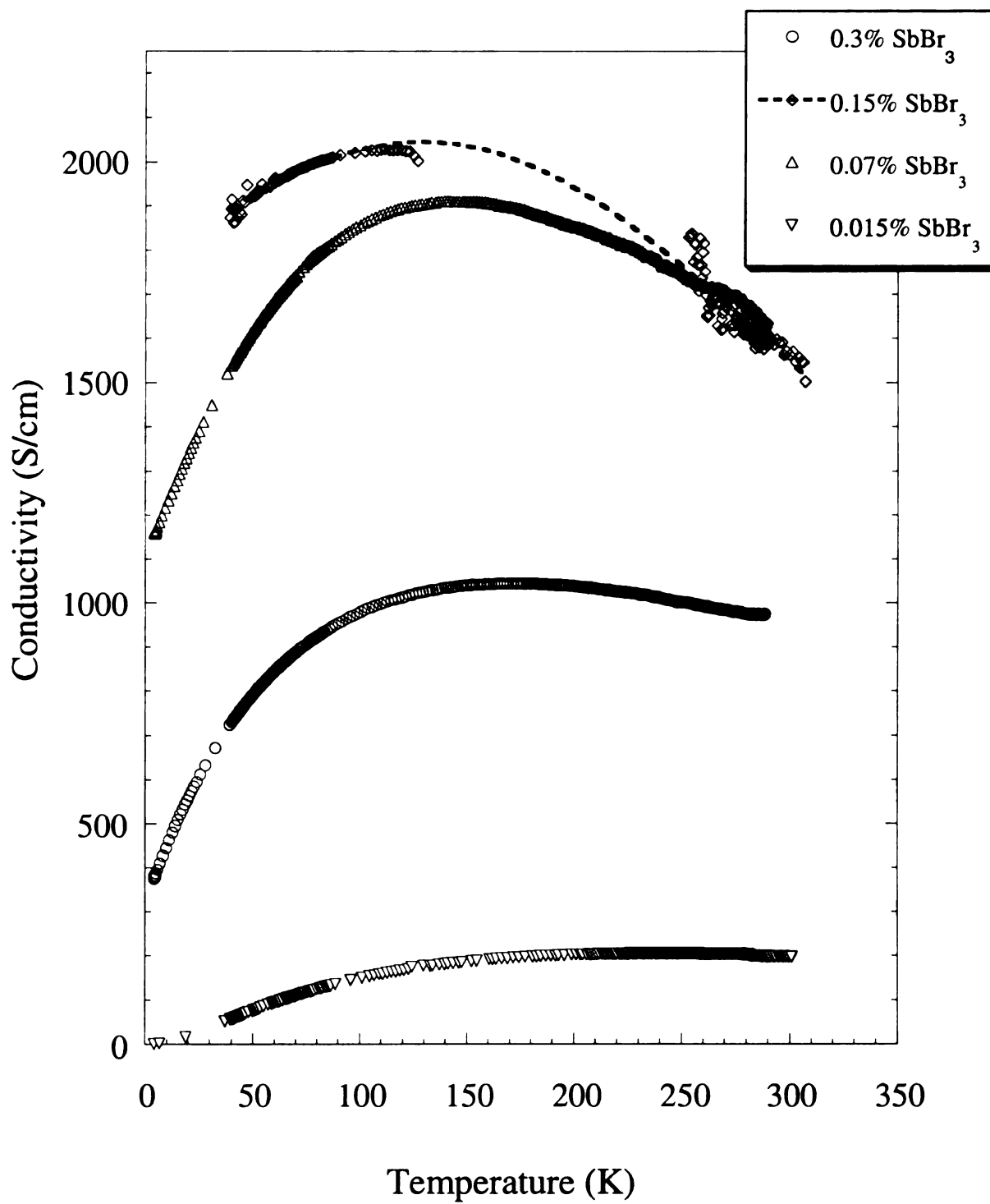


Figure 7-8. Variable temperature electrical conductivity for single crystals of $\text{Eu}_x\text{Pb}_{4-x}$.

$\text{Bi}_{4+2y}\text{Se}_{10}$ doped with various amounts of SbBr_3 .

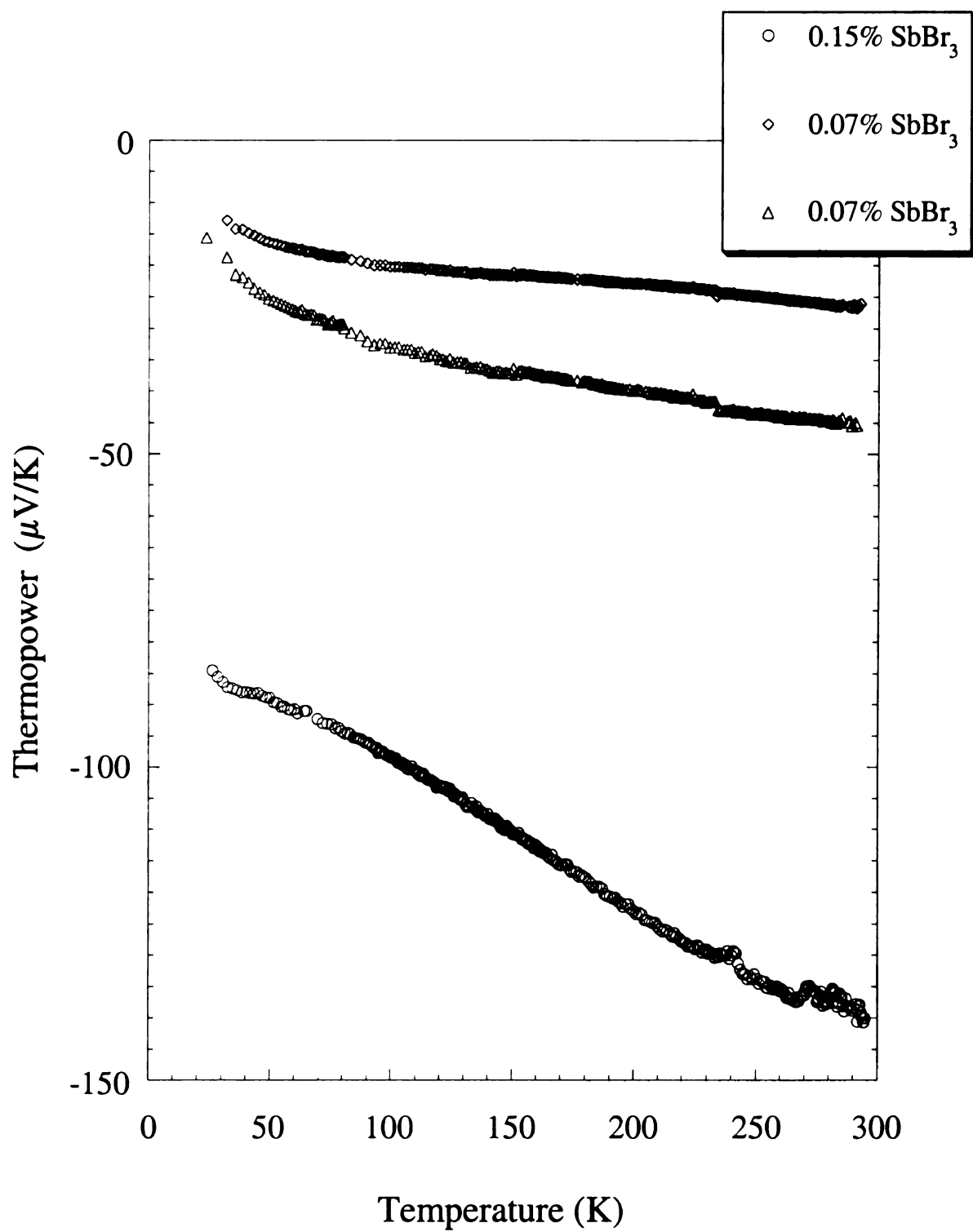


Figure 7-9. Variable temperature thermopower for single crystals of $\text{Eu}_x\text{Pb}_{4-x}$.

$_{3y}\text{Bi}_{4+2y}\text{Se}_{10}$ doped with SbBr_3 .

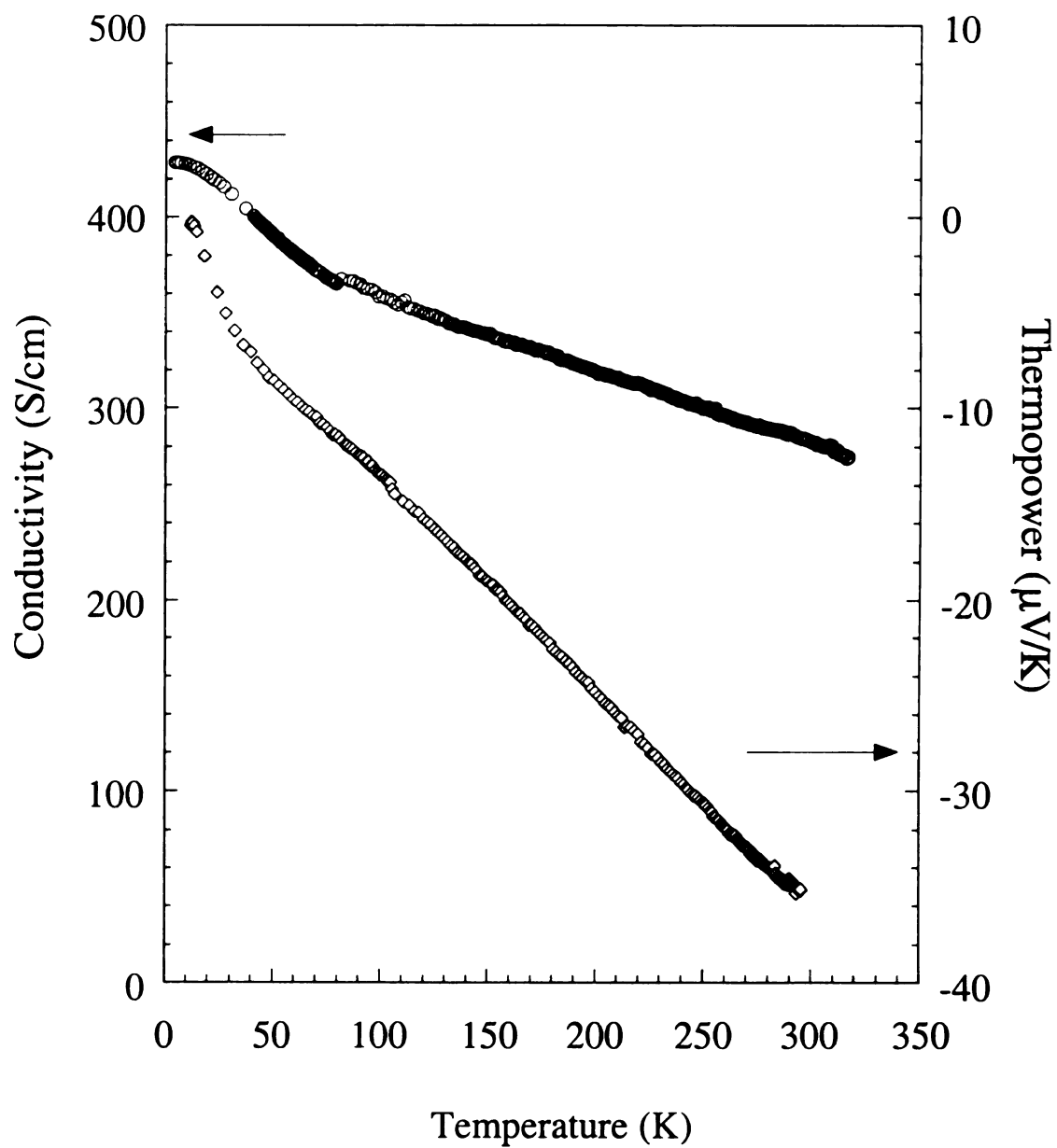


Figure 7-10. Variable temperature electrical conductivity and thermopower for a single crystal of $\text{Eu}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$.

Temperature dependent electrical conductivity and thermoelectric power measurements were also performed on single crystals of $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$. As shown in Figure 7-11 the conductivity of this system is considerably lower with ~ 15 S/cm at room temperature. At lower temperatures it increases reaching a maximum (~ 25 S/cm) between 150-200 K. The origin of the conductivity maximum is not known. Due to the fragile nature of the crystals only room temperature data for thermopower are available which is ~ 360 $\mu\text{V/K}$. Nevertheless based on the previous measurements $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ can be described as having a n-type semiconducting behavior. Compared to $\text{K}_{1+x}\text{Pb}_{4-2x}\text{Bi}_{7+x}\text{Se}_{15}$ which is considered a promising thermoelectric material, $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}$ has a higher thermopower ($\sim 2x$ more) but its conductivity is considerably lower ($\sim 15x$ less). Whether this material is subject to doping remains to be answered.

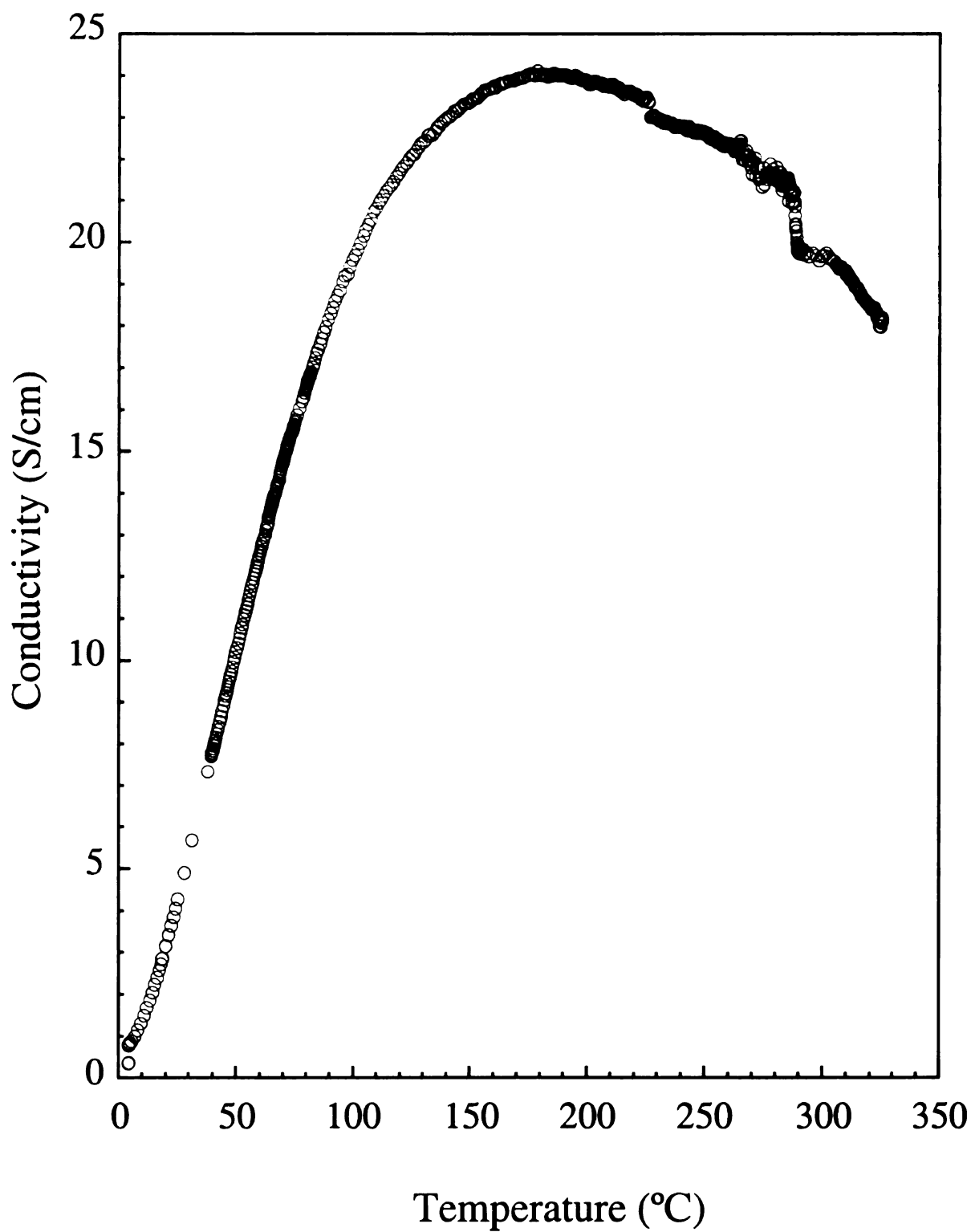


Figure 7-11. Variable temperature electrical conductivity for a single crystal of Ba_xPb_6 .

$\text{Bi}_6\text{Se}_{15}$.

5. Concluding Remarks

Five new quaternary chalcogenides were synthesized by direct combination reactions at temperatures above 800 °C. $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ and $A_xPb_{4-x}Bi_6Se_{13}$ ($A = \text{Eu, Sr}$) adopt two very stable and commonly encountered structures types, that of cosalite $Pb_2Bi_2S_5$ and $Sr_4Bi_6Se_{13}$, respectively. $Ba_xPb_{6-x}Bi_6Se_{15}$ adopts the structure of $A_{1+x}M_{4-2x}M'_{7+x}Se_{15}$ ($A = \text{K, Rb}$; $M = \text{Pb, Sn}$; $M' = \text{Bi, Sb}$) which is structurally related with $Sr_4Bi_6Se_{13}$. All three structure types contain several high (>6) coordinate and sometimes octahedral sites which display mixed occupancy and can accommodate a variety of similar sized cations without disrupting the structure. These kind of substitutions are very helpful because they allow us to study the effect of considerable compositional changes on the properties of the compounds.

The Eu analogs present a set of rather interesting charge transport properties and appear promising for thermoelectric applications. The thermal conductivity needs to be measured to further evaluate their potential.

$Ba_xPb_{6-x}Bi_6Se_{15}$ with its current properties it is not very promising due to its low conductivity. Since an isostructural compound, $K_{1+x}Pb_{4-2x}Bi_{7+x}Se_{15}$, is a promising thermoelectric material, attempts to improve its properties by doping may be worthwhile.

References

1. (a) Makovicky, E. *Fortschr. Mineral.* **1981**, *59*, 137-190. (b) Makovicky, E. *Fortschr. Mineral.* **1985**, *63*, 45-89. (c) Makovicky, E. *Z. Kristallogr.* **1985**, *173*, 1-23. (d) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, *160*, 269-297. (e) Makovicky, E. *Eur. J. Mineral.* **1993**, *5*, 545-591.
2. McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331-340.
3. (a) McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301. (b) Chondroudis, K.; Kanatzidis, M. G. *J. Solid State Chem.* **1998**, *136*, 328-332.
4. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474. (b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.
5. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
6. (a) Iordanidis, L.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1928-1930. (b) Iordanidis, L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 8319-8320.
7. Chung, D.-Y.; Jovic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
8. Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science (Washington, D. C.)* **2000**, *287*, 1024-1027.
9. Adouby, K.; Perez Vicente, C.; Jumas, J. C.; Fourcade, R.; Abba Touré, A. Z. *Kristallogr.* **1998**, *213*, 343-349.

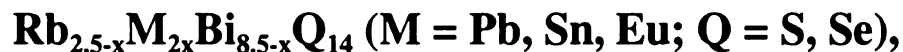
-
10. Perez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Abba Touré, A.; Kra, G. *Inorg. Chem.* **1999**, *38*, 2131-2135.
 11. Choe, W.; Lee, S.; O'Connell, P.; Covey A. *Chem. Mater.* **1997**, *9*, 2025-2030.
 12. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011-1017.
 13. Iordanidis, L.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Solid State Chem.* **1999**, *143*, 151-162.
 14. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805. See also Chapter 8.
 15. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
 16. Mrotzek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.
 17. Choi, K.-S.; Chung, D.-Y.; Mrotzek, A.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Submitted for publication*.
 18. (a) Glemser, O.; Filcek, M. Z. *Anorg. Allg. Chem.* **1955**, *279*, 321-323. (b) Gattow, G.; Zemmann, J. Z. *Anorg. Allg. Chem.* **1955**, *279*, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, *6*, 961-964. (d) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, *8*, 677-678. (e) Peresh, E. Y.; Golovei, M. I.; Berul, S. I. *Inorg. Mater.* **1971**, *7*, 27-30.
 19. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, *252*, 96-99.
 20. Schmitz, D.; Bronger, W. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29*, 438-439.
 21. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 676-683.
 22. Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 399-407.

-
23. Cook, R.; Schäfer, H. *Rev. Chim. Miner.* **1982**, *19*, 19-27.
24. Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 631-638.
25. Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 136-140.
26. The thermoelectric figure of merit is defined as: $ZT = (S^2\sigma/\kappa)T$; where S is the thermopower, σ the electrical conductivity, κ the thermal conductivity and T is the temperature. The numerator $S^2\sigma$ is called the power factor. All three of these properties are determined by the details of the electronic structure and scattering of charge carriers (electrons or holes) and thus are not independently controllable parameters. κ also has a contribution from lattice vibrations, κ_l , the phonon thermal conductivity. Thus $\kappa = \kappa_e + \kappa_l$, where κ_e is the carrier thermal conductivity.
27. *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995 and references there in.
28. (a) Iitaka, Y.; Nowacki, W. *Acta Crystallogr.* **1962**, *15*, 691-698. (b) Takeuchi, Y.; Takagi, J. *Proc. Jap. Acad.* **1974**, *50*, 222-225. (c) Takeuchi, Y.; Takagi, J.; Yamanaka, T. *Proc. Jap. Acad.* **1974**, *50*, 317-321. (d) Takeuchi, Y.; Ozawa, T.; Takagi, J. *Z. Kristallogr.* **1979**, *150*, 75-84. (e) Otto, H. H.; Strunz, H. *Neues Jahrb. Mineral., Abh.* **1968**, *108*, 1-19. (f) Srikrishnan, T.; Nowacki, W. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1974**, *140*, 114-136. (g) Tilley, R. J. D.; Wright, A. C. *J. Solid State Chem.* **1986**, *65*, 45-62. (h) Takagi, J.; Takeuchi, Y. *Acta Crystallogr., Sect. B* **1972**, *28*, 649-651. (i) Matzat, E. *Acta Crystallogr., Sect. B* **1979**, *B35*, 133-136. (j) Takeuchi, Y.; Takagi, J. *Proc. Jap. Acad.* **1974**, *50*, 76-79.

-
29. (a) For example the ionic radius of Eu is 1.17 Å, whereas the ionic radii of strontium and barium are 1.18 and 1.35 Å respectively^{29(b)}. Furthermore Eu forms EuSe₂^{29(c)} which has the same structure as SrS₂^{29(d)} and BaTe₂^{29(e)}. (b) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, A32, 751-767. (c) Aitken, J. A.; Cowen, J. A.; Kanatzidis, M. G. *Chem. Mater.* **1998**, 10, 3928-3935. (d) Kawada, I.; Kato, K.; Yamoaka, S. *Acta Crystallogr., Sect. B* **1976**, B32, 3110-3111. (e) Li, J.; Guo, H. *J. Solid State Chem.* **1995**, 117, 247-255.
30. The europium metal chunk was in the form of small pieces (< 1cm).
31. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.
32. Mar, A.; Ibers, J. A. *Acta Crystallogr., Sect. C* **1992**, C48, 771-773.
33. Guittard, M.; Benacerraf, A. *C. R. Hebd. Seances de Acad. Sci.* **1959**, 248, 2589-2591.
34. Wills, A. S.; Brown, I. D. *Valist*, CEA, France (1999). Program available from author at willsas@netscape.net.
35. Skowron, A.; Brown, I. D. *Acta Crystallogr., Sect. C* **1990**, C46, 2287-2291.
36. Chung, D.-Y.; Breshears, J. D.; Kanatzidis, M. G. work in progress.
37. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, C42, 259-261.
38. (a) Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. B* **1981**, B37, 1281-1284. (b) Cordier, G.; Schwidetzky, C.; Schäfer, H. *Rev. Chim. Miner.* **1982**, 19, 179-186.
39. See Chapter 8.
40. Wulf, R. *Mineral. Petrol.*, **1995**, 52, 187-196.

CHAPTER 8

Synthesis and Characterization of



1. Introduction

As presented in the previous chapters, in the past decade, we have extensively investigated the ternary A/Bi/Q (A = alkali or alkaline earth; Q = chalcogen) and quaternary A/M/Bi/Q (A = alkali or alkaline earth; M = Pb, Sn, rare earth; Q = chalcogen) bismuth chalcogenide systems discovering a large number of new

compounds. Our efforts have significantly expanded this previously limited and little studied class of materials.¹ The amazing feature of these systems that clearly demonstrates their remarkable structural flexibility is that we continuously uncover new compounds with new structures even in systems that we thought were thoroughly researched. Variations in the starting ratios and/or the reaction (heating) profiles lead to the formation of new phases. Our efforts to fully explore the bismuth chalcogenide are ongoing but the large number of the discovered phases have kept us from fully characterizing all them to date. Several of the compounds presented in this chapter belong in this category.

We report here the synthesis, physicochemical, spectroscopic, and structural characterization of β -K_{2.5}Bi_{8.5}Se₁₄, Rb₂MBi₈Q₁₄ (M = Pb, Sn, Eu; Q = S, Se), Rb₁₁Bi₁₅Se₂₈, Rb₄EuBi₆Se₁₂, Cs_{6-3x}Bi_{8+x}Se₁₅, Rb_xSn_{1-x}Bi_{6-x}Se₁₀, Ba_{4-x}Bi_{6+2/3x}Se₁₃, Ba_xPb_{4-x}Bi₆S₁₃, Rb_{1.5-x}Sn_{2x}Bi_{7.5-x}Se₁₂, K_xM_{4-2x-3y}Bi_{4+x+2y}S₁₀ (M = Pb, Eu), APbBi₃S₆ (A = Rb, Cs), BaLnBi₂Q₆ (Ln = La, Ce Pr; Q = S, Se) and Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z}.

2. Experimental section

Reagents. Chemicals in this work were used as obtained: bismuth powder (99.999+%, -100 mesh, Cerac, Milwaukee, WI), bismuth chunks (99.999% Noranda, Canada), bismuth chunks (99.999%, Tellurex, Traverse City, MI), lead granules (99.999%, -20 mesh, Cerac, Milwaukee, WI), sulfur powder (sublimed, Spectrum Chemical Mfg. Corp., Gardena, CA), selenium powder (99.95%, -200 mesh, Cerac, Milwaukee, WI), selenium shots (99.999%, Noranda Advanced Materials, Quebec, Canada), selenium shots (99.999%, Tellurex, Traverse City, MI), potassium metal granules (<6 mm, 99%, Aldrich Chemical, Milwaukee, WI), rubidium metal (99.8%, Alfa Aesar, Ward Hill, MA), barium metal (<6 mm, 99%, Aldrich Chemical, Milwaukee, WI), tin metal (99.999%, -200 mesh, Cerac, Milwaukee, WI), lanthanum metal (99.9%, -40 mesh, Cerac, Milwaukee, WI), cerium metal (99.9% purity, <250 micron, Alfa Aesar, Ward Hill, MA), praseodimium metal (99.9%, -40 mesh, Cerac, Milwaukee, WI), europium metal chunk² (99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), uranium metal (99.7%, -60 mesh, Cerac, Milwaukee, WI), lead sulfide (99.9%, -200 mesh, Cerac, Milwaukee, WI), barium selenide powder (99.5%, -20 mesh, Cerac, Milwaukee, WI). K_2Q , BaS , Rb_2Q , Cs_2Q ($Q = S, Se$) were prepared by a stoichiometric reaction of the alkali or alkaline earth metal and chalcogen in liquid ammonia.

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All products were washed with degassed water, methanol and ether to remove traces of excess flux. Except when stated otherwise the yield was almost quantitative and the purity and homogeneity of the samples was verified by comparing the X-ray powder diffraction patterns to those calculated by the crystallographically determined fractional atomic coordinates.

Bi₂S₃. A mixture of 11.633 g (0.056 mol) Bi and 2.677 g (0.083 mol) S was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 650 °C in 48 h, kept at 650 °C for 2 days and then cooled down to 50 °C in 10 h. The product was ground into powder and used for further reactions.

EuS. A mixture of 1.062 g (0.069 mol) Eu and 0.224 g (0.069 mol) S were combined and loaded into carbon coated fused silica tube. The tube was flamed sealed under vacuum and inserted into a computer controlled furnace. The temperature was raised from 50 to 200 °C in 24 h. The reaction was allowed to stay at this temperature for 24 h. Next, the temperature was raised to 600 °C in 24 h, held there for 24 h and decreased at a rate of 20 °C/h to 300 °C and then cooled quickly to 50 °C. The reaction of Eu with S begins at ~200 °C and is exothermic and explosive. In order to prevent an explosion a slow, stage-wise heating profile is necessary. The dark reddish brown powder was ground and stored in a nitrogen filled glove box.

Bi₂Se₃. A mixture of 9.407 g (0.045 mol) Bi and 5.331 g (0.068 mol) Se was transferred into a silica tube, which was flame-sealed under vacuum. The tube was heated to 600 °C in 12 h, kept at 600 °C for 2 days and then cooled down to 50 °C in 6 h. The product was ground into a fine powder and used for further reactions.

PbSe. A mixture of 6.114 g (0.030 mol) Pb and 2.330 g (0.030 mol) Se was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 650 °C in 12 h, kept at 650 °C for 72 h and then cooled down to 50 °C in 10 h. The product was ground into a fine powder and used for further reactions.

β-K_{2.5}Bi_{8.5}Se₁₄ (I). The compound was found as a minor phase in the synthesis of K_xBi₂Se₃. The synthetic procedure is the following: A mixture of 0.080 g (0.509 mmol) K₂Se and 0.6667 g (1.018 mmol) Bi₂Se₃ was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 670 °C in 12 h, kept at 670 °C for 48 h and then cooled down to 50 °C in 11 h. The product consists mainly of small plate-like crystals that correspond to K_xBi₂Se₃³ and a small amount (~10 %) of well shaped rods that correspond to β-K_{2.5}Bi_{8.5}Se₁₄.

Rb₂PbBi₈S₁₄ (II). A mixture of 0.050 g (0.246 mmol) Rb₂S, 0.053 g (0.222 mmol) PbS and 0.507 g (0.986 mmol) Bi₂S₃ was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated with the same profile

as in the case of (VII). The product consists of large chunk made of needle-like crystals. SEM/EDS on a number of crystals gave an average composition of $\text{Rb}_{1.4}\text{Pb}_{1.0}\text{Bi}_{8.4}\text{S}_{14}$.

$\text{Rb}_{2.5-x}\text{Pb}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$ (III). A mixture of 0.050 g (0.200 mmol) Rb_2Se , 0.057 g (0.200 mmol) PbSe and 0.524 g (0.800 mmol) Bi_2Se_3 was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated with the same profile as in the case of (VII). The product consists of large chunk made of needle-like crystals. SEM/EDS on a number of crystals gave an average composition of $\text{Rb}_{1.5}\text{Pb}_{0.9}\text{Bi}_{7.8}\text{Se}_{14}$.

$\text{Rb}_{2.5-x}\text{Sn}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$ (IV). A mixture of 0.065 g (0.260 mmol) Rb_2Se , 0.313 g (1.498 mmol) Bi , 0.012 g (0.101 mmol) Sn and 0.190 g (2.406 mmol) Se was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 700 °C in 24 h, kept at 700 °C for 60 h, then cooled down to 400 °C in 45 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals. SEM/EDS on a number of crystals gave an average composition of $\text{Rb}_{2.5}\text{Sn}_{0.5}\text{Bi}_{7.6}\text{Se}_{14}$.

$\text{Rb}_{2.5-x}\text{Eu}_{2x}\text{Bi}_{8.5-x}\text{S}_{14}$ (V). A mixture of 0.066 g (0.264 mmol) Rb_2S , 0.060 g (0.326 mmol) EuS and 0.671 g (1.025 mmol) Bi_2S_3 was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 900 °C in 12

h, kept at 900 °C for 96 h, then cooled down to 600 °C in 45 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals. SEM/EDS on a number of crystals gave an average composition of $\text{Rb}_{2.9}\text{Eu}_{0.4}\text{Bi}_{7.5}\text{S}_{14}$. The product contains a small impurity of EuBi_2S_4 .

$\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ (VI). A mixture of 0.060 g (0.509 mmol) Rb_2Se and 0.1965 g (1.018 mmol) Bi_2Se_3 was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 810 °C in 48 h, kept at 810 °C for 6 d, then cooled down to 510 °C in 45 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals.

$\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$ (VII). A mixture of 0.070 g (0.345 mmol) Rb_2S , 0.528 g (1.027 mmol) Bi_2S_3 , 0.052 g (0.342 mmol) Eu and 0.013 g (0.405 mmol) S was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 850 °C in 60 h, kept at 850 °C for 6 d, then cooled down to 500 °C in 40 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of plate-like crystals.

$\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ (VIII). A mixture of 0.040 g (0.116 mmol) Cs_2Se and 0.380 g (0.580 mmol) Bi_2Se_3 was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a natural gas-oxygen torch until the

mixture melted and then the tube was removed from the flame and let to solidify. The procedure was repeated two more times to ensure homogeneity. The product consisted of a silvery chunk with needles growing across its surface. $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ is the main phase with $\text{CsBi}_{3.67}\text{Se}_6$ ⁵ as a minor phase as evidenced by X-ray powder diffraction.

$\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$ (IX). A mixture of 0.014 g (0.056 mmol) Rb_2Se , 0.500 g (0.763 mmol) Bi_2Se_3 , 0.026 g (0.219 mmol) Sn and 0.017 g (0.215 mmol) Se was transferred into a carbon coated silica tube. The tube was placed under the flame of a natural gas-oxygen torch until the mixture melted and then the tube was removed from the flame and let to solidify. The procedure was repeated two more times to ensure homogeneity. The product consisted of a silvery chunk with needles growing across its surface.

$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ (X). A mixture of 0.100 g (0.462 mmol) BaSe and 0.378 g (0.577 mmol) Bi_2Se_3 was transferred into a carbon crucible which was inserted into a silica tube and it was flame-sealed under vacuum. The tube was heated to 990 °C in 20 h, kept at 990 °C for 72 h, then cooled down to 700 °C in 58 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals.

$\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ (XI). A mixture of 0.050 g (0.295 mmol) BaS , 0.106 g (0.443 mmol) PbS and 0.285 g (0.554 mmol) Bi_2S_3 was transferred into a carbon coated silica

tube, which was flame-sealed under vacuum. The tube was heated to 880 °C in 12 h, kept at 880 °C for 2 d, then cooled down to 580 °C in 30 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals.

Rb_{1.5-x}Sn_{2x}Bi_{7.5-x}Se₁₂ (XII). This compound was found as a minor phase (~10 %) in the synthesis of (XIII).

K_xPb_{4-2x-3y}Bi_{4+x+2y}S₁₀ (XIII). A mixture of 0.031 g (0.281 mmol) K₂S, 0.433 g (0.842 mmol) Bi₂S₃, 0.116 g (0.560 mmol) Pb and 0.020 g (0.623 mmol) S was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 830 °C in 35 h, kept at 830 °C for 6 d, then cooled down to 530 °C in 30 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals.

K_xEu_{4-2x-3y}Bi_{4+x+2y}S₁₀ (XIV). A mixture of 0.016 g (0.145 mmol) K₂S, 0.292 g (0.568 mmol) Bi₂S₃, 0.043 g (0.283 mmol) Eu and 0.014 g (0.437 mmol) S was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 850 °C in 48 h, kept at 830 °C for 5 d, then cooled down to 450 °C in 40 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals.

RbPbBi₃S₆ (XV). A mixture of 0.040 g (0.197 mmol) Rb₂S, 0.082 g (0.395 mmol) Pb, 0.246 g (1.177 mmol) Bi and 0.070 g (2.183 mmol) S was transferred to a carbon coated quartz tube and flame-sealed under vacuum. The mixture was heated for 5 days at 800 °C and cooled to 500 °C at 10 °C/h and then to 50 °C in 10 h. The product consisted of a large chunk made up of shiny gray-metallic plates.

CsPbBi₃S₆ (XVI). A mixture of 0.084 g (0.282 mmol) Cs₂S, 0.116 g (0.560 mmol) Pb, 0.433 g (0.842 mmol) Bi₂S₃ and 0.020 g (0.623 mmol) S was transferred to a carbon coated quartz tube and flame-sealed under vacuum. The mixture was heated for 6 days at 850 °C and cooled to 500 °C at 5 °C/h and then to 50 °C in 10 h. The product consisted of a large chunk made up of shiny gray-metallic plates.

BaLaBi₂S₆ (XVII). A mixture of 0.050 g (0.364 mmol) Ba, 0.152 g (0.727 mmol) Bi, 0.051 g (0.364 mmol) La and 0.072 g (2.246 mmol) S was transferred into a carbon coated silica tube. The tube was sealed under vacuum and heated to 830°C for 5 days followed by cooling to 530°C at 10°C/h and then to 100°C in 12h.

BaCeBi₂S₆ (XVIII), BaPrBi₂Se₆ (XIX) BaLaBi₂Se₆ (XX). Under the same heating profile as above a stoichiometric ratio of Ba/Bi₂Q₃/Ln/Q gave the isostructural phases BaLnBi₂Q₆ as evidenced by X-ray powder-diffraction.

Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z} (XXI). A mixture of 0.040 g (0.291 mmol) Ba, 0.080 g

(0.336 mmol) U, 0.069 g (0.873 mmol) Se and 0.095 g (1.450 mmol) Bi_2S_3 was transferred into a carbon coated silica tube, which was flame-sealed under vacuum. The tube was heated to 850 °C in 48 h, kept at 850 °C for 6 d, then cooled down to 450 °C in 48 h and further cooled down to 50 °C in 10 h. The product consists of large chunk made of needle-like crystals. The yield is around ~50% and there is a second unidentified phase as evidenced by X-ray powder diffraction.

3. Physical Measurements

The instrument and experimental setups for *Electron Microscopy*, *Differential Thermal Analysis*, *Infrared Spectroscopy*, *Charge-transport and thermal conductivity measurements*, and *Powder X-ray diffraction* are the same as that in Chapter 2 (Section 3). The instrument and experimental setup for *Solid-State UV/Vis Spectroscopy* is the same as that in Chapter 4 (Section 3).

Single-Crystal X-ray Crystallography. X-ray single crystal were collected with one of the following ways:

(a) Intensity data were collected at room temperature on a Rigaku AFC6S diffractometer with a graphite-crystal monochromator by using the ω or $\theta/2\theta$ scan mode. The unit cell parameters were determined from a least-squares refinement using the 2θ ,

ω , χ , and ϕ angles of 15~25 carefully machine-centered reflections in the $5 \leq 2\theta \leq 30^\circ$ range. An empirical absorption correction based on ψ scans of 3 reflections with $\chi \sim 90^\circ$ was applied to the data.

The intensities of three standard reflections were checked every 150 reflections to monitor crystal and instrument stability during single crystal X-ray data collection. No significant decay was observed during the data collection period. The structures of all compounds were solved by direct methods using the SHELXS-86⁶ software program. Refinements with full-matrix least-squares techniques and Fourier synthesis calculations were carried out using the TEXSAN package of crystallographic programs.⁷ After isotropic refinement of all atoms, a DIFABS correction was applied as recommended.⁸

(b) A Bruker (formerly Siemens) SMART Platform CCD diffractometer was used for data collection. Several different sets of frames covering a random area of the reciprocal space were collected using 0.3° steps in ω at a detector-to-sample distance between 4-5 cm depending on the desired resolution. The SMART⁹ software was used for data acquisition and SAINT⁹ for data extraction. The absorption correction was done with SADABS⁹ and the structure solution (direct methods) and refinement was done with the SHELXTL⁹ package of crystallographic programs. An analytical absorption correction with XPREP⁹ was applied before SABABS for (IV).

β -K_{2.5}Bi_{8.5}Se₁₄ (I). Over a hemisphere of data were collected (1641 frames) with an exposure time of 35 sec per frame to a resolution of 0.8 Å. The final cell was calculated from 3935 [$I > 10\sigma(I)$] reflections (Table 8-1). Eight bismuth atoms, three potassium and fourteen selenium atoms were found to sit on a crystallographic mirror plane. After refinement the U_{iso} of K(9) was very small (0.001 Å²) and at the same time two peaks appeared to either side of K(9) having a trigonal pyramidal coordination. These two peaks were assigned as Bi [Bi(9) and Bi(9')] and the occupancies of all three atoms in that site were refined ($R1 = 6.5\%$, 16.4%). The formula at that time was K_{2.3}Bi_{8.7}Se₁₄, very close to what was needed for electroneutrality, K_{2.5}Bi_{8.5}Se₁₄. Therefore the occupancy of the K(9) was constrained at 0.5 and also the sum of the occupancies of the two bismuth atoms Bi(9) and Bi(9') was constrained at 50% without any significant changes in the R values. All atoms with the exception of three previous atoms were refined anisotropically. Final R values $R1 = 5.8\%$ $wR2 = 12.9\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-2.

Rb₂PbBi₈S₁₄ (II). Less than a hemisphere of data were collected (988 frames) with an exposure time of 75 sec per frame to a resolution of 0.74 Å. The final cell was calculated from 2440 [$I > 8\sigma(I)$] reflections chosen from the data set (Table 8-1). Two rubidium, one lead, eight bismuth and fourteen selenium atoms were found to sit on a

crystallographic mirror plane. All atoms were refined anisotropically. Final R values, $R1 = 4.3\%$, $wR2 = 7.2\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-3.

$Rb_{2.5-x}Sn_{2x}Bi_{8.5-x}Se_{14}$ (IV). Only the cell was determined and was found to be $a = 21.74(5) \text{ \AA}$, $b = 4.101(8) \text{ \AA}$, $c = 32.42(7) \text{ \AA}$

$Rb_{2.5-x}Eu_{2x}Bi_{8.5-x}S_{14}$ (V). Only the cell was determined and was found to be $a = 21.43(2) \text{ \AA}$, $b = 4.065(3) \text{ \AA}$, $c = 31.53(2) \text{ \AA}$.

$Rb_{11}Bi_{15}Se_{28}$ (VI). Over a hemisphere of data were collected (1382 frames) with an exposure time of 40 sec per frame to a resolution of $0.80 \text{ \AA}$. The final cell was calculated from 3386 [$I > 10\sigma(I)$] reflections (Table 8-4). Eight bismuth atoms, six rubidium and fourteen selenium atoms were found to sit on a crystallographic mirror plane. After refinement the U_{iso} of Bi(1) was very high compared to that of the other Bi atoms and at the same time there was too much positive charge in the structure. Bi(1) was disordered with Rb(1) after that the formula was $Rb_{5.5}Bi_{7.5}Se_{14}$, exactly what was needed for electroneutrality. Therefore the occupancy of that site was constrained to be 50/50 with Bi and Rb without any significant changes in the R values. All atoms were refined anisotropically. Final R values, $R1 = 4.7\%$ $wR2 = 8.8\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-5.

Rb₄EuBi₆S₁₂ (VII). Four rubidium, one europium, six bismuth and twelve sulfur atoms were found to sit on a crystallographic mirror plane. All atoms were refined anisotropically. Final R values, R1 = 6.8%, wR2 = 18.3%. Tables 8-4 and 8-6 show the summary of crystallographic data collected and the fractional atomic coordinates of Rb₄EuBi₆S₁₂.

Cs_{6-3x}Bi_{8+x}Se₁₅ (VIII). Over a hemisphere of data were collected (1284 frames) with an exposure time of 40 sec per frame to a resolution of 0.74 Å. The final cell was calculated from 2512 [I>10σ(I)] reflections (Table 8-7). Five bismuth atoms, one cesium and eight selenium atoms were found to sit on a crystallographic mirror plane. After refinement a second peak appeared close to Bi(5). This peak was assigned as Cs its occupancy together with the occupancy of Bi(5) were refined. Also since the temperature factor of Cs(2) was high its occupancy was refined and it was found to be ~74 occupied. All atoms except Bi(5) and Cs(1) were refined anisotropically. Final R values R1 = 5.2%, wR2 = 14.1%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-8.

Rb_xSn_{1+x}Bi_{6-x}Se₁₀ (IX). A hemisphere of data were collected (1307 frames) with an exposure time of 30 sec per frame to a resolution of 0.74 Å. The final cell was calculated from 3414 [I>10σ(I)] reflections (Table 8-7). One rubidium, seven bismuth and ten selenium atoms were found to sit on a crystallographic mirror plane. In all the

bismuth sites Sn was introduced and only sites Bi(5) through Bi(7) contained statistically significant amounts of Sn. All atoms were refined anisotropically. Final R values, R1 = 5.4%, wR2 = 14.1%. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-9.

Ba_{4-x}Bi_{6+2/3x}Se₁₃ (X). A full sphere of data were collected (2419 frames) with an exposure time of 41 sec per frame to a resolution of 0.66 Å. The final cell was calculated from 12480 [I>8σ(I)] reflections (Table 8-10). Seven bismuth atoms, three barium and thirteen selenium atoms were found to sit on a crystallographic mirror plane. One peak appeared next to Ba(8) shifted to the site of the trigonal prismatic site and at the same time two more peaks appeared next to Ba(9) again shifted to the sides of the trigonal prismatic site. These peaks were assigned as bismuth and their occupancy together with the occupancy of the corresponding Ba atoms were refined. At that time there was too much positive charge in the structure and as a result the occupancy of the Bi sites was refined. Site Bi(7) was found to be ~76% occupied while site Bi(4) was ~95% occupied. All the atoms except those in sites 8 and 9 were refined anisotropically. Final R values, R1 = 3.7%, wR2 = 8.8%). The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-11.

Ba_xPb_{4-x}Bi₆S₁₃ (XI). A full sphere of data were collected (2110 frames) with an exposure time of 30 sec per frame to a resolution of 0.67 Å. The final cell was calculated

from 5266 [$I > 8\sigma(I)$] reflections (Table 8-10). Ten *MI* sites and thirteen selenium atoms were found to sit in a crystallographic mirror plane where *MI* is any combination of Pb, Bi or Ba. Since Pb and Bi are crystallographically indistinguishable all the metal sites *MI* were refined as Bi together with their occupancies. For sites 1 through 7 the occupancy did not change indicating that are fully occupied by Bi/Pb. For sites 8 and 9 the occupancy dropped to less than 0.500 (full theoretical occupancy) and Ba was introduced in these sites. In site 10, the occupancy dropped to less than 0.500 and at the same time a new peak appeared shifted to the side of the trigonal prismatic side. These peak was assigned as Bi/Pb. All atoms were refined anisotropically except those in site 10. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-12.

$\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ (XII). More than a hemisphere of data were collected (1936 frames) with an exposure time of 60 sec per frame to a resolution of 0.84 Å. The final cell was calculated from 1384 [$I > 10\sigma(I)$] reflections chosen from the data set (Table 8-13). One rubidium, eight bismuth and twelve selenium were found to sit on a crystallographic mirror plane. After refinement the U_{iso} of Bi(8) was considerably higher than that of the remaining bismuth atoms and as a result that site was disordered with Rb. The refinement gave that site approximately occupied by 50-50% occupied by Rb and Bi and a formula of $\text{Rb}_{1.5}\text{Bi}_{7.5}\text{Se}_{12}$. Since EDS analysis gave the presence of tin the

occupancy of all bismuth sites were refined but none of them revealed any significant changes in its occupancy. Therefore we believe that small amounts of tin are necessary for the stabilization of this structure and each bismuth site contains ever smaller amounts which is hard to be detected by X-ray crystallography. All atoms were refined anisotropically. Final R values, R1= 5.4% WR2 = 10.6 % The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-14.

$K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$ (XIII). A hemisphere of data were collected (1273 frames) with an exposure time of 12 sec per frame to a resolution of 0.71 Å. The final cell was calculated from 6515 [$I > 10\sigma(I)$] reflections (Table 8-15). Seven *Ml* sites, one potassium and ten sulfurs atoms were found to sit in a crystallographic mirror plane where *Ml* is Bi or Pb or both. Since Pb and Bi are crystallographically indistinguishable all the metal sites *Ml* with the exception of K(8) were refined as Bi. In subsequent step the occupancies of all eight sites were refined. It was found that site M(5) is only partially occupied (~93%) by Bi/Pb while M(7) contains ~49% K. Also site K(8) contains ~8% Bi/Pb. In we take into account all these results the compound should have the general formula $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$ where x and y are the crystallographically refined amount of potassium and vacancies respectively. The final formula is $K_{1.40}Pb_{0.99}Bi_{5.54}S_{10}$. All atoms were refined anisotropically. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-16.

$K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$ (XIV). A hemisphere of data were collected (1271 frames) with an exposure time of 35 sec per frame to a resolution of 0.75 Å. The final cell was calculated from 5289 [$I > 10\sigma(I)$] reflections chosen from the data set (Table 8-15). Since the compound is isostructural with (V) the fractional atomic coordination of (V) were as a starting point for refinements after replacing Pb with Eu. Later it was found that site 7 had to be split into three positions. All atoms except those in site 7 were refined anisotropically. Final R values, $R1 = 3.2\%$, $wR2 = 6.6\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-17.

$RbPbBi_3S_6$ (XV). Only the cell was determined and was found to be $a = 4.185(2)$ Å, $c = 24.985(5)$ Å, $\gamma = 120^\circ$.

$CsPbBi_3S_6$ (XVI). One bismuth atom and four "sulfur" atoms were located. Two of the "sulfur" atoms were found sitting between the Bi_2Te_3 -type layers at a distance of 2.35 Å from each other. They were subsequently assigned as Cs atoms and their occupancies were refined. Cs(1) was 26% occupied while Cs(2) was 34% occupied. Since SEM/EDS analysis showed the presence of Cs, Pb, Bi, and S atoms, the compound must have, for charge balancing reasons, the formula $Cs_{0.5}Pb_{0.5}Bi_{1.5}S_3$. This formula indicates that the total Cs occupancy should be 50% while the site assigned as Bi must actually contain 75% Bi and 25% Pb. The sum of the occupancies of the Cs atoms was

slightly higher than 50% and it was constrained to be equal to 0.0417, which corresponds to a 50% total occupancy of the Cs atoms. All atoms were refined anisotropically ($R/R_w = 11.0/13.5\%$). Averaging the data improved the R values ($R/R_w = 8.9/10.1\%$). Tables 8-18 and 8-19 show the summary of crystallographic data collected and the fractional atomic coordinates of $\text{CsPbBi}_3\text{S}_6$.

BaLaBi₂S₆ (XVII). One barium, one lanthanum, two bismuth and six sulfur atoms were found by direct methods. All atoms were refined anisotropically. Final R values, $R_1 = 4.7\%$, $wR_2 = 12.8\%$. Tables 8-20 and 8-21 show the summary of crystallographic data collected and the fractional atomic coordinates of $\text{BaLaBi}_2\text{S}_6$.

Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z} (XXI). More than a hemisphere of data were collected (1529 frames) with an exposure time of 40 sec per frame to a resolution of 0.75 Å. The final cell was calculated from 3115 [$I > 10\sigma(I)$] reflections chosen from the data set (Table 8-20). The crystal contained two fragments that were partially overlapped. The minor fragment was ignored and the subsequent integration was done on the major fragment. After integration 1529 reflections that were completely overlapped up to 0.007 Å⁻¹ in the two fragments were removed using the GEMINI⁹ software. All the refinements were done on the resulting *hkl* file after the removal of the overlapping reflections. Three M sites, three barium and nine selenium were found to sit on a crystallographic mirror site where M is

Bi or U or both. As will be further explained, in the structure description section, the quality of the data set did not allow for the distinction between Bi and U. The occupancy of all atoms was refined and it was found that Ba(4) has to be disordered with U while Se(9) was partially occupied. All atoms were refined anisotropically. Final R values, $R1 = 3.9\%$, $wR2 = 9.2\%$. The fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 8-22.

Bond Valence Calculations. The program VaList¹⁰ was used for the calculation of bond valence sums. The bond-valence parameters R_0 and B were supplied by the program. The CIF files generated by SHELXL were used as input.

Table 8-1. Crystallographic Data for β -K_{2.5}Bi_{8.5}Se₁₄ and Rb₂PbBi₈S₁₄.

Empirical formula	β -K _{2.5} Bi _{8.5} Se ₁₄ (I)	Rb ₂ PbBi ₈ S ₁₄ (II)
Formula weight	2979.52	2498.81
Temperature, K	300(2)	299(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions, Å	<i>a</i> = 22.194(2) <i>b</i> = 4.1628(7) <i>c</i> = 32.232(6)	<i>a</i> = 21.393(6) <i>b</i> = 4.023(1) <i>c</i> = 31.391(9)
Z, Volume, Å ³	2, 2977.9(9)	4, 2702(1)
Density (calculated), g/cm ³	6.646	6.143
Absorption coefficient, mm ⁻¹	67.493	62.761
F(000)	4916	4176
Crystal size, mm ³	0.02 x 0.02 x 0.20	0.01 x 0.02 x 0.30
θ range for data collection	1.56 to 26.38°	1.15 to 28.59°
Index ranges	-27 ≤ <i>h</i> ≤ 27 -5 ≤ <i>k</i> ≤ 5 -26 ≤ <i>l</i> ≤ 40	-14 ≤ <i>h</i> ≤ 28 -5 ≤ <i>k</i> ≤ 5 -41 ≤ <i>l</i> ≤ 41
Reflections collected	17963	10993
Independent reflections	3472 [<i>R</i> _(int) = 0.1251]	3455 [<i>R</i> _(int) = 0.0693]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	3472 / 0 / 154	3455 / 0 / 152
Goodness-of-fit on <i>F</i> ²	0.957	0.939
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0580 <i>wR</i> 2 = 0.1292	<i>R</i> 1 = 0.0430 <i>wR</i> 2 = 0.0720
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0949 <i>wR</i> 2 = 0.1435	<i>R</i> 1 = 0.0908 <i>wR</i> 2 = 0.0788
Extinction	0.00023(6)	0.000014(4)
Largest peak and hole, e·Å ⁻³	4.884 and -4.757	3.057 and -2.760

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.0785(1)	0.2500	0.4673(1)	21(1)	
Bi(2)	0.0661(1)	-0.7500	0.6042(1)	18(1)	
Bi(3)	-0.0856(1)	-0.2500	0.6695(1)	19(1)	
Bi(4)	-0.1993(1)	-0.7500	0.7456(1)	22(1)	
Bi(5)	0.1879(1)	-0.2500	0.6775(1)	20(1)	
Bi(6)	-0.0913(1)	-0.2500	0.8763(1)	20(1)	
Bi(7)	-0.4284(1)	-0.7500	0.6056(1)	19(1)	
Bi(8)	-0.4087(1)	-0.2500	0.4862(1)	19(1)	
Bi(9)	0.7868(8)	-0.7500	0.4719(3)	20(1)	0.229(15)
K(9)	0.7644(8)	-0.7500	0.4583(5)	20(1)	0.50
Bi(9')	0.7688(7)	-0.7500	0.4758(2)	20(1)	0.271(15)
K(10)	-0.2464(4)	-0.7500	0.6053(2)	27(2)	
K(11)	0.0543(4)	-0.2500	0.7696(3)	35(2)	
Se(1)	0.0725(2)	-0.2500	0.5336(1)	26(1)	
Se(2)	0.0831(2)	-0.2500	0.4038(1)	23(1)	
Se(3)	0.2016(2)	0.2500	0.4709(1)	22(1)	
Se(4)	0.1885(2)	-0.7500	0.6099(1)	20(1)	
Se(5)	0.0549(2)	-0.2500	0.6643(1)	17(1)	
Se(6)	-0.0665(2)	-0.7500	0.7274(1)	18(1)	
Se(7)	-0.2093(2)	-0.2500	0.6811(1)	17(1)	
Se(8)	-0.1840(2)	-0.2500	0.8080(1)	22(1)	
Se(9)	-0.3285(2)	-0.7500	0.7605(1)	20(1)	
Se(10)	-0.0199(2)	-0.7500	0.8350(1)	20(1)	
Se(11)	-0.3350(2)	-0.2500	0.4183(1)	19(1)	
Se(12)	-0.0102(2)	-0.2500	0.9438(1)	17(1)	
Se(13)	-0.3419(2)	-0.7500	0.5245(1)	23(1)	
Se(14)	-0.3642(2)	-0.2500	0.6424(1)	21(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$.

	x	y	z	$U_{\text{(eq)}}$
Bi(1)	0.0815(1)	0.2500	0.4679(1)	20(1)
Bi(2)	0.0666(1)	-0.7500	0.6012(1)	16(1)
Bi(3)	-0.0825(1)	-0.2500	0.6678(1)	17(1)
Bi(4)	-0.1945(1)	-0.7500	0.7465(1)	20(1)
Bi(5)	0.1914(1)	-0.2500	0.6745(1)	18(1)
Bi(6)	-0.0953(1)	-0.2500	0.8773(1)	17(1)
Bi(7)	-0.4316(1)	-0.7500	0.6039(1)	17(1)
Bi(8)	-0.4083(1)	-0.2500	0.4877(1)	16(1)
Pb(9)	-0.2299(1)	-0.7500	0.4663(1)	37(1)
Rb(10)	-0.2470(1)	-0.7500	0.6063(1)	28(1)
Rb(11)	0.0528(1)	-0.2500	0.7687(1)	38(1)
S(1)	0.0750(4)	-0.2500	0.5327(3)	27(2)
S(2)	0.0849(3)	-0.2500	0.4042(2)	19(2)
S(3)	0.2027(3)	0.2500	0.4743(2)	20(2)
S(4)	0.1873(3)	-0.7500	0.6062(3)	21(2)
S(5)	0.0584(3)	-0.2500	0.6597(2)	19(2)
S(6)	-0.0645(3)	-0.7500	0.7239(2)	19(2)
S(7)	-0.2046(3)	-0.2500	0.6848(3)	22(2)
S(8)	-0.1815(3)	-0.2500	0.8080(3)	25(2)
S(9)	-0.3236(3)	-0.7500	0.7675(3)	24(2)
S(10)	-0.0235(3)	-0.7500	0.8394(2)	20(2)
S(11)	-0.3341(3)	-0.2500	0.4222(2)	17(2)
S(12)	-0.0143(3)	-0.2500	0.9443(2)	16(2)
S(13)	-0.3411(3)	-0.7500	0.5231(2)	20(2)
S(14)	-0.3708(3)	-0.2500	0.6396(2)	18(2)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-4. Crystallographic Data for Rb₁₁Bi₁₅Se₂₈ and Rb₄EuBi₆Se₁₂.

Empirical formula	Rb ₁₁ Bi ₁₅ Se ₂₈ (VI)	Rb ₄ EuBi ₆ Se ₁₂ (VII)
Formula weight	6285.75	2132.44
Temperature, K	173(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
Unit cell dimensions, Å	<i>a</i> = 32.219(1) <i>b</i> = 4.2719(2) <i>c</i> = 26.6592(8) β = 112.453(1)°	<i>a</i> = 31.929(6) <i>b</i> = 4.1369(8) <i>c</i> = 21.175(4) β = 105.34(3)°
Z, Volume, Å ³	2, 3496.3(2)	4, 2697.3(9)
Density (calculated), g/cm ³	5.971	5.251
Absorption coefficient, mm ⁻¹	59.787	49.380
F(000)	5208	3604
Crystal size, mm ³	0.02 x 0.02 x 0.50	0.2 x 0.6 x 0.05
θ range for data collection	1.33 to 26.40°	1.00 to 26.00°
Index ranges	-31 ≤ <i>h</i> ≤ 40 -5 ≤ <i>k</i> ≤ 5 -33 ≤ <i>l</i> ≤ 33	0 ≤ <i>h</i> ≤ 38 0 ≤ <i>k</i> ≤ 5 -26 ≤ <i>l</i> ≤ 25
Reflections collected	10247	3087
Independent reflections	4028 [<i>R</i> _(int) = 0.0771]	3039 [<i>R</i> _(int) = 0.1491]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4028 / 0 / 168	3039 / 0 / 144
Goodness-of-fit on <i>F</i> ²	0.832	1.094
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0467 <i>wR</i> 2 = 0.0877	<i>R</i> 1 = 0.0677, <i>wR</i> 2 = 0.1829
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0851 <i>wR</i> 2 = 0.0933	<i>R</i> 1 = 0.2101 <i>wR</i> 2 = 0.2316
Extinction	0.000081(4)	-
Largest peak and hole, e·Å ⁻³	4.403 and -2.799	5.694 and -4.816

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	-0.2041(1)	0	0.0747(1)	16(1)	0.5
Rb(1)	-0.2041(1)	0	0.0747(1)	16(1)	
Bi(2)	-0.0590(1)	0	0.1131(1)	16(1)	0.5
Bi(3)	-0.3520(1)	0	0.0344(1)	16(1)	
Bi(4)	-0.2648(1)	-0.5000	0.1737(1)	15(1)	
Bi(5)	-0.1926(1)	0	0.3194(1)	13(1)	
Bi(6)	-0.1380(1)	0.5000	0.4625(1)	15(1)	
Bi(7)	0.0885(1)	0	0.3943(1)	13(1)	
Bi(8)	0.0257(1)	0.5000	0.2530(1)	12(1)	
Rb(2)	-0.1143(1)	0.5000	0.2337(1)	14(1)	
Rb(3)	-0.0369(1)	0	0.4031(1)	17(1)	
Rb(4)	-0.5000	0	0	22(1)	
Rb(5)	-0.4087(1)	-0.5000	0.1526(1)	20(1)	
Rb(6)	-0.3199(1)	0	0.3234(1)	21(1)	
Rb(7)	-0.2572(2)	0.5000	0.4819(2)	34(2)	
Se(1)	-0.1311(1)	-0.5000	0.0929(1)	45(1)	
Se(2)	-0.0855(1)	0	-0.0166(1)	20(1)	
Se(3)	-0.2805(1)	-0.5000	0.0487(1)	36(1)	
Se(4)	-0.3312(1)	0	0.1476(1)	15(1)	
Se(5)	-0.1993(1)	0	0.1959(1)	29(1)	
Se(6)	-0.2596(1)	-0.5000	0.2804(1)	14(1)	
Se(7)	-0.1257(1)	0.5000	0.3576(1)	12(1)	
Se(8)	-0.2060(1)	0	0.4167(1)	14(1)	
Se(9)	-0.0733(1)	0	0.5062(1)	11(1)	
Se(10)	-0.1539(1)	0.5000	0.5634(1)	14(1)	
Se(11)	0.0213(1)	0.5000	0.3551(1)	11(1)	
Se(12)	0.0927(1)	0	0.2829(1)	11(1)	
Se(13)	-0.0402(1)	0	0.2250(1)	11(1)	
Se(14)	0.0039(1)	0.5000	0.1270(1)	23(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3852(1)	0	0.8676(1)	24(1)	
Bi(2)	0.1320(1)	0	0.9634(1)	22(1)	
Bi(3)	0.1475(1)	0.5000	0.7969(1)	20(1)	
Bi(4)	0.3601(1)	0.5000	0.3725(1)	28(1)	
Bi(5)	0.3808(1)	0	0.5392(1)	37(1)	
Bi(6)	0.3960(1)	-0.5000	0.7042(1)	22(1)	
Eu(1)	0.2579(2)	0	0.9096(2)	29(1)	
Rb(1)	0.2652(2)	0.5000	0.7150(3)	34(2)	
Rb(2)	0.7442(5)	0	0.4775(6)	50(4)	0.5
Rb(3)	0.5000	0.5000	0	46(3)	
Rb(4)	0.5162(3)	0	0.8150(3)	44(2)	
Rb(5)	0.5117(3)	0.5000	0.6141(4)	52(2)	
S(1)	-0.1743(12)	0	0.8898(9)	81(11)	
S(2)	0.0779(6)	0.5000	0.9766(8)	36(5)	
S(3)	-0.3037(7)	-0	0.9496(9)	50(6)	
S(4)	0.0963(5)	0	0.8324(8)	25(3)	
S(5)	0.2007(8)	0	0.7657(10)	48(6)	
S(6)	0.0954(5)	0.5000	0.6775(7)	26(3)	
S(7)	0.1831(6)	-0.5000	0.5788(7)	34(4)	
S(8)	-0.0779(6)	0	0.4859(6)	35(4)	
S(9)	-0.1632(6)	0	0.5876(7)	36(4)	
S(10)	-0.0562(6)	0.5000	0.6635(7)	27(4)	
S(11)	-0.1536(6)	-0.5000	0.7402(7)	30(4)	
S(12)	-0.0591(7)	0	0.8467(8)	38(5)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-7. Crystallographic Data for $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ and $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$.

Empirical formula	$\text{Cs}_{1.11}\text{Bi}_{9.63}\text{Se}_{15}$ (VIII)	$\text{Rb}_{0.18}\text{Sn}_{1.18}\text{Bi}_{5.82}\text{Se}_{10}$ (IX)
Formula weight	3344.41	2161.30
Temperature, K	173(2)	300(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$P2_1/m$
Unit cell dimensions, Å	$a = 27.547(9)$ $b = 4.162(1)$ $c = 14.132(5)$ $\beta = 103.350(6)^\circ$	$a = 16.038(2)$ $b = 4.1540(6)$ $c = 17.028(3)$ $\beta = 116.517(2)^\circ$
Z, Volume, Å ³	2, 1576.5(9)	2, 1015.1(3)
Density (calculated), g/cm ³	7.046	7.071
Absorption coefficient, mm ⁻¹	72.112	70.021
F(000)	2741	1777
Crystal size, mm ³	0.10 x 0.12 x 0.25	0.39 x 0.06 x 0.03
θ range for data collection	1.86 to 28.49°	2.34 to 28.50°
Index ranges	$-30 \leq h \leq 36$ $-5 \leq k \leq 5$ $-18 \leq l \leq 15$	$-20 \leq h \leq 20$ $-5 \leq k \leq 5$ $-22 \leq l \leq 22$
Reflections collected	4803	10783
Independent reflections	2087 [$R_{\text{(int)}} = 0.0444$]	2654 [$R_{\text{(int)}} = 0.0862$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4803 / 2 / 88	2654 / 4 / 117
Goodness-of-fit on F^2	1.093	1.128
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0524$ $wR2 = 0.1423$	$R1 = 0.0540$ $wR2 = 0.1413$
R indices (all data)	$R1 = 0.0642$ $wR2 = 0.1499$	$R1 = 0.0607$ $wR2 = 0.1464$
Extinction	0.00016(4)	0.00099(11)
Largest peak and hole, e·Å ⁻³	3.938 and -3.738	4.083 and -2.779

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.3061(1)	0	0.9639(1)	17(1)	
Bi(2)	0.4255(1)	-0.5000	0.8886(1)	16(1)	
Bi(3)	0.4509(1)	0	0.1717(1)	19(1)	
Bi(4)	0.3133(1)	0	0.5695(1)	16(1)	
Bi(5)	0.3351(1)	-0.5000	0.3212(2)	27(1)	0.815(4)
Cs(1)	0.3252(4)	-0.5000	0.2804(9)	16(2)	0.185(4)
Cs(2)	0.5000	-0.5000	0.5000	122(5)	0.739(14)
Se(1)	0.3762(1)	-0.5000	0.0656(2)	16(1)	
Se(2)	0.3615(1)	0	0.7980(2)	15(1)	
Se(3)	0.5000	0	0	13(1)	
Se(4)	0.2623(1)	0	0.1291(2)	16(1)	
Se(5)	0.4828(1)	-0.5000	0.7409(2)	17(1)	
Se(6)	0.2590(1)	0	0.3789(2)	14(1)	
Se(7)	0.3740(1)	-0.5000	0.5210(2)	15(1)	
Se(8)	0.4077(1)	0	0.3346(2)	30(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-9. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.1120(1)	0.2500	0.0817(1)	21(1)	
Bi(2)	0.3514(1)	0.7500	0.2636(1)	20(1)	
Bi(3)	0.5921(1)	0.2500	0.4522(1)	17(1)	
Bi(4)	0.8230(1)	-0.2500	0.6339(1)	22(1)	
Bi(5)	0.9000(1)	-0.2500	0.2146(1)	43(1)	0.356(3)
Sn(5)	0.9000(1)	-0.2500	0.2146(1)	43(1)	0.644(3)
Bi(6)	0.6780(1)	0.2500	0.2382(1)	28(1)	0.775(3)
Sn(6)	0.6780(1)	0.2500	0.2382(1)	28(1)	0.225(3)
Bi(7)	0.3946(1)	0.2500	0.0022(1)	22(1)	0.686(3)
Sn(7)	0.3946(1)	0.2500	0.0022(1)	22(1)	0.314(3)
Rb	0.0022(12)	-0.2500	0.4980(10)	113(12)	0.183(5)
Se(1)	-0.0820(1)	0.2500	0.0453(1)	19(1)	
Se(2)	0.1481(2)	0.7500	0.2233(1)	20(1)	
Se(3)	0.3197(2)	0.2500	0.1399(1)	19(1)	
Se(4)	0.3851(1)	0.2500	0.4068(1)	15(1)	
Se(5)	0.5593(1)	0.7500	0.3272(1)	17(1)	
Se(6)	0.7878(1)	0.2500	0.5060(1)	19(1)	
Se(7)	0.0080(2)	-0.2500	0.6672(2)	47(1)	
Se(8)	0.8062(2)	-0.2500	0.3175(2)	23(1)	
Se(9)	0.7356(2)	0.2500	0.1093(1)	21(1)	
Se(10)	0.5245(1)	-0.2500	0.1112(1)	20(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-10. Crystallographic Data for Ba_{4-x}Bi_{6+2/3x}Se₁₃ and Ba_xPb_{4-x}Bi₆S₁₃.

Empirical formula	Ba _{2.77} Bi _{6.82} Se ₁₃ (X)	Ba _{1.58} Pb _{2.42} Bi ₆ S ₁₃ (XI)
Formula weight	2832.16	2389.06
Temperature, K	297(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/m</i>	<i>P2₁/m</i>
Unit cell dimensions, Å	<i>a</i> = 17.232(2) <i>b</i> = 4.2816(6) <i>c</i> = 18.469(2) β = 90.640(2)°	<i>a</i> = 16.507(3) <i>b</i> = 4.1134(8) <i>c</i> = 17.706(3) β = 90.570(4)°
Z, Volume, Å ³	2, 1362.6(3)	2, 1202.2(4)
Density (calculated), g/cm ³	6.903	6.600
Absorption coefficient, mm ⁻¹	65.153	65.277
F(000)	2236	1986
Crystal size, mm ³	0.10 x 0.12 x 0.25	0.39 x 0.06 x 0.03
θ range for data collection	1.18 to 32.72°	1.68 to 30.51°
Index ranges	-25 ≤ <i>h</i> ≤ 26 -6 ≤ <i>k</i> ≤ 6 -27 ≤ <i>l</i> ≤ 27	-21 ≤ <i>h</i> ≤ 21 -5 ≤ <i>k</i> ≤ 5 -25 ≤ <i>l</i> ≤ 25
Reflections collected	22682	13675
Independent reflections	5269 [<i>R</i> _(int) = 0.0499]	3946 [<i>R</i> _(int) = 0.0818]
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	5369 / 2 / 150	3946 / 0 / 143
Goodness-of-fit on <i>F</i> ²	1.097	0.977
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0369 <i>wR</i> 2 = 0.0878	<i>R</i> 1 = 0.0445 <i>wR</i> 2 = 0.1000
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0434 <i>wR</i> 2 = 0.0905	<i>R</i> 1 = 0.0682 <i>wR</i> 2 = 0.1082
Extinction	0.00030(3)	0.00097(7)
Largest peak and hole, e·Å ⁻³	3.173 and -3.699	4.934 and -3.008

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-11. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.0092(1)	-0.2500	0.6181(1)	21(1)	
Bi(2)	0.1899(1)	-0.2500	0.4577(1)	20(1)	
Bi(3)	0.3980(1)	-0.7500	0.4717(1)	25(1)	
Bi(4)	0.6714(1)	-0.7500	0.1198(1)	20(1)	
Bi(5)	0.4191(1)	0.2500	0.0767(1)	20(1)	0.947(2)
Bi(6)	0.1734(1)	-0.7500	0.0257(1)	18(1)	
Bi(7)	0.5123(1)	-0.2500	0.2487(1)	24(1)	0.757(2)
Ba(8)	0.2369(1)	-0.7500	0.6744(1)	18(1)	0.912(5)
Bi(8)	0.2222(8)	-0.7500	0.7029(11)	32(5)	0.046(4)
Bi(8')	0.2062(13)	-0.7500	0.6711(9)	25(5)	0.038(5)
Ba(9)	0.2503(1)	-0.2500	0.2344(1)	17(1)	0.855(5)
Bi(9)	0.2487(8)	-0.2500	0.2029(11)	21(5)	0.034(3)
Ba(10)	0.0191(1)	-0.7500	0.8449(1)	19(1)	
Se(1)	0.1083(1)	-0.2500	0.7324(1)	19(1)	
Se(2)	-0.0775(1)	-0.7500	0.6762(1)	18(1)	
Se(3)	0.2669(1)	-0.7500	0.3746(1)	18(1)	
Se(4)	0.4834(1)	-0.2500	0.4037(1)	21(1)	
Se(5)	0.3130(1)	-0.2500	0.5557(1)	18(1)	
Se(6)	0.1067(1)	-0.7500	0.5356(1)	19(1)	
Se(7)	0.7753(1)	-0.2500	0.1427(1)	18(1)	
Se(8)	0.6304(1)	-0.7500	0.2626(1)	19(1)	
Se(9)	0.5412(1)	-0.2500	0.0910(1)	17(1)	
Se(10)	0.3980(1)	0.2500	0.02242(1)	19(1)	
Se(11)	0.3053(1)	-0.2500	0.567(1)	18(1)	
Se(12)	0.1267(1)	-0.7500	0.1656(1)	21(1)	
Se(13)	0.0745(1)	-0.2500	-0.0126(1)	18(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-12. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)	0.0084(1)	-0.2500	0.6190(1)	15(1)	
M(2)	0.1883(1)	-0.2500	0.4591(1)	16(1)	
M(3)	0.3929(1)	-0.7500	0.4786(1)	18(1)	
M(4)	0.6733(1)	-0.7500	0.1223(1)	15(1)	
M(5)	0.4185(1)	0.2500	0.0778(1)	15(1)	
M(6)	0.1750(1)	-0.7500	0.0223(1)	15(1)	
M(7)	0.5131(1)	-0.2500	0.2552(1)	18(1)	
M(8)	0.2242(1)	-0.7500	0.6811(1)	23(1)	0.805(11)
Ba(8)	0.2242(1)	-0.7500	0.6811(1)	23(1)	0.195(11)
M(9)	0.2420(1)	-0.2500	0.2311(1)	36(1)	0.418(12)
Ba(9)	0.2420(1)	-0.2500	0.2311(1)	36(1)	0.582(12)
M(10)	-0.0073(6)	-0.7500	0.8352(4)	35(2)	0.199(9)
Ba(10)	0.0193(2)	-0.7500	0.8472(1)	18(1)	0.801(9)
S(1)	0.1086(3)	-0.2500	0.7303(2)	16(1)	
S(2)	-0.0755(3)	-0.7500	0.6816(2)	16(1)	
S(3)	0.2639(3)	-0.7500	0.3779(3)	18(1)	
S(4)	0.4765(3)	-0.2500	0.4089(3)	21(1)	
S(5)	0.3053(3)	-0.2500	0.5595(3)	18(1)	
S(6)	0.1069(3)	-0.7500	0.5417(3)	19(1)	
S(7)	0.7765(3)	-0.2500	0.1461(3)	16(1)	
S(8)	0.6373(3)	-0.7500	0.2639(2)	17(1)	
S(9)	0.5411(3)	-0.2500	0.0937(3)	17(1)	
S(10)	0.3962(3)	0.2500	0.2238(3)	18(1)	
S(11)	0.3046(3)	-0.2500	0.0619(3)	19(1)	
S(12)	0.1288(3)	-0.7500	0.1634(2)	18(1)	
S(13)	0.0774(3)	-0.2500	-0.0132(3)	16(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 8-13. Crystallographic Data for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$.

Empirical formula	$\text{Rb}_{1.5x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ (XII)
Formula weight	2643.07
Temperature, K	294(2)
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions, Å	$a = 17.596(5)$ $b = 4.169(1)$ $c = 18.568(6)$ $\beta = 114.101(5)^\circ$
Z, Volume, Å ³	2, 1243.5(7)
Density (calculated), g/cm ³	7.059
Absorption coefficient, mm ⁻¹	73.337
F(000)	2172
Crystal size, mm ³	0.10 x 0.12 x 0.25
θ range for data collection	1.27 to 25.06°
Index ranges	$-20 \leq h \leq 20$ $-4 \leq k \leq 4$ $-22 \leq l \leq 22$
Reflections collected	9358
Independent reflections	2511 [$R_{\text{int}} = 0.0949$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2511 / 0 / 127
Goodness-of-fit on F^2	0.929
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0538$, $wR2 = 0.1064$
R indices (all data)	$R1 = 0.1076$, $wR2 = 0.1192$
Largest peak and hole, e·Å ⁻³	4.325 and -2.303

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-14. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.9458(1)	-0.7500	0.3835(1)	35(1)	
Bi(2)	0.1693(1)	-0.2500	0.4326(1)	30(1)	
Bi(3)	0.3972(1)	-0.7500	0.4915(1)	33(1)	
Bi(4)	0.7319(1)	-0.2500	0.1353(1)	28(1)	
Bi(5)	0.4591(1)	0.7500	0.0859(1)	28(1)	
Bi(6)	0.8164(1)	-0.7500	-0.0215(1)	27(1)	
Bi(7)	0.6341(1)	0.2500	0.2740(1)	29(1)	
Bi(8)	0.3475(2)	0.2500	0.2308(2)	53(1)	0.5
Rb(8)	0.3475(2)	0.2500	0.2308(2)	53(1)	0.5
Rb(9)	0.0524(3)	-0.7500	0.1751(3)	39(1)	
Se(1)	0.0027(3)	-0.2500	0.3112(2)	26(1)	
Se(2)	0.2206(3)	-0.7500	0.3594(2)	28(1)	
Se(3)	0.4304(3)	-0.2500	0.3984(2)	31(1)	
Se(4)	0.3370(3)	-0.2500	0.5669(2)	32(1)	
Se(5)	0.9052(3)	-0.2500	0.4878(2)	28(1)	
Se(6)	0.8441(3)	-0.7500	0.1576(3)	29(1)	
Se(7)	0.7589(3)	-0.2500	0.2926(2)	27(1)	
Se(8)	0.5841(2)	0.2500	0.0978(2)	23(1)	
Se(9)	0.5037(3)	0.7500	0.2461(2)	26(1)	
Se(10)	0.3346(3)	0.2500	0.0643(3)	28(1)	
Se(11)	0.7759(3)	-0.7500	-0.1860(3)	47(1)	
Se(12)	0.9288(3)	-0.2500	0.0082(3)	29(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The Bi sites probably contain small amounts of Sn.

Table 8-15. Crystallographic Data for $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$ and $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$.

Empirical formula	$K_{1.40}Pb_{0.99}Bi_{5.54}Se_{10}$ (XIII)	$K_{1.16}Eu_{0.87}Bi_{5.71}Se_{10}$ (XIV)
Formula weight	1738.30	1691.10
Temperature, K	293(2)	173(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions, Å	$a = 23.905(5)$ $b = 4.0746(8)$ $c = 19.382(4)$	$a = 24.1357(4)$ $b = 4.0889(1)$ $c = 19.4661(5)$
Z, Volume, Å ³	4, 1887.9(7)	4, 1921.08(8)
Density (calculated), g/cm ³	6.116	5.847
Absorption coefficient, mm ⁻¹	61.639	56.232
F(000)	2449	2843
Crystal size, mm ³	0.13 x 0.03 x 0.03	0.65 x 0.026 x 0.26
θ range for data collection	1.35 to 30.19(	1.69 to 28.76(
Index ranges	$-31 \leq h \leq 33$ $-5 \leq k \leq 5$ $-18 \leq l \leq 27$	$-32 \leq h \leq 31$ $-4 \leq k \leq 5$ $-25 \leq l \leq 25$
Reflections collected	13540	14578
Independent reflections	2922 [R(int) = 0.0771]	2696 [R(int) = 0.0699]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2922 / 0 / 113	2696 / 0 / 117
Goodness-of-fit on F ²	1.012	0.950
Final R indices [I>2σ(I)]	R1 = 0.0437 wR2 = 0.0885	R1 = 0.0323 wR2 = 0.0660
R indices (all data)	R1 = 0.0635 wR2 = 0.0956	R1 = 0.0458 wR2 = 0.0672
Extinction	0.00049(4)	0.00082(3)
Largest peak and hole, e·Å ⁻³	3.936 and -4.816	2.446 and -2.622

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-16. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)*	0.4325(1)	-0.7500	0.4644(1)	10(1)	
M(2)	0.2994(1)	-0.2500	0.4088(1)	8(1)	
M(3)	0.3284(1)	-0.2500	-0.1888(1)	9(1)	
M(4)	0.3489(1)	0.2500	0.0156(1)	12(1)	
M(5)	0.4914(1)	-0.2500	-0.0971(1)	11(1)	0.932(3)
M(6)	0.4571(1)	0.2500	-0.2745(1)	11(1)	
M(7)	0.2168(1)	-0.2500	0.1159(1)	26(1)	0.515(4)
K(7)	0.2168(1)	-0.2500	0.1159(1)	26(1)	0.485(4)
M(8)	0.3686(1)	-0.2500	0.2131(2)	32(1)	0.082(5)
K(8)	0.3686(1)	-0.2500	0.2131(2)	32(1)	0.918(5)
S(1)	0.5007(2)	-0.7500	0.5894(2)	14(1)	
S(2)	0.3623(2)	-0.2500	0.5191(2)	13(1)	
S(3)	0.3603(2)	-0.7500	0.3529(2)	11(1)	
S(4)	0.2782(2)	-0.2500	-0.0331(3)	16(1)	
S(5)	0.2624(2)	-0.7500	-0.2295(2)	13(1)	
S(6)	0.3783(2)	-0.2500	-0.3068(2)	12(1)	
S(7)	0.4123(2)	0.2500	-0.1381(2)	12(1)	
S(8)	0.2985(2)	0.2500	0.1317(2)	14(1)	
S(9)	0.4304(2)	-0.2500	0.0559(3)	21(1)	
S(10)	0.5283(2)	-0.2500	-0.2255(2)	11(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, Pb or both.

Table 8-17. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
Bi(1)	0.4328(1)	-0.7500	0.4652(1)	17(1)	
Bi(2)	0.2998(1)	-0.2500	0.4086(1)	12(1)	
Bi(3)	0.3261(1)	-0.2500	-0.1907(1)	13(1)	
Bi(4)	0.3485(1)	0.2500	0.0170(1)	21(1)	
Bi(5)	0.4901(1)	-0.2500	-0.1002(1)	22(1)	0.735(2)
Bi(6)	0.4557(1)	0.2500	-0.2745(1)	17(1)	0.758(11)
Eu(6)	0.4557(1)	0.2500	-0.2745(1)	17(1)	0.242(11)
Eu(7)	0.2077(1)	-0.2500	0.1132(1)	16(1)	0.591(5)
K(7)	0.2077(1)	-0.2500	0.1132(1)	16(1)	0.189(5)
Bi(7')	0.2288(3)	-0.2500	0.1083(4)	12(2)	0.10
Bi(7'')	0.2245(3)	-0.2500	0.1289(3)	11(1)	0.12
K(8)	0.3716(1)	-0.2500	0.2174(2)	20(1)	0.969(4)
Eu(8)	0.3716(1)	-0.2500	0.2174(2)	20(1)	0.031(4)
S(1)	0.5025(2)	-0.7500	0.5866(2)	20(1)	
S(2)	0.3594(2)	-0.2500	0.5206(2)	16(1)	
S(3)	0.3616(1)	-0.7500	0.3533(2)	17(1)	
S(4)	0.2748(2)	-0.2500	-0.0317(2)	22(1)	
S(5)	0.2596(1)	-0.7500	-0.2308(2)	17(1)	
S(6)	0.3721(2)	-0.2500	-0.3097(2)	19(1)	
S(7)	0.4101(2)	0.2500	-0.1414(2)	23(1)	
S(8)	0.2970(1)	0.2500	0.1313(2)	17(1)	
S(9)	0.4273(2)	-0.2500	0.0569(2)	36(1)	
S(10)	0.5253(2)	-0.2500	-0.2294(2)	19(1)	

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-18. Crystallographic Data for CsPbBi₃S₆.

formula	CsPbBi ₃ S ₆ (XVI)	Temp, K	298
Formula weight	1159.41	$\lambda(\text{Mo K}\alpha)$, Å	0.71069
Crystal habit	black plate	$\mu(\text{Mo K}\alpha)$, cm ⁻¹	525.27
Crystal size, mm ³	0.50 x 0.35 x 0.02	scan mode	ω
Space group	<i>P6₃/mmc</i> (No. 194)	2 θ max, deg	59.8
<i>a</i> , Å	4.074(2)	total data measd	2420
<i>b</i> , Å	4.074(2)	total unique data	290
<i>c</i> , Å	24.549(5)	data with $I > 3\sigma(I)$	177
γ , deg	120	No. of variables	14
<i>Z</i> ; <i>V</i> , Å ³	1 ; 352.8(3)	final <i>R</i> / <i>R_w</i> , %	8.9 / 10.1
<i>D</i> calc, g/cm ⁻³	5.457	goodness of fit	3.09

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad R_w = \left\{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \right\}^{1/2}$$

Table 8-19. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²x10³) for CsPbBi₃S₆.

	x	y	z	<i>B</i> (eq)	occ.
M(1)	0.6667	0.3333	0.4251(1)	1.69(3)	1
Cs(1)	0.6667	0.3333	0.2500	7.0(7)	0.21
Cs(2)	0	0	0.7500	6.0(4)	0.29
S(1)	0.6667	0.3333	0.6359(8)	2.3(2)	1
S(2)	0	0	0.5000	2.0(3)	1

M = 75% Bi + 25% Pb

Table 8-20. Crystallographic Data for BaLaBi₂S₆ and Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z}.

Empirical formula	BaBi ₂ LaS ₆ (XVII)	Ba _{2.80} U _{0.70} Bi _{2.50} Se _{8.75} (XXI)
Formula weight	886.57	1764.52
Temperature, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/m</i>
Unit cell dimensions, Å	<i>a</i> = 4.232(4) <i>b</i> = 14.787(5) <i>c</i> = 16.360(9) β = 92.22(7)°	<i>a</i> = 13.124(2) <i>b</i> = 4.3438(5) <i>c</i> = 15.518(6) β = 95.276(2)°
Z, Volume, Å ³	4, 1023.1(12)	2, 880.86(18)
Density (calculated), g/cm ³	5.756	6.653
Absorption coefficient, mm ⁻¹	43.335	55.501
F(000)	1500	1452
Crystal size, mm ³	0.02 x 0.02 x 0.20	0.02 x 0.02 x 0.20
θ range for data collection	2.75 to 25.04°	1.32 to 28.26°
Index ranges	-16 ≤ <i>h</i> ≤ 13 -5 ≤ <i>k</i> ≤ 5 -20 ≤ <i>l</i> ≤ 20	-16 ≤ <i>h</i> ≤ 13 -5 ≤ <i>k</i> ≤ 5 -20 ≤ <i>l</i> ≤ 20
Reflections collected	3536	5359
Independent reflections	1799 [<i>R</i> _(int) = 0.2413]	1944 [<i>R</i> _(int) = 0.0447]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1799 / 0 / 91	1944 / 0 / 94
Goodness-of-fit on F ²	1.062	1.010
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0474, <i>wR</i> 2 = 0.1281	<i>R</i> 1 = 0.0394, <i>wR</i> 2 = 0.0916
R indices (all data)	<i>R</i> 1 = 0.1007, <i>wR</i> 2 = 0.1639	<i>R</i> 1 = 0.0522, <i>wR</i> 2 = 0.0956
Extinction	-	0.00189(16)
Largest peak and hole, e.Å ⁻³	5.029 and -5.046	3.029 and -2.369

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 8-21. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for BaLaBi₂S₆.

	x	y	z	U _(eq)
Bi(1)	0.2673(3)	0.3706(1)	0.0303(1)	14(1)
Bi(2)	-0.7506(3)	0.4769(1)	-0.1993(1)	13(1)
La	-0.2948(4)	0.3738(1)	-0.4056(1)	14(1)
Ba	0.7440(4)	0.2901(1)	0.3294(1)	14(1)
S(1)	-0.2554(18)	0.3280(5)	0.1301(4)	14(2)
S(2)	0.2352(18)	0.2069(5)	-0.0206(4)	14(2)
S(3)	0.2967(19)	0.5867(5)	0.0900(4)	19(2)
S(4)	-0.2231(17)	0.6735(4)	0.2804(4)	10(1)
S(5)	-0.6832(19)	0.4618(5)	0.2969(4)	19(2)
S(6)	0.1605(19)	-0.0135(5)	0.0509(5)	20(2)

U_(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8-22. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$.

	x	y	z	$U_{\text{(eq)}}$	occ.
M(1)	0.7272(1)	0.2500	0.9548(1)	18(1)	
M(2)	0.0354(1)	-0.7500	0.8817(1)	22(1)	
M(3)	0.3868(1)	0.2500	0.5550(1)	24(1)	
Ba(4)	0.1250(1)	-0.2500	0.6505(1)	22(1)	0.795(10)
U(4)	0.1250(1)	-0.2500	0.6505(1)	22(1)	0.205(10)
Ba(5)	0.2271(1)	0.2500	0.3028(1)	20(1)	
Ba(6)	0.5546(1)	0.2500	0.1741(1)	17(1)	
Se(1)	0.6092(2)	-0.2500	0.0125(1)	19(1)	
Se(2)	0.6293(1)	0.2500	0.7932(1)	16(1)	
Se(3)	0.8735(2)	-0.2500	0.9117(1)	25(1)	
Se(4)	0.8288(1)	0.2500	0.1422(1)	21(1)	
Se(5)	0.9666(2)	-0.7500	0.7119(1)	26(1)	
Se(6)	0.2943(2)	0.2500	0.7066(1)	24(1)	
Se(7)	0.4812(2)	0.2500	0.3861(1)	24(1)	
Se(8)	0.2566(2)	-0.2500	0.4779(2)	44(1)	
Se(9)	0.0550(4)	0.2500	0.4908(3)	73(2)	0.753(12)

$U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

*M = Bi, U or both.

4. Results and discussion

Synthesis, thermal behavior and energy gaps. $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$, $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$, $\text{K}_x\text{M}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$ ($\text{M} = \text{Pb}, \text{Eu}$), APbBi_3S_6 ($\text{A} = \text{Rb}, \text{Cs}$), $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$, $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$, $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$, $\text{Rb}_{2.5-x}\text{Pb}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$, $\text{BaLnBi}_2\text{Q}_6$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$; $\text{Q} = \text{S}, \text{Se}$) can be made in pure form by stoichiometric reaction of the elements or the binaries at temperatures above 700 °C. $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$, and $\text{Rb}_x\text{Sn}_{1-x}\text{Bi}_{6-x}\text{Se}_{10}$ can be made by quenching a melt of the corresponding composition. $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ contains a small amount of $\text{CsBi}_{3.67}\text{Se}_6$ ⁵. $\text{Rb}_{2.5-x}\text{Sn}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$ and $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ are found as a mixture by reacting $\text{Rb}_2\text{Se}/\text{Bi}/\text{Sn}/\text{Se}$ in a 1.3:7.5:0.5:12 ratio. $\text{Rb}_{2.5-x}\text{Eu}_{2x}\text{Bi}_{8.5-x}\text{S}_{14}$ has a impurity of EuBi_2S_4 ⁴ while $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ is found a minor phase in the synthesis of $\text{K}_x\text{Bi}_2\text{Se}_3$ ³. $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$ was synthesized by reacting $\text{Ba}/\text{U}/\text{Bi}/\text{Se}$ in 1:1:0.5:3 ratio and a second identified phase exists.

In Table 8-23 there is a summary of the band-gap and differential thermal analysis data. These measurements could only be done when a pure phase was possible.

In general the sulfides compounds present higher band gaps and higher melting points compared to the selenide compounds.

Table 8-23. Optical Band-Gaps and Melting Points for (I) through (XXI).

Compound	E_g (eV)	Melting point ($^{\circ}\text{C}$)
$\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}^*$	—	—
$\text{Rb}_2\text{PbBi}_8\text{S}_{14}$	?	?
$\text{Rb}_{2.5-x}\text{Pb}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$	0.6	700
$\text{Rb}_{2.5-x}\text{Sn}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$	—	—
$\text{Rb}_{2.5-x}\text{Eu}_{2x}\text{Bi}_{8.5-x}\text{S}_{14}$	1.1	?
$\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$	1.1	?
$\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$	1.2	680
$\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$	—	—
$\text{Rb}_x\text{Sn}_{1-x}\text{Bi}_{6-x}\text{Se}_{10}$	—	—
$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$	0.3	842
$\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	?	?
$\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$	—	—
$\text{K}_x\text{Pb}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	1.0	739
$\text{K}_x\text{Eu}_{4-2x-3y}\text{Bi}_{4+x+2y}\text{S}_{10}$	—	—
$\text{RbPbBi}_3\text{S}_6$	0.9	739
$\text{CsPbBi}_3\text{S}_6$	0.9	726
$\text{BaLaBi}_2\text{S}_6$	0.8	910
$\text{BaCeBi}_2\text{S}_6$	1.0	890
$\text{BaPrBi}_2\text{S}_6$	1.1	864
$\text{BaLaBi}_2\text{Se}_6$	0.1	866
$\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$	—	—

*For the compounds that are not made in pure form these measurements could not be made.

Structure Description.

β -K_{2.5}Bi_{8.5}Se₁₄ (I), Rb₂PbBi₈S₁₄ (II), Rb_{2.5-x}Pb_{2x}Bi_{8.5-x}Se₁₄ (III), Rb_{2.5-x}Sn_{2x}Bi_{8.5-x}Se₁₄ (IV) and Rb_{2.5-x}Eu_{2x}Bi_{8.5-x}S₁₄ (V). All compounds are isostructural and adopt a new structure type. Single crystal X-ray data were only collected for β -K_{2.5}Bi_{8.5}Se₁₄ and Rb₂PbBi₈S₁₄. For the other members due to small size of the crystals this was not possible. For Rb_{2.5-x}Sn_{2x}Bi_{8.5-x}Se₁₄ and Rb_{2.5-x}Eu_{2x}Bi_{8.5-x}S₁₄ only the unit cell parameters were determined. Nevertheless, all compounds are isostructural as evidenced by X-ray powder diffraction and EDS analysis. Here we will describe in detail Rb₂PbBi₈S₁₄ and will compare it with β -K_{2.5}Bi_{8.5}Se₁₄.

The structure of Rb₂PbBi₈S₁₄ consists of NaCl-, CdI₂- and Bi₂Te₃- type infinite rods running along the b-axis and creating tunnels filled by Rb atoms, see Figure 8-1. The CdI₂-type blocks are running diagonally in two opposite directions in the ac-plane. In the point where they intercept the NaCl-type blocks are formed. The arrangement of the CdI₂-type and NaCl-type blocks creates large tunnels with a square-like cross section filled by the Rb atoms and the Bi₂Te₃- fragments. Similar arrangements are also found in Sr₂La_xBi_{8-x}S₁₄¹¹, α -RbBi₃Se₅¹² and KBi₃S₅¹³.

Similar to what is observed in the majority of Bi chalcogenides, the BiS_6 octahedra are distorted in various degrees. The least distorted BiS_6 octahedron is that of Bi(4) with Bi(4)-Se distances varying between 2.800(6)-2.870(7) Å and Se-Bi(4)-Se angles between 84.48(17)°-94.24(18)° (Tables 8-24 and 8-25). The next least distorted octahedron is that of Bi(6) with six bonds between 2.725(6)-2.882(5) Å. The distortion in the rest of the BiS_6 octahedra can be classified into three categories; those octahedra that are distorted towards a trigonal pyramid having three short bonds *trans* to three longer ones, those octahedra that have one short bond *trans* to a longer one and four more bonds equal in distance and those that the distortion resembles a “see-saw” geometry. The majority of the BiS_6 octahedra, Bi(2), Bi(3), Bi(7) and Bi(8) belong to the first category. This kind of distortion is more pronounced in the bismuth sulfides and less encountered in the bismuth selenides and bismuth tellurides. Bi(1) and Bi(5) belong to the second and third category respectively.

The Pb(9) atom has a bicapped trigonal prismatic coordination with Pb-S distances varying between 2.803(5)-3.314(8) Å.

The Rb atoms have also bicapped trigonal prismatic coordination with distances varying between 3.298(8)-3.487(6) Å for Rb(10) and 3.310(8)-3.512(6) Å for Rb(11).

Because Pb and Bi are crystallographically indistinguishable, bond-valence calculations were performed in order to check the atoms assignments. The bond-valence

sums are between 2.901 and 3.177 for Bi(1) through Bi(8), 1.959 for Pb(9), 1.248 for Rb(10) and 1.024 for Rb(11) agreeing very well with our atom assignments.

Several others compounds adopt the same structure type. In β - $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ the Pb(9) site is 50-50% occupied by K and Bi. Furthermore the better quality of the data set allowed the splitting of this site in three positions, two shifted to the side of the bicapped trigonal prismatic site assigned as Bi [Bi(9) and Bi(9')] and one sitting in the center assigned as K(9), see Figure 8-2. Also the two Rb sites are now occupied by K while the rest of the structure is identical with the majority of the BiSe_6 octahedra having the same octahedral distortions found in $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ and the Bi-Q bonds increased by ~ 0.1 - 0.15 Å. The corresponding Rb analogs, $\text{Rb}_{2.5}\text{Bi}_{8.5}\text{Q}_{14}$ (Q = S, Se) could be made. Instead we were able to make the analogs with Pb, Sn and Eu, $\text{Rb}_{2.5-x}\text{Pb}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$, $\text{Rb}_{2.5-x}\text{Sn}_{2x}\text{Bi}_{8.5-x}\text{Se}_{14}$ and $\text{Rb}_{2.5-x}\text{Eu}_{2x}\text{Bi}_{8.5-x}\text{S}_{14}$. For these three compounds the poor quality of the crystals did not allowed structural determination. We were able only to determine the cells for the Sn and Eu analogs which are $a = 21.74(5)$ Å, $b = 4.101(8)$ Å, $c = 32.42(7)$ Å and $a = 21.43(2)$ Å, $b = 4.065(3)$ Å, $c = 31.53(2)$ Å, respectively.

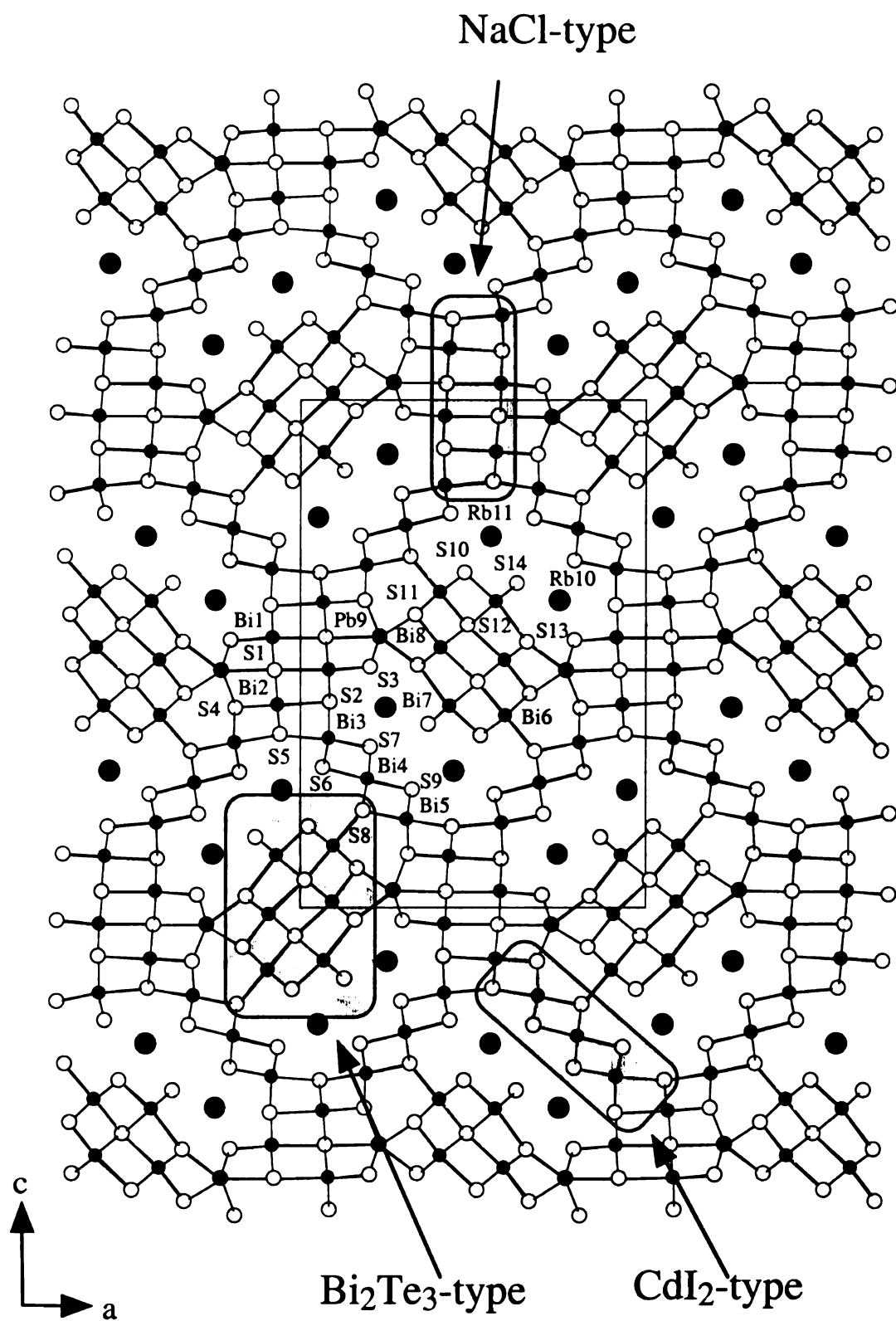


Figure 8-1. Projection of the structure of $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ down the b -axis. The shaded areas indicate the NaCl-, Bi_2Te_3 - and CdI_2 -type building blocks.

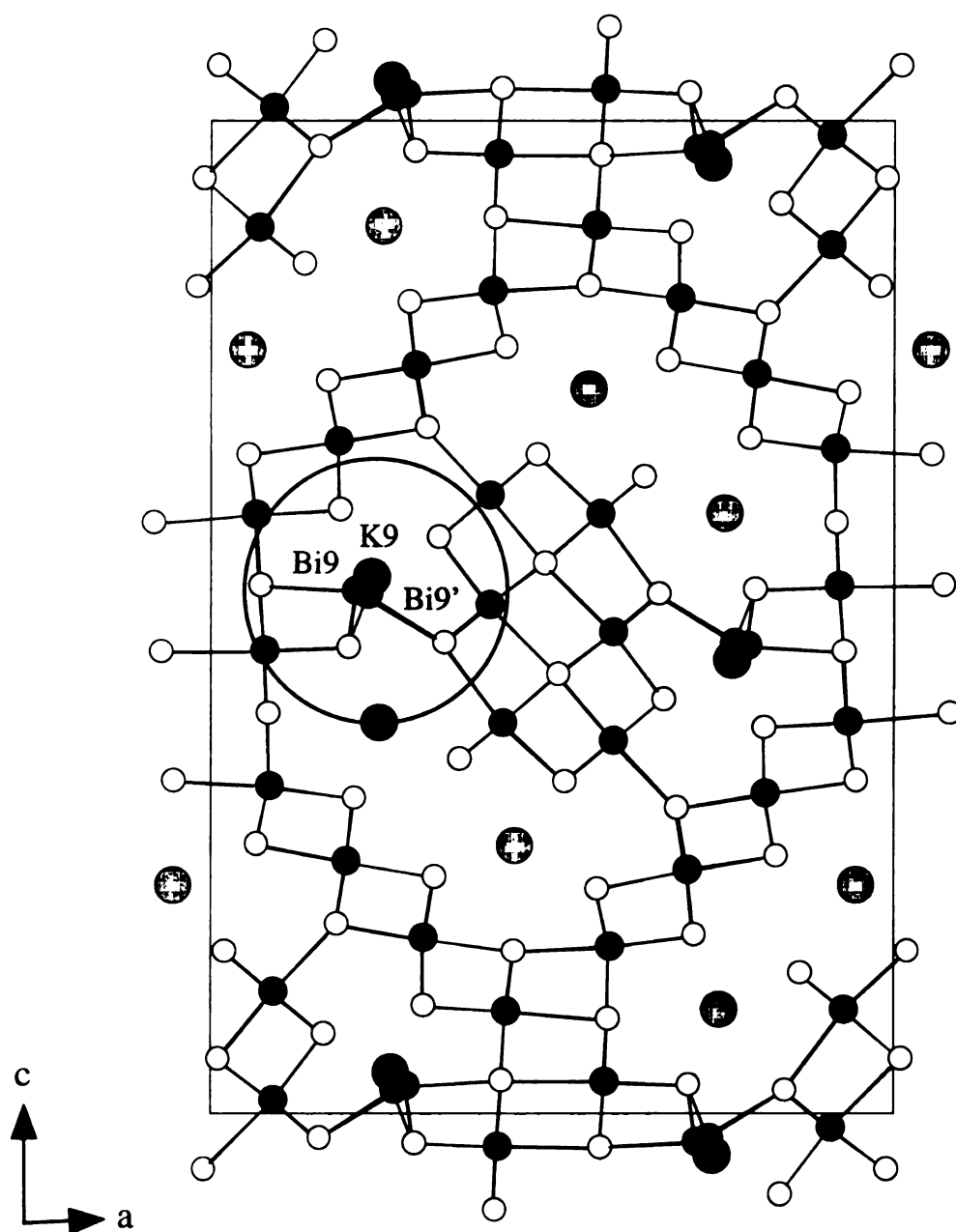


Figure 8-2. Projection of the unit cell of $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ down the b-axis. The circular shaded area shows the splitting in site 9. The rest of the atom labeling is the same as in $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$.

Table 8-24. Bond Distances (Å) for Rb₂PbBi₈S₁₄ and β-K_{2.5}Bi_{8.5}Se₁₄.

Rb ₂ PbBi ₈ S ₁₄		β-K _{2.5} Bi _{8.5} Se ₁₄	
Bi(1)-S(3)	2.601(6)	Bi(1)-Se(3)	2.735(4)
Bi(1)-S(2)	2.838(5)x2	Bi(1)-Se(2)	2.920(2)x2
Bi(1)-S(1)	2.864(6)x2	Bi(1)-Se(1)	2.986(3)x2
Bi(1)-S(1)	3.347(8)	Bi(1)-Se(1)	3.351(4)
Bi(2)-S(4)	2.587(7)	Bi(2)-Se(4)	2.722(4)
Bi(2)-S(5)	2.731(5)x2	Bi(2)-Se(5)	2.854(2)x2
Bi(2)-S(1)	2.950(6)x2	Bi(2)-Se(1)	3.088(3)x2
Bi(2)-S(2)	3.246(7)	Bi(2)-Se(2)	3.321(4)
Bi(3)-S(7)	2.667(7)	Bi(3)-Se(7)	2.771(4)
Bi(3)-S(6)	2.701(5)x2	Bi(3)-Se(6)	2.825(2)x2
Bi(3)-S(5)	3.024(6)	Bi(3)-Se(5)	3.122(4)
Bi(3)-S(2)	3.025(5)x2	Bi(3)-Se(2)	3.151(3)x2
Bi(4)-S(7)	2.800(6)x2	Bi(4)-Se(9)	2.908(4)
Bi(4)-S(8)	2.804(6)x2	Bi(4)-Se(8)	2.916(3)x2
Bi(4)-S(9)	2.838(7)	Bi(4)-Se(7)	2.949(2)x2
Bi(4)-S(6)	2.870(7)	Bi(4)-Se(6)	3.004(4)
Bi(5)-S(9)	2.734(6)x2	Bi(5)-Se(8)	2.880(4)
Bi(5)-S(8)	2.775(7)	Bi(5)-Se(9)	2.908(3)x2
Bi(5)-S(5)	2.883(6)	Bi(5)-Se(5)	2.981(4)
Bi(5)-S(4)	2.941(6)x2	Bi(5)-Se(4)	3.013(3)x2
Bi(6)-S(12)	2.725(7)	Bi(6)-Se(12)	2.825(3)
Bi(6)-S(10)	2.797(5)x2	Bi(6)-Se(10)	2.935(3)x2
Bi(6)-S(8)	2.850(7)	Bi(6)-Se(11)	2.973(3)x2
Bi(6)-S(11)	2.882(5)x2	Bi(6)-Se(8)	3.012(4)
Bi(7)-S(14)	2.646(4)x2	Bi(7)-Se(14)	2.787(2)x2
Bi(7)-S(10)	2.652(7)	Bi(7)-Se(10)	2.791(4)
Bi(7)-S(12)	3.076(5)x2	Bi(7)-Se(12)	3.189(3)x2
Bi(7)-S(13)	3.191(8)	Bi(7)-Se(13)	3.244(4)

Table 8-24. (cont'd).

Bi(8)-S(11)	2.596(7)	Bi(8)-Se(11)	2.732(4)
Bi(8)-S(13)	2.711(5)x2	Bi(8)-Se(13)	2.837(3)x2
Bi(8)-S(12)	2.940(5)x2	Bi(8)-Se(12)	3.073(3)x2
Bi(8)-S(12)	3.116(7)	Bi(8)-Se(12)	3.188(3)
		K(9)-Bi(9')	0.573(17)
		K(9)-Bi(9)	0.662(18)
Pb(9)-S(3)	2.803(5)x2	K(9)-Se(13)	3.179(19)
Pb(9)-S(13)	2.973(7)	K(9)-Se(3)	3.180(13)x2
Pb(9)-S(4)	3.171(6)x2	K(9)-Se(4)	3.204(14)x2
Pb(9)-S(11)	3.308(5)x2	K(9)-Se(11)	3.295(14)x2
Pb(9)-S(1)	3.314(8)	K(9)-Se(1)	3.630(19)
		Bi(9)-Se(3)	2.794(6)x2
		Bi(9)-Se(1)	3.128(18)
		Bi(9)-Se(13)	3.321(18)
		Bi(9)-Se(4)	3.404(9)x2
		Bi(9')-Se(3)	2.777(5)x2
		Bi(9')-Se(13)	2.914(15)
		Bi(9')-Se(1)	3.535(16)
		Bi(9')-Se(4)	3.588(9)x2
		Bi(9')-Se(11)	3.616(9)x2
Rb(10)-S(13)	3.298(8)	K(10)-Se(7)	3.315(6)x2
Rb(10)-S(7)	3.308(7)x2	K(10)-Se(13)	3.357(8)
Rb(10)-S(3)	3.369(7)x2	K(10)-Se(3)	3.368(7)x2
Rb(10)-S(2)	3.482(7)	K(10)-Se(14)	3.549(7)x2
Rb(10)-S(14)	3.487(6)x2	K(10)-Se(2)	3.637(9)
Rb(11)-S(14)	3.310(8)	K(11)-Se(14)	3.364(10)
Rb(11)-S(10)	3.412(6)x2	K(11)-Se(10)	3.389(7)x2
Rb(11)-S(5)	3.422(9)	K(11)-Se(5)	3.395(9)
Rb(11)-S(6)	3.510(6)x2	K(11)-Se(9)	3.471(8)x2
Rb(11)-S(9)	3.512(6)x2	K(11)-Se(6)	3.658(8)x2

Table 8-25. Selected Angles (deg) for $\text{Rb}_2\text{PbBi}_8\text{S}_{14}$ and $\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$.

$\text{Rb}_2\text{PbBi}_8\text{S}_{14}$		$\beta\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$	
S(1)-Bi(1)-S(1)	87.42(19)	Se(1)-Bi(1)-Se(1)	87.80(9)
S(3)-Bi(1)-S(2)	91.65(18)	Se(2)-Bi(1)-Se(1)	91.66(9)
S(3)-Bi(1)-S(1)	175.9(2)	Se(3)-Bi(1)-Se(1)	178.07(10)
S(1)-Bi(2)-S(1)	86.0(2)	Se(1)-Bi(2)-Se(1)	84.76(9)
S(5)-Bi(2)-S(5)	94.9(2)	Se(5)-Bi(2)-Se(5)	93.63(10)
S(5)-Bi(2)-S(1)	175.53(16)	Se(5)-Bi(2)-Se(1)	174.82(8)
S(2)-Bi(3)-S(2)	83.38(18)	Se(5)-Bi(3)-Se(2)	86.68(9)
S(7)-Bi(3)-S(2)	97.62(18)	Se(7)-Bi(3)-Se(2)	96.81(9)
S(6)-Bi(3)-S(2)	169.92(17)	Se(6)-Bi(3)-Se(2)	168.24(10)
S(8)-Bi(4)-S(9)	84.48(17)	Se(7)-Bi(4)-Se(6)	86.34(8)
S(8)-Bi(4)-S(6)	94.24(18)	Se(9)-Bi(4)-Se(7)	92.42(9)
S(7)-Bi(4)-S(8)	178.7(2)	Se(8)-Bi(4)-Se(7)	177.51(11)
S(5)-Bi(5)-S(4)	81.59(17)	Se(5)-Bi(5)-Se(4)	84.35(8)
S(8)-Bi(5)-S(4)	99.98(18)	Se(8)-Bi(5)-Se(4)	96.46(9)
S(9)-Bi(5)-S(4)	170.40(19)	Se(9)-Bi(5)-Se(4)	172.64(10)
S(11)-Bi(6)-S(11)	88.5(2)	Se(11)-Bi(6)-Se(8)	87.53(9)
S(10)-Bi(6)-S(10)	92.0(2)	Se(10)-Bi(6)-Se(8)	92.17(9)
S(10)-Bi(6)-S(11)	175.9(2)	Se(12)-Bi(6)-Se(8)	176.53(11)
S(12)-Bi(7)-S(12)	81.69(17)	Se(12)-Bi(7)-Se(13)	86.23(8)
S(14)-Bi(7)-S(14)	99.0(2)	Se(14)-Bi(7)-Se(14)	96.62(11)
S(10)-Bi(7)-S(13)	169.54(19)	Se(10)-Bi(7)-Se(13)	169.58(10)
S(12)-Bi(8)-S(12)	84.68(18)	Se(12)-Bi(8)-Se(12)	84.26(8)
S(13)-Bi(8)-S(12)	96.01(19)	Se(13)-Bi(8)-Se(12)	93.54(9)
S(11)-Bi(8)-S(12)	170.9(2)	Se(11)-Bi(8)-Se(12)	171.77(10)

Rb₁₁Bi₁₅Se₂₈ (VI) and Rb₄EuBi₆Se₁₂ (VII). These compounds adopt new structures which can be thought as modification of the RbBiS₂^{1(d)} structure type. Rb₁₁Bi₁₅Se₂₈ has a two dimensional character and its made of CdI₂-type infinite layers, see Figure 8-3. These layers are slightly undulated along the ac-diagonal and are separated by "layers" of Rb atoms that occupy trigonal prismatic or octahedral sites. Every two CdI₂-type layers there is a connection between them (essentially through intercalated Bi atoms) and this is due to the fact that one of the Rb sites, Rb(1) is disordered 50-50 with Bi. This essentially creates a situation that half of time we have thicker layers that contain tunnels with four Rb ions.

All Bi atoms have distorted octahedral geometries while the Rb ions reside in trigonal prismatic or distorted octahedral sites. Rb(1) is disordered with Bi(1) and has an octahedral coordination with distances between 3.127(3)-3.184(3) Å (Table 8-26). These distances are shorter than the usual Rb-Se bonds (for the other Rb atoms in the structure, the shorter Rb-Se bond varies between 3.3-3.4 Å) and longer than the usual Bi-Se bonds. These distances are an average and are caused by the fact that Bi and Rb occupy the same site. Furthermore the Se atoms bonded to Rb(1)/Bi(1) have large temperature factors along the direction of the bonds indicating that occupy different positions depending to which kind of atom (Rb or Bi) are bonded to.

The least distorted BiSe_6 octahedron is that of Bi(6) followed by that of Bi(7). Bi(6) has six distances between 2.933(2)-3.007(2) Å and angles between 88.10(5)-93.29(8)°. Both octahedra belong to the "straight" part of the CdI_2 -type layers. The remaining BiSe_6 octahedra can be classified into two categories. Those octahedra that are distorted towards a square pyramid with four similar in length bonds and a shorter bond *trans* to a longer one and those octahedra that have three short bonds *trans* to three longer ones. The majority of the BiSe_6 octahedra, Bi(2), Bi(4), Bi(5) and Bi(7) belong to the first category while that of Bi(3) belongs to the second category. For example Bi(5) has four Bi(5)-Se bonds between 2.967(2)-2.972(2) Å and a bond at 2.794(3) Å *trans* to a long one at 3.214(4) Å. All these octahedra belong to the part of the CdI_2 -layer that bends slightly to form an undulation.

Rb(2), Rb(4) and Rb(5) are six coordinate residing in distorted octahedral sites while Rb(3), Rb(6) and Rb(7), also being six coordinate, have a trigonal prismatic coordination. The Rb-Se distances are similar in both cases, e.g. in Rb(2) the Rb-Se distances vary between 3.334(3)-3.577(4) Å while in Rb(3) the Rb-Se distances vary between 3.400(3)-3.534(3) Å.

As mentioned above $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ can be viewed as a modification of the $\text{RbBiS}_2^{1(d)}$ structure. In RbBiS_2 , the CdI_2 -type layers are perfectly flat. The Se analog

$\text{RbBiSe}_2^{1(d)}$, has been reported and it is interesting that both structures, RbBiSe_2 and $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ exist. The $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ compensates for the fact that it has less alkali metal by bending the layers and disordering Rb with Bi.

The structure of $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$ is related to that of $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ and is shown in Figure 8-4. In this case the connection between two adjacent CdI_2 -type fragments is made by a Eu atom while the tunnels formed between the two CdI_2 -type layers are narrower in the direction of the layers containing one less Rb atom. If we compare the formulas, the general formula for $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ is $\text{M}_{26}\text{Se}_{28}$ or $\text{M}_{13}\text{Se}_{14}$ and for $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$, $\text{M}_{11}\text{Se}_{12}$ so $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ has an extra M_2Se_2 or RbBiQ_2 fragment that results to wider tunnels. This relationship is very interesting since we can envision a class of compounds with the same motif but with longer or smaller tunnels formed between the layers differing by RbBiQ_2 units. Bond distances and selected angles for $\text{Rb}_4\text{EuBi}_6\text{Se}_{12}$ are shown on Table 8-27.

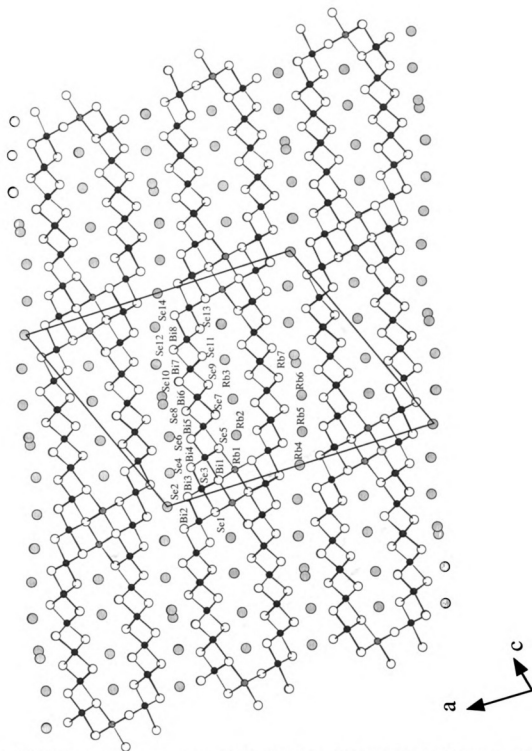


Figure 8-3. Projection of the structure of $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$ down the b -axis. The corrugated

CdI_2 -type layers connect to form tunnels every other layer.

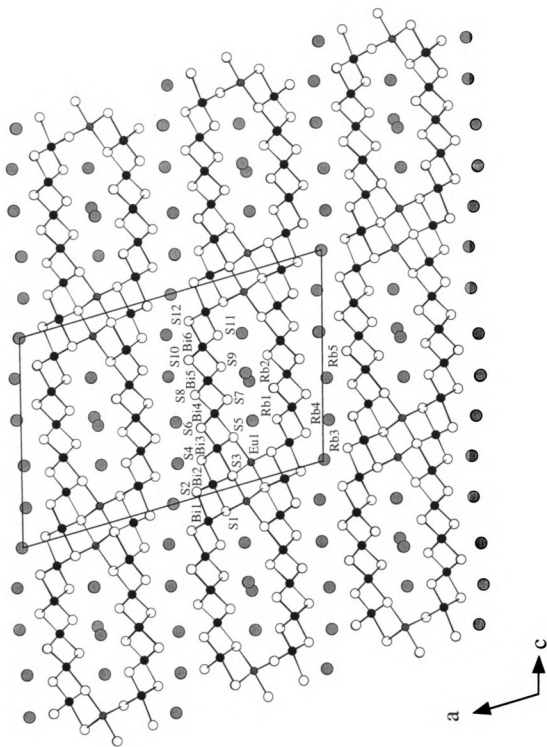


Figure 8-4. Projection of the structure of $\text{Rb}_4\text{EuBi}_6\text{S}_{12}$ down the b -axis. The corrugated

CdI_2 -type layers connect to form smaller tunnels compared to $\text{Rb}_{11}\text{Bi}_{15}\text{Se}_{28}$.

Table 8-26. Bond Distances (Å) and Selected Angles (deg) for Rb₁₁Bi₁₅Se₂₈.

Bi(1)/Rb(1)-Se(1)	3.127(3)x2	Se(3)-Bi(1)/Rb(1)-Se(3)	84.26(11)
Bi(1)/Rb(1)-Se(3)	3.130(3)	Se(1)-Bi(1)/Rb(1)-Se(5)	96.14(8)
Bi(1)/Rb(1)-Se(5)	3.173(4)	Se(3)-Bi(1)/Rb(1)-Se(5)	173.95(11)
Bi(1)/Rb(1)-Se(3)	3.184(3)x2		
Bi(2)-Se(13)	2.804(3)	Se(1)-Bi(2)-Se(2)	86.42(7)
Bi(2)-Se(14)	2.911(2)x2	Se(14)-Bi(2)-Se(14)	94.41(10)
Bi(2)-Se(1)	3.099(3)x2	Se(14)-Bi(2)-Se(1)	175.89(8)
Bi(2)-Se(2)	3.224(3)		
Bi(3)-Se(4)	2.828(3)	Se(3)-Bi(3)-Se(3)	86.79(11)
Bi(3)-Se(2)	2.888(2)x2	Se(2)-Bi(3)-Se(2)	95.41(9)
Bi(3)-Se(3)	3.109(3)x2	Se(2)-Bi(3)-Se(3)	174.86(7)
Bi(3)-Se(1)	3.221(3)		
Bi(4)-Se(6)	2.785(3)	Se(4)-Bi(4)-Se(3)	86.82(7)
Bi(4)-Se(5)	2.944(2)x2	Se(5)-Bi(4)-Se(5)	93.03(10)
Bi(4)-Se(4)	2.957(2)x2	Se(6)-Bi(4)-Se(3)	174.54(10)
Bi(4)-Se(3)	3.169(3)		
Bi(5)-Se(8)	2.794(3)	Se(6)-Bi(5)-Se(5)	83.86(6)
Bi(5)-Se(7)	2.967(2)x2	Se(7)-Bi(5)-Se(5)	95.84(6)
Bi(5)-Se(6)	2.972(2)x2	Se(8)-Bi(5)-Se(5)	167.89(9)
Bi(5)-Se(5)	3.214(4)		
Bi(6)-Se(10)	2.933(2)	Se(9)-Bi(6)-Se(8)	88.10(5)
Bi(6)-Se(9)	2.9377(19)x2	Se(9)-Bi(6)-Se(9)	93.29(8)
Bi(6)-Se(7)	2.976(2)	Se(10)-Bi(6)-Se(7)	177.72(8)
Bi(6)-Se(8)	3.007(2)x2		
Bi(7)-Se(9)	2.883(2)	Se(9)-Bi(7)-Se(11)	87.20(6)
Bi(7)-Se(10)	2.947(2)x2	Se(10)-Bi(7)-Se(12)	94.11(6)
Bi(7)-Se(11)	2.976(2)x2	Se(9)-Bi(7)-Se(12)	173.16(8)
Bi(7)-Se(12)	3.026(3)		

Table 8-26. (cont'd).

Bi(8)-Se(11)	2.783(2)	Se(13)-Bi(8)-Se(14)	83.31(6)
Bi(8)-Se(13)	2.943(2)x2	Se(12)-Bi(8)-Se(14)	97.46(6)
Bi(8)-Se(12)	2.965(2)x2	Se(11)-Bi(8)-Se(14)	164.91(9)
Bi(8)-Se(14)	3.154(3)		
Rb(2)-Se(13)	3.334(3)	Se(13)-Rb(2)-Se(1)	75.53(8)
Rb(2)-Se(13)	3.335(3)	Se(13)-Rb(2)-Se(7)	114.78(8)
Rb(2)-Se(5)	3.372(3)x2	Se(13)-Rb(2)-Se(5)	160.21(11)
Rb(2)-Se(7)	3.466(3)		
Rb(2)-Se(1)	3.577(4)		
Rb(3)-Se(9)	3.400(3)		
Rb(3)-Se(11)	3.437(3)x2		
Rb(3)-Se(7)	3.464(3)x2		
Rb(3)-Se(9)	3.534(3)		
Rb(4)-Se(14)	3.338(2)x2	Se(2)-Rb(4)-Se(2)	76.63(6)
Rb(4)-Se(2)	3.445(2)x4	Se(2)-Rb(4)-Se(2)	103.37(6)
		Se(2)-Rb(4)-Se(2)	180.00(6)
Rb(5)-Se(4)	3.387(3)x2	Se(4)-Rb(5)-Se(2)	72.87(7)
Rb(5)-Se(14)	3.455(3)x2	Se(4)-Rb(5)-Se(12)	108.71(8)
Rb(5)-Se(12)	3.455(3)	Se(12)-Rb(5)-Se(2)	177.89(10)
Rb(5)-Se(2)	3.557(3)		
Rb(6)-Se(6)	3.411(3)x2		
Rb(6)-Se(12)	3.429(3)x2		
Rb(6)-Se(10)	3.446(3)		
Rb(6)-Se(8)	3.650(4)		
Rb(7)-Rb(7)	2.318(4)x2		
Rb(7)-Se(10)	3.286(6)		
Rb(7)-Se(8)	3.370(6)		
Rb(7)-Se(10)	3.468(5)x2		
Rb(7)-Se(8)	3.569(5)x2		

Table 8-27. Bond Distances (Å) and Selected Angles (deg) for Rb₄EuBi₆Se₁₂.

Bi(1)-S(11)	2.653(16)	S(1)-Bi(1)-S(2)	85.0(4)
Bi(1)-S(12)	2.838(15)x2	S(12)-Bi(1)-S(2)	94.9(4)
Bi(1)-S(1)	2.93(2)x2	S(11)-Bi(1)-S(2)	174.1(5)
Bi(1)-S(2)	3.197(17)		
Bi(2)-S(4)	2.706(16)	S(2)-Bi(2)-S(3)	87.5(5)
Bi(2)-S(2)	2.756(12)x2	S(2)-Bi(2)-S(2)	97.3(6)
Bi(2)-S(3)	2.983(19)x2	S(2)-Bi(2)-S(3)	175.2(4)
Bi(2)-S(1)	3.04(2)		
Bi(3)-S(6)	2.634(15)	S(4)-Bi(3)-S(3)	83.9(5)
Bi(3)-S(4)	2.857(10)x2	S(5)-Bi(3)-S(3)	94.2(6)
Bi(3)-S(5)	2.862(15)x2	S(6)-Bi(3)-S(3)	170.5(6)
Bi(3)-S(3)	3.198(17)		
Bi(4)-S(8)	2.677(16)	S(6)-Bi(4)-S(5)	84.1(4)
Bi(4)-S(7)	2.828(13)x2	S(7)-Bi(4)-S(5)	95.8(4)
Bi(4)-S(6)	2.866(13)x2	S(7)-Bi(4)-S(6)	179.2(4)
Bi(4)-S(5)	3.05(2)		
Bi(5)-S(7)	2.779(16)	S(9)-Bi(5)-S(8)	86.5(4)
Bi(5)-S(9)	2.841(14)x2	S(8)-Bi(5)-S(10)	94.5(4)
Bi(5)-S(8)	2.841(12)x2	S(7)-Bi(5)-S(10)	177.5(5)
Bi(5)-S(10)	2.857(17)		
Bi(6)-S(9)	2.683(15)	S(11)-Bi(6)-S(12)	83.2(4)
Bi(6)-S(11)	2.829(12)x2	S(10)-Bi(6)-S(12)	98.9(5)
Bi(6)-S(10)	2.836(11)x2	S(9)-Bi(6)-S(12)	164.9(6)
Bi(6)-S(12)	2.978(18)		
Eu(1)-S(3)	2.952(18)	S(3)-Eu(1)-S(3)	83.0(7)
Eu(1)-S(1)	3.10(3)x2	S(1)-Eu(1)-S(3)	96.2(5)
Eu(1)-S(5)	3.11(2)	S(1)-Eu(1)-S(3)	172.3(5)
Eu(1)-S(3)	3.12(2)x2		

Table 8-27. (cont'd).

Rb(1)-S(11)	3.250(16)x2		
Rb(1)-S(5)	3.293(16)x2		
Rb(1)-S(7)	3.344(17)		
Rb(1)-S(1)	3.69(2)		
Rb(1)-S(9)	3.97(2)		
Rb(2)-Rb(2)	2.266(11)x2		
Rb(2)-S(9)	3.24(2)		
Rb(2)-S(7)	3.26(2)		
Rb(2)-S(9)	3.315(18)x2		
Rb(2)-S(7)	3.54(2)x2		
Rb(3)-S(12)	3.295(18)x2	S(2)-Rb(3)-S(2)	75.7(4)
Rb(3)-S(2)	3.370(14)x4	S(2)-Rb(3)-S(2)	104.3(4)
		S(12)-Rb(3)-S(12)	179.998(2)
Rb(4)-S(4)	3.235(13)x2	S(4)-Rb(4)-S(2)	70.2(4)
Rb(4)-S(12)	3.370(18)x2	S(4)-Rb(4)-S(10)	115.1(4)
Rb(4)-S(10)	3.422(18)	S(4)-Rb(4)-S(12)	162.6(5)
Rb(4)-S(2)	3.469(19)		
Rb(5)-S(10)	3.358(14)x2		
Rb(5)-S(8)	3.365(17)		
Rb(5)-S(6)	3.365(15)x2		
Rb(5)-S(8)	3.38(2)		

Cs_{6-3x}Bi_{8+x}Se₁₅ (VIII) and Rb_xSn_{1+x}Bi_{6-x}Se₁₀ (IX). These two compounds adopt two new different new structures but they will be described together because they share several structural features.

The structure of Cs_{6-3x}Bi_{8+x}Se₁₅ is shown in Figure 8-5. It consists of CdI₂-, Bi₂Te₃- and NaCl-type fragments. The CdI₂- and Bi₂Te₃-type fragments create stepped layers along the a-axis while the NaCl-type blocks connect the layers together. Between the blocks we have the formation of tunnels filled by Cs⁺ ions.

As it can be seen on Table 8-28, sites Bi(1) through Bi(4) have a distorted octahedral coordination while site Bi(5) is square pyramidal. The least distorted site is that of Bi(1) with six bonds between 2.864(3)-3.078(3) and the most distorted that of Bi(4) with six distances between 2.762(3)-3.195(3) Å.

Site Bi(5) is partially occupied and disordered with Cs(1). The coordination of Cs(1) is bicapped trigonal prismatic with distances between 3.046(8)-3.627(12) Å. These distances are short for Cs-Se bonds and are an artifact of the disorder found in that site. The Cs-Se distances in Cs(2) are between 3.544(3)-3.677(3), slightly higher than the normal Cs-Se bonds. As a result Cs(2) is rattling inside the tunnels and has a large temperature factor along the direction of the tunnels.

The structure of $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$, as shown in Figure 8-6, is related to that of $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$. It consists from the same kind of building blocks but now the Bi_2Te_3 - and NaCl-type fragments are longer while the CdI_2 -type has the same length. Again we have the same tunnels now filled by Rb^+ ions. In comparison with $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ the BiSe_6 are more distorted, e.g. Bi(4) in $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$ has a short Bi-Se bond at 2.759(3) Å *trans* to a longer one at 3.091(2) Å and four bonds between 2.8873(15)-3.0729(16) Å (Table 8-29). In $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$ based on the crystallographic data the sites that belong to the CdI_2 - and Bi_2Te_3 -type blocks are occupied exclusively by Bi while the sites in the NaCl-type are disordered between Bi and Sn. The relationship between these two compounds is very interesting because we can envision a whole series of compounds where the length of the two fragments is increased by bismuth octahedra units. Furthermore there are other compounds such as $\text{A}_{1-x}\text{M}_{4-x}\text{Bi}_{11+x}\text{Se}_{21}$ ¹⁴ and $\text{A}_{1-x}\text{M}_{5-x}\text{Bi}_{11+x}\text{Se}_{22}$ ¹⁵ (A = K, Rb, Cs; M = Sn, Pb) where the same motif is preserved but the stepped layers made of the Bi_2Te_3 - and CdI_2 -type are thicker (essentially the Bi_2Te_3 -type fragment gets longer while the CdI_2 -type gets shorter).

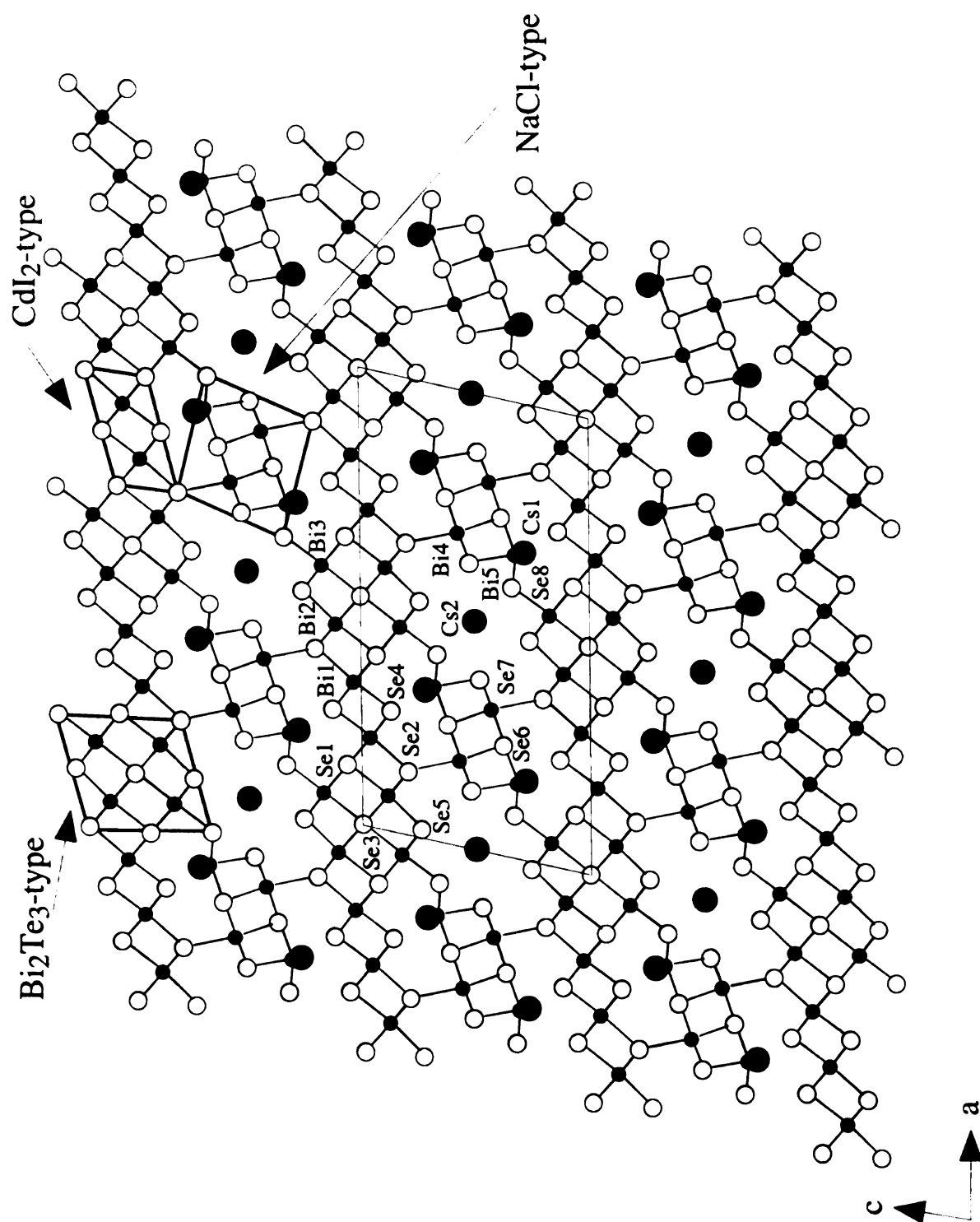


Figure 8-5. Projection of the structure of $\text{Cs}_{6-3x}\text{Bi}_{8+x}\text{Se}_{15}$ down the b-axis. The shaded areas indicate the NaCl-, Bi_2Te_3 - and CdI_2 -type building blocks.

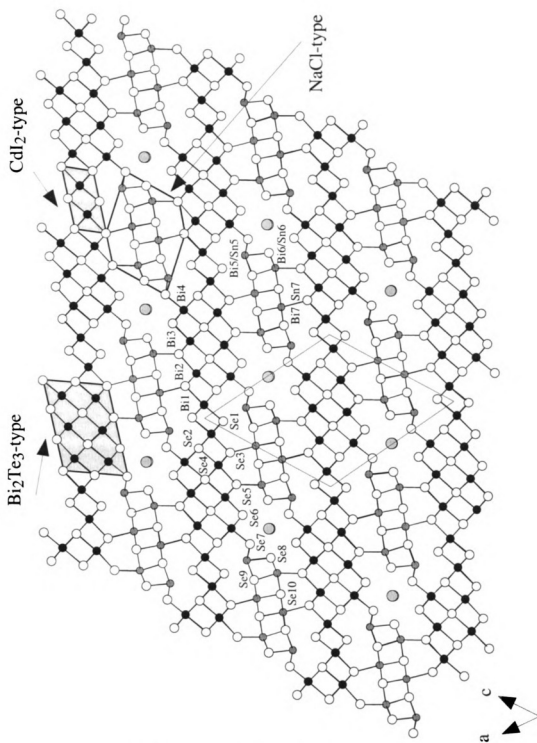


Figure 8-6. Projection of the structure of $\text{Rb}_x\text{Sn}_{1-x}\text{Bi}_{6-x}\text{Se}_{10}$ down the b -axis. The shaded areas indicate the NaCl -, Bi_2Te_3 - and CdI_2 -type building blocks.

Table 8-28. Bond Distances (Å) and Selected Angles (deg) for Cs_{6-3x}Bi_{8+x}Se₁₅.

Bi(1)-Se(4)	2.864(3)	Se(4)-Bi(1)-Se(1)	87.40(6)
Bi(1)-Se(4)	2.9105(18)x2	Se(4)-Bi(1)-Se(2)	92.25(6)
Bi(1)-Se(1)	2.9737(18)x2	Se(4)-Bi(1)-Se(2)	175.38(7)
Bi(1)-Se(2)	3.078(3)		
Bi(2)-Se(2)	2.8352(17)x2	Se(3)-Bi(2)-Se(1)	87.26(4)
Bi(2)-Se(5)	2.893(3)	Se(2)-Bi(2)-Se(2)	94.44(8)
Bi(2)-Se(3)	3.0869(9)x2	Se(5)-Bi(2)-Se(1)	173.07(7)
Bi(2)-Se(1)	3.109(3)		
Bi(3)-Se(8)	2.827(3)	Se(1)-Bi(3)-Se(1)	85.56(6)
Bi(3)-Se(5)	2.8544(18)x2	Se(5)-Bi(3)-Se(5)	93.61(8)
Bi(3)-Se(3)	3.0381(12)	Se(5)-Bi(3)-Se(1)	175.60(6)
Bi(3)-Se(1)	3.0640(18)x2		
Bi(4)-Se(6)	2.762(3)	Se(6)-Bi(4)-Se(2)	84.32(6)
Bi(4)-Se(7)	2.8498(18)x2	Se(7)-Bi(4)-Se(2)	96.51(6)
Bi(4)-Se(6)	3.0832(18)x2	Se(6)-Bi(4)-Se(2)	172.03(7)
Bi(4)-Se(2)	3.195(3)		
Bi(5)-Cs(1)	0.579(11)		
Bi(5)-Se(7)	2.779(3)	Se(7)-Bi(5)-Se(8)	80.40(9)
Bi(5)-Se(8)	2.861(2)x2	Se(8)-Bi(5)-Se(8)	93.35(10)
Bi(5)-Se(6)	3.190(2)x2	Se(8)-Bi(5)-Se(6)	161.37(10)
Cs(1)-Se(8)	3.046(8)x2		
Cs(1)-Se(4)	3.192(9)x2		
Cs(1)-Se(6)	3.280(8)x2		
Cs(1)-Se(7)	3.356(13)		
Cs(1)-Se(1)	3.627(12)		
Cs(2)-Se(5)	3.544(3)x2		
Cs(2)-Se(7)	3.552(2)x2		
Cs(2)-Se(8)	3.677(3)x4		

Table 8-29. Bond Distances (Å) and Selected Angles (deg) for $\text{Rb}_x\text{Sn}_{1+x}\text{Bi}_{6-x}\text{Se}_{10}$.

Bi(1)-Se(1)	2.8798(15)x2	Se(2)-Bi(1)-Se(2)	86.37(6)
Bi(1)-Se(1)	2.888(2)	Se(1)-Bi(1)-Se(1)	92.31(6)
Bi(1)-Se(3)	3.023(2)	Se(1)-Bi(1)-Se(3)	174.04(6)
Bi(1)-Se(2)	3.0349(16)x2		
Bi(2)-Se(3)	2.8379(15)x2	Se(4)-Bi(2)-Se(4)	85.42(5)
Bi(2)-Se(5)	3.011(2)	Se(3)-Bi(2)-Se(3)	94.09(6)
Bi(2)-Se(2)	3.017(2)	Se(5)-Bi(2)-Se(2)	172.97(6)
Bi(2)-Se(4)	3.0620(14)x2		
Bi(3)-Se(5)	2.8502(14)x2	Se(4)-Bi(3)-Se(4)	85.11(5)
Bi(3)-Se(6)	2.851(2)	Se(5)-Bi(3)-Se(5)	93.56(6)
Bi(3)-Se(4)	3.054(2)	Se(5)-Bi(3)-Se(4)	174.20(5)
Bi(3)-Se(4)	3.0711(15)x2		
Bi(4)-Se(7)	2.759(3)	Se(2)-Bi(4)-Se(4)	86.73(5)
Bi(4)-Se(6)	2.8773(15)x2	Se(7)-Bi(4)-Se(2)	93.95(7)
Bi(4)-Se(2)	3.0729(16)x2	Se(6)-Bi(4)-Se(2)	175.27(5)
Bi(4)-Se(4)	3.091(2)		
Bi(5)/Sn(5)-Se(8)	2.772(3)	Se(8)-Bi(5)/Sn(5)-Se(7)	78.89(9)
Bi(5)/Sn(5)-Se(7)	2.809(3)x2	Se(7)-Bi(5)/Sn(5)-Se(7)	95.37(11)
Bi(5)/Sn(5)-Se(9)	3.203(2)x2	Se(7)-Bi(5)/Sn(5)-Se(9)	156.73(9)
Bi(5)/Sn(5)-Se(1)	3.668(2)x2		
Bi(6)/Sn(6)-Se(9)	2.735(2)	Se(10)-Bi(6)/Sn(6)-Se(10)	80.68(5)
Bi(6)/Sn(6)-Se(8)	2.8086(16)x2	Se(8)-Bi(6)/Sn(6)-Se(8)	95.38(7)
Bi(6)/Sn(6)-Se(10)	3.2086(18)x2	Se(8)-Bi(6)/Sn(6)-Se(10)	168.41(6)
Bi(6)/Sn(6)-Se(5)	3.5789(18)x2		
Bi(7)/Sn(7)-Se(10)	2.766(2)	Se(10)-Bi(7)/Sn(7)-Se(3)	85.79(5)
Bi(7)/Sn(7)-Se(10)	2.9401(16)x2	Se(9)-Bi(7)/Sn(7)-Se(3)	94.90(5)
Bi(7)/Sn(7)-Se(9)	2.9564(16)x2	Se(10)-Bi(7)/Sn(7)-Se(3)	175.66(7)
Bi(7)/Sn(7)-Se(3)	3.074(2)		

Table 8-29. (cont'd).

Rb-Rb	2.0803(18)x2
Rb-Se(7)	2.842(15)
Rb-Se(8)	3.270(17)
Rb-Se(6)	3.399(16)
Rb-Se(7)	3.442(12)x2
Rb-Se(8)	3.874(14)x2
Rb-Se(6)	4.070(14)x2

There is a known mineral junosite $\text{Cu}_2\text{Pb}_3\text{Bi}_8(\text{S},\text{Se})_{16}$ ¹⁶ with a very similar structure but now its tunnels instead of having alkali metal ions are filled with pairs of copper atoms shifted off center towards either the walls of the tunnels. Junosite forms a homologous series with $\text{Cu}_2\text{Pb}_6\text{Bi}_8\text{S}_{19}$ ¹⁷. Therefore these structures have three different degrees of variability, first the ratio of the Bi_2Te_3 -type to the CdI_2 -type fragment, second the length of the NaCl -type and CdI_2 -type fragments and third the content of the tunnels can be a variety of cations e.g. K^+ , Rb^+ , Cs^+ or Cu^+ .

$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ (X), $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ (XI) and $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ (XII).

The first two compounds, (IV) and (VII), are isostructural and adopt the $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ ¹⁽ⁱ⁾ structure type, as shown in Figures 8-7 and 8-8, respectively. The structure of (IX) is very closely related and will be compared with those of (IV) and (VII).

The structure adopted by (IV) and (VII) is very stable and is one of the most commonly encountered in the ternary and quaternary bismuth chalcogenide systems having several members such as $\text{K}_2\text{Bi}_8\text{S}_{13}$ ¹⁸, $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ¹⁹, $\text{Ba}_3\text{Bi}_{6.67}\text{Se}_{13}$ ²⁰, $\text{Ba}_3\text{MBi}_6\text{Se}_{13}$ ²⁰ (M = Sn, Pb) and $\text{A}_x\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{13}$ ²¹ (A = Eu, Sr) adopting this structure. The main characteristic is that the $[\text{Bi}_6\text{Se}_{13}]^{8-}$ part of the structure remains intact while the remaining four Sr^{2+} positions can be substituted with a variety of similarly sized ions

such as Ba^{2+} , K^+ , Bi^{3+} , Pb^{2+} etc. Often these substitutions result in mixed occupancy between the alkali or alkaline earth metal and the bismuth atoms.

Since compounds $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ are isostructural only $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ will be described in detail. The structure of $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ consists of NaCl- and CdI_2 -type infinite rods which connect with each other to form a three-dimensional network. The CdI_2 -type rods alternate with NaCl-type fragments forming layers with steps perpendicular to the c-axis. The different kinds of blocks are connected with each other with high (>6) coordinate sites which exhibit mixed occupancy between the Ba and the Bi/Pb atoms.

The structure contains 10 metal sites, seven of them M(1)-M(7) are six coordinate having distorted octahedral coordination while the remaining three, M(8)-M(10) have higher coordination residing in bicapped or tricapped trigonal prismatic environments. These three sites, M(8), M(9) and M(10) display an mixed occupancy with Ba and Bi/Pb. The rest of the octahedral sites M(1)-M(7) are fully occupied by Bi/Pb.

From the octahedral sites, M(7) is the least distorted with M(7)-Se distances varying between 2.794(5)-2.907(3) and Se-M(7)-Se angles between 86.16(11)-96.18(11) $^\circ$ (Tables 8-30 and 8-31). This specific site in the majority of the compounds that adopt this structure exhibits the least distortion. The next least distorted site is M(3) with M(3)-Se

distances between 2.763(5)-2.921(5) Å. The remaining five sites can be divided into two categories, those that are distorted towards an square pyramid and those that are distorted towards a trigonal pyramid. Sites M(2) and M(5) belong to first category having a short bond *trans* to longer one for example, M(2) has a bond at 2.611(5) Å *trans* to one at 3.096(4) Å. M(1), M(4) and M(6) have a distortion towards a trigonal pyramid with three short bond *trans* to three longer ones e.g. M(6) has one bond at 2.619(4) Å, two bonds at 2.684(3) Å, two bonds at 3.044(3) Å and one bond at 3.095(5) Å.

M(8)/Ba(8) and M(9)/Ba(9) are bicapped trigonal prismatic with M-Se distances varying between 2.943(3)-3.274(4) Å for M(8)/Ba(8) and 3.018(4)-3.331(4) Å for M(9)/Ba(9). Some of the distances are short for Ba-Se bonds but this is an averaging effect due to mixed occupancy. The remaining site exhibits a splitting to two positions M(10) and Ba(10). The coordination of Ba(10) is tricapped trigonal prismatic with distances varying between 3.200(4)-3.371(5) Å while M(10) has three short bonds between 2.874(7)-2.934(9) Å and three longer ones between 3.369(7)-3.378(6) Å.

Ba_{4-x}Bi_{6+2/3x}Se₁₃ has many similar characteristics with Ba_xPb_{4-x}Bi₆S₁₃. In this case the charge-neutrality is maintained by a combination of partial and mixed occupancy. Site Bi(4) is ~95% occupied by Bi while Bi(7) which has the least distorted octahedral coordination is ~76% occupied by Bi. In two of the three high (>6) coordinate sites there is a splitting while the third site, Ba(10), is fully occupied by Ba and there is

no splitting or mixed occupancy. Position Ba(8) has a bicapped trigonal prismatic coordination while Bi(8) and Bi(8') which are 0.5-0.6 Å away from Ba(8) have a trigonal pyramidal coordination. Position Ba(9) is again bicapped trigonal prismatic while Bi(9) which ~0.6 Å away from Ba(9) has a square pyramidal coordination.

The structure of $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ is shown in Figure 8-9 and as mentioned above is related to that of the two previous compounds. It consists of the same 2x3 NaCl-type and the same CdI_2 -type blocks but the other NaCl-type block that belongs to the "stepped" layers is thinner. The coordination of Bi(1) is square pyramidal while the remaining Bi sites have distorted octahedral coordination similar to what was found above (Table 8-32). Site M(8) is seven-coordinate having a monocapped trigonal prismatic coordination.

Four different structures types form a homologous series. In all different structures the 2x3 NaCl type is retained but the thickness of the stepped layers is gradually increasing. The four different structures types are that of $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ with the general formula M_9Q_{12} , that of $\text{Sr}_4\text{Bi}_6\text{Se}_{13}^{1(i)}$ where $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ belong with the formula $\text{M}_{10}\text{Q}_{13}$, the structure of $\alpha\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}^{19}$ with the formula $\text{M}_{11}\text{Q}_{14}$ and the structure of $\text{A}_{1+x}\text{M}_{4-2x}\text{M}'_{7+x}\text{Se}_{15}^{22}$ ($\text{A} = \text{K, Rb}$; $\text{M} = \text{Pb, Sn}$; $\text{M}' = \text{Bi, Sb}$) and $\text{Ba}_x\text{Pb}_{6-x}\text{Bi}_6\text{Se}_{15}^{21}$ with the formula $\text{M}_{12}\text{Q}_{15}$. As it can be seen from the

general formulae the "stepped" layers get thicker by one MQ unit going from one structure type to another.

Again for the purpose of evaluating the distribution of Pb (Sn) and Bi in the metal sites bond valence calculations were performed for (XI) and (XII). The results are summarized in Table 8-33 and 8-34. The octahedral sites in $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$, M(1)-M(6) exhibit bond valence sums ≥ 3 , therefore there should be occupied by Bi. Site M(7) which is the least distorted octahedral one, has a bond valence sum ~ 2.5 indicating a mixture of Bi (3+) and Pb (2+). For sites M(8) and M(9) with trigonal prismatic coordination the varying range of the bond-valence sums make its difficult to assign specific atoms. In the last site where there is a splitting the position in the side of the trigonal prismatic site can be assigned as Pb and the one in the center as Ba based on the bond-valence sums. In $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ is difficult to assign the sites that contain Sn. Since SEM/EDS analysis shows the presence of a small amount of Sn probably the Sn is distributed at all sites and such small amounts are hard to be detected by X-ray crystallography.

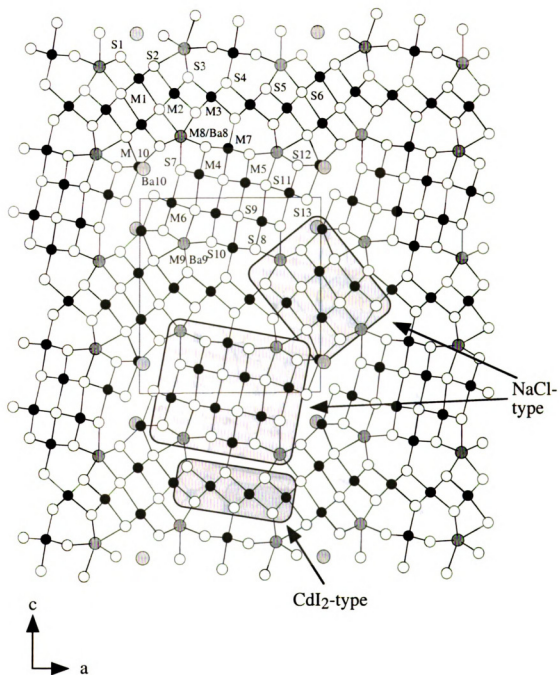


Figure 8-7. Projection of the structure of $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$ down the b -axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.

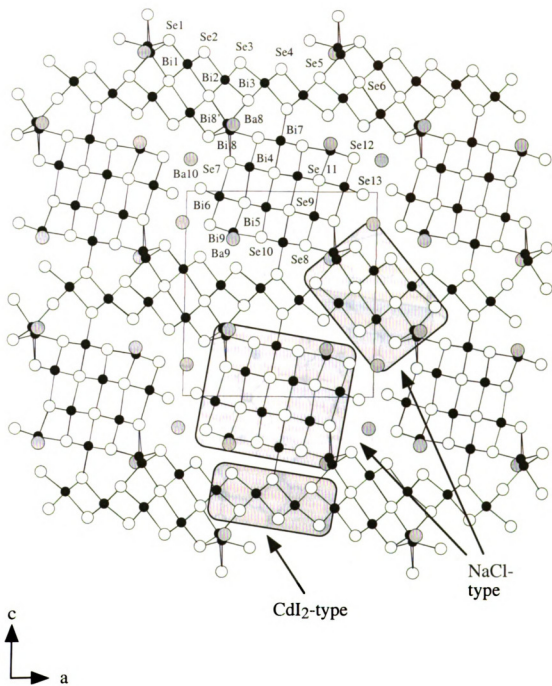


Figure 8-8. Projection of the structure of $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ down the b -axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.

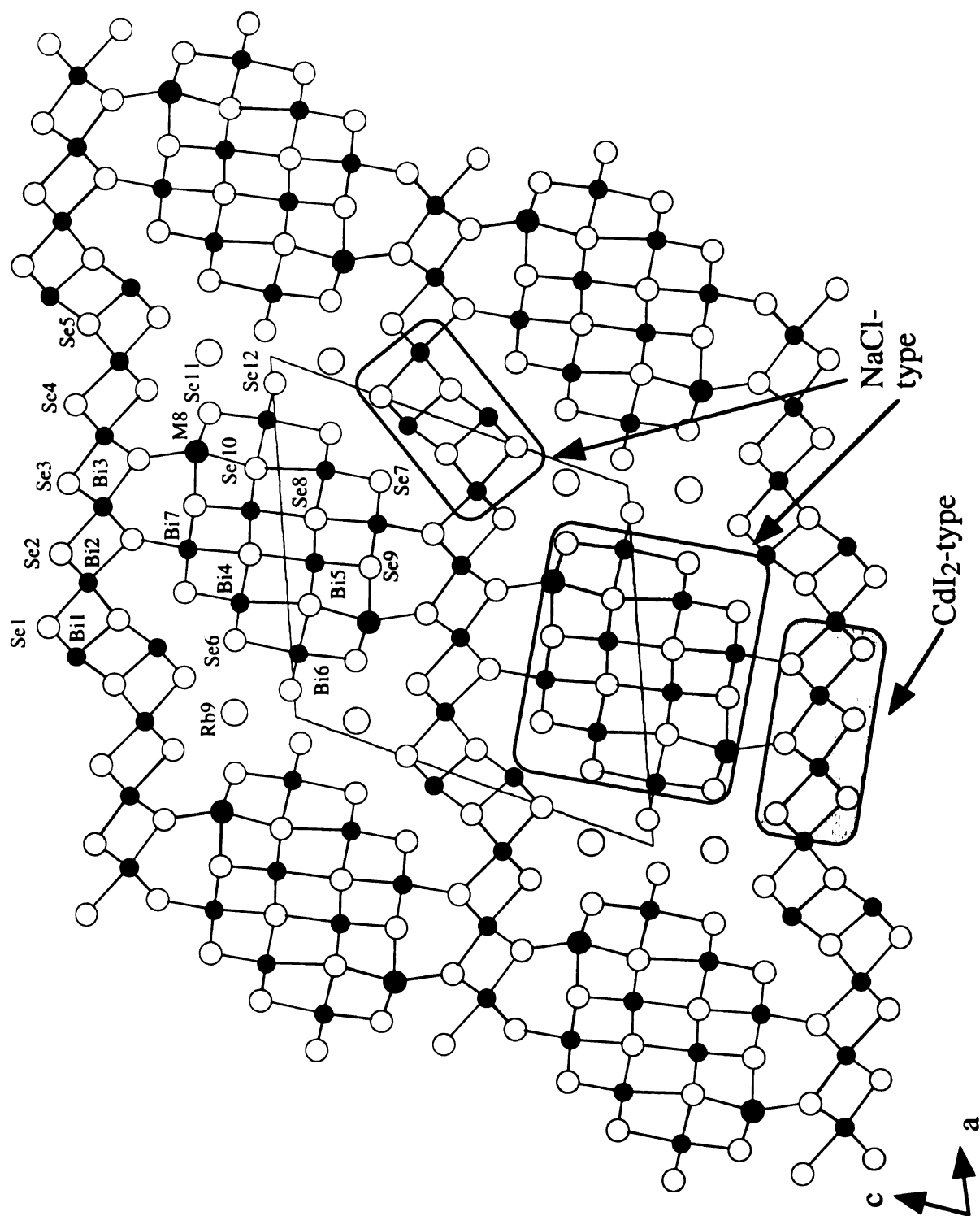


Figure 8-9. Projection of the structure of $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$ down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.

Table 8-30. Bond Distances (Å) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$.

$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$		$\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	
Bi(1)-Se(1)	2.7002(13)	M(1)-S(1)	2.561(4)
Bi(1)-Se(2)	2.8295(8)x2	M(1)-S(2)	2.721(3)x2
Bi(1)-Se(6)	3.1272(9)x2	M(1)-S(6)	2.965(3)x2
Bi(1)-Se(6)	3.4519(13)	M(1)-S(6)	3.407(5)
Bi(2)-Se(5)	2.7742(12)	M(2)-S(5)	2.611(5)
Bi(2)-Se(3)	2.9569(8)x2	M(2)-S(3)	2.809(3)x2
Bi(2)-Se(6)	2.9593(8)x2	M(2)-S(6)	2.866(3)x2
Bi(2)-Se(2)	3.1241(12)	M(2)-S(2)	3.096(4)
Bi(3)-Se(3)	2.8690(13)	M(3)-S(3)	2.763(5)
Bi(3)-Se(4)	2.8919(9)x2	M(3)-S(4)	2.774(3)x2
Bi(3)-Se(5)	3.0308(9)x2	M(3)-S(5)	2.901(3)x2
Bi(3)-Se(4)	3.0606(13)	M(3)-S(4)	2.921(5)
Bi(4)-Se(8)	2.7373(12)	M(4)-S(8)	2.582(4)
Bi(4)-Se(7)	2.8196(8)x2	M(4)-S(7)	2.701(3)x2
Bi(4)-Se(9)	3.1423(9)x2	M(4)-S(9)	3.037(3)x2
Bi(4)-Se(11)	3.2894(13)	M(4)-S(11)	3.284(5)
Bi(5)-Se(10)	2.7523(13)	M(5)-S(10)	2.614(4)
Bi(5)-Se(11)	2.9247(8)x2	M(5)-S(11)	2.799(3)x2
Bi(5)-Se(9)	3.0108(9)x2	M(5)-S(9)	2.897(3)x2
Bi(5)-Se(9)	3.1786(13)	M(5)-S(9)	3.116(5)
Bi(6)-Se(12)	2.7143(13)	M(6)-S(12)	2.619(4)
Bi(6)-Se(13)	2.8211(8)x2	M(6)-S(13)	2.684(3)x2
Bi(6)-Se(11)	3.1698(9)x2	M(6)-S(11)	3.044(3)x2
Bi(6)-Se(7)	3.2418(13)	M(6)-S(7)	3.095(5)
Bi(7)-Se(4)	2.9133(13)	M(7)-S(4)	2.794(5)
Bi(7)-Se(10)	2.9412(9)x2	M(7)-S(10)	2.871(3)x2
Bi(7)-Se(9)	2.9601(13)	M(7)-S(9)	2.901(5)
Bi(7)-Se(8)	2.9629(9)x2	M(7)-S(8)	2.907(3)x2

Table 8-30. (cont'd).

Ba(8)-Bi(8')	0.53(2)		
Ba(8)-Bi(8)	0.588(19)		
		M(8)/Ba(8)-S(1)	2.943(3)x2
Ba(8)-Se(1)	3.2711(13)x2	M(8)/Ba(8)-S(7)	3.060(5)
Ba(8)-Se(8)	3.3323(13)x2	M(8)/Ba(8)-S(6)	3.123(5)
Ba(8)-Se(5)	3.3420(13)x2	M(8)/Ba(8)-S(8)	3.219(4)x2
Ba(8)-Se(6)	3.3875(17)	M(8)/Ba(8)-S(5)	3.274(4)x2
Ba(8)-Se(7)	3.3888(16)		
Bi(8)-Bi(8')	0.647(18)		
Bi(8)-Se(7)	2.85(2)		
Bi(8)-Se(1)	2.959(11)x2		
Bi(8)-Se(8)	3.377(12)x2		
Bi(8')-Se(1)	2.959(12)x2		
Bi(8')-Se(6)	3.02(2)		
Bi(8')-Se(7)	3.452(17)		
Bi(8')-Se(5)	3.550(13)x2		
Ba(9)-Bi(9)	0.582(19)		
		M(9)/Ba(9)-S(12)	3.018(4)x2
Ba(9)-Se(12)	3.2667(12)x2	M(9)/Ba(9)-S(2)	3.168(5)
Ba(9)-Se(10)	3.3327(11)x2	M(9)/Ba(9)-S(11)	3.179(5)
Ba(9)-Se(3)	3.3701(13)x2	M(9)/Ba(9)-S(10)	3.276(4)x2
Ba(9)-Se(2)	3.4205(14)	M(9)/Ba(9)-S(3)	3.331(4)x2
Ba(9)-Se(11)	3.4252(17)		
Bi(9)-Se(11)	2.880(19)		
Bi(9)-Se(12)	3.074(10)x2		
Bi(9)-Se(10)	3.366(10)x2		

Table 8-30. (cont'd).

		M(10)-Ba(10)	0.486(8)
		M(10)-S(12)	2.874(7)x2
		M(10)-S(2)	2.934(9)
		M(10)-S(13)	3.369(7)
		M(10)-S(1)	3.378(6)x2
Ba(10)-Se(12)	3.3049(11)x2	Ba(10)-S(12)	3.200(4)x2
Ba(10)-Se(1)	3.3662(11)x2	Ba(10)-S(1)	3.277(4)x2
Ba(10)-Se(13)	3.5086(14)	Ba(10)-S(2)	3.310(5)
Ba(10)-Se(2)	3.5155(14)	Ba(10)-S(13)	3.348(4)x2
Ba(10)-Se(13)	3.5165(11)x2	Ba(10)-S(13)	3.360(5)
Ba(10)-Se(7)	3.5467(14)	Ba(10)-S(7)	3.371(5)

*M = Bi, Pb or both.

Table 8-31. Selected Angles (deg) for $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$ and $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$.

$\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$		$\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$	
Se(6)-Bi(1)-Se(6)	84.75(3)	S(6)-M(1)-S(6)	85.33(11)
Se(2)-Bi(1)-Se(2)	98.33(4)	S(2)-M(1)-S(2)	98.21(14)
Se(2)-Bi(1)-Se(6)	172.57(3)	S(1)-M(1)-S(6)	173.70(13)
Se(3)-Bi(2)-Se(2)	82.35(3)	S(3)-M(2)-S(2)	81.65(11)
Se(6)-Bi(2)-Se(2)	94.92(3)	S(6)-M(2)-S(2)	97.41(11)
Se(5)-Bi(2)-Se(2)	168.41(3)	S(5)-M(2)-S(2)	169.30(13)
Se(5)-Bi(3)-Se(4)	86.42(3)	S(3)-M(3)-S(5)	86.21(11)
Se(3)-Bi(3)-Se(4)	97.45(3)	S(4)-M(3)-S(4)	95.72(16)
Se(3)-Bi(3)-Se(4)	169.95(4)	S(4)-M(3)-S(5)	176.64(12)
Se(9)-Bi(4)-Se(11)	85.80(3)	S(9)-M(4)-S(9)	85.24(12)
Se(7)-Bi(4)-Se(11)	93.66(3)	S(7)-M(4)-S(7)	99.19(15)
Se(8)-Bi(4)-Se(11)	172.06(3)	S(7)-M(4)-S(9)	173.00(9)
Se(9)-Bi(5)-Se(9)	85.85(3)	S(9)-M(5)-S(9)	86.47(11)
Se(10)-Bi(5)-Se(11)	91.65(3)	S(11)-M(5)-S(11)	94.57(14)
Se(10)-Bi(5)-Se(9)	175.21(4)	S(10)-M(5)-S(9)	175.74(14)
Se(11)-Bi(6)-Se(11)	84.97(3)	S(11)-M(6)-S(11)	85.01(12)
Se(13)-Bi(6)-Se(13)	98.73(4)	S(12)-M(6)-S(13)	92.53(12)
Se(13)-Bi(6)-Se(11)	170.96(3)	S(13)#3-M(6)-S(11)	172.16(10)
Se(9)-Bi(7)-Se(8)	87.85(3)	S(9)-M(7)-S(8)	86.16(11)
Se(10)-Bi(7)-Se(10)	93.41(4)	S(4)-M(7)-S(8)	96.18(11)
Se(10)-Bi(7)-Se(8)	176.03(4)	S(10)-M(7)-S(8)	171.68(12)

*M = Bi, Pb or both.

Table 8-32. Bond Distances (Å) and Selected Angles (deg) for $\text{Rb}_{1.5-x}\text{Sn}_2\text{Bi}_{7.5-x}\text{Se}_{12}$.

Bi(1)-Se(5)	2.732(5)	Se(5)-Bi(1)-Se(5)	83.85(11)
Bi(1)-Se(1)	2.872(3)x2	Se(1)-Bi(1)-Se(1)	93.06(13)
Bi(1)-Se(5)	3.120(3)x2	Se(1)-Bi(1)-Se(5)	170.73(12)
Bi(2)-Se(2)	2.830(3)x2	Se(1)-Bi(2)-Se(5)	83.14(10)
Bi(2)-Se(1)	2.877(5)	Se(2)-Bi(2)-Se(2)	94.91(13)
Bi(2)-Se(4)	2.985(5)	Se(2)-Bi(2)-Se(5)	173.12(10)
Bi(2)-Se(5)	3.135(3)x2		
Bi(3)-Se(3)	2.884(5)	Se(3)-Bi(3)-Se(2)	84.76(11)
Bi(3)-Se(3)	2.915(3)x2	Se(3)-Bi(3)-Se(4)	98.17(11)
Bi(3)-Se(4)	2.940(3)x2	Se(3)-Bi(3)-Se(4)	171.08(14)
Bi(3)-Se(2)	3.074(5)		
Bi(4)-Se(7)	2.760(4)	Se(8)-Bi(4)-Se(10)	82.81(9)
Bi(4)-Se(6)	2.785(3)x2	Se(6)-Bi(4)-Se(10)	93.99(11)
Bi(4)-Se(8)	3.180(3)x2	Se(7)-Bi(4)-Se(10)	170.76(12)
Bi(4)-Se(10)	3.400(5)		
Bi(5)-Se(9)	2.749(4)	Se(8)-Bi(5)-Se(8)	85.69(10)
Bi(5)-Se(10)	2.930(3)x2	Se(9)-Bi(5)-Se(8)	92.53(11)
Bi(5)-Se(8)	2.972(3)x2	Se(10)-Bi(5)-Se(8)	176.48(14)
Bi(5)-Se(8)	3.178(4)		
Bi(6)-Se(12)	2.770(3)x2	Se(10)-Bi(6)-Se(10)	80.95(10)
Bi(6)-Se(11)	2.839(5)	Se(12)-Bi(6)-Se(12)	97.63(14)
Bi(6)-Se(6)	3.157(5)	Se(12)-Bi(6)-Se(10)	171.61(10)
Bi(6)-Se(10)	3.212(3)x2		
Bi(7)-Se(4)	2.786(5)	Se(9)-Bi(7)-Se(8)	87.08(10)
Bi(7)-Se(7)	2.944(3)x2	Se(4)-Bi(7)-Se(7)	94.08(11)
Bi(7)-Se(9)	2.985(3)x2	Se(4)-Bi(7)-Se(8)	174.16(14)
Bi(7)-Se(8)	3.020(4)		

Table 8-32. (cont'd)

Bi(8)/Rb(8)-Se(11)	2.877(5)x2
Bi(8)/Rb(8)-Se(10)	3.008(5)
Bi(8)/Rb(8)-Se(9)	3.368(4)x2
Bi(8)/Rb(8)-Se(3)	3.528(4)x2
Rb(9)-Se(2)	3.493(6)
Rb(9)-Se(6)	3.545(6)
Rb(9)-Se(12)	3.550(6)
Rb(9)-Se(11)	3.607(6)x2
Rb(9)-Se(12)	3.630(5)x2
Rb(9)-Se(1)	3.648(5)x2

Table 8-33. Bond-Valence Sums for $\text{Ba}_x\text{Pb}_{4-x}\text{Bi}_6\text{S}_{13}$.

Site Number	Atom type	Oxidn. state assumed	Bond-Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	3.147	5
	Pb	(2)	2.909	45
2	Bi	(3)	3.082	3
	Pb	(2)	2.851	43
3	Bi	(3)	2.951	2
	Pb	(2)	2.729	36
4	Bi	(3)	3.083	3
	Pb	(2)	2.851	43
5	Bi	(3)	3.021	1
	Pb	(2)	2.792	40
6	Bi	(3)	3.144	5
	Pb	(2)	2.906	45
7	Bi	(3)	2.645	12
	Pb	(2)	2.447	22
8	Bi	(3)	1.864	38
	Pb	(2)	3.191	60
	Ba	(2)	1.723	14
9	Bi	(3)	1.540	49
	Pb	(2)	1.422	29
	Ba	(2)	2.636	32
10	Bi	(3)	1.595	47
	Pb	(2)	1.475	26
	Ba	(2)	2.179	9

The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Table 8-34. Bond-Valence Sums for $\text{Rb}_{1.5-x}\text{Sn}_{2x}\text{Bi}_{7.5-x}\text{Se}_{12}$.

Site Number	Atom type	Oxidn. state assumed	Bond-Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	2.739	9
	Sn	(2)	2.093	5
2	Bi	(3)	3.004	0
	Sn	(2)	2.308	15
3	Bi	(3)	3.025	1
	Sn	(2)	2.059	3
4	Bi	(3)	3.053	2
	Sn	(2)	2.330	17
5	Bi	(3)	3.080	3
	Sn	(2)	2.161	8
6	Bi	(3)	3.045	1
	Sn	(2)	2.142	7
7	Bi	(3)	3.065	2
	Sn	(2)	2.358	18
8	Bi	(3)	2.105	30
	Sn	(2)	1.645	18
	Rb	(1)	2.984	198
9	Rb	(1)	1.088	9

The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

$K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$ (XIII) and $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$ (XIV). The two compounds adopt the cosalite $Pb_2Bi_2S_5$ ²³ structure, see Figures 8-10 and 8-11. Since they are isostructural only (V) will be described in detail. This structure type is very stable and several compounds such as $Pb_4Sb_4Se_{10}$ ²⁴, $KBi_{6.33}S_{10}$ ¹⁸, $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ²¹ (A = Eu, Sr) and $TlBi_3Se_5$ ²⁵ crystallize in the same type. The structure consists of elongated NaCl-type infinite blocks that are arranged in a zigzag fashion. The space that is formed between the NaCl-type blocks is filled up with CdI_2 -type fragments. There are several sites, mainly located on the outside (surface) of the NaCl-type block that exhibit mixed occupancy between the K and the Bi/Pb atoms.

Sites M(1)-M(6) have a octahedral coordination while M(7) and M(8) are eight coordinate having a bicapped trigonal prismatic coordination. Sites M(1)-M(4) and M(6) are fully occupied by Bi/Pb. Site M(5) is partially occupied by Bi/Pb while sites M(7) and M(8) display mixed occupancy and contain K.

All the octahedral sites exhibit some distortion varying in degree (Table 8-35). M(1) is slightly distorted with M(1)-Se distances varying between 2.764(4)-2.922(5) Å and Se-M(1)-Se angles varying between 85.62(11)-93.76(13)°. M(2), M(3) and M(4) distorted towards a trigonal pyramid having three short bonds *trans* to three longer ones e.g. M(3) has a short bond at 2.580(4) Å *trans* to a long one at 3.247(5) and two bonds at

2.694(3) Å *trans* to two bonds at 3.024(3) Å. M(5) is distorted towards a square pyramid having a short bond of 2.580(4) Å *trans* to a longer one (3.305 Å) and four almost equal bonds between 2.877(3)-2.890(3) Å. M(6) is the least distorted atom approaching the ideal octahedral coordination with six equidistant bonds and all angles at 90°. M(6) has six bonds varying between 2.818(3)-2.852(4) Å and angles varying between 85.09(11)-95.25(11)°. Sites M(7)/K(7) and M(8)/K(8) have bicapped trigonal prismatic coordination with distances varying between 2.839(3)-3.400(4) Å and 3.073(5)-3.397(5) Å respectively. Site M(7)/K(7) contains ~50 K while site M(8)/K(8) is mainly occupied by K.

The Eu analog has many similar characteristics with (V) and is shown in Figure 8-11. As shown in Table 8-36 the bond distances are very similar in both compounds.

If we compare $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$ with other isostructural compounds we notice that the trigonal prismatic sites exhibit mixed occupancy e.g. in $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ the sites M(7) and M(8) display A/Pb (A = Eu, Sr) mixed occupancy. Also M(5) is partially occupied in other compounds e.g. 81% in $KBi_{6.33}S_{10}$, ~92% in $Eu_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ and ~96% $Sr_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$.

Pb and Bi are crystallographically indistinguishable and in an attempt to evaluate the distribution of Pb and Bi in two structures the bond valence sums for all metal sites

were calculated. Tables 8-37 and 8-38 summarizes these calculations. As it can be seen for (XIII) sites M(1)-M(4) (octahedral sites with full occupancy) have bond valence sums around ~3 indicating that most probably are exclusively occupied by Bi. Site M(5) has a bond valence sum ~2.6 indicating a mixture of 3+ ion (Bi) and a 2+ ion (Pb). Since this site has bonds around 2.65 Å which are short for K⁺-S bonds we think that M(5) is partially occupied containing only Bi and Pb. The partial occupancy in that site as mentioned above is a feature encountered in other compounds adopting this structure type. Site M(6) has also a bond valence sum less than 3, ~2.3 indicating a mixture of 3+ and 2+ ions. As mentioned above this site is the least distorted with six almost equal M(5)-S bonds between 2.818(3)-2.852(4) Å. These kind of distances are found in PbS therefore site M(6) contains also Bi and Pb. The two remaining trigonal prismatic sites have bond valence sums less than 2. This indicates that most probably these two sites are mainly occupied by Pb and K.

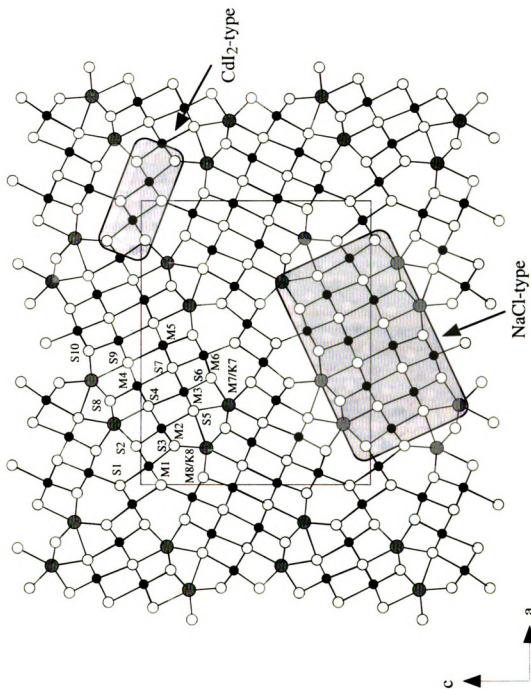


Figure 8-10. Projection of the structure of $K_xPb_{4-2x-3y}Bi_{4-x+2y}Se_{10}$ down the b-axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks.

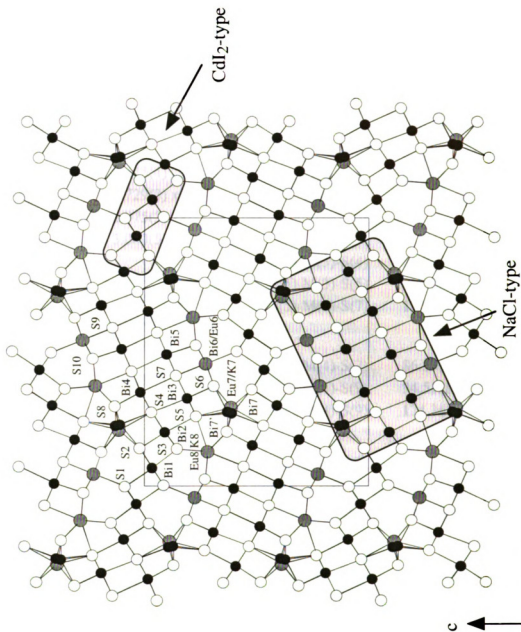


Figure 8-11. Projection of the structure of $K_xEu_{4-2x-3y}Bi_{4-x+2y}Se_{10}$ down the b -axis. The shaded areas indicate the NaCl- and CdI_2 -type building blocks. Site 7 is split in three different positions compared to $K_xEu_{4-2x-3y}Bi_{4-x+2y}Se_{10}$.

Table 8-35. Bond Distances (Å) and Selected Angles (deg) for $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$.

M(1)-S(3)	2.764(4)	S(3)-M(1)-S(2)	85.62(11)
M(1)-S(1)	2.791(3) x2	S(1)-M(1)-S(1)	93.76(13)
M(1)-S(2)	2.844(3) x2	S(3)-M(1)-S(1)	175.35(13)
M(1)-S(1)	2.922(5)		
		S(3)-M(2)-S(5)	84.85(11)
M(2)-S(2)	2.615(4)	S(3)-M(2)-S(3)	96.60(13)
M(2)-S(3)	2.729(3) x2	S(2)-M(2)-S(5)	173.71(13)
M(2)-S(4)	2.975(3) x2		
M(2)-S(5)	3.060(5)		
		S(7)-M(3)-S(4)	86.75(10)
M(3)-S(6)	2.580(4)	S(5)-M(3)-S(5)	98.28(14)
M(3)-S(5)	2.694(3) x2	S(5)-M(3)-S(7)	173.20(9)
M(3)-S(7)	3.024(3) x2		
M(3)-S(4)	3.247(5)		
		S(9)-M(4)-S(7)	86.33(12)
M(4)-S(8)	2.553(5)	S(8)-M(4)-S(9)	94.51(13)
M(4)-S(4)	2.810(3) x2	S(4)-M(4)-S(9)	174.36(14)
M(4)-S(9)	2.926(4) x2		
M(4)-S(7)	3.342(5)		
		S(7)-M(5)-S(9)	87.62(11)
M(5)-S(10)	2.640(4)	S(10)-M(5)-S(9)	92.57(12)
M(5)-S(9)	2.877(3) x2	S(10)-M(5)-S(9)	173.35(13)
M(5)-S(7)	2.890(3) x2		
M(5)-S(9)	3.305(5)		
		S(6)-M(6)-S(7)	87.45(11)
M(6)-S(10)	2.818(3) x2	S(10)-M(6)-S(10)	92.58(13)
M(6)-S(1)	2.836(5)	S(10)-M(6)-S(6)	172.51(13)
M(6)-S(6)	2.846(3) x2		
M(6)-S(7)	2.852(4)		
M(7)/K(7)-S(8)	2.839(3) x2	M(8)/K(8)-S(8)	3.073(5) x2
M(7)/K(7)-S(5)	3.037(5)	M(8)/K(8)-S(10)	3.208(4) x2
M(7)/K(7)-S(4)	3.240(5)	M(8)/K(8)-S(5)	3.324(5)
M(7)/K(7)-S(2)	3.354(4) x2	M(8)/K(8)-S(9)	3.386(7)
M(7)/K(7)-S(6)	3.400(4) x2	M(8)/K(8)-S(3)	3.397(5) x2

M = Pb, Bi or both.

Table 8-36. Bond Distances (Å) and Selected Angles (deg) for $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$.

Bi(1)-S(1)	2.763(3)x2	S(3)-Bi(1)-S(2)	85.06(9)
Bi(1)-S(3)	2.774(4)	S(1)-Bi(1)-S(1)	95.46(11)
Bi(1)-S(1)	2.902(4)	S(1)-Bi(1)-S(2)	176.70(8)
Bi(1)-S(2)	2.912(3)x2		
Bi(2)-S(2)	2.611(4)	S(3)-Bi(2)-S(5)	84.65(9)
Bi(2)-S(3)	2.750(2)x2	S(3)-Bi(2)-S(3)	96.06(11)
Bi(2)-S(4)	2.961(3)x2	S(2)-Bi(2)-S(5)	174.38(10)
Bi(2)-S(5)	3.070(4)		
Bi(3)-S(6)	2.568(4)	S(7)-Bi(3)-S(4)	87.40(9)
Bi(3)-S(5)	2.714(2)x2	S(5)-Bi(3)-S(5)	97.73(11)
Bi(3)-S(7)	3.035(3)x2	S(5)-Bi(3)-S(7)	173.48(8)
Bi(3)-S(4)	3.334(4)		
Bi(4)-S(8)	2.548(4)	S(9)-Bi(4)-S(7)	87.52(10)
Bi(4)-S(4)	2.871(3)x2	S(8)-Bi(4)-S(9)	94.94(11)
Bi(4)-S(9)	2.898(3)x2	S(4)-Bi(4)-S(9)	175.86(12)
Bi(4)-S(7)	3.424(4)		
Bi(5)-S(10)	2.655(4)	S(10)-Bi(5)-S(7)	87.22(10)
Bi(5)-S(7)	2.925(3)x2	S(10)-Bi(5)-S(9)	93.05(11)
Bi(5)-S(9)	2.978(4)x2	S(10)-Bi(5)-S(9)	172.32(12)
Bi(5)-S(9)	3.413(5)		
Bi(6)/Eu(6)-S(10)	2.789(3)x2	S(10)-Bi(6)/Eu(6)-S(7)	86.90(9)
Bi(6)/Eu(6)-S(7)	2.814(4)	S(10)-Bi(6)/Eu(6)-S(10)	94.28(11)
Bi(6)/Eu(6)-S(1)	2.931(4)	S(10)-Bi(6)/Eu(6)-S(6)	172.99(10)
Bi(6)/Eu(6)-S(6)	2.952(3)x2		

Table 8-36. (cont'd).

Eu(7)-Bi(7')	0.508(6)
Eu(7)-Bi(7)	0.519(7)
Eu(7)/K(7)-S(8)	2.992(3)x2
Eu(7)/K(7)-S(5)	3.137(4)
Eu(7)/K(7)-S(2)	3.171(3)x2
Eu(7)/K(7)-S(6)	3.184(3)x2
Eu(7)/K(7)-S(4)	3.253(4)
Bi(7')-S(8)	2.662(6)x2
Bi(7')-S(4)	2.942(9)
Bi(7')-S(5)	3.144(9)
Bi(7')-S(2)	3.411(8)x2
Bi(7'')-S(8)	2.692(5)x2
Bi(7'')-S(5)	2.757(8)
Bi(7'')-S(6)	3.323(7)x2
Bi(7'')-S(4)	3.353(8)
K(8)/Eu(8)-S(8)	3.199(4)x2
K(8)/Eu(8)-S(10)	3.229(4)x2
K(8)/Eu(8)-S(5)	3.322(5)
K(8)/Eu(8)-S(3)	3.353(4)x2
K(8)/Eu(8)-S(9)	3.401(6)

Table 8-37. Selected Bond-Valence Sums for $K_xPb_{4-2x-3y}Bi_{4+x+2y}S_{10}$.

Site Number	Atom type	Oxidn. state assumed	Bond-Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	3.032	1
	Pb	(2)	2.804	40
2	Bi	(3)	3.123	4
	Pb	(2)	2.887	44
3	Bi	(3)	3.149	5
	Pb	(2)	2.912	46
4	Bi	(3)	2.981	1
	Pb	(2)	2.755	38
5	Bi	(3)	2.679	11
	Pb	(2)	2.476	24
6	Bi	(3)	2.926	2
	Pb	(2)	2.706	35
7	Pb	(2)	1.725	14
	K	(1)	1.970	97
8	Pb	(2)	1.224	39
	K	(1)	1.398	40

The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Table 8-38. Selected Bond-Valence Sums for $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$.

Site Number	Atom type	Oxidn. state assumed	Bond-Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	2.966	1
	Eu	(2)	3.077	54
2	Bi	(3)	3.080	3
	Eu	(2)	3.197	60
3	Bi	(3)	3.056	2
	Eu	(2)	3.174	59
4	Bi	(3)	2.870	4
	Eu	(2)	2.981	49
5	Bi	(3)	2.327	22
	Eu	(2)	2.417	21
6	Bi	(3)	2.712	10
	Eu	(2)	2.818	41
7	Eu	(2)	1.858	7
	K	(1)	1.887	89
7'	Bi	(3)	2.344	22
7''	Bi	(3)	2.425	19
8	Eu	(2)	1.226	39
	K	(1)	1.246	25

The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Similar atom assignments can be made for the Eu analog, $K_xEu_{4-2x-3y}Bi_{4+x+2y}S_{10}$ using the bond-valence results. The atoms assignments in two compounds agree well with other compounds that adopt the cosalite structure type $A_xPb_{4-x-3y}Bi_{4+2y}Se_{10}$ ($A =$ Eu, Sr). These assignments also agree with a recent paper²⁶ where synchrotron radiation was used to distinguish between Pb and Bi in cosalite $Pb_2Bi_2S_5$, taking advantage of anomalous dispersion effects near absorption edges.

RbPbBi₃S₆ (XV) and CsPbBi₃S₆ (XVI). The structure of $CsPbBi_3S_6$ ²⁷ is made up of hexagonal $[PbBi_3S_6]_n$ slabs, which are five atomic layers thick. Cs atoms are distributed between the layers. This structure can be considered as intercalated Bi_2Te_3 -type, see Figure 8-12. Substitution of a Pb^{2+} atom for a Bi^{3+} atom in $2[Bi_2Se_3]$ slabs requires another cation to balance charge and the resulting rigid Bi_2Te_3 -type $[PbBi_3S_6]^-$ layers accept monovalent alkali cations between them.

The Cs atoms in $CsPbBi_3S_6$ occupy, partially, two crystallographically distinct sites between the layers both of which have trigonal prismatic coordination (Table 8-39). The occupancy of the Cs^+ ions in the interlayer gallery is only one half of the total capacity of the interlayer space for such ions.

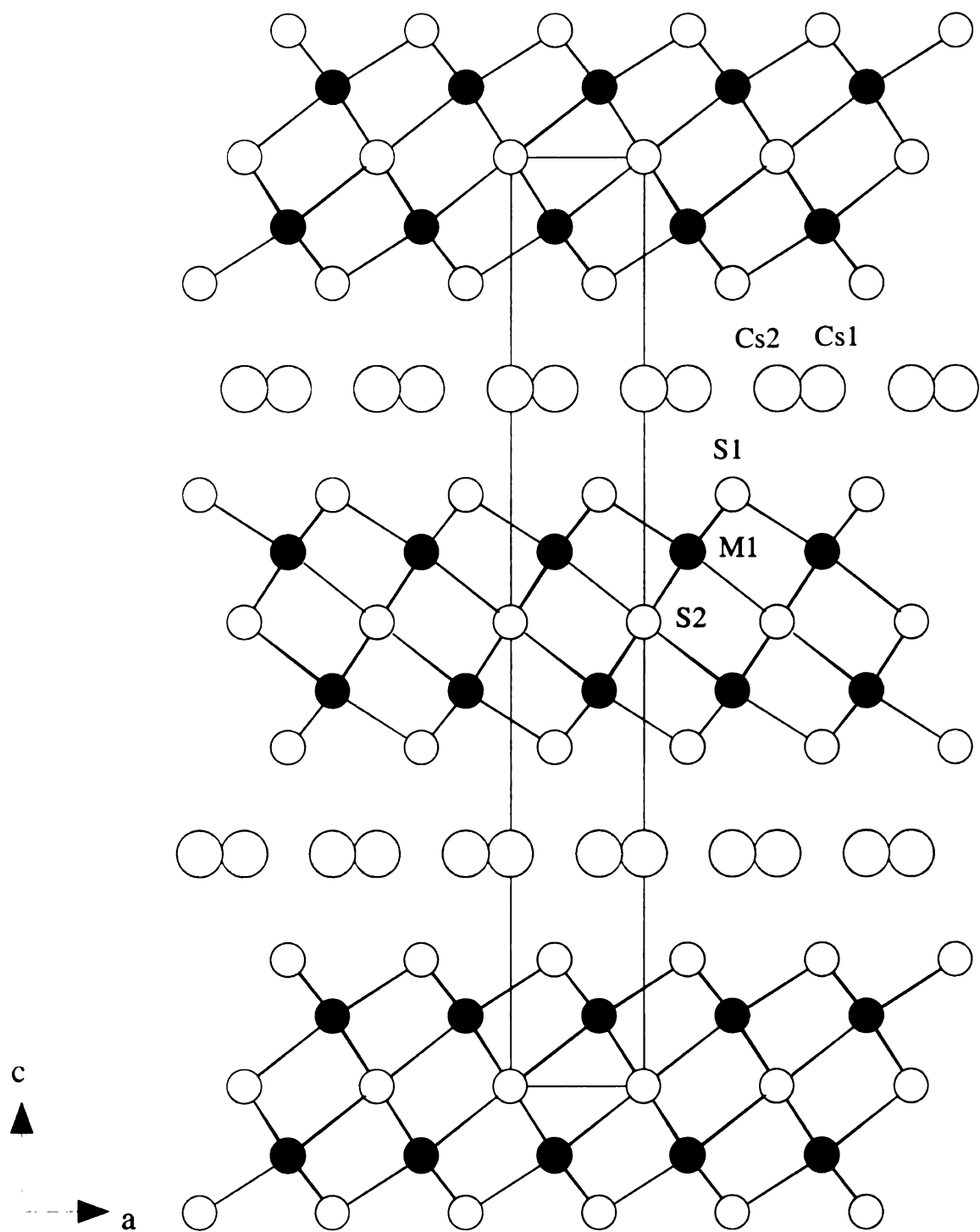


Figure 8-12. Projection of the structure of $\text{CsPbBi}_3\text{S}_6$ down the b -axis. The Cs atoms are disordered between the Bi_2Te_3 -type layers.

Long range ordering of Cs atoms between the layers was probed with electron diffraction performed on crystals $\text{CsPbBi}_3\text{S}_6$ using a Transmission Electron Microscope and no evidence of a superlattice was observed.

For $\text{RbPbBi}_3\text{S}_6$ only the cell was determined and was found to be $a = 4.185(2) \text{ \AA}$, $c = 24.985(5) \text{ \AA}$, $\gamma = 120^\circ$.

Table 8-39. Bond Distances ($\text{\AA}$) and Selected Angles (deg) for $\text{CsPbBi}_3\text{S}_6$.

M(1)-S(1)	2.79(1) x 3	S(1)-M(1)-S(1)	94.1(5)
M(1)-S(2)	2.985(2) x 3	S(1)-M(1)-S(2)	89.8(2)
		S(2)-M(1)-S(2)	86.02(6)
		S(1)-M(1)-S(2)	174.2(4)
Cs(1)-Cs(2)	2.352(1)x 3		
Cs(1)-S(1)	3.66(1) x 6		
Cs(2)-S(1)	3.66(1) x 6		

BaLaBi₂S₆ (XVII), BaCeBi₂S₆ (XVIII), BaPrBi₂S₆ (XIX) and BaLaBi₂Se₆ (XX). X-ray single crystal data were only collected for (XVII). $\text{BaLaBi}_2\text{S}_6$ ²⁸ has a three dimensional tunnel framework with trivalent La centers. Its structure can be thought as a modification of the BaBiSe_3 ^{1(g)} structure by replacing one of the Ba^{2+} with La^{3+} and is shown in Figure 8-13. In order to compensate for the extra positive charge the chalcogenide (selenium) net in BaBiSe_3 break apart forming dichalcogenides (disulfides).

Other compounds such as $\text{KThSb}_2\text{Se}_6$ ²⁸ and $\text{K}_2\text{Ln}_{2-x}\text{Sb}_{4+x}\text{Se}_{12}$ (Ln = La, Ce, Pr and Gd) adopt or are derivatives of the same BaBiSe_3 structure type having diselenides and triselenides respectively. The Ba^{2+} filled tunnels run parallel to the a-axis. As mentioned above $\text{BaLaBi}_2\text{S}_6$ contains disulfide ions, S_2^{2-} , and so it could be described as $\text{Ba}^{2+}\text{La}^{3+}\text{Bi}_2^{3+}(\text{S}^{2-})_5(\text{S}_2)^{2-}_{0.5}$. The La atom is coordinated by nine sulfur atoms and it is best described as a tricapped trigonal prism, see Figure 8-14.

Three of the sulfide atoms bound to La belong to disulfide groups. A notable feature in this structure is that La atoms form one-dimensional infinite double columns parallel to the [100] direction, see Figure 8-14. The disulfide ligands play an important role in the construction of the double columns, see Figure 8-13, by bridging single columns composed of LaS_6 prisms sharing opposite triangular faces. The La double columns are separated by bridging $[\text{Bi}_4\text{S}_{10}]_n$ blocks. Each S_2^{2-} is simultaneously connected to four La atoms in an arrangement unusual for a dichalcogenide. This extensive bonding gives rise to a longer S-S of 2.15(2)Å compared to the normal 2.05Å.

The Bi^{3+} ion occupies two different sites in this structure. Both of them have a distorted octahedral coordination with three short Bi-S bonds *trans* to longer ones (Table 8-40).

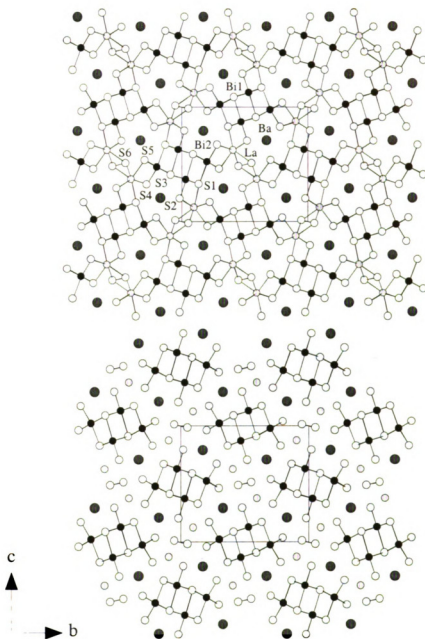


Figure 8-13. Projection of the structure of $\text{BaLaBi}_2\text{S}_6$ down the a -axis (top). The same projection after removing the La-S bonds (bottom).

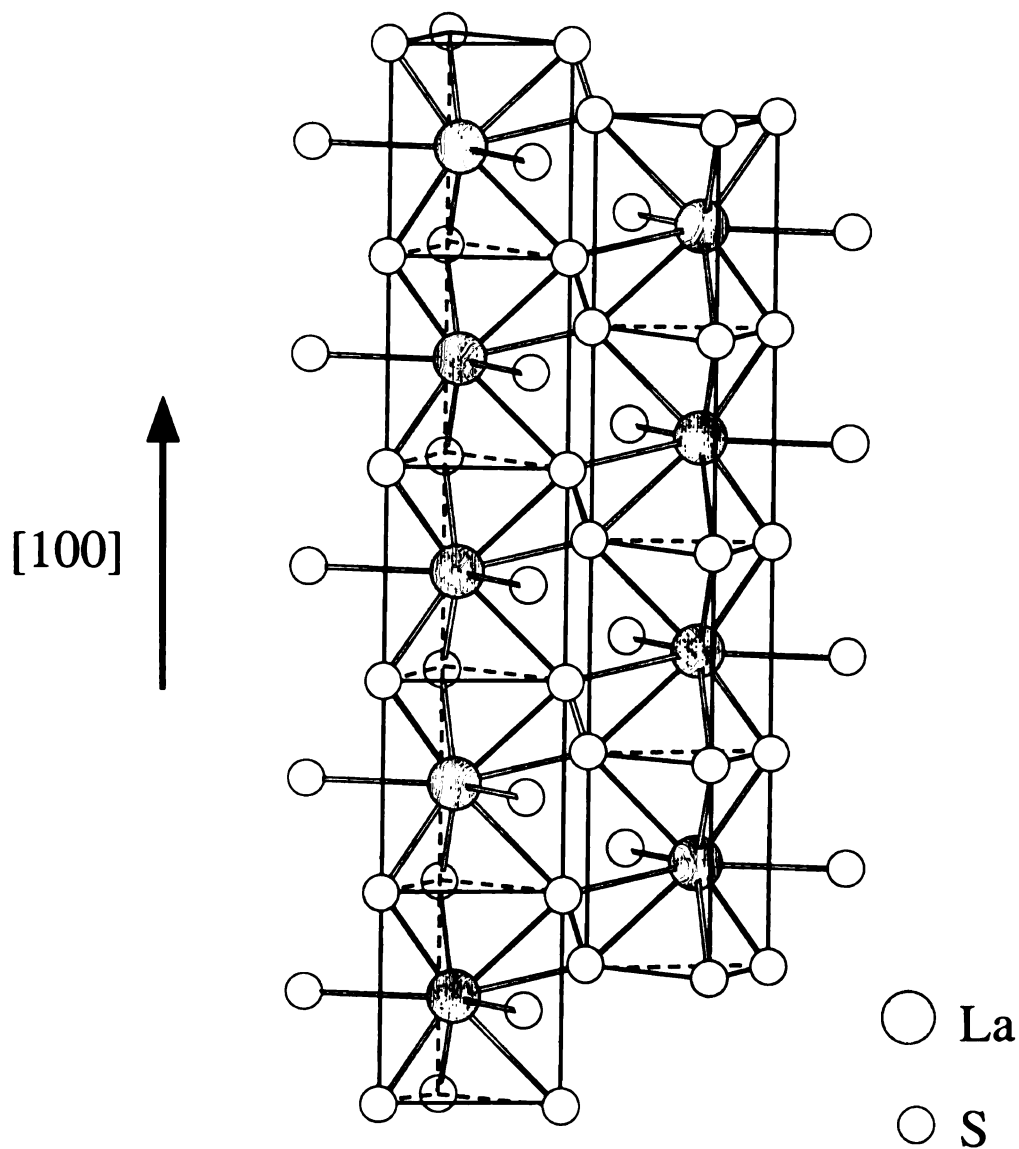


Figure 8-14. The double columns of La atoms running along the [100] direction in $\text{BaLaBi}_2\text{S}_6$. Each single column is composed of LaS_6 prisms sharing opposite triangular faces. The capped S atoms are also shown.

Table 8-40. Bond Distances (Å) and Selected Angles (deg) for BaLaBi₂S₆.

Bi(1)-S(2)	2.562(7)	S(1)-Bi(1)-S(3)	79.3(2)
Bi(1)-S(1)	2.624(8)	S(1)-Bi(1)-S(1)	100.7(2)
Bi(1)-S(3)	2.821(8)	S(3)-Bi(1)-S(1)	170.2(2)
Bi(1)-S(1)	2.870(8)		
Bi(1)-S(3)	3.100(8)		
Bi(1)-S(3)	3.342(7)		
Bi(2)-S(4)	2.590(6)	S(5)-Bi(2)-S(3)	78.5(2)
Bi(2)-S(5)	2.639(8)	S(5)-Bi(2)-S(5)	97.8(2)
Bi(2)-S(3)	2.740(8)	S(4)-Bi(2)-S(1)	170.51(19)
Bi(2)-S(5)	2.969(8)		
Bi(2)-S(1)	3.099(7)		
Bi(2)-S(3)	3.122(8)		
La-S(6)	2.931(8)	Ba-S(5)	3.150(8)
La-S(2)	2.938(8)	Ba-S(2)	3.155(8)
La-S(6)	2.975(8)	Ba-S(4)	3.254(7)
La-S(5)	3.016(7)	Ba-S(4)	3.279(7)
La-S(4)	3.025(7)	Ba-S(3)	3.292(7)
La-S(4)	3.029(7)	Ba-S(1)	3.308(7)
La-S(1)	3.044(7)	Ba-S(2)	3.327(8)
La-S(6)	3.156(8)	Ba-S(6)	3.517(8)
La-S(2)	3.213(8)	Ba-S(5)	3.564(8)
S(6)-S(6)	2.146(15)		

The gross distortion of BiS_6 octahedra is due to the stereochemically active lone pair of Bi^{3+} ions. The BiS_6 octahedra share edges with neighboring octahedra.

The Ba^{2+} ions are also coordinated by 9 sulfurs atoms in tricapped trigonal prismatic sites with Ba-S distances between 3.150(8)-3.564(8) Å.

$\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$ (XXI). This compound adopts a new structure type that is related with the structure of BaBiQ_3 ($\text{Q} = \text{Se}^{1(\text{g})}, \text{Te}^{29},$) and its derivative, $\text{BaLaBi}_2\text{S}_6$ described above. It consists of very narrow CdI_2 and NaCl -type infinite rods running along the b-axis, see Figure 8-15. These two different fragments are separated by Ba^{2+} ions. Similar fragments but with slightly longer dimensions are found in α, β - $\text{BaBi}_2\text{S}_4^{1(\text{h})}$, $\text{BaBi}_2\text{Se}_4^{30}$ and SrBiSe_3^{31} . Also there is a formation of infinite Se-Se chains in a zigzag arrangement running along the b-axis. The Se(9)-Se(9) distances in the chain are 2.637(6) Å with a Se(9)-Se(9)-Se(9) angle of $110.9(4)^\circ$. These distances are too long to be actual Se-Se bonds. These Se atoms have high anisotropic thermal parameters and are only ~75 % occupied. Furthermore the anisotropic thermal parameters of the nearby Se(8) atoms are also high suggesting a possible interaction with the chain. Therefore we suspect the existence of a superstructure in which the Se atoms are found to oligomerize, however, no superstructure is necessary for oligomerization. No evidence of

superstructure could be seen by X-ray diffraction so Transmission Electron Microscopy (TEM) experiments are necessary.

While the task of assigning formal charges in compounds that contain Q-Q interactions is not simple, it becomes even more complicated in the case of $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$ because the exact amount of U and its oxidation state are not known. Although U is not very close to Bi in the periodic table the quality of the X-ray data set make it impossible to distinguish them. The fact that $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$ cannot be made pure in bulk quantities does not allow for magnetic experiments that will help us determine the U oxidation state. Nevertheless bond-valence calculations in combination with the X-ray single crystal data allow for some atom assignments. Sites M(1), M(2) and M(3) are distorted octahedral with distances between 2.704(19)-3.087(2) Å for M(1), 2.707(2)-3.1031(15) Å for M(2) and 2.745(2)-3.001(2) Å for M(3) (Table 8-41). For all these three octahedra the M-Se bonds are on the short side for Bi-Se bonds and this is shown by the bond-valence sums that are greater than 3, reaching 3.5 for the case of M(3) (Table 8-42). This suggests that U exists at least in sites M(1) and M(3) and probably in M(2). Site 4 contains both U and Ba and this assignment was done based on the X-ray single crystal data assuming that Bi would not probably occupy a tricapped trigonal prismatic site. For this site the bond-valence calculations results were not conclusive.

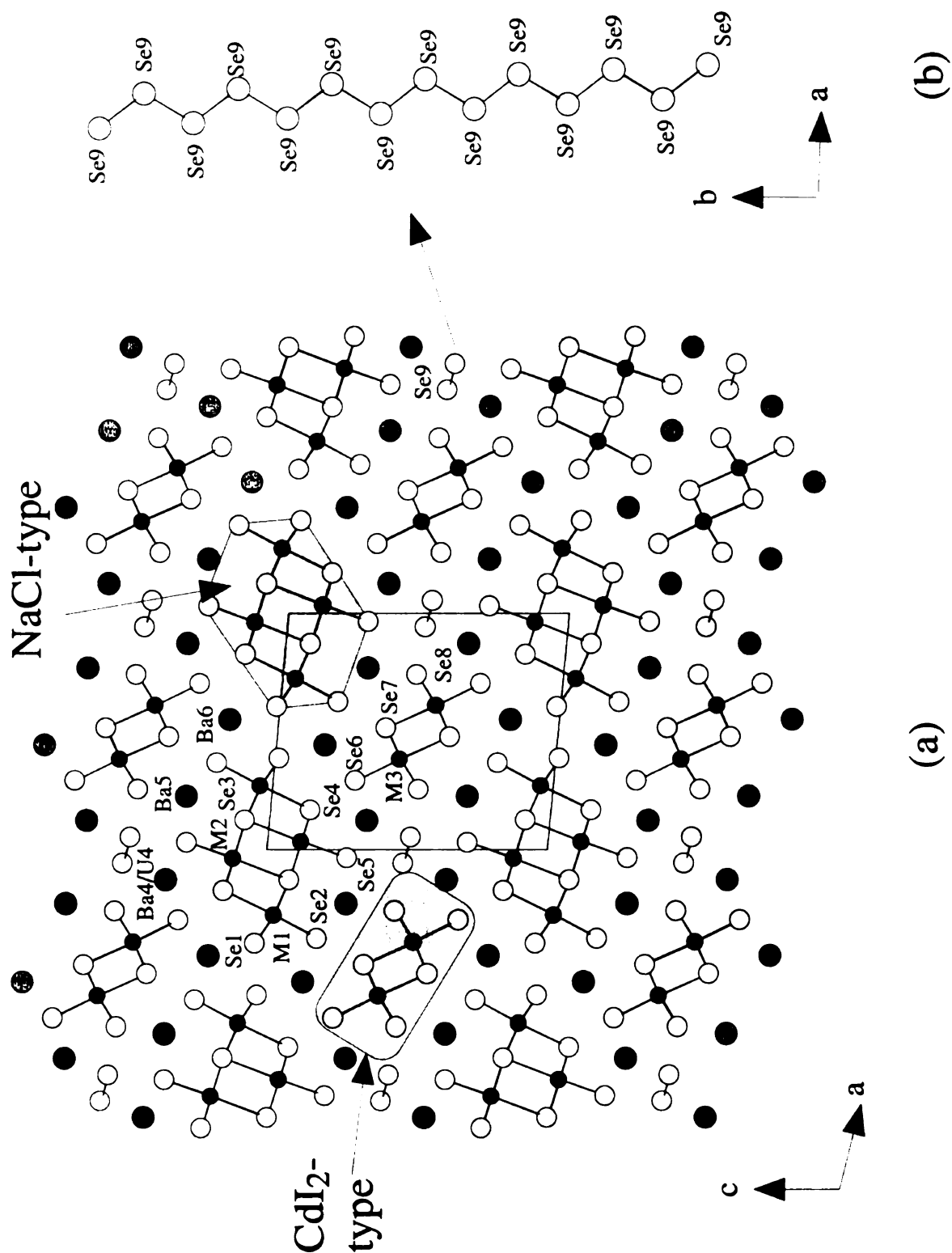


Figure 8-15. (a) Projection of the structure of $\text{Ba}_{3-x}\text{U}_{x-y}\text{Bi}_{3-y}\text{Se}_{9-z}$ down the b -axis. (b)

The Se(9)-Se(9) zigzag chains running along the c -axis.

Table 8-41. Bond Distances (Å) and Selected Angles (deg) for Ba_{3-x}U_{x+y}Bi_{3-y}Se_{9-z}.

M(1)-Se(2)	2.7104(19)	Se(1)-M(1)-Se(4)	84.48(5)
M(1)-Se(1)	2.8593(14)x2	Se(1)-M(1)-Se(1)	98.86(6)
M(1)-Se(3)	3.0135(15)x2	Se(1)-M(1)-Se(3)	172.43(6)
M(1)-Se(4)	3.087(2)		
M(2)-Se(5)	2.707(2)	Se(4)-M(2)-Se(3)	86.07(4)
M(2)-Se(4)	2.8559(14)x2	Se(4)-M(2)-Se(4)	99.02(6)
M(2)-Se(3)	3.1031(15)x2	Se(4)-M(2)-Se(3)	174.90(5)
M(2)-Se(3)	3.317(2)		
M(3)-Se(6)	2.745(2)	Se(7)-M(3)-Se(8)	83.24(5)
M(3)-Se(7)	2.8741(13)x2	Se(7)-M(3)-Se(7)	98.17(6)
M(3)-Se(8)	2.9486(18)x2	Se(7)-M(3)-Se(8)	174.61(7)
M(3)-Se(7)	3.001(2)		
Ba(4)/U(4)-Se(9)	3.071(6)		
Ba(4)/U(4)-Se(6)	3.1706(17)x2		
Ba(4)/U(4)-Se(5)	3.2106(18)x2		
Ba(4)/U(4)-Se(8)	3.317(3)x2		
Ba(4)/U(4)-Se(9)	3.360(4)x2		
Ba(5)-Se(2)	3.3164(17)x2		
Ba(5)-Se(5)	3.3357(18)x2		
Ba(5)-Se(7)	3.464(2)		
Ba(5)-Se(3)	3.465(2)		
Ba(5)-Se(8)	3.473(2)x2		
Ba(6)-Se(2)	3.3207(17)x2	Se(9)-Se(9)	2.637(6)x2
Ba(6)-Se(6)	3.3769(18)x2		
Ba(6)-Se(1)	3.4419(17)x2	Se(9)-Se(9)-Se(9)	110.9(4)°
Ba(6)-Se(1)	3.445(2)		
Ba(6)-Se(7)	3.511(2)		
Ba(6)-Se(4)	3.677(2)		

*M = Bi, U or both.

Table 8-42. Selected Bond-Valence Sums for $\text{Ba}_{3-x}\text{U}_{x+y}\text{Bi}_{3-y}\text{Se}_{9-z}$.

Site Number	Atom type	Oxidn. state assumed	Bond-Valence Sum	% Deviation from assumed oxid. state
1	Bi	(3)	3.389	13
	U	(?)	3.131	
2	Bi	(3)	3.064	2
	U	(?)	3.154	
3	Bi	(3)	3.500	17
	U	(?)	3.155	
4	Bi	(3)	2.034	32
	U	(?)	2.033	
	Ba	(2)	3.307	65
5	Ba	(2)	2.014	1
6	Ba	(2)	1.967	2

The atoms in bold indicate the most probably metal assignments taking in consideration the bond-valence sums and the crystallographic (occupancy) data.

Finally both X-ray single crystal and bond valence show that the tricapped trigonal prismatic sites 5 and 6 are exclusively occupied by Ba. If we try to incorporate these results into a formula we have $Ba_2(Ba,U)_1(Bi,U)_3Se_8Se_{0.75}$ or $Ba_2(Ba_{0.8}U_{0.2})[(Bi,U)_2Bi]Se_8Se_{0.75}$ assuming that one of the three octahedral sites is only occupied by Bi and finally $Ba_{2.8}U_{0.2}(Bi,U)_2BiSe_{8.75}$. We know from SEM/EDS analysis that the Ba:U:Bi ratio is ~3:1:3, therefore we can propose as a final formula $Ba_{2.8}U_{0.8}Bi_{2.4}Se_{8.75}$.

Charge transport properties and thermal conductivity. Temperature dependent electrical conductivity and thermoelectric power measurements were carried out needle shaped single crystals of $Ba_{4-x}Bi_{6+2/3x}Se_{13}$ and polycrystalline ingots of $BaLaBi_2Se_6$. In the case of $BaLaBi_2Se_6$ the thermal conductivity of the ingots was also measured.

As it can be seen in Figure 8-16, $Ba_{4-x}Bi_{6+2/3x}Se_{13}$ has a n-type metallic behavior with a room temperature conductivity of ~2000 S/cm and a thermopower of ~-30 $\mu V/K$. The heavy doping and metallic behavior observed for $Ba_{4-x}Bi_{6+2/3x}Se_{13}$ could be to non-stoichiometry and can be difficult to control and can vary from preparation to preparation or even from crystal to crystal if serious precautions during synthesis and crystal growth are not taken.

The temperature dependence of the electrical conductivity and thermopower for polycrystalline ingots of $\text{BaLaBi}_2\text{Se}_6$ is shown in Figure 8-17. The room temperature values for the electrical conductivity and thermopower are 10^{-2} S/cm and $\sim 140 \mu\text{V/K}$ respectively. The behavior of $\text{BaLaBi}_2\text{Se}_6$ suggests an p-type semiconductor. The thermal conductivity κ of $\text{BaBi}_2\text{LaSe}_6$ is significantly lower (0.7 W/mK) of that of Bi_2Te_3 that has a value of 1.7 W/mK .

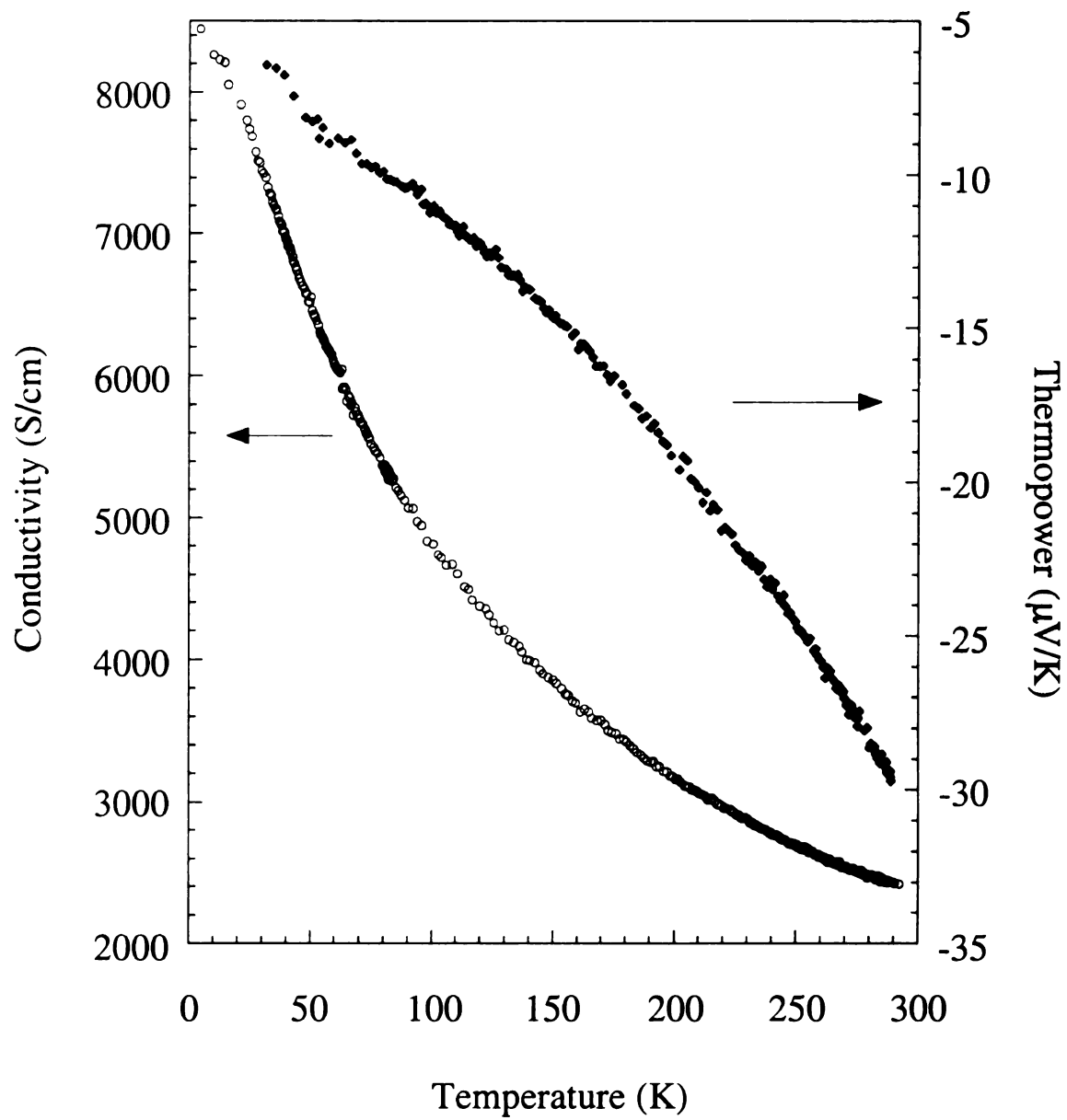


Figure 8-16. Variable temperature electrical conductivity and thermopower for single crystals of $\text{Ba}_{4-x}\text{Bi}_{6+2/3x}\text{Se}_{13}$.

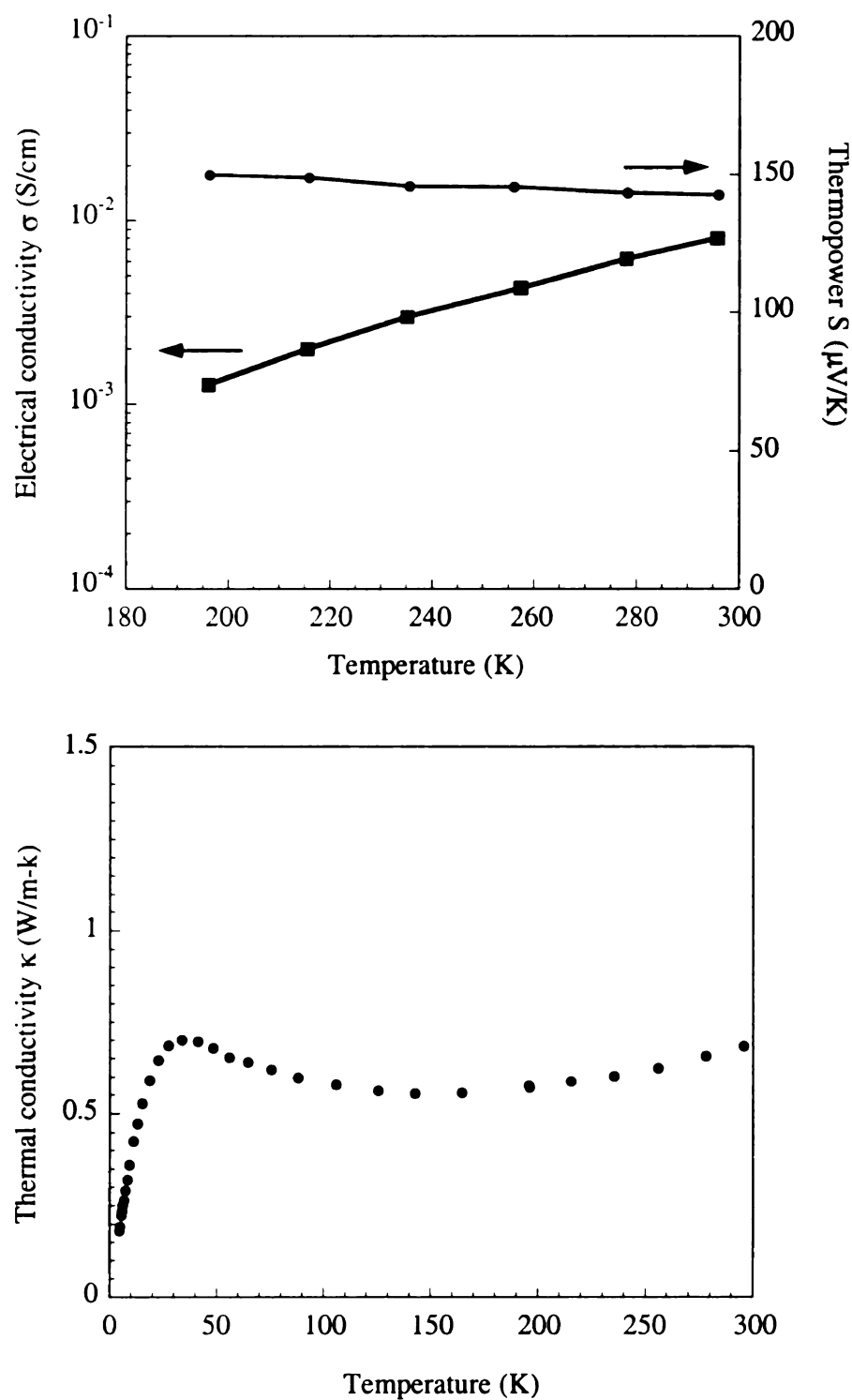


Figure 8-17. (a) Variable temperature electrical conductivity and thermopower for an ingot (hot pressed) of $\text{BaLaBi}_2\text{Se}_6$. (b) Variable temperature thermal conductivity for an ingot (hot pressed) of $\text{BaLaBi}_2\text{Se}_6$.

5. Concluding Remarks

It should have been already apparent that bismuth chalcogenides exhibit a remarkable structural variety forming in several cases unusual homologous series. Some structures types such as that of cosalite or $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ are very stable and will form with a variety of similar sized ions as long as the charge balance requirements are met. In other cases the incorporation of the fourth element such as Sn, for example, will result in the formation of new structures types. The different building blocks will combine with each other in several different ways forming new structures based on the composition of the reaction mixture and heating profile. Although we have done a lot of work in these systems there is definitely more to be discovered!

References

1. (a) Glemser, O.; Filcek, M. *Z. Anorg. Allg. Chem.* **1955**, 279, 321-323. (b) Gattow, G.; Zemmann, J. *Z. Anorg. Allg. Chem.* **1955**, 279, 324-327. (c) Golovei, M. I.; Berul, S. I.; Luzhnaya, N. P.; Peresh, E. Y. *Inorg. Mater.* **1970**, 6, 961-964. (d) Voroshilov, Y. V.; Peresh, E. Y.; Golovei, M. I. *Inorg. Mater.* **1972**, 8, 677-678. (e) Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk SSSR* **1980**, 252, 96-99. (f) Schmitz, D.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, 29, 438-439. (g) Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 676-683. (h) Aurivillius, B. *Acta Chem. Scand., Ser. A* **1983**, A37, 399-407. (i) Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, 22, 631-638. (j) Volk, K.; Cordier, G.; Cook, R.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, 35, 136-140.
2. The europium metal chunk was in the form of small pieces (< 1cm).
3. Chung, D.-Y.; Iordanidis, L.; Kanatzidis, M. G. work in progress.
4. Lemoine, P.; Carre, D.; Guittard, M. *Acta Crystallogr., Sect. C* **1986**, C42, 259-261.
5. See Chapter 3.
6. Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M.; Kruger, C.; Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175-189.
7. teXsan v1.8, 1996 Molecular Structure Corporation, The Woodlands, Texas 77831 USA.
8. Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, A39, 158-166.
9. SMART v4 and 5 1996-1999, SAINT v4, 5 and 6 1994-1999, SADABS, XPREP, SHELXTL V-5.1, GEMINI, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA.

-
10. Wills, A. S.; Brown, I. D. *Valist*, CEA, France (1999). Program available from author at willsas@netscape.net.
 11. See Chapter 6.
 12. See Chapter 3.
 13. (a) McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301. (b) Chondroudis, K.; Kanatzidis, M. G. *J. Solid State Chem.* **1998**, *136*, 328-332.
 14. Mrozek, A.; Chung, D.-Y.; Ghelani, N.; Hogan, T.; Kanatzidis, M. G. Submitted for publication.
 15. Mrozek, A.; Chung, D.-Y.; Hogan, T.; Kanatzidis, M. G. *J. Mater. Chem.* **2000**, *10*, 1667-1672.
 16. Mumme, W. G. *Amer. Mineral.* **1975**, *60*, 548-558.
 17. Topa, D.; Makovicky, E.; Balic-Zunic, T.; Berlepsch, P. *Eur. J. Mineral.* **2000**, *12*, 825-833.
 18. (a) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465-1474. (b) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655-1658.
 19. Chung, D.-Y.; Choi, K.-S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B.; Hu, S.; Uher, C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 3060-3071.
 20. Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011-1017.
 21. See Chapter 7.
 22. Choi, K.-S.; Chung, D.-Y.; Mrozek, A.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. Submitted for publication.

-
23. Srikrishnan, T.; Nowacki, W. Z. *Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1974**, *140*, 114-136.
 24. Skowron, A.; Brown, I. D. *Acta Crystallogr., Sect. C* **1990**, *C46*, 2287-2291.
 25. Chung, D.-Y.; Kanatzidis, M. G. work in progress.
 26. Wulf, R. *Mineral. Petrol.*, **1995**, *52*, 187-196.
 27. Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352-1362.
 28. Choi, K.-S.; Iordanidis, L.; Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 3804-3805.
 29. Chung, D.-Y.; Jobic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2505-2515.
 30. See Chapter 2.
 31. Cook, R.; Schäfer, H. *Rev. Chim. Miner.* **1982**, *19*, 19-27.