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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW MULTINARY GROUP 15 (BISMUTH AND ANTIMONY) CHALCOGENIDES

presented by

SUMOHAN MISRA

has been accepted towards fulfillment
of the requirements for the

MASTER OF SCIENCE degree in CHEMISTRY

Major Professor's Signature

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Date

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW MULTINARY GROUP 15 (BISMUTH AND ANTIMONY) CHALCOGENIDES

By

Sumohan Misra

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ABSTRACT

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW MULTINARY GROUP 15 (BISMUTH AND ANTIMONY) CHALCOGENIDES

By

Sumohan Misra

Multinary bismuth chalcogenides are an attractive class of compounds due to their rich compositional and structural variety which makes them some of the most adaptable and versatile systems. Together with this rich structural heterogeneity, their potential as leading thermoelectric materials led us to the investigation of these multinary bismuth chalcogenide.

Three new compounds $KPb_2Bi_5S_{10}$, $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$, and $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$ all having $KBi_{6.33}S_{10}$ type structure and showing variation in either the metal or the chalcogenide site were obtained. Physicochemical characterization of $KPb_2Bi_5S_{10}$ is reported. We also obtained two derivatives of the $K_{2.5}Bi_{8.5}Se_{14}$ structure type: $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ and $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$. Physicochemical characterization of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ is reported. We also employed solvothermal synthetic conditions to study the system $Cs_2Se/M/Se$ (M = Bi, Sb). $Cs_3Sb_5Se_9$ was obtained which is an ordered structural variant than the one previously reported.

This thesis describes the synthesis and structural characterization of the above mentioned compounds.

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I would like to thank my advisor, Professor Mercouri G. Kanatzidis for all his help, support and advice. I would also like to thank all my past and present group members for their help and support.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

Multin

Introduction

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CHAPTER 1

Multinary Bismuth Chalcogenides and Their Application as Thermoelectric Materials

Introduction

The general formula for multinary bismuth chalcogenide family can be expressed as $M_wM'_xBi_yQ_z$ where M & M′ could be any metal and Q is a chalcogen (S, Se, Te). This family is an interesting class of materials due to their compositional and structural diversity and complexity and this makes them attractive for investigations for thermoelectric applications.

Multinary Bismuth Chalcogenides

Bismuth chalcogenides from a solid state chemistry perspective are an attractive class of compounds due to their rich compositional and structural variety which makes them some of the most adaptable and versatile systems. In nature these characteristics are very well expressed in the sulfosalts family[1] where Bi compounds constitute 20% of them. Bismuth atoms both in naturally occurring sulfosalts and in the synthetically derived compounds show an amazing flexibility in bonding. This fact is an underlying reason for the unparalleled diversity and complexity that bismuth chalcogenide compounds possess. Bismuth atom adopt several different coordination environments ranging from trigonal

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pyramidal, to square pyramidal, to octahedral (usually distorted) to trigonal prismatic to higher coordination number extending to nine. The cause of such a variety of coordination environments can be pinned down to the $6s^2$ lone pair of electrons of bismuth. This lone pair can be stereochemically expressed to locally distort the bismuth coordination geometry or can be suppressed by hybridizing with energetically adjacent p- and d-orbitals to form sp^3d^2 hybrid orbitals thereby producing a regular octahedral Bi^{3+} center. Almost any intermediate stage in the continuum is observed between the full stereochemical expression and complete suppression of the lone pair. This property gives rise to probably the most malleable coordination geometry in the periodic table. It is therefore interesting to observe the role of Bi^{3+} and its role in stabilizing various structure types.

Some of the different types of coordination environment for Bi atoms that can be observed in various multinary bismuth chalcogenides can range from trigonal pyramidal in β-$CsBiS_2$,[2] to square pyramidal in $RbBi_2Bi_8Se_{13}$,[3] to perfect octahedral in $RbBiS_2$,[4] to distorted octahedral in β-$K_2Bi_8Se_{13}$,[5] to bicapped trigonal prismatic in $KBi_{6.33}S_{10}$,[6] to monocapped trigonal prismatic in $Pb_2La_xBi_{8-x}S_{14}$.[7] These are shown in Figure 1-1. With reference to the figure, for (a) and (b) the lone pair is being completely expressed while for (c) it is completely suppressed. For (d) it is only partially expressed leading to short bonds (solid lines) trans to longer bonds (dotted line).

Another interesting feature of these families of compounds is the ability of BiQ_6 octahedra to combine with each other by sharing their edges thereby forming various building blocks. NaCl-type, Bi_2Te_3-type and CdI_2-type fragment is the most common and in some cases Sb_2Se_3-type fragment can also be seen (see figure 1-2.).

Figure 1-1. Som

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Figure 1-1. Some of the different types of coordination environment that Bi atoms adopt in various multinary bismuth chalcogenides: (a) trigonal pyramidal in β-$CsBiS_2$, (b) square pyramidal in $Rb_2Bi_8Se_{13}$, (c) perfect octahedral in $RbBiS_2$, (d) distorted octahedral in β-$K_2Bi_8Se_{13}$, (e) bicapped trigonal prismatic in $KBi_{6.33}S_{10}$, (f) monocapped trigonal prismatic in $Pb_2La_xBi_{8-x}S_{14}$.

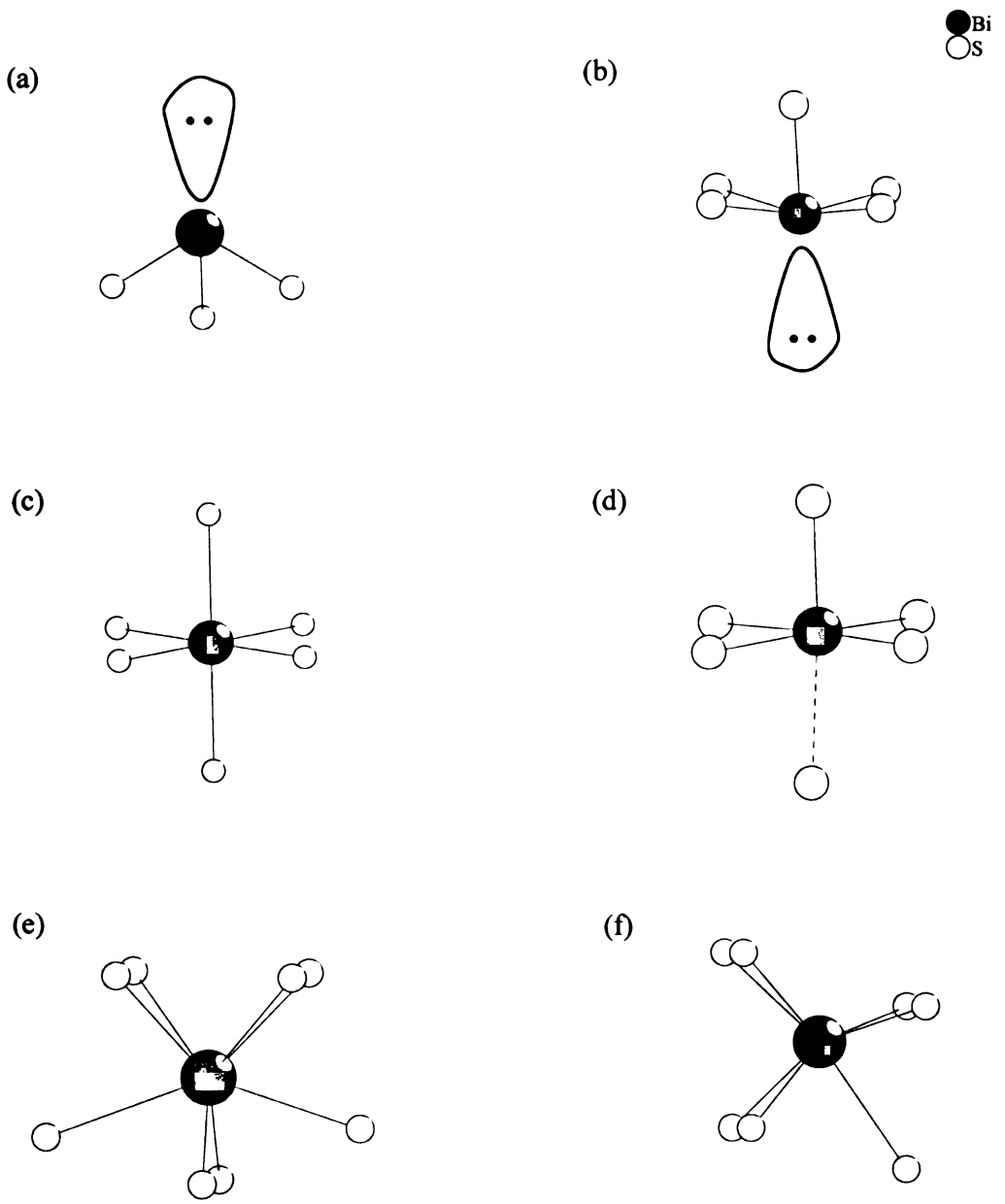

Figure 1-2.

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Figure 1-2. Different building blocks that are found in multinary bismuth chalcogenides: (a) NaCl-type fragment, (b) Bi_2Te_3-type fragment, (c) CdI_2-type fragment, (d) Sb_2Se_3-type fragment.

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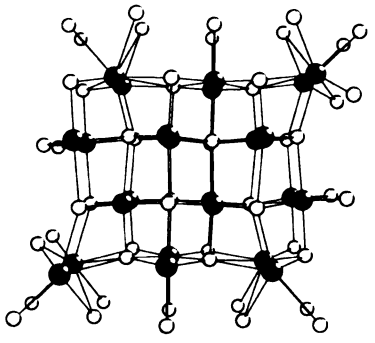

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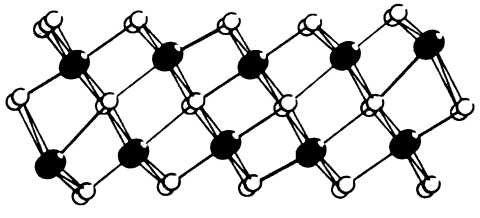

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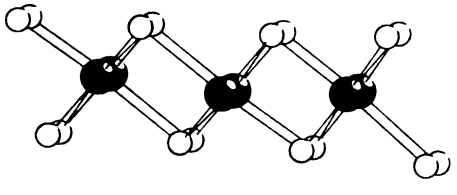

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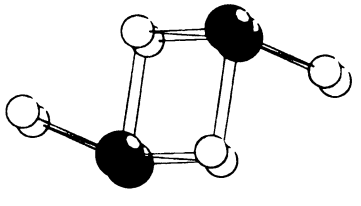

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The third characteristic property of bismuth atoms is its ability to display mixed occupancy leading to structural disorder with a variety of similar sized ions like alkali metals, [5,6] alkaline earth metals,[8] Pb,[8, 9, 10] Sn[8, 10, 11] or rare earth metals.[12] This mixed occupancy often results in the formation of new structure types that do not exist in the simpler systems. Also this kind of positional disorder in the structure generates randomness in mass, size and charge of the atoms on a particular lattice position and this can strongly scatter acoustic lattice phonons carrying heat and thus lower the thermal conductivity.[13] The lowering of thermal conductivity is important in maximizing the figure of merit (ZT) of thermoelectric materials (explained later in this chapter).

This rich structural heterogeneity that these compounds possess together with their potential as leading thermoelectric materials led us to the investigation of these multinary bismuth chalcogenide.

Application of Multinary Bismuth chalcogenides as Thermoelectric Materials

When two dissimilar conductors are in contact with each other then at the junction a voltage gradient is generated automatically whose values depend on the type of conductors used and the temperature. Also if a temperature gradient exists along a conductor, a voltage difference is generated which again depends on the type of conductor and the temperature gradient. These effects are known as thermoelectric effects and they can be distinguished as Thomson, Peltier and Seebeck effects. The applications of these are in thermocouples, refrigeration devices and in power generation.

The best materials for thermoelectric cooling applications currently used in the industry are solid solutions of Bi_2Te_3 and $Bi_{2-x}Sb_xTe_{3-y}Se_y$.[14] These materials possess high

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electrical conductivity and thermoelectric power (Seebeck coefficient) and low thermal conductivity. These properties define the dimensionless figure of merit:

$$ZT = (S^2\sigma)\, T / \kappa$$

where S is the thermoelectric power or Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the temperature. These alloys have a $ZT \sim 1.0$ at 300 K. The above properties are determined by the details of the electronic structure and scattering of charge carriers (electrons and holes) and thus are not independently controllable parameters. An increase in the electrical conductivity leads to a simultaneous decrease in the thermoelectric power and a comparable increase in the thermal conductivity. Hence it is not easy to improve the value of ZT. Moreover it is now believed that the Bi_2Te_3 compounds may be nearing the limit of their potential performance[15] and the requirement for a thermoelectric material to be commercially useful is a $ZT \geq 1.5$.

Our approach in improving ZT is to identify new multinary bismuth chalcogenides with higher compositional and structural complexity containing heavy atoms, large unit cells and disorder in the crystal lattice. This rationale is based on the proposition that materials with more complex compositions and structures may have complex electronic structure which may give rise to high thermoelectric power and low thermal conductivities.[16] Another concept which helps in lowering the thermal conductivity was introduced by Slack as the limiting characteristic for a superior thermoelectric.[13] In these materials a weakly bound atom or molecule 'rattler' is used. These 'rattlers' create low-frequency vibration modes that scatter acoustic lattice phonons

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carrying heat thereby lowering the thermal conductivity of the solid without severely affecting the electrical conduction, thus leading to improved thermoelectric efficiency.[17]

The compounds β-$K_2Bi_8Se_{13}$,[5] $CsBi_4Te_6$,[18] $KBi_{6.33}S_{10}$ [6] reported earlier by our group shows all the above mentioned characteristics and exhibit promising thermoelectric properties. This has leaded us to investigate more complicated multinary systems.

In Chapters 2 and 3 we will describe the multinary bismuth chalcogenides found during these synthetic investigations and their structural characterization. In Chapter 4 we will discuss the 'solvothermal' synthesis technique and how it is used to synthesize a ternary antimony chalcogenide.

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CHAPTER 2

Synthesis and Structure of $KPb_2Bi_5S_{10}$, $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$, and $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$ belonging to the Cosalite structure type.

A. Introduction

Bismuth chalcogenides have a wide range of applications including thermoelectrics,[1] and non-linear optical materials.[2] From the point of view of their application in thermoelectrics our approach has been to focus on new semiconducting multinary bismuth chalcogenides. These materials are an interesting class of compounds due to their compositional and structural complexity arising due to the presence of an inert $6s^2$ lone pair of electrons on bismuth which may or may not be stereochemically active which in turn affects the lattice structure, the electronic structure and thus the properties of the resulting compounds.

A superior thermoelectric material has high electrical conductivity (σ), high seebeck coefficient (S) and low thermal conductivity (κ). These together define the TE figure of merit $ZT = (\sigma S^2/\kappa) T$. Factors contributing to low thermal conductivity and thus higher ZT are the presence of heavy atoms like Bi and Pb, large unit cells and disorder in the crystal lattice. The rationale behind using lead is that in addition to being very heavy it has similar electronic properties as Bi and has a well known tendency to disorder with Bi or alkali metals, depending on the local environment.[3-5] This kind of site occupancy disorder in the structure generates randomness in mass, size and charge of the atoms on a

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particular lattice position that can strongly scatter acoustic lattice phonons carrying heat and thus lower the thermal conductivity.[6] Another approach in lowering the thermal conductivity in these materials is to incorporate alkali or alkaline earth metals in the channels or layers formed by these infinite anionic bismuth-chalcogen frameworks. These ions make relatively weak ionic bonds with chalcogens due to which they rattle around in their channels or in between the layers thereby creating low-frequency vibration modes that scatter acoustic lattice phonons carrying heat, thus reducing the thermal conductivity.[7]

Reports previously from our group showed that $KBi_{6.33}S_{10}$[8] which has a cosalite like structure has thermal conductivity substantially lower than Bi_2Te_3 making it attractive for further investigations for thermoelectric applications. We report here three new compounds $KPb_2Bi_5S_{10}$, $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$, and $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$ all having $KBi_{6.33}S_{10}$ type structure showing variation in either the metal or the chalcogenide site.

B. Experimental Section

Reagents: Chemicals were used as obtained: (i) bismuth chunks, 99.999% purity, Cerac, Milwaukee, WI, (ii) sulfur powder, sublimed, Spectrum Chemical Mfg. Corp., Gardena, CA, (iii) selenium shots (99.999% purity, Cerac, Milwaukee, WI), (iv) tellurium chunks 99.999% purity, Cerac, Milwaukee, WI, (v) potassium metal, Aldrich, Milwaukee, WI, (vi) lead metal, Cerac, Milwaukee, WI, (vii) strontium selenide powder 99.5% purity, -20 mesh, Cerac, Milwaukee, WI. Na_2Se was prepared by a stoichiometric reaction of sodium metal and selenium shots in liquid ammonia.

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Synthesis: All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. 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_2Se_3: A mixture of 6.383g (0.031 mol) of bismuth and 3.617g (0.046 mol) of selenium was transferred into a 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 800°C in 10 hours, held at that temperature for 10 hours and then cooled down to 50°C in 10 hours. The product was used for further reactions.

PbTe: A mixture of 12.378g (0.060 mol) of lead and 7.622g (0.060 mol) of tellurium was transferred into a 13mm carbon coated quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 1100°C in 8 hours, isothermed there for 12 hours and then cooled down to 50°C in 24 hours. The product was used for further reactions.

$K_2Bi_8S_{13}$: A mixture of 0.180g (4.60 mmol) of potassium, 3.858g (0.018 mol) of bismuth and 0.962g (0.030 mol) of sulfur was transferred into 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 150°C in 6 hours, and then further heated upto 850°C in 6 hours, isothermed there for 1 hour and then cooled down to 50°C in 48 hours. The product was used for further reactions.

$KPb_2Bi_5S_{10}$: A pure synthesis of $KPb_2Bi_5S_{10}$ was achieved with a mixture of 0.05g (1.280 mmol) of potassium, 0.265g (1.280 mmol) of lead, 0.668g (3.20 mmol) of bismuth and 0.205g (6.40 mmol) of sulfur in the ratio 2:2:5:10 which were transferred into a 13mm quartz tube and was flame sealed under vacuum (~10^{-4} Torr). The tube was

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heated to 850°C in 10 hours and isothermed there for 48 hours and then cooled slowly to 550°C in 30 hours and finally to 50°C in 3 hours. The product consisted of silvery-gray needle like crystals. A quantitative analysis by Energy Dispersive Spectroscopy (EDS) using a Scanning Electron Microscope (SEM) was performed on several of these crystals which gave an approximate composition of "$KPb_{3.80}Bi_{3.36}S_{8.03}$".

$K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$: A mixture of 0.4g (0.185 mmol) of $K_2Bi_8S_{13}$ and 0.185g (.553 mmol) of PbTe in the ratio 1:3 was transferred into a 9mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 850°C in 10 hours and isothermed there for 48 hours and then cooled slowly to 500°C in 96 hours and finally to 50°C in 5 hours. The product consisted of silvery-gray needle like crystals. A quantitative analysis by Energy Dispersive Spectroscopy (EDS) using a Scanning Electron Microscope (SEM) was performed on several of these crystals which gave an approximate composition of "$KPb_{4.62}Bi_{3.95}S_{9.73}Te_{0.27}$".

$Na_xSr_{4-2x}Bi_{4+x}Se_{10}$: A mixture of 0.03g (0.24 mmol) of Na_2Se, 0.2g (1.2 mmol) of SrSe and 0.472g (7.2 mmol) of Bi_2Se3 in the ratio 1:5:3 were transferred into a graphite tube which was placed in a 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 800°C in 24 hours, held at that temperature for 24 hours and then cooled to 50°C in 25 hours. The product consisted of silvery-gray rod like crystals. Energy Dispersive Spectroscopy (EDS) on several of these crystals gave an approximate composition of "$NaSr_{1.96}Bi_{4.60}Se_{9.68}$".

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C. Physical Measurements

Energy Dispersive Spectroscopy: Quantitative microprobe analyses of the compound were performed with a JEOL JSM-6400V Scanning Electron Microscope equipped with a Tracor Northern Energy Dispersive Spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 30 seconds accumulation time.

Differential Thermal Analysis: Differential Thermal Analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50 thermal analyzer. Ground single crystals (30-40 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 1000°C at 10°C/min, isothermed for 1 minute followed by cooling at 10°C/min. The reported DTA temperature is the peak temperature. After DTA, the samples were examined with powder X-ray diffraction. Reproducibility of results was checked with multiple heating / cooling cycles.

Charge Transport Measurements: Thermopower was measured using an instrument from MMR Technologies, Inc., Mountain View, CA. The sample and the reference (constantan wire) were mounted on a Seebeck stage with conductive silver paste. The temperature gradient across the sample was built up by a computer controlled heater which is controlled by the MMR Programmable Seebeck Controller SB100. The Seebeck stage was attached to the MMR stage, which provides a given stable temperature for the measurement. The MMR K20A Programmable Temperature Controller controls this MMR stage. The voltage across the sample resulting from the temperature gradient was measured.

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Table 2-2.

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Pb 1-4, K 1,

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Powder X-ray diffraction: The compounds were examined by X-ray powder diffraction for identification and to assess phase purity. Powder patterns were obtained using a CPS 120 INEL diffractometer using Cu-Kα radiation and 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 CERIUS^2 software.[9]

Single-Crystal X-ray Crystallography: Single crystals of $KPb_2Bi_5S_{10}$, $K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$ and $Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$ were mounted on the tip of a glass fiber. The intensity data were collected at 293 K on a Bruker SMART Platform CCD diffractometer using graphite monochromatized Mo K_α (λ = 0.71073 Å) radiation over a full sphere of reciprocal space. Individual frames were measured using 0.3° steps in ω. The SMART software was used for data acquisition and SAINT[10] for data extraction and reduction. The absorption correction was done with SADABS[10], and the structure solution was done with the SHELXTL[10] package of crystallographic programs.

$KPb_2Bi_5S_{10}$: A full sphere of data was collected with an exposure time of 30 seconds per frame. Structure refinement was straightforward in orthorhombic space group Pnma. After anisotropic refinement final R values, R1 = 2.75% and wR2 = 6.91%. The fractional atomic coordinates and isotropic displacement parameters are shown in Table 2-2.

$K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$: A full sphere of data was collected with an exposure time of 20 seconds per frame. Eighteen crystallographically independent positions (Bi 1-5, Pb 1-4, K 1, S 1-9 and Te 10) were found to sit on a crystallographic mirror plane. Pb(3) & Pb(4) and Bi(1) & K(1) were found to be disordered over a single site. After

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anisotropic refinement final R values, R1 = 2.96% and wR2 = 6.06%. The fractional atomic coordinates and isotropic displacement parameters are shown in Table 2-3.

$Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$: A full sphere of date was collected with an exposure time of 30 seconds per frame. Eighteen crystallographically independent positions were found to sit on a crystallographic mirror plane. Bi(1) & Sr(1), Bi(3) & Sr(3), Bi(4) & Sr(4), Sr(5) & Na(5), Sr(6) & Na(6) and Sr(7) & Na(7) were all found to be disordered over a single site. After anisotropic refinement final R values, R1 = 7.00% and wR2 = 12.61%. The fractional atomic coordinates and isotropic displacement parameters are shown in Table 2-4.

Table 2-1. Cry

$Na_xSr_{4-2x}Bi_{4+x}S$

Chemical form	
Formula weigh	
T, K	
λ, Å	
Crystal system	
Space group	
a, Å	
b, Å	
c, Å	
α, deg	
β, deg	
γ, deg	
V, Å3	
Z	
ρ_{calcd}, g cm^3	
μ, mm^{-1}	
Total reflecti	
Unique reflec	
R_{int}	
No. of param	
Goodness-of-	
Refinement m	
R1[a]	
wR2[b]	

[a] $R1 = \sum F_o$

Table 2-1. Crystallographic Data for $KPb_2Bi_5S_{10}$, $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$, and $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$.

Chemical formula	$KPb_2Bi_5S_{10}$	$K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$	$Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$
Formula weight	487.33	614.93	8172.56
T, K	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system		Orthorhombic	
Space group	Pnma	Pnma	Pnma
a, Å	23.927(10)	24.111(12)	24.512(15)
b, Å	4.1103(16)	4.089(2)	4.247(3)
c, Å	19.315(8)	19.371(9)	20.205(13)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, $Å^3$	1899.6(13)	1909.8(16)	2104(2)
Z	14	11	1
ρ_{calcd}, g/cm^3	5.964	5.881	6.451
μ, mm^{-1}	64.327	54.397	64.625
Total reflections	21493	20504	16913
Unique reflections	2674	2536	2788
$R_{(int)}$	0.0452	0.0577	0.1820
No. of parameters	110	114	117
Goodness-of-fit on F^2	1.031	0.911	1.013
Refinement method		Full-matrix least-squares on F^2	
R1[a]	0.0275	0.0296	0.0700
wR2[b]	0.0691	0.0606	0.1261

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

Table 2-2. Ato

($Å^2 \times 10^3$) for K

Bi(1)	
Bi(2)	
Bi(3)	
Bi(4)	
Bi(5)	
Pb(1)	
Pb(2)	
K(1)	
S(1)	
S(2)	
S(3)	
S(4)	
S(5)	
S(6)	
S(7)	
S(8)	
S(9)	
S(10)	

U_{eq} is defin

Table 2-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KPb_2Bi_5S_{10}$.

	x	y	z	U(eq)
Bi(1)	1507(1)	2500	161(1)	17(1)
Bi(2)	1716(1)	-2500	-1897(1)	15(1)
Bi(3)	93(1)	-2500	-961(1)	19(1)
Bi(4)	2020(1)	-2500	4090(1)	14(1)
Bi(5)	688(1)	-7500	4651(1)	18(1)
Pb(1)	428(1)	2500	-2751(1)	18(1)
Pb(2)	2865(1)	-2500	1157(1)	29(1)
K(1)	1301(1)	-2500	2171(2)	18(1)
S(1)	885(1)	2500	-1367(2)	19(1)
S(2)	1402(1)	-7500	3536(2)	17(1)
S(3)	-272(1)	-2500	-2252(2)	17(1)
S(4)	2219(1)	-2500	-326(2)	20(1)
S(5)	1409(1)	-12500	5211(2)	18(1)
S(6)	1235(1)	-2500	-3094(2)	17(1)
S(7)	-35(1)	-7500	5893(2)	22(1)
S(8)	-699(1)	-7500	-564(2)	25(1)
S(9)	2376(1)	-7500	-2312(2)	16(1)
S(10)	2046(1)	2500	1321(2)	17(1)

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

Table 2-3. Ato

($Å^2 \times 10^3$) for

Pb(1)	
Pb(2)	
Pb(3)	
Pb(4)	
K(1)	
Bi(1)	
Bi(2)	
Bi(3)	
Bi(4)	
Bi(5)	
S(1)	
S(2)	
S(3)	
S(4)	
S(5)	
S(6)	
S(7)	
S(8)	
S(9)	
Te(10)	

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Table 2-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$.

	x	y	z	U(eq)	Occ.
Pb(1)	4899(1)	-2500	10957(1)	23(1)	
Pb(2)	2143(1)	-2500	8834(1)	32(1)	0.42601
Pb(3)	5681(1)	-2500	14587(4)	19(1)	0.46327
Pb(4)	5701(1)	-2500	14725(4)	22(1)	0.53673
K(1)	3706(2)	-2500	7802(3)	25(1)	0.87487
Bi(1)	3708(3)	-2500	8034(4)	36(2)	0.12513
Bi(2)	3490(1)	2500	9831(1)	20(1)	
Bi(3)	3271(1)	-2500	11889(1)	18(1)	
Bi(4)	7015(1)	-7500	14097(1)	17(1)	
Bi(5)	4564(1)	2500	12726(1)	25(1)	
S(1)	4110(1)	2500	11359(2)	21(1)	
S(2)	6384(1)	-2500	13521(2)	17(1)	
S(3)	5270(1)	-2500	12243(2)	23(1)	
S(4)	2769(2)	-2500	10318(2)	24(1)	
S(5)	2612(1)	-7500	12304(2)	19(1)	
S(6)	6409(2)	-7500	15219(2)	23(1)	
S(7)	3758(1)	-2500	13073(2)	20(1)	
S(8)	4283(2)	-2500	9426(2)	25(1)	
S(9)	2971(2)	2500	8670(2)	21(1)	
Te(10)	4984(1)	-2500	15908(1)	27(1)	0.18924

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

Table 2-4

($Å^2 \times 10^3$)

Bi(1)	
Sn(1)	
Bi(2)	
Bi(3)	
Sn(3)	
Bi(4)	
Sn(4)	
Bi(5)	
Sn(5)	
Na(5)	
Sn(6)	
Na(6)	
Sn(7)	
Na(7)	
Se(1)	
Se(2)	
Se(3)	
Se(4)	
Se(5)	
Se(6)	
Se(7)	
Se(8)	
Se(9)	
Se(10)	

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Table 2-4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$.

	x	y	z	U(eq)	Occ.
Bi(1)	1513(1)	2500	9824(1)	14(1)	0.89828
Sr(1)	1513(1)	2500	9824(1)	14(1)	0.10172
Bi(2)	1719(1)	-2500	11920(1)	16(1)	0.49244
Bi(3)	99(1)	-2500	11006(1)	17(1)	0.89034
Sr(3)	99(1)	-2500	11006(1)	17(1)	0.10966
Bi(4)	2998(1)	-7500	10934(1)	17(1)	0.93817
Sr(4)	2998(1)	-7500	10934(1)	17(1)	0.06183
Bi(5)	4358(1)	-12500	10390(1)	23(1)	
Sr(5)	3708(2)	-7500	12897(2)	20(2)	0.79289
Na(5)	3708(2)	-7500	12897(2)	20(2)	0.20711
Sr(6)	2968(1)	-2500	8864(2)	15(1)	0.95836
Na(6)	2968(1)	-2500	8864(2)	15(1)	0.04164
Sr(7)	5423(2)	-17500	12283(2)	21(2)	0.77261
Na(7)	5423(2)	-17500	12283(2)	21(2)	0.22739
Se(1)	885(1)	2500	11308(2)	15(1)	
Se(2)	2257(2)	-2500	10313(2)	18(1)	
Se(3)	3613(2)	-7500	9789(2)	15(1)	
Se(4)	2411(2)	-7500	12301(2)	15(1)	
Se(5)	5033(2)	-17500	10874(2)	19(1)	
Se(6)	-346(2)	-2500	12223(2)	18(1)	
Se(7)	723(2)	-2500	9438(2)	19(1)	
Se(8)	2018(1)	2500	8628(2)	15(1)	
Se(9)	3628(2)	-12500	11563(2)	19(1)	
Se(10)	1244(2)	-2500	13116(2)	16(1)	

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

D. Results

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D. Results and discussion

Structure Description of $KPb_2Bi_5S_{10}$

This compound is isostructural with $KBi_{6.33}S_{10}$ and has a three dimensional structure made up of NaCl-type blocks and CdI_2-type fragments that connect to form tunnels filled with eight-coordinate K^+ cations. The bond distances and selected bond angles are given in Tables 2-7 and 2-8. The structural diagram down the b-axis is shown in Figure 2-1. The existence of these types of NaCl- and CdI_2-type fragments with Bi in an octahedral coordination site is a very common structural motif found in most bismuth chalcogenides. The two different fragments of NaCl-type and CdI_2-type are joined by eight coordinated Pb atoms (i.e., Pb(2)) which are in a bicapped prismatic geometry, in the same way as Bi is found in $KBi_{6.33}S_{10}$ [8] and various mineral sulfo salts.[11] The $[Pb_2Bi_5S_{10}]^-$ framework is made of edge-sharing MS_6 (M = Bi, Pb) octahedra, as shown in Figure 2.2. An interesting feature is the presence of small triangular shaped empty channels which are lined by Bi(5)-S(7)-Pb(1)-S(6)-Pb(2)-S(5). These types of channels are similar to the $KBi_{6.33}S_{10}$ structure.

Atoms Pb(1) and Bi(5) are present in a slightly distorted octahedral coordination where the M-S (M = Bi, Pb) distances range from 2.820(2) to 2.897(2) Å for Pb(1) and 2.749(3) to 2.957(4) Å for Bi(5). On the other hand Bi(1), Bi(2), Bi(3) and Bi(4) are present in a highly distorted octahedral coordination with a short bond trans to a long bond. Pb(2) is present in a bicapped prismatic geometry where its coordination sphere is filled by eight sulfur atoms and the bond length ranges from 2.856(2) to 3.310(1) Å.

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Thermal Analysis of $KPb_2Bi_5S_{10}$

Differential thermal analysis was performed on pure $KPb_2Bi_5S_{10}$ samples to ascertain their thermal behavior. At the end of two heating cycles the compound was checked for decomposition by taking its powder X-ray diffraction pattern. $KPb_2Bi_5S_{10}$ shows an endothermic (melting) peak at 728°C and on cooling shows an exothermic (recrystallization) peak at 703°C. The powder pattern of the compound after DTA indicated no decomposition. (See Figure 2-3.)

Charge Transport Measurement of $KPb_2Bi_5S_{10}$

Thermoelectric power measurements were carried on polycrystalline oriented ingots (grown by Bridgman technique) [12] of $KPb_2Bi_5S_{10}$. It is a n-type conductor and at room temperature the thermopower has a value of -133 μV/K. It shows a linear trend till 400 K. (See Figure 2.4.)

Figure 2-1. P

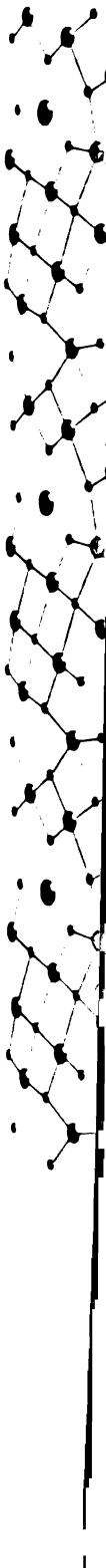


Figure 2-1. Projection of the structure of $KPb_2Bi_5S_{10}$ down the b-axis.

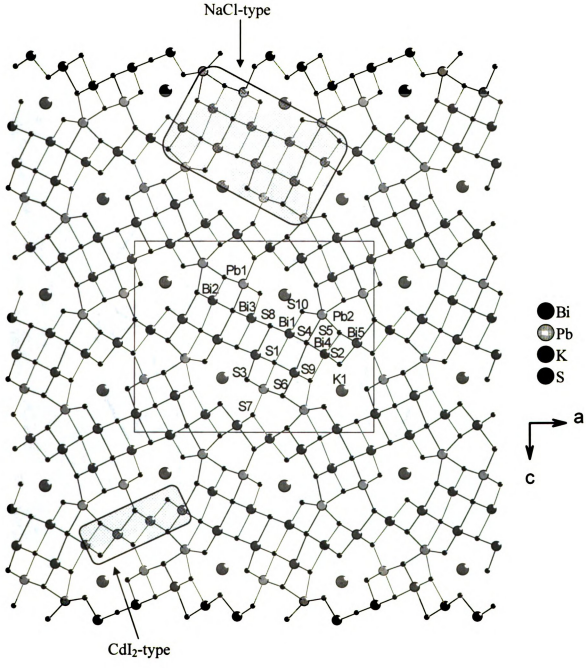


Figure 2-2. Polyhedral representation of $KPb_2Bi_5S_{10}$ down the b-axis showing the connectivity of the MS_6 octahedra (M = Bi, Pb).

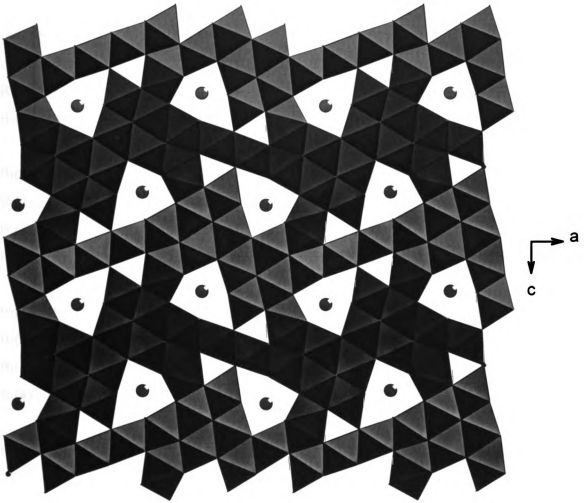


Table 2-5. Bor

Bu(1)-S(10)

Bu(1)-S(4) x 2

Bu(1)-S(8) x 2

Bu(1)-S(1)

Bu(2)-S(6)

Bu(2)-S(9) x 2

Bu(2)-S(1) x 2

Bu(2)-S(4)

Bu(3)-S(3)

Bu(3)-S(8) x 2

Bu(3)-S(1) x 2

Bu(3)-S(8)

Bu(4)-S(5)

Bu(4)-S(2) x

Bu(4)-S(4) x

Bu(4)-S(9)

Bu(5)-S(2)

Table 2-5. Bond distances (Å) for $KPb_2Bi_5S_{10}$.

Bi(1)-S(10)	2.586(3)	Bi(5)-S(7) x 2	2.786(2)
Bi(1)-S(4) x 2	2.830(2)	Bi(5)-S(5) x 2	2.894(2)
Bi(1)-S(8) x 2	2.927(3)	Bi(5)-S(7)	2.957(4)
Bi(1)-S(1)	3.305(1)		
		Pb(1)-S(3) x 2	2.820(2)
Bi(2)-S(6)	2.583(3)	Pb(1)-S(6) x 2	2.897(2)
Bi(2)-S(9) x 2	2.713(2)	Pb(1)-S(7)	2.844(3)
Bi(2)-S(1) x 2	3.038(3)	Pb(1)-S(1)	2.888(3)
Bi(2)-S(4)	3.264(1)		
		Pb(2)-S(10) x 2	2.856(2)
Bi(3)-S(3)	2.643(3)	Pb(2)-S(5) x 2	3.253(1)
Bi(3)-S(8) x 2	2.899(2)	Pb(2)-S(6) x 2	3.310(1)
Bi(3)-S(1) x 2	2.903(2)	Pb(2)-S(9)	3.012(3)
Bi(3)-S(8)	3.282(1)	Pb(2)-S(4)	3.254(1)
Bi(4)-S(5)	2.612(3)	K(1)-S(10) x 2	3.178(3)
Bi(4)-S(2) x 2	2.748(2)	K(1)-S(3) x 2	3.211(3)
Bi(4)-S(4) x 2	2.969(2)	K(1)-S(2) x 2	3.352(3)
Bi(4)-S(9)	3.069(3)	K(1)-S(9)	3.319(4)
		K(1)-S(8)	3.423(5)
Bi(5)-S(2)	2.749(3)		

Table 2-6. Se

Si(9)-Bi(1)-S
Si(4)-Bi(1)-S(
Si(9)-Bi(1)-S
Si(4)-Bi(1)-S(
Si(4)-Bi(1)-S(
Si(8)-Bi(1)-S(

Si(6)-Bi(2)-S(
Si(9)-Bi(2)-S(
Si(6)-Bi(2)-S(
Si(9)-Bi(2)-S(
Si(9)-Bi(2)-S(
Si(1)-Bi(2)-S(

Si(3)-Bi(3)-S(
Si(8)-Bi(3)-S(
Si(8)-Bi(3)-S(
Si(3)-Bi(3)-S(
Si(8)-Bi(3)-S(
Si(1)-Bi(3)-S(

Si(5)-Bi(4)-S
Si(2)-Bi(4)-S
Si(2)-Bi(4)-S
Si(5)-Bi(4)-S
Si(2)-Bi(4)-S
Si(4)-Bi(4)-S

Table 2-6. Selected Angles (deg) for $KPb_2Bi_5S_{10}$.

S(10)-Bi(1)-S(4)	89.24(9)	S(5)-Bi(4)-S(9)	174.06(9)
S(4)-Bi(1)-S(4)	93.13(10)	S(2)-Bi(4)-S(9)	84.82(8)
S(10)-Bi(1)-S(8)	95.68(9)	S(4)-Bi(4)-S(9)	92.68(8)
S(4)-Bi(1)-S(8)	88.63(7)		
S(4)-Bi(1)-S(8)	174.80(10)	S(2)-Bi(5)-S(7)	93.07(9)
S(8)-Bi(1)-S(8)	89.21(10)	S(7)-Bi(5)-S(7)	95.07(10)
		S(7)-Bi(5)-S(5)	177.39(8)
S(6)-Bi(2)-S(9)	89.69(8)	S(2)-Bi(5)-S(5)	85.51(8)
S(9)-Bi(2)-S(9)	98.49(10)	S(7)-Bi(5)-S(5)	87.20(7)
S(6)-Bi(2)-S(1)	90.52(8)	S(5)-Bi(5)-S(5)	90.50(9)
S(9)-Bi(2)-S(1)	173.33(7)	S(2)-Bi(5)-S(7)	177.33(9)
S(9)-Bi(2)-S(1)	88.18(7)	S(7)-Bi(5)-S(7)	88.74(8)
S(1)-Bi(2)-S(1)	85.15(9)	S(5)-Bi(5)-S(7)	92.61(8)
S(3)-Bi(3)-S(8)	91.93(9)	S(3)-Pb(1)-S(3)	93.57(10)
S(8)-Bi(3)-S(8)	90.29(10)	S(3)-Pb(1)-S(7)	94.81(8)
S(8)-Bi(3)-S(1)	89.78(7)	S(3)-Pb(1)-S(1)	84.74(8)
S(3)-Bi(3)-S(1)	87.72(8)	S(7)-Pb(1)-S(1)	179.34(10)
S(8)-Bi(3)-S(1)	179.64(10)	S(7)-Pb(1)-S(6)	92.83(8)
S(1)-Bi(3)-S(1)	90.14(10)	S(3)-Pb(1)-S(6)	87.52(7)
		S(3)-Pb(1)-S(6)	172.16(9)
S(5)-Bi(4)-S(2)	91.24(8)	S(1)-Pb(1)-S(6)	87.63(8)
S(2)-Bi(4)-S(2)	96.80(10)	S(6)-Pb(1)-S(6)	90.37(9)
S(2)-Bi(4)-S(4)	174.60(8)		
S(5)-Bi(4)-S(4)	91.60(8)	S(10)-Pb(2)-S(10)	92.02(10)
S(2)-Bi(4)-S(4)	87.72(7)	S(10)-Pb(2)-S(9)	76.14(7)
S(4)-Bi(4)-S(4)	87.61(9)		

Figure 2.3. D

The heating a

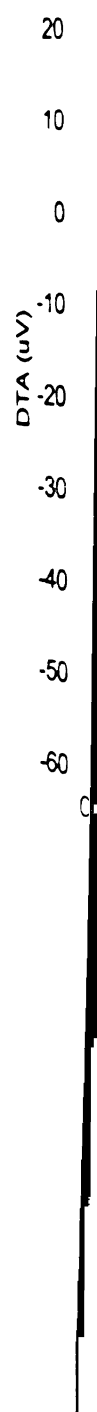


Figure 2.3. DTA diagram of $KPb_2Bi_5S_{10}$ showing the endothermic and exothermic peaks. The heating and cooling rates were 10°C/min.

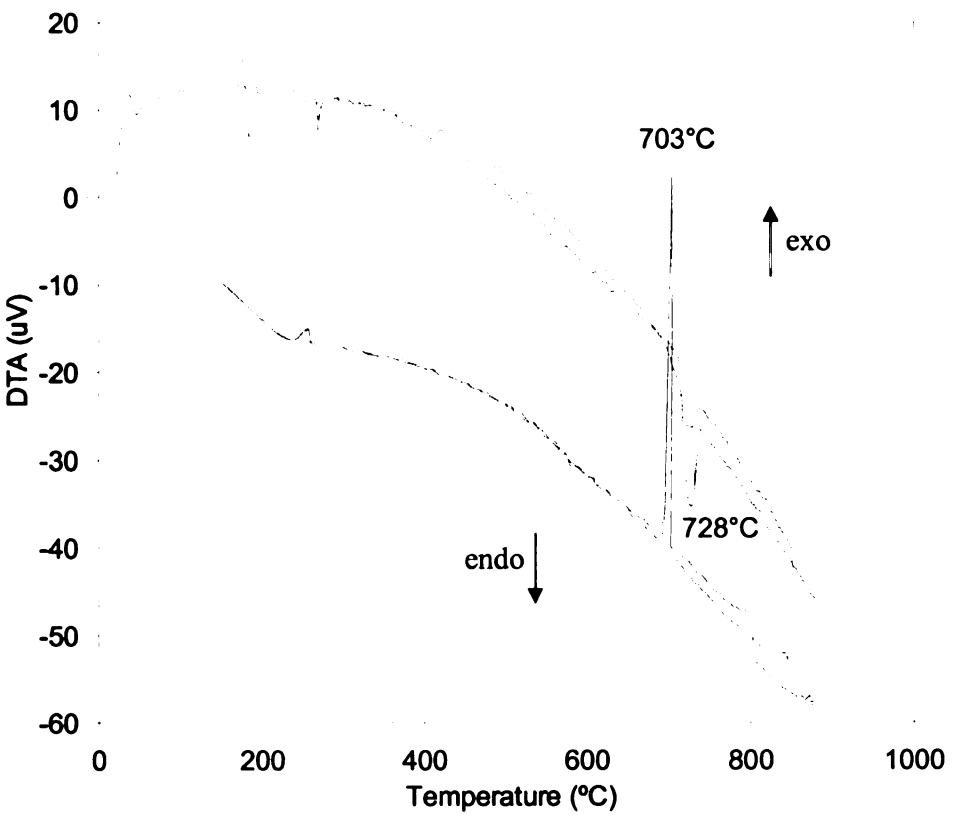


Figure 2.4.

$KPb_2Bi_2S_5$

-130

-135

-140

-145

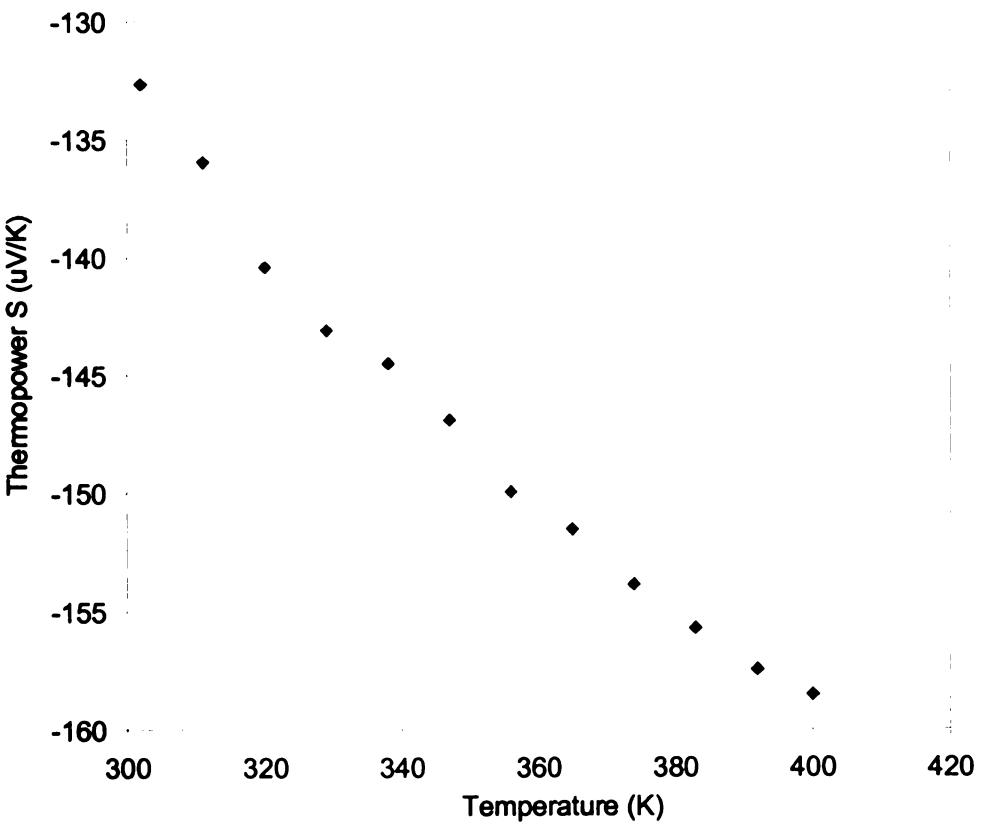
-150

-155

-160

Thermopower S (uV/K)

Figure 2.4. Variable temperature thermopower for a polycrystalline oriented ingot of $KPb_2Bi_5S_{10}$.



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Structure Description of $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$

The idea of using tellurium here was to investigate whether it goes to a different site than sulfur thereby creating a new structure or whether it goes to the same chalcogen site thereby creating a known structure. In our research we ended up in getting a known structure with a small uptake of tellurium in the sulfur site. The compound has a similar structure as $KPb_2Bi_5S_{10}$ where we have a three dimensional network made up of NaCl-type and CdI_2-type fragments. But here unlike $KPb_2Bi_5S_{10}$ these fragments do not form tunnels but instead the K^+ cations are disordered with one of the Bi^{3+} ions (i.e., Bi(1) & K(1)). The bond distances and selected angles are given in Table 2.9 and 2.10. The structural diagram down the b-axis is shown in Figure 2.6.

Atoms K(1) and Bi(1) are disordered in the highly coordinated bicapped prismatic site with 87% K and 13% Bi. The other highly coordinated site is occupied by Pb(2) with 43% Pb. In these sites similar to $KPb_2Bi_5S_{10}$ the metal coordination sphere is filled by eight sulfur atoms. Here the CdI_2-type fragments are made of disordered Pb atoms (Pb(3) and Pb(4)) and Te atoms (Te(10)). The lead sites have 46% of Pb(3) and 54% Pb(4) and the tellurium site is a partially filled site with 19% Te(10). Bi(5), Pb(3) and Pb(4) are present in a slightly distorted octahedral coordination. On the other hand Pb(1), Bi(2), Bi(3) and Bi(4) are present in a highly distorted octahedral coordination with a short bond trans to a long bond.

Figure 2-5. Projection of the structure of $K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$ down the b-axis.

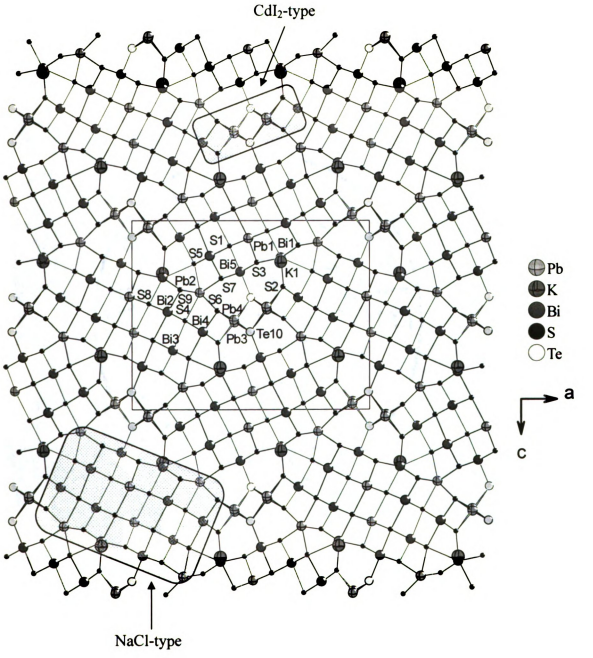

Figure 2-6. Polyhedral representation of $K_{0.93}Pb_{3.04}Bi_{4.34}S_{9.60}Te_{0.40}$ down the b-axis showing the connectivity of the MS_6 octahedra (M = Bi, Pb, Bi/K).

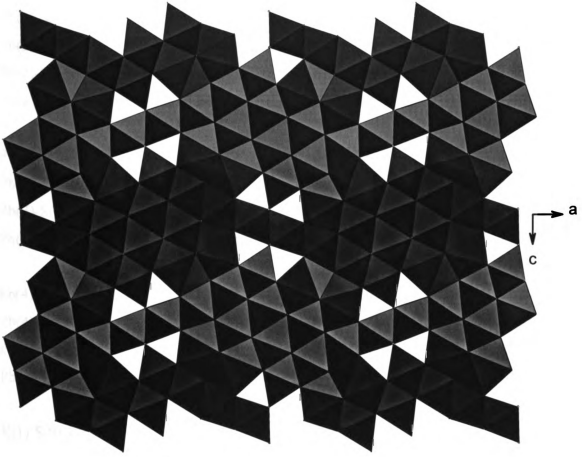

Table 2-7. Bond distances (Å) for $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$.

Pb(1)-S(3)	2.647(4)	Bi(1)-S(9) x 2	2.975(6)
Pb(1)-S(1) x 2	2.899(3)	Bi(1)-S(3) x 2	3.248(1)
Pb(1)-S(8) x 2	2.936(3)	Bi(1)-S(2) x 2	3.648(1)
Pb(1)-S(8)	3.316(1)	Bi(1)-S(5)	3.483(1)
		Bi(1)-S(8)	3.031(8)
Pb(2)-S(9) x 2	2.875(3)		
Pb(2)-S(6) x 2	3.267(1)	Bi(2)-S(1)	3.316(1)
Pb(2)-S(7) x 2	3.328(1)	Bi(2)-S(9)	2.574(4)
Pb(2)-S(5)	3.022(4)	Bi(2)-S(4) x 2	2.844(3)
Pb(2)-S(4)	3.247(1)	Bi(2)-S(8) x 2	2.907(3)
Pb(3)-S(2)	2.671(7)	Bi(3)-S(4)	3.274(1)
Pb(3)-Te(10) x 2	2.769(4)	Bi(3)-S(7)	2.577(4)
Pb(3)-S(6) x 2	2.960(5)	Bi(3)-S(5) x 2	2.712(2)
Pb(3)-Te(10)	3.061(7)	Bi(3)-S(1) x 2	3.054(3)
Pb(4)-S(6) x 2	2.831(4)	Bi(4)-S(6)	2.620(4)
Pb(4)-Te(10) x 2	2.899(5)	Bi(4)-S(2) x 2	2.782(2)
Pb(4)-S(2)	2.855(7)	Bi(4)-S(4) x 2	2.962(3)
Pb(4)-Te(10)	2.869(6)	Bi(4)-S(5)	3.072(4)
K(1)-S(9) x 2	3.186(5)	Bi(5)-S(3) x 2	2.820(3)
K(1)-S(3) x 2	3.207(4)	Bi(5)-Te(10)	2.862(3)
K(1)-S(2) x 2	3.287(5)	Bi(5)-S(1)	2.865(4)
K(1)-S(5)	3.322(6)	Bi(5)-S(7) x 2	2.900(3)
K(1)-S(8)	3.439(7)		

Tabl

Si3-

Si1-

Si3-

Si1-

Si1-

Si5-

Si9-

Si9-

Si2-

Te1

Si2-

Te1

Te1

Si6-

Si2-

Te1

Si6-

Si6-

Si6-

Si5-

Si1-

Si6-E

Si2-E

Si4-E

Si6-E

Table 2-8. Selected Angles (deg) for $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$.

S(3)-Pb(1)-S(1)	88.18(9)	S(6)-Pb(4)-Te(10)	95.4(2)
S(1)-Pb(1)-S(1)	89.71(10)	S(2)-Pb(4)-Te(10)	178.2(2)
S(3)-Pb(1)-S(8)	90.61(9)	S(6)-Pb(4)-Te(10)	88.69(7)
S(1)-Pb(1)-S(8)	91.01(8)	S(2)-Pb(4)-Te(10)	89.0(2)
S(1)-Pb(1)-S(8)	178.57(10)	Te(10)-Pb(4)-Te(10)	89.72(8)
S(8)-Pb(1)-S(8)	88.26(11)	S(6)-Pb(4)-Te(10)	174.6(3)
		Te(10)-Pb(4)-Te(10)	89.68(18)
S(9)-Pb(2)-S(9)	90.66(11)	S(9)-Bi(1)-S(9)	86.8(2)
S(9)-Pb(2)-S(5)	75.89(8)	S(9)-Bi(1)-S(8)	84.53(19)
S(2)-Pb(3)-Te(10)	95.7(2)	S(9)-Bi(2)-S(4)	89.59(10)
Te(10)-Pb(3)-Te(10)	95.2(2)	S(4)-Bi(2)-S(4)	91.92(11)
S(2)-Pb(3)-S(6)	86.75(10)	S(9)-Bi(2)-S(8)	94.80(10)
Te(10)-Pb(3)-S(6)	175.2(3)	S(4)-Bi(2)-S(8)	175.49(11)
Te(10)-Pb(3)-S(6)	88.65(7)	S(4)-Bi(2)-S(8)	89.18(8)
S(6)-Pb(3)-S(6)	87.4(2)	S(8)-Bi(2)-S(8)	89.39(11)
S(2)-Pb(3)-Te(10)	173.9(3)		
Te(10)-Pb(3)-Te(10)	88.39(10)	S(7)-Bi(3)-S(5)	90.16(9)
S(6)-Pb(3)-Te(10)	88.9(2)	S(5)-Bi(3)-S(5)	97.87(11)
		S(7)-Bi(3)-S(1)	89.87(9)
S(6)-Pb(4)-S(6)	92.48(19)	S(5)-Bi(3)-S(1)	89.04(8)
S(6)-Pb(4)-S(2)	85.88(10)		
S(5)-Bi(3)-S(1)	173.09(7)	S(2)-Bi(4)-S(2)	94.60(11)
S(1)-Bi(3)-S(1)	84.06(10)	S(6)-Bi(4)-S(4)	91.44(10)
		S(2)-Bi(4)-S(4)	175.26(8)
S(6)-Bi(4)-S(2)	91.58(9)		
S(2)-Bi(4)-S(4)	88.97(8)	S(2)-Bi(4)-S(5)	84.40(8)
S(4)-Bi(4)-S(4)	87.30(10)	S(4)-Bi(4)-S(5)	92.86(9)
S(6)-Bi(4)-S(5)	174.05(10)		

Table 2

Si3+Bi

Si3+Bu

Si3+Bi

Ta10+

Table 2-8. (cont'd)

S(3)-Bi(5)-S(3)	92.96(11)	S(3)-Bi(5)-S(7)	88.30(8)
S(3)-Bi(5)-Te(10)	94.43(8)	Te(10)-Bi(5)-S(7)	92.35(8)
S(3)-Bi(5)-S(1)	85.61(9)	S(1)-Bi(5)-S(7)	87.61(9)
Te(10)-Bi(5)-S(1)	179.94(9)	S(3)-Bi(5)-S(7)	172.99(10)
		S(7)-Bi(5)-S(7)	89.64(10)

Structure Description of $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$

The structure of this compound is very similar to the two previous one but considering only ionic interactions between the alkali and alkaline earth metals with chalcogenides the structure reduces to two dimensional structure having layers of NaCl-type and CdI_2-type fragments joined together. The alkali and alkaline earth metals occupy the sites in between these layers. The bond distances and selected angles are given in Table 2-11 and 2-12. The structural diagram down the b-axis is shown in Figure 2-8.

All the three crystallographic sites between the layers are mixed occupied by the alkali and alkaline earth metals. Sr(5) is mixed occupied with Na(5) with 79% Sr(5) and 21% Na(5), Sr(6) is mixed occupied with Na(6) with 96% Sr(6) and 4% Na(6) and Sr(7) is mixed occupied with Na(7) with 77% Sr(7) and 23% Na(7). The Bi_2Te_3-type fragment also has mixed occupation, by strontium and bismuth with one site containing only bismuth (i.e., Bi(2)). Bi(1) is mixed occupied with Sr(1) with 90% Bi(1) and 10% Sr(1), Bi(3) is mixed occupied with Sr(3) with 89% Bi(3) and 11% Sr(3) and Bi(4) is mixed occupied with Sr(4) with 94% Bi(4) and 6% Sr(4).

Bi(5) is the only atom to be present in a slightly distorted octahedral coordination where the Bi-Se distances range from 2.863(3) to 3.054(3). The remaining atoms Bi(1)/Sr(1), Bi(2), Bi(3)/Sr(1) and Bi(4)/Sr(1) are all present in a highly distorted octahedral coordination.

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Figure 2-7. Projection of the structure of $Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$ down the b-axis.

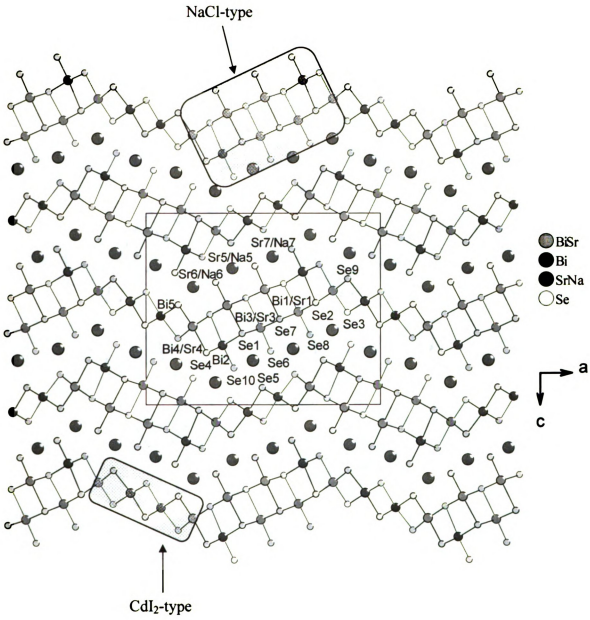


Figure 2-8. Polyhedral representation of $Na_{0.475}Sr_{2.798}Bi_{4.713}Se_{10}$ down the b-axis showing the connectivity of the MS_6 octahedra (M = Bi, Bi/Sr).

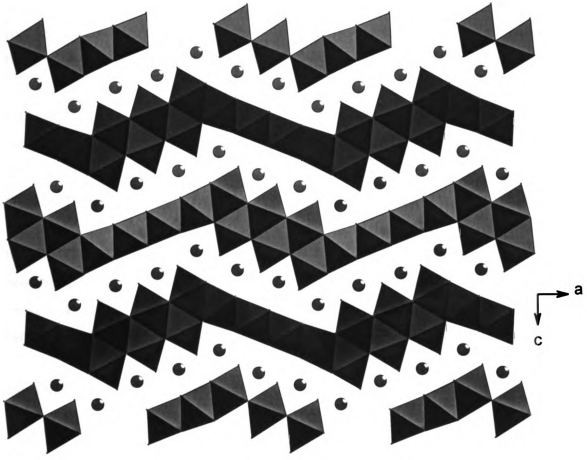


Table 2-9. Bond distances (Å) for $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$.

Bi(1)/Sr(1)-Se(8)	2.715(4)	Bi(5)-Se(9)	2.971(4)
Bi(1)/Sr(1)-Se(1)	3.371(1)	Bi(5)-Se(5) x 2	2.863(3)
Bi(1)/Sr(1)-Se(2) x 2	2.968(3)	Bi(5)-Se(3) x 2	3.054(3)
Bi(1)/Sr(1)-Se(7) x 2	2.977(3)		
		Sr(5)/Na(5)-Se(8) x 2	3.139(4)
Bi(2)-Se(10)	2.682(4)	Sr(5)/Na(5)-Se(6) x 2	3.153(4)
Bi(2)-Se(2)	3.503(1)	Sr(5)/Na(5)-Se(9) x 2	3.438(5)
Bi(2)-Se(4) x 2	2.825(3)	Sr(5)/Na(5)-Se(4)	3.400(6)
Bi(2)-Se(1) x 2	3.196(3)	Sr(5)/Na(5)-Se(7)	3.410(7)
Bi(3)/Sr(3)-Se(6)	2.691(4)	Sr(6)/Na(6)-Se(8) x 2	3.187(4)
Bi(3)/Sr(3)-Se(7)	3.518(1)	Sr(6)/Na(6)-Se(3) x 2	3.241(4)
Bi(3)/Sr(3)-Se(1) x 2	2.931(3)	Sr(6)/Na(6)-Se(10) x 2	3.245(4)
Bi(3)/Sr(3)-Se(7) x 2	3.063(3)	Sr(6)/Na(6)-Se(4)	3.293(6)
		Sr(6)/Na(6)-Se(2)	3.408(6)
Bi(4)/Sr(4)-Se(3)	2.761(4)		
Bi(4)/Sr(4)-Se(4)	3.113(4)	Sr(7)/Na(7)-Se(5)	3.002(6)
Bi(4)/Sr(4)-Se(9) x 2	2.918(3)	Sr(7)/Na(7)-Se(6) x 2	3.010(4)
Bi(4)/Sr(4)-Se(2) x 2	3.063(3)	Sr(7)/Na(7)-Se(10) x 2	3.035(4)
		Sr(7)/Na(7)-Se(1)	3.065(6)
Bi(5)-Se(5)	2.958(5)		

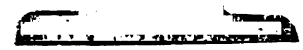
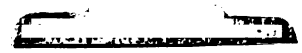


Table 2-10. Selected Angles (deg) for $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$.

Se(8)-Bi(1)-Se(2)	90.96(10)	Se(7)-Bi(3)-Se(7)	87.80(12)
Se(2)-Bi(1)-Se(2)	91.36(12)	Se(3)-Bi(4)-Se(9)	94.35(11)
Se(2)-Bi(1)-Se(7)	175.42(12)	Se(9)-Bi(4)-Se(9)	93.42(13)
Se(2)-Bi(1)-Se(7)	88.64(9)	Se(3)-Bi(4)-Se(2)	88.89(11)
Se(8)-Bi(1)-Se(7)	93.62(11)	Se(9)-Bi(4)-Se(2)	89.30(8)
Se(7)-Bi(1)-Se(7)	91.00(12)	Se(9)-Bi(4)-Se(2)	175.59(11)
		Se(2)-Bi(4)-Se(2)	87.78(11)
Se(10)-Bi(2)-Se(4)	90.88(10)	Se(3)-Bi(4)-Se(4)	174.43(11)
Se(4)-Bi(2)-Se(4)	97.48(13)	Se(9)-Bi(4)-Se(4)	81.86(10)
Se(4)-Bi(2)-Se(1)	89.42(9)	Se(2)-Bi(4)-Se(4)	95.11(10)
Se(10)-Bi(2)-Se(1)	94.06(10)		
Se(4)-Bi(2)-Se(1)	171.45(9)	Se(5)-Bi(5)-Se(5)	95.75(13)
Se(1)-Bi(2)-Se(1)	83.27(10)	Se(5)-Bi(5)-Se(5)	90.21(11)
		Se(5)-Bi(5)-Se(9)	94.30(11)
Se(6)-Bi(3)-Se(1)	94.38(10)	Se(5)-Bi(5)-Se(9)	173.26(12)
Se(1)-Bi(3)-Se(1)	92.86(12)	Se(5)-Bi(5)-Se(3)	87.65(10)
Se(6)-Bi(3)-Se(7)	90.00(11)	Se(5)-Bi(5)-Se(3)	88.02(9)
Se(1)-Bi(3)-Se(7)	174.85(12)	Se(5)-Bi(5)-Se(3)	175.68(10)
Se(1)-Bi(3)-Se(7)	89.49(9)	Se(9)-Bi(5)-Se(3)	87.50(10)
Se(6)-Bi(3)-Se(7)	90.00(11)	Se(3)-Bi(5)-Se(3)	88.13(12)



E. Conclusion

The synthesis and structure of three new quaternary bismuth chalcogenides have been presented. Variations in the cosalite structure type are observed whereby replacing the softer Pb^{2+} with harder Sr^{2+} collapses the three dimensional character of the cosalite structure to a layered type. The charge-transport properties of $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$ and $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$ need to be investigated. Also it would be interesting to do some ion-exchange reactions with $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$.

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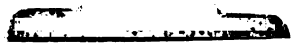

CHAPTER 3

Variation in the $K_{2.5}Bi_{8.5}Se_{14}$ structure type: Synthesis and Structure of $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ and $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$.

A. Introduction

Bismuth compounds constitute a great part of the sulfosalt family.[1] These naturally occurring minerals present a remarkable structural diversity and complexity. These characteristics are also found in the great number of ternary[2-8] and quaternary[8-12] bismuth chalcogenides synthesized during the last decade. The rich compositional and structural variety makes them some of the most adaptable and versatile systems in solid state chemistry. Bismuth atoms both in naturally occurring sulfosalts and in the above mentioned compounds show an amazing flexibility in bonding. Although they usually exhibit a distorted octahedral geometry, however they also adopt variety of other coordination ranging from trigonal pyramidal in β-$CsBiS_2$[3], to square pyramidal in $Rb_2Bi_8Se_{13}$[13], to trigonal prismatic in $ALn_{1\pm x}Bi_{4\pm x}S_8$ (A = K, Rb; Ln = La, Ce, Pr, Nd)[9] and sometimes the coordination number can range upto nine.[2-12] These high-coordination sites (> 6) serves to connect with each other the several NaCl-, Bi_2Te_3 and CdI_2-type blocks, formed by the BiQ_6 (Q = chalcogen) octahedra when combined together by sharing edges. These above mentioned blocks come in different sizes creating even more structural possibilities. Another reason for the structural heterogeneity is the mixed

occupancy that bismuth atoms can display with a variety of similar sized ions such as alkali[4a,14] or alkaline earth metals[8], Pb[8, 11, 15], Sn[8, 12, 15], or lanthanides.[9]

Examples of the above mentioned structural diversity and complexity can be found in compounds reported earlier from our group such as KBi_3S_5,[3] $KBi_{6.33}S_{10}$,[4a] α-,β-$K_2Bi_8Se_{13}$,[2, 14] $K_{2.5}Bi_{8.5}Se_{14}$ [14], $KPb_2Bi_5S_{10}$,[16] $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$,[16] $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$[16] and many more. Our idea to move from ternary systems to quaternary system was that the latter would give a much more complex structure thereby strongly scattering acoustic lattice phonons carrying heat and thus lowering the thermal conductivity. This would lead to better thermoelectric materials.

We report here the synthesis and structural characterization of $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ and $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ belonging to the $K_{2.5}Bi_{8.5}Se_{14}$ structure type.

B. Experimental Section

Reagents: Chemicals were used as obtained: (i) bismuth chunks, 99.999% purity, Cerac, Milwaukee, WI. (ii) selenium shots 99.999% purity, Cerac, Milwaukee, WI. (iii) tellurium chunks 99.999% purity, Cerac, Milwaukee, WI. (iv) lead metal, Cerac, Milwaukee, WI. (v) rubidium metal, 99.8% purity, Alfa Aesar, Ward Hill, MA. (vi) sodium metal, Aldrich, Milwaukee, WI. (vii) barium selenide powder 99.5% purity, -20 mesh, Cerac, Milwaukee, WI. A_2Se (A = Na, Rb) was prepared by a stoichiometric reaction of alkali metal and selenium shots in liquid ammonia.

Synthesis: All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. 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_2Se_3: A mixture of 6.383g (0.045 mol) of bismuth and 3.617g (0.068 mol) of selenium was transferred into a 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 800°C in 10 hours and isothermed there for 10 hours and then cooled down to 50°C in 10 hours. The product was used for further reactions.

PbTe: A mixture of 12.378g (0.060 mol) of lead and 7.622g (0.060 mol) of tellurium was transferred into a 13mm carbon coated quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 1100°C in 8 hours, held there for 12 hours and then cooled down to 50°C in 24 hours. The product was used for further reactions.

$Rb_2Bi_8Se_{13}$: A mixture of 0.871g (3.50 mmol) of rubidium selenide and 9.129g (0.140 mol) of bismuth selenide was transferred into a 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). 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 the molten mixture was allowed to solidify. The procedure was repeated two more times to ensure homogeneity. The product was used for further reactions.

$Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$: A mixture of 0.4g (0.140 mmol) of $Rb_2Bi_8Se_{13}$ and 0.047g (0.140 mmol) of lead telluride in the ratio 1:1 was transferred into a 9mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 850°C in 10 hours and isothermed there for 48 hours and then cooled slowly to 350°C in

96 hours and finally to 50°C in 3 hours. The product consisted of silvery-gray needle like crystals. A quantitative analysis by Energy Dispersive Spectroscopy (EDS) using a Scanning Electron Microscope (SEM) was performed on several of these crystals which gave an approximate composition of "$Rb_{1.67}Pb_{1.43}Bi_{7.89}Se_{13.31}Te_{0.70}$".

$Na_xBa_{5-2x}Bi_{6+x}Se_{14}$: A mixture of 0.03g (0.240 mmol) of Na_2Se, 0.286g (1.32 mmol) of barium selenide and 0.472g (0.720 mmol) of bismuth selenide in the ratio 0.5:2.79:3.69 were transferred into a graphite tube which was placed in a 13mm quartz tube, which was then flame sealed under vacuum (~10^{-4} Torr). The tube was heated to 800°C in 24 hours and isothermed there for 24 hours and then cooled 50°C in 25 hours. The product consisted of silvery-gray needle like crystals. Energy Dispersive Spectroscopy (EDS) on several of these crystals gave an approximate composition of "$Na_1Ba_{5.53}Bi_{7.42}Se_{15.47}$".

C. Physical Measurements

Energy Dispersive Spectroscopy: Quantitative microprobe analyses of the compound were performed with a JEOL JSM-6400V Scanning Electron Microscope equipped with a Tracor Northern Energy Dispersive Spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 30 seconds accumulation time.

Differential Thermal Analysis: Differential Thermal Analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50 thermal analyzer. Ground single crystals (30-40 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 1000°C at 10°C/min, then isothermed for 1 minute followed by cooling at 10°C/minute. The reported DTA temperature is the peak temperature. After DTA, the samples were examined with powder X-ray diffraction. Reproducibility of results was checked with multiple heating / cooling cycles.

Charge Transport Measurements: Thermopower was measured using an instrument from MMR Technologies, Inc., Mountain View, CA. The sample and the reference (constantan wire) were mounted on a Seebeck stage with conductive silver paste. The temperature gradient across the sample was built up by a computer controlled heater which is controlled by the MMR Programmable Seebeck Controller SB100. The Seebeck stage was attached to the MMR stage, which provides a given stable temperature for the measurement. The MMR K20A Programmable Temperature Controller controls this MMR stage. The voltage across the sample resulting from the temperature gradient was measured.

Room temperature electrical conductivity was measured by a four probe technique using a Keithley 236 Source Measure Unit. 0.003 inch copper wires were used for the current and voltage electrodes. Measurements of the pellet cross-sectional area and voltage probe separation were made with a calibrated binocular microscope.

Powder X-ray diffraction: The compounds were examined by X-ray powder diffraction for identification and to assess phase purity. Powder patterns were obtained using a CPS 120 INEL diffractometer using Cu-Kα radiation and 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 CERIUS^2 software.[17]

Single-Crystal X-ray Crystallography: Intensity data were collected at 293 K on a Bruker SMART Platform CCD diffractometer using graphite monochromatized Mo K_α (λ = 0.71073Å) radiation over a full sphere of reciprocal space. Individual frames were measured using 0.3° steps in ω. The SMART software was used for data acquisition and SAINT[18] for data extraction and reduction. The absorption correction was done with SADABS[18], and the structure solution was done with the SHELXTL[18] package of crystallographic programs.

$Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$: A full sphere of data was collected with an exposure time of 45 seconds per frame. The crystallographic data is shown in Table 3-1. Twenty five crystallographically independent positions were found to sit on a crystallographic mirror plane. Pb1 & Rb2, Pb2, Rb3 & Pb3, Te2 & Se2 and Te14 & Se14 were all found to be disordered over a single site. After anisotropic refinement final R values, R1 = 5.17% and wR2 = 11.75%. The fractional coordinates and isotropic displacement parameters along with occupancies for disordered atoms are shown in table 3-2.

$Na_1Ba_{2.79}Bi_{7.37}Se_{14}$: A hemisphere of data was collected with an exposure time of 30 seconds per frame. The crystallographic data is shown in Table 3-1. Twenty seven crystallographically independent positions were found to sit on a crystallographic mirror plane. Bi6 & Na6, Bi7 &Na7, Bi8 & Na8 and Se15, Se16 & Se17 were all found to be disordered over a single site. After anisotropic refinement final R values, R1 = 5.29% and wR2 = 10.78%. The fractional coordinates and isotropic displacement parameters along with occupancies for disordered atoms are shown in table 3-3.

Table 3-1. Crystallographic Data for $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ and $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$.

Chemical formula	$Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$	$Na_1Ba_{2.79}Bi_{7.37}Se_{14}$
Formula weight	798.10	3554.62
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	
Space group	P2(1)/m	P2(1)/m
a, Å	17.610(11)	17.407(6)
b, Å	4.213(3)	4.3165(15)
c, Å	21.398(13)	21.747(7)
α, deg	90	90
β, deg	109.348(9)	98.768(6)
γ, deg	90	90
V, Å3	1497.9(16)	1614.9(10)
Z	8	2
ρ_{calcd}, g/cm^3	7.078	7.310
μ, mm^{-1}	73.827	64.326
Total reflections	16731	14160
Unique reflections	3890	4245
$R_{(int)}$	0.0860	0.1181
No. of parameters	151	171
Goodness-of-fit on F^2	1.009	1.294
Refinement method	Full-matrix least-squares on F^2	
R1[a]	0.0517	0.0529
wR2[b]	0.1175	0.1078

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

Table 3-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$

	x	y	z	U(eq)	Occ
Rb(1)	4216(2)	2500	3546(2)	29(1)	
Bi(1)	5215(1)	2500	913(1)	21(1)	
Bi(2)	7203(1)	-2500	632(1)	28(1)	
Bi(3)	3367(1)	-2500	1387(1)	24(1)	
Bi(4)	8913(1)	-12500	4290(1)	21(1)	
Bi(5)	8756(1)	-7500	6155(1)	21(1)	
Bi(6)	9180(1)	-7500	2701(1)	24(1)	
Bi(7)	9083(1)	-7500	135(1)	23(1)	
Bi(8)	6659(1)	-12500	4816(1)	21(1)	
Pb(1)	6679(2)	-17500	3101(2)	33(1)	0.69871
Rb(2)	6617(7)	-17500	2855(8)	13(2)	0.30129
Pb(2)	1663(5)	-7500	2104(9)	34(2)	0.40436
Rb(3)	1375(7)	-7500	1933(6)	12(2)	0.43145
Pb(3)	1645(9)	-7500	1895(17)	31(5)	0.18427
Se(1)	8305(2)	-7500	1262(2)	22(1)	
Te(2)	4512(2)	2500	1958(2)	22(1)	0.08409
Se(2)	4512(2)	2500	1958(2)	22(1)	0.91591
Se(3)	7872(2)	-7500	4486(2)	21(1)	
Se(4)	9716(2)	-7500	7457(2)	21(1)	
Se(5)	10173(2)	-12500	842(2)	22(1)	
Se(6)	8124(2)	-12500	2952(2)	21(1)	
Se(7)	4210(2)	-12500	4916(2)	19(1)	
Se(8)	7811(2)	-12500	6372(2)	22(1)	
Se(9)	4010(2)	-2500	150(2)	19(1)	
Se(10)	10068(2)	-17500	4147(2)	17(1)	
Se(11)	7896(2)	-2500	-595(2)	28(1)	
Se(12)	2833(2)	-2500	2435(2)	25(1)	
Se(13)	5794(2)	-12500	3480(2)	29(1)	

Table 3-2. (cont'd)

	x	y	z	U(eq)	Occ
Te(14)	6333(2)	-2500	1600(2)	21(1)	0.20309
Se(14)	6333(2)	-2500	1600(2)	21(1)	0.79691

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

Table 3-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Na_1Ba_{2.79}Bi_{7.37}Se_{14}$.

	x	y	z	U(eq)	Occ.
Bi(1)	3225(1)	7500	4771(1)	12(1)	
Bi(2)	4553(1)	-2500	11723(1)	17(1)	
Bi(3)	1894(1)	2500	6034(1)	16(1)	
Bi(4)	696(1)	-2500	14326(1)	20(1)	
Bi(5)	3929(1)	2500	9695(1)	25(1)	
Bi(6)	2483(1)	2500	11117(1)	22(1)	0.68214
Na(6)	2483(1)	2500	11117(1)	22(1)	0.31786
Bi(7)	-503(1)	2500	12842(1)	19(1)	0.53889
Na(7)	-503(1)	2500	12842(1)	19(1)	0.46111
Bi(8)	1809(2)	7500	9440(1)	40(1)	0.70179
Na(8)	1809(2)	7500	9440(1)	40(1)	0.29821
Bi(9)	362(1)	-2500	10936(1)	42(1)	
Ba(1)	2159(1)	2500	12982(1)	14(1)	
Ba(2)	3153(1)	7500	7776(1)	13(1)	
Ba(3)	5043(1)	7500	6315(1)	14(1)	
Se(1)	3262(2)	-2500	10420(2)	18(1)	
Se(2)	2962(2)	7500	6200(2)	15(1)	
Se(3)	1884(2)	2500	4510(2)	15(1)	
Se(4)	5360(2)	-7500	10983(2)	20(1)	
Se(5)	3742(2)	-7500	12192(2)	15(1)	
Se(6)	2641(2)	2500	8826(2)	18(1)	
Se(7)	1824(2)	-2500	11766(2)	26(1)	
Se(8)	4274(2)	2500	5112(2)	13(1)	
Se(9)	1734(2)	2500	7265(2)	16(1)	
Se(10)	3500(2)	7500	3572(2)	12(1)	
Se(11)	5663(2)	-2500	12737(2)	11(1)	
Se(12)	1075(2)	2500	10143(2)	21(1)	
Se(13)	720(2)	-2500	13069(2)	18(1)	

Table 3-3. (cont'd.)

	x	y	z	U(eq)	Occ
Se(14)	531(2)	-2500	5778(2)	14(1)	
Se(15)	-399(16)	-7500	11481(6)	47(6)	0.68043
Se(16)	-606(18)	-6200(110)	11513(13)	24(10)	0.24310
Se(17)	-70(50)	-7500	11540(20)	45(17)	0.16378

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

D. Results and discussion

Structure Description of $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$

The compound is isostructural to $K_{2.5}Bi_{8.5}Se_{14}$ [1] and possesses a complex 3D anionic framework which is very similar to that of β- $K_2Bi_8Se_{13}$[1] (see Figure 3-1.). The main difference being the presence of only NaCl- and Bi_2Te_3-type fragments in case of $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ whereas the presence of additional CdI_2-type fragments in case of β- $K_2Bi_8Se_{13}$. These different types of fragments are common in other multinary bismuth chalcogenides such as $Cs_3Bi_7Se_{12}$ [19] and $KBi_{6.33}S_{10}$.[4a] The Bi_2Te_3-type fragments in $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ are arranged side by side to form layers. The NaCl-type fragments connect these layers which run perpendicular to the c-axis, to build a three dimensional framework with tunnels which are filled by the alkali (Rb^+) cations. The NaCl-type fragments in $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ are three bismuth octahedra wide whereas the Bi_2Te_3-type fragments are five bismuth octahedra wide. The latter is an important structural difference with the β- $K_2Bi_8Se_{13}$ structure where these fragments are three Bi octahedra wide.

Among the Rb^+ cations in $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$, Rb(1) is fully occupied by Rb^+ while Rb(2) is disordered with Pb(1) and Rb(3) is disordered with Pb(2) and Pb(3) (see figure 3-1). The Rb(2) site contains 70% Pb and 30% Rb while the Rb(3) site contains 43% of Rb, 40% of Pb(2) and 18% of Pb(3). There are two eight coordinate sites. One is occupied by Pb(1) and Rb(2) in a distorted bicapped trigonal prismatic coordination by Se(6), Se(6)′, Se(13), Se(13)′, Te14/Se(14), Te(14)/Se(14)′, Se(3) and Te(2)/Se(2) (the atoms primed outside parentheses are the symmetrically equivalent ones). Pb(1) is disordered with Rb(2) at 0.499(1)Å. The other site has Rb(3), Pb(2) and Pb(3)

atoms in a similar kind of coordination. The prism is defined by Se(4), Se(5), Se(12) and their symmetry equivalent atoms while the capping atoms are Se(8) and Se(11). Here Rb(3) is disordered with Pb(2) and Pb(3) at a distance of 0.518(3) and 0.51(2)Å respectively. These high-coordinate sites serve to stitch together the layers formed by Bi_2Te_3-type fragments.

Two of the chalcogenide sites in the Bi_2Te_3-type fragments close to Pb(1)/Rb(1) disordered site has mixed occupancy. The Se(2) site contains 92% of Se(2) and 8% of Te(2). The Se(14) site contains 80% of Se(14) and 20% of Te(14). Apart from Bi(6) all the bismuth atoms in both types of fragments are present in a highly distorted octahedral coordination with a short bond trans to a long bond. In contrast Bi(6) is in a slightly distorted octahedral coordination where the Bi-Se distances range from 2.953(4) to 2.974(3) (see Table 3-4. & 3-5.). This site also serves as the second joining point for the two types of fragments.

Figure 3-1. Projection of the structure of $Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$ down the b-axis.

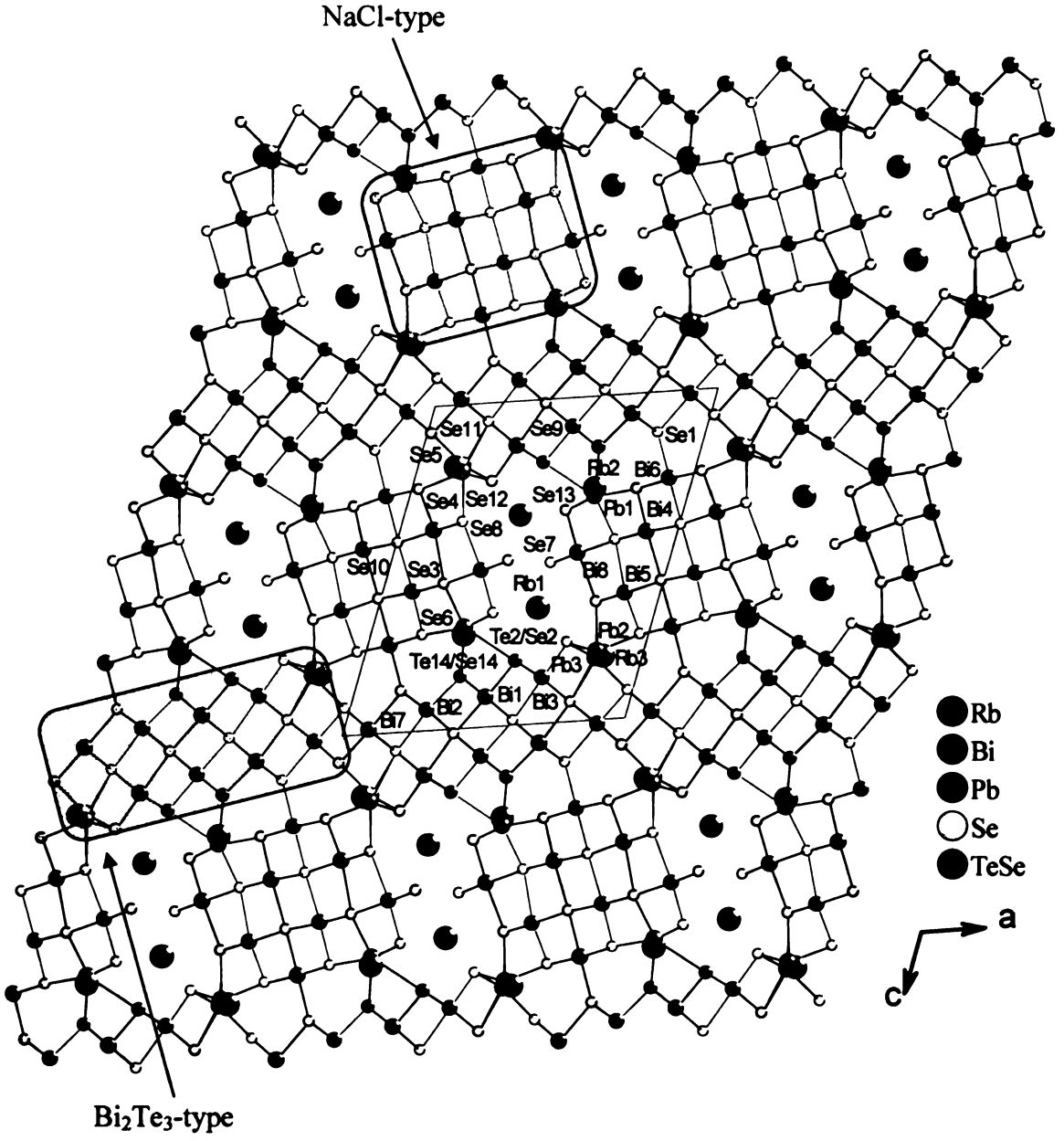

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Table 3-4. Bond distances (Å) for $Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$.

Rb(1)-Se(12)	3.491(4)	Bi(2)-Se(11)	3.241(5)
Rb(1)-Se(13)	3.527(4)		
Rb(1)-Se(7)	3.532(5)	Bi(3)-Te(2)/Se(2) x 2	2.892(3)
Rb(1)-Te(2)/Se(2)	3.603(5)	Bi(3)-Se(11) x 2	3.124(3)
Rb(1)-Se(7)	3.613(4)	Bi(3)-Se(9)	3.206(4)
Rb(1)-Se(8)	3.632(5)	Bi(3)-Se(12)	2.702(4)
Rb(2)-Se(13)	3.099(10)	Bi(4)-Se(3) x 2	2.913(3)
Rb(2)-Te(14)/Se(14)	3.319(13)	Bi(4)-Se(10) x 2	3.013(3)
Rb(2)-Se(6)	3.341(9)	Bi(4)-Se(6)	2.736(4)
Rb(2)-Se(3)	3.457(16)	Bi(4)-Se(10)	3.231(4)
Rb(2)-Te(2)/Se(2)	3.565(12)		
		Bi(5)-Se(8) x 2	2.817(3)
Rb(3)-Pb(3)	0.51(2)	Bi(5)-Se(10) x 2	3.167(3)
Rb(3)-Pb(2)	0.518(3)	Bi(5)-Se(4)	2.740(4)
Rb(3)-Se(12) x 2	3.219(10)	Bi(5)-Se(3)	3.389(1)
Rb(3)-Se(5) x 2	3.331(10)		
Rb(3)-Se(4) x 2	3.390(10)	Bi(6)-Se(4) x 2	2.961(3)
Rb(3)-Se(8)	3.428(13)	Bi(6)-Se(6) x 2	2.974(3)
Rb(3)-Se(11)	3.505(13)	Bi(6)-Se(1)	2.953(4)
		Bi(6)-Se(10)	2.968(4)
Bi(1)-Te(14)/Se(14) x 2	2.925(3)		
Bi(1)-Se(9) x 2	3.051(3)	Bi(7)-Se(5) x 2	2.914(3)
Bi(1)-Te(2)/Se(2)	2.893(4)	Bi(7)-Se(11) x 2	3.013(3)
Bi(1)-Se(9)	3.016(4)	Bi(7)-Se(1)	3.142(4)
		Bi(7)-Se(5)	2.811(4)
Bi(2)-Se(1) x 2	2.879(3)		
Bi(2)-Se(9) x 2	3.071(3)	Bi(8)-Se(7) x 2	2.773(2)
Bi(2)-Te(14)/Se(14)	2.955(4)	Bi(8)-Se(3) x 2	3.240(3)

Table 3-4. (Cont'd)

Bi(8)-Se(13)	2.759(4)	Pb(2)-Se(12) x 2	2.867(6)
Bi(8)-Se(8)	3.275(1)	Pb(2)-Se(8)	3.079(18)
Pb(1)-Se(13) x 2	2.892(3)	Pb(3)-Pb(2)	0.439(1)
Pb(1)-Se(6) x 2	3.398(2)	Pb(3)-Se(12) x 2	2.923(11)
Pb(1)-Se(3)	3.012(5)	Pb(3)-Se(11)	3.14(4)
Pb(1)-Rb(2)	0.499(1)		

Table 3-5. Selected Angles (deg) for $Rb_{1.73}Pb_{1.29}Bi_8Se_{13.42}Te_{0.59}$.

Te(2)-Bi(1)-Te(14)	90.08(9)	Te(2)-Bi(3)-Se(9)	87.76(9)
Te(14)-Bi(1)-Te(14)	92.13(10)	Se(11)-Bi(3)-Se(9)	86.26(10)
Te(2)-Bi(1)-Se(9)	178.57(10)		
Te(14)-Bi(1)-Se(9)	88.93(9)	Se(6)-Bi(4)-Se(3)	91.46(10)
Te(2)-Bi(1)-Se(9)	90.78(9)	Se(3)-Bi(4)-Se(3)	92.63(11)
Te(14)-Bi(1)-Se(9)	90.27(7)	Se(6)-Bi(4)-Se(10)	91.12(9)
Te(2)-Bi(1)-Se(9)	90.78(9)	Se(3)-Bi(4)-Se(10)	176.76(10)
Te(14)-Bi(1)-Se(9)	177.45(8)	Se(3)-Bi(4)-Se(10)	89.27(8)
Se(9)-Bi(1)-Se(9)	90.26(9)	Se(10)-Bi(4)-Se(10)	88.71(10)
Se(9)-Bi(1)-Se(9)	87.32(10)	Se(6)-Bi(4)-Se(10)	176.96(10)
		Se(3)-Bi(4)-Se(10)	90.64(9)
Se(1)-Bi(2)-Se(1)	94.05(12)	Se(10)-Bi(4)-Se(10)	86.71(9)
Se(1)-Bi(2)-Te(14)	95.60(9)		
Se(1)-Bi(2)-Se(9)	175.08(10)	Se(4)-Bi(5)-Se(8)	91.78(10)
Se(1)-Bi(2)-Se(9)	89.58(8)	Se(8)-Bi(5)-Se(8)	96.79(11)
Te(14)-Bi(2)-Se(9)	87.33(9)	Se(4)-Bi(5)-Se(10)	88.98(9)
Se(9)-Bi(2)-Se(9)	86.61(10)	Se(8)-Bi(5)-Se(10)	89.91(8)
Se(1)-Bi(2)-Se(11)	90.15(9)	Se(8)-Bi(5)-Se(10)	173.23(7)
Te(14)-Bi(2)-Se(11)	171.55(10)	Se(8)-Bi(5)-Se(10)	173.23(7)
Se(9)-Bi(2)-Se(11)	86.52(9)	Se(10)-Bi(5)-Se(10)	83.37(9)
Se(12)-Bi(3)-Te(2)	92.02(10)	Se(1)-Bi(6)-Se(4)	90.91(9)
Te(2)-Bi(3)-Se(2)	93.51(12)	Se(4)-Bi(6)-Se(4)	90.70(11)
Se(12)-Bi(3)-Se(11)	93.98(10)	Se(1)-Bi(6)-Se(10)	179.69(10)
Te(2)-Bi(3)-Se(11)	172.65(11)	Se(4)-Bi(6)-Se(10)	88.87(9)
Te(2)-Bi(3)-Se(11)	90.54(8)	Se(1)-Bi(6)-Se(6)	92.70(9)
Se(12)-Bi(3)-Se(11)	93.98(10)	Se(4)-Bi(6)-Se(6)	176.39(12)
Se(11)-Bi(3)-Se(11)	84.80(10)	Se(4)-Bi(6)-Se(6)	89.43(8)
Se(12)-Bi(3)-Se(9)	179.68(11)	Se(1)-Bi(6)-Se(6)	92.70(9)

Table 3-5. (Cont'd)

Se(10)-Bi(6)-Se(6)	87.52(9)	Se(13)-Bi(8)-Se(3)	87.21(10)
Se(6)-Bi(6)-Se(6)	90.20(11)	Se(7)-Bi(8)-Se(3)	171.04(7)
		Se(7)-Bi(8)-Se(3)	90.00(8)
Se(5)-Bi(7)-Se(5)	89.82(10)	Se(3)-Bi(8)-Se(3)	81.11(9)
Se(5)-Bi(7)-Se(5)	92.59(12)		
Se(5)-Bi(7)-Se(11)	91.65(10)	Se(13)-Pb(1)-Se(13)	93.50(14)
Se(5)-Bi(7)-Se(11)	177.58(9)	Se(13)-Pb(1)-Se(3)	89.35(13)
Se(5)-Bi(7)-Se(11)	89.33(8)	Rb(3)-Pb(2)-Se(12)	129.1(7)
Se(11)-Bi(7)-Se(11)	88.71(11)	Se(12)-Pb(2)-Se(12)	94.6(3)
Se(5)-Bi(7)-Se(1)	178.16(11)	Rb(3)-Pb(2)-Se(8)	128.9(18)
Se(5)-Bi(7)-Se(1)	88.90(9)	Se(12)-Pb(2)-Se(8)	78.4(4)
Se(11)-Bi(7)-Se(1)	89.67(10)		
		Se(12)-Pb(3)-Se(12)	92.2(5)
Se(13)-Bi(8)-Se(7)	93.52(10)	Se(12)-Pb(3)-Se(11)	89.4(7)
Se(7)-Bi(8)-Se(7)	98.86(11)		

Structure Description of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$

The structure of this compound is very similar to $Rb_xPb_{5-2x}Bi_{6+x}Se_{14-y}Te_y$ structure. In the previous compound lead replaces the bismuth atoms in the high-coordinate sites. In $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ moving from lead to barium the trend remains the same but the bonding becomes more ionic. Barium too, replaces the high-coordinate bismuth sites but due to its more ionic nature the resultant structure is different from the previous one. Here too, only NaCl- and Bi_2Te_3-type fragments exist and the former fragment is three bismuth octahedra wide while the latter is five bismuth octahedra wide which is a point of structural difference with the β-$K_2Bi_8Se_{13}$ structure. The NaCl-type fragments connect the layers formed by Bi_2Te_3-type fragments to generate a three dimensional framework with tunnels which are filled by the alkaline earth (Ba^{2+}) cations.

Among the alkaline earth (Ba^{2+}) cations, Ba(1) and Ba(2) occupy the bismuth high-coordinate sites while Ba(3) occupies the tunnels (see figure 3-2). All these three sites are fully occupied. Ba(1,2) is present in a bicapped trigonal prism like coordination with eight Se atoms in the range between 3.293(3) – 3.464(4)Å for Ba(1) and between 3.295(3) – 3.443(5)Å for Ba(2). The coordination environment of Ba(3) is a little different and can be described as a distorted tricapped trigonal prism. The prism is defined by Se(8), Se(10), Se(11) and their symmetry-equivalent atoms, while the capping atoms are Se(2), Se(5) and Se(8). The alkali (Na^+) cations have mixed occupancy over three sites with Bi(6, 7, 8). The Bi(6) site contains 68% of Bi and 32% of Na, the Bi(7) site contains 54% of Bi and 46% of Na and the Bi(8) site contains 70% of Bi and 30% of Na. The Bi(7) mixed site is present in the NaCl fragment whereas the other two mixed sites are present in the Bi_2Te_3 fragment. This disorder can be attributed to very similar

ionic sizes of Na^+ and Bi^{3+} in octahedral coordination (r_{Na^+} = 1.16Å, $r_{Bi^{3+}}$ = 1.17Å).[20] Bi(1-5) are present in a highly distorted octahedral coordination with a short bond trans to a long bond. The other interesting feature of this structure is the disordered selenium site containing three selenium atoms, Se(15), Se(16) and Se(17) which also makes up the coordination sphere for the mixed site of Bi(7)/Na(7) and Bi(8)/Na(8). For bond lengths and selected angles see Table 3-6. & 3-7.

Thermal Analysis of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$

Differential thermal analysis was performed on pure $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ to ascertain its thermal behavior. At the end of two heating cycles the compound was checked for decomposition by taking its powder X-ray diffraction pattern. $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ show an endothermic (melting) peak at 819°C and on cooling shows an exothermic (recrystallization) peak at 788°C (see Figure 3-3.). The powder pattern of the compound after DTA indicated no decomposition.

Charge Transport Measurement of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$

Thermoelectric power measurements were carried on polycrystalline oriented ingots (grown by Bridgman technique) [21] of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$. It is a n-type conductor and at room temperature the thermopower has a value of -24.22 μV/K. It shows a linear trend till 400 K. (See Figure 3-4.).

Electrical conductivity measurements were carried on polycrystalline oriented ingots along the needle axis and at room temperature value of 183.61 S/cm was obtained.

Figure 3-2. Projection of the structure of $Na_1Ba_{2.79}Bi_{7.37}Se_{14}$ down the b-axis.

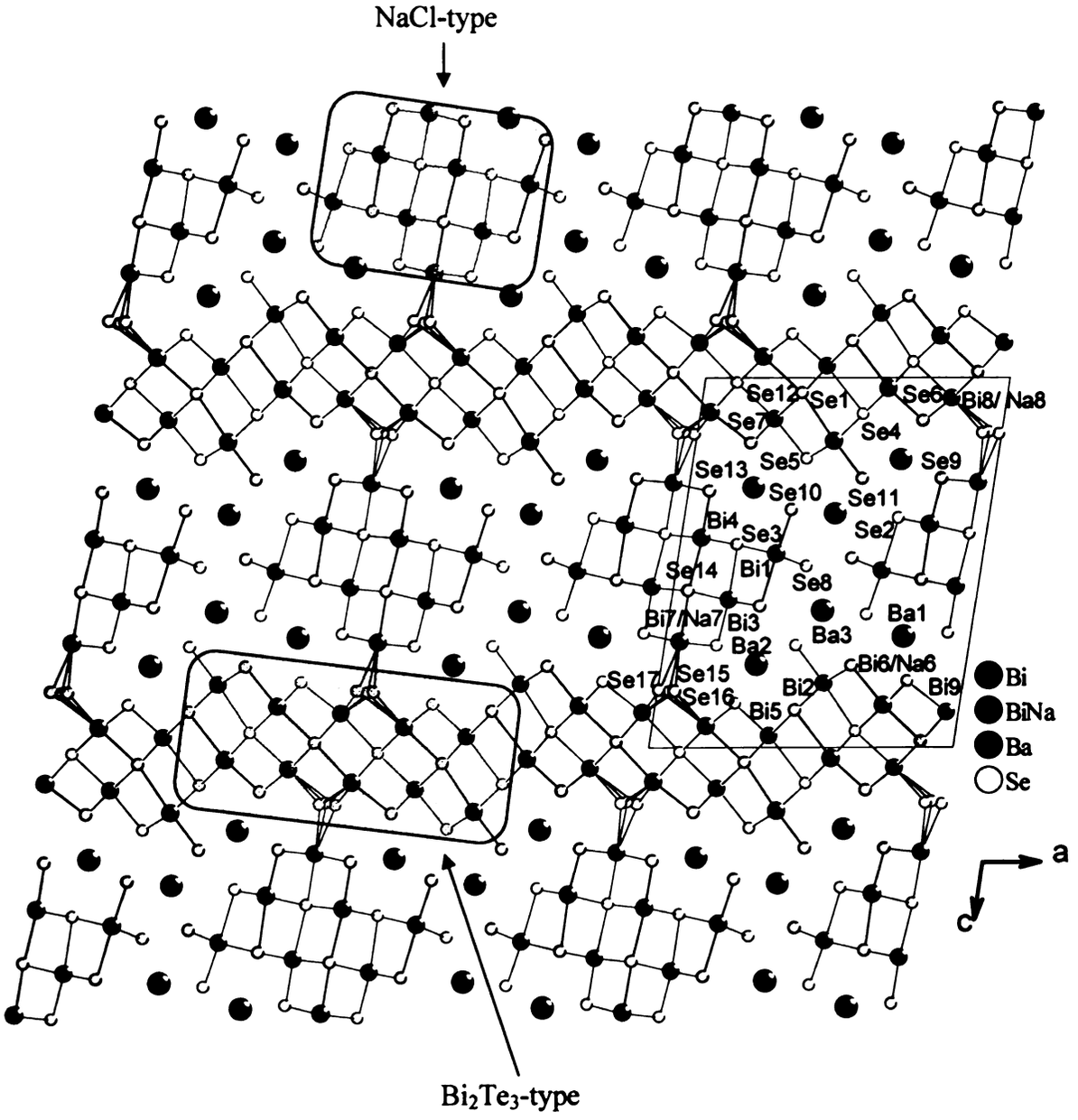


Table 3-6. Bond distances (Å) for $Na_1Ba_{2.79}Bi_{7.37}Se_{14}$.

Bi(1)-Se(10)	2.722(4)	Bi(7)/Na(7)-Se(16) x 2	2.92(3)
Bi(1)-Se(8) x 2	2.851(3)	Bi(7)/Na(7)-Se(13) x 2	3.019(3)
Bi(1)-Se(3) x 2	3.167(3)	Bi(7)/Na(7)-Se(9) x 2	3.025(3)
Bi(1)-Se(2)	3.208(4)	Bi(7)/Na(7)-Se(15)	2.992(12)
		Bi(7)/Na(7)-Se(14)	3.009(5)
Bi(2)-Se(11)	2.701(4)	Bi(7)/Na(7)-Se(17)	3.05(4)
Bi(2)-Se(5) x 2	2.851(2)		
Bi(2)-Se(4) x 2	3.147(3)	Bi(8)/Na(8)-Se(16) x 2	2.77(3)
Bi(2)-Se(1)	3.337(1)	Bi(8)/Na(8)-Se(15)	2.92(2)
		Bi(8)/Na(8)-Se(17)	3.429(11)
Bi(3)-Se(9)	2.733(4)	Bi(8)/Na(8)-Se(6) x 2	3.022(3)
Bi(3)-Se(2) x 2	2.836(3)	Bi(8)/Na(8)-Se(12) x 2	3.036(3)
Bi(3)-Se(14) x 2	3.193(3)	Bi(8)/Na(8)-Se(1)	3.049(5)
Bi(3)-Se(3)	3.313(1)		
		Bi(9)-Se(17) x 2	2.69(3)
Bi(4)-Se(13)	2.740(4)	Bi(9)-Se(16) x 2	2.76(3)
Bi(4)-Se(3) x 2	2.974(3)	Bi(9)-Se(15) x 2	2.880(14)
Bi(4)-Se(14) x 2	3.020(3)	Bi(9)-Se(7)	2.887(5)
Bi(4)-Se(14)	3.215(4)	Bi(9)-Se(12) x 2	3.135(3)
		Bi(9)-Se(12)	3.159(5)
Bi(5)-Se(6)	2.704(4)		
Bi(5)-Se(4) x 2	2.987(3)	Ba(1)-Se(10) x 2	3.293(3)
Bi(5)-Se(1) x 2	3.008(3)	Ba(1)-Se(13) x 2	3.334(3)
Bi(5)-Se(4)	3.453(1)	Ba(1)-Se(7) x 2	3.395(4)
		Ba(1)-Se(3)	3.427(4)
Bi(6)/Na(6)-Se(7) x 2	2.908(3)	Ba(1)-Se(5)	3.464(4)
Bi(6)/Na(6)-Se(1) x 2	3.070(3)		
Bi(6)/Na(6)-Se(5)	2.950(5)	Ba(2)-Se(11) x 2	3.295(3)
Bi(6)/Na(6)-Se(12)	2.984(5)	Ba(2)-Se(9) x 2	3.340(3)

Table 3-6. (cont'd)

Ba(2)-Se(6) x 2	3.359(3)	Ba(3)-Se(11) x 2	3.345(3)
Ba(2)-Se(2)	3.395(4)	Ba(3)-Se(8)	3.488(4)
Ba(2)-Se(4)	3.443(5)	Ba(3)-Se(8) x 2	3.497(4)
		Ba(3)-Se(2)	3.593(4)
Ba(3)-Se(10) x 2	3.310(3)	Ba(3)-Se(5)	3.594(5)

Table 3-7. Selected Angles (deg) for $Na_1Ba_{2.79}Bi_{7.37}Se_{14}$.

Se(10)-Bi(1)-Se(8)	92.84(9)	Se(13)-Bi(4)-Se(14)	92.49(10)
Se(8)-Bi(1)-Se(8)	98.39(12)	Se(3)-Bi(4)-Se(14)	176.37(12)
Se(10)-Bi(1)-Se(3)	93.45(9)	Se(3)-Bi(4)-Se(14)	87.74(7)
Se(8)-Bi(1)-Se(3)	171.16(9)	Se(14)-Bi(4)-Se(14)	91.24(11)
Se(8)-Bi(1)-Se(3)	87.50(7)	Se(13)-Bi(4)-Se(14)	175.79(12)
Se(3)-Bi(1)-Se(3)	85.93(10)	Se(3)-Bi(4)-Se(14)	91.86(9)
Se(10)-Bi(1)-Se(2)	178.09(11)	Se(14)-Bi(4)-Se(14)	84.57(9)
Se(8)-Bi(1)-Se(2)	85.92(9)		
Se(3)-Bi(1)-Se(2)	87.94(9)	Se(6)-Bi(5)-Se(4)	90.95(11)
Se(10)-Bi(1)-Ba(3)	122.58(9)	Se(4)-Bi(5)-Se(4)	92.52(11)
Se(8)-Bi(1)-Ba(3)	54.85(7)	Se(6)-Bi(5)-Se(1)	91.22(10)
Se(3)-Bi(1)-Ba(3)	125.60(7)	Se(4)-Bi(5)-Se(1)	177.79(13)
Se(2)-Bi(1)-Ba(3)	55.51(7)	Se(4)-Bi(5)-Se(1)	87.84(7)
		Se(1)-Bi(5)-Se(1)	91.71(11)
Se(11)-Bi(2)-Se(5)	92.24(10)		
Se(5)-Bi(2)-Se(5)	98.39(11)	Se(7)-Bi(6)-Se(7)	95.82(13)
Se(11)-Bi(2)-Se(4)	95.64(10)	Se(7)-Bi(6)-Se(5)	85.20(12)
Se(5)-Bi(2)-Se(4)	170.29(11)	Se(7)-Bi(6)-Se(12)	90.14(12)
Se(5)-Bi(2)-Se(4)	86.99(7)	Se(5)-Bi(6)-Se(12)	173.03(13)
Se(4)-Bi(2)-Se(4)	86.60(10)	Se(7)-Bi(6)-Se(1)	176.39(10)
		Se(7)-Bi(6)-Se(1)	87.40(8)
Se(9)-Bi(3)-Se(2)	92.20(10)	Se(5)-Bi(6)-Se(1)	93.45(10)
Se(2)-Bi(3)-Se(2)	99.10(12)	Se(12)-Bi(6)-Se(1)	91.51(11)
Se(9)-Bi(3)-Se(14)	89.25(9)	Se(1)-Bi(6)-Se(1)	89.34(11)
Se(2)-Bi(3)-Se(14)	172.78(9)		
Se(2)-Bi(3)-Se(14)	87.90(7)	Se(16)-Bi(7)-Se(16)	22(2)
Se(14)-Bi(3)-Se(14)	85.05(10)	Se(16)-Bi(7)-Se(15)	13.1(10)
		Se(16)-Bi(7)-Se(14)	168.1(10)
Se(13)-Bi(4)-Se(3)	91.04(10)	Se(15)-Bi(7)-Se(14)	177.5(5)
Se(3)-Bi(4)-Se(3)	93.06(11)	Se(16)-Bi(7)-Se(13)	103.6(10)

Table 3-7. (cont'd)

Se(16)-Bi(7)-Se(13)	87.7(7)	Se(15)-Bi(8)-Se(1)	179.0(4)
Se(15)-Bi(7)-Se(13)	90.8(4)	Se(6)-Bi(8)-Se(1)	84.62(11)
Se(14)-Bi(7)-Se(13)	87.42(11)	Se(12)-Bi(8)-Se(1)	90.91(11)
Se(16)-Bi(7)-Se(13)	103.6(10)		
Se(13)-Bi(7)-Se(13)	91.28(13)	Se(17)-Bi(9)-Se(17)	106.9(17)
Se(16)-Bi(7)-Se(9)	97.2(7)	Se(17)-Bi(9)-Se(16)	23(2)
Se(15)-Bi(7)-Se(9)	94.2(4)	Se(17)-Bi(9)-Se(16)	90.6(16)
Se(14)-Bi(7)-Se(9)	87.59(10)	Se(16)-Bi(9)-Se(16)	71(2)
Se(13)-Bi(7)-Se(9)	175.00(14)	Se(17)-Bi(9)-Se(15)	102.9(12)
Se(13)-Bi(7)-Se(9)	88.63(8)	Se(17)-Bi(9)-Se(15)	11.2(16)
Se(16)-Bi(7)-Se(9)	81.4(10)	Se(16)-Bi(9)-Se(15)	84.0(13)
Se(9)-Bi(7)-Se(9)	91.03(12)	Se(16)-Bi(9)-Se(15)	13.6(9)
Se(16)-Bi(7)-Se(17)	20.9(18)	Se(15)-Bi(9)-Se(15)	97.1(6)
Se(15)-Bi(7)-Se(17)	10.9(14)	Se(17)-Bi(9)-Se(7)	88.8(19)
Se(14)-Bi(7)-Se(17)	166.6(18)	Se(16)-Bi(9)-Se(7)	104.9(7)
Se(13)-Bi(7)-Se(17)	83.2(12)	Se(15)-Bi(9)-Se(7)	99.2(5)
Se(9)-Bi(7)-Se(17)	101.7(12)	Se(17)-Bi(9)-Se(12)	82.9(9)
		Se(17)-Bi(9)-Se(12)	169.4(13)
Se(16)-Bi(8)-Se(16)	23(2)	Se(16)-Bi(9)-Se(12)	99.9(10)
Se(16)-Bi(8)-Se(15)	13.3(10)	Se(16)-Bi(9)-Se(12)	165.8(9)
Se(16)-Bi(8)-Se(6)	100.0(7)	Se(15)-Bi(9)-Se(12)	171.1(3)
Se(16)-Bi(8)-Se(6)	83.3(10)	Se(7)-Bi(9)-Se(12)	87.61(10)
Se(15)-Bi(8)-Se(6)	96.1(3)	Se(15)-Bi(9)-Se(12)	87.5(3)
Se(6)-Bi(8)-Se(6)	91.16(12)	Se(12)-Bi(9)-Se(12)	87.02(11)
Se(16)-Bi(8)-Se(12)	101.1(10)	Se(17)-Bi(9)-Se(12)	96.6(18)
Se(16)-Bi(8)-Se(12)	84.5(7)	Se(16)-Bi(9)-Se(12)	82.4(6)
Se(6)-Bi(8)-Se(12)	175.50(15)	Se(15)-Bi(9)-Se(12)	86.8(4)
Se(6)-Bi(8)-Se(12)	88.94(8)	Se(7)-Bi(9)-Se(12)	170.90(13)
Se(12)-Bi(8)-Se(12)	90.60(13)	Se(12)-Bi(9)-Se(12)	85.80(10)
Se(16)-Bi(8)-Se(1)	167.1(11)		

Figure 3-3. DTA diagram of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$ showing the endothermic and exothermic peaks. The heating and cooling rates were 10°C/min.

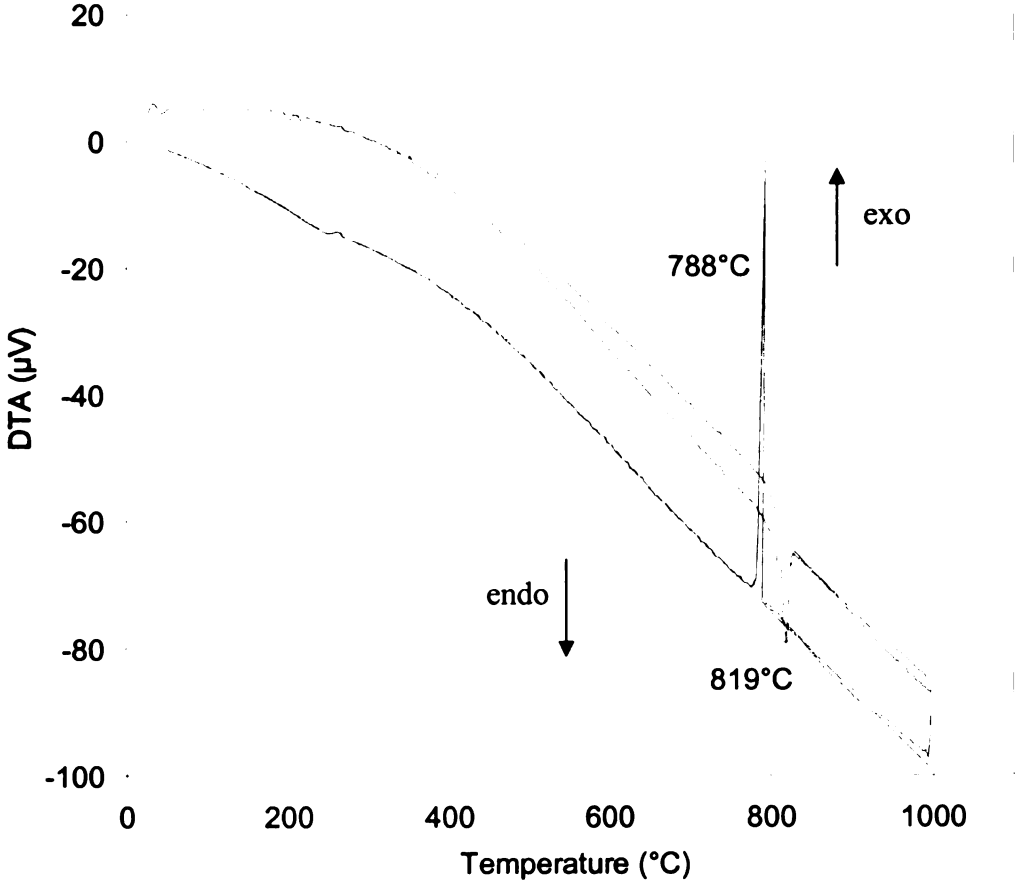
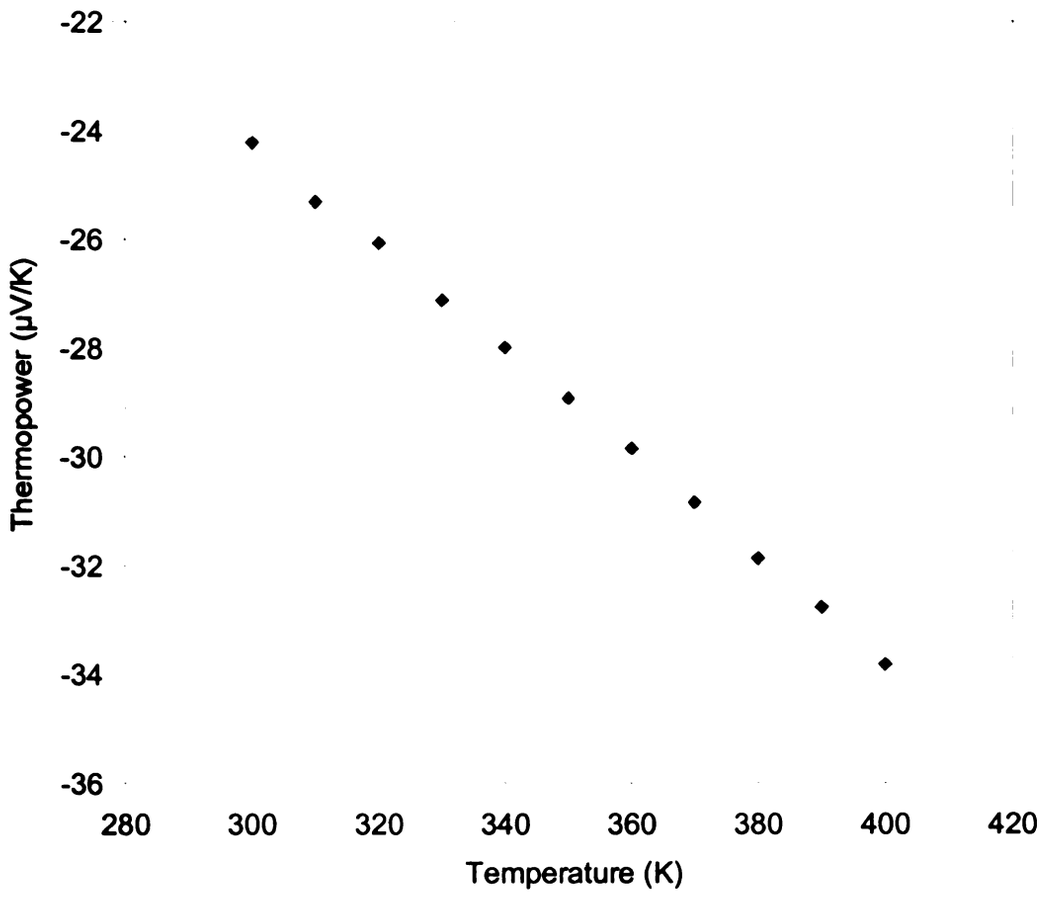


Figure 3-4. Variable temperature thermopower for a polycrystalline oriented ingot of $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$.



E. Conclusion

Two new quaternary bismuth chalcogenides that are derivatives of the $K_{2.5}Bi_{8.5}Se_{14}$ structure type have been prepared. In $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$ structure the bigger Rb^+ cations occupy the tunnels and are disordered with Bi atoms similar to the parent structure. Pb atoms occupy the high-coordination sites. When we move to smaller cations (Na^+) in $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$, they get disordered with Bi atoms and reside in the NaCl- and Bi_2Te_3-type fragments rather than the tunnels. The tunnels and the high-coordination sites are occupied by the alkaline earth (Ba^{2+}) cations.

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CHAPTER 4

Solvothermal Synthesis of Ordered Structure of $Cs_3Sb_5Se_9$

A. Introduction

Solid state reactions involve solid reactants and are characterized by slow nucleation and diffusion processes. High temperatures are usually required so that the reactants have enough mobility for sufficient diffusion to take place. This high-temperature diffusion control leads to restrictions in the number and complexity of the structural building blocks available for the construction of solid-state frameworks. Thus one has very little control in the rational design and prediction of the structures coming out of this traditional solid-state reactions.[1] Such experimental conditions lead almost invariably to thermodynamically stable phases which have simple lattice structures of high symmetry and high density.[1] Usually these reactions occur at temperatures typically above 600°C which allows adequate diffusion of ions and atoms to the site of product formation.

In comparison to the results obtained from such high temperature synthetic methods, alternative methods like chemical vapor deposition (CVD), molten salt flux synthesis and hydrothermal synthesis have allowed the solid-state chemist to use lower temperature regime where kinetically stable or metastable phases can be accessible. These lower temperatures make possible the use of molecular assemblies as building blocks, for incorporation in solid state structures.

Hydrothermal synthesis usually refers to heterogeneous reactions involving water as a solvent at elevated temperatures and pressures in a closed system, often in the vicinity of its critical point.[2] There are certain fundamental differences in the reaction conditions involved in comparison to traditional solid-state reactions.[1] First, using a suitable solvent removes diffusion control and allows the starting materials to mix properly. Second, the reactions are restricted to one or more functional groups by the employment of relatively low temperatures. This leaves the majority of the chemical bonds intact.

'Solvothermal' is a more general term and it refers to similar reaction but in which a different solvent, can be either inorganic or organic, is used. Certain properties of the solvent under these conditions (hydro- or solvothermal), like viscosity, density and diffusion coefficient changes appreciably and the solvent behaves much differently as compared to what is expected at ambient conditions.[3] As a result of this, the chemical reactivity and the solubility of the reactants are greatly enhanced and this enables the reaction to take place at a much lower temperature. This methodology is being applied for the growth of various inorganic materials like metal carbonates, phosphates, oxides, halides, quartz and zeolites.[2, 4]

A growing interest in solvothermal methods has been motivated by the fact that these lead to materials containing regularly spaced pores and cavities, which have a distinct technological potential.[5] For example, these mild and soft conditions make it possible to leave polychalcogen building-blocks intact while they reorganize themselves to form various new structures, many of which might be promising for applications in catalysis, electronic, magnetic, optical and thermalelectronic devices.[6] Water and alcohol

so far have been solvents of choice and a number of alkali metal, alkaline-earth metal, group 14-15 sulfides and selenides and other metal based chalcogenides have been isolated both by our group[7] and other groups.[8] These reactions were carried out in the temperature range of 110-220°C. Only recently ethylenediamine[9] and ammonia[10] have been used as reaction medium to crystallize polychalcogenides at lower temperature range of 160-170°C.

The structure of $Cs_3Sb_5Se_9$ which was reported by Sheldrick and Häusler[11] shows disorder in the Sb and chalcogen sites and this disorder extends to all the layers in the structure. The structure of $Cs_3Sb_5Se_9$ presented here has a more ordered structure in the sense that the disorder in the metal and chalcogen site is extended only in alternate layers.

B. Experimental Section

Reagents: Chemicals were used as obtained: (i) antimony shots, 99.999% purity, Cerac, Milwaukee, WI. (ii) selenium shots, 99.999% purity, Cerac, Milwaukee, WI. (iii) cesium metal, 99.999% purity, Alfa Aesar, Ward Hill, MA. (iv) ethylenediamine, Spectrum Chemical Mfg. Corp., Gardena, CA. Cs_2Se was prepared by a stoichiometric reaction of cesium metal and selenium shots in liquid ammonia.

Solvent: Ethylenediamine ($H_2NCH_2CH_2NH_2$) is a very good solvent for solvothermal synthesis of metal chalcogenides. Some of the physical constants of the solvent are shown in Table 4-1.[12] It has a relatively low critical pressure which makes it possible to run these reactions in thick-walled pyrex tubes under mild temperature conditions.

Synthesis: All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All starting materials were ground to fine powder and then loaded in thick walled pyrex tubes for efficient mixing with the solvent.

$Cs_3Sb_5Se_9$: A mixture of 0.09g (0.261 mol) of Cs_2Se, 0.159g (1.31 mol) of antimony and 0.206g (2.61 mol) of selenium in the ratio of 0.2:1:2 was transferred into a 9mm thick walled pyrex tube. 0.30ml (mol) of ethylene diamine was added to this and the tube was cooled under liquid N_2 until the solvent solidifies. This was then flame sealed under vacuum (~10^{-4} Torr). The tube was then wrapped in aluminum foil and kept in an oven maintained at a constant temperature of 154°C. The progress of the reaction was monitored by checking for crystal growth inside the tube. The product consisted of reddish brown hexagonal rods (see Figure 4-1.) and orange crystals. The rods were stable in air whereas the orange crystals were sensitive to air as it lost its color when left outside. These orange crystals were Cs_3SbSe_4.[13] Energy Dispersive Spectroscopy (EDS) on several of these hexagonal rod type crystals gave an approximate composition of "$CsSb_{1.68}Se_{2.94}$".

C. Physical Measurements

Energy Dispersive Spectroscopy: Quantitative microprobe analyses of the compound were performed with a JEOL JSM-6400V Scanning Electron Microscope equipped with a Tracor Northern Energy Dispersive Spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 30 seconds accumulation time.

Single-Crystal X-ray Crystallography: Intensity data were collected at 293 K on a Bruker SMART Platform CCD diffractometer using graphite monochromatized Mo K_α (λ = 0.71073Å) radiation. Individual frames were measured using 0.3° steps in ω using the SMART software. SAINT[14] was used for data extraction and reduction. The absorption correction was done with SADABS[14], and the structure solution was done with the SHELXTL[14] package of crystallographic programs.

A hemisphere of data was collected with an exposure time of 30 seconds per frame. The crystallographic data is shown in Table 4-2. The structure was first solved in C2 space group. Then the TEXSAN[15] package of crystallographic program was used to find missing symmetry elements and an inversion center was found at (0.0001, 0.2845, -0.0013) suggesting a higher centrosymmetric space group C2/m. The origin was shifted to the inversion point and the coordinates of all the atoms were recalculated based on this origin. $1/8^{th}$ of this cell was chosen and refined in C2/m. Forty six crystallographically independent positions were found out of which thirteen positions were found to sit on a crystallographic mirror plane. The remaining sat on a general position. Sb(13) & Sb(14), Se(18) & Se(19), Se(20) & Se(21), Se(22) & Se(23) and Se(24) & Se(25) were all found to be disordered over a single site. After anisotropic refinement final R values, R1 = 8.18% and wR2 = 22.68%. The fractional coordinates and isotropic displacement parameters along with occupancies for disordered atoms are shown in Table 4-3.

Table 4-1. Physical constants for ethylene diamine.

Molecular formula	$C_2H_8N_2$
Formula weight (g.mol-^{1})	60.10
Melting point (°C)	8.5
Boiling point (°C)	117.3
Flash point (°C)	43
Critical temp. (°C)	319.9
Critical pressure (atm)	62.1
Critical volume ($cm^3.mol^{-1}$)	206

Figure 4-1. SEM image of the hexagonal rod type crystal of $Cs_3Sb_5Se_9$.

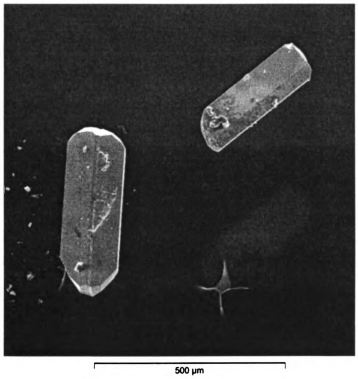


Table 4-2. Crystallographic data for the ordered $Cs_3Sb_5Se_9$ and the structure reported by Sheldrick and Häusler.[11]

Empirical formula	$Cs_3Sb_5Se_9$	$Cs_3Sb_5Se_9$ (From ref. 11)
Formula weight	412.58	-
T, K	293(2)	-
λ, Å	0.71073	0.71073
Crystal System	Monoclinic	
Space group	C2/m	C2/m
a, Å	19.156(4)	9.587(4)
b, Å	51.647(12)	25.855(4)
c, Å	11.615(3)	9.638(1)
α, deg	90	90
β, deg	126.974(4)	105.58(2)
γ, deg	90	90
V, Å3	9180(4)	2301(1)
Z	70	4
ρ_{calcd}, g/cm^3	5.224	4.96
μ, mm^{-1}	25.789	24.57
Total reflections	38167	1862
Unique reflections	11209	1582
$R_{(int)}$	0.0708	-
No. of parameters	371	99
Goodness-of-fit on F^2	1.064	-
Refinement method	Full-matrix least-squares on F^2	
R1[a]	0.0818	0.064
wR2[b]	0.2268	0.061

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

Table 4-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å2x 103) for $Cs_3Sb_5Se_9$.

	x	y	z	U(eq)	Occ.
Cs(1)	2638(1)	1080(1)	7563(2)	20(1)	
Cs(2)	2353(1)	1076(1)	2328(2)	18(1)	
Cs(3)	0	408(1)	5000	24(1)	
Cs(4)	5000	411(1)	5000	25(1)	
Cs(5)	10102(1)	1425(1)	7574(2)	22(1)	
Cs(6)	7486(1)	2091(1)	4999(2)	33(1)	
Cs(7)	5155(1)	1419(1)	7618(2)	22(1)	
Sb(1)	7493(1)	1886(1)	8394(2)	22(1)	
Sb(2)	0	-2886(1)	5000	33(1)	
Sb(3)	2417(1)	380(1)	4743(1)	8(1)	
Sb(4)	2589(1)	380(1)	-86(1)	7(1)	
Sb(5)	1168(1)	0	637(2)	7(1)	
Sb(6)	3833(1)	0	8297(2)	8(1)	
Sb(7)	4893(1)	615(1)	8283(2)	9(1)	
Sb(8)	-96(1)	611(1)	1510(2)	9(1)	
Sb(9)	7501(1)	1888(1)	11612(2)	23(1)	
Sb(10)	0	-2880(1)	0	36(1)	
Sb(11)	5000	-2879(1)	15000	33(1)	
Sb(12)	5000	-2878(1)	10000	36(1)	
Sb(13)	6334(3)	-2497(1)	18311(4)	27(1)	0.51744
Sb(14)	6333(3)	-2499(1)	19350(4)	22(1)	0.48256
Se(1)	3801(2)	0	1134(3)	11(1)	
Se(2)	1217(2)	0	3569(3)	11(1)	
Se(3)	2290(1)	376(1)	1877(2)	8(1)	
Se(4)	1165(2)	0	-1620(3)	8(1)	
Se(5)	3832(2)	0	6024(3)	8(1)	
Se(6)	7518(2)	1533(1)	10030(2)	18(1)	
Se(7)	1226(2)	773(1)	4001(2)	14(1)	

Table 4-3. (cont'd)

	x	y	z	U(eq)	Occ.
Se(8)	3766(2)	771(1)	1546(3)	16(1)	
Se(9)	0	965(1)	0	13(1)	
Se(10)	1233(2)	823(1)	-1620(3)	14(1)	
Se(11)	3775(2)	836(1)	5939(2)	13(1)	
Se(12)	8735(2)	1707(1)	8442(3)	26(1)	
Se(13)	5000	967(1)	10000	15(1)	
Se(14)	8717(2)	1700(1)	14034(3)	30(1)	
Se(15)	6257(2)	1706(1)	11559(3)	26(1)	
Se(16)	6276(2)	1692(1)	5991(3)	29(1)	
Se(17)	2709(1)	377(1)	7297(2)	9(1)	
Se(18)	-191(4)	-2881(1)	2719(6)	21(2)	0.48593
Se(19)	-180(4)	-2878(1)	1904(6)	25(2)	0.51407
Se(20)	4809(4)	-2872(1)	12712(6)	22(2)	0.48630
Se(21)	4819(4)	-2874(1)	11909(6)	25(2)	0.51370
Se(22)	6315(8)	-2503(1)	16110(50)	24(5)	0.66742
Se(23)	6279(11)	-2489(5)	16510(50)	10(6)	0.33258
Se(24)	6334(9)	-2497(4)	11620(50)	16(4)	0.43799
Se(25)	6313(7)	-2500(2)	11150(60)	20(6)	0.56201

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

D. Results and discussion

Structure Description of $Cs_3Sb_5Se_9$:

The structure of $Cs_3Sb_5Se_9$ consists of complex selenoantimonate layers and builds up in the following manner: it has three kinds of building blocks which are $(Sb_2Se_6)^{6-}$; $(SbSe_4)^{5-}$ and $(Sb_2Se_5)^{4-}$ (see Figure 4-3.). Each $(Sb_2Se_6)^{6-}$ unit is bridged by $(SbSe_4)^{5-}$ anion to another $(Sb_2Se_6)^{6-}$ unit to form chains which run along the c-direction. The $(SbSe_4)^{5-}$ bridging unit are positioned in an alternate fashion along this chain. These linear chains are connected along the a-direction by two $(Sb_2Se_5)^{4-}$ anions to form layers parallel to the ac-plane. Alternate layers in this structure have disordered Sb- and Se-sites.

The antimony atoms in the $(Sb_2Se_6)^{6-}$ unit are in a distorted octahedral coordination with a long Sb-Se bond trans to a short Sb-Se bond. Sb-Se distances in this unit ranges between 2.435(6)-3.189(1)Å. In the $(SbSe_4)^{5-}$ unit the antimony atoms are in see-saw type coordination. Sb-Se distances in this unit ranges between 2.596(2)-3.332(1)Å. The $(Sb_2Se_5)^{4-}$ unit is formed by the corner sharing of two trigonal pyramidal $SbSe_3$ units. Sb-Se distances in this unit ranges between 2.508 (3)-2.617(3)Å. For bond distances and selected bond angles see Table 4-3. and Table 4-4. respectively.

For the alkali (Cs^+) atoms, Cs(3), Cs(4) & Cs(6) lies in the tunnels running along the b-direction (see Figure 4-4.) which are within the layers and all the remaining alkali atoms lie between the layers.

An interesting feature in this structure is the presence of disorder in the Sb- and Se-sites. Specifically Sb is disordered in the $(SbSe_4)^{5-}$ unit while Se is disordered in both $(Sb_2Se_6)^{6-}$ and $(SbSe_4)^{5-}$ units (see Figure 4-3.). The Sb-site in $(SbSe_4)^{5-}$ unit has 52%

Sb(13) and 48% Sb(14). Both the atoms are disordered at 1.207(1)Å. In the Se-sites, Se(18) (49%)is disordered with Se(19) (51%) and Se(20) (49%) is disordered with Se(21) (51%). Se(18) is disordered with Se(19) at 0.959(1)Å and Se(20) is disordered with Se(21) at 0.945(1)Å. In case of the $(Sb_2Se_6)^{6-}$ unit the disordered Se-sites are occupied by Se(22)/Se(23) and Se(24)/Se(25). The Se(22) site contains 67% Se(22) and 33% Se(23) whereas the Se(24) site has 44% Se(24) and 56% Se(25). Se(22) is disordered with Se(23) at 0.512(1)Å and Se(24) is disordered with Se(25) at 0.524(1)Å.

Sheldrick and Häusler[11] in their report on the structure of $Cs_3Sb_5Se_9$ have noted disorder in the Sb- and Se-site and this disorder is present in all the layers. They also reported the disorder of Se-site to be present only in the $(SbSe_4)^{5-}$ unit. In our structural solution we observe the disorder in Sb- and Se-sites to be present in alternate layers and this is probably a distinct structural difference with that reported earlier. Also the disorder in the Se-sites is observed to be present in $(Sb_2Se_6)^{6-}$ unit as well as in $(SbSe_4)^{5-}$ unit. Moving from disordered layers as reported earlier to ordered layers, probably explains the doubling from 25.855(4)Å to 51.647(12)Å in the b-parameter of the unit cell.

Figure 4-2. Projection of the structure of $Cs_3Sb_5Se_9$ down the c-axis.

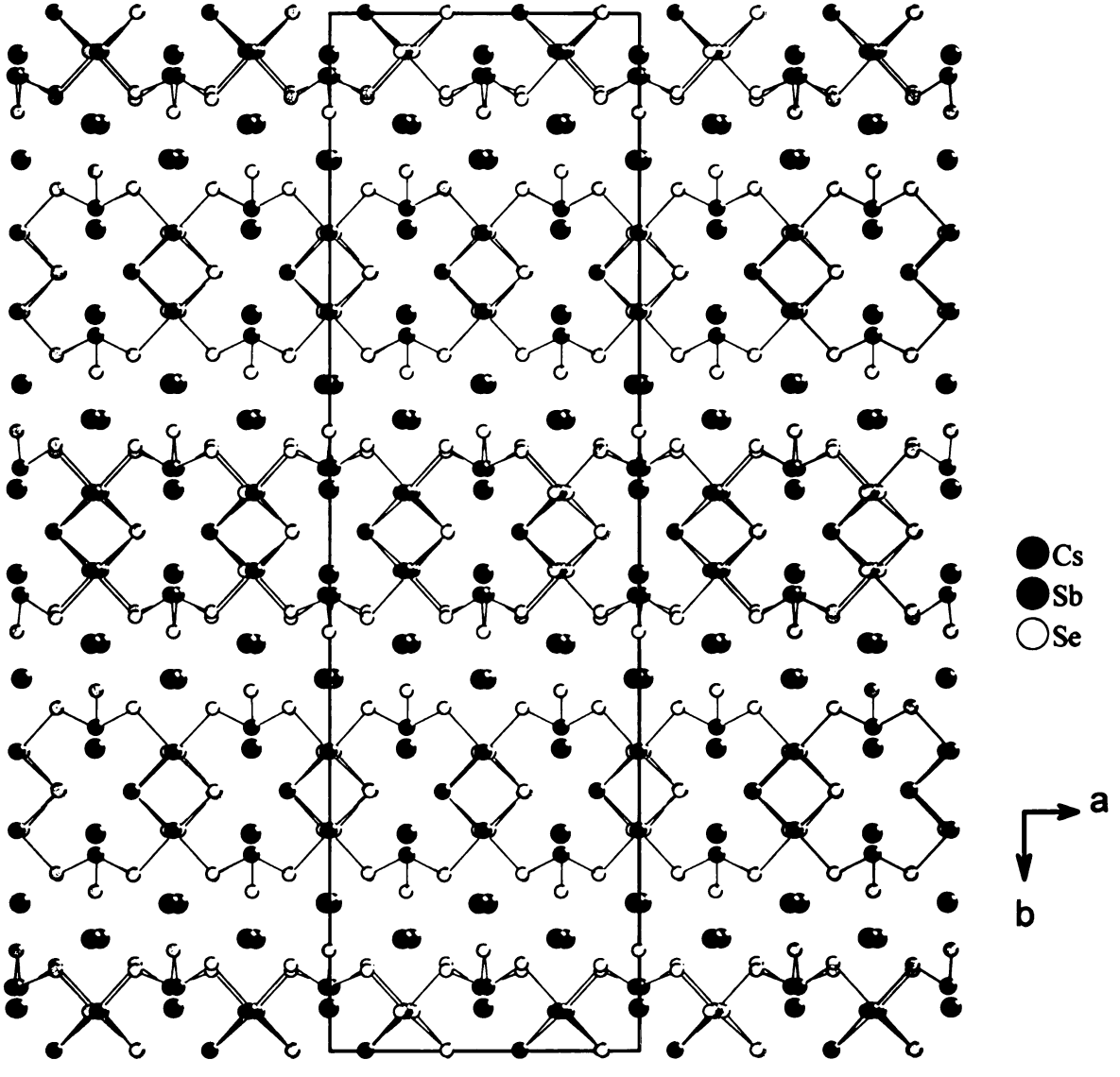
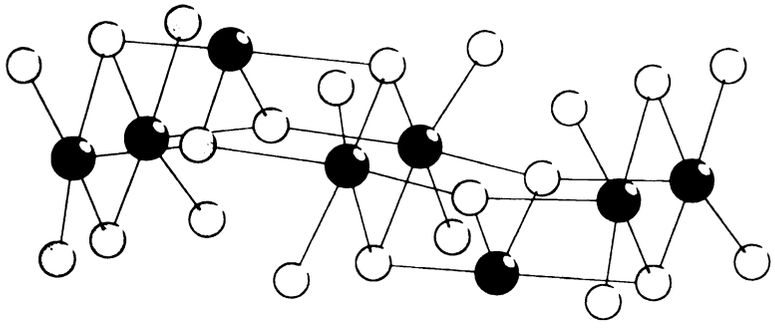
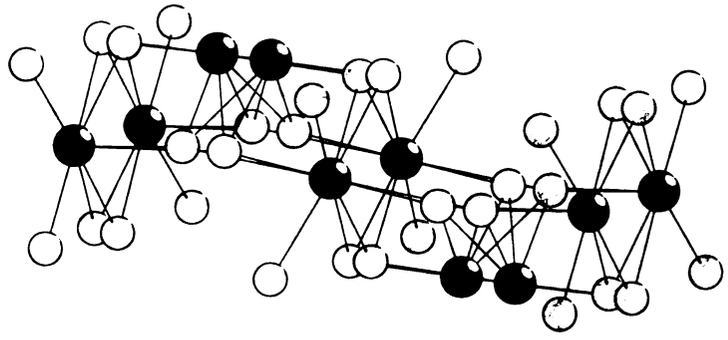


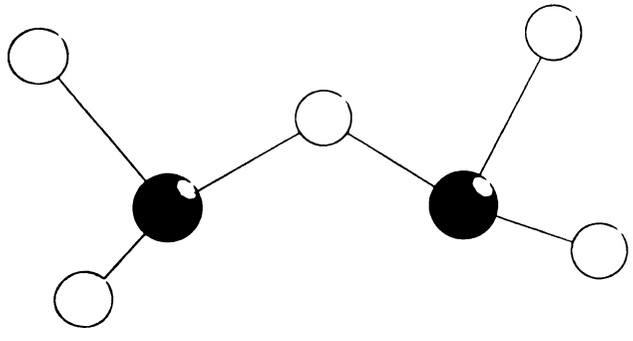
Figure 4-3. Different selenoantimonate units which act as building-blocks.



a) Linear chains composed of $(Sb_2Se_6)^{6-}$ units joined by $(SbSe_4)^{5-}$ unit.

b) Similar chains showing disorder in the Sb- and Se-sites





(c) $(Sb_2Se_5)^{4-}$ unit, this joins the two chains to form a layer.

Figure 4-4. Projection of one of the layers in $Cs_3Sb_5Se_9$ down the b-axis showing the tunnels occupied by the alkali atoms. It also shows the chains connected by the $(Sb_2Se_5)^{4-}$ unit.

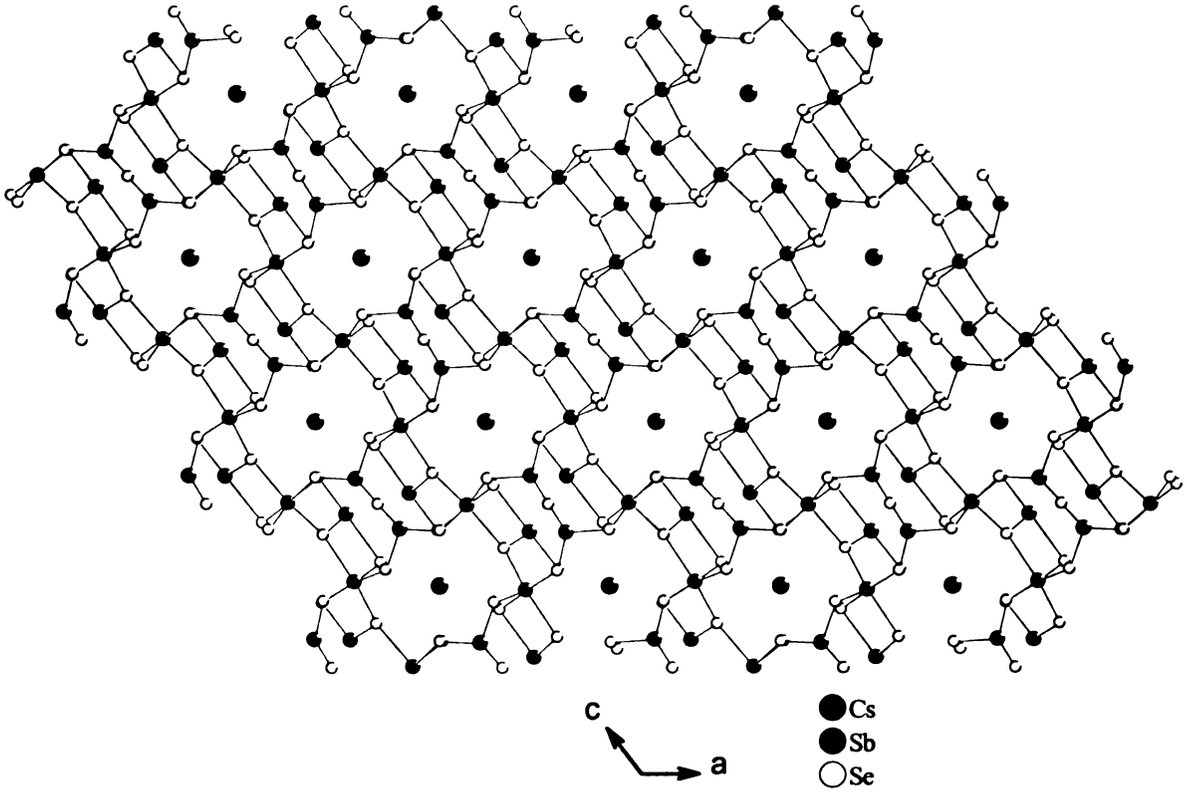


Table 4-4. Bond distances (Å) for $Cs_3Sb_5Se_9$.

Sb(1)-Se(12)	2.521(3)	Sb(6)-Se(1)	3.332(1)
Sb(1)-Se(16)	2.531(3)		
Sb(1)-Se(6)	2.614(3)	Sb(7)-Se(11)	2.508(3)
		Sb(7)-Se(8)	2.583(3)
Sb(2)-Se(18) x 2	2.447(6)	Sb(7)-Se(13)	2.615(3)
Sb(2)-Se(23)	2.765(19)		
Sb(2)-Se(22)	2.849(14)	Sb(8)-Se(10)	2.509(3)
Sb(2)-Se(16) x 2	2.948(4)	Sb(8)-Se(7)	2.584(3)
		Sb(8)-Se(9)	2.617(3)
Sb(3)-Se(17)	2.668(2)		
Sb(3)-Se(2)	2.687(3)	Sb(9)-Se(15)	2.529(3)
Sb(3)-Se(7)	2.775(3)	Sb(9)-Se(14)	2.530(3)
Sb(3)-Se(5)	2.926(3)	Sb(9)-Se(6)	2.610(3)
Sb(3)-Se(3)	3.189(1)		
Sb(3)-Se(11)	3.149(4)	Sb(10)-Se(19) x 2	2.435(6)
		Sb(10)-Se(25)	2.812(10)
Sb(4)-Se(3)	2.665(2)	Sb(10)-Se(24)	2.843(12)
Sb(4)-Se(1)	2.700(3)	Sb(10)-Se(15) x 2	2.901(3)
Sb(4)-Se(8)	2.760(3)		
Sb(4)-Se(4)	2.936(3)	Sb(11)-Se(20) x 2	2.455(6)
Sb(4)-Se(17)	3.181(1)	Sb(11)-Se(22)	2.807(12)
Sb(4)-Se(10)	3.097(5)	Sb(11)-Se(23)	2.82(2)
		Sb(11)-Se(14) x 2	2.952(4)
Sb(5)-Se(3) x 2	2.596(2)		
Sb(5)-Se(4)	2.617(3)	Sb(12)-Se(21) x 2	2.441(6)
Sb(5)-Se(2)	3.350(1)	Sb(12)-Se(25)	2.809(12)
		Sb(12)-Se(24)	2.86(2)
Sb(6)-Se(17) x 2	2.601(2)	Sb(12)-Se(12) x 2	2.909(4)
Sb(6)-Se(5)	2.640(3)		

Table 4-4. (cont'd)

Sb(13)-Sb(14)	1.207(5)	Cs(2)-Se(8)	3.686(3)
Sb(13)-Se(23)	2.03(6)	Cs(2)-Se(6)	3.735(3)
Sb(13)-Se(22)	2.53(6)	Cs(2)-Se(16)	3.827(3)
Sb(13)-Se(20)	2.612(7)	Cs(2)-Se(10)	3.937(3)
Sb(13)-Se(18)	2.623(7)	Cs(2)-Se(7)	3.991(3)
Sb(13)-Se(19)	2.834(7)		
Sb(13)-Se(21)	2.836(7)	Cs(3)-Se(7) x 2	3.701(3)
		Cs(3)-Se(4) x 2	3.780(3)
Sb(14)-Se(25)	2.11(6)	Cs(3)-Se(10) x 2	3.800(3)
Sb(14)-Se(21)	2.623(7)	Cs(3)-Se(2) x 2	4.159(3)
Sb(14)-Se(19)	2.629(6)	Cs(3)-Se(17) x 2	4.173(2)
Sb(14)-Se(24)	2.64(6)		
Sb(14)-Se(20)	2.818(7)	Cs(4)-Se(8) x 2	3.706(3)
Sb(14)-Se(18)	2.841(6)	Cs(4)-Se(5) x 2	3.758(3)
		Cs(4)-Se(11) x 2	3.820(3)
Cs(1)-Se(10)	3.604(3)	Cs(4)-Se(3) x 2	4.182(2)
Cs(1)-Se(15)	3.654(3)	Cs(4)-Se(1)	4.188(3)
Cs(1)-Se(17)	3.657(3)		
Cs(1)-Se(13)	3.6633(19)	Cs(5)-Se(10)	3.577(3)
Cs(1)-Se(7)	3.673(3)	Cs(5)-Se(14)	3.583(3)
Cs(1)-Se(6)	3.790(3)	Cs(5)-Se(12)	3.629(3)
Cs(1)-Se(14)	3.824(3)	Cs(5)-Se(20)	3.659(6)
Cs(1)-Se(11)	3.853(3)	Cs(5)-Se(21)	3.660(6)
Cs(1)-Se(8)	4.073(3)	Cs(5)-Se(6)	3.686(3)
		Cs(5)-Se(9)	3.779(3)
Cs(2)-Se(11)	3.577(3)	Cs(5)-Se(7)	3.944(3)
Cs(2)-Se(3)	3.645(3)	Cs(5)-Se(14)	3.964(4)
Cs(2)-Se(9)	3.6458(19)	Cs(5)-Se(12)	4.012(3)
Cs(2)-Se(12)	3.677(3)		

Table 4-4. (cont'd)

Cs(6)-Se(14)	3.751(4)	Cs(7)-Se(18)	3.644(5)
Cs(6)-Se(12)	3.759(3)	Cs(7)-Se(6)	3.664(3)
Cs(6)-Se(15)	3.762(3)	Cs(7)-Se(19)	3.670(5)
Cs(6)-Se(16)	3.764(4)	Cs(7)-Se(15)	3.677(3)
Cs(6)-Se(24)	3.79(3)	Cs(7)-Se(11)	3.694(3)
Cs(6)-Se(22)	3.84(4)	Cs(7)-Se(8)	3.741(3)
Cs(6)-Se(19)	4.118(6)	Cs(7)-Se(13)	3.764(3)
Cs(6)-Se(18)	4.124(6)	Cs(7)-Se(16)	3.879(4)
		Cs(7)-Se(15)	3.996(3)
Cs(7)-Se(16)	3.639(3)		

Table 4-5. Selected Angles (deg) for $Cs_3Sb_5Se_9$.

Se(12)-Sb(1)-Se(16)	96.29(11)	Se(3)-Sb(4)-Se(1)	95.99(9)
Se(12)-Sb(1)-Se(6)	97.10(10)	Se(3)-Sb(4)-Se(8)	85.72(8)
Se(16)-Sb(1)-Se(6)	97.26(10)	Se(1)-Sb(4)-Se(8)	94.74(8)
		Se(3)-Sb(4)-Se(4)	85.07(8)
Se(18)-Sb(2)-Se(18)	178.8(3)	Se(1)-Sb(4)-Se(4)	91.38(8)
Se(18)-Sb(2)-Se(23)	78.8(13)	Se(8)-Sb(4)-Se(4)	169.42(9)
Se(18)-Sb(2)-Se(23)	100.3(13)		
Se(23)-Sb(2)-Se(23)	91.3(10)	Se(3)-Sb(5)-Se(3)	96.81(11)
Se(18)-Sb(2)-Se(22)	89.1(12)	Se(3)-Sb(5)-Se(4)	93.32(8)
Se(18)-Sb(2)-Se(22)	90.0(12)		
Se(18)-Sb(2)-Se(16)	88.83(14)	Se(17)-Sb(6)-Se(17)	96.86(12)
Se(18)-Sb(2)-Se(16)	92.06(15)	Se(17)-Sb(6)-Se(5)	92.96(8)
Se(23)-Sb(2)-Se(16	167.4(13)		
Se(23)-Sb(2)-Se(16)	93.5(3)	Se(11)-Sb(7)-Se(8)	95.81(9)
Se(22)-Sb(2)-Se(16)	92.6(3)	Se(11)-Sb(7)-Se(13)	97.75(8)
Se(22)-Sb(2)-Se(16)	176.2(5)	Se(8)-Sb(7)-Se(13)	96.06(8)
Se(16)-Sb(2)-Se(16)	84.33(14)		
		Se(10)-Sb(8)-Se(7)	95.57(9)
Se(17)-Sb(3)-Se(2)	95.93(9)	Se(10)-Sb(8)-Se(9)	98.09(8)
Se(17)-Sb(3)-Se(7)	86.16(7)	Se(7)-Sb(8)-Se(9)	96.13(8)
Se(2)-Sb(3)-Se(7)	94.85(8)		
Se(17)-Sb(3)-Se(5)	85.43(8)	Se(15)-Sb(9)-Se(14)	96.17(11)
Se(2)-Sb(3)-Se(5)	90.95(8)	Se(15)-Sb(9)-Se(6)	97.55(10)
Se(7)-Sb(3)-Se(5)	170.24(9)	Se(14)-Sb(9)-Se(6)	96.90(11)
Se(17)-Sb(3)-Cs(2)	127.21(7)		
Se(2)-Sb(3)-Cs(2)	124.79(7)	Se(19)-Sb(10)-Se(19)	179.5(3)
Se(7)-Sb(3)-Cs(2)	60.96(6)	Se(19)-Sb(10)-Se(25)	98.1(13)
Se(5)-Sb(3)-Cs(2)	121.34(6)	Se(19)-Sb(10)-Se(25)	81.6(13)
		Se(25)-Sb(10)-Se(25)	91.6(5)

Table 4-5. (cont'd)

Se(24)-Sb(10)-Se(24)	93.5(10)	Se(21)-Sb(12)-Se(21)	178.9(3)
Se(19)-Sb(10)-Se(15)	93.01(15)	Se(21)-Sb(12)-Se(25)	81.4(13)
Se(19)-Sb(10)-Se(15)	87.39(14)	Se(21)-Sb(12)-Se(25)	97.9(13)
Se(25)-Sb(10)-Se(15)	168.6(13)	Se(25)-Sb(12)-Se(25)	91.8(4)
Se(25)-Sb(10)-Se(15)	92.8(2)	Se(21)-Sb(12)-Se(24)	87.4(11)
Se(24)-Sb(10)-Se(15)	175.6(3)	Se(21)-Sb(12)-Se(24)	91.9(11)
Se(24)-Sb(10)-Se(15)	90.8(5)	Se(25)-Sb(12)-Se(24)	91.4(2)
Se(15)-Sb(10)-Se(15)	84.87(14)	Se(21)-Sb(12)-Se(24)	87.4(11)
Se(19)-Sb(10)-Se(24)	87.6(12)	Se(24)-Sb(12)-Se(24)	92.9(5)
Se(19)-Sb(10)-Se(24)	92.1(12)	Se(21)-Sb(12)-Se(12)	92.97(15)
		Se(21)-Sb(12)-Se(12)	87.82(15)
Se(20)-Sb(11)-Se(20)	178.4(3)	Se(25)-Sb(12)-Se(12)	168.8(12)
Se(20)-Sb(11)-Se(22)	89.0(12)	Se(25)-Sb(12)-Se(12)	92.5(4)
Se(20)-Sb(11)-Se(22)	89.8(12)	Se(24)-Sb(12)-Se(12)	176.1(3)
Se(22)-Sb(11)-Se(22)	92.3(6)	Se(24)-Sb(12)-Se(12)	91.0(2)
Se(20)-Sb(11)-Se(23)	78.9(12)	Se(12)-Sb(12)-Se(12)	85.15(14)
Se(20)-Sb(11)-Se(23)	99.9(12)		
Se(22)-Sb(11)-Se(23)	89.7(5)	Sb(14)-Sb(13)-Se(23)	177.4(7)
Se(20)-Sb(11)-Se(23)	99.9(12)	Sb(14)-Sb(13)-Se(22)	178.8(4)
Se(23)-Sb(11)-Se(23)	88.9(8)	Sb(14)-Sb(13)-Se(20)	86.9(3)
Se(20)-Sb(11)-Se(14)	88.26(15)	Se(23)-Sb(13)-Se(20)	92.1(6)
Se(20)-Sb(11)-Se(14)	92.94(15)	Se(22)-Sb(13)-Se(20)	91.9(3)
Se(22)-Sb(11)-Se(14)	175.4(5)	Sb(14)-Sb(13)-Se(18)	87.6(3)
Se(22)-Sb(11)-Se(14)	91.4(3)	Se(23)-Sb(13)-Se(18)	90.1(8)
Se(23)-Sb(11)-Se(14)	167.1(12)	Se(22)-Sb(13)-Se(18)	92.7(3)
Se(23)-Sb(11)-Se(14)	94.4(6)	Se(20)-Sb(13)-Se(18)	95.9(2)
Se(20)-Sb(11)-Se(14)	92.94(15)	Sb(14)-Sb(13)-Se(19)	67.8(3)
Se(14)-Sb(11)-Se(14)	85.07(14)	Se(23)-Sb(13)-Se(19)	109.8(8)
		Se(22)-Sb(13)-Se(19)	112.4(3)

Table 4-5. (cont'd)

Se(20)-Sb(13)-Se(19)	94.1(2)	Se(21)-Sb(14)-Se(19)	95.3(2)
Sb(14)-Sb(13)-Se(21)	67.5(3)	Sb(13)-Sb(14)-Se(20)	67.8(3)
Se(23)-Sb(13)-Se(21)	111.5(5)	Se(25)-Sb(14)-Se(20)	111.9(3)
Se(18)-Sb(13)-Se(21)	94.5(2)	Se(21)-Sb(14)-Se(20)	19.58(15)
Se(19)-Sb(13)-Se(21)	86.4(2)	Se(19)-Sb(14)-Se(20)	94.1(2)
		Se(24)-Sb(14)-Se(20)	112.6(4)
Sb(13)-Sb(14)-Se(25)	179.2(5)	Sb(13)-Sb(14)-Se(18)	67.3(3)
Sb(13)-Sb(14)-Se(21)	87.4(3)	Se(25)-Sb(14)-Se(18)	112.0(4)
Se(25)-Sb(14)-Se(21)	92.3(3)	Se(21)-Sb(14)-Se(18)	94.4(2)
Sb(13)-Sb(14)-Se(19)	87.0(3)	Se(20)-Sb(14)-Se(18)	86.8(2)

E. Conclusion

$Cs_3Sb_5Se_9$ was prepared by the solvothermal reaction of Cs_2Se, Sb and Se using ethylene diamine as the solvent at a temperature of 154°C. It has a more ordered structure than previously described and it consists of selenoantimonate layers parallel to the ac-plane. The alkali atoms are present both in between these layers and also in the tunnels formed within the layers. This type of low temperature reaction technique helps in retaining these selenoantimonate building bocks, which may not survive under traditional high temperature solid state reaction conditions.

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APPENDICES

APPENDIX A. CIF FILE FOR $KPb_2Bi_5S_{10}$

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'x, -y-1/2, z'
'-x-1/2, y-1/2, z-1/2'
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_cell_length_b                  4.1103(16)
_cell_length_c                  19.315(8)
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_cell_angle_gamma               90.00
_cell_volume                    1899.6(13)
_cell_formula_units_Z           14
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_diffrn_standards_interval_time ?
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Bi5 S7 2.957(4) . ?
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Pb1 S1 2.888(3) . ?
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S5 Bi5 2.894(2) 1_545 ?
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APPENDIX B. CIF FILE FOR $K_xPb_{4-2x}Bi_{4+x}S_{10-y}Te_y$

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 _atom_type_description
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 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Te' 'Te' -0.5308  1.6751
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Pb' 'Pb' -3.3944  10.1111
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Bi' 'Bi' -4.1077  10.2566
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_symmetry_space_group_name_H-M  ?
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'-x, y+1/2, -z'
'x+1/2, -y+1/2, -z+1/2'
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'x-1/2, y, -z-1/2'
'x, -y-1/2, z'
'-x-1/2, y-1/2, z-1/2'
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_cell_length_b                  4.089(2)
_cell_length_c                  19.371(9)
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_cell_angle_beta                90.00
_cell_angle_gamma               90.00
_cell_volume                    1909.8(16)
_cell_formula_units_Z           11
_cell_measurement_temperature   293(2)
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_exptl_crystal_colour           ?
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_exptl_crystal_density_diffrn   5.881
_exptl_crystal_density_method   'not measured'
_exptl_crystal_F_000            2772
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_diffrn_radiation_source 'fine-focus sealed tube'
_diffrn_radiation_monochromator graphite
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_diffrn_standards_number ?
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_diffrn_standards_decay_% ?
_diffrn_reflns_number 20504
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_diffrn_reflns_av_sigmaI/netI 0.0392
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_diffrn_reflns_limit_k_max 5
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_reflns_threshold_expression >2sigma(I)

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_computing_cell_refinement ?
_computing_data_reduction ?
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
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_computing_publication_material ?
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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
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_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment mixed
_refine_ls_extinction_method SHELXL
_refine_ls_extinction_coef 0.00029(2)

_refine_ls_extinction_expression
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S2 S 0.63836(13) -0.2500 1.35214(17) 0.0171(7) Uani 1 2 d S . .
S3 S 0.52695(14) -0.2500 1.22427(19) 0.0234(8) Uani 1 2 d S . .
S4 S 0.27693(15) -0.2500 1.03183(19) 0.0239(8) Uani 1 2 d S . .
S5 S 0.26120(13) -0.7500 1.23040(17) 0.0185(7) Uani 1 2 d S . .
S6 S 0.64089(15) -0.7500 1.52194(18) 0.0225(7) Uani 1 2 d S . .
S7 S 0.37577(14) -0.2500 1.30733(17) 0.0195(7) Uani 1 2 d S . .

S8 S 0.42828(15) -0.2500 0.94260(19) 0.0252(8) Uani 1 2 d S . .
S9 S 0.29711(15) 0.2500 0.86703(18) 0.0214(7) Uani 1 2 d S . .
Te10 Te 0.49837(11) -0.2500 1.59079(13) 0.0272(9) Uani 0.378(4) 2 d SP . .
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Bi2 0.0217(3) 0.0188(3) 0.0199(3) 0.000 0.0014(2) 0.000
Bi3 0.0192(2) 0.0173(3) 0.0173(3) 0.000 -0.00132(19) 0.000
Bi4 0.0172(2) 0.0171(3) 0.0176(3) 0.000 0.00059(18) 0.000
Bi5 0.0220(3) 0.0203(3) 0.0331(3) 0.000 0.0020(2) 0.000
S1 0.0214(16) 0.0182(17) 0.0236(18) 0.000 -0.0003(13) 0.000
S2 0.0208(16) 0.0123(15) 0.0181(17) 0.000 0.0026(13) 0.000
S3 0.0192(16) 0.0236(19) 0.0275(19) 0.000 -0.0045(14) 0.000
S4 0.0251(18) 0.0218(18) 0.0250(19) 0.000 0.0056(14) 0.000
S5 0.0192(16) 0.0168(17) 0.0194(17) 0.000 0.0003(13) 0.000
S6 0.0268(18) 0.0211(18) 0.0197(18) 0.000 0.0034(14) 0.000
S7 0.0202(16) 0.0184(17) 0.0199(17) 0.000 -0.0012(13) 0.000
S8 0.0285(19) 0.0216(19) 0.025(2) 0.000 0.0032(15) 0.000
S9 0.0293(18) 0.0180(17) 0.0168(17) 0.000 0.0012(13) 0.000
Te10 0.0302(15) 0.0268(16) 0.0246(15) 0.000 -0.0031(10) 0.000
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
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Pb1 S8 2.936(3) 5_657 ?
Pb1 S8 2.936(3) 5_647 ?

Pb2 S9 2.875(3) 1_545 ?
Pb2 S9 2.875(3) . ?
Pb2 S5 3.022(4) 2_544 ?
Pb2 K1 4.266(5) . ?
Pb3 S2 2.671(7) . ?
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Pb3 Te10 2.769(4) 5_658 ?
Pb3 S6 2.960(5) 1_565 ?
Pb3 S6 2.960(5) . ?
Pb3 Te10 3.061(7) . ?
Pb4 S6 2.831(4) 1_565 ?
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Pb4 S2 2.855(7) . ?
Pb4 Te10 2.869(6) . ?
Pb4 Te10 2.899(5) 5_648 ?
Pb4 Te10 2.899(5) 5_658 ?
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K1 S3 3.207(4) 5_657 ?
K1 S3 3.207(4) 5_647 ?
K1 S2 3.287(5) 5_647 ?
K1 S2 3.287(5) 5_657 ?
K1 S5 3.322(6) 2_544 ?
K1 S8 3.439(7) . ?
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K1 K1 4.089(2) 1_545 ?
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Bi4 S4 2.962(3) 6_648 ?
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Bi4 K1 4.069(6) 5_647 ?
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Bi5 S3 2.820(3) . ?
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S5 Bi4 3.072(4) 6_558 ?
S5 K1 3.322(6) 2_545 ?
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S8 Bi2 2.907(3) 1_545 ?
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Te10 Pb3 2.769(4) 5_648 ?
Te10 Pb3 2.769(4) 5_658 ?
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Te10 Bi5 S7 92.35(8) 5_658 1_565 ?
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K1 S2 K1 76.94(14) 5_647 5_657 ?
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Bi2 S8 Pb1 178.63(15) 1_545 5_657 ?
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Bi2 S8 Bi1 86.53(13) 1_545 . ?
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Pb1 S8 Bi1 94.75(13) 5_647 . ?
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Bi2 S8 K1 88.93(10) 1_545 . ?
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Bi1 S9 K1 7.39(13) 1_565 1_565 ?
Bi1 S9 K1 83.70(14) . 1_565 ?

Bi2 S9 K1 100.99(13) . . ?
Pb2 S9 K1 89.33(7) . . ?
Pb2 S9 K1 154.29(16) 1_565 . ?
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Bi1 S9 K1 7.39(13) . . ?
K1 S9 K1 79.84(14) 1_565 . ?
Pb3 Te10 Pb3 95.2(2) 5_648 5_658 ?
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Bi5 Te10 Pb4 127.45(15) 5_658 5_648 ?
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Pb3 Te10 Pb4 4.82(6) 5_658 5_658 ?
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APPENDIX C. CIF FILE FOR $Na_xSr_{4-2x}Bi_{4+x}Se_{10}$

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'x, -y-1/2, z'
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Sr3 Sr 0.00994(6) -0.2500 1.10059(8) 0.0167(5) Uani 0.11 2 d SP . .
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Sr5 Sr 0.37082(17) -0.7500 1.2897(2) 0.0197(16) Uani 0.793(15) 2 d SP . .
Na5 Na 0.37082(17) -0.7500 1.2897(2) 0.0197(16) Uani 0.21 2 d SP . .
Sr6 S r 0.29675(14) -0.2500 0.88642(18) 0.0148(12) Uani 0.958(13) 2 d SP . .
Na6 Na 0.29675(14) -0.2500 0.88642(18) 0.0148(12) Uani 0.04 2 d SP . .
Sr7 Sr 0.54225(18) -1.7500 1.2283(2) 0.0212(16) Uani 0.773(14) 2 d SP . .
Na7 Na 0.54225(18) -1.7500 1.2283(2) 0.0212(16) Uani 0.23 2 d SP . .
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Se4 Se 0.24111(15) -0.7500 1.23006(18) 0.0148(8) Uani 1 2 d S . .

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Se9 Se 0.36282(15) -1.2500 1.1563(2) 0.0188(9) Uani 1 2 d S . .
Se10 Se 0.12440(15) -0.2500 1.31159(19) 0.0163(8) Uani 1 2 d S . .
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Bi2 0.0156(8) 0.0127(8) 0.0182(9) 0.000 0.0002(6) 0.000
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Na5 0.015(3) 0.011(2) 0.033(3) 0.000 0.002(2) 0.000
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Na6 0.013(2) 0.0086(18) 0.023(2) 0.000 0.0005(15) 0.000
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Na7 0.019(3) 0.018(2) 0.027(3) 0.000 -0.001(2) 0.000
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Se2 0.0145(19) 0.0145(18) 0.024(2) 0.000 -0.0052(16) 0.000
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Se4 0.0154(19) 0.0125(18) 0.017(2) 0.000 0.0012(15) 0.000
Se5 0.017(2) 0.0153(19) 0.023(2) 0.000 -0.0030(16) 0.000
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Se1 Bi3 2.931(3) 1_565 ?
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Se4 Bi2 Sr7 137.67(11) . 6_578 ?
Se1 Bi2 Sr7 90.02(9) 1_545 6_578 ?
Se1 Bi2 Sr7 47.16(9) . 6_578 ?
Sr7 Bi2 Sr7 61.59(8) 6_568 6_578 ?
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Se7 Bi3 Sr7 136.64(11) 5_547 6_578 ?
Se7 Bi3 Sr7 90.85(9) 5_557 6_578 ?
Se6 Bi3 Sr7 46.65(9) . 6_568 ?
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Se7 Bi3 Sr7 90.85(9) 5_547 6_568 ?
Se7 Bi3 Sr7 136.64(11) 5_557 6_568 ?
Sr7 Bi3 Sr7 61.81(8) 6_578 6_568 ?
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Se7 Bi3 Sr3 133.90(6) 5_557 1_545 ?
Sr7 Bi3 Sr3 120.91(4) 6_578 1_545 ?
Sr7 Bi3 Sr3 59.09(4) 6_568 1_545 ?
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Se8 Sr5 Na5 132.57(7) 2 1_545 ?
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Se6 Sr5 Na5 47.65(7) 6_648 1_545 ?
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Se9 Sr5 Na5 128.15(7) 1_565 1_545 ?
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Sr5 Sr5 Na5 180.0(2) 1_565 1_545 ?
Se8 Sr5 Na5 132.57(7) 2_545 1_565 ?
Se8 Sr5 Na5 47.43(7) 2 1_565 ?
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Se6 Sr5 Na5 132.35(7) 6_648 1_565 ?
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Se2 Sr6 Na6 90.0 . 1_565 ?
Se8 Sr6 Sr6 48.22(6) 1_545 1_545 ?
Se8 Sr6 Sr6 131.78(6) . 1_545 ?
Se3 Sr6 Sr6 130.94(6) 1_565 1_545 ?
Se3 Sr6 Sr6 49.06(6) . 1_545 ?
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Se2 Sr6 Sr6 90.0 . 1_545 ?
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Se8 Sr6 Sr6 131.78(6) 1_545 1_565 ?
Se8 Sr6 Sr6 48.22(6) . 1_565 ?
Se3 Sr6 Sr6 49.06(6) 1_565 1_565 ?
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Se2 Sr6 Sr6 90.0 . 1_565 ?
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Se8 Sr6 Na6 48.22(6) 1_545 1_545 ?
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Se3 Sr6 Na6 130.94(6) 1_565 1_545 ?
Se3 Sr6 Na6 49.06(6) . 1_545 ?
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Se2 Sr6 Na6 90.0 . 1_545 ?
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Se5 Sr7 Se1 176.85(19) . 6_638 ?
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Se6 Sr7 Bi3 40.54(9) 6_648 6_648 ?
Se10 Sr7 Bi3 89.40(10) 6_648 6_648 ?
Se10 Sr7 Bi3 135.09(15) 6_638 6_648 ?
Se1 Sr7 Bi3 45.07(8) 6_638 6_648 ?
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Se6 Sr7 Sr3 87.98(13) 6_638 6_648 ?
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Se10 Sr7 Sr3 89.40(10) 6_648 6_648 ?
Se10 Sr7 Sr3 135.09(15) 6_638 6_648 ?
Se1 Sr7 Sr3 45.07(8) 6_638 6_648 ?
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Se5 Sr7 Bi3 137.05(11) . 6_638 ?
Se6 Sr7 Bi3 40.54(9) 6_638 6_638 ?
Se6 Sr7 Bi3 87.98(13) 6_648 6_638 ?
Se10 Sr7 Bi3 135.09(15) 6_648 6_638 ?
Se10 Sr7 Bi3 89.40(10) 6_638 6_638 ?
Se1 Sr7 Bi3 45.07(8) 6_638 6_638 ?
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Se6 Sr7 Sr3 87.98(13) 6_648 6_638 ?
Se10 Sr7 Sr3 135.09(15) 6_648 6_638 ?
Se10 Sr7 Sr3 89.40(10) 6_638 6_638 ?
Se1 Sr7 Sr3 45.07(8) 6_638 6_638 ?
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Se10 Sr7 Bi2 40.23(9) 6_648 6_648 ?
Se10 Sr7 Bi2 87.30(12) 6_638 6_648 ?
Se1 Sr7 Bi2 49.89(8) 6_638 6_648 ?
Bi3 Sr7 Bi2 63.82(7) 6_648 6_648 ?
Sr3 Sr7 Bi2 63.82(7) 6_648 6_648 ?
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Sr3 Sr7 Bi2 94.86(10) 6_638 6_648 ?
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Se6 Sr7 Bi2 89.40(10) 6_638 6_638 ?
Se6 Sr7 Bi2 135.39(16) 6_648 6_638 ?
Se10 Sr7 Bi2 87.30(12) 6_648 6_638 ?
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Bi3 Se7 Sr3 87.80(12) 5_547 5_557 ?
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Bi3 Se7 Na5 90.11(11) 5_547 2_544 ?
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APPENDIX D. CIF FILE FOR $Rb_{1+x}Pb_{3-2x}Bi_{7+x}Se_{14-y}Te_y$

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Bi3 Se12 Rb1 102.07(12) . 1_545 ?
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Pb3 Se12 Rb1 161.9(7) 1_565 1_545 ?
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Pb1 Se13 Rb1 94.66(7) 1_565 1_545 ?
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APPENDIX E. CIF FILE FOR $Na_xBa_{5-2x}Bi_{6+x}Se_{14}$

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'Ba'  'Ba'  -0.3244  2.2819
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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'x, -y-1/2, z'
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
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Bi7 Se17 Na7 0.00(8) 1_545 1_545 ?
Se15 Se17 Na8 26(4) . 3_557 ?
Se16 Se17 Na8 45(4) . 3_557 ?
Se16 Se17 Na8 45(4) 4_545 3_557 ?
Bi9 Se17 Na8 89.0(16) . 3_557 ?
Bi9 Se17 Na8 89.0(16) 1_545 3_557 ?
Bi7 Se17 Na8 105(2) 1_545 3_557 ?
Na7 Se17 Na8 105(2) 1_545 3_557 ?
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_diffrn_reflns_theta_full 28.42
_diffrn_measured_fraction_theta_full 0.927
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APPENDIX F. CIF FILE FOR $Cs_3Sb_5Se_9$

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_chemical_name_common           ?
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_chemical_formula_moiety        ?
_chemical_formula_sum
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_chemical_formula_weight        412.58
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 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
'Se'  'Se'  -0.0929   2.2259
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Sb'  'Sb'  -0.5866   1.5461
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cs'  'Cs'  -0.3680   2.1192
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
_symmetry_cell_setting          ?
_symmetry_space_group_name_H-M   ?
loop_
 _symmetry_equiv_pos_as_xyz
'x, y, z'
'x, -y, z'
'x+1/2, y+1/2, z'
'x+1/2, -y+1/2, z'
'-x, -y, -z'
'-x, y, -z'
'-x+1/2, -y+1/2, -z'
'-x+1/2, y+1/2, -z'
_cell_length_a                  19.156(4)
_cell_length_b                  51.647(12)
_cell_length_c                  11.615(3)
_cell_angle_alpha               90.00
_cell_angle_beta                126.974(4)
_cell_angle_gamma               90.00
_cell_volume                    9180(4)
_cell_formula_units_Z           70
_cell_measurement_temperature   293(2)
_cell_measurement_reflns_used   ?
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_cell_measurement_theta_max     ?
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_exptl_crystal_colour           ?
_exptl_crystal_size_max         ?
_exptl_crystal_size_mid         ?
_exptl_crystal_size_min         ?
_exptl_crystal_density_meas     ?
_exptl_crystal_density_diffrn   5.224
_exptl_crystal_density_method   'not measured'
_exptl_crystal_F_000            12180
_exptl_absorpt_coefficient_mu   25.789
_exptl_absorpt_correction_type  ?
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_exptl_absorpt_process_details  ?
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_diffrn_radiation_wavelength 0.71073
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_diffrn_radiation_source 'fine-focus sealed tube'
_diffrn_radiation_monochromator graphite
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_diffrn_measurement_method ?
_diffrn_detector_area_resol_mean ?
_diffrn_standards_number ?
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_diffrn_standards_interval_time ?
_diffrn_standards_decay_% ?
_diffrn_reflns_number 38167
_diffrn_reflns_av_R_equivalents 0.0708
_diffrn_reflns_av_sigmaI/netI 0.0771
_diffrn_reflns_limit_h_min -25
_diffrn_reflns_limit_h_max 23
_diffrn_reflns_limit_k_min -66
_diffrn_reflns_limit_k_max 68
_diffrn_reflns_limit_l_min -15
_diffrn_reflns_limit_l_max 15
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_reflns_number_gt 5923
_reflns_threshold_expression >2sigma(I)
_computing_data_collection ?
_computing_cell_refinement ?
_computing_data_reduction ?
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics ?
_computing_publication_material ?
_refine_special_details
Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
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_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.1172P)^2^+508.9427P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment mixed
_refine_ls_extinction_method SHELXL
_refine_ls_extinction_coef 0.000095(8)
_refine_ls_extinction_expression
'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'
_refine_ls_number_reflns 11209

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_refine_ls_number_restraints     0
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_refine_ls_R_factor_gt           0.0818
_refine_ls_wR_factor_ref         0.2611
_refine_ls_wR_factor_gt          0.2268
_refine_ls_goodness_of_fit_ref   1.064
_refine_ls_restrained_S_all      1.064
_refine_ls_shift/su_max          1.846
_refine_ls_shift/su_mean         0.008
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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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 _atom_site_disorder_group
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Uani 1 1 d . . .
Cs2 Cs 0.23527(10) 0.10759(3) 0.23280(16) 0.0178(3)
Uani 1 1 d . . .
Cs3 Cs 0.0000 0.04075(4) 0.5000 0.0235(5) Uani 1 2 d S . .
Cs4 Cs 0.5000 0.04112(4) 0.5000 0.0245(5) Uani 1 2 d S . .
Cs5 Cs 1.01016(11) 0.14249(3) 0.75741(17) 0.0223(4)
Uani 1 1 d . . .
Cs6 Cs 0.74863(12) 0.20908(4) 0.49992(17) 0.0325(5)
Uani 1 1 d . . .
Cs7 Cs 0.51549(11) 0.14191(3) 0.76184(17) 0.0222(4)
Uani 1 1 d . . .
Sb1 Sb 0.74932(13) 0.18861(3) 0.83939(18) 0.0219(4)
Uani 1 1 d . . .
Sb2 Sb 0.0000 -0.28855(5) 0.5000 0.0333(7) Uani 1 2 d
S . .
Sb3 Sb 0.24167(9) 0.03799(3) 0.47428(14) 0.0079(3) Uani
1 1 d . . .
Sb4 Sb 0.25894(9) 0.03801(3) -0.00863(14) 0.0069(3)
Uani 1 1 d . . .
Sb5 Sb 0.11682(12) 0.0000 0.0637(2) 0.0070(4) Uani 1 2 d
S . .
Sb6 Sb 0.38329(12) 0.0000 0.8297(2) 0.0075(4) Uani 1 2 d
S . .
Sb7 Sb 0.48929(9) 0.06150(3) 0.82826(15) 0.0088(3) Uani
1 1 d . . .
Sb8 Sb -0.00958(9) 0.06105(3) 0.15100(15) 0.0091(3)
Uani 1 1 d . . .
Sb9 Sb 0.75014(13) 0.18880(3) 1.16117(19) 0.0232(4)
Uani 1 1 d . . .
Sb10 Sb 0.0000 -0.28799(5) 0.0000 0.0355(7) Uani 1 2 d
S . .
Sb11 Sb 0.5000 -0.28790(5) 1.5000 0.0332(7) Uani 1 2 d
S . .
Sb12 Sb 0.5000 -0.28783(5) 1.0000 0.0359(7) Uani 1 2 d
S . .
```

Sb13 Sb 0.6334(3) -0.24974(6) 1.8311(4) 0.0269(12) Uani 0.517(7) 1 d P . .
Sb14 Sb 0.6333(3) -0.24989(6) 1.9350(4) 0.0221(12) Uani 0.483(7) 1 d P . .
Se1 Se 0.3801(2) 0.0000 0.1134(3) 0.0106(6) Uani 1 2 d S . .
Se2 Se 0.1217(2) 0.0000 0.3569(3) 0.0109(6) Uani 1 2 d S . .
Se3 Se 0.22902(14) 0.03759(4) 0.1877(2) 0.0084(4) Uani 1 1 d . . .
Se4 Se 0.1165(2) 0.0000 -0.1620(3) 0.0077(6) Uani 1 2 d S . .
Se5 Se 0.3832(2) 0.0000 0.6024(3) 0.0079(6) Uani 1 2 d S . .
Se6 Se 0.75178(15) 0.15328(5) 1.0030(2) 0.0182(6) Uani 1 1 d . . .
Se7 Se 0.12262(16) 0.07729(4) 0.4001(2) 0.0138(5) Uani 1 1 d . . .
Se8 Se 0.37660(16) 0.07713(4) 0.1546(3) 0.0161(5) Uani 1 1 d . . .
Se9 Se 0.0000 0.09650(6) 0.0000 0.0134(7) Uani 1 2 d S . .
Se10 Se 0.12325(16) 0.08230(4) -0.1620(3) 0.0136(5) Uani 1 1 d . . .
Se11 Se 0.37754(16) 0.08364(4) 0.5939(2) 0.0133(5) Uani 1 1 d . . .
Se12 Se 0.87346(18) 0.17070(6) 0.8442(3) 0.0261(6) Uani 1 1 d . . .
Se13 Se 0.5000 0.09674(6) 1.0000 0.0148(7) Uani 1 2 d S . .
Se14 Se 0.87169(19) 0.16998(6) 1.4034(3) 0.0300(7) Uani 1 1 d . . .
Se15 Se 0.62569(18) 0.17056(6) 1.1559(3) 0.0261(6) Uani 1 1 d . . .
Se16 Se 0.62761(19) 0.16915(6) 0.5991(3) 0.0294(7) Uani 1 1 d . . .
Se17 Se 0.27087(14) 0.03767(4) 0.7297(2) 0.0085(4) Uani 1 1 d . . .
Se18 Se -0.0191(4) -0.28805(10) 0.2719(6) 0.0209(18) Uani 0.486(11) 1 d P . .
Se19 Se -0.0180(4) -0.28777(10) 0.1904(6) 0.0251(18) Uani 0.514(11) 1 d P . .
Se20 Se 0.4809(4) -0.28722(10) 1.2712(6) 0.0216(18) Uani 0.486(11) 1 d P . .
Se21 Se 0.4819(4) -0.28738(10) 1.1909(6) 0.0254(18) Uani 0.514(11) 1 d P . .
Se22 Se 0.6315(8) -0.25027(14) 1.611(5) 0.024(5) Uani 0.67(12) 1 d P . .
Se23 Se 0.6279(11) -0.2489(5) 1.651(5) 0.010(6) Uani 0.33(12) 1 d P . .
Se24 Se 0.6334(9) -0.2497(4) 1.162(5) 0.016(4) Uani 0.44(12) 1 d P . .
Se25 Se 0.6313(7) -0.2500(2) 1.115(6) 0.020(6) Uani 0.56(12) 1 d P . .
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_atom_site_aniso_U_12

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Cs2 0.0150(8) 0.0151(7) 0.0171(7) 0.0013(6) 0.0063(6) 0.0007(6)
Cs3 0.0333(13) 0.0196(12) 0.0151(10) 0.000 0.0133(10) 0.000
Cs4 0.0368(14) 0.0195(12) 0.0341(13) 0.000 0.0302(12) 0.000
Cs5 0.0212(9) 0.0163(8) 0.0265(9) 0.0032(6) 0.0129(7) 0.0027(6)
Cs6 0.0422(13) 0.0325(11) 0.0288(10) -0.0015(6) 0.0245(10) -0.0010(7)
Cs7 0.0232(9) 0.0145(8) 0.0259(8) 0.0016(6) 0.0132(7) -0.0010(6)
Sb1 0.0343(11) 0.0166(8) 0.0216(9) 0.0007(6) 0.0203(8) 0.0020(7)
Sb2 0.0260(15) 0.0176(13) 0.065(2) 0.000 0.0316(15) 0.000
Sb3 0.0066(7) 0.0123(7) 0.0000(5) -0.0004(5) -0.0006(5) -0.0004(5)
Sb4 0.0060(7) 0.0107(7) 0.0098(7) 0.0004(5) 0.0078(6) -0.0009(5)
Sb5 0.0011(9) 0.0076(10) 0.0104(9) 0.000 0.0024(8) 0.000
Sb6 0.0013(9) 0.0063(9) 0.0061(9) 0.000 -0.0024(8) 0.000
Sb7 0.0027(6) 0.0102(7) 0.0091(6) 0.0002(5) 0.0012(5) 0.0007(5)
Sb8 0.0036(7) 0.0101(7) 0.0098(7) -0.0010(5) 0.0019(6) -0.0007(5)
Sb9 0.0361(11) 0.0185(9) 0.0208(9) -0.0015(7) 0.0202(8) -0.0030(8)
Sb10 0.0332(16) 0.0162(13) 0.0235(13) 0.000 -0.0007(12) 0.000
Sb11 0.0300(15) 0.0168(13) 0.064(2) 0.000 0.0345(16) 0.000
Sb12 0.0348(16) 0.0168(13) 0.0228(13) 0.000 -0.0003(12) 0.000
Sb13 0.022(2) 0.027(2) 0.021(2) -0.0056(12) 0.0073(17) -0.0016(13)
Sb14 0.019(2) 0.022(2) 0.028(2) 0.0068(13) 0.0160(19) 0.0014(13)
Se1 0.0081(15) 0.0133(15) 0.0088(14) 0.000 0.0042(13) 0.000
Se2 0.0079(15) 0.0147(15) 0.0064(14) 0.000 0.0024(13) 0.000
Se3 0.0130(11) 0.0030(9) 0.0098(10) -0.0034(7) 0.0070(9) -0.0050(8)
Se4 0.0033(14) 0.0166(16) 0.0000(13) 0.000 -0.0007(11) 0.000
Se5 0.0026(14) 0.0197(16) 0.0056(14) 0.000 0.0048(12) 0.000
Se6 0.0186(15) 0.0188(14) 0.0171(13) -0.0001(8) 0.0106(12) 0.0002(9)
Se7 0.0150(12) 0.0077(10) 0.0113(11) -0.0032(8) 0.0039(10) 0.0045(8)
Se8 0.0158(13) 0.0126(11) 0.0244(13) -0.0080(9) 0.0145(11) -0.0056(9)
Se9 0.0148(17) 0.0117(16) 0.0145(16) 0.000 0.0092(14) 0.000
Se10 0.0141(12) 0.0091(11) 0.0209(12) 0.0026(8) 0.0122(11) 0.0013(9)

Se11 0.0128(12) 0.0114(11) 0.0096(11) 0.0018(8) 0.0035(9) -0.0004(8)
Se12 0.0147(14) 0.0322(15) 0.0309(15) -0.0027(12) 0.0135(13) -0.0024(11)
Se13 0.0214(19) 0.0110(16) 0.0141(16) 0.000 0.0118(15) 0.000
Se14 0.0170(14) 0.0442(18) 0.0171(14) -0.0021(12) 0.0041(12) -0.0013(12)
Se15 0.0155(14) 0.0314(15) 0.0315(15) 0.0037(12) 0.0143(13) 0.0055(11)
Se16 0.0164(14) 0.0428(17) 0.0160(13) 0.0015(11) 0.0027(12) -0.0014(12)
Se17 0.0136(11) 0.0048(10) 0.0083(9) 0.0016(7) 0.0072(9) 0.0042(8)
Se18 0.031(3) 0.021(3) 0.016(3) 0.0005(19) 0.017(2) 0.004(2)
Se19 0.034(3) 0.023(3) 0.027(3) 0.008(2) 0.023(3) 0.007(2)
Se20 0.034(3) 0.019(3) 0.015(3) 0.0025(19) 0.016(2) 0.000(2)
Se21 0.037(3) 0.025(3) 0.020(3) -0.004(2) 0.020(3) 0.002(2)
Se22 0.018(3) 0.014(2) 0.029(9) -0.007(2) 0.009(4) 0.0003(15)
Se23 0.008(5) 0.016(5) 0.009(10) -0.004(4) 0.006(4) 0.000(3)
Se24 0.018(4) 0.016(4) 0.015(9) 0.007(3) 0.010(4) 0.002(2)
Se25 0.008(3) 0.017(3) 0.026(13) -0.004(3) 0.006(4) -0.0010(16)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
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Cs1 Se15 3.654(3) 6_657 ?
Cs1 Se17 3.657(3) . ?
Cs1 Se13 3.6633(19) . ?
Cs1 Se7 3.673(3) . ?
Cs1 Se6 3.790(3) 6_657 ?
Cs1 Se14 3.824(3) 6_657 ?
Cs1 Se11 3.853(3) . ?
Cs1 Se8 4.073(3) 1_556 ?
Cs1 Sb9 4.323(2) 6_657 ?
Cs1 Sb7 4.560(2) . ?
Cs1 Cs7 4.878(2) 6_657 ?
Cs2 Se11 3.577(3) . ?
Cs2 Se3 3.645(3) . ?
Cs2 Se9 3.6458(19) . ?
Cs2 Se12 3.677(3) 6_656 ?
Cs2 Se8 3.686(3) . ?
Cs2 Se6 3.735(3) 6_656 ?
Cs2 Se16 3.827(3) 6_656 ?

Cs2 Se10 3.937(3) . ?
Cs2 Se7 3.991(3) . ?
Cs2 Sb1 4.312(2) 6_656 ?
Cs2 Sb3 4.516(2) . ?
Cs2 Cs5 4.867(2) 1_454 ?
Cs3 Se7 3.701(3) 6_556 ?
Cs3 Se7 3.701(3) . ?
Cs3 Se4 3.780(3) 5 ?
Cs3 Se4 3.780(3) 1_556 ?
Cs3 Se10 3.800(3) 1_556 ?
Cs3 Se10 3.800(3) 6 ?
Cs3 Sb8 4.0827(18) 6_556 ?
Cs3 Sb8 4.0827(18) . ?
Cs3 Se2 4.159(3) 5_556 ?
Cs3 Se2 4.159(3) . ?
Cs3 Se17 4.173(2) 6_556 ?
Cs3 Se17 4.173(2) . ?
Cs4 Se8 3.706(3) 6_656 ?
Cs4 Se8 3.706(3) . ?
Cs4 Se5 3.758(3) . ?
Cs4 Se5 3.758(3) 5_656 ?
Cs4 Se11 3.820(3) 6_656 ?
Cs4 Se11 3.820(3) . ?
Cs4 Sb7 4.0777(17) . ?
Cs4 Sb7 4.0777(17) 6_656 ?
Cs4 Se3 4.182(2) . ?
Cs4 Se3 4.182(2) 6_656 ?
Cs4 Se1 4.188(3) . ?
Cs4 Se1 4.188(3) 5_656 ?
Cs5 Se10 3.577(3) 1_656 ?
Cs5 Se14 3.583(3) 1_554 ?
Cs5 Se12 3.629(3) . ?
Cs5 Se20 3.659(6) 8_657 ?
Cs5 Se21 3.660(6) 8_657 ?
Cs5 Se6 3.686(3) 6_757 ?
Cs5 Se9 3.779(3) 1_656 ?
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Cs5 Se14 3.964(4) 6_757 ?
Cs5 Se12 4.012(3) 6_757 ?
Cs5 Sb8 4.340(2) 6_656 ?
Cs5 Cs2 4.867(2) 1_656 ?
Cs6 Se14 3.751(4) 1_554 ?
Cs6 Se12 3.759(3) . ?
Cs6 Se15 3.762(3) 1_554 ?
Cs6 Se16 3.764(4) . ?
Cs6 Se24 3.78(5) 2_554 ?
Cs6 Se24 3.79(3) 8_657 ?
Cs6 Se22 3.84(4) 2_554 ?
Cs6 Se22 3.86(5) 8_657 ?
Cs6 Sb1 4.075(2) . ?
Cs6 Sb9 4.088(2) 1_554 ?
Cs6 Se19 4.118(6) 3 ?
Cs6 Se18 4.124(6) 3 ?
Cs7 Se16 3.639(3) 6_656 ?
Cs7 Se18 3.644(5) 8_556 ?
Cs7 Se6 3.664(3) . ?
Cs7 Se19 3.670(5) 8_556 ?
Cs7 Se15 3.677(3) 6_657 ?
Cs7 Se11 3.694(3) . ?
Cs7 Se8 3.741(3) 6_656 ?
Cs7 Se13 3.764(3) . ?
Cs7 Se16 3.879(4) . ?

Cs7 Se15 3.996(3) . ?
Cs7 Sb7 4.308(2) . ?
Cs7 Cs1 4.878(2) 6_657 ?
Sb1 Se12 2.521(3) . ?
Sb1 Se16 2.531(3) . ?
Sb1 Se6 2.614(3) . ?
Sb1 Cs2 4.312(2) 6_656 ?
Sb2 Se18 2.447(6) 6_556 ?
Sb2 Se18 2.447(6) . ?
Sb2 Se23 2.765(19) 4_444 ?
Sb2 Se23 2.765(19) 7_547 ?
Sb2 Se22 2.849(14) 4_444 ?
Sb2 Se22 2.849(14) 7_547 ?
Sb2 Se16 2.948(4) 8_546 ?
Sb2 Se16 2.948(4) 3_445 ?
Sb3 Se17 2.668(2) . ?
Sb3 Se2 2.687(3) . ?
Sb3 Se7 2.775(3) . ?
Sb3 Se5 2.926(3) . ?
Sb4 Se3 2.665(2) . ?
Sb4 Se1 2.700(3) . ?
Sb4 Se8 2.760(3) . ?
Sb4 Se4 2.936(3) . ?
Sb5 Se3 2.596(2) . ?
Sb5 Se3 2.596(2) 2 ?
Sb5 Se4 2.617(3) . ?
Sb6 Se17 2.601(2) 2 ?
Sb6 Se17 2.601(2) . ?
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Se21 Cs5 Sb8 157.65(10) 8_657 6_656 ?
Se6 Cs5 Sb8 98.39(6) 6_757 6_656 ?
Se9 Cs5 Sb8 36.79(4) 1_656 6_656 ?
Se7 Cs5 Sb8 35.94(4) 6_656 6_656 ?
Se14 Cs5 Sb8 123.30(6) 6_757 6_656 ?
Se12 Cs5 Sb8 98.67(6) 6_757 6_656 ?
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Se14 Cs5 Cs2 171.05(7) 1_554 1_656 ?
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Se21 Cs5 Cs2 105.03(10) 8_657 1_656 ?
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Se7 Cs5 Cs2 95.41(5) 6_656 1_656 ?
Se14 Cs5 Cs2 107.45(6) 6_757 1_656 ?
Se12 Cs5 Cs2 47.73(5) 6_757 1_656 ?
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Se14 Cs6 Se16 114.20(9) 1_554 . ?

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Se22 Cs6 Se22 113.4(9) 2_554 8_657 ?
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Se18 Cs7 Cs1 114.83(10) 8_556 6_657 ?
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Se18 Sb2 Se23 78.8(13) . 7_547 ?
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Se7 Sb3 Se5 170.24(9) . . ?
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Se11 Sb7 Se13 97.75(8) . . ?
Se8 Sb7 Se13 96.06(8) 6_656 . ?
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Se8 Sb7 Cs4 62.99(6) 6_656 . ?
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Se8 Sb7 Cs7 59.68(6) 6_656 . ?
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Se11 Sb7 Cs1 57.65(7) . . ?
Se8 Sb7 Cs1 129.63(7) 6_656 . ?
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Cs7 Sb7 Cs1 70.04(4) . . ?
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Se25 Sb10 Se15 92.8(2) 7_546 8_546 ?
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Se21 Sb12 Se12 87.82(15) 6_657 3_445 ?
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Se25 Sb12 Se12 92.5(4) 6_657 3_445 ?
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Se21 Sb12 Se12 92.97(15) 6_657 8_647 ?
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Se24 Sb12 Se12 176.1(3) 6_657 8_647 ?
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Se23 Sb13 Se19 109.8(8) . 7_547 ?
Se22 Sb13 Se19 112.4(3) . 7_547 ?
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Sb13 Sb14 Se19 87.0(3) . 7_547 ?
Se25 Sb14 Se19 92.3(4) 1_556 7_547 ?
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Cs4 Se1 Cs4 60.94(7) . 5_656 ?
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Sb4 Se3 Cs2 96.30(7) . . ?
Sb5 Se3 Cs4 134.06(8) . . ?
Sb4 Se3 Cs4 87.03(6) . . ?
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Sb4 Se4 Cs3 90.61(5) . 1_554 ?
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Sb3 Se5 Cs4 139.81(9) 2 . ?
Sb3 Se5 Cs4 90.36(5) . . ?
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Sb9 Se6 Cs5 96.21(8) . 6_757 ?
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Cs7 Se6 Cs5 162.07(9) . 6_757 ?
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Cs7 Se6 Cs2 86.24(6) . 6_656 ?
Cs5 Se6 Cs2 81.97(6) 6_757 6_656 ?
Sb9 Se6 Cs1 82.79(7) . 6_657 ?
Sb1 Se6 Cs1 172.45(10) . 6_657 ?
Cs7 Se6 Cs1 81.72(6) . 6_657 ?
Cs5 Se6 Cs1 87.73(6) 6_757 6_657 ?
Cs2 Se6 Cs1 102.76(7) 6_656 6_657 ?
Sb8 Se7 Sb3 100.31(8) . . ?
Sb8 Se7 Cs1 164.47(10) . . ?
Sb3 Se7 Cs1 93.20(7) . . ?
Sb8 Se7 Cs3 78.82(7) . . ?
Sb3 Se7 Cs3 95.03(7) . . ?
Cs1 Se7 Cs3 92.50(6) . . ?
Sb8 Se7 Cs5 80.41(7) . 6_656 ?
Sb3 Se7 Cs5 161.57(9) . 6_656 ?
Cs1 Se7 Cs5 89.19(6) . 6_656 ?
Cs3 Se7 Cs5 103.12(7) . 6_656 ?
Sb8 Se7 Cs2 91.99(8) . . ?
Sb3 Se7 Cs2 81.60(7) . . ?
Cs1 Se7 Cs2 97.56(7) . . ?
Cs3 Se7 Cs2 169.54(7) . . ?
Cs5 Se7 Cs2 79.97(6) 6_656 . ?
Sb7 Se8 Sb4 100.82(9) 6_656 . ?
Sb7 Se8 Cs2 163.31(10) 6_656 . ?
Sb4 Se8 Cs2 93.69(8) . . ?
Sb7 Se8 Cs4 78.61(7) 6_656 . ?
Sb4 Se8 Cs4 95.84(8) . . ?
Cs2 Se8 Cs4 91.84(6) . . ?
Sb7 Se8 Cs7 83.73(7) 6_656 6_656 ?
Sb4 Se8 Cs7 158.21(10) . 6_656 ?
Cs2 Se8 Cs7 85.84(6) . 6_656 ?
Cs4 Se8 Cs7 105.95(7) . 6_656 ?
Sb7 Se8 Cs1 91.94(8) 6_656 1_554 ?
Sb4 Se8 Cs1 81.41(7) . 1_554 ?
Cs2 Se8 Cs1 98.39(7) . 1_554 ?
Cs4 Se8 Cs1 169.54(7) . 1_554 ?
Cs7 Se8 Cs1 77.12(6) 6_656 1_554 ?
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Cs2 Se9 Cs5 86.75(5) 6 1_454 ?
Cs5 Se9 Cs5 102.11(9) 6_656 1_454 ?
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Sb8 Se10 Cs3 77.68(7) 6 1_554 ?
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Cs7 Se13 Cs7 103.40(9) 6_657 . ?
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Cs6 Se14 Cs1 103.31(8) 1_556 6_657 ?
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Cs5 Se14 Cs5 99.23(8) 1_556 6_757 ?
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Cs1 Se14 Cs5 83.39(7) 6_657 6_757 ?
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Sb9 Se15 Cs7 166.70(12) . 6_657 ?
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