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SYNTHESIS OF THIOARSENATE COMPOUNDS FROM THE REACTIONS OF
MAIN-GROUP, TRANSITION AND RARE-EARTH METALS IN ALKALI
POLYTHIOARSENATE FLUXES

By

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ABSTRACT

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The use of alkali metal polychalcophosphate fluxes as media for synthesizing Group 15 chalcogenides has resulted in the discovery of a large number of new compounds that feature an astonishing variety of structures and chalcophosphate anion building blocks. It was therefore appropriate to question how the corresponding chalcoarsenate fluxes would behave under similar conditions. Though P and As belong to the same group, there seems to be a considerable divide in their reactivity in a chalcogen environment. Thus P mostly exists in the +4 and +5 oxidation state, whereas As usually exhibits the +3 and the +5 oxidation states with the former being predominant. Therefore, we expected the chalcoarsenate anion, $As_xQ_y^{n-}$, to be different from the chalcophosphate anions formed under similar conditions. An interesting structural aspect of As is the tendency to stereochemically express its lone pair of electrons. Another interesting property of arsenic chalcogenides is the propensity to form glasses. We therefore set out on a systematic investigation of main-group, transition and rare-earth metals in alkali polythioarsenate fluxes.

In this dissertation, the syntheses, structures, and properties of the various compounds that we obtained during the course of this research are described. The reaction of the

main-group metals Sn, Pb, In, and Bi resulted in the isolation of compounds containing molecular anions such as $\text{Cs}_2\text{SnAs}_2\text{S}_9$, $\text{A}_6\text{InAs}_3\text{S}_{13}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) and $\text{A}_9\text{BiAs}_4\text{S}_{16}$ ($\text{A} = \text{K}, \text{Rb}$), the one-dimensional compounds NaSnAsS_4 , ASnAsS_5 ($\text{A} = \text{K}, \text{Rb}$) and $\text{A}_4\text{PbAs}_2\text{S}_8$ ($\text{A} = \text{Rb}, \text{Cs}$), the two-dimensional compounds $\text{A}_2\text{SnAs}_2\text{S}_6$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$) and APbAsS_4 ($\text{A} = \text{Rb}, \text{Cs}$). The transition metals Mn, Cd, Cu, Ag and Au, gave $\text{A}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), $\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$, $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$, $\text{Cs}_2\text{CuAsS}_5$ and $\text{Cs}_2\text{AgAsS}_5$, which contain molecular anions, and the one-dimensional compound $\text{Cs}_2\text{AuAsS}_4$. Finally, we sought to study the reactivity of Eu with Ag and Cu as the counter-cations. This resulted in the formation of the three-dimensional compounds AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$. These compounds feature thioarsenate building blocks such as the pyramidal AsS_3^{3-} , AsS_4^{3-} , and AsS_5^{3-} and the tetrahedral AsS_4^{3-} and AsS_5^{3-} anions. $\text{Cs}_2\text{SnAs}_2\text{S}_9$, $\text{Rb}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ exhibit reversible glass to crystal transition. These compounds melt on heating; however, upon cooling, they do not recrystallize and form glasses. The glasses convert to the crystalline form on heating.

Our results suggest that the polythioarsenate fluxes are as interesting and promising as the chalcophosphate fluxes and provide foundation for further exploratory studies.

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LIST OF ABBREVIATIONS

DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectroscopy
SEM	Scanning Electron Microscope
SQUID	Superconducting Quantum Interference Device

Chapter 1

An Introduction to the Polythioarsenate Flux Method for the Synthesis of Complex Metal Thioarsenate Compounds

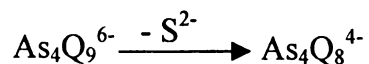
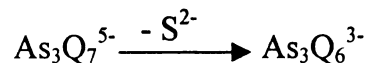
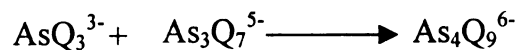
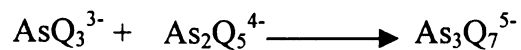
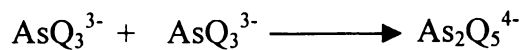
A. Introduction

Thioarsenates belong to the vast class of naturally occurring minerals called sulfosalts. These minerals exhibit an astounding variety of structures and some have recently been shown to have interesting optical properties.¹ For example, Ag_3AsS_3 and Ag_3AsSe_3 are well known for their non-linear optical properties.² $\text{Pb}_7\text{As}_9\text{S}_{20}$ and $\text{Pb}_8\text{As}_8\text{S}_{20}$ have been reported to exhibit strong piezoelectricity.³ Tl_3AsS_4 has shown promise as a photoacoustic material.⁴ The sulfosalts can be denoted by the formula MAs_xS_y or $\text{MM}'\text{As}_x\text{S}_y$, where M and M' are metals. In the case of the naturally occurring minerals, M and M' are both soft metals like Pb, Tl, Ag, Hg etc. Some examples are $\text{TlHgAs}_3\text{S}_6$,⁵ $\text{TlPbAs}_5\text{S}_9$,⁶ $\text{TlPbAs}_3\text{S}_6$,⁷ TlHgAsS_3 ,⁸ $\text{Tl}_2\text{Sb}_6\text{As}_4\text{S}_{16}$,⁹ AgPbAsS_3 ,¹⁰ $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$,¹¹ PbAs_2S_4 ,¹² $\text{Pb}_9\text{As}_{13}\text{S}_{28}$,¹³ $\text{Pb}_5\text{As}_9\text{S}_{18}$ etc.¹⁴ Therefore the bonding in these minerals is primarily covalent. It is possible to substitute one of the metals by an alkali or alkaline earth metal leading to ionic bonding in the lattice and subsequently a different structure. The large class of arsenic sulfosalts mainly arises from the strong tendency of As^{3+} to stereochemically express its lone pair. Another advantage of this expression is that the resulting compounds may be non-centrosymmetric. The structural variety found in naturally occurring sulfosalts, is a major driving force in the quest to further explore synthetic multinary chalcogenates.

Conventionally, solid state materials were made by the ceramic route which involved heating the reactants to a high temperature ($>600^{\circ}\text{C}$). High temperatures were required because solid state reactions are usually diffusion limited and in order for the reactants to diffuse sufficiently they have to be melted. Under such conditions the resulting products tend to be the thermodynamically stable simple binary or ternary phases with building blocks usually limited to the atoms themselves. In order to avoid these thermodynamic phases and pursue more complex ones, it was necessary to overcome the diffusion control barrier. Low temperature techniques such as the solventothermal method¹⁵ and the molten flux method¹⁶ sought to present mild conditions in which complex building blocks such as chains and rings remain intact for incorporation into the final structure. The advent of these methods gave a big fillip to synthetic inorganic solid state chemistry.

B. Solventothermal Pathway

Over the last decade, numerous ternary and quaternary chalcoarsenate compounds have been reported.^{15, 17} These compounds, like their natural counterparts, have shown astounding structural diversity. Most of these compounds have been prepared by solventothermal techniques that tend to mimic the conditions in which sulfosalts were made in the earth's crust (i.e. hydrothermally). The structural variation found in the chalcoarsenates made by this method derives from the condensation ability of AsQ_3^{3-} to form novel anionic units. Scheme 1 depicts the condensation reactions of the AsQ_3^{3-} anion:



Scheme 1

Each of these ligands differs in its mode of coordination to the metal leading to isolation of different structures. In these reactions, the cation not only serves to counterbalance the negative charge but also acts as a structure-directing agent. The complexity of the chalcoarsenate ligands and their elaborate bonding modes can be observed in the compounds $(\text{Ph}_4\text{P})_2\text{Hg}_2\text{As}_4\text{S}_9$ ¹⁸ and $\text{RbAg}_2\text{As}_3\text{Se}_6$.¹⁹

$(\text{Ph}_4\text{P})_2\text{Hg}_2\text{As}_4\text{S}_9$ was obtained by reacting HgCl_2 , K_3AsS_3 and Ph_4PBr in 0.3 mL water at 130°C for a week. In this compound, trigonal planar Hg is coordinated by $[\text{As}_4\text{S}_9]^{6-}$ ligands to form chains running along the a-axis, see Figure 1a. The $[\text{As}_4\text{S}_9]^{6-}$ ligand is formed by the corner sharing of 4 $[\text{AsS}_3]^{3-}$ units as shown in Figure 1b.

$\text{RbAg}_2\text{As}_3\text{Se}_6$ was synthesized by heating RbCl , AgBF_4 and Li_3AsSe_3 in methanol at 130°C for 2h. This compound features a very complicated three-dimensional framework formed by distorted trigonal planar Ag^+ cations and $[\text{As}_3\text{Se}_6]^{3-}$ rings. The As_3Se_6 ring

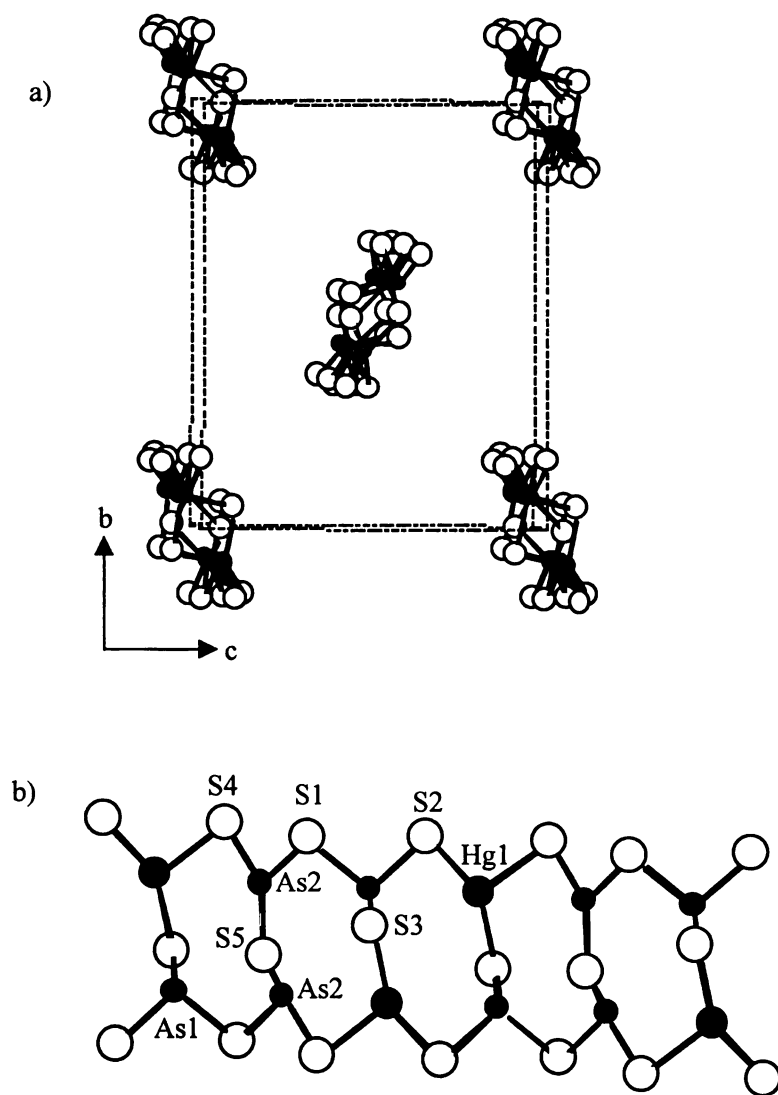


Figure 1. a) Unit cell of $(\text{Ph}_4\text{P})_2\text{Hg}_2\text{As}_4\text{S}_9$ looking down the a-axis with the organic cations removed. b) Single constituent chain of the structure consisting of the tetramer $(\text{As}_4\text{S}_9)^{6-}$ coordinating to trigonal planar Hg.

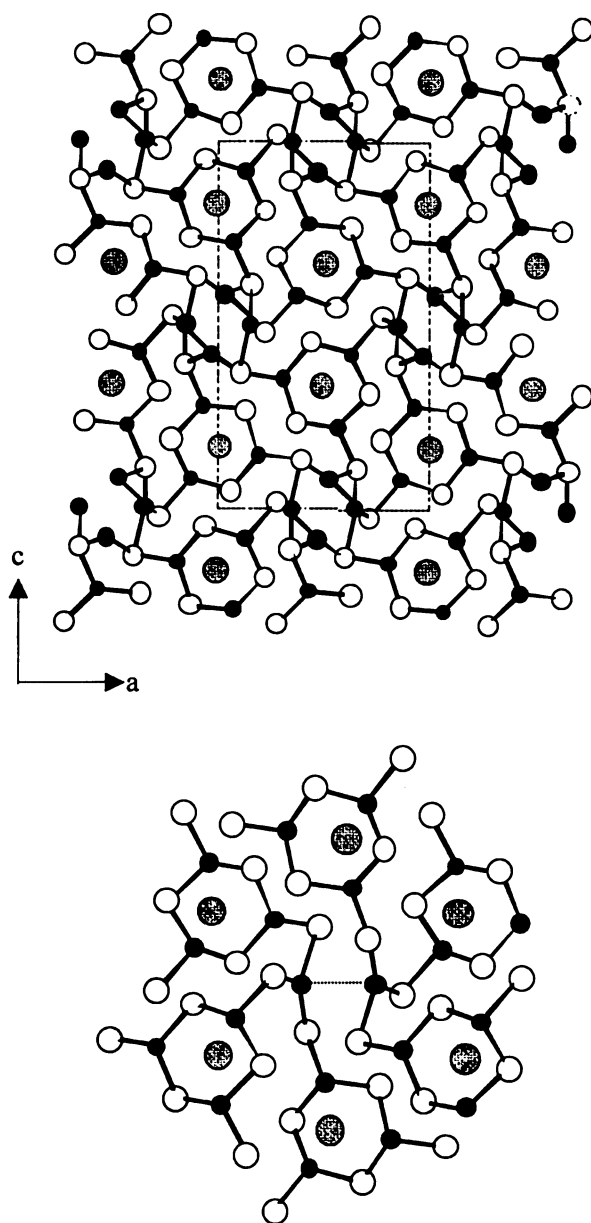


Figure 2. a) Unit cell of $\text{RbAg}_2\text{As}_3\text{Se}_6$ down the b -axis showing the three dimensional framework of the compound. b) Coordination of the cyclic $(\text{As}_3\text{Se}_6)^{3-}$ ligand and short range Ag-Ag interactions.

consists of 3 As atoms bridged by 3 Se atoms in a chair conformation. The $[\text{As}_3\text{Se}_6]^{3-}$ ring can be formally obtained by the condensation of 3 $[\text{AsS}_3]^{3-}$ anions followed by a ring closure reaction and elimination of Se^{2-} . Figure 2a shows the three-dimensional framework of the compound. The extended coordination of Ag and As_3Se_6 is shown in Figure 2b.

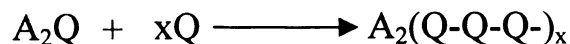
There are several other chalcoarsenates that have been made solvothermally and that showcase the remarkable structural diversity of these compounds. Some of them include $[(n\text{-Bu})_4\text{N}]_2\text{MoAs}_2\text{Se}_{10}$,²⁰ featuring the molecular anion $[\text{Mo}(\text{AsSe}_5)_2]^{2-}$ consisting of an octahedral Mo coordinated by two pyramidal AsSe_5^{3-} ligands; KCu_2AsS_3 ²¹ consists of a complex layered structure formed by tetrahedral Cu bound by pyramidal AsS_3^{3-} units; the molecule $(\text{Ph}_4\text{P})_4[\text{Pd}_7\text{As}_{10}\text{S}_{22}]$ ²² presents two kinds of thioarsenate anions viz., $\text{As}_2\text{S}_5^{4-}$ and $\text{As}_3\text{S}_6^{5-}$ that bind to the Pd atoms through S and As; $(\text{Ph}_4\text{P})_2\text{Pt}(\text{As}_3\text{S}_5)_2$ ²³ is molecular cage compound with an octahedral Pt^{4+} bound by cyclic $\text{As}_3\text{S}_5^{3-}$ ligands.

C. The Molten Flux Method

C.1 The Polychalcogenide Flux

The application of the alkali polychalcogenide flux to synthesize new compounds has contributed to an exponential increase in the number of ternary and quaternary chalcogenides.²⁴ This method is also called the reactive flux method because it supplies the chalcogenide for incorporation into the final product. The flux acts like a solvent and allows for better diffusion of the reactants. However unlike the solventothermal method, where the temperature range is limited due to solvent loss, the flux method readily allows

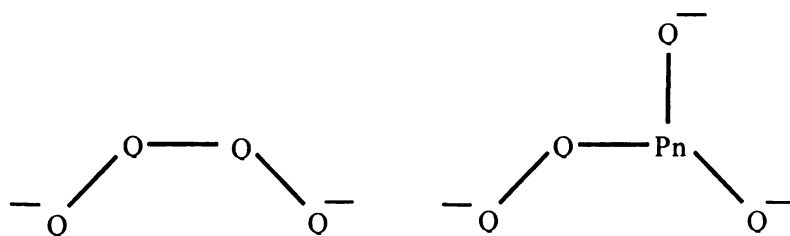
for a wide variation in the temperature (200-700°C). The flux also acts as a mineralizer and helps in crystal growth. The polychalcogenide flux is formed in the reaction:



In this reaction, A is an alkali, alkaline earth metal or even an organic cation.²⁵ Q is the chalcogen S, Se or Te. As shown in the reaction, an alkali chalcogenide reacts with excess of chalcogen to form polychalcogenide chains of different lengths. The length of the chain is a function of the amount of alkali chalcogenide (also known as the flux basicity) present. The greater the flux basicity the shorter are the chains. In other words, the more the amount of A_2Q , the more the basicity of the flux and less the number of Q-Q bonds. At lower concentrations of A_2Q , there will be more Q-Q bonds and the flux will have a greater oxidizing power. The inner chalcogen atoms of the chain have a formal oxidation state of 0. Therefore, they can oxidize the metals present. In this process, they get reduced thereby breaking the chain. The metal ion is then coordinated by the Q_x^{2-} fragments present. The other superb feature of this method is that it can be applied to any metal, thereby allowing us to study trends in the periodic table. Using this method, a plethora of compounds containing various metal ions have been prepared like $Cs_3Ti_3Te_{11}$, Cs_2SnS_{14} , $K_2Hg_3S_4$, $CsBiS_2$ etc.²⁶

C.2 The Polychalcophosphate Flux

The idea of using a polychalcophosphate flux basically involved the additional bonding possibilities that a group 15 element would offer. For example,



Scheme 2

This idea led to the discovery of KBiP_2S_7 .²⁷ Since then, we and others have advanced this field to include numerous new quaternary chalcophosphate phases that display novel P_xQ_y ligands in various binding modes and structures of different dimensionalities.²⁸

The polychalcophosphate flux is more basic than a polychalcogenide flux and is generated by the fusion of A_2Q , P_2Q_5 and excess Q. A more appropriate description of this flux would be a polychalcogenide flux in which various $\text{P}_x\text{Q}_y^{n-}$ anions are solubilized.

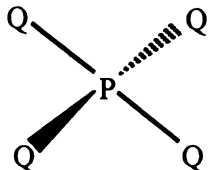
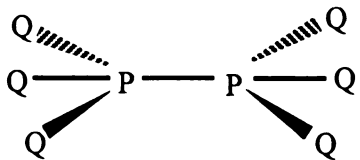
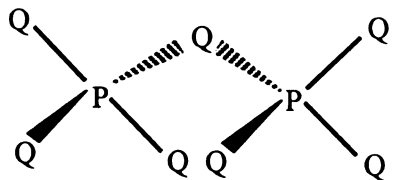
The nature of the chalcophosphate ligand usually depends on the basicity of the flux and there is now a fair understanding of the conditions that promote a certain kind of chalcophosphate ligand. Table 1a gives a list of chalcophosphate ligands and the synthetic conditions that give rise to them. Each of these ligands exhibits different modes of connectivity to the metal giving rise to solid state compounds having molecular, chains, layers or framework structures. Chalcophosphate ligands other than those mentioned in the table such as $\text{P}_2\text{S}_6^{2-}$,³⁴ $\text{P}_2\text{S}_7^{2-}$,³⁵ $\text{P}_2\text{Se}_8^{2-}$,³⁶ etc have also been reported. The structures of these ligands are shown in Table 1b.

Table 1a. Reaction conditions leading to the different chalcophosphate ligands

Reactant ratio $A_2Se/M/P_2Se_5/Se$	Chalcophosphate anion $P_xSe_y^{n-}$
1-2/1/1-3/10	$P_2Se_6^{4-} (P^{4+})^{29}$
3-4/1/1.5-2/10	$PSe_4^{3-}, PSe_5^{3-}, P_2Se_8^{4-} (P^{5+})^{30}$
2/1/2-3/10	$P_2Se_7^{4-}, P_2Se_9^{4-} (P^{5+})^{31}$

$A_2S/M/P_2S_5/S$	$P_xS_y^{n-}$
2-4/1/1.5-3/4-12	$PS_4^{3-}, P_2S_7^{4-}, P_2S_9^{4-} (P^{5+})^{32}$
2/1/3/4	$P_2S_6^{4-} (P^{4+})^{33}$

Table 1b. Structures of various reported chalcophosphate ligands

P_xQ_y ligands	Structure
PQ_4^{3-} 30a, 32a	 A central phosphorus atom (P) is bonded to four chalcogen atoms (Q) in a tetrahedral arrangement. Two bonds are shown as solid lines, and two are shown as dashed lines.
$P_2Q_6^{4-}$ 29, 33	 Two phosphorus atoms (P) are bridged by two chalcogen atoms (Q). Each phosphorus atom is also bonded to two terminal chalcogen atoms (Q), resulting in a total of six P-Q bonds. The bonds are represented by solid and dashed lines to indicate stereochemistry.
$P_2Q_7^{4-}$ 31, 32b	 Two phosphorus atoms (P) are bridged by two chalcogen atoms (Q). Each phosphorus atom is also bonded to three terminal chalcogen atoms (Q), resulting in a total of seven P-Q bonds. The bonds are represented by solid and dashed lines to indicate stereochemistry.

$P_2Q_9^{4-31, 32c}$	
$P_2Se_8^{4-30c}$	
PSe_5^{3-30b}	
$P_2S_6^{2-34}$	
$P_2S_7^{2-35}$	
$P_2Se_8^{2-36}$	

C.3 The Polythioarsenate Flux

Given the considerable success in using a polychalcophosphate flux, it was inevitable that the question of what happens in a polychalcoarsenate flux should arise. A few ternary and quaternary chalcoarsenate compounds have been made via direct combination of the elements.³⁷ It is surprising that even though literature is abound with the structural diversity shown by chalcoarsenate compounds, there were almost no attempts to prepare chalcoarsenates by the flux method. We therefore became interested in such an investigation. There seems to be a considerable divide in the electronegativities of P and As. Thus while P exists in the +4 or +5 oxidation state in its compounds, this cannot be the case for As which does not show the +4 state. The most favored oxidation states of As are +3 and +5. This implies that the chalcoarsenate ligands would be quite different from the corresponding chalcophosphate ligands and so would the resulting compounds that are formed by these ligands. The only ligand that is common to both P and As is the PnQ_4^{3-} anion with the pnictogen in the +5 oxidation state.

We also expect the chalcoarsenate fluxes to yield ligands that are not simple condensation products of the AsS_3^{3-} ligand. Since these fluxes have solubilized polychalcogenide anions along with $\text{As}_x\text{Q}_y^{n-}$ anions, we can expect compounds with chalcoarsenate ligands that contain Q-Q bonds.

We therefore began a systematic investigation of the reactivity of main group, transition and rare earth metals in alkali polythioarsenate fluxes. The remainder of the chapter deals with the details of the flux and a summary of the compounds we have obtained during the course of this research.

C.3-1 The formation of a polythioarsenate flux

Conceptually, the alkali polythioarsenate flux can be generated by an insitu reaction of A_2S , As_2S_3 and excess of S, in a manner similar to the polychalcophosphate flux. This reaction leads to the formation of various $As_xS_y^{n-}$ anions along with S_z^{2-} anions. The metal that is present in the flux is oxidized by both $As_xS_y^{n-}$ and S_z^{2-} anions. The resulting metal ion is then coordinated by the thioarsenate ligands present in the solution according to its coordination preferences. Since the flux is oxidizing, frequently we observe the metal in its highest possible oxidation state. There is usually an excess of sulfur in the flux, because it helps lower its melting point and if needed acts as an electron acceptor. The excess of sulfur can also get incorporated into the structure in the form of polysulfide ligands. The structure therefore presents an interesting mix of thioarsenate and polysulfide ligands.

The high basicity of the fluxes generally implies that $As_xS_y^{n-}$ ligands of high charge are isolated. The basicity of the flux is also affected by the kind and amount of alkali sulfide used. Generally, the greater the amount of A_2S , the greater the flux basicity and greater is the likelihood of obtaining highly charged thioarsenate ligands. This high basicity also leads to the formation of molecular phases. As we go from Na_2S to Cs_2S , the basicity of the flux increases. This increases the probability of incorporating the alkali metal in the final structure. Thus it has generally proved difficult to form compounds with Na and Li. Another governing principle for dimensionality of the observed structures is the counter-ion effect.³⁸ The counter-ion effect explains that the dimensionality of the structure is inversely proportional to the size of the counter ion. Thus the possibility of obtaining a 3-

D framework is highest for Li/Na, and molecular phases will most probably be obtained with Cs.

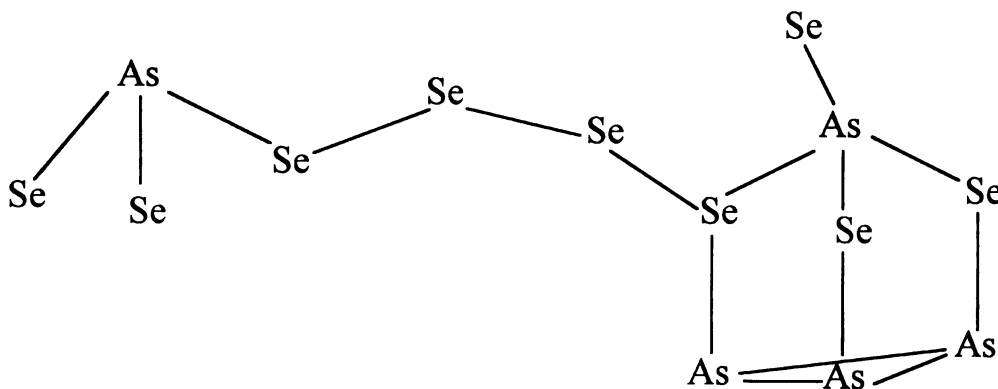
The general method of setting up an alkali thioarsenate flux reaction is as follows:

The starting materials, alkali sulfide (A_2S), the metal, As_2S_3 and excess of S are weighed in a glove box and loaded into a fused-silica tube. The tube is then flame sealed under vacuum ($\sim 10^{-4}$ Torr). This tube is put in a computer-controlled furnace and heated according to a desired temperature profile. After cooling, usually well-formed crystals are visible inside tube, embedded in a matrix. Isolation of these crystals is done by opening the tube in *N, N*-dimethyl formamide, which has been previously degassed by bubbling N_2 through it. The excess of flux gets dissolved away in this solvent. After the flux is washed off (this can be observed when the solution loses all its color and usually takes about 8-10 h), the crystals are washed with ether and dried. Ofcourse, this method assumes that the product is insoluble in the solvent. If the product dissolves in DMF, then we need to use another solvent, but usually it is possible to find atleast one solvent in which the product is stable. If this fails then a manual extraction of the crystals should be attempted.

At this point, it is important to consider the As-S speciation in the flux. The flux can be considered to be a liquid glass with different kinds of As-S units present. Two questions arise from this consideration: 1) What are the different units present in the melt? 2) Which one gets incorporated in the final product? Spectroscopic investigations done on arsenic and phosphorus chalcogenide glassy systems can provide us with some clues to answer the above questions. This will be the topic of the next section.

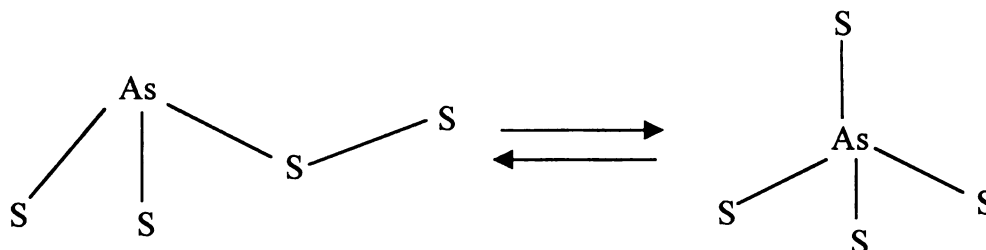
C.3-2 Spectroscopic investigations in arsenic and phosphorus chalcogenide glasses.

Raman spectroscopic studies done on arsenic chalcogenide glasses have shed some light on the kind of As-Q units present in the glass. Though these studies were done to understand asymmetries in local bonding sites of the arsenic chalcogenide glass, it is still constructive to our purpose. According to one Raman study³⁹ done on $\text{As}_x\text{Se}_{100-x}$ glass system, it was found that all the glasses consist of a band at 227cm^{-1} corresponding to pyramidal AsSe_3 units. As the content of the Se was increased in the glass, the AsSe_3 peak overlapped with a peak due to $-\text{Se}-\text{Se}-\text{Se}-$ chains. At very high concentrations of Se, a strong band at 252cm^{-1} appeared which showed the presence of Se_8 rings. As the As content was increased, the AsSe_3 band became weaker with simultaneous increase in the intensity of peaks due to As_4Se_3 and As_4Se_4 cage units formed in the glass. The As rich glass also showed a narrow Raman band at 280 cm^{-1} corresponding to Se-Se bridges that link AsSe_3^{3-} units and/or $\text{As}_4\text{Se}_3/\text{As}_4\text{Se}_4$ cages. This configuration of the glass can be empirically represented as follows:



Scheme 3

It is quite possible that the thioarsenate flux has AsS_x units similar to the ones seen in the glassy systems. In addition, internal redox equilibria between the different thioarsenate anions might also be taking place as shown below:



In a Raman investigation conducted on $\text{As}_x\text{S}_{100-x}$ glasses,⁴⁰ it was found that for $x < 25\%$, the glasses contained S_8 rings indicated by the characteristic peaks at 155, 234 and 474 cm^{-1} . When $x = 40\%$, the Raman spectrum shows a single broad peak at 343 cm^{-1} , corresponding to the pyramidal AsS_3 units. There are also very weak peaks due to As-As and S-S bonds. However at $x > 40\%$, there are distinct peaks due to As-As bond formation. The authors also conducted differential scanning calorimetric experiments on these glasses. They found that for $x < 25\%$, the glasses consist of two phases: one whose glass transition temperature depends on the concentration of As and another that has a fixed composition of $\sim \text{As}_2\text{S}_5$. Based on the Raman spectrum, it has been proposed that the structure of the glassy As_2S_5 consists of tetrahedral AsS_4 units that are linked polymerically or pyramidal AsS_3 units linked by S-S chains or an equilibrium between these two possibilities.

High temperature liquid state ^{77}Se NMR performed on $\text{As}_x\text{Se}_{1-x}$ glassy melts⁴¹ have also shed some light on the type of AsSe units present in the liquid. It was found that the

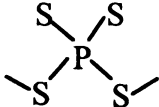
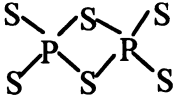
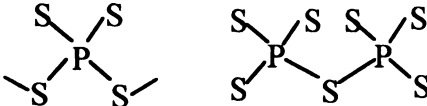
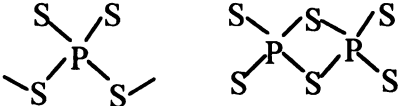
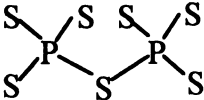
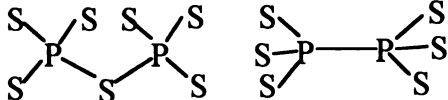
average chemical shift showed a linear dependence on the amount of As in the range $0 < x < 40\%$. This shift corresponds to the progressive dismantling of Se-Se-Se chains to form As-Se-Se and As-Se-As fragments as the amount of As is increased. The chemical shift remains constant at $x > 40\%$ indicating a chemically ordered network consisting of pyramidal AsSe_3 units. Since the ^{77}Se peak remains constant at higher concentrations of As, this can only mean that addition of As leads to As-As bonds. ^{75}As NQR measurements on arsenic sulfide glasses with As $> 40\%$, have proved the existence of As-As bonds.⁴⁴

In chalcophosphate systems, ^{31}P NMR has contributed advantageously to understand short-range order in different glassy systems like P-S, P-Se, $\text{Ag}_2\text{S-P}_2\text{S}_5$, $\text{Li}_2\text{S-P}_2\text{S}_5$ etc.⁴² In the P-S glassy system, it was reported that up to about 12 at% of P, the glass consisted of PS_4 units connected by S-S chains. However as the phosphorous content is increased, there is a marked decrease in the glass transition temperatures, implying that the structure of the glass does not contain as many bonds. The chemical shifts observed in the NMR of these glasses at high concentration of phosphorous point to the formation of clusters of the type P_4S_x ($x = 3, 4, 5, 7, 9, 10$). This behavior is very similar to arsenic chalcogenide glasses, which show a tendency to form $\text{As}_4\text{Q}_4/\text{As}_4\text{Q}_3$ cages at high concentrations of arsenic.

^{31}P NMR of ternary $\text{Ag}_2\text{S-P}_2\text{S}_5$ system⁴² has revealed some interesting facts about the different thiophosphate units found in the glass and the corresponding crystalline compound obtained through annealing of the glass. Shown below is a table (Table 2) of thiophosphate units observed in glassy and crystalline $(\text{Ag}_2\text{S})_x(\text{P}_2\text{S}_5)_{1-x}$ compounds for different values of x . As seen, the tendency to form dimeric $\text{P}_2\text{S}_6^{2-}$ groups does not exist

in the glass. Instead it seems that the sulfur atoms of the PS_4^{3-} groups form polymeric chains. We can infer from this table that the short range order in these glasses is unique and some of these species may not stable in the crystalline forms of the same composition.

Table 2. Thiophosphate ligands observed in the glassy and crystalline compounds belonging to the system $(\text{Ag}_2\text{S})_x(\text{P}_2\text{S}_5)_{1-x}$ for different values of x .

Glass	Crystal	x
		0.5
		0.6
		0.67

From the standpoint of a thioarsenate flux, the above discussion tells us that a) the flux consists of different structural units like AsS_3 , S_n chains, As_4S_4 molecular cages, which are probably in dynamic equilibrium. These units may or may not be linked with each other. b) It is quite possible that the structural units that finally get incorporated in the compound may not necessarily be the ones observed in the melt.

A very pertinent question to the flux methodology is the role of the metals present and how they affect the structural units. We can attempt to obtain some answers by observing how does the introduction of a metal in an arsenic chalcogenide glass change its structure.

Refractive index measurements on thin films of Tl-As-S glasses,⁴³ ^{75}As NQR measurements on Cu-As-S and Cu-As-Se systems⁴⁴ and IR absorption measurements on $\text{Ag}_2\text{S-As}_2\text{S}_3\text{-AgI}$ glasses⁴⁵ have shown that the introduction of a metal leads to the breaking of the As-S bond and formation of the M-S bond. There are also homopolar As-As and S-S bonds formed as a result. Since most of the M-S bonds have a different degree of covalency compared to As-S bonds, the covalent glassy network of the pure arsenic chalcogenide glass is modified. The addition of these metals also leads to the formation of additional structural units such as Ag_3AsS_3 , AgAsS_2 , TlAsS_2 , Tl_3AsS_3 etc.

We can infer from the above studies that the presence of two kinds of metals in our reactions will significantly alter the makeup of the thioarsenate melt and the final outcome will depend on the amount ratio of the metal to the thioarsenate composition.

D. Conclusion

The large family of natural sulfosalts and the synthetically obtained metal chalcoarsenates are evidences of the exciting structural chemistry observed in these compounds. Chalcophosphate compounds have been successfully prepared using molten polychalcophosphate fluxes. In fact, since the advent of these fluxes the number of chalcophosphate compounds has more than doubled. However similar efforts, though logical, are lacking in the area of chalcoarsenate fluxes. In a sulfur environment, the chemistry of arsenic is mainly dominated by the $\text{As}^{3+}/\text{As}^{5+}$ couple as compared to the $\text{P}^{4+}/\text{P}^{5+}$ couple observed for phosphorus. Thus we can expect that there will be a difference in the reactivities of the two fluxes. Even for the well-studied chalcophosphate flux there are some issues that need answering. These are concerned with the kind of ligand observed for a particular flux ratio and the influence of the metal on the isolation of a certain kind of ligand. NMR and Raman spectroscopic investigations on glassy P-Q and ternary $\text{Ag}_2\text{S-P}_2\text{S}_5$ systems have shown what kind of chalcophosphate units are present in the local structures of these glasses and what units are observed when these glasses crystallize. However there has been no study of high temperature flux melts to prove that they have units similar to the short range order observed in the above mentioned glasses. Insitu experiments in the future can hope to clarify this situation.

Thioarsenate systems face the same issues mentioned above, even more so. Based on Raman and NMR studies of arsenic chalcogenide glasses, we can possibly predict that under sulfur rich conditions, we will observe AsS_3 pyramidal ligands along with S-S linkages. In sulfur poor conditions, in other words when the flux basicity is high, we

should probably expect compounds that contain As_xS_y cages and a tendency to form molecular phases. Ofcourse, these predictions can only be used as guidelines and we hope to observe a wide structural variety depending on different flux conditions and the type of metal used. Compared to the polychalcophosphate fluxes, the thioarsenate flux is still in its infancy and extensive studies are warranted.

During the course of this Ph.D. dissertation, a number of quaternary thioarsenates were discovered. These compounds will be presented in Chapters 2-8 and the Appendix.

Chapter 2 describes the synthesis, structural and physical characterization of four new tin thioarsenates, NaSnAsS_4 , RbSnAsS_5 , $\text{Rb}_2\text{SnAs}_2\text{S}_6$ and $\text{Cs}_2\text{SnAs}_2\text{S}_9$. These compounds feature the pyramidal AsS_3^{3-} , AsS_4^{3-} and AsS_5^{3-} ligands. The latter two are derived from the AsS_3^{3-} anion by the substitution of one and two S atoms by disulfide units, respectively. $\text{Cs}_2\text{SnAs}_2\text{S}_9$ is an interesting compound that crystallizes in a non-centrosymmetric space group and exhibits reversible crystal - glass transition.

The compounds obtained from a flux can give us ideas to make useful materials.

$\text{Rb}_2\text{SnAs}_2\text{S}_6$ crystallizes in the trigonal space group P-3 and consists of SnAs_2S_6 layers.

We reasoned that if we could substitute Rb with Tl, then we should obtain a better semiconductor material due to the tendency of Tl to form covalent bonds compared to Rb. Chapter 3 describes the synthesis of $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$. During our attempts to prepare $\text{Tl}_2\text{SnSb}_2\text{Se}_6$, we obtained a new layered compound, $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

This compound is discussed in the Appendix.

Chapter 4 presents the compounds obtained from the investigation of Pb in Rb and Cs thioarsenate fluxes. The compounds APbAsS_4 and $\text{A}_4\text{PbAs}_2\text{S}_8$ prepared from these fluxes are isostructural or very similar to their thiophosphate counterparts. Since Eu reactivity is

similar to Pb in chalcophosphate systems, we decided to forgo the reaction of Eu in thioarsenate fluxes. Instead, we decided to study the reaction of Ag, Cu/Eu/As₂S₃/S which yielded us the framework compound AgEuAsS₄ and a surprising ternary compound Eu₃As₂S₈ with a unique structure. These compounds are discussed in Chapter 5. Chapter 6 deals with A₆InAs₃S₁₃, A₃BiAs₂S₈ and A₉BiAs₄S₁₆. A₆InAs₃S₁₃ and A₉BiAs₄S₁₆ contain molecular anions [In(AsS₄)₂(AsS₅)]⁶⁻ and [Bi(AsS₄)₄]⁹⁻ respectively. The reactions of transition metals Cd and Mn resulted in the molecular phases A₈MnAs₄S₁₆ and A₈Cd₂As₄S₁₈. The latter compound displays a rare octahedral Cd geometry. This is the subject of Chapter 7. Chapter 8 talks about the reaction of coinage metals Cu, Ag and Au in cesium thioarsenate fluxes.

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Chapter 2

Reactivity of Sn in Alkali Polythioarsenate Fluxes: Synthesis and Characterization of NaSnAsS₄, ASnAsS₅ (A = K, Rb), A₂SnAs₂S₆ (A = K, Rb), and Cs₂SnAs₂Q₉ (Q = S, Se)

Abstract

Six new quaternary tin thioarsenates have been prepared by heating Sn in alkali polythioarsenate fluxes at intermediate temperatures. The one-dimensional NaSnAsS₄ (I) crystallizes in *Pnnm* with cell parameters $a = 11.859(4)$ Å, $b = 7.318(2)$ Å and $c = 7.508(2)$ Å. It consists of centrosymmetric [Sn₂(AsS₃)₂] centers linked together by μ_2 -S to form a chain. A variation of this chain is observed in KSnAsS₅ (II), *Pbam* with $a = 8.1369(2)$ Å, $b = 13.784(4)$ Å and $c = 7.428(2)$ Å and RbSnAsS₅ (III), *P2₁/c* with $a = 7.373(4)$ Å, $b = 15.694(8)$ Å, $c = 7.486(4)$ Å and $\beta = 102.61(14)^\circ$. Both II and III contain chains made up of [Sn(AsS₄)₂] cores linked by μ_2 -S. The β -[AsS₄]³⁻ ligand featured in these chains is derived from the pyramidal [AsS₃]³⁻ ion by substituting a terminal sulfur atom with a disulfide unit. A₂SnAs₂S₆ (IV) is layered and crystallizes in *P-3* with $a = 6.717(5)$ Å, $c = 7.204(8)$ Å for A = K and $a = 6.7358(18)$ Å, $c = 7.454(3)$ Å for A = Rb. The layers consist of edge sharing [SnS₆] octahedra and [AsS₃] pyramids charged balanced by K or Rb ions. Cs₂SnAs₂Q₉ (V) is molecular: *s.g Pmc2₁*, $a = 7.386(3)$ Å, $b = 14.614(5)$ Å, $c = 14.417(5)$ Å for Q = S and *s.g P2₁*, $a = 7.175(5)$ Å, $b = 17.555(12)$ Å, $c = 7.663(5)$ Å, $\beta = 115.857(11)^\circ$ for Q = Se. The molecule consists of Sn coordinated by β -[AsQ₄]³⁻ and [AsQ₅]³⁻ ligands. The [AsQ₅]³⁻ ligand is obtained by substitution of two

terminal Q atoms in $[\text{AsQ}_3]$ with disulfide arms. Compounds **I-V** are semiconductors with optical bandgaps of 2.17, 2.11, 2.07, 1.89 and 1.98 eV respectively.

A. Introduction

In view of the considerable body of information now available on polychalcophosphate fluxes,¹ it is timely to ask how the corresponding polychalcoarsenate fluxes perform as synthetic tools and what type of phases are likely to form. Because P and As are members of the same group in the periodic table, one might expect simple analogues both in composition and structure. However, there seems to be a significant divide at the P-As boundary in terms of chemical and electronic behavior in these two elements. For example, whereas the most stable oxidation states of P as evidenced by the frequency of the $[\text{P}_2\text{Q}_6]^{4-}$ ² and $[\text{PQ}_4]^{3-}$ ³ ($\text{Q} = \text{S}, \text{Se}$) anions in known phases are +4 and +5, this is not likely to be the case for As because of the greater stability of the +3 state and the extreme rarity of the +4 state. The corresponding ethane-like unit $[\text{As}_2\text{Q}_6]^{4-}$ (ubiquitous in P chemistry) does not exist; however, other anions such as $[\text{As}_2\text{Q}_5]^{4-}$, $[\text{AsQ}_3]^{3-}$ are known and might form in the melt.^{4,5} Conversely, in P chemistry, these species are unknown or are extremely rare. The only species common in both elements are the classical tetrahedral $[\text{PQ}_4]^{3-}$ and $[\text{AsQ}_4]^{3-}$ ⁶ anions with P and As in the +5 oxidation state. Therefore, we anticipate a sharp contrast between $[\text{As}_x\text{Q}_y]^{z-}$ and $[\text{P}_x\text{Q}_y]^{z-}$ chemistry. The number of naturally occurring thioarsenates is quite large, and this diversity is a harbinger of what could be expected in synthetically based systems. Structures with $[\text{As(III)Q}_x]^{3-}$ ($x = 3, 4, 5$) units are expected to have unique structural chemistry because of the strong tendency of As^{3+} lone pair to be stereochemically expressed. To date, the solventothermal technique⁷ has been the primary means for the formation of ternary or quaternary chalcoarsenate phases. We expect the structures obtained from a flux to be quite different

from that obtained by the solution route. We therefore set forth on a systematic study of the reactivity of different metals in these fluxes.

Tin has proven to be an extremely versatile metal for use in the flux method. The reactions of Sn in polychalcogenide fluxes have yielded compounds like $A_2Sn_4S_9$ ($A = K, Rb, Cs$)⁸, α, β - $Rb_2Sn_2S_8$, $K_2Sn_2S_5$, $Cs_2Sn_2S_6$, Cs_2SnS_{14} ⁹. In a polychalcophosphate flux, compounds such as $Rb_3Sn(PSe_5)(P_2Se_6)$ ¹⁰, $Rb_4Sn_2Ag_4(P_2Se_6)_3$ ¹¹, $K_5Sn(PSe_5)_3$ ¹², $Rb_6Sn_2Se_4(PSe_5)_2$ ¹², $K_4Sn_2P_6S_{25}$ ¹³ have been isolated. All these compounds feature Sn in an octahedral or tetrahedral or a Ψ -trigonal bipyramidal geometry bound by chalcophosphate anions. Our studies with Sn in AA_sS_y ($A = \text{alkali metal}$) fluxes have proven to be very rewarding and yielded us with six new quaternary phases, $NaSnAsS_4$, $(K, Rb)SnAsS_5$, $(K, Rb)_2SnAs_2S_6$ and $Cs_2SnAs_2S_9$. Each of these compounds features an octahedral, diamagnetic Sn^{4+} ion bound to a thioarsenate $[As^{3+}S_x]^{3-}$ ($x = 3, 4, 5$) ligand. The structures and physical properties of these compounds are discussed here.

B. Experimental Section

B.1 Reagents

All manipulations were done in a nitrogen-filled dry-vac glove box. Reagents: Sn (99.999 %; Cerac, Milwaukee, WI), As_2S_3 (99.9 %; Strem Chemicals, Newburyport, MA), As (99.9%; Aldrich Chemical Co, Milwaukee, WI), S (99.9 %; Strem Chemicals, Newburyport, MA). *N,N*-dimethylformamide (Spectrum Chemicals, ACS reagent grade); diethyl ether (CCI, ACS grade). Na_2S , K_2S , Rb_2S and Cs_2S were prepared by dissolving the alkali metal in liquid NH_3 and reacting it with a stoichiometric amount of sulfur according to a modified literature procedure.¹⁴

B.2 Physical Measurements

Powder X-ray Diffraction

X-ray powder diffraction patterns were recorded on a CPS 120 INEL diffractometer (Cu K α radiation) operating at 40kV/20mA and equipped with a position sensitive detector and a flat sample geometry.

Energy Dispersive Spectroscopy

Semiquantitative microprobe analyses on the compounds were done with a JEOL JSM-35C scanning electron microscope equipped with a Tracor Northern Energy Dispersive Spectroscopy detector. Elemental compositions were obtained from an average of three readings. Acquisition times were 30s or 45s per reading.

Diffuse Reflectance Spectroscopy

Solid state diffuse reflectance spectra were measured using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as reference. Finely ground sample was spread on a sample holder preloaded with the reference. Energy gap was determined from a plot of absorbance vs energy by converting reflectance to absorbance using the Kubelka-Munk function.¹⁵

Infrared and Raman Spectroscopy

Far IR spectra of the compounds were recorded as CsI pellets on a Nicolet 740 FT-IR spectrometer with a TSG/PE detector and silicon beam splitter. Raman spectra were recorded on a Bio-rad FT- Raman spectrometer equipped with a Germanium detector and using 633nm radiation from a HeNe laser for excitation with a 4cm⁻¹ resolution.

Differential Thermal Analysis

The thermal behavior of the compounds was investigated by differential thermal analysis using a Shimadzu DTA-50 thermal analyzer. Typically a sample (~20 mg) of ground crystalline material was sealed in a silica ampule under vacuum. A similar ampoule of equal mass filled with Al_2O_3 was sealed and placed on the reference side of the detector. The sample was heated to the desired temperature at $10^\circ\text{C}/\text{min}$, and after 1-3 min it was cooled at a rate of $-10^\circ\text{C}/\text{min}$ to 50°C . Residues of the DTA experiments were examined by X-ray powder diffraction. Reproducibility of the results was checked by running multiple heating/cooling cycles.

B.3 Synthesis

NaSnAsS₄ (I): A pure synthesis of I was achieved by heating a mixture of Na_2S (0.07g, 0.9mmol), Sn (0.108g, 0.9mmol), As (0.136g, 1.8mmol), S (0.288g, 9mmol) in the ratio 1/1/2/10 at 500°C . The reactants were held at this temperature for 3 d and then cooled to 250°C at the rate of $3^\circ\text{C}/\text{h}$ followed by rapid cooling to room temperature. Isolation of the product using degassed *N,N*-dimethylformamide and diethyl ether afforded orange needles in almost 70% yield. The crystals are stable in air and water. Energy Dispersive Spectroscopic analysis on several crystals gave an average composition of $\text{Na}_{1.0}\text{Sn}_{1.0}\text{As}_{1.0}\text{S}_{4.1}$.

KSnAsS₅ (II): KSnAsS_5 was synthesized by reacting K_2S , Sn, As_2S_3 and S in the ratio 1/1/1/10. The reactants were soaked at 500°C for 60h, followed by cooling to 250°C at $5^\circ\text{C}/\text{h}$ and then fast cooled to room temperature. Golden-brown rectangular crystals were

obtained as the product after washing the excess of flux. Electron microprobe analysis on these crystals gave a composition of $K_{1.0}Sn_{1.0}As_{1.0}S_{5.1}$. Yield > 85%

RbSnAsS₅ (III): $RbSnAsS_5$ was obtained as dark red rod-like crystals by fusing $Rb_2S/Sn/As_2S_3/S$ in a 1/1/1/10 ratio using the same procedure mentioned above with a yield of ~60%. EDS measurement gave an average reading of $Rb_{1.1}Sn_{1.0}As_{1.0}S_{5.4}$.

As₂SnAs₂S₆ (IV): $K_2SnAs_2S_6$ was obtained by combining a 4/1/3/10 mixture of K_2S , Sn, As_2S_3 and S at 500°C for 60h. For $Rb_2SnAs_2S_6$, Rb_2S , Sn, As and S were mixed stoichiometrically in a 1/1/2/5 ratio and isothermed at 500°C for 72h. Both phases were isolated as dark red hexagonal crystals. EDS analysis indicated $K_{2.0}Sn_{1.0}As_{1.9}S_{6.0}$ and $Rb_{2.1}Sn_{1.0}As_{2.0}S_{5.9}$. The crystals are air stable and insoluble in common solvents like water and acetone. Both compounds were obtained in pure phase with yields greater than 80%.

Cs₂SnAs₂Q₉ (V): Red plates of $Cs_2SnAs_2S_9$ were initially obtained from a reaction of 2/1/1/10 ratio of $Cs_2S/Sn/As_2S_3/S$ at 500°C. The product also contained yellow plates of a ternary phase $Cs_4As_2S_{10}$ (see Appendix). A pure synthesis for V was achieved by a direct combination of Cs_2S , Sn, As and S in the ratio 1:1:2:8 at 550°C. The product is insoluble in water, acetone and alcohol but soluble in DMF after exposure of more than a day. Elemental analysis using EDS gave an average composition of $Cs_{2.1}Sn_{1.0}As_{1.9}S_{8.5}$.

$Cs_2SnAs_2Se_9$ was obtained as black plate-like crystals in pure form from a reaction of the stoichiometric amounts of $Cs_2Se/Sn/As/Se$ at 500°C. The product was stable in air and water.

B.4 X-ray Diffraction Analysis

The homogeneity of compounds **I-V** were ascertained by comparing the experimental powder diffraction patterns to their theoretical patterns calculated from their single crystal structures.

The single crystal diffraction data on these compounds were collected on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. The crystals were mounted on glass fiber tips. The data were acquired using the SMART software and integrated using the SAINT program. An empirical absorption correction was done using SADABS and all refinements were done using the SHELXTL¹⁶ package of crystallographic programs.

The structural refinement of **I**, **II**, **III** and **IV** was straightforward with final R1/wR2 values of 0.0203/0.0429, 0.0314/0.0785, 0.0296/0.0729 and 0.0209/0.0462 respectively. In the case of Cs₂SnAs₂S₉ (**V**), systematic absences indicated the orthorhombic *Pmc*2₁ space group. After anisotropic refinement of all atom positions, there was one high-intensity peak remaining in the electron density map. This peak (assigned as S13) was observed between the disulfide ion in the [AsS(S₂)₂]³⁻ fragment and was 1.04 Å and 1.15 Å away from atoms S11 and S12, respectively. A disordered model was considered and structure refinement led to 80% occupancy for S11 and S12 and 40% occupancy of S13 which resulted in a drop in the R values from R1 = 0.0499, wR2 = 0.1369 to R1 = 0.0399, wR2 = 0.1068. However, the structure refinement result considering the disordered disulfide ions did not give any reasonable structural models. It is not clear why the disulfide ion in one cluster anion shows an unusual disorder. A possible

supercell structure was sought, however zone photos with long exposure times (5 min) gave no evidence for supercell reflections. The structure of $\text{Cs}_2\text{SnAs}_2\text{Se}_9$ was refined in the space group $P2_1$. No disorder was observed in this compound. Crystallographic details for **I-V** are listed in Table 1. Fractional atomic coordinates and isotropic displacement parameters are given in Table 2. Anisotropic displacement parameters are given in Table 3.

Table 1. Crystallographic data for NaSnAsS₄, RbSnAsS₅, Rb₂SnAs₂S₆, Cs₂SnAs₂S₉ and Cs₂SnAs₂Se₉

empirical formula	NaSnAsS ₄	RbSnAsS ₅	Rb ₂ SnAs ₂ S ₆	Cs ₂ SnAs ₂ S ₉	Cs ₂ SnAs ₂ Se ₉
fw	344.84	439.38	631.83	822.89	1244.99
space group	<i>Pnmm</i>	<i>P2₁/c</i>	<i>P-3</i>	<i>Pmc2₁</i>	<i>P2₁</i>
<i>a</i> , Å	11.859(4)	7.373(4)	6.7358(18)	7.386(3)	7.175(5)
<i>b</i> , Å	7.318(2)	15.694(8)	6.7358(18)	14.614(5)	17.555(12)
<i>c</i> , Å	7.508(2)	7.486(4)	7.454(3)	14.417(5)	7.663(5)
α , deg	90	90	90	90	90
β , deg	90	102.61(14)	90	90	115.857(11)
γ , deg	90	90	120	90	90
<i>V</i> , Å ³	651.6(4)	845.3(8)	292.89(16)	1556.2(9)	868.5(11)
<i>Z</i>	4	4	2	4	2
ρ_{calcd} , g/cm ³	3.515	3.453	3.582	3.512	4.761
μ , mm ⁻¹	10.174	13.766	17.051	11.643	11.643
<i>T</i> , K	293(2)	293(2)	293(2)	293(2)	293(2)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073
Total reflections	6080	4615	2898	9626	6787
Total unique	859	1956	480	3730	3670
R(int)	0.0389	0.0313	0.0292	0.0635	0.1449
No. of parameters	39	73	19	158	129
Goodnes of fit on F ²	1.030	1.015	1.121	1.062	0.802
Refinement method	Full-matrix least-squares on F ²				
R1 ^a	0.0203	0.0296	0.0209	0.0399	0.0739
wR2 ^b	0.0429	0.0729	0.0462	0.1068	0.1442

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

Table 2. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for NaSnAsS₄, RbSnAsS₅, Rb₂SnAs₂S₆, Cs₂SnAs₂S₉ and Cs₂SnAs₂Se₉.

Atom	x	y	z	Ueq ^a
NaSnAsS ₄				
Sn	0.5	0.5	0.2646(1)	16(1)
Na	0.1635(2)	0.6003(3)	0	32(1)
As	0.3433(1)	0.1945(1)	0	18(1)
S(1)	0.4414(1)	0.7221(1)	0.5	18(1)
S(2)	0.5330(1)	0.2601(2)	0	18(1)
S(3)	0.3028(1)	0.3802(1)	0.2328(1)	18(1)
RbSnAsS ₅				
Sn	0.2309(1)	0.5062(1)	0.4958(1)	20(1)
As	0.5203(1)	0.2095(1)	1.1383(1)	25(1)
Rb	0.0501(1)	0.3396(1)	0.9878(1)	40(1)
S(1)	0.0596(2)	0.5093(1)	0.7417(2)	23(1)
S(2)	0.4479(2)	0.4981(1)	0.2533(2)	22(1)
S(3)	0.2682(2)	0.3445(1)	0.4580(2)	28(1)
S(4)	0.2464(2)	0.6681(1)	0.4811(2)	28(1)
S(5)	0.5511(2)	0.1132(1)	1.3734(2)	30(1)
Rb ₂ SnAs ₂ S ₆				
Sn	0	0	0	12(1)
As	0.3333	0.6667	0.068(1)	15(1)

S	0.1945(2)	0.336(2)	0.2204(1)	22(1)
Rb	0.3333	0.6667	-0.3927(1)	27(1)
Cs ₂ SnAs ₂ S ₉				
Sn(1)	0.5	0.1783(1)	0.4739(1)	27(1)
Sn(2)	0	0.6543(1)	0.4425(1)	27(1)
Cs(1)	0.5	0.4917(1)	0.4793(1)	45(1)
Cs(2)	0	-0.0645(1)	-0.1801(1)	46(1)
Cs(3)	0.5	0.1417(1)	0.9851(1)	50(1)
Cs(4)	0	0.2935(1)	-0.3878(1)	41(1)
As(1)	0	0.4507(1)	0.2995(1)	36(1)
As(2)	0	0.2542(1)	0.1495(1)	41(1)
As(3)	0.5	0.1616(1)	0.7103(1)	51(1)
As(4)	0.5	0.2901(1)	0.2771(1)	58(1)
S(1)	0.5	0.2790(2)	0.6158(2)	34(1)
S(2)	0.5	0.0608(2)	0.3395(3)	40(1)
S(3)	0	0.4830(2)	0.4481(2)	30(1)
S(4)	0.2795(4)	0.2760(2)	0.3812(2)	48(1)
S(5)	-0.2224(3)	0.6712(2)	0.5794(2)	39(1)
S(6)	0	0.1247(2)	0.0584(3)	51(1)
S(7A)	0.5454(8)	0.1409(4)	0.2252(3)	49(2)
S(8)	0	0.8307(2)	0.4238(3)	46(1)
S(9)	-0.2527(3)	0.6557(2)	0.3243(2)	42(1)
S(10)	-0.2446(3)	0.5335(2)	0.2525(2)	43(1)

S(11)	0.2428(6)	0.0819(3)	0.5322(2)	62(1)
S(12)	0.2523(6)	0.0867(3)	0.6724(3)	67(1)
S(13)	0.3046(11)	0.0878(6)	0.5970(6)	59(2)

Cs₂SnAs₂Se₉

Cs(1)	1.3085(6)	0.4374(3)	0.2439(6)	82(2)
Cs(2)	1.0817(6)	0.2044(3)	0.5131(6)	79(1)
Sn	0.6805(6)	0.3322(3)	-0.1170(6)	60(1)
As(1)	1.1824(10)	0.6429(4)	0.0570(9)	68(2)
As(2)	0.6419(9)	0.5495(4)	-0.01573(9)	66(2)
Se(1)	0.8129(9)	0.3942(4)	0.2374(9)	73(2)
Se(2)	0.8021(9)	0.4544(4)	0.7519(8)	65(2)
Se(3)	0.2953(9)	0.3814(5)	-0.2163(10)	79(2)
Se(4)	1.0360(10)	0.2470(5)	-0.0017(9)	73(2)
Se(5)	1.2869(10)	0.5080(4)	0.6990(12)	85(2)
Se(6)	1.3746(10)	0.6454(4)	0.4103(9)	73(2)
Se(7)	0.7591(13)	0.5233(5)	0.1839(10)	88(2)
Se(8)	0.5688(9)	0.2070(4)	0.0172(9)	66(2)
Se(9)	0.5917(10)	0.2737(4)	0.5285(9)	72(2)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for NaSnAsS₄, RbSnAsS₅, Rb₂SnAs₂S₆, Cs₂SnAs₂S₉ and Cs₂SnAs₂Se₉.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
NaSnAsS₄						
Sn(1)	16(1)	19(1)	11(1)	0	0	-2(1)
Na(1)	39(1)	31(1)	25(1)	0	0	12(1)
As(1)	22(1)	16(1)	15(1)	0	0	-2(1)
S(1)	21(1)	17(1)	14(1)	0	0	2(1)
S(2)	20(1)	18(1)	17(1)	0	0	2(1)
S(3)	17(1)	22(1)	15(1)	-2	1	-2(1)
RbSnAsS₅						
Sn(1)	17(1)	20(1)	23(1)	-1(1)	3(1)	0(1)
As(1)	27(1)	17(1)	29(1)	-2(1)	1(1)	0(1)
Rb(1)	56(1)	25(1)	37(1)	1(1)	4(1)	9(1)
S(1)	22(1)	28(1)	19(1)	-1(1)	2(1)	0(1)
S(2)	23(1)	20(1)	21(1)	-3(1)	3(1)	0(1)
S(3)	26(1)	19(1)	34(1)	-2(1)	-4(1)	-1(1)
S(4)	27(1)	20(1)	38(1)	-6(1)	8(1)	1(1)
S(5)	41(1)	26(1)	21(1)	-3(1)	3(1)	0(1)
Rb₂SnAsS₆						
Sn(1)	9(1)	9(1)	16(1)	0	0	5(1)
As(1)	15(1)	15(1)	14(1)	0	0	7(1)

S(1)	30(1)	11(1)	19(1)	-2	-5	6(1)
Rb(1)	31(1)	31(1)	19(1)	0	0	15(1)
Cs ₂ SnAs ₂ S ₉						
Sn(1)	27(1)	22(1)	31(1)	-1(1)	0	0
Sn(2)	28(1)	23(1)	31(1)	2(1)	0	0
Cs(1)	35(1)	33(1)	68(1)	-2(1)	0	0
Cs(2)	49(1)	40(1)	48(1)	-6(1)	0	0
Cs(3)	60(1)	48(1)	42(1)	-10(1)	0	0
Cs(4)	35(1)	44(1)	44(1)	-1(1)	0	0
As(1)	42(1)	28(1)	38(1)	-3(1)	0	0
As(2)	54(1)	33(1)	35(1)	7(1)	0	0
As(3)	66(1)	46(1)	41(1)	16(1)	0	0
As(4)	112(2)	33(1)	30(1)	2(1)	0	0
S(1)	46(2)	27(1)	29(1)	-1(1)	0	0
S(2)	51(2)	24(1)	45(2)	-9(1)	0	0
S(3)	36(1)	20(1)	35(1)	2(1)	0	0
S(4)	51(1)	34(1)	58(1)	-3(1)	-23	13
S(5)	38(1)	38(1)	40(1)	-2(1)	8	-1
S(6)	72(2)	22(2)	59(2)	6(2)	0	0
S(7A)	77(6)	39(2)	32(2)	-10(2)	1	-5
S(8)	63(2)	23(2)	52(2)	7(1)	0	0
S(9)	40(1)	43(1)	43(1)	0(1)	-10	12
S(10)	41(1)	39(1)	50(1)	-3(1)	-14	-1

S(11)	69(2)	75(3)	42(2)	-1(2)	3	-42
S(12)	76(3)	81(3)	45(2)	22(2)	0	-34
Cs ₂ SnAs ₂ Se ₉						
Cs(1)	65(2)	96(4)	77(3)	-4(3)	21(2)	8(3)
Cs(2)	63(2)	94(4)	69(3)	3(3)	20(2)	-6(2)
Sn	51(2)	63(3)	58(2)	1(2)	17(2)	1(2)
As(1)	70(4)	64(5)	65(4)	-12(4)	26(3)	0(4)
As(2)	69(4)	65(5)	62(4)	0(3)	25(3)	4(3)
Se(1)	63(4)	91(6)	55(4)	6(4)	16(3)	9(4)
Se(2)	60(3)	72(6)	68(4)	0(4)	33(3)	-1(4)
Se(3)	45(4)	100(7)	80(5)	6(4)	16(3)	0(4)
Se(4)	53(4)	91(6)	66(4)	-4(4)	17(3)	5(3)
Se(5)	58(4)	79(6)	112(6)	9(5)	31(4)	0(4)
Se(6)	74(4)	81(6)	63(4)	9(4)	30(3)	-4(4)
Se(7)	121(6)	72(6)	66(4)	3(4)	35(4)	-7(4)
Se(8)	76(4)	59(5)	70(4)	5(4)	38(4)	-7(4)
Se(9)	82(5)	70(5)	63(4)	-5(4)	31(4)	9(4)

* The anisotropic displacement factor exponent takes the form:

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

C. Results and Discussion

C.1 Synthesis

The syntheses and crystallization of I-V were carried out in $A_2As_xS_y$ fluxes that were generated by an *in situ* reaction of A_2S , As_2S_3 and S. These fluxes act as reaction media allowing for easy diffusion of reactants and also as oxidizing agents. They are termed as reactive fluxes because they are an essential part of the reaction outcome. The different $[As_xS_y]^{n-}$ anions that are generated in these fluxes bind to the metal based on its preferred coordination geometry and oxidation charge to give structurally variant compounds. $NaSnAsS_4$ was synthesized from a ratio of 1:1:2:10 of Na_2S :Sn:As:S in almost pure form. Increasing the amount of Na_2S , thereby increasing the flux basicity leads to the formation of $NaSnS_2$ and SnS_2 exclusively. However reducing the amount of sulfur from 10 equivalents to 5 equivalents, but keeping the ratios of the metals intact gives a stoichiometric mixture of $NaSnAsS_4$ (68% based on Sn) and $NaAsS_2$. Since both the phases have a needle morphology and are orange in color, it is difficult to separate them. The use of As_2S_3 instead of As leads to the formation of ternary $NaAsS_2$ and $NaSnS_2$ but no quaternary phases were found. The one-dimensional $ASnAsS_5$ ($A = K, Rb$) phase, which features the $\beta-[AsS_4]^{3-}$ ligand, forms from a flux ratio 1:1:1:10 of A_2S :Sn: As_2S_3 :S. Increasing the flux basicity leads to the formation of $A_2SnAs_2S_6$ and A_3AsS_4 in the case of K. In the case of Rb, the addition of Rb_2S usually led to the formation of glasses and Rb_3AsS_4 . Using Cs_2S , we obtained the molecular $Cs_2SnAs_2S_9$, consisting of $\beta-[AsS_4]^{3-}$ and $[AsS_5]^{3-}$ ligands, from a $Cs_4As_2S_{15}$ flux. This flux also gave a ternary phase, $Cs_4As_2S_{10}$ (Appendix, Page 270). Any change in the flux basicity led to the formation of glassy products. A pure

quantitative synthesis of this compound was achieved by a direct combination of the reactants. We attempted to use a mixed rubidium-cesium thioarsenate flux with the hope that we might be able to obtain the clusters that are connected together to form chains. But these reactions gave red glasses as products. Attempts to prepare CsSnAsS_5 and $\text{Cs}_2\text{SnAs}_2\text{S}_6$ also failed, giving glasses as products.

C.2 Structure description of NaSnAsS_4 (I)

NaSnAsS_4 crystallizes in the orthorhombic space group $Pn\bar{n}m$, Figure 1. The structure of I is made up of $[\text{Sn}(\text{AsS}_3)]_2$ dimers which are linked together by bidentate S atoms to form chains running along the c-axis. These chains are separated by charge balancing Na^+ ions. The $[\text{Sn}(\text{AsS}_3)]_2$ core is formed by the coordination of Sn with the pyramidal $[\text{AsS}_3]^{3-}$ ion. Each AsS_3 ligand utilizes all three of its sulfur atoms to bind to two Sn atoms. One sulfur atom forms a bridge between the two Sn atoms within the dimeric unit, while the other two sulfur atoms each bind to one tin to complete the core. These cores are then sewed together by two μ_2 -S atoms to form the chain. Sn is in a distorted octahedral site with Sn - S bond distances varying from 2.4997(9) to 2.6802(10) Å. S-Sn-S bond angles range from 80.6(3)° to 172.18(3)°. The Sn - Sn distance within the core is 3.973 Å. The Na^+ cation is surrounded by six sulfur atoms with Na-S bond lengths between 2.8948(18) to 3.034(3) Å. The average As-S bond distance is normal at 2.2772(11) Å. Tables 4 and 5 give selected bond lengths and bond angles for compounds I, III, IV and V.

The structure of NaSnAsS_4 is reminiscent of the one dimensional $\text{K}_3\text{Cr}_2(\text{PS}_4)_3$ ¹⁷ that features $[\text{Cr}(\text{PS}_4)]_2$ centers that are stitched together by $[\text{PS}_4]^{3-}$ tetrahedra. A similar

comparison can be made with the chains of KTiPSe_5 .¹⁸ This compound contains $[\text{Ti}(\text{PSe}_4)]_2$ units that are connected by μ^2 -Se atoms on either side to form a chain. TiSe_6 octahedra share edges with two $[\text{PSe}_4]^{3-}$ tetrahedra, each employing 3 Se atoms to bridge the two Ti atoms while one Se remains non-bonding.

C.3 Structure description of RbSnAsS_5 (III)

The structures of **II** and **III** are similar; therefore, we will discuss the structural details of **III** here. The structure of **III** was solved in the monoclinic space group $P2_1/c$. This structure is one-dimensional and similar to the structure of **I**. It is composed of chains, running down the c-axis, consisting of centrosymmetric $[\text{Sn}(\text{AsS}_2(\text{S}_2))_2]$ dimeric cores linked together by two μ_2 -bridging S^{2-} ions, Figure 2. The major difference between the structures of **I** and **III** is the type of thioarsenate ligand. In the case of **III**, this ligand is a pyramidal β - $[\text{AsS}_4]^{3-}$ ligand which is a derivative of the $[\text{AsS}_3]^{3-}$ ligand in **I**. It is obtained by substituting one terminal S atom in $[\text{AsS}_3]$ by a disulfide arm. In these cores, two $[\text{AsS}_2(\text{S}_2)]^{3-}$ ligands bridge two octahedral tin atoms employing three sulfur atoms each, of which one of the sulfur atoms is the terminal sulfur atom of the disulfide unit.

The adjacent chains are separated by hepta-coordinated Rb^+ ions with Rb-S distances varying from 3.2468(18) to 3.710(2) Å. Sn is coordinated by six S atoms at distances of 2.4503(9) to 2.6831(17) Å. (Table 3) The S-S distance is normal at 2.0415(19) Å. Sn^{4+} is distorted with S-Sn-S bond angles ranging from 84.65° to 174.18°. The Sn-Sn distances within the dimeric unit and between the dimeric units are 3.959 Å and 3.425 Å respectively; Table 4. As-S distances range from 2.2024(17) Å to 2.2924(16) Å with S-As-S angles between 98.36(6)° and 105.45(7)°.

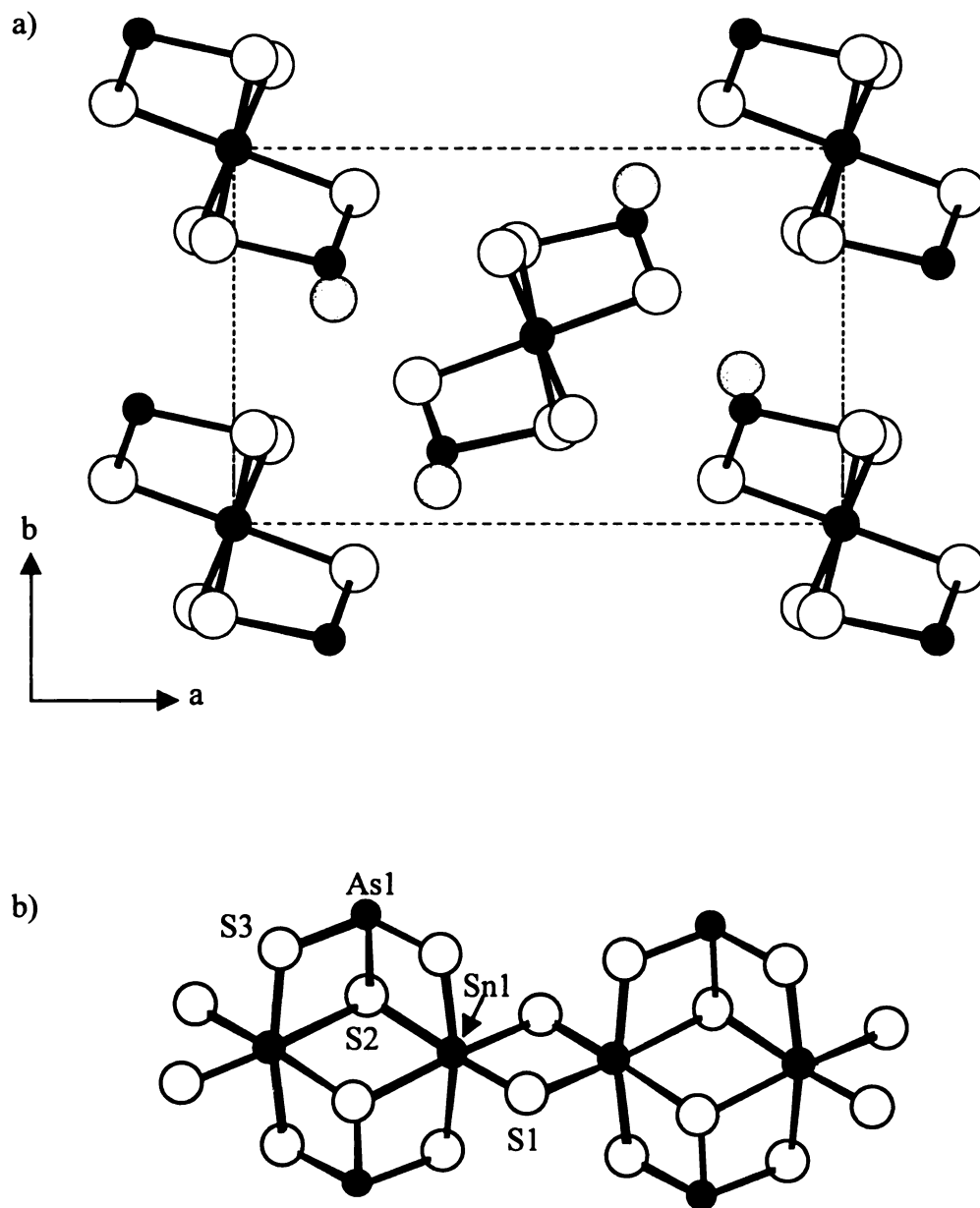


Figure 1. a) View of the unit cell of NaSnAsS_4 down c -axis. b) Single chain of NaSnAsS_4 .

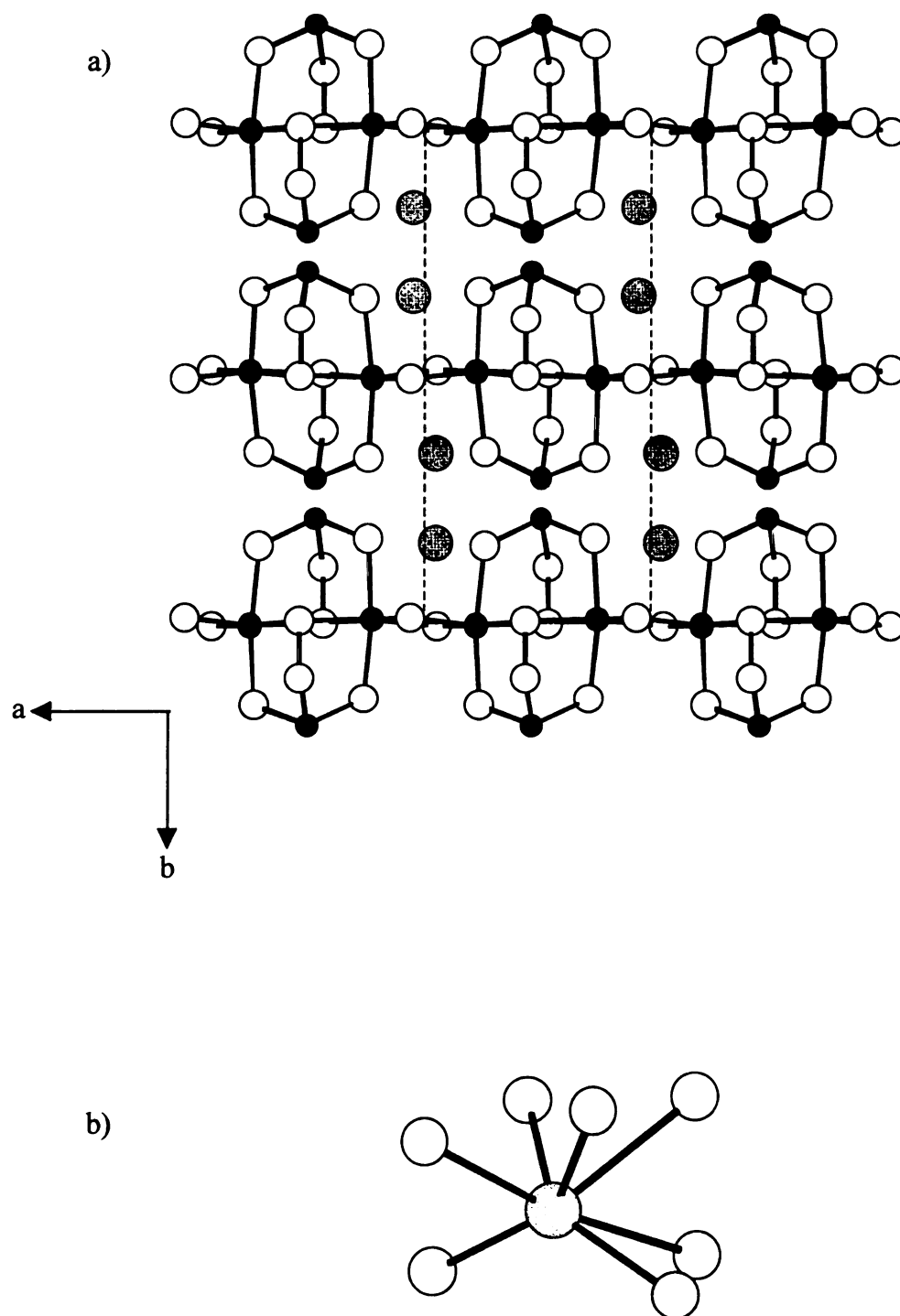


Figure 2. a) Unit cell of RbSnAsS_5 showing chains running along the a-axis. b) Coordination environment of the Rb^+ cation.

KSnAsS₅ (II) crystallizes in the orthorhombic space group *Pbam*. The lowering of symmetry going to Rb can be attributed to the bigger size of Rb, which does not allow the chains to pack as efficiently as in the potassium analog. This is also observed in the cation coordination environment. The K ion sits in a regular six-coordinate trigonal prismatic geometry whereas the Rb sits in an irregular seven-coordinate site, Figure 2.

NaSnAsS₄ and RbSnAsS₅ have very similar chain structures. The major difference comes from the type of the thioarsenate ligand present in these two compounds. In the case of RbSnAsS₅, there is more S present in the flux as compared to NaSnAsS₄. Therefore the AsS₃³⁻ anion can take another S atom to form AsS₄³⁻ thereby releasing the strain on the Sn⁴⁺ ion upon coordination.

C.4 Structure description of Rb₂SnAs₂S₆ (IV): Rb₂SnAs₂S₆ is a layered material that crystallizes in the trigonal space group *P-3*. The layers are made up of edge sharing SnS₆ octahedra and [AsS₃] pyramids. This compound is isostructural to the mineral ernigillite, Tl₂SnAs₂S₆.¹⁹ It was synthesized from a direct combination of Rb₂S/Sn/As/S mixture in the ratio 1/1/2/5. It could not be made from any other ratio of the starting materials. Attempts to obtain the compound by using As₂S₃ instead of As ended up yielding glassy products. Figure 3a shows the unit cell of Rb₂SnAs₂S₆ down the a-axis. The anionic [Sn(AsS₃)₂]_n²ⁿ⁻ lie perpendicular to the c-axis. Two rows of Rb⁺ cations sit between adjacent anionic sheets. The structure belongs to the TiS₂ structure type with Sn occupying the position of Ti and AsS₃ taking up the S position. Octahedral SnS₆ and pyramidal [AsS₃] units alternate forming eight membered -S-Sn-S-As-S-Sn-S-As- rings that have a chair like conformation. These rings share As-S-Sn edges with each other to

form the condensed rings running along the ab-plane forming the two-dimensional network. Each $[\text{AsS}_3]^{3-}$ unit binds to 3 Sn atoms, while each Sn is bonded to 6 $[\text{AsS}_3]^{3-}$ anions, Figure 3b. The $[\text{AsS}_3]^{3-}$ pyramids lie in such a way that the lone pair on the As points towards the Rb^+ ions between the layers, Figure 3c.

Sn-S bond distances are equal at 2.564(10) Å. As-S bond distance is 2.2458(10) Å. The closest interlayer distance is 4.4609 Å and the closest Sn-Sn distance within the layer and between the layers is 6.736 Å and 7.454 Å. S-Sn-S bond angles are 83.33(3)° and 96.67(3)°. S-As-S angles are equal at 96.66(4)°. (Tables 3 and 4) The layers are separated by ten-coordinate Rb^+ ions with Rb-S bond lengths from 3.4380(13) Å to 3.720(14) Å. The Rb sits between a hexagonal plane created by 6 S atoms and a trigonal plane created by 3 S atoms. In addition, Rb^+ shows a significant bonding interaction at a distance of 3.4385 Å with the lone pair on As. (Figure 3c) The structure has also been encountered in $\text{A}_2\text{Mn}(\text{TeS}_3)_2$ ²⁰ (A = Rb, Cs). In these compounds the Sn is substituted by Mn, which is octahedrally bound by pyramidal $[\text{TeS}_3]^{2-}$ units.

C.5 Structure description of $\text{Cs}_2\text{SnAs}_2\text{S}_9$ (V): The structure of V was solved in the noncentrosymmetric space group $Pmc2_1$. The structure is built up of molecular complex anions $\{\text{Sn}[\text{AsS}_2(\text{S}_2)][\text{AsS}(\text{S}_2)_2]\}^{2-}$ separated by Cs^+ cations. Figure 4 shows the unit cell and a single cluster anion. The Sn^{4+} ion is in a distorted octahedral environment coordinated by two pyramidal-shaped tridentate ligands, $[\text{AsS}_2(\text{S}_2)]^{3-}$ and $[\text{AsS}(\text{S}_2)_2]^{3-}$ forming a cage-like structure. The Sn-S bond lengths range from 2.510(4) Å to 2.589(5) Å for Sn1 and 2.504(4) Å to 2.592(5) Å for Sn2.

Table 4. Selected bond distances for NaSnAsS₄, RbSnAsS₅, Rb₂SnAs₂S₆ and Cs₂SnAs₂S₉

NaSnAsS ₄			
Sn(1) - S(1)	2 x 2.4997(9)	As(1) - S(3)	2 x 2.2655(10)
Sn(1) - S(3)	2 x 2.5088(10)	As(1) - S(2)	2.3006(14)
Sn(1) - S(2)	2 x 2.6802(10)	Na(1) - S(1)	2.937(2)
Na(1) - S(3)	4 x 2.8949(19)	Na(1) - S(1)	3.034(3)
RbSnAsS ₅			
Sn(1) - S(1)	2.4503(15)	As(1) - S(5)	2.2924(16)
Sn(1) - S(1)	2.4790(16)	Rb(1) - S(1)	3.2468(18)
Sn(1) - S(4)	2.5465(19)	Rb(1) - S(1)	3.3308(17)
Sn(1) - S(3)	2.5754(18)	Rb(1) - S(3)	3.338(2)
Sn(1) - S(2)	2.6714(16)	Rb(1) - S(4)	3.5071(19)
Sn(1) - S(2)	2.6831(17)	Rb(1) - S(3)	3.537(18)
As(1) - S(4)	2.2024(17)	Rb(1) - S(5)	3.666(3)
As(1) - S(3)	2.2130(16)	Rb(1) - S(1)	3.710(2)
S(2) - S(5)	2.0415(19)		
Rb ₂ SnAs ₂ S ₆			
Sn(1) - S(1)	6 x 2.5640(10)	Rb(1) - S(1)	3 x 3.4737(14)
As(1) - S(1)	3 x 2.2458(10)	Rb(1) - S(1)	3 x 3.7720(14)
Rb(1) - S(1)	3 x 3.4380(13)	Rb(1) - As(1)	3.4345(15)
Cs ₂ SnAs ₂ S ₉			
Sn(1) - S(11)	2 x 2.510(3)	Cs(1) - S(5)	2 x 3.628(3)

Sn(1) - S(1)	2.520(3)	Cs(1) - S(1)	3.679(3)
Sn(1) - S(4)	2 x 2.545(2)	Cs(1) - S(3)	2 x 3.7225(13)
Sn(1) - S(2)	2.589(4)	Cs(1) - S(9)	2 x 3.752(3)
Sn(1) - S(13)	2 x 2.641(8)	Cs(1) - S(4)	2 x 3.820(3)
Sn(2) - S(3)	2.504(3)	Cs(1) - S(10)	2 x 3.825(3)
Sn(2) - S(9)	2 x 2.528(3)	Cs(1) - As(4)	4.145(2)
Sn(2) - S(5)	2 x 2.579(3)	Cs(2) - S(11)	2 x 3.557(4)
Sn(2) - S(8)	2.592(4)	Cs(2) - S(12)	2 x 3.589(4)
As(1) - S(3)	2.194(4)	Cs(2) - As(2)	3.7038(18)
As(1) - S(10)	2 x 2.278(3)	Cs(2) - S(2)	2 x 3.7043(13)
As(2) - S(5)	2 x 2.216(3)	Cs(2) - S(8)	2 3.732(4)
As(2) - S(6)	2.304(4)	Cs(2) - S(7)	2 x 3.792(6)
As(3) - S(1)	2.190(3)	Cs(2) - S(4)	2 x 3.820(3)
As(3) - S(12)	2 x 2.201(4)	Cs(3) - S(7)	2 x 3.478(5)
As(3) - S(13)	2 x 2.432(8)	Cs(3) - S(2)	3.628(4)
As(4) - S(4)	2 x 2.224(3)	Cs(3) - S(5)	2 x 3.678(3)
As(4) - S(7)	2.328(5)	Cs(3) - S(8)	2 x 3.8185(16)
S(2) - S(7)	2.049(7)	Cs(3) - S(11)	2 x 3.841(5)
S(6) - S(8)	2.046(6)	Cs(3) - S(6)	2 x 3.8492(17)
Cs(3) - As(3)	3.972(2)	Cs(4) - S(3)	3.643(3)
Cs(4) - S(12)	2 x 3.655(5)	Cs(4)-S(9)	2 x 3.658(3)
Cs(4) - S(1)	2 x 3.6995(13)	Cs(4) - S(10)	2 x 3.707(3)
Cs(4) - S(11)	2 x 3.756(5)	Cs(4) - S(13)	3.762(8)

Table 5. Selected bond angles for NaSnAsS₄, RbSnAsS₅, Rb₂SnAs₂S₆ and Cs₂SnAs₂S₉

NaSnAsS ₄			
S(1) - Sn(1) - S(1)	90.01(4)	S(1) - Sn(1) - S(3)	2 x 95.71(3)
S(1) - Sn(1) - S(3)	2 x 92.02(3)	S(3) - Sn(1) - S(3)	169.07(4)
S(1) - Sn(1) - S(2)	2 x 93.30(3)	S(1) - Sn(1) - S(2)	2 x 172.18(3)
S(3) - Sn(1) - S(2)	2 x 80.60(3)	S(3) - Sn(1) - S(2)	2 x 91.26(3)
S(2) - Sn(1) - S(2)	84.32(4)	S(3) - As(1) - S(3)	100.97(5)
S(3) - As(1) - S(2)	94.72(3)	S(3) - As(1) - S(2)	94.72(3)
RbSnAsS ₅			
S(1) - Sn(1) - S(1)	91.96(6)	S(1) - Sn(1) - S(4)	92.78(4)
S(1) - Sn(1) - S(4)	96.12(4)	S(1) - Sn(1) - S(3)	100.73(4)
S(1) - Sn(1) - S(3)	85.46(4)	S(1) - Sn(1) - S(2)	93.43(6)
S(4) - Sn(1) - S(3)	166.35(5)	S(1) - Sn(1) - S(2)	174.18(4)
S(4) - Sn(1) - S(2)	88.82(4)	S(3) - Sn(1) - S(2)	77.54(4)
S(1) - Sn(1) - S(2)	89.73(6)	S(1) - Sn(1) - S(2)	172.76(4)
S(4) - Sn(1) - S(2)	90.83(4)	S(3) - Sn(1) - S(2)	87.31(4)
S(2) - Sn(1) - S(2)	84.65(6)	S(4) - As(1) - S(3)	105.45(7)
S(4) - As(1) - S(5)	99.32(6)	S(3) - As(1) - S(5)	98.36(6)
Rb ₂ SnAs ₂ S ₆			
S(1) - Sn(1) - S(1)	6 x 83.33(3)	S(1) - Sn(1) - S(1)	3 x 180.0
S(1) - Sn(1) - S(1)	6 x 96.67(3)	S(1) - As(1) - S(1)	3 x 96.66(4)

$\text{Cs}_2\text{SnAs}_2\text{S}_9$

S(11) - Sn(1) - S(11')	98.4(2)	S(1) - Sn(1) - S(11)	93.2(10)
S(4) - Sn(1) - S(4')	79.56(15)	S(2) - Sn(1) - S(4)	88.79(9)
S(1) - Sn(1) - S(2)	174.20(12)	S(11) - Sn(1) - S(4)	167.17(12)
S(3) - Sn(2) - S(9)	91.70(8)	S(9) - Sn(2) - S(9')	95.20(13)
S(5) - Sn(2) - S(5')	79.14(12)	S(5) - Sn(2) - S(8)	89.11(9)
S(3) - Sn(2) - S(8)	175.87(12)	S(5) - Sn(2) - S(9)	170.19(9)
S(3) - As(1) - S(10')	100.13(9)	S(10) - As(1) - S(10')	104.95(15)
S(5) - As(2) - S(6)	98.28(10)	S(5) - As(2) - S(5')	95.72(13)
S(1) - As(3) - S(12)	103.57(13)	S(12) - As(3) - S(12')	112.4(3)
S(4) - As(4) - S(7)	103.64(16)	S(4) - As(4) - S(4')	94.14(14)

There are four crystallographically unique Cs^+ cations surrounded by eleven S atoms in the range of 3.628(3) Å - 3.825(3) Å for Cs1, 3.557(4) Å - 3.820(3) Å for Cs2, 3.478(5) Å - 3.972(2) Å for Cs3, and 3.643(3) Å - 3.756(5) Å for Cs4. Weak interactions, similar to the one observed in IV between Rb^+ and As, are observed for Cs1, Cs2 and Cs3 with As4, As2 and As3, respectively at distances of 4.145 Å, 3.703 Å and 3.976 Å. The average S-S distance is normal at 2.0475 Å. The structure of the double cage-like $[\text{SnAs}_2\text{S}_9]^{2-}$ cluster anion is reminiscent of those in the centrosymmetric compounds $[(n\text{-Bu})_4\text{N}]_2[\text{MAS}_2\text{Se}_{10}]^{21}$ (M=Mo, W), which also have two $[\text{AsSe}(\text{Se}_2)_2]^{3-}$ ligands.

The structure of $\text{Cs}_2\text{SnAs}_2\text{Se}_9$ is similar to $\text{Cs}_2\text{SnAs}_2\text{S}_9$ and consists of the same structural motif, $\{\text{Sn}[\text{AsSe}_2(\text{Se}_2)][\text{AsSe}(\text{Se}_2)_2]^{2-}$ anions. This compound crystallizes in the monoclinic space group $P2_1$.

An important feature of the flux method is the freedom it allows the metal to choose its own ligands for lattice construction. In this context, an issue that deserves comment is the composition of the cluster anion, $[\text{SnAs}_2\text{S}_9]^{2-}$, which contains both $[\text{AsS}_5]^{3-}$ and $[\text{AsS}_4]^{3-}$ instead of only one type of ligand. A speculative explanation of this behavior can be based on electronic and steric considerations of the ligands involved. $[\text{AsS}_5]^{3-}$ being more electron donating than $[\text{AsS}_4]^{3-}$, because of the additional chalcogen atom, coupled with its ability to form a larger cage, might be preferred by the electrophilic Sn^{4+} ion. Coordination to this ligand reduces the electron density requirement of the central metal atom and allows for the relatively less electron-rich and less bulky $[\text{AsS}_4]^{3-}$ to bind.

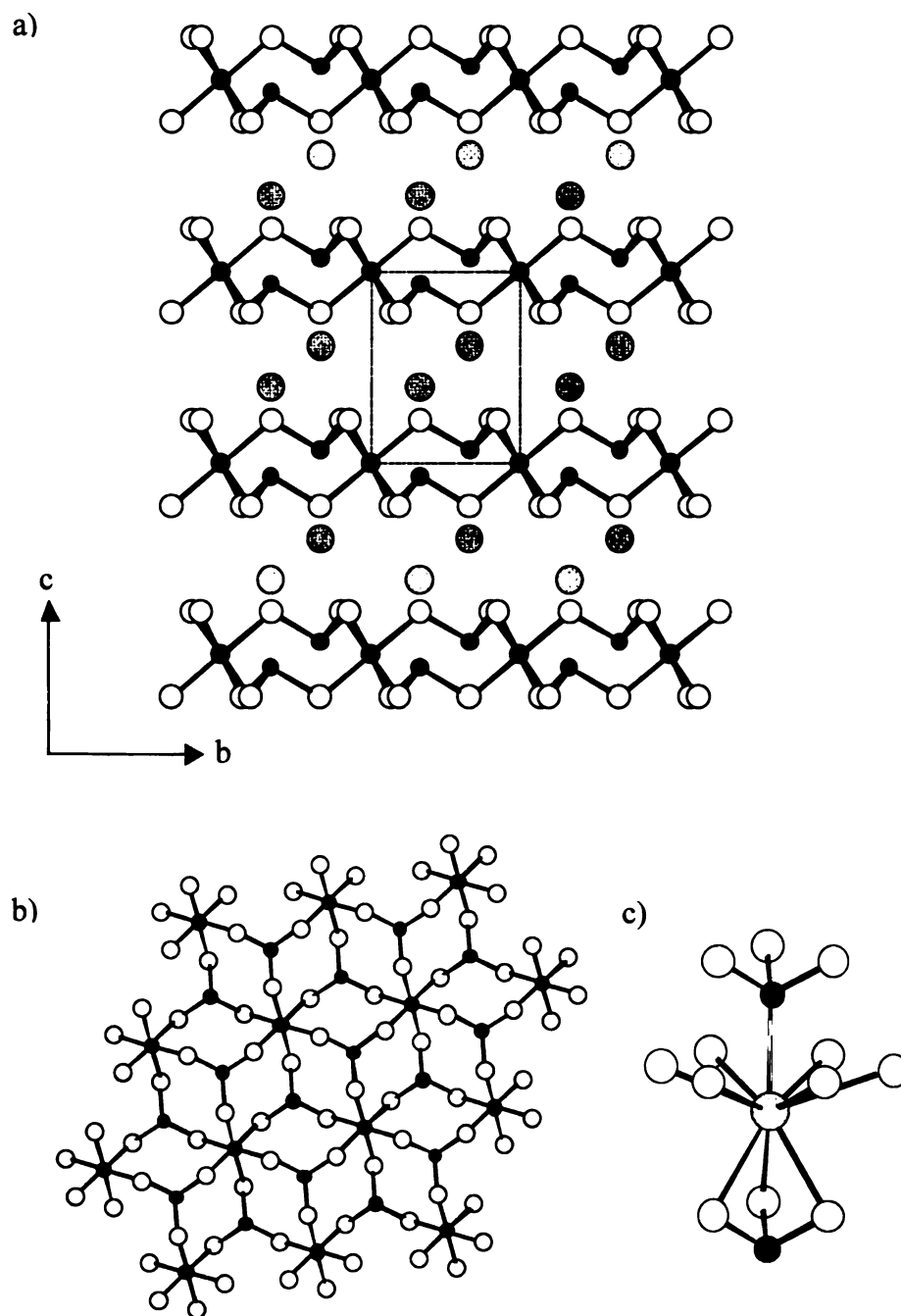


Figure 3. a) Layers of $\text{Rb}_2\text{SnAs}_2\text{S}_6$ parallel to the ab plane and stacked perpendicular to the c - axis. b) A single layer showing octahedral Sn bound by pyramidal AsS_3 ligands. c) Coordination environment of Rb

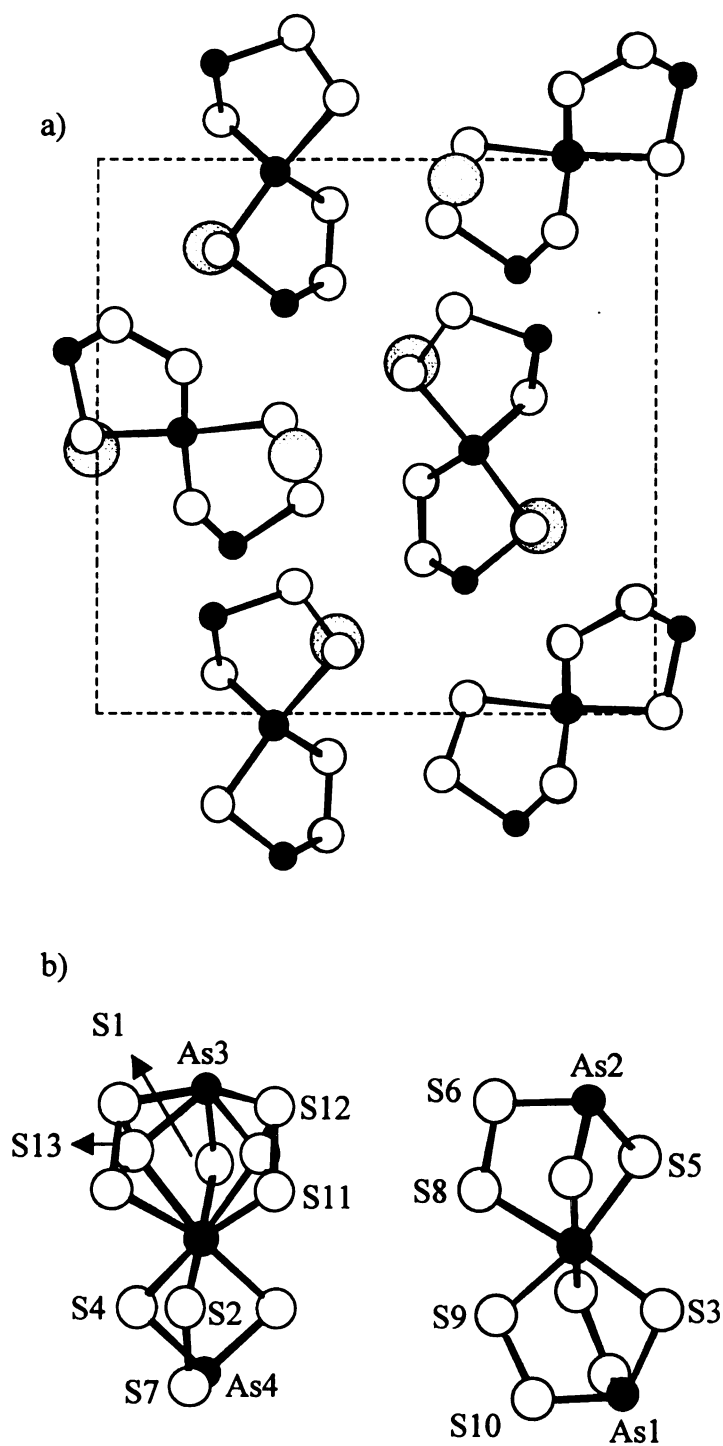


Figure 4. a) The unit cell of $\text{Cs}_2\text{SnAs}_2\text{S}_9$ showing the two crystallographically unique clusters. b) The individual clusters with one showing a disorder in the disulfide linkage.

C.6 Thermal Analysis

Differential thermal analyses (DTA) were performed on pure samples of all the compounds to ascertain their thermal behavior. In each case, the compound was checked for decomposition at the end of two heating cycles by taking its powder X-ray diffraction pattern. NaSnAsS₄ (I) melts at 488°C and on cooling shows a recrystallization peak at 375°C, Figure 5a. The powder pattern of the compound taken after the DTA indicated that the compound had decomposed to NaAsS₂ and SnS₂. RbSnAsS₅ (II) shows an endothermic (melting) peak at 380°C. On cooling, however, no recrystallization is observed implying glass formation. When this glass is heated again, an exothermic peak is observed at 320°C which is followed by melting at 372°C, Figure 5b. The powder pattern of the product after cooling showed that the compound had decomposed to a glassy matrix along with SnS₂. The DTA of Rb₂SnAs₂S₆ (IV) shows a melting point of 482°C and recrystallization at 365°C. As seen in Figure 5c, the recrystallization is partial. A slower heating rate allowed complete recrystallization of the compound. A powder pattern taken after the DTA matched the one before, indicating congruent melting. The DTA of V, Figure 5d, showed that it melted at 351°C but no recrystallization was observed on cooling implying the formation of a glassy phase. The glass crystallizes on heating at 268°C. Comparison of the powder patterns of the pristine compound, the glassy phase and recrystallized phase indicate that the glass-crystal transformation is reversible, Figure 7a.

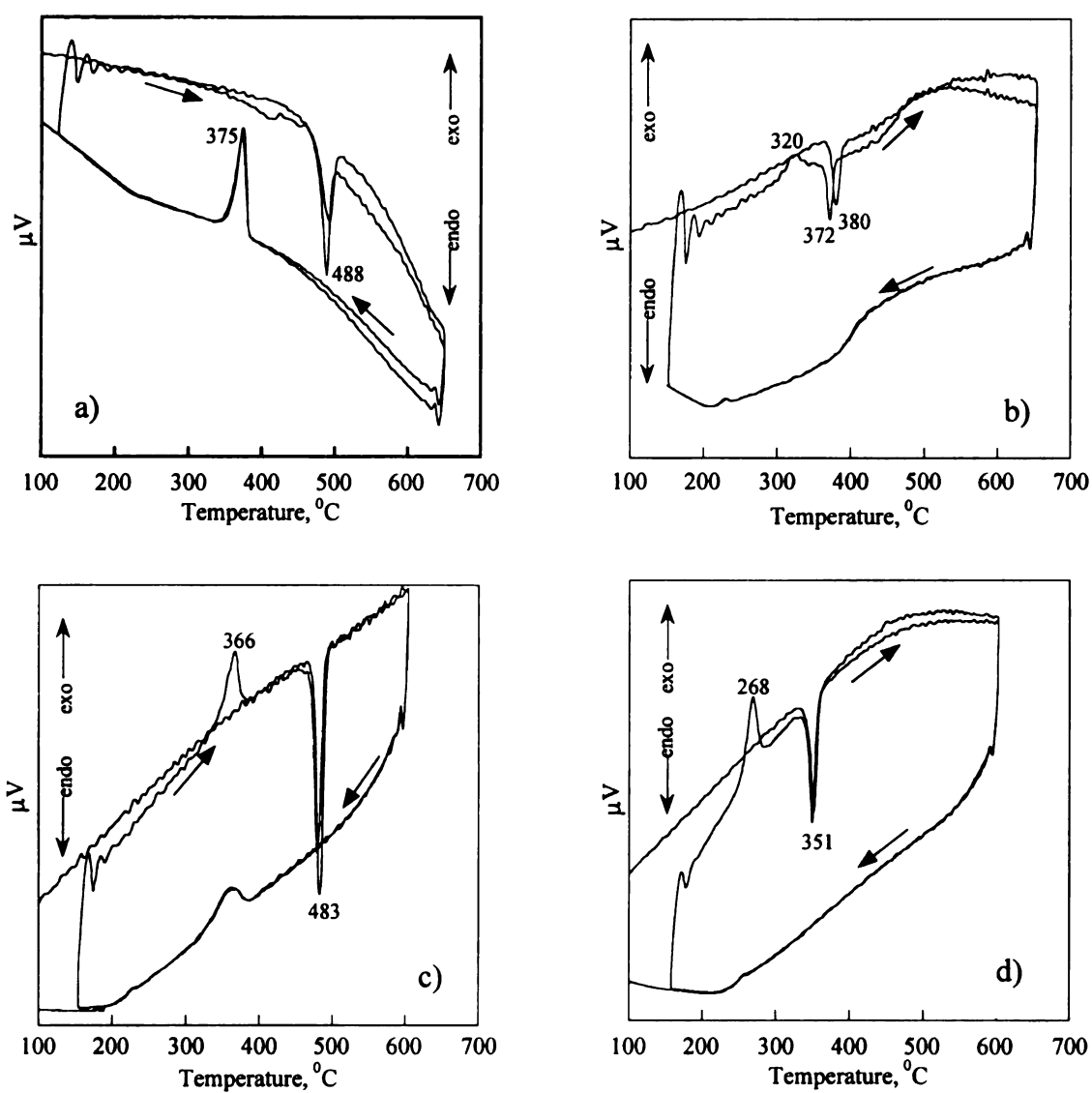


Figure 5. Differential Thermal Analysis of a) NaSnAsS₄ b) RbSnAsS₅ c) Rb₂SnAs₂S₆ d) Cs₂SnAs₂S₉

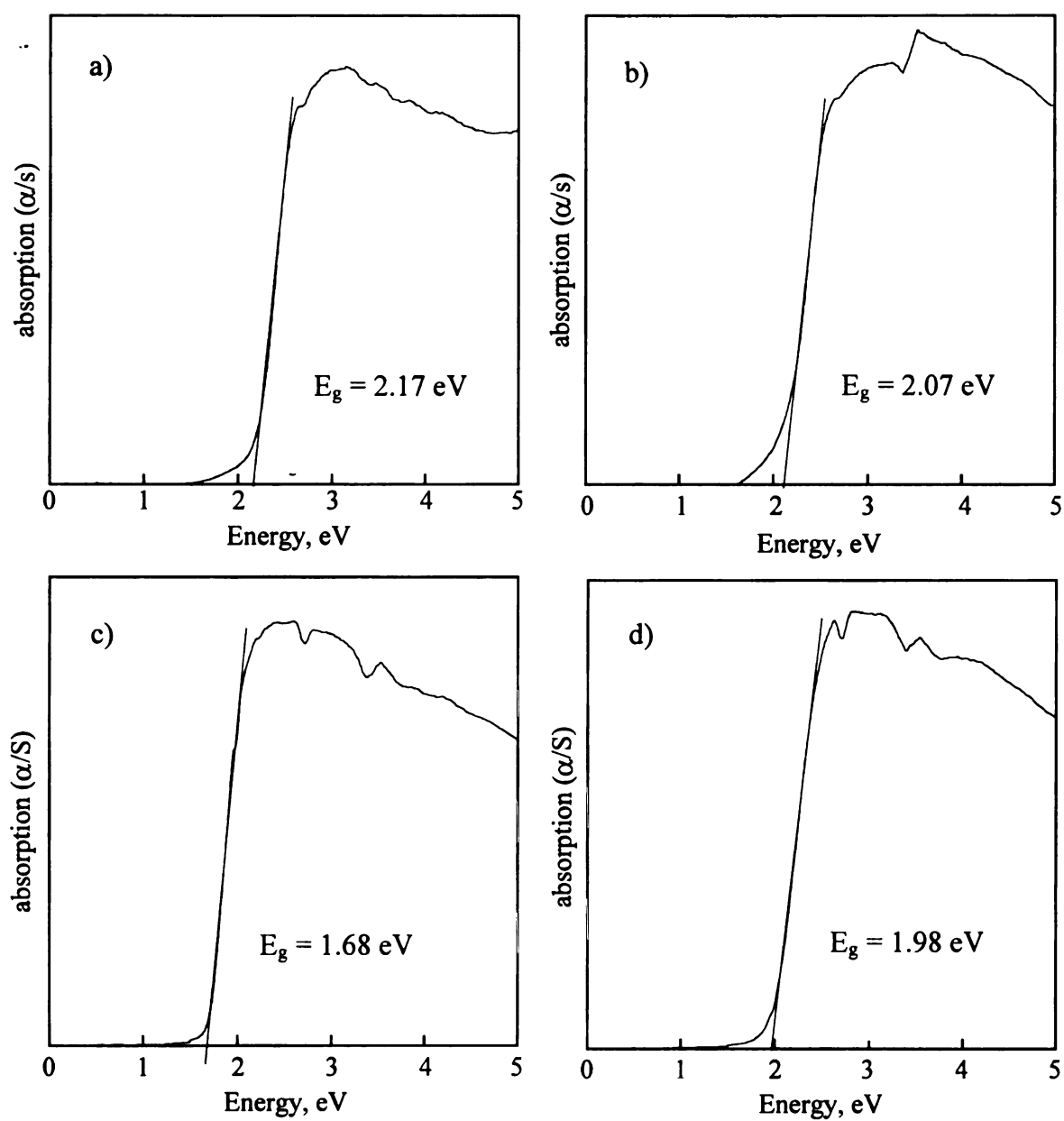


Figure 6. Optical absorption spectra of a) NaSnAsS_4 b) RbSnAsS_5 c) $\text{Rb}_2\text{SnAs}_2\text{S}_6$ and d) $\text{Cs}_2\text{SnAs}_2\text{S}_9$. Energy gaps are calculated as 2.17 eV, 2.07 eV, 1.68 eV and 1.98 eV respectively.

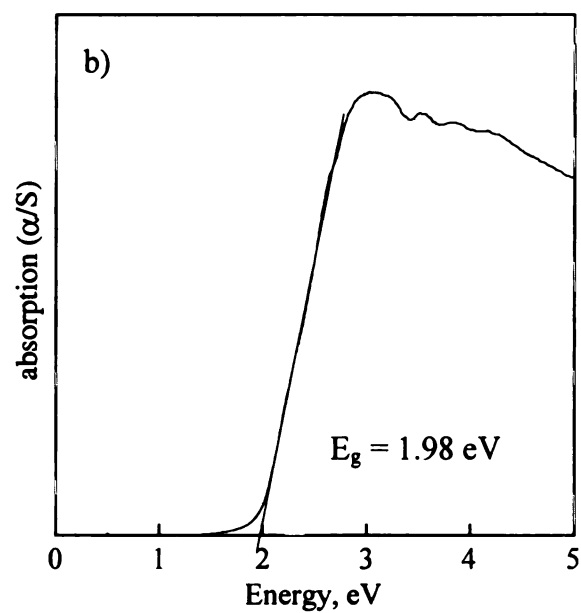
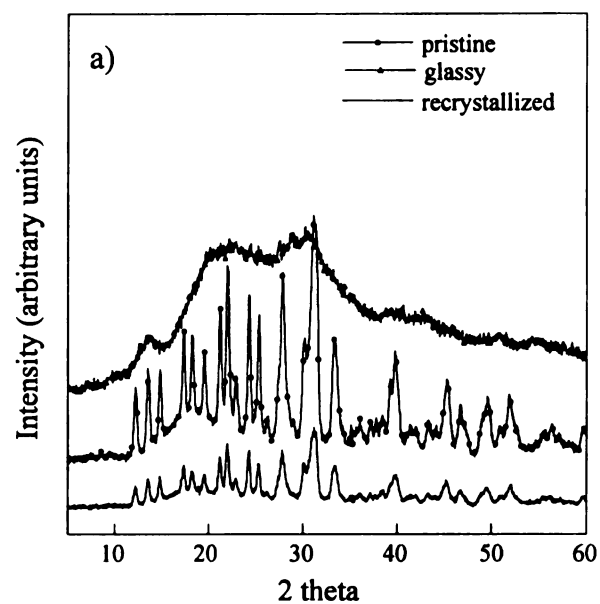


Figure 7. a) Comparison of the powder patterns of pristine, glassy and re-crystallized $\text{Cs}_2\text{SnAs}_2\text{S}_9$ shows that the glass-crystal transition is reversible. b) Optical spectrum of the glassy $\text{Cs}_2\text{SnAs}_2\text{S}_9$ shows an absorption onset at 1.98 eV.

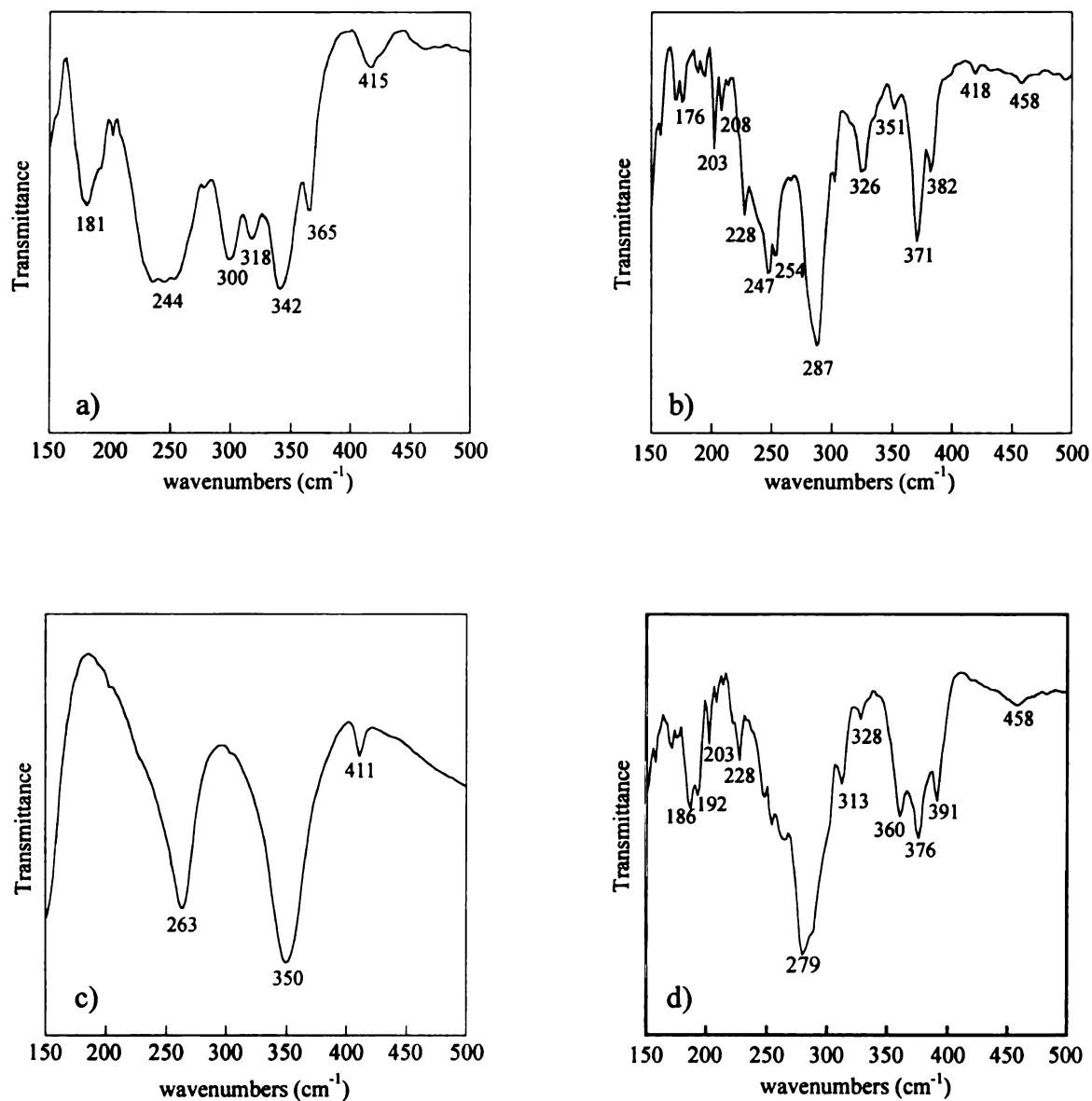


Figure 8. Far Infrared spectra of a) NaSnAsS_4 b) RbSnAsS_5 c) $\text{Rb}_2\text{SnAs}_2\text{S}_6$ and d) $\text{Cs}_2\text{SnAs}_2\text{S}_9$

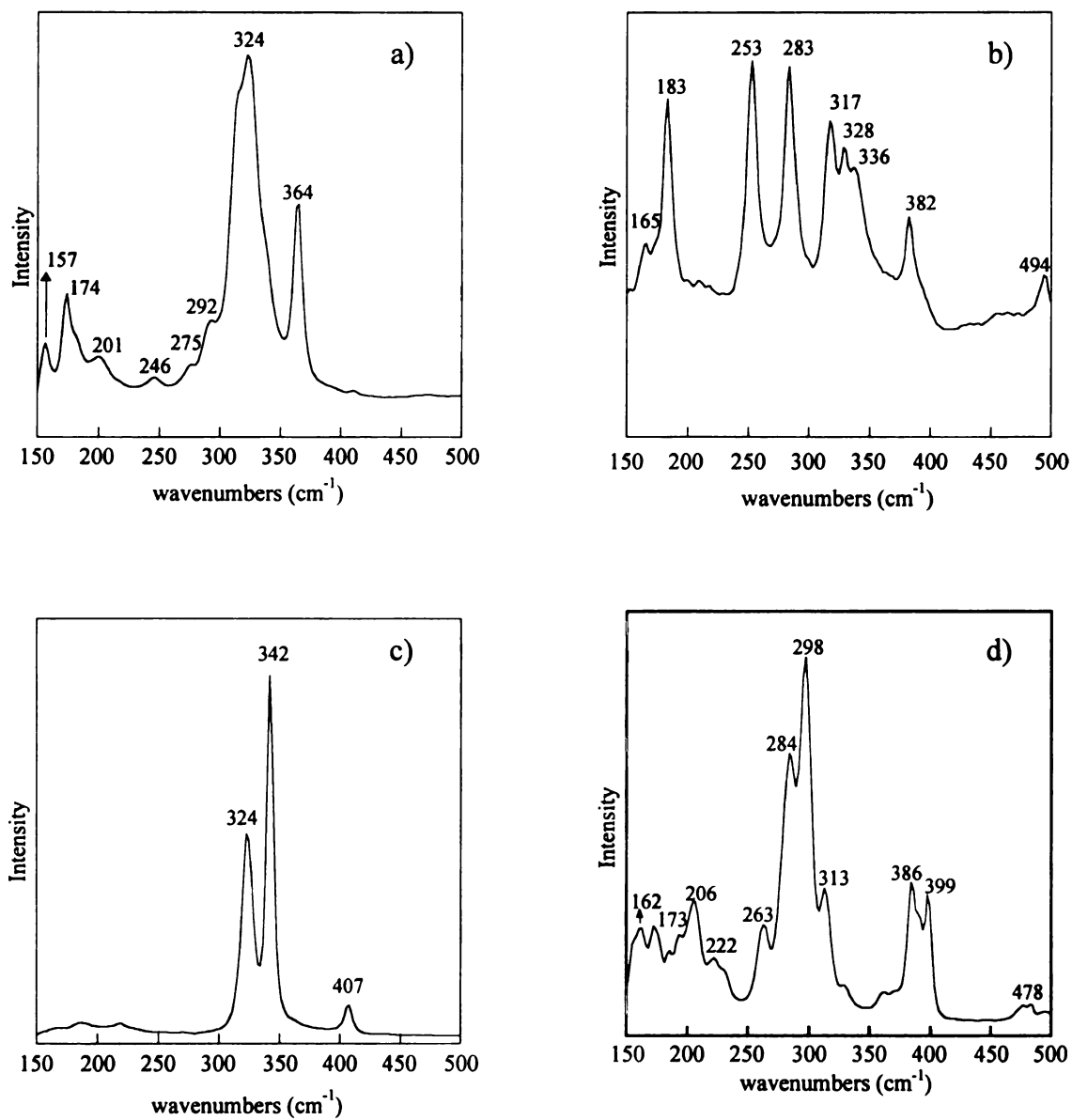


Figure 9. Raman Spectra of a) NaSnAsS_4 b) RbSnAsS_5 c) $\text{Rb}_2\text{SnAs}_2\text{S}_6$ and d) $\text{Cs}_2\text{SnAs}_2\text{S}_9$.

C.7 Optical Spectroscopy

The energy gaps in these compounds were estimated by recording their diffuse reflectance spectra. As seen in Figure 6, these compounds are semiconductors with band gaps ranging from 1.68 eV for $\text{Rb}_2\text{SnAs}_2\text{S}_6$ to 2.17 eV for NaSnAsS_4 . For $\text{Cs}_2\text{SnAs}_2\text{S}_9$, this energy gap arises from localized levels and therefore can be considered as a HOMO-LUMO transition. The glassy form of **V** also shows an absorption onset at 1.98 eV, Figure 7b. The absence of the typical red shift in the absorption edge, as is typically observed in the glassy forms of compounds with extended solid state structures,²² also supports the notion that the electronic properties of **V** are intracuster in nature. In extended systems with a well-developed band structure, the crystal to glass conversion produces a red-shift because of the large number of defect-induced midgap states generated in the glass. The discrete molecular nature of $\text{Cs}_2\text{SnAs}_2\text{S}_9$ does not generate such states and the glass structure probably represents a disordered arrangement of $[\text{SnAs}_2\text{S}_9]^{2-}$ anions and Cs^+ cations. Table 6 gives the band gaps for all these compounds. Table 7 gives the peaks observed in the IR and Raman spectra of compounds **I**, **III**, **IV** and **V**. The IR spectra for the above compounds are shown in Figure 8. Based on previous reports,²³ the vibrations between 420 cm^{-1} and 300 cm^{-1} can be assigned to As-S stretching vibrations. Below 300 cm^{-1} , the peaks can be attributed to either Sn-S stretching or As-S bending modes. The Raman spectra are shown in Figure 9. Assignments similar to the IR spectra can be made here. RbSnAsS_5 and $\text{Cs}_2\text{SnAs}_2\text{S}_9$ show peaks at 494 and 478, respectively. These peaks are diagnostic of S-S stretching vibrations.²⁴

D. Conclusion

The synthesis, structural characterization and optical properties of six new quaternary alkali metal tin thioarsenates have been presented. The dimensionality of these compounds ranges from molecules to layers. This is the first time that the ligands, $[\text{AsS}_4]^{3-}$ and $[\text{AsS}_5]^{3-}$ have been observed in the flux methodology. NaSnAsS_4 , KSnAsS_5 and RbSnAsS_5 are one-dimensional materials that might give anionic chains when exfoliated in polar solvents. $\text{Cs}_2\text{SnAs}_2\text{S}_9$ crystallizes in the non-centrosymmetric space group $Pmc2_1$ and needs to be investigated for its non-linear optical behavior. It also displays a reversible glass to crystal transition, a requisite condition for energy storage systems. The compounds presented here have no known thiophosphate analogs indicating that these fluxes have a promising potential that needs to be exploited.

Table 6. Band gaps for I-V

Compound	Band gap (eV)
NaSnAsS ₄	2.17
KSnAsS ₅	2.11
RbSnAsS ₅	2.07
K ₂ SnAs ₂ S ₆	1.89
Rb ₂ SnAs ₂ S ₆	1.68
Cs ₂ SnAs ₂ S ₉	1.98

Table 7. Far IR and Raman bands of I, III, IV and V

Compound	Far-IR (cm ⁻¹)	Raman (cm ⁻¹)
NaSnAsS ₄	415, 365, 342, 318, 300, 279, 254, 244, 236, 203, 181	157, 174, 201, 246, 275, 292, 324, 364
RbSnAsS ₅	458, 418, 382, 371, 351, 326, 287, 254, 247, 228, 208, 203, 176	165, 183, 253, 283, 317, 328, 336, 382, 494
Rb ₂ SnAs ₂ S ₆	411, 350, 263	324, 342, 407
Cs ₂ SnAs ₂ S ₉	458, 391, 376, 360, 328, 313, 279, 228, 203, 192, 186	162, 173, 206, 222, 263, 284, 298, 313, 386, 399, 478

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Chapter 3

Synthesis, Characterization of the layered compounds $\text{Tl}_2\text{SnAs}_2\text{Q}_6$ ($\text{Q} = \text{S}, \text{Se}$)

Abstract

The reaction of Sn in potassium and rubidium thioarsenate fluxes gave the trigonal compound $\text{K(Rb)}_2\text{SnAs}_2\text{S}_6$, which consists of $[\text{SnAs}_2\text{S}_6]^{2-}$ layers with the alkali cations lying between the layers. Given the high symmetry of this compound, we reasoned that if we could substitute the alkali cations with Tl and S with Se, we would be able to obtain better semiconductor that might possibly have some interesting thermoelectric properties. We were successful in discovering $\text{Tl}_2\text{SnAs}_2\text{S}_6$ (**I**) and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ (**II**) which crystallize in the space group $P\bar{3}$ with $a = 6.706(4) \text{ \AA}$, $c = 7.187(6) \text{ \AA}$ for **I** and $a = 6.996(3) \text{ \AA}$, $c = 7.232(4) \text{ \AA}$ for **II**. These compounds are semiconductors with band gaps of 1.68 eV for **I** and 1.08 eV for **II**, corresponding to their dark red and black colors respectively. **II**, on melting followed by cooling forms a glass, which has a band gap of 0.87 eV. This glass can be crystallized back on heating.

A. Introduction

The ultimate goal in solid state chemistry is the ability to predict and prepare materials with pre-designed structures and properties. This requires that we have a good understanding of different structure types. Therefore it is important that new structures be discovered. In the case of multinary chalcogenides, this purpose is served by the hugely successful alkali metal polychalcogenide¹ and polychalcophosphate flux methods.² These fluxes allow reactions to be done at lower temperatures and reduce or eliminate thermodynamic control over the reaction pathway. Under such conditions molecular building blocks rather than atoms are available for bonding. These building blocks can show a variety of binding modes resulting in different structural assemblies. Recently we began investigating the reactivity of main group and transition metals in alkali polythioarsenate fluxes.³ The driving force for this investigation was the dissimilar redox behavior of the $\text{As}^{3+}/\text{As}^{5+}$ couple in a sulfur environment compared to the $\text{P}^{4+}/\text{P}^{5+}$ couple. We anticipate the structures of thioarsenate compounds to be quite different from those observed in chalcophosphate chemistry. We therefore set forth on a systematic study of the reactivity of different metals in these fluxes.

We chose Sn because of our success with this metal in polychalcogenide and polychalcophosphate fluxes.⁴ The reactions of Sn in AAs_xS_y ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) fluxes gave the one-dimensional compounds NaSnAsS_4 and ASnAsS_5 ($\text{A} = \text{K}, \text{Rb}$), the layered compounds $\text{A}_2\text{SnAs}_2\text{S}_6$ ($\text{A} = \text{K}, \text{Rb}$) and the molecular $\text{Cs}_2\text{SnAs}_2\text{S}_9$, which features discrete molecules.³

The layered phase, $\text{A}_2\text{SnAs}_2\text{S}_6$, crystallizes in the trigonal space group $P\bar{3}$. The band gap of $\text{K}_2\text{SnAs}_2\text{S}_6$ is 1.89 eV. Because of the highly symmetrical crystal structure of this

phase, we became interested in them as possible semiconductors. If Tl could be substituted for the alkali metal, there will be a lowering of the band gap because of the tendency of Tl to act in a more covalent fashion compared to the alkali metals. Additional reduction in the band gap can be achieved by substituting Se for S. Compounds with low band gaps and high symmetry are desirable for thermoelectric applications.⁵ Another useful class of thallium thioarsenate materials which has gained considerable interest is the glassy system $\text{Tl}_2\text{S}-\text{As}_2\text{S}_3$, where Tl is used as a modifier to modify the glassy As_2S_3 network and hence change its properties.⁶ Thin films of Tl-As-S glasses have shown potential as high-resolution photoresist. Most of the known thallium thioarsenates are minerals. These minerals include $\text{TlPbAs}_5\text{S}_9$,⁷ TlHgAsS_3 ,⁸ $\text{Tl}_2\text{Sb}_6\text{As}_4\text{S}_{16}$,⁹ $\text{TlHgAs}_3\text{S}_6$,¹⁰ TlAs_5S_8 ,¹¹ $\text{Tl}_2\text{SnAs}_2\text{S}_6$,¹² $\text{Tl}_2\text{MnAs}_2\text{S}_5$,¹³ Tl_3AsS_4 ,¹⁴ $\text{TlPbAs}_3\text{S}_6$,¹⁵ Tl_3AsS_3 ,¹⁶ and TlAsS_2 .¹⁷ Some of these minerals like $\text{Tl}_2\text{MnAs}_2\text{S}_5$, $\text{TlPbAs}_3\text{S}_6$, Tl_3AsS_4 , Tl_3AsS_3 and TlAsS_2 have been synthesized in the laboratory. Here we present the synthesis and characterization of $\text{Tl}_2\text{SnAs}_2\text{Q}_6$ ($\text{Q} = \text{S}, \text{Se}$), which are the synthetic equivalents of the mineral ernigillite ($\text{Tl}_2\text{SnAs}_2\text{S}_6$).¹² A highlight of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ is its ability to form glass on melting. During our attempts to make the analogous $\text{Tl}_2\text{SnSb}_2\text{Se}_6$, we discovered a new phase $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ that has an interesting layered structure. The structure of this compound is discussed in the appendix.

B. Experimental Section

B.1 Reagents

All manipulations were done in a nitrogen-filled dri-vac glove box. Reagents: Tl, Sn (99.999 %; Cerac, Milwaukee, WI); As (99.9%; Aldrich Chemical Co, Milwaukee, WI);

S (99.9 %; Strem Chemicals, Newburyport, MA); Se (99.999 %; Noranda Advanced Materials, Quebec, Canada); N,N-dimethylformamide (Spectrum Chemicals, ACS reagent grade); diethyl ether (CCI, ACS grade).

Caution: Thallium and its compounds are extremely toxic and proper precautions need to be taken when handling these compounds.

B.2 Physical Measurements

Powder X-ray Diffraction

X-ray powder diffraction patterns were recorded on a CPS 120 INEL diffractometer (Cu K α radiation) operating at 40kV/20mA and equipped with a position sensitive detector with a flat sample geometry.

Energy Dispersive Spectroscopy

Semiquantitative microprobe analyses on the compounds were done with a JEOL 6400V scanning electron microscope equipped with a Noran Vantage Energy Dispersive Spectroscopy detector.

Diffuse Reflectance Spectroscopy

Solid state diffuse reflectance spectra were measured using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as reference. Band gaps were computed according to a procedure described elsewhere.¹⁸

Differential Thermal Analysis

The thermal behavior of the compounds was investigated by differential thermal analysis with a Shimadzu DTA-50 thermal analyzer. Typically ~ 20mg of the sample was sealed

in fused-silica tube. An equal amount of a reference material, Al_2O_3 , was also sealed in another tube. The sample and the reference were then heated/cooled at the rate of $10^\circ\text{C}/\text{min}$. Melting and recrystallization events result in a difference in the temperatures of the sample and the reference, which is recorded. Congruent melting of the compound was analyzed by recording powder patterns before and after the DTA experiment. Reproducibility of the result was checked by running multiple heating/cooling cycles.

Band structure calculations

Band structure calculations were performed on $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ using the self-consistent, full-potential linearized augmented plane wave method (LAPW)¹⁹ within density functional theory (DFT) with a generalized gradient approximation (GGA) for the exchange and correlation potential within the Perdew-Burke-Ernzerhof model.²⁰ Scalar relativistic corrections were added and spin-orbit interactions (SOI) were incorporated using a second variational procedure.²¹ The calculations were performed with the WIEN97 program.²² Self-consistent iterations were performed with 24 k points in the reduced Brillouin zone with a cutoff between valence and core states of -6.0 Ry; convergence was assumed when the total energy difference between cycles was within 0.0001 Ry.

B.3 Synthesis

Tl₂SnAs₂S₆ (I): $\text{Tl}_2\text{SnAs}_2\text{S}_6$ was prepared by reacting stoichiometric amounts of Tl, Sn, As and S at 500°C . The reactants were loaded in a fused-silica tube in a nitrogen atmosphere and the tube sealed under vacuum. The tube was then heated to 500°C in 10h, held at that temperature for 60h and cooled down to 250°C at the rate of $5^\circ\text{C}/\text{h}$ followed

by rapid cooling to room temperature. The product consisted of homogeneous red plates. The average composition, as determined by EDS analysis using a scanning electron microscope on several red plates, was " $\text{Tl}_2\text{SnAs}_{2.1}\text{S}_6$ ". The powder pattern of the product was compared to the pattern simulated on the basis of single crystal structure and revealed an almost pure phase, the minor impurity being Tl_2SnS_3 .

$\text{Tl}_2\text{SnAs}_2\text{Se}_6$ (II): $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ was made by a direct combination of the elements using a slightly different heating profile from above. The reactants were sealed in an evacuated silica tube, heated to 600°C and maintained there for 4 days. On cooling the tube to 200°C at the rate of 5°C/h followed by rapid cooling to room temperature, shiny black plate like crystals of the targeted phase were obtained. Energy dispersive spectroscopy gave an average composition of " $\text{Tl}_2\text{SnAs}_{1.7}\text{Se}_{5.9}$ ". The powder pattern of the compound matched the simulated powder pattern based on the crystal structure revealing a pure phase with a 100% yield.

B.4 X-ray Crystallography

Single crystal diffraction data for the title phases were collected on a Bruker SMART Platform CCD diffractometer, operating at 50kV/40mA and employing graphite monochromatized Mo $K\alpha$ radiation. A full sphere of data was collected with scan widths of 0.3 in ω and an exposure time of at least 45s per frame. The SMART program was used to extract reflections and obtain an initial cell. The program SAINT was used to integrate data using the orientation matrix obtained from SMART. An empirical absorption correction was done using SADABS. All refinements were carried out using the SHELXTL package of crystallographic programs. Intensity statistics and systematic

absence conditions pointed to the trigonal space group $P\bar{3}$ for **I** and **II**.²³ The structure solution was straightforward and all atoms were found in two least squares cycles. After complete anisotropic refinement of all the atoms, the final $R1/wR2$ values were 4.92/11.84 for **I** and 4.14/10.19 for **II**. Table 1 lists the crystallographic refinement data for the two compounds. Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Anisotropic displacement parameters are given in Table 3.

C. Results and Discussion

C.1 Synthesis

$Tl_2SnAs_2S_6$ was achieved by the fusion of Tl, Sn, As and S in the ratio 2/1/2/6 at 500°C for 60h. A similar heating profile failed to produce pure $Tl_2SnAs_2Se_6$. Instead, along with the required phase, we always formed Tl_2SnSe_3 as a byproduct. Pure synthesis of $Tl_2SnAs_2Se_6$ was realized by heating the elements at 600°C for 4 days. We also attempted to prepare $Tl_2SnAs_2Te_6$, $Tl_2SnSb_2S_6$, $Tl_2SnSb_2Se_6$ and $Tl_2SnSb_2Te_6$, however the reactions yielded inhomogeneous products along with Tl_2SnQ_3 ($Q = S, Se, Te$).

C.2 Structure description of $Tl_2SnAs_2Q_6$ ($Q = S, Se$)

$Tl_2SnAs_2Q_6$ ($Q = S, Se$) is isostructural to $K_2SnAs_2S_6$ and consists of layers formed by edge sharing SnQ_6 octahedra and AsQ_3 pyramids. Another compound that has the same structure as $Tl_2SnAs_2Q_6$ is $Cs_2Mn(TeS_3)_2$.²⁴ The Tl^+ cations act as spacers and lie between the layers, Figure 1. Each layer is made up of an octahedral Sn^{4+} ion which is coordinated by six different $[AsQ_3]^{3-}$ ligands, each utilizing one of its terminal Q atoms.

Thus an eight-membered ring of alternating -Q-Sn-Q-As-Q-Sn-Q-As- is formed. The orientation of the AsQ₃ ligands are such that apex of the pyramid, where the As is located, points towards the Tl between the layers. This leads to significant Tl-As interactions through the lone pair of electrons on As. As a result, Tl-As distance is comparable to Tl-Q distances.

Sn has a slightly distorted octahedral geometry with 6 equivalent Sn-Q bond distance of 2.564(5) Å for S and 2.6873(15) Å for Se, see Table 4. The equatorial and axial Q-Sn-Q bond angles are exactly 180°, while the Q-Sn-Q bond angles between equatorial and axial atoms are 82.77(15)° and 97.23(15)° for S and 82.83(5)° and 97.17(5)° for Se, see Table 5. As-Q distance is 2.256(5) Å for S and 2.3854(17) Å for Se. The AsQ₃ pyramid is distorted from the ideal with Q-As-Q bond angle of 97.03(18)° for S and 96.58(7)° for Se. Tl sits in a irregular seven coordinate pocket and is bonded to 3 Se atoms at distances of 3.2856(18) Å, 3 Se atoms at 3.422(2) Å and one As atom at a distance of 3.287(3) Å. The corresponding Tl-S and Tl-As distances are 3.274 Å, 3.395 Å and 3.277(4) Å respectively. The distance between two adjacent layers is 4.341 Å for Tl₂SnAs₂S₆ and 4.287 Å for Tl₂SnAs₂Se₆.

Comparison of isostructural Rb₂SnAs₂S₆ and Tl₂SnAs₂S₆ can give us important clues as to the role of Tl⁺ in the structure. Does it act as an inert counter-cation or is it involved in bonding? Since Tl and Rb have almost the same ionic radii, one would expect the cell parameters to be almost identical.²⁵ The cell volume of Tl₂SnAs₂S₆ is nearly 4.4% smaller than Rb₂SnAs₂S₆. Also the interlayer distance in Rb₂SnAs₂S₆ is longer at 4.4609 Å. This implies that there exist stronger forces of attraction between Tl⁺ and the AsQ₃ anions as compared to Rb. Some more understanding of these bonding forces can come

from comparison with other Tl-As-Q compounds. In $\text{Tl}_2\text{MnAs}_2\text{S}_5$,¹³ the Tl-S distances range from 2.933(5) to 3.531(8) Å. Similarly, Tl-As distance in this compound is 3.580(1) Å. The shortest Tl-S distance in $\text{Tl}_2\text{Au}_4\text{S}_3$ ²⁶ is 2.978(1) Å and as observed from the density of states plot, there is a strong interaction between the Tl s and S p orbitals. The density of states plot and the band structure plots of TlTaS_3 ²⁷ indicate there is very little Tl-S contribution. The Tl-S bond lengths in this compound are in the range 3.128(3) to 3.331(3) Å. Another interesting set of compounds are the thallium polysulfides, $(\text{Ph}_4\text{P})_2\text{Tl}_2(\text{S}_4)_2$ and $\text{K}_{0.68}\text{Tl}_{1.32}\text{S}_5$.²⁸ Tl-S bond lengths in the former are significantly shorter with a mean distance of 2.926 Å whereas in the latter it is 3.316 Å. The average Tl-S distance is 3.334 Å in $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and the average Tl-Se distance is 3.354 Å in $\text{Tl}_2\text{SnAs}_2\text{Se}_6$. From the above discussion we can interpret that the Tl-Q interactions in the title compounds, though stronger than $\text{A}_2\text{SnAs}_2\text{S}_6$ (A = K, Rb), are predominantly ionic. A better idea of the extent of involvement in bonding of Tl- based orbitals can be obtained from band-structure calculations.

C.3 Differential Thermal Analysis and Phase Change Properties

The differential thermal analysis of $\text{Tl}_2\text{SnAs}_2\text{S}_6$, Figure 2, shows a melting point of about 490°C and recrystallization point around 424°C. The powder pattern taken after the DTA matches with the one taken before the experiment indicating a congruent melting compound. The thermal behavior of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ showed a reversible crystal -glass transition. On heating, the compound melts at 350°C, however on cooling does not crystallize. Crystallization occurs on heating the sample in a second cycle at 297°C. The X-ray powder diffraction pattern of the compound after cooling from 325°C matches very

well with the parent pattern indicating a congruently melting compound, Figure 3.

Interestingly, the compound $\text{Rb}_2\text{SnAs}_2\text{S}_6$ also shows partial glass formation on heating while $\text{Cs}_2\text{SnAs}_2\text{S}_6$ shows a complete and reversible glass-crystal transformation. It is therefore possible that $\text{Tl}_2\text{SnAs}_2\text{S}_6$ may also form a glass if we quench it in ice-cold water from a molten state. Such compounds are potentially interesting candidates for use in memory storage devices²⁹ and further studies need to be done in this direction.

It is probably not surprising that these compounds form glasses readily. Structural studies on As_2S_3 glasses have shown that the local structure in these glasses is dominated by AsS_3^{3-} units.³⁰ Given that the above mentioned compounds contain the same anions, they are perhaps predisposed to form glassy structures. It is also possible that the glassy and the crystalline forms do not have a large thermodynamic disparity since they can be converted reversibly.

C.4 Optical Spectroscopy

The diffused reflectance spectra of **I**, **II** and the glassy form of **II** are shown in Figure 4. As seen in the figure, **I** shows a steep absorption starting at 1.68 eV. This corresponds to its dark red color. $\text{K}_2\text{SnAs}_2\text{S}_6$ shows a band gap of 1.89 eV, which indicates that the Tl^+ ions interact with the layers through bonding interactions that are only slightly stronger than those of the alkali metals. **II** shows a steep absorption edge at 1.08 eV. The glassy form of **II** absorbs at 0.84 eV. This is expected because in glasses the large number of defects create significant midgap states and "band-tailing" in the electronic structure.³¹ This leads to a red shift in the band gap. The change in the band gap results in a sharp difference in the reflection coefficient or conductivity between the amorphous and

crystalline states and is the principle on which memory storage devices like $\text{Ge}_2\text{Sb}_2\text{Te}_5$ work.³² In this context, $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ is a promising compound.

We also performed thermoelectric power measurements on the crystalline and glassy forms of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$. While we could not measure the thermoelectric power of the crystalline form due to its very high electrical resistivity, the Seebeck coefficient of the glassy form was very small, $\sim 0.5 \mu\text{V/K}$ at room temperature.

Table 1. Crystallographic refinement details of $\text{Ti}_2\text{SnAs}_2\text{S}_6$, $\text{Ti}_2\text{SnAs}_2\text{Se}_6$.

Formula	$\text{Ti}_2\text{SnAs}_2\text{S}_6$	$\text{Ti}_2\text{SnAs}_2\text{Se}_6$
Space Group	<i>P</i> -3	<i>P</i> -3
<i>a</i> , Å	6.706 (4)	6.996 (3)
<i>b</i> , Å	6.706 (4)	6.996 (3)
<i>c</i> , Å	7.187 (6)	7.232 (4)
α , deg	90	90
β , deg	90	90
γ , deg	120	120
<i>Z</i> , V	1, 279.9(3)	1, 306.5 (3)
<i>D</i> , mg/m ³	5.159	6.236
Temp, K	293	293
λ , Å	0.71073	0.71073
μ , mm ⁻¹	37.846	51.354
<i>F</i> (000)	374	482
θ_{max} , deg	28.26	28.15
Total reflections	2648	2283
Total unique reflections	453	484
No. of parameters	18	18
Refinement method	Full-matrix least-squares on F^2	
Final R indices(<i>I</i> >2 <i>s</i> (<i>I</i>))	$R1^a = 0.0492$, $wR2^b = 0.1184$	$R1 = 0.0414$, $wR2 = 0.1019$
R indices (all data)	$R1 = 0.0890$, $wR2 = 0.1293$	$R1 = 0.0579$, $wR2 = 0.1126$
Goodness of fit on F^2	1.085	1.060

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

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Factors ($\text{\AA}^2 \times 10^3$) for $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$.

Atom	x	y	z	Ueq ^a
$\text{Tl}_2\text{SnAs}_2\text{S}_6$				
Sn(1)	0	0	0	14(1)
Tl(1)	0.3333	0.6667	0.3829(2)	29(1)
As(1)	0.3333	0.6667	-0.0730(4)	16(1)
S(1)	0.2070(8)	0.3339(7)	-0.2305(7)	23(1)
$\text{Tl}_2\text{SnAs}_2\text{Se}_6$				
Sn(1)	0	0	0	16(1)
Tl(1)	0.3333	-0.3333	-0.6180(1)	45(1)
As(1)	0.3333	-0.3333	-1.0726(3)	19(1)
Se(1)	0.2204(2)	-0.1126(2)	-0.2398(2)	27(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{Tl}_2\text{SnAs}_2\text{S}_6$						
Sn(1)	11(1)	11(1)	19(2)	0	0	6(1)
Tl(1)	32(1)	32(1)	24(1)	0	0	16(1)
As(1)	13(1)	13(1)	23(2)	0	0	6(1)
S(1)	31(3)	9(2)	22(2)	1(2)	-1(2)	4(2)
$\text{Tl}_2\text{SnAs}_2\text{Se}_6$						
Sn(1)	13(1)	13(1)	22(1)	0	0	6(1)
Tl(1)	55(1)	55(1)	24(1)	0	0	27(1)
As(1)	20(1)	20(1)	17(1)	0	0	10(1)
Se(1)	37(1)	33(1)	26(1)	6(1)	10(1)	28(1)

* The anisotropic displacement factor exponent takes the form:

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

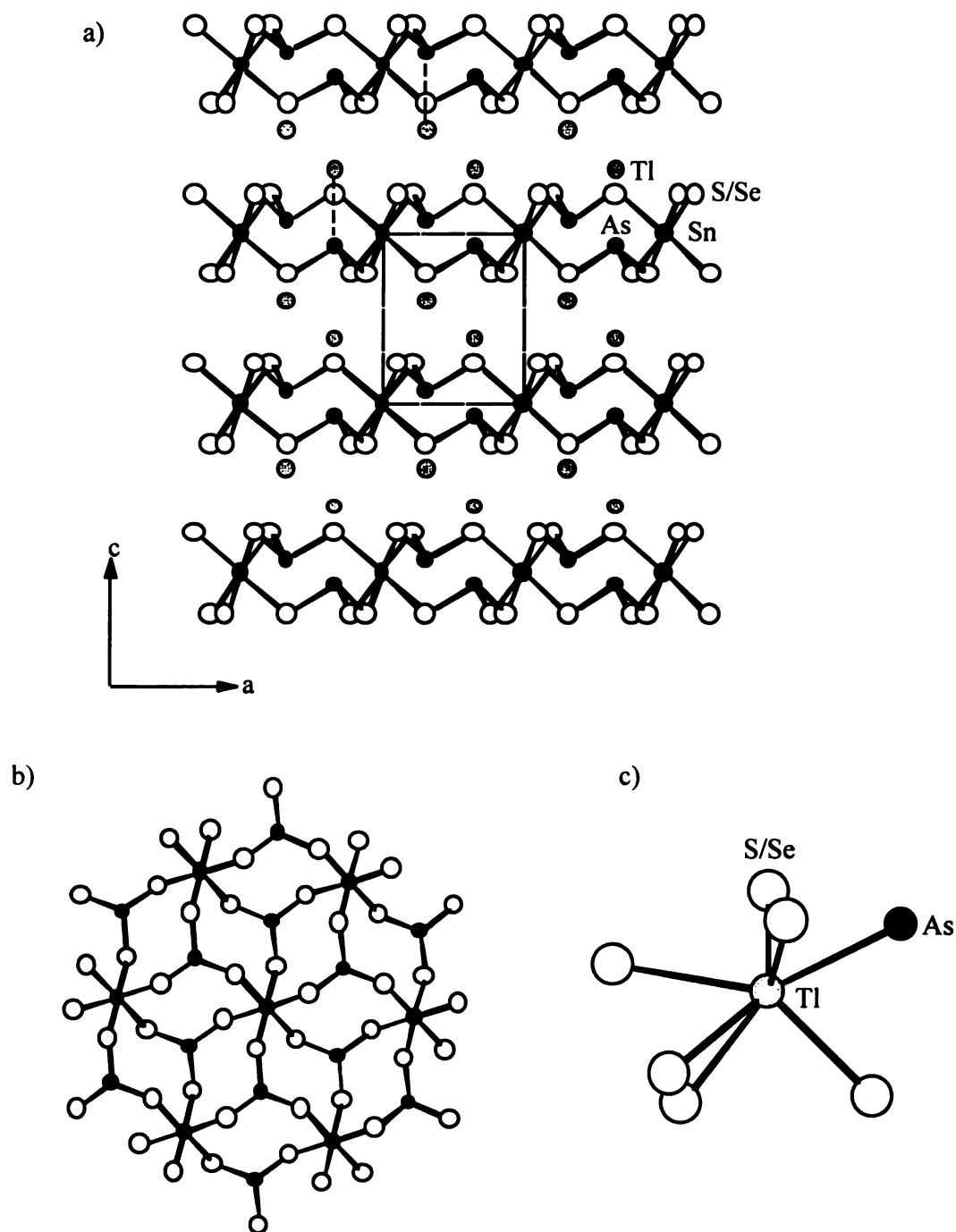


Figure 1. a) Unit cell of $\text{Tl}_2\text{SnAs}_2\text{Q}_6$ looking down the b -axis. The As lone pair is oriented towards the Tl cations between the layers. b) A single layer showing an octahedral Sn coordinated by 6 AsQ_3^{3-} anions. c) The irregular seven coordination pocket of Tl created by 6 Q atoms and an As atom.

Table 4. Selected bond distances (Å) for $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$.

	$\text{Tl}_2\text{SnAs}_2\text{S}_6$	$\text{Tl}_2\text{SnAs}_2\text{Se}_6$
Tl(1)-Q(1)	3 x 3.274(2)	3 x 3.2856(18)
	3 x 3.395(2)	3 x 3.422(2)
Tl(1)-As(1)	3.277(4)	3.287(3)
Sn(1)-Q(1)	6 x 2.564(5)	6 x 2.6873(15)
As(1)-Q(1)	3 x 2.256(5)	3 x 2.3854(17)

Table 5. Selected bond angles (deg) for $\text{Tl}_2\text{SnAs}_2\text{S}_6$ and $\text{Tl}_2\text{SnAs}_2\text{Se}_6$.

$\text{Tl}_2\text{SnAs}_2\text{S}_6$		$\text{Tl}_2\text{SnAs}_2\text{Se}_6$	
S(1)-Sn(1)-S(1)	3 x 180.0	Se(1)-Sn(1)-Se(1)	3 x 180.0
S(1)-Sn(1)-S(1)	6 x 82.77(15)	Se(1)-Sn(1)-Se(1)	6 x 82.83(5)
S(1)-Sn(1)-S(1)	6 x 97.23(15)	Se(1)-Sn(1)-Se(1)	6 x 97.17(5)
S(1)-As(1)-S(1)	3 x 97.03(18)	Se(1)-As(1)-Se(1)	3 x 96.58(7)

C. 5 Band structure calculations

We performed band structure calculations to get a better understanding of the type of gap present in this material and the orbital character and nature of the conduction and valence bands near the gap. Figure 5 shows the band structure plot of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$. As can be seen, the minimum in the conduction band occurs at point A of the Brillouin zone while the maximum in the valence band occurs at general points in the region between H and T and T and L. There is another maximum between A and H which is very close to the above two maxima. Given the almost vertical nature of the diffuse reflectance spectrum of the compound, it seems more likely the band gap transition involves the maxima in the AH region and the point A in the conduction band giving rise to an indirect gap of about 0.6 eV. Because they are ground state calculations, usually the LAPW method tends to underestimate energy gaps in semiconductors and therefore this value can be qualitatively acceptable. Figure 8 shows the total density of states plot while Figures 6 and 7 plot the contribution of the s and p orbitals of Tl, Sn, As and Se to the total density of states. As can be seen from Figure 6a, there is some interaction of the Tl 6s orbital with As p- and Se p- orbitals. However these interactions are relatively weak. Figure 6b shows that the As s electrons lie much below the Fermi level (~ -10 eV) and therefore are unavailable for bonding. Figures 7a and 7b reveal that the top energy levels of the valence bands are constructed mainly from Se based p- orbitals whereas the conduction band closest to the Fermi level is constructed from Sn based s- orbitals and Se based p- orbitals (see peak at ~ 0.5 eV) with the main contribution coming from Sn s- orbitals. We can therefore attribute the absorption spectrum of the compound to charge-transfer transition from Se to Sn.

D. Conclusion

$\text{Tl}_2\text{SnAs}_2\text{Q}_6$ was predicted and obtained based on the synthesis of $\text{A}_2\text{SnAs}_2\text{S}_6$ ($\text{A} = \text{K}, \text{Rb}$) from a polythioarsenate flux. It was expected that the tendency of Tl to form covalent bonds would lead to lowering of the bandgap as compared to $\text{A}_2\text{SnAs}_2\text{S}_6$ and better semiconducting properties. Tl-Q interactions, though stronger, are mainly ionic in nature. $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ shows a crystal to glass transition. It is possible that $\text{Tl}_2\text{SnAs}_2\text{S}_6$ may also exhibit this property at faster quenching rates. Further studies are needed to probe the phase change properties of these compounds as well as to determine conditions under which $\text{Tl}_2\text{SnAs}_2\text{Te}_6$, $\text{Tl}_2\text{SnSb}_2\text{Q}_6$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) may be isolated.

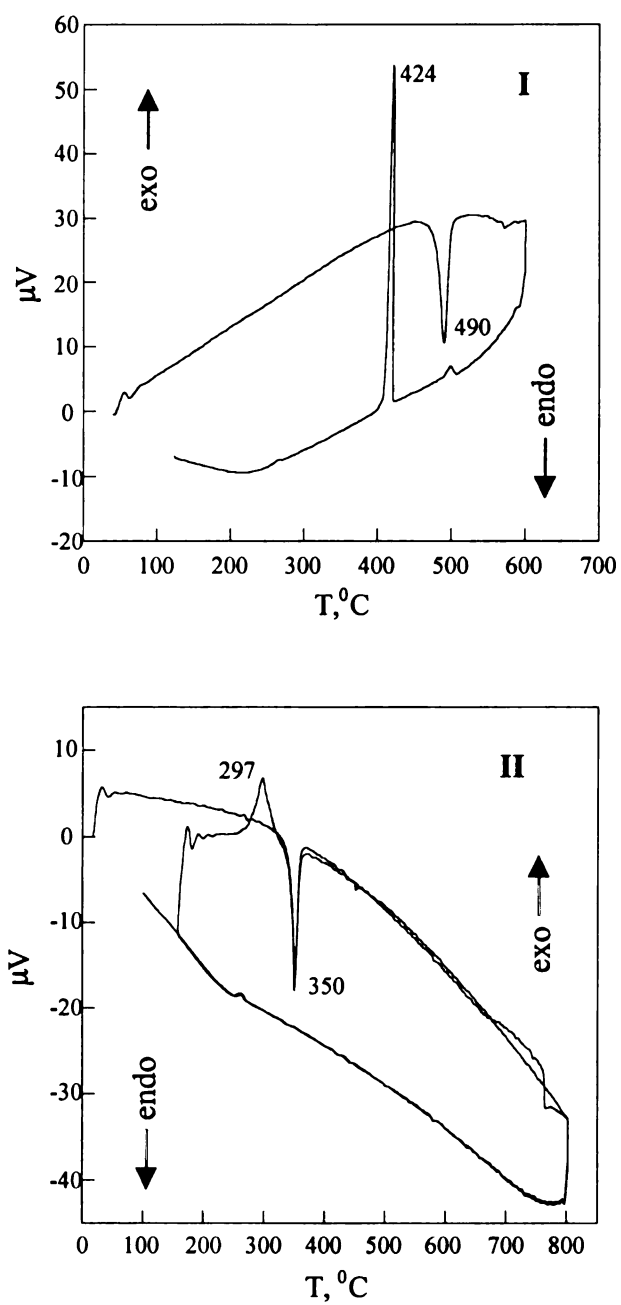


Figure 2. Differential Thermal Analysis of (I) $\text{Tl}_2\text{SnAs}_2\text{S}_6$ showing a melting point of 490°C and a recrystallization point of 424°C and (II) $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ showing that the compound melts at 350°C but does not crystallize on cooling. Crystallization occurs on heating the compound at 297°C .

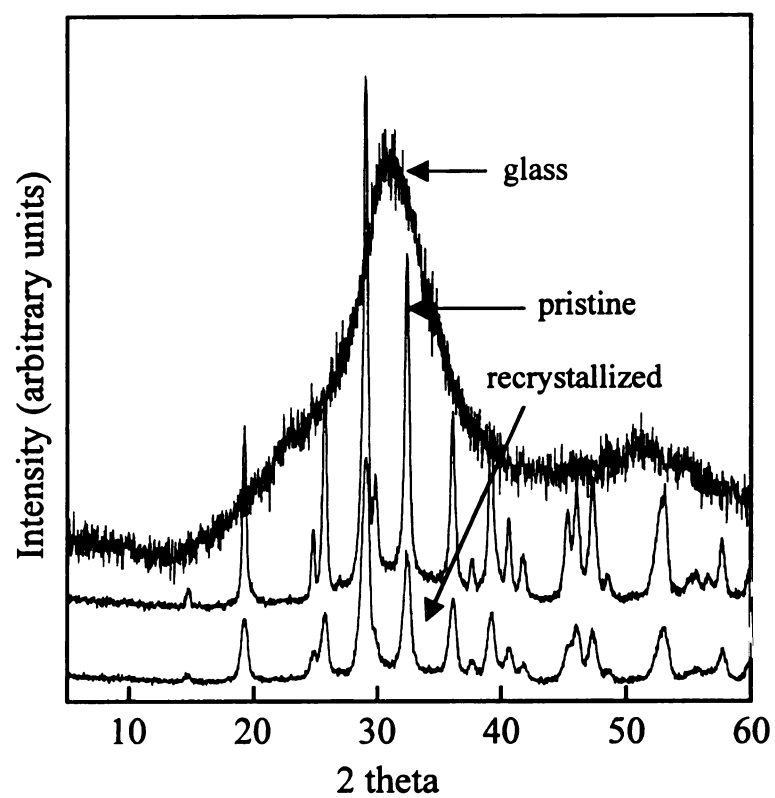


Figure 3. Comparison of the powder patterns of the pristine, glassy and recrystallized forms of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ shows that the compound switches reversibly between crystalline and glassy states upon heating.

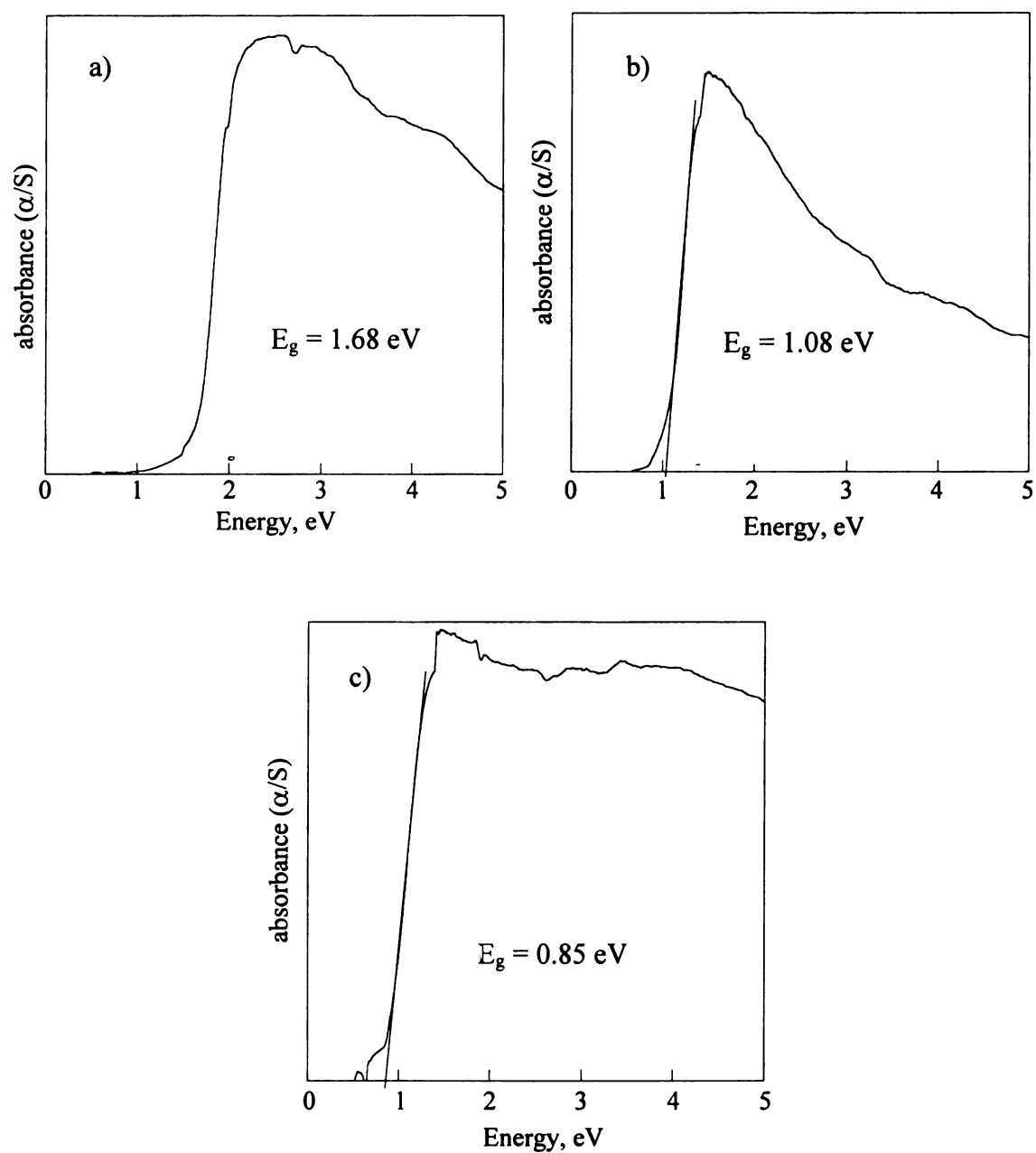


Figure 4. Optical absorption spectra of a) $\text{Tl}_2\text{SnAs}_2\text{S}_6$ showing a steep absorption edge at 1.68 eV corresponding to its dark red color b) $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ with a energy gap of 1.08 eV c) the glassy form of $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ shows a red shift compared to the crystalline form and absorbs at 0.85 eV.

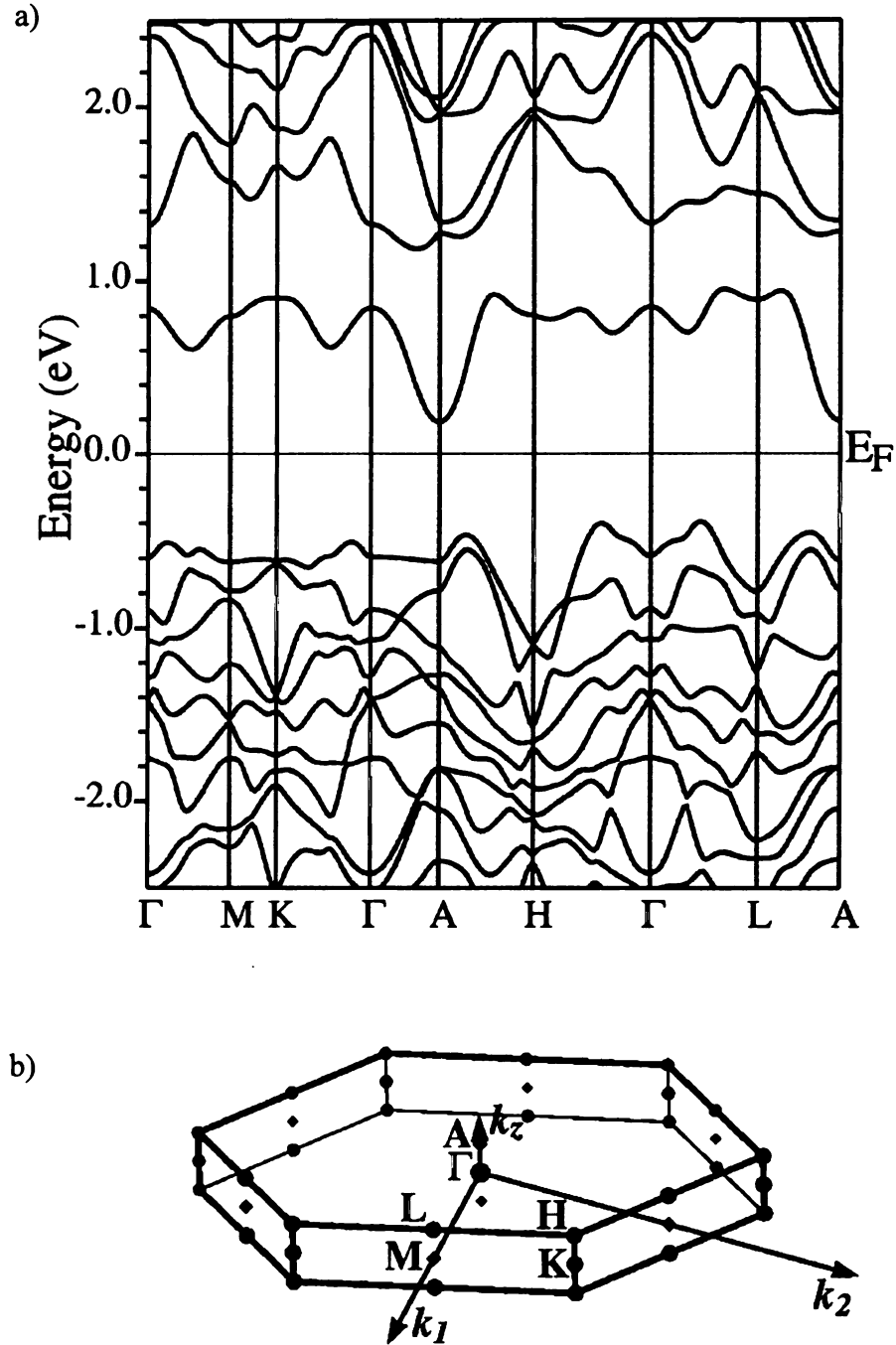


Figure 5. a) Band structure plot for $\text{Tl}_2\text{SnAs}_2\text{Se}_6$ shows that the band gap is an indirect gap with an approximate energy of 0.6 eV arising from a transition from a general point in the region AH to the point A of the Brillouin zone. b) The Brillouin zone for a trigonal system.

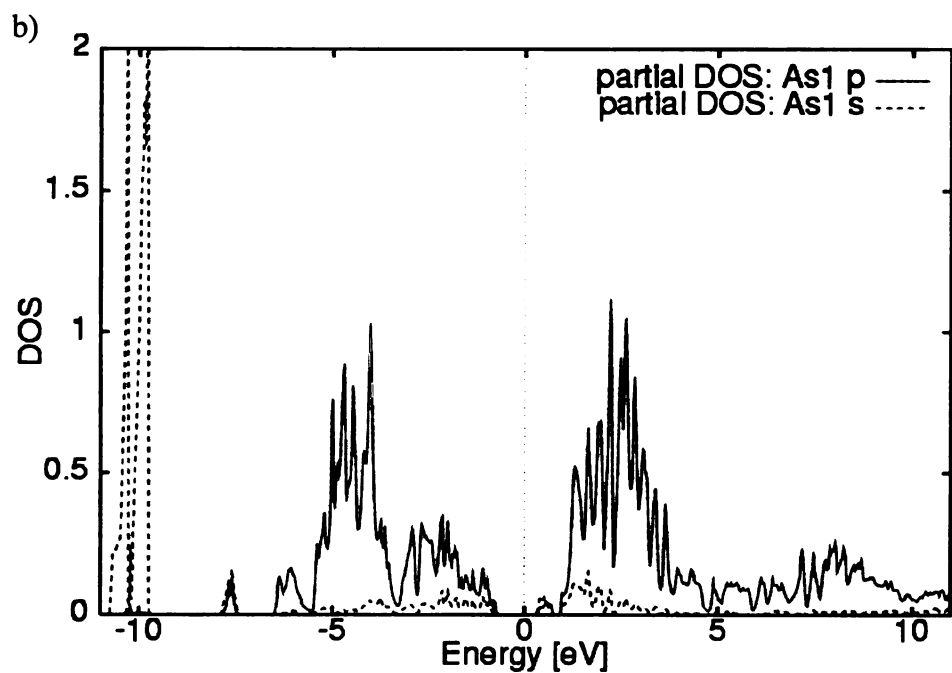
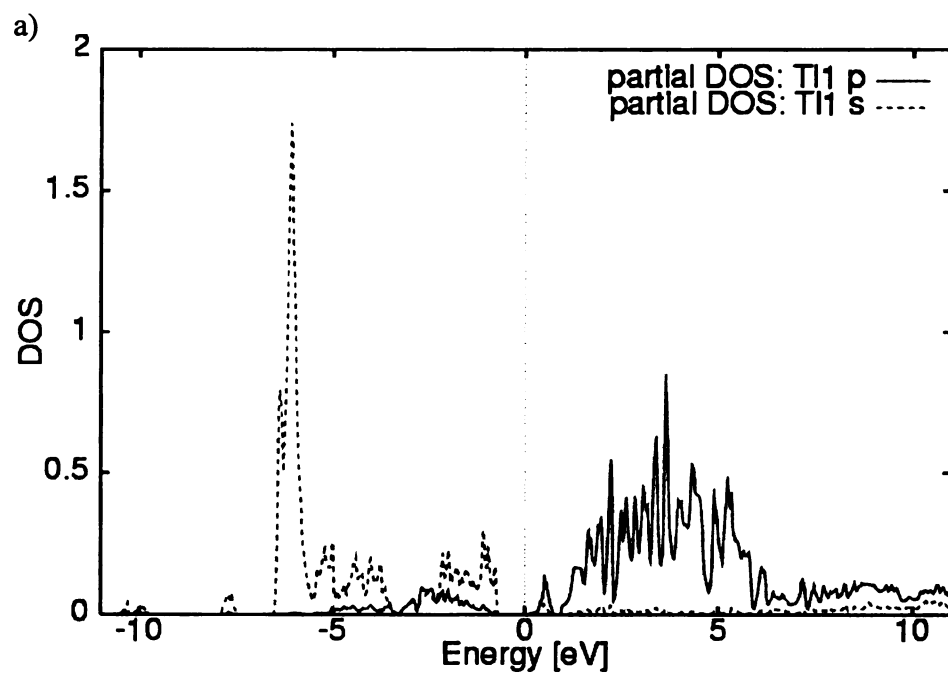


Figure 6. a) Density of states for Tl s and p orbitals showing that the s electrons are below the Fermi level and interact weakly with As p orbitals. b) Density of states for As s and p orbitals showing that the As s electrons lie much below the Fermi level.

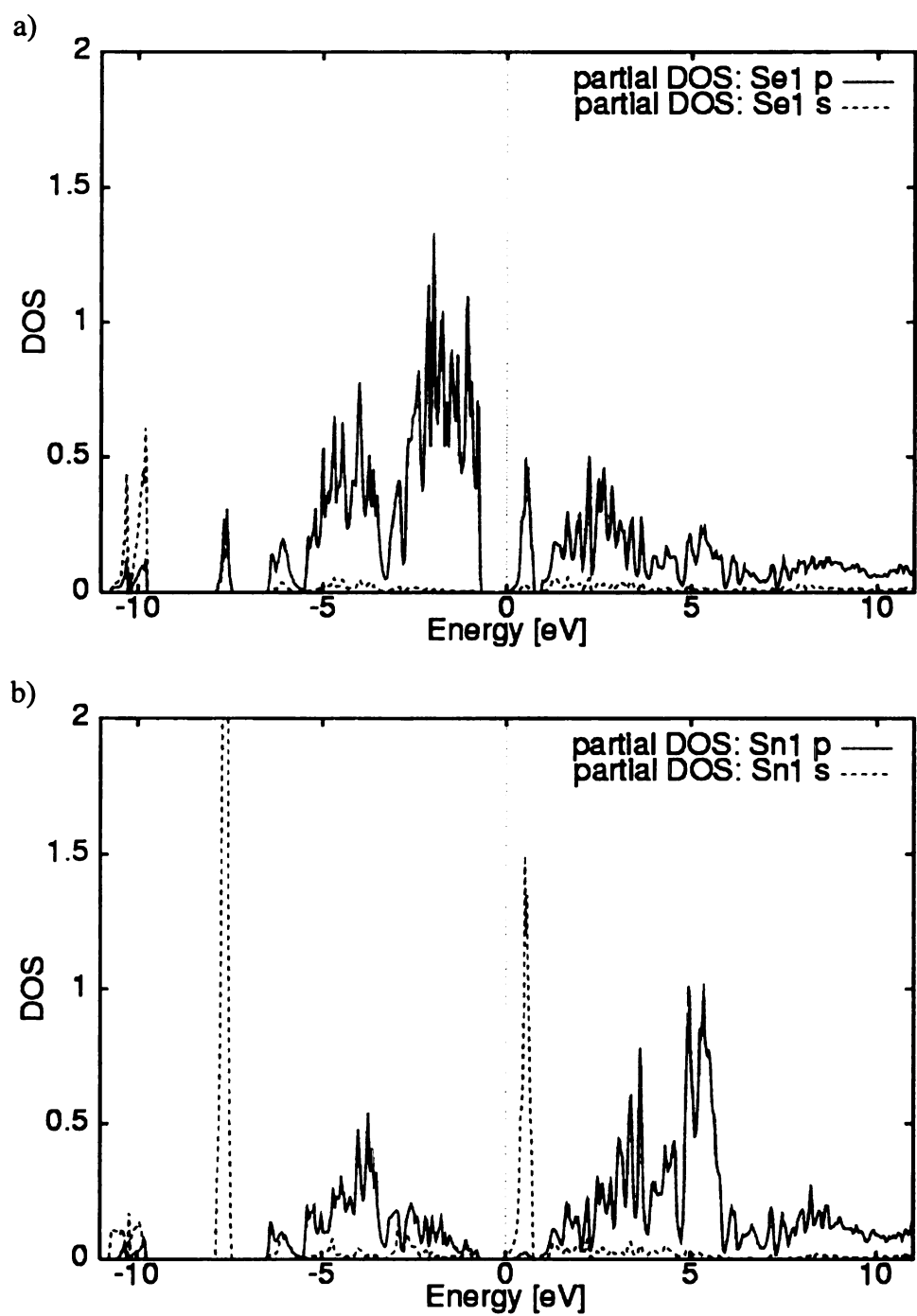


Figure 7. a) Density of states for Se s and p orbitals showing that the p orbitals form the energy levels closest to the Fermi level in the valence band. B) Density of states for Sn s and p orbitals showing that Sn orbitals contribute mainly to the conduction band.

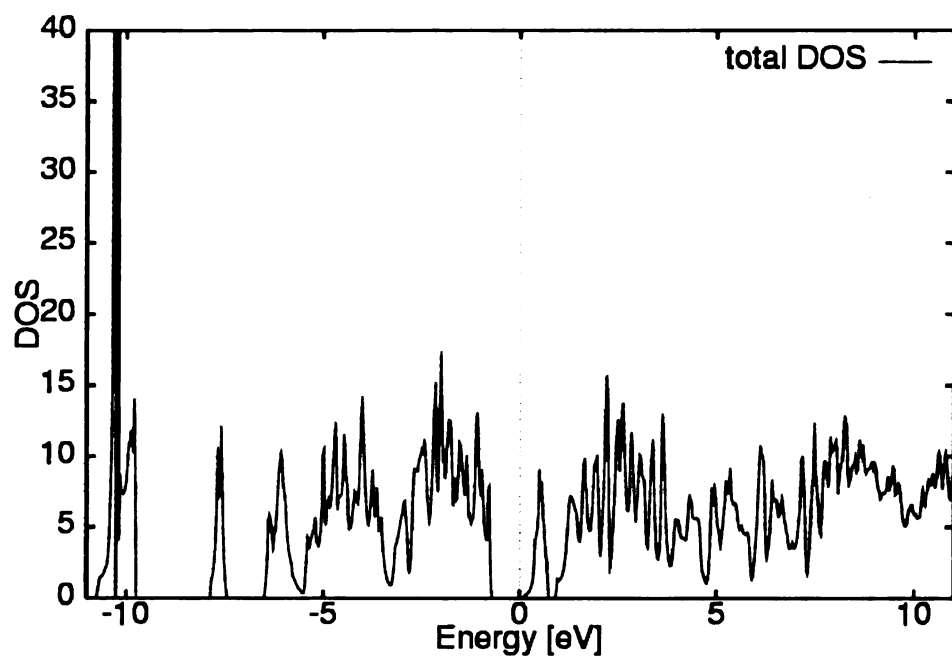


Figure 8. Total density of states for $\text{Tl}_2\text{SnAs}_2\text{Se}_6$.

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Chapter 4

Chemistry of Pb in Alkali Thioarsenate Fluxes: Isolation and Characterization of

APbAsS₄ (A = Rb, Cs) and A₄PbAs₂S₈ (A = Rb, Cs)

Abstract

The reaction of Pb in AAs_xS_y fluxes (A = Rb, Cs) yielded four new compounds. APbAsS₄ crystallizes as yellow plates in *Pnma* with $a = 17.360(5)$ Å, $b = 6.7925(18)$ Å, $c = 6.6090(17)$ Å for A = Rb and $a = 18.170(9)$ Å, $b = 6.890(4)$ Å, $c = 6.486(3)$ Å for A = Cs. This compound consists of trigonal bipyramidal Pb coordinated by tetrahedral (AsS₄)³⁻ ligands to form two-dimensional [Pb(AsS₄)]ⁿ⁻ layers which are separated by the alkali cations. Rb₄PbAs₂S₈ crystallizes in *Ibam* with $a = 18.754(9)$ Å, $b = 9.142(4)$ Å and $c = 10.143(5)$ Å. This compound is made up of [Pb(AsS₄)₂] motifs that are connected together to form chains running along the *c*-axis. Cs₄PbAs₂S₈ has a similar one-dimensional structure as the Rb compound and crystallizes in the monoclinic space group *C2/c* with $a = 13.994(5)$ Å, $b = 19.106(6)$ Å, $c = 9.423(3)$ Å, $\beta = 131.414(4)^\circ$. Rb₄PbAs₂S₈ and Cs₄PbAs₂S₈ form as yellow chunks. All the compounds are semiconductors with bandgap ranging from 2.26 eV to 2.58 eV. The compounds are air stable and insoluble in water and DMF.

A. Introduction

Lead arsenosulfide minerals form a considerable subclass of the sulfosalt family.¹ These minerals have an extensive structural variation arising due to the stereochemically active lone pairs on both As and Pb. Some of these compounds like $\text{Pb}_7\text{As}_9\text{S}_{20}$ ² and $\text{Pb}_8\text{As}_8\text{S}_{20}$ ³ exhibit strong piezoelectric effect. The structural variety found in natural lead thioarsenates promotes the need to explore synthetic analogs. The use of polythioarsenate fluxes is well suited to synthesize new alkali lead thioarsenates. In these fluxes, different kinds of $[\text{As}_x\text{S}_y]^n$ anions are generated from an in-situ fusion of As_2S_3 , As_2S_3 and S. These anions coordinate to the metal ion present, according to its coordination preference, to give compounds with varying dimensionalities. Before the advent of the flux method, thioarsenates have been prepared mainly by solventothermal techniques.⁴

We started investigating the reactivity of different metals in polythioarsenate fluxes with an aim to compare the results with the well-documented chalcophosphate flux.⁵ We expect the thioarsenate flux to behave differently from the chalcophosphate flux mainly due to the different oxidation states exhibited by P (+4 and +5) and As (+3 and +5) in their compounds. This is observed in the reaction of Sn in thioarsenate fluxes where we observe thioarsenate ligands based on the pyramidal $(\text{AsS}_3)^{3-}$ anion.⁶ In the case of tin thiophosphates, the thiophosphate ligands are derived from the $(\text{PS}_4)^{3-}$ anion.⁷ The reaction of Pb in polychalcophosphate fluxes has yielded the phases APbPQ_4 ⁸, $\text{A}_4\text{PbP}_2\text{Q}_8$ ($\text{Q} = \text{S}, \text{Se}$)⁸, $\text{Na}_{1.5}\text{Pb}_{0.75}\text{PSe}_4$ ⁹, α - and β - $\text{Na}_6\text{Pb}_3(\text{PS}_4)_4$ ¹⁰. Each of these compounds consists of Pb coordinated by the tetrahedral $(\text{PQ}_4)^{3-}$ ligand to form 1-D 2-D or 3-D compounds.

Here we present the synthesis, structure and physical characterization of APbAsS₄ and A₄PbAs₂S₈ (A = Rb, Cs). Rb₄PbAs₂S₈ is isostructural to its thiophosphate counterpart whereas APbAsS₄ represents a centrosymmetric version of APbPS₄. All the compounds are air and water stable.

B. Experimental Section

B.1 Reagents

The chemicals used in this work were as follows: Pb powder (Spectrum, Gardena, CA), As₂S₃ (99.9%; Strem Chemicals, Newburyport, MA), S (99.9%; Strem Chemicals, Newburyport, MA), N, N-dimethylformamide (Spectrum Chemicals, ACS reagent grade), diethyl ether (CCI, ACS grade). K₂S, Rb₂S and Cs₂S were made by reacting stoichiometric amounts of the elements in liquid ammonia following a modified literature procedure.¹¹

B.2 Physical Measurements

Energy Dispersive Spectroscopy was performed on a JEOL JSM-35C Scanning Electron Microscope equipped with a Tracor Northern Energy Dispersive Spectroscopy Detector. Acquisition time per reading was 30s. The composition of the compound was determined as an average of several readings on atleast 3 crystals.

Powder X-ray Diffraction patterns were obtained on a CPS INEL 120 diffractometer with graphite monochromatized Cu K α radiation, operating at 40kV and 20mA.

Differential Thermal Analysis was performed using a Shimadzu DTA-50 thermal analyzer. The reproducibility of the thermal behavior of the compounds was monitored

by running two heating/cooling cycles. To check for congruent melting, powder X-ray diffraction patterns taken after the DTA cycle were compared to the ones recorded before the DTA.

Diffuse Reflectance Spectra were recorded using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrometer. Energy gaps were extracted from a plot of absorbance vs energy.

Single Crystal UV/Vis Spectra were obtained at room temperature on single crystals using a Hitachi U-6000 microscopic FT spectrophotometer with an Olympus BH-2 metallurgical microscope over a range of 380-900 nm.

Far-Infrared Spectra were obtained in the 600-100 cm^{-1} range (4 cm^{-1} resolution) on a Nicolet 740 FT-IR spectrophotometer with a TSG/PE detector and silicon beam splitter. Samples were prepared by grinding the compounds with CsI and pressing the mixtures into translucent pellets.

B.3 Synthesis

RbPbAsS₄: In a N₂ filled glove box, Rb₂S (0.061g, 0.3mmol), Pb (0.062g, 0.3mmol), As₂S₃ (0.074g, 0.3mmol) and S (0.096g, 3mmol) were loaded in a fused silica tube. The tube was sealed under vacuum and put in computer controlled furnace. The furnace was ramped up to 500°C and held there for 60h. It was then slow cooled at the rate of 5°C/h to 250°C and then rapidly cooled to room temperature. Isolation of the product with N₂-bubbled N, N-dimethylformamide, revealed yellow transparent crystals and a small amount of black crystals. EDS analysis on several of the yellow crystals gave an average composition of Rb_{1.2}PbAs_{1.1}S_{4.3}. The black crystals were identified as PbS. The yield of

the product was about 60% based on Pb and product purity based on powder X-ray diffraction pattern was ~ 95%.

Rb₄PbAs₂S₈: An optimum synthesis with a yield of ~65% for Rb₄PbAs₂S₈ was obtained by reacting a mixture of Rb₂S, Pb, As₂S₃ and S in the ratio 3.5/1/1.5/4 using the heating profile as above. The product consisted of golden brown crystals of average composition Rb_{4.4}PbAs_{1.9}S_{7.9} and light yellow crystals of Rb₃AsS₄.

CsPbAsS₄: This compound is obtained as the majority product (>95% phase purity) from a reaction of Cs₂S, Pb, As₂S₃ and S in the ratio 2/1/1/8. The reactants were heated to 600°C and held there for 4 days. The reaction mixture was then cooled to 200°C at the rate of 5°C/h and then fast cooled to room temperature. The product on isolation revealed almost pure yellow transparent crystals, some colorless and black crystals. Elemental analysis on several of the yellow crystals gave an average composition of Cs_{1.3}Pb_{1.0}As_{1.0}S_{4.5}. The colorless crystals were Cs₃AsS₄ and the black crystals were PbS. The yield of the reaction was ~ 60%.

Cs₄PbAs₂S₈: A reaction of Cs₂S, Pb, As₂S₃ and S in the ratio 3/1/1/10 using the above heating profile afforded mostly Cs₄PbAs₂S₈, with a small amount of Cs₃AsS₄, in nearly 70% yield. The EDS analysis gave a composition of Cs_{4.3}PbAs_{2.4}S₈.

B.4 Single Crystal Diffraction

Single crystal X-ray diffraction data on the compounds were collected at room temperature on a SMART platform diffractometer with a 1K CCD area detector using monochromatized Mo K α (λ = 0.71073 Å) radiation. Reflection data were recorded using the SMART software. Data integration was done with SAINT and an empirical

Table 1. Crystallographic data for RbPbAsS₄, CsPbAsS₄, Rb₄PbAs₂S₈ and Cs₄PbAs₂S₈

empirical formula	RbPbAsS ₄	CsPbAsS ₄	Rb ₄ PbAs ₂ S ₈	Cs ₄ PbAs ₂ S ₈
fw	495.82	543.26	955.39	1145.15
space group	<i>Pnma</i>	<i>Pnma</i>	<i>Ibam</i>	<i>C2/c</i>
<i>a</i> , Å	17.360(5)	18.170(9)	18.754(9)	13.994(5)
<i>b</i> , Å	6.7925(18)	6.890(4)	9.142(4)	19.106(6)
<i>c</i> , Å	6.6090(17)	6.486(3)	10.143(5)	9.423(3)
α, deg	90	90	90	90
β, deg	90	90	90	131.414(4)
γ, deg	90	90	90	90
<i>V</i> , Å ³	779.3(4)	812.0(7)	1739.1(14)	1889.4(10)
<i>Z</i>	4	4	4	4
ρ _{calcd} , g/cm ³	4.226	4.444	3.649	4.026
μ, mm ⁻¹	33.027	30.162	25.530	20.857
<i>T</i> , K	293(2)	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Total reflections	7279	7440	8368	9574
Total unique	1020	1045	1130	2325
R(int)	0.0672	0.0354	0.0431	0.0343
No. of parameters	40	41	43	72
Goodnes of fit on F ²	1.063	1.128	1.080	1.135
Refinement method	Full-matrix least-squares on F ²			
R1 ^a	0.0348	0.0327	0.0279	0.0300
wR2 ^b	0.0809	0.0702	0.0668	0.0676

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

Table 2. Fractional atomic coordinates and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RbPbAsS_4 , CsPbAsS_4 , $\text{Rb}_4\text{PbAs}_2\text{S}_8$ and $\text{Cs}_4\text{PbAs}_2\text{S}_8$

Atom	x	y	z	Ueq ^a
RbPbAsS₄				
Pb(1)	-0.0204(1)	0.2500	0.7862(1)	38(1)
As(1)	-0.0952(1)	0.2500	1.2837(2)	20(1)
Rb(1)	0.2120(1)	0.2500	0.5009(3)	46(1)
S(1)	-0.1661(2)	0.2500	0.5512(5)	31(1)
S(2)	0.1179(2)	0.0047(3)	0.9012(4)	30(1)
S(3)	0.0262(2)	0.2500	0.3619(6)	46(1)
CsPbAsS₄				
Pb(1)	0.0165(1)	0.2500	0.2095(1)	41(1)
As(1)	0.0941(1)	0.2500	-0.2855(2)	21(1)
Cs(1)	0.2911(1)	0.2500	-0.0405(2)	50(1)
S(1)	0.1585(1)	0.2500	0.4373(4)	28(1)
S(2)	-0.1158(1)	0.0031(3)	0.1000(3)	31(1)
S(3)	-0.0224(2)	0.2500	-0.3580(5)	60(1)
Rb₄PbAs₂S₈				
Pb(1)	0	-1.0000	0.2500	39(1)
As(1)	-0.1274(1)	-0.7954(1)	0	18(1)
Rb(1)	-0.0836(1)	-0.3754(1)	0	32(1)

Rb(2)	0.2411(1)	0	0.2500	45(1)
S(1)	-0.2396(1)	-0.7504(2)	0	31(1)
S(2)	-0.0774(1)	-0.7047(2)	0.1720(1)	36(1)
S(3)	-0.1045(1)	-1.0276(2)	0	41(1)

Cs₄PbAs₂S₈

Pb(1)	0.5000	-0.2362(1)	-0.2500	32(1)
Cs(1)	0.2389(1)	-0.1619(1)	0.1102(1)	30(1)
Cs(2)	0.5000	0.0020(1)	-0.2500	35(1)
Cs(3)	0.5000	-0.4709(9)	-0.2500	34(1)
Cs(33)	0.5000	-0.4862(7)	-0.2500	34(1)
As(1)	0.2580(1)	-0.1262(1)	-0.2914(1)	17(1)
S(1)	0.2494(2)	0.0168(1)	0.2534(3)	28(1)
S(2)	0.4246(2)	-0.1746(1)	-0.0350(2)	27(1)
S(3)	0.4126(2)	-0.3221(1)	0.3866(3)	33(1)
S(4)	0.2776(2)	-0.1438(1)	-0.4995(3)	33(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor

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Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for RbPbAsS₄, CsPbAsS₄, Rb₄PbAs₂S₈ and Cs₄PbAs₄S₈.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
RbPbAsS₄						
Pb(1)	30(1)	59(1)	24(1)	0	0(1)	0
As(1)	22(1)	17(1)	22(1)	0	1(1)	0
Rb(1)	29(1)	31(1)	77(1)	0	12(1)	0
S(1)	27(2)	34(2)	30(2)	0	10(2)	0
S(2)	38(1)	17(1)	36(1)	-5(1)	-4(1)	1(1)
S(3)	20(2)	88(4)	32(2)	0	5(2)	0
CsPbAsS₄						
Pb(1)	29(1)	70(1)	24(1)	0	1(1)	0
As(1)	20(1)	22(1)	21(1)	0	2(1)	0
Cs(1)	27(1)	31(1)	92(1)	0	-15(1)	0
S(1)	23(1)	33(1)	27(1)	0	6(1)	0
S(2)	39(1)	22(1)	33(1)	5(1)	-3(1)	-4(1)
S(3)	16(1)	132(4)	31(2)	0	2(1)	0
Rb₄PbAs₂S₈						
Pb(1)	37(1)	39(1)	42(1)	0	0	0
As(1)	17(1)	16(1)	22(1)	0	0	0(1)

Rb(1)	38(1)	24(1)	34(1)	0	0	5(1)
Rb(2)	63(1)	42(1)	30(1)	-7(1)	0	0
S(1)	19(1)	36(1)	39(1)	0	0	10(1)
S(2)	50(1)	37(1)	22(1)	-3(1)	-8(1)	-6(1)
S(3)	27(1)	18(1)	78(2)	0	0	3(1)

Cs₄PbAs₂S₈

Pb(1)	34(1)	28(1)	41(1)	0	28(1)	0
Cs(1)	33(1)	34(1)	28(1)	-4(1)	22(1)	-2(1)
Cs(2)	24(1)	45(1)	33(1)	0	18(1)	0
Cs(3)	24(1)	45(4)	26(1)	0	13(1)	0
Cs(33)	24(1)	45(4)	26(1)	0	13(1)	0
As(1)	17(1)	19(1)	17(1)	0(1)	12(1)	1(1)
S(1)	30(1)	23(1)	32(1)	3(1)	20(1)	-3(1)
S(2)	19(1)	36(1)	22(1)	6(1)	11(1)	6(1)
S(3)	20(1)	44(1)	31(1)	-4(1)	16(1)	-8(1)
S(4)	49(1)	36(1)	30(1)	7(1)	33(1)	13(1)

* The anisotropic displacement factor exponent takes the form:

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

absorption correction was applied using SADABS. The structures were solved by direct methods using the SHELXTL package of programs.¹² Based on the intensity statistics, centrosymmetric spacegroups were assigned to all the four compounds. RbPbAsS₄ and CsPbAsS₄ were refined in *Pnma* with final R1/wR2 values of 0.0348/0.0809 and 0.0327/0.0702 respectively. Rb₄PbAs₂S₈ was refined in the orthorhombic spacegroup *Ibam* with R1/wR2 = 0.0279/0.0668 while Cs₄PbAs₂S₈ was refined as monoclinic *C2/c* with R1/wR2 = 0.0300/0.0676. Table 1 lists crystal refinement details and Table 2 lists the fractional atomic coordinates and isotropic displacement parameters for all the compounds. Anisotropic displacement factors are listed in Table 3. Selected bond distances and angles are given in Tables 4 and 5 respectively.

C. Results and Discussion

C.1 Synthesis

RbPbAsS₄ and CsPbAsS₄ were both synthesized initially from a 1/1/1/10 ratio of A₂S/Pb/As₂S₃/S. For RbPbAsS₄, this flux composition proved to be optimum for maximum yield of the compound. CsPbAsS₄ could be obtained in a better yield and purity from a composition of 2/1/1/8 of Cs₂S/Pb/As₂S₃/S at 600°C. In both the fluxes, increasing the basicity by adding A₂S gave products consisting of APbAsS₄ and A₄PbAs₂S₈. The amount of A₄PbAs₂S₈ increased as the amount of A₂S was increased. Rb₄PbAs₂S₈ was initially obtained from a composition of 4/1/1/10 of Rb₂S/Pb/As₂S₃/S. This reaction also gave PbS and Rb₃AsS₄. A better synthesis was achieved by heating a mixture with formal composition Rb₇PbAs₃S₁₂. This gave Rb₄PbAs₂S₈ as well-formed, irregular golden-yellow crystals along with light yellow crystals of Rb₃AsS₄. Cs₄PbAs₂S₈

was obtained as irregular yellow crystals, along with some Cs_3AsS_4 , from a flux composition of $\text{Cs}_6\text{As}_2\text{S}_{16}$.

We also performed reactions with Pb in KAs_xS_y flux. These reactions resulted in the formation of a 3-D compound KPbAsS_4 and the molecular $\text{K}_4\text{PbAs}_2\text{S}_8$. However the structures of these compounds could not be refined satisfactorily. Repeated attempts to obtain good quality crystals and better data were unsuccessful. The crystal details of these two compounds along with their structures are shown in Appendix B.

C.2 Structure description of APbAsS_4

Since RbPbAsS_4 and CsPbAsS_4 are isostructural, we will discuss the structure of RbPbAsS_4 . The structure of this compound consists of $[\text{PbAsS}_4]^{n-}$ layers stacked along the a-axis and parallel to the bc- plane, Figure 1a. Each layer consists of a trigonal prismatic Pb coordinated by tetrahedral $(\text{AsS}_4)^{3-}$ ligands, Figure 1b. A better understanding of the bonding can be seen in Figure 1c. As shown in this figure, Pb is coordinated by four $(\text{AsS}_4)^{3-}$ ligands. Two of these ligands are bidentate and use two of its sulfur atoms to link to the metal, the other two are monodentate and use one sulfur to link to the metal thus forming the trigonal prismatic geometry around Pb. Each $(\text{AsS}_4)^{3-}$ ligand uses all its sulfur atoms to bind 4 Pb atoms. It uses two sulfur atoms to bind to one Pb in a bidentate fashion. The other two sulfur atoms bridge three Pb atoms. In other words, the $(\text{AsS}_4)^{3-}$ tetrahedron uses one edge and two corners to bind to 4 Pb, Figure 1d. Pb-S bond distances range from 2.918(4) to 3.182(1) Å while As-S bond lengths are in the range 2.154(3) to 2.169(4) Å. Rb sits in a 8 coordinate site generated by S atoms at distances ranging from 3.355(4) to 3.639(4) Å. There is a weak Rb-As interaction at

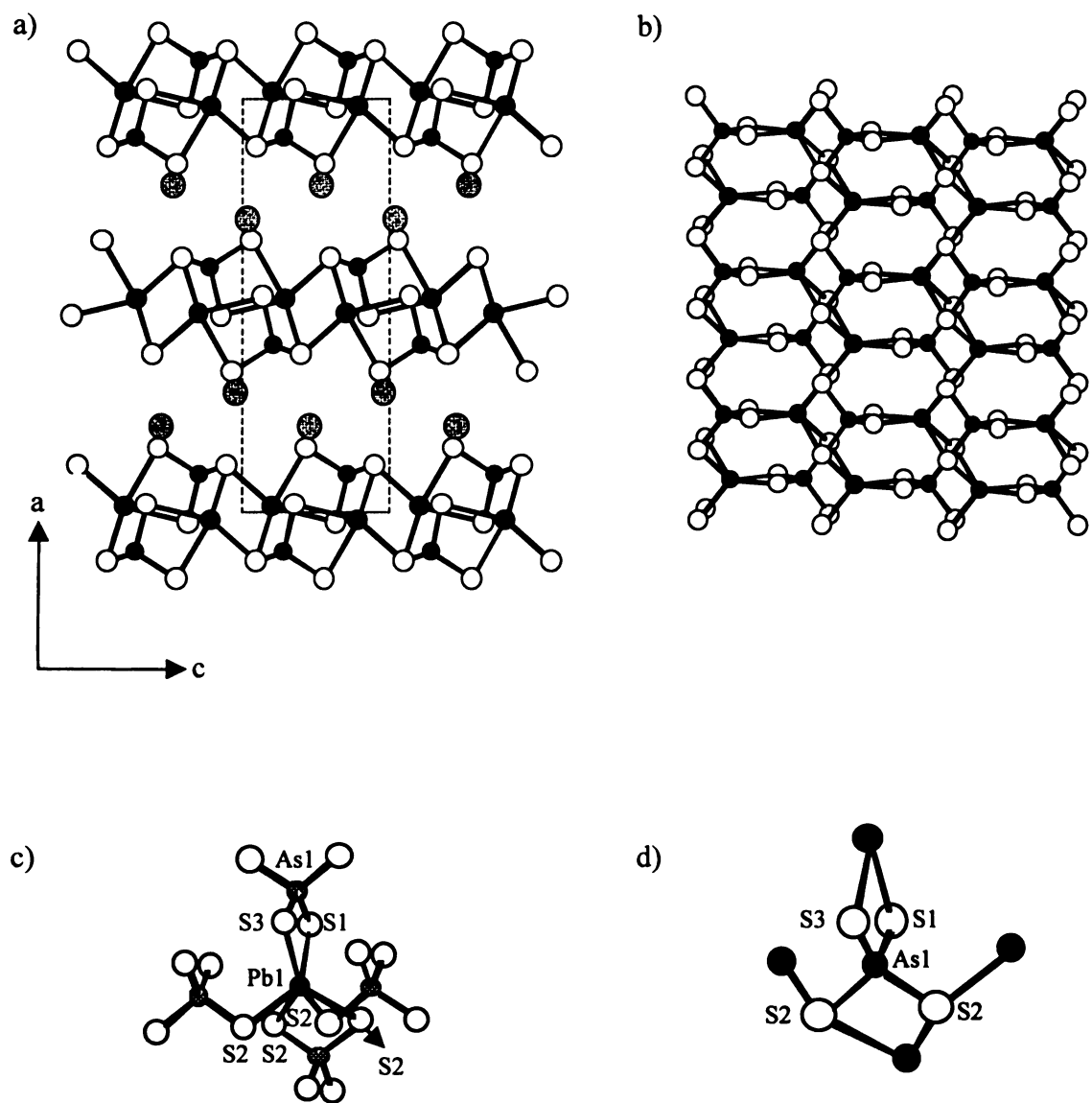


Figure 1. a) Unit cell down the a - axis for APbAsS_4 b) A single $[\text{PbAsS}_4]^{n-}$ layer c) Trigonal prismatic geometry of Pb d) Coordination of $(\text{AsS}_4)^{3-}$

Table 4. Selected bond distances for RbPbAsS₄, CsPbAsS₄, Rb₄PbAs₂S₈ and Cs₄PbAs₂S₈

RbPbAsS ₄			
Pb(1) - S(3)	2.918(4)	Rb(1) - S(3)	3.355(4)
Pb(1) - S(1)	2.968(4)	Rb(1) - S(2)	2 x 3.484(3)
Pb(1) - S(2)	2 x 3.020(3)	Rb(1) - S(1)	2 x 3.5057(13)
Pb(1) - S(2)	2 x 3.182(1)	Rb(1) - S(2)	2 x 3.528(3)
As(1) - S(2)	3 x 2.154(3)	Rb(1) - S(1)	3.639(4)
As(1) - S(3)	2.169(4)	Rb(1) - As(1)	3.839(2)
CsPbAsS ₄			
Pb(1) - S(3)	2.893(4)	As(1) - S(3)	2.168(3)
Pb(1) - S(1)	2.972(3)	Cs(1) - S(2)	2 x 3.730(3)
Pb(1) - S(2)	2 x 3.030(2)	Cs(1) - S(2)	2 x 3.652(3)
Pb(1) - S(2)	2 x 3.213(1)	Cs(1) - S(3)	3.451(4)
As(1) - S(1)	2.145(3)	Cs(1) - S(1)	2 x 3.5675(18)
As(1) - S(2)	2 x 2.155(2)	Cs(1) - As(1)	3.918(2)
Rb ₄ PbAs ₂ S ₈			
Pb(1) - S(2)	4 x 3.1656(19)	Rb(1) - S(2)	2 x 3.481(2)
Pb(1) - S(3)	4 x 3.2144(17)	Rb(1) - S(1)	3.508(3)
As(1) - S(1)	2.143(2)	Rb(1) - S(2)	2 x 3.563(2)
As(1) - S(2)	2 x 2.1478(15)	Rb(2) - S(1)	2 x 3.4115(18)

As(1) - S(3)	2.166(2)	Rb(2) - S(1)	2 x 3.4353(17)
Rb(1) - S(3)	3.204(3)	Rb(2) - S(3)	2 x 3.614(2)
Rb(1) - S(2)	2 x 3.409(2)	Rb(2) - As(1)	2 x 3.8040(13)

Cs₄PbAs₂S₈

Pb(1) - S(4)	2 x 2.940(2)	Cs(1)-S(3)	3.699(2)
Pb(1) - S(2)	2 x 3.0710(18)	Cs(1)-S(3)	3.657(2)
Pb(1) - S(3)	2 x 3.220(2)	Cs(1)-S(2)	3.654(2)
As(1) - S(1)	2.1519(19)	Cs(2) - S(4)	2 x 3.647(2)
As(1) - S(3)	2.1554(19)	Cs(2) - S(1)	2 x 3.545(2)
As(1) - S(2)	2.1616(17)	Cs(2) - S(1)	2 x 3.547(2)
As(1) - S(4)	2.1778(19)	Cs(3) - Cs(33)	0.293(1)
Cs(1)-S(4)	3.363(2)	Cs(3) - S(1)	2 x 3.577(5)
Cs(1)-S(3)	3.558(2)	Cs(3) - S(1)	2 x 3.583(2)
Cs(1)-S(1)	3.639(2)	Cs(3) - S(4)	2 x 3.652(11)
Cs(1)-S(2)	3.6490(19)	Cs(3) - As(1)	2 x 3.809(9)
Cs(1)-S(2)	3.658(2)		

Table 5. Selected bond angles for RbPbAsS₄, CsPbAsS₄, Rb₄PbAs₂S₈ and Cs₄PbAs₂S₈

RbPbAsS ₄			
S(3) - Pb(1) - S(1)	74.51(10)	S(2) - As(1) - S(2)	106.82(15)
S(3) - Pb(1) - S(2)	2 x 91.24(8)	S(2) - As(1) - S(1)	2 x 111.14(10)
S(1) - Pb(1) - S(2)	2 x 144.02(5)	S(2) - As(1) - S(3)	2 x 108.27(10)
S(2) - Pb(1) - S(2)	66.98(10)	S(1) - As(1) - S(3)	111.04(16)
CsPbAsS ₄			
S(3) - Pb(1) - S(1)	74.34(8)	S(1) - As(1) - S(2)	2 x 111.58(8)
S(3) - Pb(1) - S(2)	2 x 91.90(7)	S(2) - As(1) - S(2)	108.01(12)
S(1) - Pb(1) - S(2)	2 x 143.62(4)	S(1) - As(1) - S(3)	110.52(13)
S(2) - Pb(1) - S(2)	68.31(8)	S(2) - As(1) - S(3)	2 x 107.48(8)
Rb ₄ PbAs ₂ S ₈			
S(2) - Pb(1) - S(2)	125.414(1)	S(2) - Pb(1) - S(3)	65.82(5)
S(2) - Pb(1) - S(2)	151.054(1)	S(2) - Pb(1) - S(3)	81.411(1)
S(2) - Pb(1) - S(2)	62.964(1)	S(2) - Pb(1) - S(3)	122.93(2)
S(3) - Pb(1) - S(3)	170.997(1)	S(1) - As(1) - S(2)	2 x 110.77(6)
S(3) - Pb(1) - S(3)	104.875(1)	S(2) - As(1) - S(2)	108.63(9)
S(3) - Pb(1) - S(3)	75.855(1)	S(1) - As(1) - S(3)	112.56(8)
S(2) - Pb(1) - S(3)	90.886(1)	S(2) - As(1) - S(3)	2 x 106.96(6)

Cs₄PbAs₂S₈

S(4) - Pb(1) - S(4)	106.27(9)	S(1) - As(1) - S(2)	110.79(7)
S(4) - Pb(1) - S(2)	2 x 69.73(5)	S(3) - As(1) - S(2)	110.36(8)
S(4) - Pb(1) - S(2)	2 x 83.49(5)	S(1) - As(1) - S(4)	112.56(7)
S(2) - Pb(1) - S(2)	134.93(7)	S(3) - As(1) - S(4)	108.58(8)
S(1) - As(1) - S(3)	109.64(8)	S(2) - As(1) - S(4)	104.80(8)

3.839(2) Å. The two AsS₄ tetrahedra are slightly distorted with S-As-S angles between 106.82(15)° and 111.14(10)°. S-Pb-S angles vary from 65.86(1)° to 144.02(5)°.

APbAsS₄ crystallizes in the CsPbPSe₄^{8a} structure type. This structure type is also found in AEuPS₄^{8b} (A = Rb, Cs). Distortions of this structure type are seen in the compounds APbPS₄^{8b} (A = Rb, Cs) which crystallize in the non-centrosymmetric space group *P2₁2₁2₁*. These compounds differ from APbAsS₄ with respect to the binding mode of the (PS₄)³⁻ ligand. In APbPS₄, each Pb is still coordinated by 4 (PS₄)³⁻ ligands. However each of the (PS₄)³⁻ unit uses two edges and one corner to ligate to 4 Pb atoms. Another compound CsSmGeS₄¹³ shows a striking similarity to this structure type. This compound crystallizes in *P2₁2₁2₁* and consists of a monocapped trigonal prismatic Sm³⁺ coordinated by 4 (GeS₄)⁴⁻ tetrahedra. Each (GeS₄)⁴⁻ uses three edges and one corner to 4 Sm³⁺ ions.

C.3 Structure description of A₄PbAs₂S₈

Rb₄PbAs₂S₈ crystallizes in the orthorhombic space group *Ibam*. The structure is composed of 1-D chains running parallel to the c- axis, Figure 2a. Each chain is made up of eight coordinate Pb ligated by 4 tetrahedral (AsS₄)³⁻ units. This gives rise to a distorted dodecahedral geometry for Pb, Figure 2b. Each (AsS₄)³⁻ anion employs three of its sulfur atoms to bridge to two adjacent Pb atoms while the remaining sulfur remains non-bonding, Figure 2c.

There are four Pb-S distances at 3.1656(19) Å and four distances at 3.2144(17) Å. As-S distances vary between 2.143(2) to 2.166(2) Å. There are two Rb ions, one coordinated by sulfur atoms in a bicapped trigonal prismatic geometry and the other in an irregular six-coordinate site with average Rb-S distances of 3.45(1) Å and 3.49(1) Å, Figure 2d.

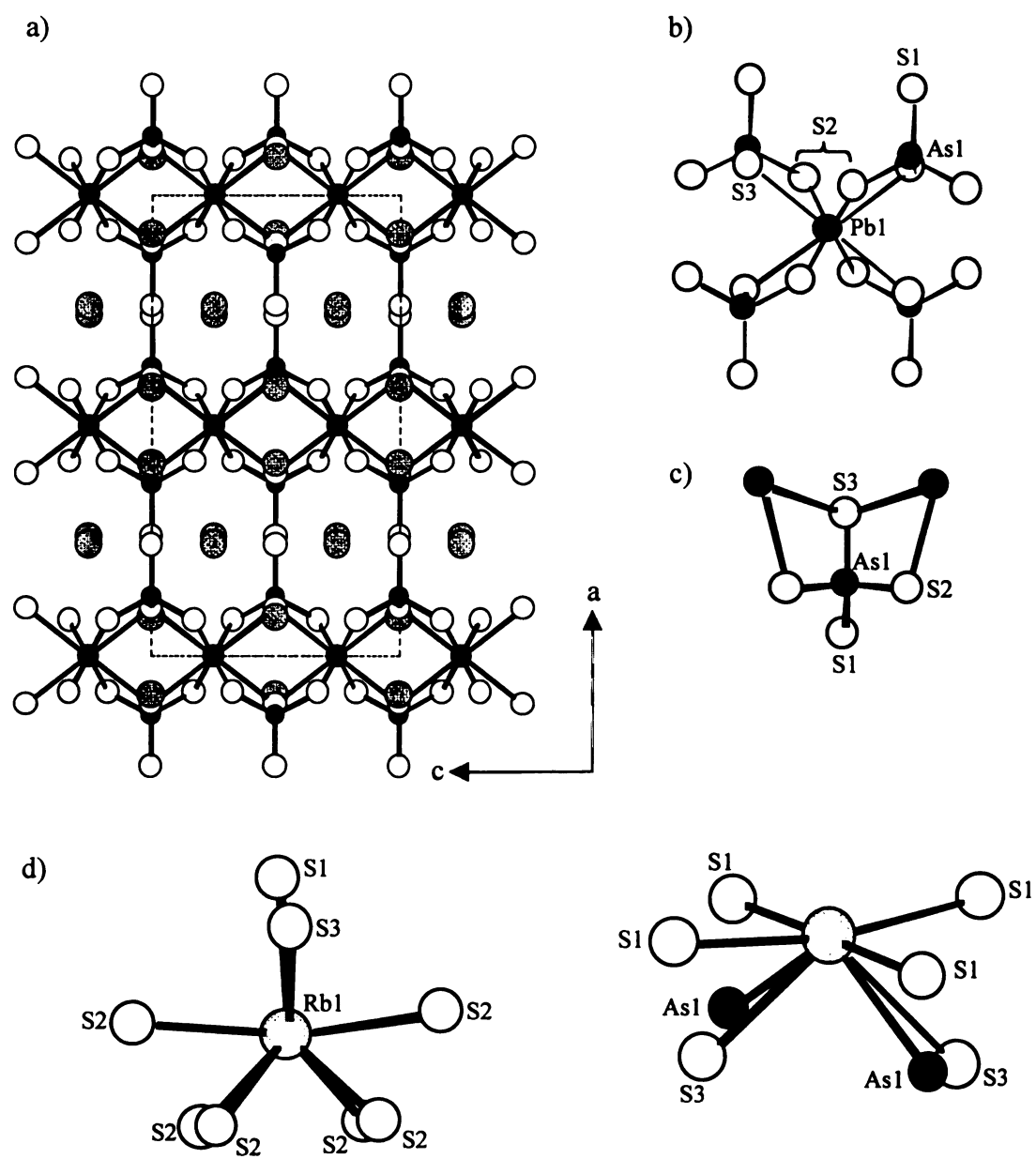


Figure 2. a) Unit cell of $\text{Rb}_4\text{PbAs}_2\text{S}_8$ b) Distorted dodecahedral environment around Pb
c) Coordination of $(\text{AsS}_4)^{3-}$ d) Coordination of K^+ cations

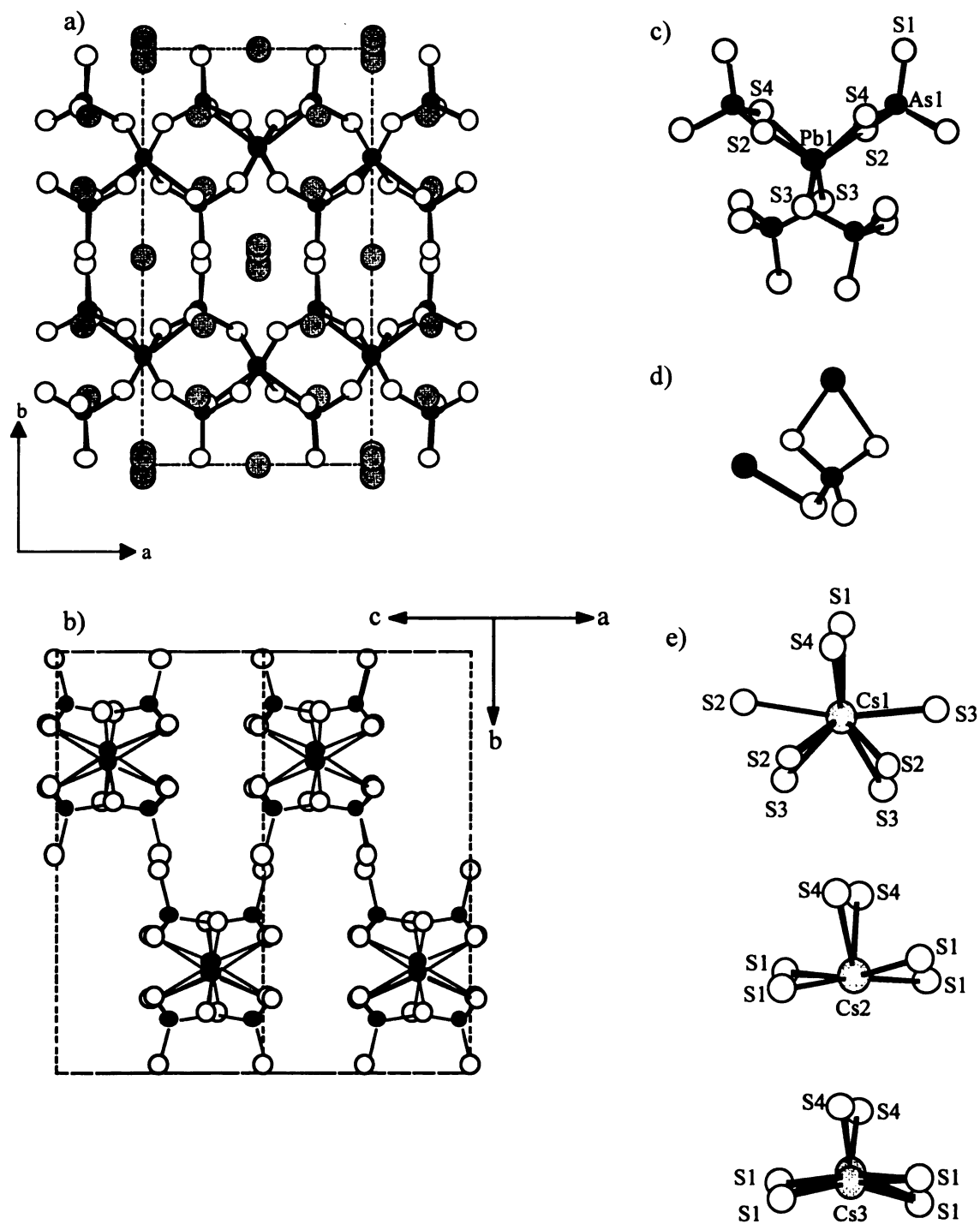


Figure 3. a) Unit cell of $\text{Cs}_4\text{PbAs}_2\text{S}_8$ along the a - axis b) View of the unit cell along the ac - plane, Cs atoms have been omitted for clarity c) Coordination geometry around Pb d) Coordination of $(\text{AsS}_4)^{3-}$ e) Coordination environments of Cs^+

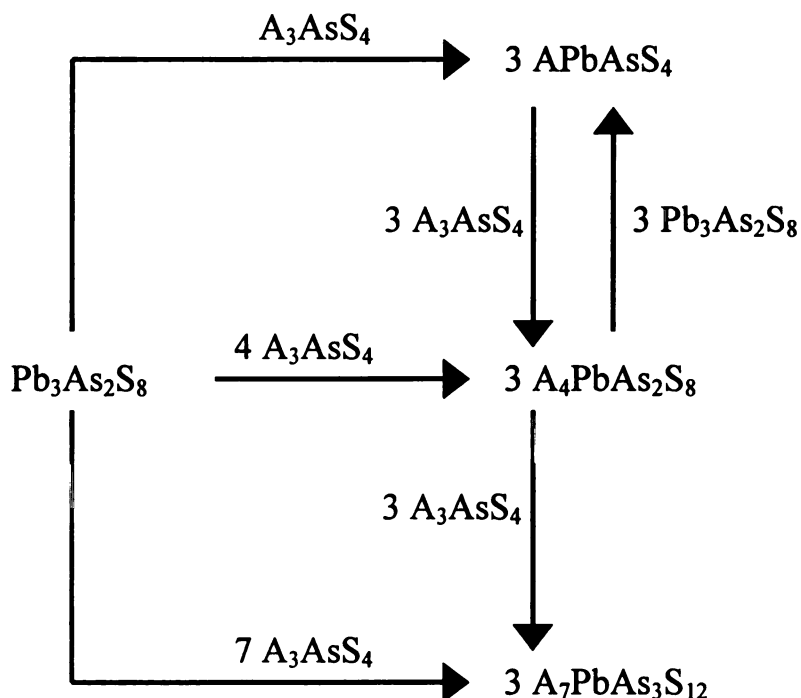
There is also a weak interaction of one of the Rb ions with As at a distance of 3.8040(13) Å. S-As-S bond angles of 110.77(6)° and 106.96(6)° are close to tetrahedral angles. S-Pb-S angles range from 62.964(1)° to 170.997(1)°. The Pb-S bond distances are longer than those found APbAsS₄ however the other distances and angles are similar.

The structure of Cs₄PbAs₂S₈ is similar to the Rb compound. There is a lowering of the symmetry going from Rb to Cs owing to the bigger size of the Cs⁺ ion which does not allow better packing of the chains. The chains run along the ac- direction and the Pb atoms have a kink-like arrangement along this chain, Figure 3a and 3b. The Pb-Pb distance in the chain is 5.275 Å compared to 5.072 Å for the Rb compound. The other significant difference comes from the coordination environment of Pb. In Cs₄PbAs₂S₈, Pb has a trigonal prismatic geometry similar to that found in APbAsS₄, Figure 3c. Each (AsS₄)³⁻ anion uses one edge and one corner to bridge two Pb atoms while the fourth sulfur atoms remains non-bonding, Figure 3d. Figure 3e shows bonding geometry of the three crystallographically unique Cs cations.

Rb₄PbAs₂S₈ is isostructural to A₄PbP₂S₈ (A= K, Rb, Cs). Cs₄PbAs₂S₈ represents a distorted version of this structure type. A closely related structure is observed in the one-dimensional compounds K₃LaP₂Se₈¹⁴, K₃PuP₂S₈¹⁵, A₃REP₂Se₈ (A = Rb, Cs; RE = Ce, Gd).¹⁶ In these compounds, the rare-earth metal is in a bicapped trigonal prismatic environment coordinated by 4 tetrahedral (PQ₄)³⁻ anions in a bidentate manner. The rare-earth metals are arranged in a kink-like fashion along the chain, akin to Cs₄PbAs₂S₈.

C.4 Pb Series

Based on the Pb compounds we have obtained so far, it is possible to envision a series of Pb compounds belonging to the general formula $(A_3AsS_4)_n(Pb_3As_2S_8)_m$ where the first compound of the series is $Pb_3As_2S_8$ ($m = 1, n = 0$), Scheme 1. By adding one equivalent of A_3AsS_4 , we can obtain the compound $APbAsS_4$ ($m = 1, n = 1$). For $m = 1, n = 2$, we should get the compound $A_4PbAs_2S_8$, further addition of A_3AsS_4 should give $A_7PbAs_3S_{12}$. We can think of this series as a gradual dismantling of the 3-D framework of $Pb_3As_2S_8$ to give the 2-D $APbAsS_4$, the 1-D $A_4PbAs_2S_8$ and $A_7PbAs_3S_{12}$ which is probably molecular. A similar series has been postulated for lead chalcophosphate compounds.⁸



Scheme 1. Flow chart showing the different members belonging to the series $(A_3AsS_4)_n(Pb_3As_2S_8)_m$

C.5 Thermal Analysis

The thermal behavior of RbPbAsS_4 and $\text{Cs}_4\text{PbAs}_2\text{S}_8$ were monitored by DTA. RbPbAsS_4 melts at 435°C and recrystallizes at 397°C , Figure 4a. The powder pattern of the compound after DTA contained peaks belonging to the parent compound along with some PbS and $\text{Rb}_4\text{PbAs}_2\text{S}_8$. $\text{Cs}_4\text{PbAs}_2\text{S}_8$ melts at 547°C and recrystallizes at 524°C . As seen in Figure 4b, the melting point shifts to 540°C on the second heating cycle. The powder pattern after DTA matched the one before indicating no decomposition of the compound.

C.6 Optical Spectroscopy

Since RbPbAsS_4 was obtained as yellow transparent plates, suitable crystals could be picked up for single-crystal band gap measurements. Figure 5a shows that RbPbAsS_4 is a semiconductor with a sharp absorption at 2.53 eV. This value corresponds well to its yellow color. The band gaps of $\text{Rb}_4\text{PbAs}_2\text{S}_8$, CsPbAsS_4 and $\text{Cs}_4\text{PbAs}_2\text{S}_8$ were determined by diffuse reflectance spectroscopy. These compounds absorb at 2.26 eV (figure 5c), 2.42 eV (figure 5b) and 2.58 eV (figure 5d) respectively. As a general rule, for the same structure, the band gap should decrease as we go down a group. This is observed in the case of RbPbAsS_4 and CsPbAsS_4 . Like wise $\text{Rb}_4\text{PbP}_2\text{S}_8$ has a higher band gap (2.68 eV) compared to $\text{Rb}_4\text{PbAs}_2\text{S}_8$.

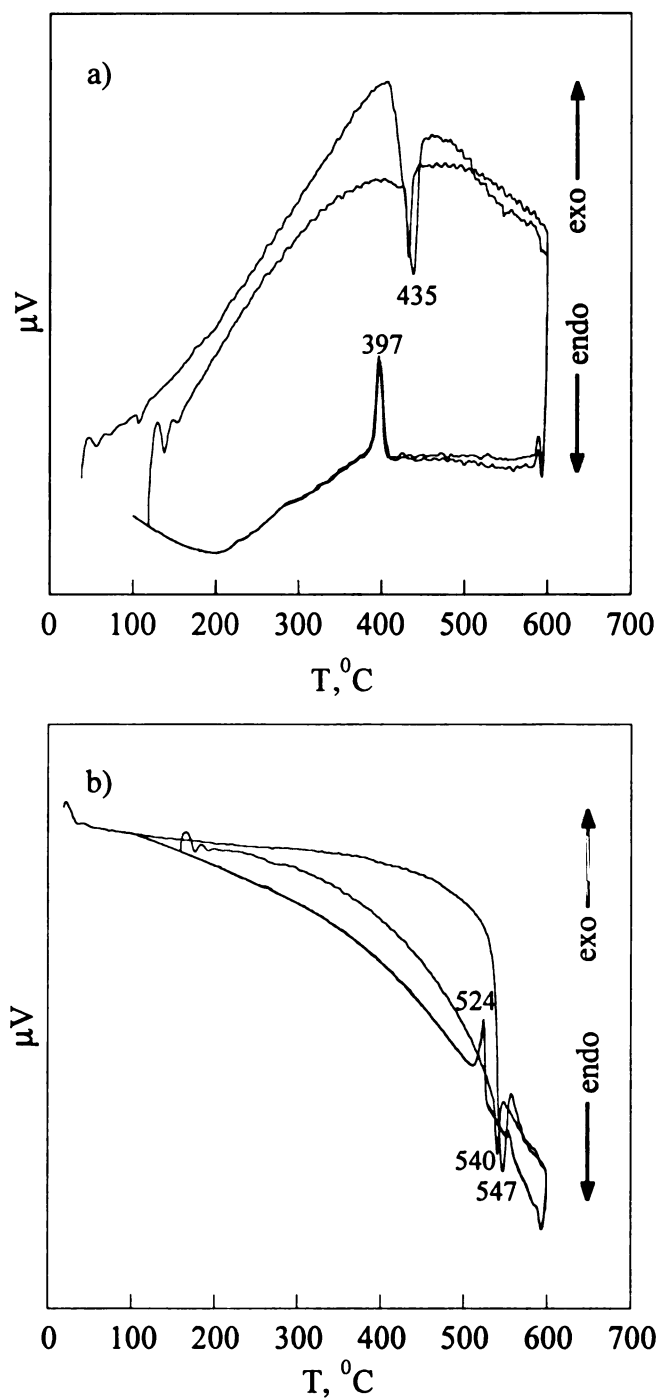


Figure 4. a) DTA of $RbPbAsS_4$ showing a melting point at $435^\circ C$ and recrystallization point at $397^\circ C$. b) DTA of $Cs_4PbAs_2S_8$ showing that it melts at around $543^\circ C$ and recrystallizes at $524^\circ C$.

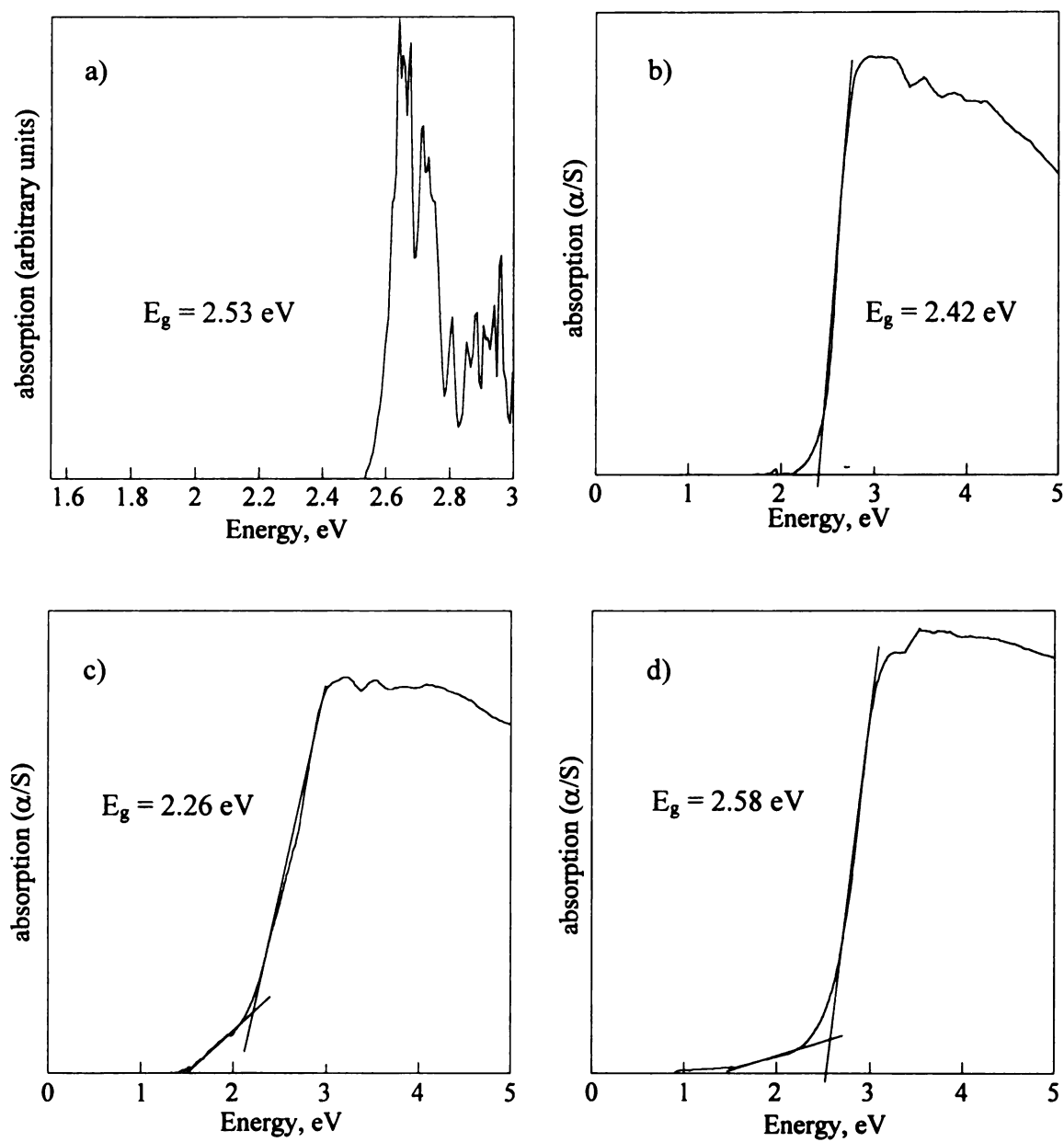


Figure 5. a) Single crystal UV-Vis spectrum of RbPbAsS_4 showing a sharp absorption at 2.53 eV. Diffuse reflectance spectra of b) CsPbAsS_4 c) $\text{Rb}_4\text{PbAs}_2\text{S}_8$ d) $\text{Cs}_4\text{PbAs}_2\text{S}_8$

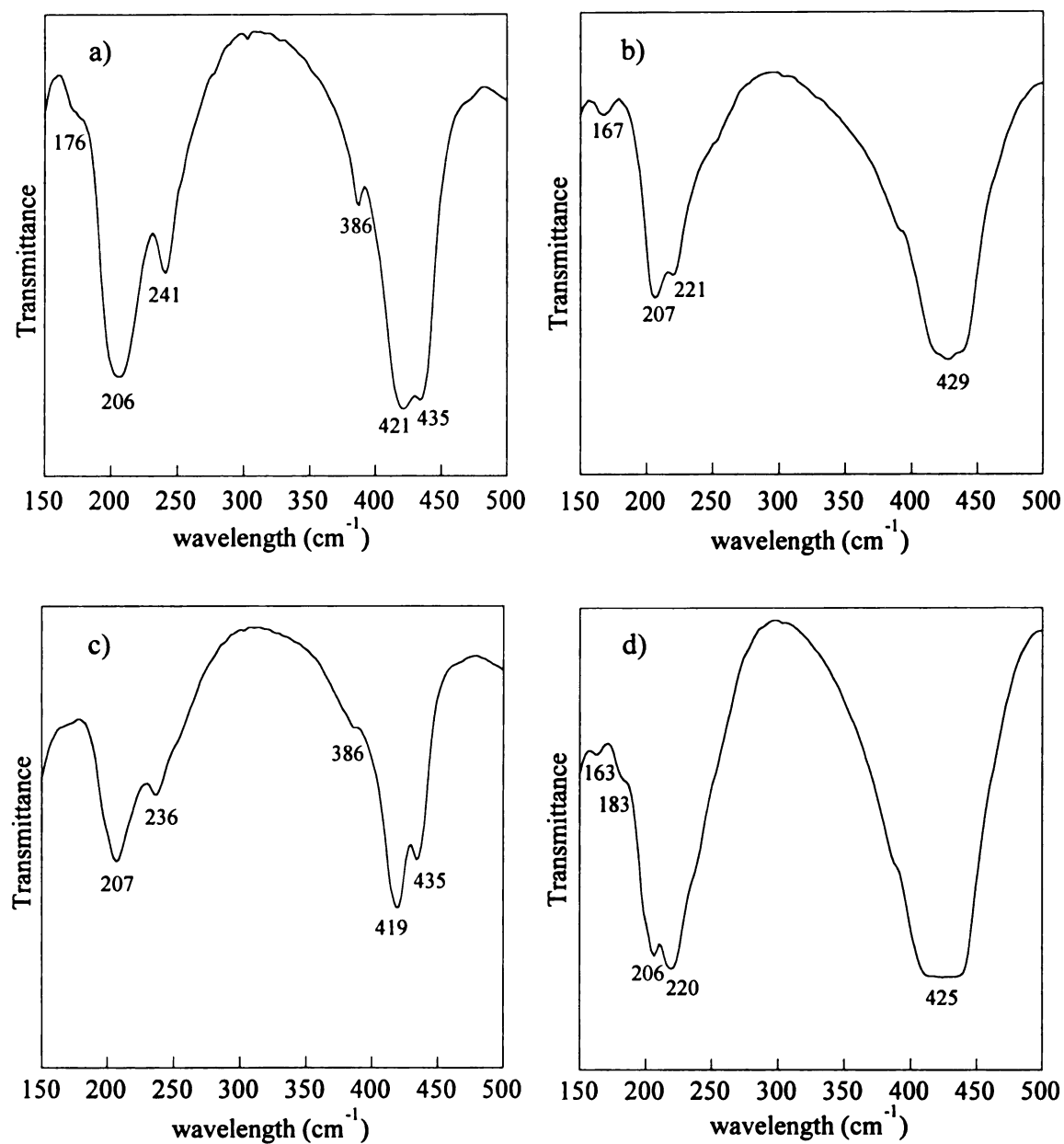


Figure 6. Far-IR spectra of a) RbPbAsS₄ b) Rb₄PbAs₂S₈ c) CsPbAsS₄ d) Cs₄PbAs₂S₈

The Far-IR spectra of APbAsS_4 and $\text{A}_4\text{PbAs}_2\text{S}_8$ are shown in Figure 6. As seen in the figure, the spectra compare very well to each other. There are three strong peaks in the range $380\text{--}440\text{ cm}^{-1}$, which can be attributed to As-S stretching. The peaks in the $160\text{--}250\text{ cm}^{-1}$ range belong to either Pb-S or As-S vibrations. The simplicity of these spectra point to the very symmetrical coordination environments of As and Pb. Similar vibrational energies are observed for APbPS_4 and $\text{A}_4\text{PbP}_2\text{S}_8$.

D. Conclusion

The reaction of Pb in thioarsenate fluxes formed compounds that are isostructural to their thiophosphate counterparts. This similarity has its foundation on the type of ligand that is formed in both these fluxes. The formation of the tetrahedral $(\text{PnS}_4)^{3-}$ ($\text{Pn} = \text{P}, \text{As}$) ligand can be explained on the basis of the ease of oxidation of the metal. Since Pb is easily oxidized to Pb^{2+} , the flux can further oxidize As (or P) to As^{5+} (or P^{5+}). The As(P)^{5+} ion forms the well known tetrahedral $(\text{PnS}_4)^{3-}$ ligand which then coordinates to Pb^{2+} . The other significant observation that can be made here is the prediction of a series of Pb compounds. Usually predicting the outcome of a solid state reaction is very difficult. Varying the flux basicity in our system allowed us to isolate two members of the series $(\text{A}_3\text{AsS}_4)_n(\text{Pb}_3\text{As}_2\text{S}_8)_m$ whereby we can now predict the composition of the other members and try to target their synthesis.

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Chapter 5

Synthesis and Characterization of Two New Europium Thioarsenates Featuring the Tetrahedral AsS_4^{3-} Ligand: AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$

Abstract

AgEuAsS_4 (I) was obtained from a direct combination of Ag, Eu, As and S at 650°C. It crystallizes in the orthorhombic space group $Ama2$ with $a = 10.198(4)$ Å, $b = 10.084(4)$ Å, $c = 6.479(3)$ Å. The structure consists of tetrahedral AsS_4^{3-} anions coordinating to Ag^+ ions in a distorted tetrahedral geometry and Eu^{2+} ions in a bicapped trigonal prismatic geometry to form a complex 3-D framework. $\text{Eu}_3\text{As}_2\text{S}_8$ (II) crystallizes in the rhombohedral space group $R\bar{3}c$ with $a = 9.254(3)$ Å, $c = 27.698(12)$ Å, $\gamma = 120^\circ$. It is prepared by heating Eu, As and S in the required ratio at 650°C. This compound presents a new structure type consisting of 8 coordinate Eu^{2+} and tetrahedral AsS_4^{3-} ligands. The magnetic susceptibility measurements on these compounds confirm that the Eu ions have a +2 charge. Both compounds are stable in air and water over extended periods.

A. Introduction

Rare-earth chalcogenides are a subject of extensive investigation since the past decade. These compounds exhibit a rich structural chemistry arising from the variable coordination environment, ranging from 6-coordinate to 9-coordinate, of the rare-earth ions. Some of these compounds include LiEuGeS_4 ¹, $\text{Eu}_8\text{Sn}_4\text{Se}_{20}$ ², Eu_2CuS_3 ³, K_2EuTSe_5 , KEuTS_4 ($\text{T} = \text{Si, Ge}$)⁴, CePS_4 ⁵, Ce_2SiS_5 ⁶, EuSe_2 ⁷, Eu_2GeS_4 ⁸, AEuPSe_4 ($\text{A} = \text{K, Li}$)⁹, $\text{K}_4\text{EuP}_2\text{Q}_8$, KEuPQ_4 ($\text{Q} = \text{S, Se}$)^{10, 11}, $\text{NaCeP}_2\text{Se}_6$, $\text{Ce}_{1.33}\text{P}_2\text{Se}_6$, $\text{AgCeP}_2\text{Se}_6$, $\text{Cu}_{0.4}\text{Ce}_{1.2}\text{P}_2\text{Se}_6$ ¹², $\text{Rb}_9\text{CeP}_4\text{Se}_{16}$ ¹³, $\text{BaLaBi}_2\text{Q}_6$ ($\text{Q} = \text{S, Se}$)¹⁴, $\text{A}_3\text{REP}_2\text{Se}_8$ and $\text{A}_2\text{REP}_2\text{Se}_7$ ($\text{RE} = \text{Ce, Gd}$; $\text{A} = \text{Rb, Cs}$)¹⁵, $\text{A}_2\text{REP}_2\text{Se}_6$ ¹⁶, BaGdCuSe_3 ¹⁷, BaLnMQ_3 ¹⁸, $\text{K}_2\text{Cu}_2\text{CeS}_4$ ¹⁹, $\text{K}_2\text{Ag}_3\text{CeTe}_4$ ²⁰, KCuCeTe_4 ²¹, $\text{Ca}_4(\text{RE})_2\text{In}_4\text{Q}_{13}$ ²², CsCuCeS_3 ²³, KLnMQ_4 ²⁴, ALnQ_4 ($\text{A} = \text{K, Rb}$; $\text{Ln} = \text{Ce, Tb}$; $\text{Q} = \text{Se, Te}$), NaLnS_3 ²⁵, ALn_3Te_8 ($\text{A} = \text{K, Rb, Cs}$; $\text{Ln} = \text{Ce, Nd}$)²⁶, $\text{Cu}_{0.66}\text{EuTe}_2$ ²⁷, $\text{Cs}_3\text{Pr}_5(\text{PS}_4)_6$ ²⁸, AYbZnQ_3 ²⁹, La_2CuS_4 ³⁰, $\text{K}_2\text{Ln}_4\text{Cu}_4\text{S}_9$ etc.³¹ A recent review by Ibers et al. details the exquisite structural variety of transition metal-rare-earth chalcogenides.³² These compounds can exhibit many interesting properties. For example, EuSe_2 ⁷ exhibits meta-magnetic transition. Ce_2SiS_5 , $\text{Ce}_6\text{Si}_4\text{S}_{17}$ and $\text{Ce}_4\text{Si}_3\text{S}_{12}$ ⁶ are potentially important as pigment materials. Eu_2GeS_4 ⁸ displays ferroelectric behavior while Eu_2CuS_3 ³ consists of Eu in mixed valent states. KCuCeTe_4 ²¹ and $\text{KCu}_2\text{EuTe}_4$ ²⁷ consist of square Te nets, which show superstructure modulations arising from charge density waves in the Te nets. Rare-earth sulfides have shown promise as optical and electronic materials.³³ Incorporation of rare-earth cations led to increased thermal stability in oxygen-atmosphere.²² Yet another important area where rare-earth cations have found application are the lanthanide containing non-oxide glasses.³⁴ These glasses are potentially useful as fiber lasers and optical amplifiers.

The use of the solid state reactive flux technique for the synthesis of new materials at low to intermediate temperatures³⁵ has contributed immensely to the advancement of this class of materials. Recently we started exploring the reactivity of different main group, transition and rare earth metals in alkali metal thioarsenate fluxes.³⁶ We undertook such an endeavor in order to compare the behavior of the thioarsenate fluxes vis-à-vis the thiophosphate fluxes. We were successful in isolating ASnAsS_5 , $\text{A}_2\text{SnAs}_2\text{S}_6$, $\text{A}_6\text{InAs}_3\text{S}_{13}$, APbAsS_4 , $\text{A}_4\text{PbAs}_2\text{S}_8$, $\text{A}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ and $\text{A}_8\text{Cd}_2\text{As}_4\text{S}_{18}$. The structures range from molecular anions to layers. The reaction of Ce in Rb and Cs thioarsenate fluxes gave the one-dimensional compound $\text{A}_3\text{CeAs}_2\text{S}_8$ (see Appendix), which is isostructural to its thiophosphate counterpart. The reactions of Eu in thiophosphate fluxes yield AEuPS_4 , $\text{A}_4\text{EuP}_2\text{S}_8$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$)³⁷ which are similar or isostructural to their Pb counterparts. Since Pb and Eu have a similar chemistry, we realized that the reaction of Eu in thioarsenate fluxes may yield compounds similar to APbAsS_4 and $\text{A}_4\text{PbAs}_2\text{S}_8$. We therefore decided to study the reaction of Eu with Ag and Cu as the counter cation instead of the alkali metals.

Ag and Cu have ionic radii similar to the alkali metals, K and Na, however their interactions with chalcogens are covalent compared to the ionic bonding shown by the alkali metals. In addition, Ag and Cu prefer low coordination environments and belong to the d^{10} class of cations, which are known to exhibit interesting d^{10} - d^{10} homoatomic interactions.³⁸ They are also known for their anomalous high atomic displacement parameters attributed to anharmonic thermal vibrations.³⁹ There are a very few synthetic quaternary sulfides that contain both a coinage metal and As. These are K_2AuAsS_4 ⁴⁰, KAg_2AsS_4 ⁴¹, $\text{Cs}_2\text{AgAsS}_4$ ⁴², $\text{KAg}_3\text{As}_2\text{S}_5$ ⁴³, $[\text{Fe}(\text{NH}_3)_6]\text{AgAsS}_4$ ⁴⁴, $(\text{NH}_4)\text{Ag}_2\text{AsS}_4$ ⁴⁵,

$(\text{NH}_4)\text{Ag}_2\text{As}_3\text{S}_6$, $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ ⁴⁶, $(\text{enH}_2)\text{AgAsS}_4$ ⁴⁷, KCu_2AsS_3 and KCu_4AsS_4 .⁴⁸ Copper or silver containing europium sulfides are even fewer such as KCuEu_2S_6 ⁴⁹, Eu_2CuS_3 ³ and EuCu_2MS_4 ($\text{M} = \text{Ge}, \text{Sn}$).⁵⁰ In view of this paucity, $\text{Eu}_3\text{As}_2\text{S}_8$ and AgEuAsS_4 represent welcome additions to this class of compounds. AgEuAsS_4 is isostructural to LiEuPSe_4 whereas $\text{Eu}_3\text{As}_2\text{S}_8$ presents a new structure type. The structures and physical properties of these two compounds are discussed.

B. Experimental Section

B.1 Reagents

The following reagents were used as obtained: Eu (metal chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Ag (99.999% purity, Liberty coins, Lansing, MI), As_2S_3 (99.9 %; Strem Chemicals, Newburyport, MA), As (99.9%; Aldrich Chemical Co, Milwaukee, WI), S (99.9 %; Strem Chemicals, Newburyport, MA).

B.2 Physical Measurements

Powder X-ray Diffraction

X-ray powder diffraction patterns were recorded on a CPS 120 INEL diffractometer (Cu $\text{K}\alpha$ radiation) operating at 40kV/20mA and equipped with a position sensitive detector and a flat sample geometry.

Energy Dispersive Spectroscopy

Semiquantitative microprobe analyses on the compounds were done with a JEOL JSM-6400V scanning electron microscope equipped with a Tracor Noran Energy Dispersive

Spectroscopy detector. Elemental compositions were obtained from an average of three readings. Acquisition times were 30s or 45s per reading.

Diffuse Reflectance Spectroscopy

Solid state diffuse reflectance spectra were measured using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as reference. Finely ground sample was spread on a sample holder preloaded with the reference. Energy gap was determined from a plot of absorbance vs energy by converting reflectance to absorbance using the Kubelka-Munk function.⁵¹

Differential Thermal Analysis

The thermal behavior of the compounds was investigated by differential thermal analysis using a Shimadzu DTA-50 thermal analyzer. Typically a sample (~20 mg) of ground crystalline material was sealed in a silica ampule under vacuum. A similar ampoule of equal mass filled with Al₂O₃ was sealed and placed on the reference side of the detector. The sample was heated to the desired temperature at 10°C/min, and after 1-3 min it was cooled at a rate of -10°C/min to 50°C. Residues of the DTA experiments were examined by X-ray powder diffraction. Reproducibility of the results was checked by running multiple heating/ cooling cycles.

Magnetic Susceptibility Measurements

Magnetization measurements as a function of applied magnetic field and temperature were made on a MPMS Quantum Design SQUID susceptometer in the temperature range of 2 to 300 K and magnetic fields of 0 to ±55 kG. The samples consisted of about 70 - 80mg of each compound. For AgEuAsS₄, the crystals were picked under the microscope to eliminate any impurities in the sample.

B.3 Synthesis

AgEuAsS₄ (I): *AgEuAsS₄* was synthesized by reacting a mixture consisting of Ag (0.032g, 0.3mmol), Eu (0.045g, 0.3mmol), As₂S₃ (0.074g, 0.3mmol) and S (0.038g, 1.2mmol). The starting materials were loaded in a fused-silica tube in a nitrogen-filled dry glove box. The tube was then evacuated ($<10^{-4}$ Torr) and sealed. The sealed tube was put in a computer-controlled furnace and heated to 650°C. It was maintained at this temperature for 60h. The tube was then cooled at the rate of 5°C/h to room temperature. The product consisted of ruby-red rectangular rods (Figure 1), dark-red chunks and yellow glass. The rectangular crystals constituted ~30% of the product. Semiquantitative microprobe analysis using energy dispersive spectroscopy on the red rods gave an average composition of "Ag_{1.4}Eu_{1.4}AsS_{5.5}". The average composition of the dark-red chunks was "Eu_{1.1}AsS_{2.9}" while the yellow glass had a composition of "AsS₆". The powder pattern of the product revealed that the dark red chunks were Eu₃As₂S₈.

Eu₃As₂S₈ (II): Eu₃As₂S₈ was prepared by combining Eu (0.091g, 0.6mmol), As (0.03g, 0.4mmol) and S (0.051g, 1.6mmol) at 650°C following the same procedure as described above. The compound forms as ruby-red chunks with an average composition, as determined by EDS, of "Eu_{3.4}As₂S_{7.2}".

B.4 X-ray Crystallography

Single crystal data for *AgEuAsS₄* and Eu₃As₂S₈ were collected on Bruker SMART CCD diffractometer with Mo K α radiation. A full sphere of data was collected for both the compounds. For *AgEuAsS₄*, a rectangular rod with dimensions of 1.2 x 0.6 x 0.7 mm³ was mounted on a goniometer head and a full sphere of data was collected using the SMART

software. An empirical absorption correction was applied using SADABS. The structure was solved by direct methods using the SHELXTL package.⁵² Systematic absences and E^2-1 statistics indicated a non-centrosymmetric space group. The two choices were $Cmc2_1$ and $Ama2$. Based on the combined figure of merit (CFOM) value, the space group $Cmc2_1$ was chosen. However a suitable structural refinement could not be obtained. Hence the space group $Ama2$ was chosen and after an initial round of refinement, one Ag, one Eu, one As and three S atoms were found. The thermal displacement parameter for Ag was found to be very high and it occupied a position just slightly off the mirror plane (1/4,y,z). Hence its occupancy was allowed to refine freely. This reduced its site occupancy factor to 50% and generated a symmetry equivalent site 0.556 Å away. Anisotropic refinement of all the atoms gave a final R1/wR2 value of 4.69/12.71. We suspected merohedral twinning of the crystal due to the fact that a and b are very close to each other. Analysis of the structure using the program JANA2000⁵³ found no rotational twinning.

For $Eu_3As_2S_8$, a red crystal chunk was mounted on a goniometer head and a full sphere of data was collected. The space group $R-3c$ was chosen based on intensity statistics and systematic absences. The structure solution was straight-forward and after anisotropic refinement of all the atoms, the final R1/wR2 value was 2.38/5.80.

The relevant crystallographic data for **I** and **II** are presented in Table 1. Table 2 gives the coordinates of the atoms along with their isotropic displacement values. Anisotropic displacement parameters are listed in Table 3.

Table 1. Crystallographic refinement data for AgEuAsS₄ and Eu₃As₂S₈.

Formula	AgEuAsS ₄	Eu ₃ As ₂ S ₈
Space Group	<i>Ama2</i>	<i>R-3c</i>
a, Å	10.198 (4)	9.254(3)
b, Å	10.084 (4)	9.254(3)
c, Å	6.479 (3)	27.698 (12)
γ, deg	90	120
Z, V	2, 666.3 (5)	3, 2054.2 (13)
D, mg/m ³	4.615	4.182
Temp, K	293	293
λ, Å	0.71073	0.71073
μ, mm ⁻¹	18.314	19.540
F(000)	828	2298
θ _{max} , deg	28.23	28.15
Total reflections	2388	1834
Total unique reflections	776	541
No. of parameters	44	21
Refinement method	Full-matrix least-squares on F ²	
Final R indices(I>2σ(I))	R1 ^a = 0.0469, wR2 ^b = 0.1217	R1 = 0.0238, wR2 = 0.0580
R indices (all data)	R1 = 0.0513, wR2 = 0.1271	R1 = 0.0272, wR2 = 0.0598
Absolute structure parameter	0.09(4)	
Goodness of fit on F ²	1.064	1.088

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

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$.

Atom	x	y	z	Ueq ^a
AgEuAsS₄				
Eu(1)	0.5000	0	0.9494(3)	18(1)
As(1)	0.7500	-0.2864(2)	0.9705(3)	12(1)
Ag(1)	0.2770(20)	0.1611(3)	1.5051(4)	106(6)
S(1)	0.5757(3)	0.2165(3)	1.2796(6)	20(1)
S(2)	0.7500	0.0604(4)	0.7034(8)	18(1)
S(3)	0.2500	0.0993(4)	1.1424(7)	14(1)
Eu₃As₂S₈				
Eu(1)	0.3456(1)	0.0122(1)	0.0833	18(1)
As(1)	0	0	0.1595(1)	16(1)
S(1)	0	0	0.0806(1)	19(1)
S(2)	0.7035(1)	0.1330(1)	0.0182(1)	20(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for AgEuAsS₄ and Eu₃As₂S₈.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
AgEuAsS ₄						
Eu(1)	14(1)	16(1)	24(1)	0	0	3(1)
As(1)	12(1)	12(1)	14(1)	1(1)	0	0
Ag(1)	257(19)	45(2)	16(1)	-1(1)	-34(5)	-37(5)
S(1)	16(2)	20(2)	25(2)	-4(1)	-9(1)	3(1)
S(2)	14(2)	18(2)	21(3)	6(2)	0	0
S(3)	15(2)	12(2)	16(2)	2(2)	0	0
Eu ₃ As ₂ S ₈						
Eu(1)	21(1)	21(1)	15(1)	1(1)	-1(1)	11(1)
As(1)	17(1)	17(1)	13(1)	0	0	9(1)
S(1)	21(1)	21(1)	13(1)	0	0	11(1)
S(3)	23(1)	18(1)	20(1)	0(1)	-6(1)	10(1)

* The anisotropic displacement factor exponent takes the form:

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

C. Results and Discussion

C.1 Synthesis

The synthesis of AgEuAsS_4 was achieved by combining Ag, Eu, As_2S_3 and S in the ratio 2/1/1/4. This ratio gave the best yield for the compound. Even a direct combination of the reactants failed to give a pure product as the product was contaminated with $\text{Eu}_3\text{As}_2\text{S}_8$. Other ratios of the starting materials were attempted, but the reactions produced almost always a mixture of the title compound, AgAsS_2 and $\text{Eu}_3\text{As}_2\text{S}_8$. We made numerous attempts to make CuEuAsS_4 but always ended up with Cu_3AsS_4 , Eu_2CuS_3 and $\text{Eu}_3\text{As}_2\text{S}_8$. $\text{Eu}_3\text{As}_2\text{S}_8$ was a surprise find from the reaction of Cu, Eu, As_2S_3 and S in the ratio 1/1/1/4. A pure synthesis of this compound was possible by combining Eu, As and S in a 3/2/8 ratio at 650°C . Both AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$ are valence precise compounds and possess Eu in +2, Ag in +1, As in +5 and S in -2 oxidation states.

We also attempted reactions of Ag/Cu, $\text{As}_2\text{S}_3/\text{As}$ and S with Ce and Yb. For both the metals, the reactions only gave Ce_2S_3 , YbS or glassy products.

C.2 Structure description of AgEuAsS_4

Figure 1b shows the unit cell of AgEuAsS_4 looking down the c-axis. As seen in the figure, columns of edge sharing AgS_4 and AsS_4 tetrahedra are arranged parallel to the b - axis. Adjacent columns are staggered with respect to each other. These columns are held together by EuS_8 bicapped trigonal prisms to form the three dimensional network. The edge sharing AgS_4 and AsS_4 tetrahedra form layers parallel to the bc- plane, Figure 2a. The layers are made up of fused 12- member rings. These layers form channels down the a -axis within which the Eu atoms reside. Also figure 2a shows that all the AgS_4 and AsS_4

tetrahedra point in the same direction showing the lack of a center of symmetry. Figure 2b shows the extended coordination of Eu. As can be seen, each Eu atom shares two edges and four corners with 6 AsS_4 ligands. Each AsS_4 ligand binds to 6 Eu atoms by utilizing all its S atoms, Figure 2d. All the four S atoms connect to two Eu and one Ag atom. Three of these S atoms do so in an edge-corner sharing fashion while one S atom is purely corner sharing. AgS_4 tetrahedron is highly distorted with three short Ag-S bonds at 2.447(5) Å, 2.592(7) Å and 2.633(12) Å and one long Ag-S bond at 2.985(14) Å, Figure 2c. Similar distortions in the AgS_4 tetrahedra are also observed in $\text{Cs}_2\text{AgAsS}_4$ ²¹ and $\text{Fe}(\text{NH}_3)_6\text{AgAsS}_4$.²³ The bond angles in the AgS_4 tetrahedron range from 78.2(2)° to 146.4(7)°, Table 5. As-S bond lengths are normal at 2.160(5) and 2.165(3) Å. There are 8 Eu-S distances between 3.011(3) and 3.160(4) Å, Table 4. Similar Eu-S distances are observed in $\text{K}_4\text{EuP}_2\text{S}_8$ and KEuPS_4 . The Eu-Eu distance is 5.993 Å, too long for electron exchange interactions to occur.

This compound is isostructural to LiEuPSe_4 , Figure 1c.⁹ Comparison of Figures 1b and 1c shows that there are two important differences between this structure and AgEuAsS_4 . i) There is no disorder in the LiEuPSe_4 structure and ii) In LiEuPSe_4 , Li and Eu sit in the *4a* crystallographic site whereas in AgEuAsS_4 , Ag (*8c*) and Eu (*4a*) occupy different crystallographic sites. The other difference comes from the physical stability of the two compounds. LiEuPSe_4 is extremely air-sensitive whereas AgEuAsS_4 is very stable in air. In view of the fact that these compounds are non-centrosymmetric and can be potentially useful NLO materials, the air-stability of AgEuAsS_4 is an advantage.

Table 4. Selected bond distances for AgEuAsS₄ and Eu₃As₂S₈.

AgEuAsS ₄			
Eu(1) - S(3)	2 x 3.011(3)	As(1) - S(3)	2.191(4)
Eu(1) - S(2)	2 x 3.068(3)	Ag(1) - Ag(1)	0.56(4)
Eu(1) - S(1)	2 x 3.153(4)	Ag(1) - S(3)	2.447(5)
Eu(1) - S(1)	2 x 3.160(4)	Ag(1) - S(2)	2.592(6)
As(1) - S(2)	2.160(5)	Ag(1) - S(1)	2.633(12)
As(1) - S(1)	2 x 2.165(3)	Ag(1) - S(1)	2.985(14)
Eu ₃ As ₂ S ₈			
Eu(1) - S(2)	2 x 2.9549(13)	Eu(1) - S(2)	2 x 3.4309(14)
Eu(1) - S(2)	3.0519(16)	As(1) - S(2)	3 x 2.1630(12)
Eu(1) - S(2)	3.0522(16)	As(1) - S(1)	2.187(2)
Eu(1) - S(1)	2 x 3.1438(10)		

Table 5. Selected bond angles for AsEuAsS₄ and Eu₃As₂S₈

AgEuAsS ₄			
S(3) - Eu(1) - S(3)	130.93(17)	S(2) - Eu(1) - S(1)	2 x 80.95(10)
S(3) - Eu(1) - S(2)	2 x 65.05(10)	S(1) - Eu(1) - S(1)	2 x 143.42(12)
S(3) - Eu(1) - S(2)	2 x 148.58(12)	S(1) - Eu(1) - S(1)	2 x 70.71(6)
S(2) - Eu(1) - S(2)	117.40(17)	S(1) - Eu(1) - S(1)	139.24(15)
S(3) - Eu(1) - S(1)	2 x 75.00(10)	S(2) - As(1) - S(1)	2 x 114.13(13)
S(3) - Eu(1) - S(1)	2 x 72.26(10)	S(1) - As(1) - S(1)	110.3(2)
S(2) - Eu(1) - S(1)	2 x 90.66(12)	S(2) - As(1) - S(3)	105.1(2)
S(2) - Eu(1) - S(1)	2 x 133.92(9)	S(1) - As(1) - S(3)	2 x 106.19(12)
S(1) - Eu(1) - S(1)	94.53(15)	S(3) - Ag(1) - S(2)	104.2(2)
S(3) - Eu(1) - S(1)	2 x 68.69(10)	S(3) - Ag(1) - S(1)	146.4(7)
S(3) - Eu(1) - S(1)	2 x 130.75(9)	S(2) - Ag(1) - S(1)	97.5(3)
S(2) - Eu(1) - S(1)	2 x 78.20(11)	S(2) - Ag(1) - S(1)	89.26(2)
S(3) - Ag(1) - S(1)	126.8(2)	S(1) - Ag(1) - S(1)	78.2(2)
Eu ₃ As ₂ S ₈			
S(3) - Eu(1) - S(3)	109.59(5)	S(3) - Eu(1) - S(3)	2 x 66.92(4)
S(3) - Eu(1) - S(3)	2 x 126.52(3)	S(3) - Eu(1) - S(3)	2 x 69.37(4)
S(3) - Eu(1) - S(3)	2 x 75.20(3)	S(3) - Eu(1) - S(3)	2 x 144.54(3)
S(3) - Eu(1) - S(3)	145.73(4)	S(3) - Eu(1) - S(3)	2 x 64.27(4)
S(3) - Eu(1) - S(1)	2 x 141.28(4)	S(1) - Eu(1) - S(3)	2 x 83.23(2)
S(3) - Eu(1) - S(1)	2 x 80.04(3)	S(1) - Eu(1) - S(3)	2 x 142.93(3)

S(3) - Eu(1) - S(1)	2 x 92.11(3)	S(3) - Eu(1) - S(3)	99.57(4)
S(3) - Eu(1) - S(1)	2 x 69.68(4)	S(3) - As(1) - S(3)	3 x 109.97(3)
S(1) - Eu(1) - S(1)	116.446(10)	S(3) - As(1) - S(1)	3 x 108.97(3)

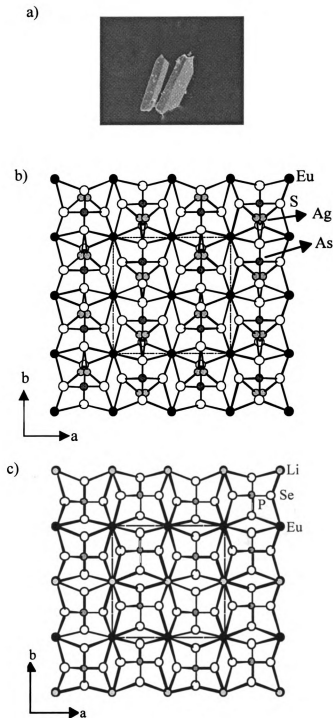


Figure 1. a) The red rectangular rods of AgEuAsS_4 b) Unit cell of AgEuAsS_4 viewed down the c - axis. c) Unit cell of LiEuPSe_4 looking down the c -axis showing that it is isostructural to AgEuAsS_4 . The two structures differ in the positions of the univalent cations (Li^+ and Ag^+).

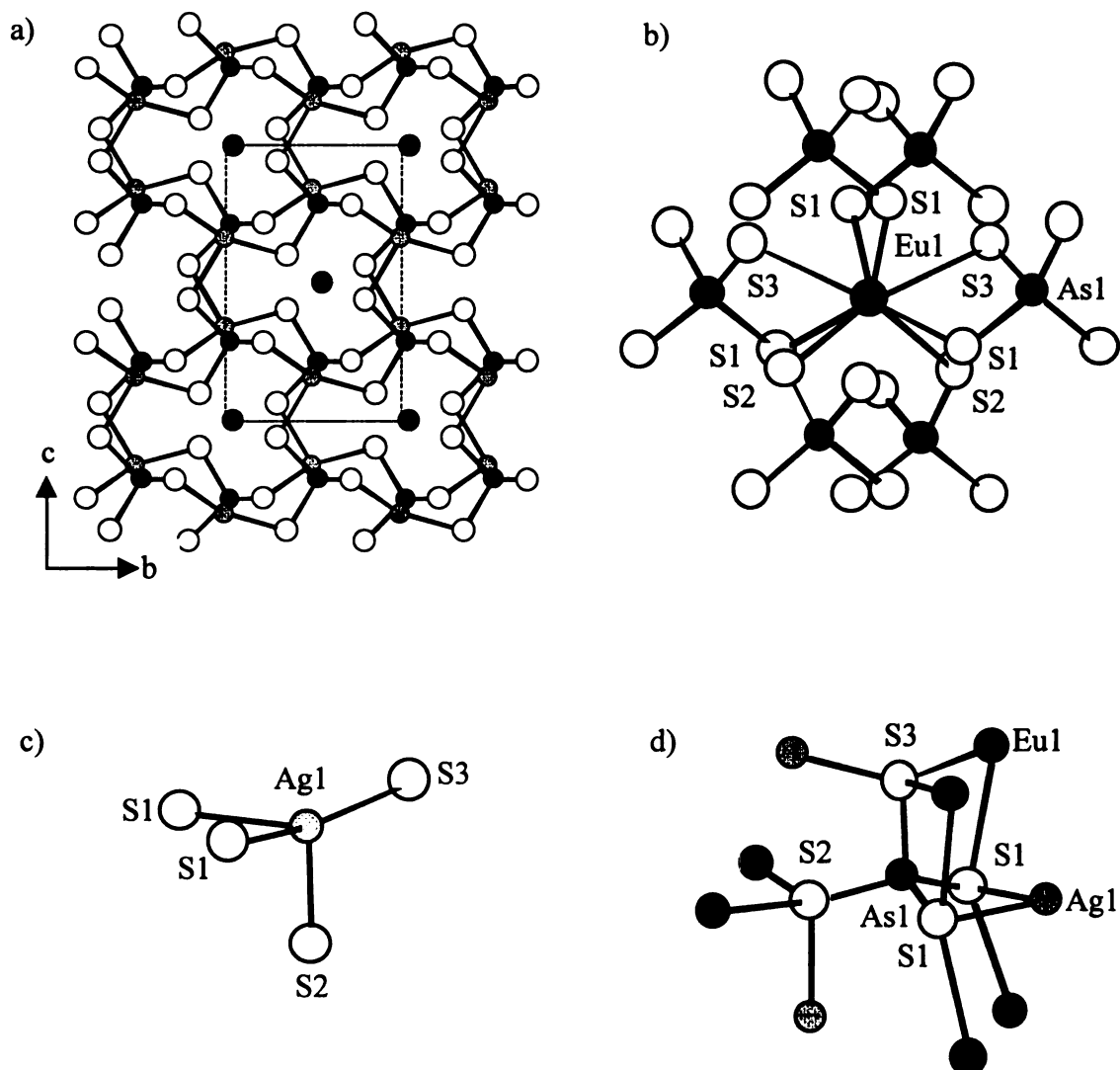


Figure 2. a) AgS₄ and AsS₄ tetrahedra fuse to form layers parallel to the bc- plane. These tetrahedra point in the same direction implying lack of center of symmetry. b) Extended coordination sphere of Eu showing that it is coordinated by 6 AsS₄ ligands in a bicapped trigonal prismatic geometry. c) The distorted tetrahedral environment around Ag d) Coordination sphere of an AsS₄ ligand

C.3 Structure description of $\text{Eu}_3\text{As}_2\text{S}_8$

$\text{Eu}_3\text{As}_2\text{S}_8$ belongs to a new structure type in which tetrahedral AsS_4^{3-} ligands coordinate to Eu to form a three dimensional framework, Figure 3a. The unique and interesting feature of this structure is the arrangement of the AsS_4^{3-} anions down the c- axis. Figure 5a shows the repeat unit of the AsS_4^{3-} anions in a unit cell. As seen, the first two tetrahedra, labelled m, are staggered by an angle of $\sim 17^\circ$. The next two tetrahedra, labelled n, are also staggered by $\sim 17^\circ$ with respect to each other. The second tetrahedron of m and the first tetrahedron of n are staggered by about 60° . The Eu atoms are arranged in a hexagonal fashion around the AsS_4 tetrahedra.

Each Eu is bound to 8 S atoms in a bicapped trigonal prismatic geometry with Eu-S distances of 2.9549(13), 3.0519(16), 3.0522(16), 3.1438(10) and 3.4309(14) Å. The As-S bond lengths are 2.1630(12) and 2.187(2) Å, Table 4. S-As-S angles are almost an ideal tetrahedral angles with values of 109.97° and 108.97° , Table 5. Figures 5b and 5c show the coordination spheres around Eu and As atoms.

A number of compounds have the molecular formula $\text{A}_3\text{B}_2\text{X}_8$ and consist of tetrahedral anions coordinating to heavy metal cations. Some include $\text{Pb}_3\text{P}_2\text{O}_8$ ⁵⁴, $\text{Ca}_3\text{As}_2\text{O}_8$ ⁵⁵, $\text{Pb}_3\text{V}_2\text{O}_8$ ⁵⁶, $\text{Ba}_3\text{As}_2\text{O}_8$ ⁵⁷, $\text{Ba}_3\text{Nb}_2\text{O}_8$ ⁵⁸, $\text{Sr}_3\text{V}_2\text{O}_8$ ⁵⁹ etc. These compounds also have the tetrahedral ligands staggered with respect to each other however the repeat distance for such staggering is only two anions compared to the four in $\text{Eu}_3\text{As}_2\text{S}_8$.

It is very surprising indeed that this compound could be made so easily. The corresponding chalcophosphate analog, $\text{Eu}_3\text{P}_2\text{S}_8$ and $\text{Eu}_3\text{P}_2\text{Se}_8$, have not yet been reported. Similarly we were unable to make $\text{Pb}_3\text{As}_2\text{S}_8$. Though $\text{Pb}_3\text{P}_2\text{S}_8$ ⁶⁰ exists, the structure of this compound is very different from $\text{Eu}_3\text{As}_2\text{S}_8$. $\text{Pb}_3\text{P}_2\text{S}_8$ crystallizes in the

cubic space group $P2_13$. The structure of $\text{Pb}_3\text{P}_2\text{S}_8$ viewed down the diagonal axis is shown in Figure 3b. Figure 4 shows the unit cells of $\text{Eu}_3\text{As}_2\text{S}_8$ and $\text{Pb}_3\text{P}_2\text{S}_8$ along the $[110]$ direction.

C.4 Magnetism

To determine the oxidation state of Eu conclusively and to check if it exhibits mixed valency, we conducted magnetic susceptibility measurements on AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$. Figure 6 shows the plots of inverse magnetic susceptibility ($1/\chi_m$) versus temperature. Both the compounds follow Curie law from 2K to 300K. The effective magnetic moment (μ_{eff}) for AgEuAsS_4 comes out to be 7.2 BM, which is very close to the calculated 7.9 BM for Eu^{2+} , Figure 6a. The ~10% difference in the calculated and experimental susceptibilities probably arise from the presence of minor amount of impurities. The μ_{eff} for $\text{Eu}_3\text{As}_2\text{S}_8$ was 12.53 BM which agrees reasonably well with the calculated 13.68 BM for 3 Eu^{2+} ions, Figure 6b.

C.5 Diffuse Reflectance Spectroscopy and Thermal Analysis

The ruby red crystals of $\text{Eu}_3\text{As}_2\text{S}_8$ were ground to a fine powder and loaded on a BaSO_4 surface. The optical absorption spectrum of this compound showed a very strong absorption onset at 1.9 eV, Figure 7. This corresponds very well to its red color. The absorption spectrum of AgEuAsS_4 indicated an energy gap at about 1.87 eV. However the sample displayed considerable tailing near the edge due to the presence of $\text{Eu}_3\text{As}_2\text{S}_8$ as an impurity. Hence we were not able to determine the band gap of AgEuAsS_4 conclusively. Optically, AgEuAsS_4 has a very similar color as $\text{Eu}_3\text{As}_2\text{S}_8$ and therefore the

bandgap of 1.87eV is probably close to its actual value.

We analyzed the thermal behavior of $\text{Eu}_3\text{As}_2\text{S}_8$ by differential thermal analysis. The DTA plot is shown in Figure 8. The plot shows two melting and recrystallization points in both the cycles. This is indicative of the decomposition of the sample on heating. To confirm this observation, we compared the powder pattern of the sample after DTA to the one before the experiment. The powder pattern revealed that along with the peaks due to the parent compound, there were a couple other strong peaks belonging to an unidentified phase. We can therefore conclude that $\text{Eu}_3\text{As}_2\text{S}_8$ melts incongruently on heating.

D. Concluding Remarks

AgEuAsS_4 and $\text{Eu}_3\text{As}_2\text{S}_8$ are valence-precise compounds built from tetrahedral AsS_4^{3-} building blocks. It is noteworthy that AgEuAsS_4 can be conceptually obtained by an addition of one equivalent of Ag_3AsS_4 to $\text{Eu}_3\text{As}_2\text{S}_8$. AgEuAsS_4 crystallizes in a non-centrosymmetric space group and is air-stable. It can therefore be a promising non-linear optical compound. $\text{Eu}_3\text{As}_2\text{S}_8$ has a unique structure type and it needs to be seen if $\text{Eu}_3\text{As}_2\text{Se}_8$ and $\text{Eu}_3\text{As}_2\text{Te}_8$ can form with the same structure. Other rare earth metals like Ce and Yb need to be investigated in view of their propensity to exhibit mixed valence states.

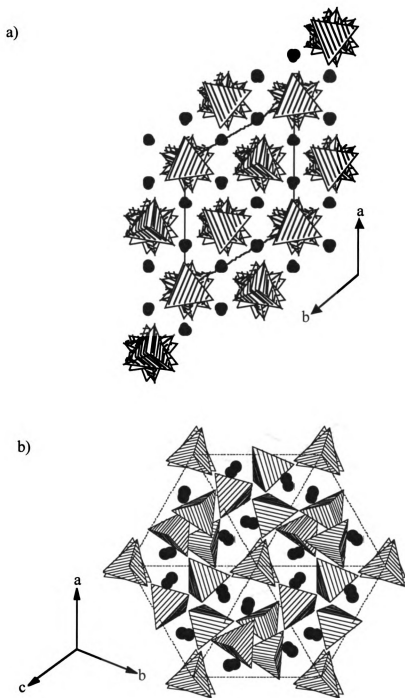


Figure 3. a) Unit cell of $\text{Eu}_3\text{As}_2\text{S}_8$ viewed down the c -axis showing the hexagonal arrangement of Eu atoms around the staggered AsS_4 tetrahedra b) Unit cell view of $\text{Pb}_3\text{P}_2\text{S}_8$ down the diagonal.

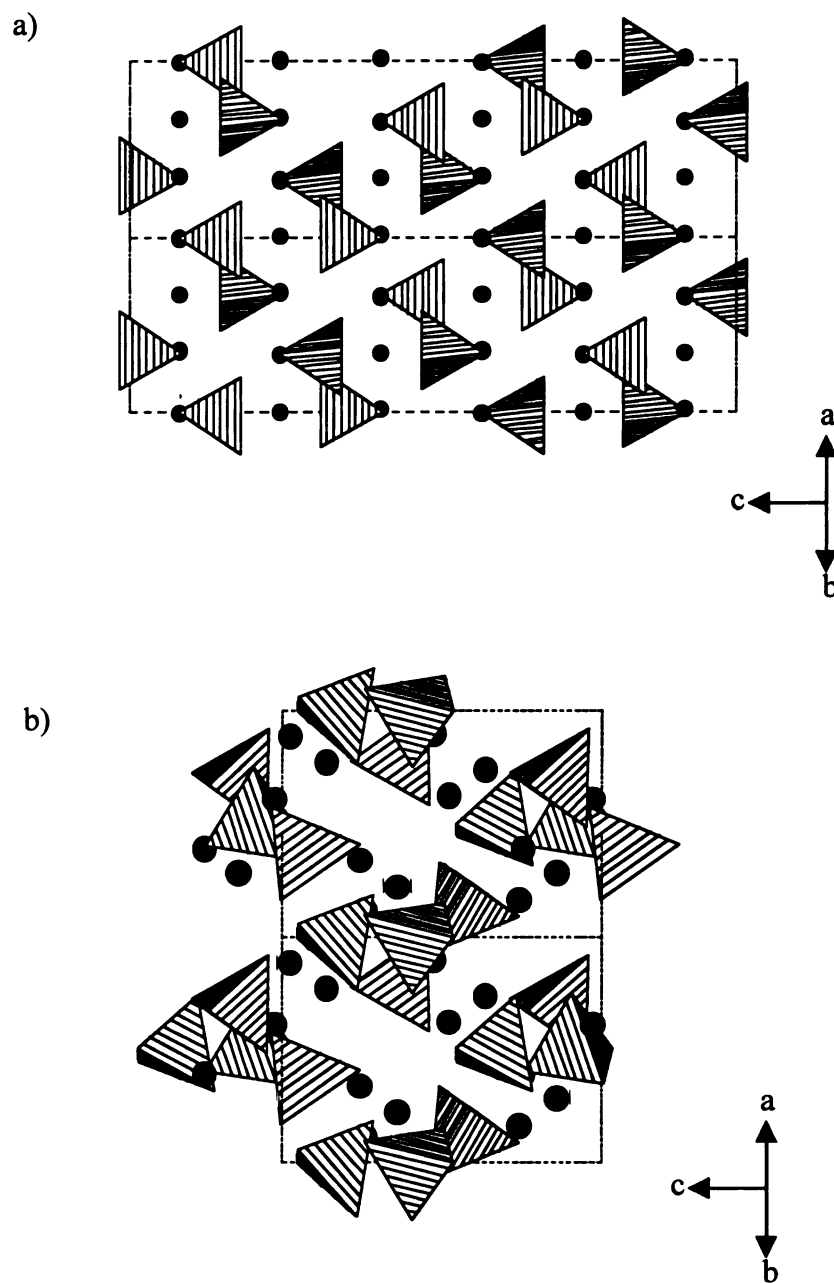


Figure 4. a) Unit cell view of $\text{Eu}_3\text{As}_2\text{S}_8$ down the 110 direction. b) Unit cell view of $\text{Pb}_3\text{P}_2\text{S}_8$ down the 110 direction. The figure shows that the two compounds are structurally different.

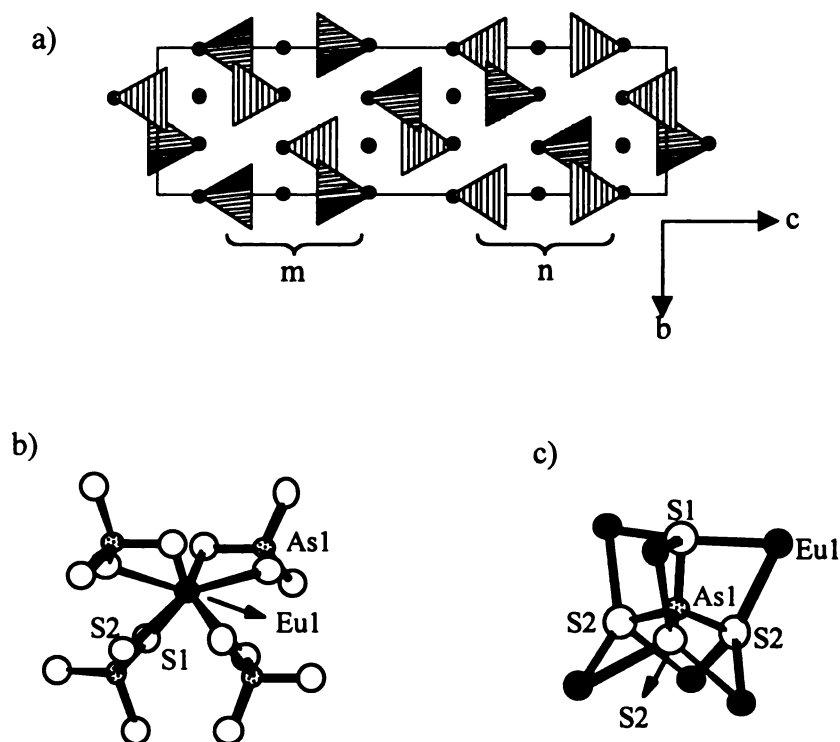


Figure 5. a) Unit cell view down the a- axis shows the repeating unit of four AsS_4 tetrahedra. The pairs of tetrahedra labelled m and n are staggered 17° with respect to each other. The second tetrahedron of m and the first tetrahedron of n are staggered 60° with respect to each other. b) Extended coordination sphere of Eu c) Coordination of the AsS_4 ligand.

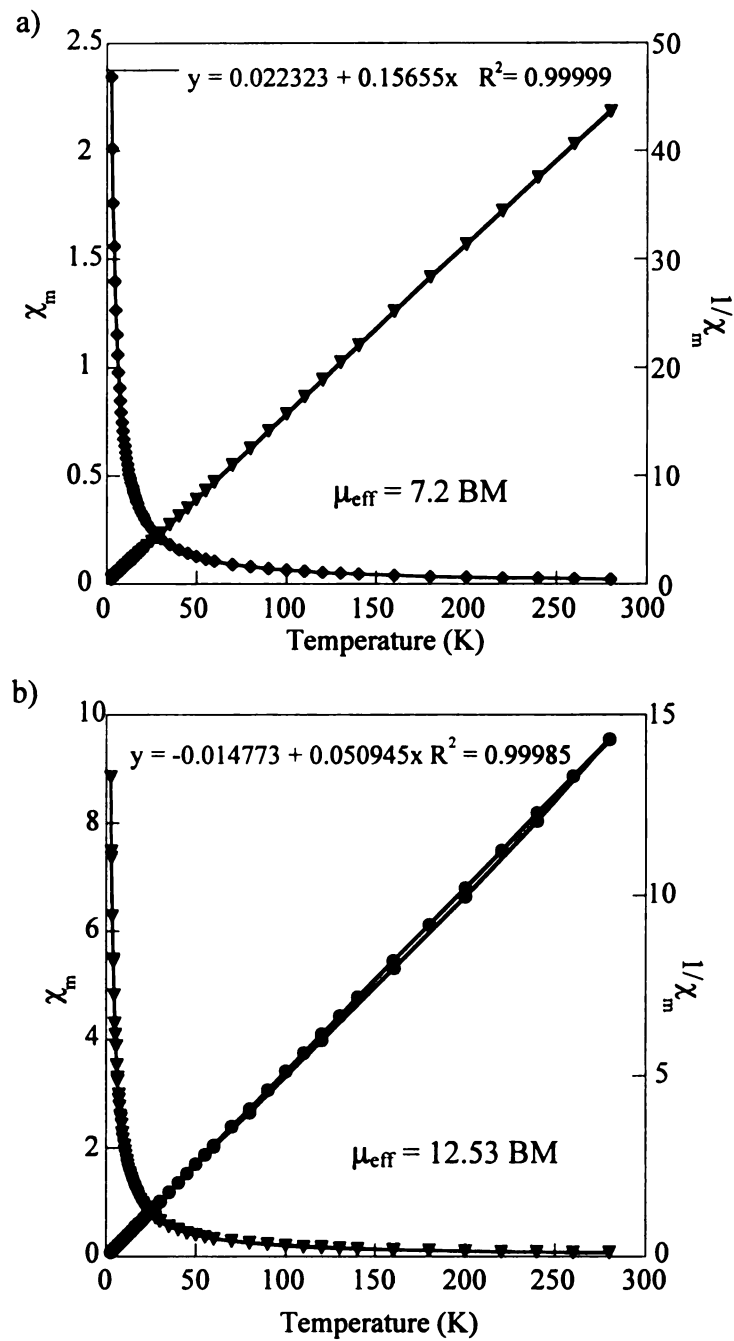


Figure 6. Plots of the inverse magnetic susceptibility and magnetic susceptibility of a) AgEuAsS₄ showing a μ_{eff} of 7.2 BM b) Eu₃As₂S₈ showing a μ_{eff} of 12.53 BM.

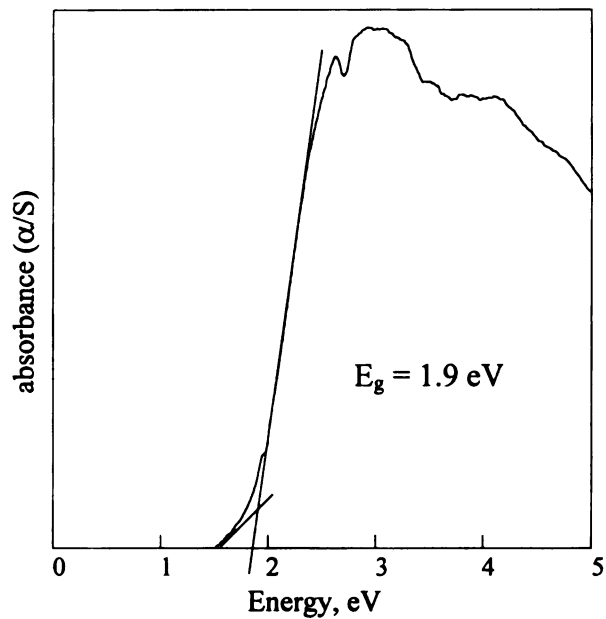


Figure 7. Optical absorption spectrum of $\text{Eu}_3\text{As}_2\text{S}_8$ shows that it absorbs strongly at 1.9 eV corresponding to its red color.

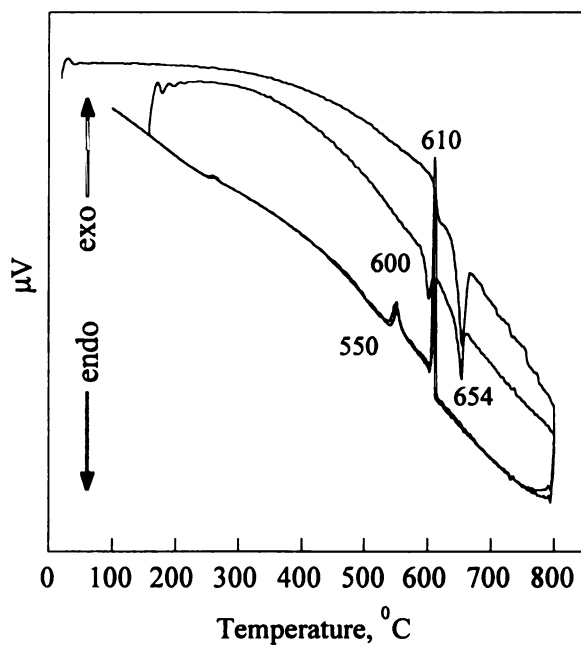


Figure 8. DTA plot of $\text{Eu}_3\text{As}_2\text{S}_8$ showing two melting and two recrystallization points. The powder pattern of the residue after DTA indicated that the compound decomposes on heating.

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Chapter 6

Chemistry of Trivalent Main Group Metals: Discovery of $A_6\text{InAs}_3\text{S}_{13}$ ($A = \text{K, Rb,}$

Cs), $A_3\text{BiAs}_2\text{S}_8$ ($A = \text{Rb, Cs}$) and $A_9\text{BiAs}_4\text{S}_{16}$ ($A = \text{K, Rb}$) from Alkali

Polythioarsenate Fluxes

Abstract

The reactions of In in K, Rb and Cs thioarsenate fluxes yielded three new compounds containing molecular anions with the general formula $A_6[\text{In}(\text{AsS}_4)_2(\text{AsS}_5)]$ ($A = \text{K, Rb, Cs}$). They crystallize in the triclinic space group $P\bar{1}$ with $a = 10.959(3) \text{ \AA}$, $b = 11.376(3) \text{ \AA}$, $c = 12.909(3) \text{ \AA}$, $\alpha = 64.822(4)^\circ$, $\beta = 86.025(4)^\circ$, $\gamma = 63.805(3)^\circ$ for $A = \text{K}$; $a = 11.128(3) \text{ \AA}$, $b = 11.532(3) \text{ \AA}$, $c = 13.396(3) \text{ \AA}$, $\alpha = 65.102(4)^\circ$, $\beta = 85.987(4)^\circ$, $\gamma = 64.045(4)^\circ$ for $A = \text{Rb}$; $a = 10.959(3) \text{ \AA}$, $b = 11.376(3) \text{ \AA}$, $c = 12.909(3) \text{ \AA}$, $\alpha = 64.822(4)^\circ$, $\beta = 86.025(4)^\circ$, $\gamma = 63.805(3)^\circ$ for $A = \text{Cs}$. The compounds form as yellow crystals with band gaps in the 2.6 eV region. They decompose on dissolution in water. The reactions of Bi in these fluxes yielded the one-dimensional phase $A_3\text{Bi}(\text{AsS}_4)_2$ ($A = \text{Rb, Cs}$) and the molecular phase $A_9\text{Bi}(\text{AsS}_4)_4$ ($A = \text{K, Rb}$). $A_3\text{BiAs}_2\text{S}_8$ crystallizes in the orthorhombic space group $Pnma$ with $a = 9.337(4) \text{ \AA}$, $b = 7.002(3) \text{ \AA}$, $c = 24.904(12) \text{ \AA}$ for $A = \text{Rb}$ and $a = 9.665(3) \text{ \AA}$, $b = 7.152(2) \text{ \AA}$, $c = 25.365(8) \text{ \AA}$ for $A = \text{Cs}$. $A_9\text{BiAs}_4\text{S}_{16}$ crystallizes in $P2_12_12$ with $a = 18.716(14) \text{ \AA}$, $b = 9.109(8) \text{ \AA}$, $c = 9.864(9) \text{ \AA}$ for $A = \text{K}$ and $a = 18.877(4) \text{ \AA}$, $b = 9.351(2) \text{ \AA}$, $c = 10.137(2) \text{ \AA}$ for $A = \text{Rb}$. $A_3\text{BiAs}_2\text{S}_8$ formed as yellow needles whereas $A_9\text{BiAs}_4\text{S}_{16}$ formed as red blocks/plates. $A_9\text{BiAs}_4\text{S}_{16}$ dissolve in water to form a reddish-brown colored solution that is stable for more than a day.

A. Introduction

Following our success in establishing the broad synthetic scope of polychalcophosphate fluxes¹ in stabilizing a variety of building blocks and diverse structures, we decided to investigate how the corresponding polychalcoarsenate, in particular thioarsenate, fluxes would perform. Our results with main group metals, Sn and Pb, gave enough evidence that these fluxes were as rich and promising as their chalcophosphate counterparts and their potential needed to be exploited.^{2, 3} Sn gave compounds that were molecular ($\text{Cs}_2\text{SnAs}_2\text{S}_9$), one-dimensional (NaSnAsS_4 , KSnAsS_5 and RbSnAsS_5) or two dimensional ($\text{K}_2\text{SnAs}_2\text{S}_6$ and $\text{Rb}_2\text{SnAs}_2\text{S}_6$) with Sn in the +4 oxidation state. Pb reacted very differently to give two-dimensional APbAsS_4 and chains of $\text{A}_4\text{PbAs}_2\text{S}_8$ ($\text{A} = \text{Rb}, \text{Cs}$) with Pb in the +2 oxidation state. The marked difference between the compounds of these two metals, other than their structures, was the type of thioarsenate ligand formed. In the case of Sn, we isolated pyramidal $\beta\text{-AsS}_4^{3-}$ and AsS_5^{3-} ligands, which feature As in the +3 oxidation state and a disulfide unit, whereas in the case of Pb the well-known tetrahedral AsS_4^{3-} ligand with As in the +5 oxidation state was observed. These results indicated that the metal might have a significant role to play in defining the final thioarsenate ligand. We therefore chose In and Bi to study the outcome of the reaction of M^{3+} in polythioarsenate fluxes and see what kind of ligands are generated.

The chemistry of indium and bismuth chalcogenides has been extensively investigated. The photovoltaic material CuInSe_2 ⁴ and the thermoelectric material Bi_2Te_3 ⁵ are probably the most investigated compounds of Cu and Bi. While a major portion of research on indium and bismuth chalcogenides have focussed on efforts to improve the efficiencies of the above compounds, a significant amount of work has been done on discovering new

ternary and quaternary indium and bismuth chalcogenides. These metals display a rich structural chemistry in their compounds. Indium has shown a great tendency to form open cavity frameworks such as $[\text{In}(\text{Se}_6)_2]^-$, $[\text{M}_4\text{In}_{16}\text{S}_{33}]^{10-}$, $[\text{Cu}_3\text{In}_{17}\text{S}_{33}]^{10-}$ etc.⁶ Some other known indium chalcogenides are AlIn_3S_5 , AlIn_5S_8 ,⁷ AlInS_2 ⁸ (A = alkali metal), KInGeS_4 ,⁹ KInSnSe_4 ,¹⁰ $[\text{Fe}(\text{en})_3]\text{In}_2\text{Te}_6$ ¹¹ etc. The field of bismuth chalcogenides has been advanced to a great degree of complexity by our group in the last decade. We have gradually increased the compositional and structural complexity to include KBi_3S_5 ,¹² $\text{K}_2\text{Bi}_8\text{Se}_{13}$,¹³ CsBi_4Te_6 ,¹⁴ $\text{CsMBi}_3\text{Te}_6$ (M = Pb, Sn),¹⁵ $\text{CsPb}_3\text{Bi}_3\text{Te}_8$,¹⁶ $\text{KSn}_5\text{Bi}_5\text{Se}_{13}$ ¹⁷ etc.

Using In and Bi in a polychalcophosphate flux we synthesized $(\text{Ph}_4\text{P})\text{InP}_2\text{Se}_6$,¹⁸ $\text{Cs}_5\text{In}(\text{P}_2\text{Se}_6)_2$,¹⁸ $\text{K}_4\text{In}_2(\text{PSe}_5)_2(\text{P}_2\text{Se}_6)$,¹⁹ KBiP_2S_7 ,²⁰ KMP_2Se_6 (M = Sb, Bi),²¹ $\beta\text{-Bi}_4(\text{P}_2\text{Se}_6)_3$,²² $\text{Cs}_3\text{Bi}_2(\text{PS}_4)_3$, $\text{A}_3\text{M}(\text{PS}_4)_2$, $\text{Na}_{0.16}\text{Bi}_{1.28}\text{P}_2\text{S}_6$ ²³ and $\text{Cs}_8\text{M}_4(\text{P}_2\text{Se}_6)_5$.²⁴ Other known compounds include InPS_4 ,²⁵ KInP_2S_7 ,²⁶ CuInP_2S_6 ,²⁷ $\text{In}_4(\text{P}_2\text{S}_6)_3$ ²⁸ and BiPS_4 .²⁹ Some of these compounds have shown interesting properties. InPS_4 exhibits high NLO susceptibility and piezo-coefficients,²⁵ CuInP_2S_6 displays ferroelectric - paraelectric transition²⁷ and KSbP_2Se_6 shows reversible glass to crystal transformation.³⁰

In comparison to the In and Bi chalcophosphates, the corresponding the chalcoarsenates are woefully an extremely small class. Only a few compounds are known such as $\text{Cs}_4\text{BiAs}_3\text{Se}_7$,³¹ $(\text{Ph}_4\text{P})_2\text{InAs}_3\text{S}_7$, $(\text{Me}_4\text{N})_2\text{RbBiAs}_6\text{S}_{12}$.³² There are some solid solutions of In, As and S however a concerted effort to discover new In and Bi chalcoarsenates has been lacking. Here we report the synthesis and characterization of $\text{A}_6\text{InAs}_3\text{S}_{13}$, $\text{A}_3\text{BiAs}_2\text{S}_8$ and $\text{A}_9\text{BiAs}_4\text{S}_{16}$, which represent important additions to the quaternary thioarsenate class of compounds.

B. Experimental Section

B.1 Reagents

All manipulations were done in a nitrogen-filled dri-vac glove box. Reagents: In (99.999%; Cerac, Milwaukee, WI), Bi (99.999%; Noranda Advanced Materials, St. Laurent, Quebec, Canada), As₂S₃ (99.9%; Strem Chemicals, Newburyport, MA), As (99.9%; Aldrich Chemical Co, Milwaukee, WI), S (99.9%; Strem Chemicals, Newburyport, MA). N,N-dimethylformamide (Spectrum Chemicals, ACS reagent grade); diethyl ether (CCI, ACS grade). K₂S, Rb₂S and Cs₂S were prepared by dissolving the alkali metal in liquid NH₃ and reacting it with a stoichiometric amount of sulfur according to a modified literature procedure.³³

B.2 Physical Measurements

Powder X-ray Diffraction

X-ray powder diffraction patterns were recorded on a CPS 120 INEL diffractometer (Cu K α radiation) operating at 40kV/20mA and equipped with a position sensitive detector and a flat-sample geometry.

Energy Dispersive Spectroscopy

Semiquantitative microprobe analyses on the compounds were done with a JEOL JSM-6400V scanning electron microscope equipped with a Tracor Noran Energy Dispersive Spectroscopy detector with an ultrathin window. Elemental compositions were obtained from an average of three readings. Acquisition times were 30s or 45s per reading.

Diffuse Reflectance Spectroscopy

Solid state diffuse reflectance spectra were measured using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as reference. Finely ground sample was spread on a sample holder preloaded with the reference. Energy gap was determined from a plot of absorbance vs energy by converting reflectance to absorbance using the Kubelka-Munk function.³⁴

Infrared Spectroscopy

Far IR spectra of the compounds were recorded as CsI pellets on a Nicolet 740 FT-IR spectrometer with a TSG/PE detector and silicon beam splitter. Raman spectra were recorded on a Bio-rad FT- Raman spectrometer equipped with a Germanium detector and using 633nm radiation from a HeNe laser for excitation with a 4cm⁻¹ resolution.

B.3 Synthesis

K₆InAs₃S₁₃ (I): K₆InAs₃S₁₃ was synthesized from a reaction mixture consisting of K₂S, In, As₂S₃ and S in the ratio 3/1/1/10. The mixture was loaded in a fused-silica tube and sealed under vacuum (<10⁻⁴ Torr). The sealed tube was then placed in a computer-controlled furnace and heated to 500°C. It was maintained at this temperature for 60h and then cooled to 250°C at the rate of 5°C/h followed by fast-cooling to room temperature. The product on isolation with N₂-bubbled DMF revealed yellow crystals, colorless crystals and pale brown crystals in equal amounts. The yellow crystals were air-sensitive and decomposed in a few minutes. Energy dispersive spectroscopy (EDS) on the yellow crystals gave an average reading of "K_{6.7}In_{1.4}As_{2.8}S_{13.02}". The brown crystals were KInS₂ while the colorless crystals were K₃AsS₄.

Rb₆InAs₃S₁₃ (II): *Rb₆InAs₃S₁₃* was obtained on heating *Rb₂S*, *In*, *As* and *S* in the ratio 3:1:3:10 using the same heating profile as above. The product consisted of pale yellow crystals of average composition "*Rb_{5.7}InAs_{2.1}S_{13.4}*" and pale orange crystals of *RbInS₂* as determined by EDS. The product was air-stable however the yield of the compound was very low (~15%).

Cs₆InAs₃S₁₃ (III): *Cs₆InAs₃S₁₃* was the product of the reaction of *Cs₂S*, *In*, *As₂S₃* and *S* in the ratio 4/1/2/10. This mixture was heated at 500°C for 7days, after an initial isotherm at 250°C for 12h, followed by cooling to 200°C at the rate of 3°C/h and finally fast-cooling to room temperature. Isolation of the product with degassed DMF gave yellow crystals, which were stable in air. EDS on a several of the yellow crystals gave an average composition of "*Cs_{6.2}In_{0.5}As_{3.5}S₁₄*". Comparison of the powder pattern to that obtained from single crystal refinement indicated that this was the majority phase (~80%).

Rb₃BiAs₂S₈ (IV): *Rb₃BiAs₂S₈* was obtained as transparent yellow plates from a reaction of *Rb₂S*(0.046g, 0.225mmol), *Bi*(0.031g, 0.15mmol), *As₂S₃*(0.037g, 0.15mmol), *S*(0.017g, 0.525mmol) in the ratio 1.5/1/1/3.5. The starting materials, loaded and sealed in a fused-silica tube, were heated to 500°C and isothermed at that temperature for 60h. This tube was then cooled to 250°C at the rate of 5°C/h, followed by rapid cooling to room temperature. On isolation of the product with degassed DMF, transparent orange plates and red cubic crystals were obtained. EDS on the plates gave an average composition of "*Rb_{3.4}BiAs_{2.2}S_{8.3}*" whereas the red cubes gave a reading of "*Rb_{8.8}BiAs_{3.6}S_{15.7}*". The yield of the yellow plates was <10% of the total product.

Cs₃BiAs₂S₈ (V): *Cs₃BiAs₂S₈* was obtained from a stoichiometric combination of the starting materials *Cs₂S*, *Bi*, *As₂S₃* and *S* in the ratio 1.5/1/1/3.5 using the same heating

profile as above. The compound is isolated as transparent yellow plates in ~40% yield along with red chunks and black rods. The average composition, as determined by EDS analysis, was " $\text{Cs}_{3.1}\text{BiAs}_{2.2}\text{S}_{8.4}$ " for the yellow crystals and " $\text{Cs}_9\text{BiAs}_4\text{S}_{16}$ " for the red chunks. The black rods were Bi_2S_3 .

K₉BiAs₄S₁₆ (VI): $\text{K}_9\text{BiAs}_4\text{S}_{16}$ was prepared by heating a mixture consisting of K_2S , Bi, As_2S_3 and S in the ratio 1.5/1/1/3.5 at 500°C according to the heating profile mentioned above. The compound forms as red cubes with an average composition of " $\text{K}_9\text{BiAs}_{3.9}\text{S}_{16.3}$ " along with black wires of Bi_2S_3 in equal measure.

Rb₉BiAs₄S₁₆ (VII): $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ is the product of the reaction of a 2/1/1/10 ratio of Rb_2S /Bi/As/S at 500°C. The procedure remains the same as the preceding compounds. The compound is obtained as red plates (yield ~30%) along with black rods of Bi_2S_3 . The average composition from several red plates was " $\text{Rb}_{9.8}\text{BiAs}_{3.8}\text{S}_{16.8}$ ".

B.4 Single Crystal X-ray Crystallography

A full sphere of data comprising of 2424 frames, scanning 180 in 2θ and a scan width of 0.3° in ω , was collected for all the compounds except $\text{K}_9\text{BiAs}_4\text{S}_{16}$ on a Bruker SMART CCD diffractometer employing Mo $\text{K}\alpha$ radiation. For $\text{K}_9\text{BiAs}_4\text{S}_{16}$, a hemisphere of data was obtained. For $\text{K}_6\text{InAs}_3\text{S}_{13}$ and $\text{Rb}_6\text{InAs}_3\text{S}_{13}$, the data were collected at 173K. The remaining compounds were measured at room temperature. The data were merged using the SAINT program and an absorption correction applied using SADABS. The structures were solved by direct methods with the SHELXTL package of programs.³⁵

For $\text{Cs}_6\text{InAs}_3\text{S}_{13}$, after an initial round of least squares refinement, three high electron density peaks were found close to S11 and S12. They were labeled S13, S14 and S15

respectively. S13 and S14 were 0.75 Å and 1.575 Å away from S11 and 2.056 Å away from each other. S14 was at a distance of 1.979 Å from As3. Similarly S15 was at a distance of 1.408 Å from S12 and 2.350 Å from As3. Therefore S13, S14 and S15 formed an AsS₅ unit along with S10 and S16. This ligand was disordered with the original AsS₄ ligand formed by S10, S11, S12 and S16. After least squares refinement, the final occupancy for the AsS₄ ligand was 80% while the AsS₅ ligand occupied 20% of the site. Another disorder was found in the Cs6 site. This position was disordered with another Cs (Cs7) at a distance of 0.723(8) Å. The final R1/wR2 values, after anisotropic refinement, were 0.0322/0.0744. The structures of K₆InAs₃S₁₃ and Rb₆InAs₃S₁₃ were solved similarly. Cs₃BiAs₂S₈ and Rb₉BiAs₄S₁₆ were solved in the orthorhombic space groups *Pnma* and *P2₁2₁2* respectively. All the atoms were found in the first two least-squares cycles. The thermal displacement parameter for Bi was found to be high and hence its occupancy was released. Upon refinement, the Bi atom occupied only 50% of the site and created another equivalent site due to the presence of a mirror plane. Anisotropic refinement of all the atoms gave final R1/wR2 values of 0.0404/0.0848 for Cs₃BiAs₂S₈ and 0.0433/0.0888 for Rb₉BiAs₄S₁₆.

Tables 1 to 9 list the crystallographic data, fractional atomic coordinates and anisotropic thermal parameters for **I** to **VII**.

Table 1. Crystallographic refinement details for $K_6InAs_3S_{13}$, $Rb_6InAs_3S_{13}$ and $Cs_6InAs_3S_{13}$

empirical formula	$K_6InAs_3S_{13}$	$Rb_6InAs_3S_{13}$	$Cs_6InAs_3S_{13}$
fw	990.96	1279.60	1560.40
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	10.959(3)	11.128(3)	8.565(4)
<i>b</i> , Å	11.376(3)	11.532(3)	11.026(5)
<i>c</i> , Å	12.909(3)	13.396(3)	16.875(7)
α , deg	64.822(4)	65.102(4)	78.388(7)
β , deg	86.025(4)	85.987(4)	77.357(7)
γ , deg	63.805(3)	64.045(4)	80.454(12)
<i>V</i> , Å ³	1292.8(6)	1388.2(6)	1510.7(11)
<i>Z</i>	2	2	2
ρ_{calcd} , g/cm ³	2.546	3.061	3.430
μ , mm ⁻¹	6.730	15.845	12.073
<i>T</i> , K	173(2)	173(2)	293(2)
λ , Å	0.71073	0.71073	0.71073
Total reflections	12757	12361	15207
Total unique	6025	6464	6876
R(int)	0.0474	0.1296	0.0308
No. of parameters	236	236	246
Goodnes of fit on <i>F</i> ²	0.933	0.909	1.028
Refinement method	Full-matrix least-squares on <i>F</i> ²		
R1 ^a	0.0506	0.0628	0.0322
wR2 ^b	0.1055	0.0999	0.0744

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

Table 2. Crystallographic refinement details for Rb₃BiAs₂S₈ and Cs₃BiAs₂S₈

empirical formula	Rb ₃ BiAs ₂ S ₈	Cs ₃ BiAs ₂ S ₈
fw	871.71	1014.03
space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> , Å	9.337(4)	9.665(3)
<i>b</i> , Å	7.002(3)	7.152(2)
<i>c</i> , Å	24.904(12)	25.365(8)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
<i>V</i> , Å ³	1628.2(13)	1753.3(9)
<i>Z</i>	4	4
ρ _{calcd} , g/cm ³	3.556	3.842
μ, mm ⁻¹	24.762	20.860
<i>T</i> , K	293(2)	293(2)
λ, Å	0.71073	0.71073
Total reflections	14223	17085
Total unique	2131	2285
R(int)	0.1122	0.0587
No. of parameters	85	85
Goodnes of fit on F ²	1.002	1.031
Refinement method	Full-matrix least-squares on F ²	
R1 ^a	0.0518	0.0404
wR2 ^b	0.1058	0.0848

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

Table 3. Crystallographic refinement details for K₉BiAs₄S₁₆ and Rb₉BiAs₄S₁₆

empirical formula	K ₉ BiAs ₄ S ₁₆	Rb ₉ BiAs ₄ S ₁₆
fw	1373.52	1790.85
space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2
<i>a</i> , Å	18.716(14)	18.877(4)
<i>b</i> , Å	9.109(8)	9.351(2)
<i>c</i> , Å	9.864(9)	10.137(2)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
<i>V</i> , Å ³	1682(2)	1789.3(7)
<i>Z</i>	2	2
ρ _{calcd} , g/cm ³	2.713	3.324
μ, mm ⁻¹	11.256	21.695
<i>T</i> , K	293(2)	293(2)
λ, Å	0.71073	0.71073
Total reflections	4852	15381
Total unique	2900	4158
R(int)	0.0623	0.0751
No. of parameters	142	142
Goodnes of fit on F ²	1.006	1.008
Refinement method	Full-matrix least-squares on F ²	
R1 ^a	0.0543	0.0433
wR2 ^b	0.1004	0.0888

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

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_6\text{InAs}_3\text{S}_{13}$, $\text{Rb}_6\text{InAs}_3\text{S}_{13}$ and $\text{Cs}_6\text{InAs}_3\text{S}_{13}$

Atom	x	y	z	Ueq ^a
$\text{K}_6\text{InAs}_3\text{S}_{13}$				
In(1)	0.6874(1)	-0.0007(1)	0.2648(1)	15(1)
As(1)	0.4021(1)	0.3214(1)	0.2031(1)	14(1)
As(2)	1.0344(1)	0.0007(1)	0.2214(1)	17(1)
As(3)	0.7515(1)	-0.3467(1)	0.3099(1)	32(1)
K(1)	0.6894(2)	0.4536(2)	0.1618(2)	25(1)
K(2)	0.8878(2)	-0.2330(2)	0.6510(2)	29(1)
K(3)	1.1882(2)	-0.2642(2)	0.0682(2)	28(1)
K(4)	1.1254(2)	-0.3919(2)	0.3710(2)	30(1)
K(5)	0.4514(2)	-0.2239(2)	0.4677(2)	30(1)
K(6)	0.7284(2)	-0.1499(2)	-0.0450(2)	37(1)
S(1)	0.5617(2)	0.2640(2)	0.0951(2)	23(1)
S(2)	0.9979(2)	-0.0574(2)	0.4056(2)	23(1)
S(3)	0.8008(2)	-0.2773(2)	0.4285(2)	22(1)
S(4)	0.2063(2)	0.4174(2)	0.1051(2)	22(1)
S(5)	0.9050(2)	-0.0561(2)	0.1510(2)	17(1)
S(6)	0.4541(2)	0.1083(2)	0.3514(2)	21(1)
S(7)	1.2458(2)	-0.1444(2)	0.2401(2)	22(1)
S(8)	0.4173(2)	0.4604(2)	0.2675(2)	20(1)

S(9)	0.9828(2)	0.2256(2)	0.1370(2)	23(1)
S(10)	0.7892(2)	0.0715(3)	0.3857(2)	26(1)
S(11)	0.5946(3)	-0.1182(4)	0.1812(4)	22(1)
S(12)	0.9143(2)	-0.4226(3)	0.2191(2)	29(1)
S(13)	0.6527(4)	-0.4756(4)	0.3930(3)	32(1)
S(14)	0.5636(9)	-0.2398(10)	0.2171(7)	24(3)
S(15)	0.7629(11)	-0.5847(11)	0.4212(8)	31(3)
S(16)	0.5712(10)	-0.0458(13)	0.1272(10)	23(2)

Rb₆InAs₃S₁₃

In(1)	0.6872(1)	0.0030(1)	0.2670(1)	14(1)
As(1)	0.4052(2)	0.3187(2)	0.2086(1)	14(1)
As(2)	1.0300(2)	0.0067(2)	0.2222(1)	14(1)
As(3)	0.7515(2)	-0.3435(2)	0.3091(2)	31(1)
Rb(1)	0.1880(2)	0.7386(2)	0.0697(1)	26(1)
Rb(2)	0.6867(2)	0.4663(2)	0.1526(1)	23(1)
Rb(3)	0.1073(2)	0.2307(2)	0.3553(1)	25(1)
Rb(4)	0.4476(2)	-0.2213(2)	0.4668(1)	27(1)
Rb(5)	1.1272(2)	-0.3924(2)	0.3732(2)	29(1)
Rb(6)	0.2757(2)	0.1497(2)	0.0449(2)	38(1)
S(1)	1.2383(4)	-0.1353(4)	0.2412(3)	19(1)
S(2)	0.4217(4)	0.4556(4)	0.2698(3)	17(1)
S(3)	0.9948(4)	-0.0458(4)	0.3994(3)	18(1)

S(4)	0.9032(4)	-0.0539(4)	0.1596(3)	15(1)
S(5)	0.5603(4)	0.2621(4)	0.1022(3)	19(1)
S(6)	0.2101(4)	0.4135(4)	0.1174(4)	24(1)
S(7)	0.4588(4)	0.1088(4)	0.3491(3)	18(1)
S(8)	0.9824(4)	0.2263(4)	0.1373(4)	19(1)
S(9)	0.7880(4)	0.0769(5)	0.3807(4)	22(1)
S(10)	0.7942(4)	-0.2701(4)	0.4226(4)	21(1)
S(11)	0.9118(4)	-0.4144(5)	0.2205(4)	29(1)
S(12)	0.5964(7)	-0.1148(9)	0.1862(7)	16(2)
S(13)	0.6545(10)	-0.4679(10)	0.3866(6)	29(2)
S(14)	0.5668(14)	-0.2291(15)	0.2172(11)	23(5)
S(15)	0.7420(20)	-0.5610(20)	0.4127(12)	26(5)
S(16)	0.5763(16)	-0.0370(20)	0.1273(14)	24(4)

Cs₆InAs₃S₁₃

Cs(1)	0.7623(1)	0.4363(1)	-0.0014(1)	37(1)
Cs(2)	0.7541(1)	0.9937(1)	0.0555(1)	44(1)
Cs(3)	0.4431(1)	0.6389(1)	0.2283(1)	49(1)
Cs(4)	0.9588(1)	0.0643(1)	-0.3353(1)	50(1)
Cs(5)	0.5029(1)	0.1022(1)	0.3283(1)	57(1)
Cs(6)	0.6851(6)	-0.3515(1)	0.4695(1)	65(1)
Cs(7)	0.7604(12)	-0.3818(9)	0.4809(3)	91(2)
In(1)	0.9698(1)	0.3777(1)	0.2645(1)	29(1)

As(1)	1.0666(1)	0.3058(1)	-0.2130(1)	26(1)
As(2)	0.6902(1)	0.7911(1)	-0.1125(1)	28(1)
As(3)	0.7795(1)	0.2454(1)	0.4598(1)	43(1)
S(1)	1.0635(2)	0.2355(2)	0.0787(1)	35(1)
S(2)	1.0370(2)	0.5709(1)	0.3126(1)	33(1)
S(3)	0.9055(2)	0.2131(2)	0.1902(1)	36(1)
S(4)	0.8898(2)	0.2003(2)	-0.1323(1)	38(1)
S(5)	0.8658(2)	0.5550(1)	0.1536(1)	29(1)
S(6)	0.5395(2)	0.7466(2)	0.0051(1)	40(1)
S(7)	0.7137(2)	0.6508(1)	-0.1901(1)	36(1)
S(8)	0.6371(2)	0.9768(1)	-0.1712(1)	38(1)
S(9)	1.2746(2)	0.1880(2)	-0.2631(1)	40(1)
S(10)	0.6764(2)	0.3651(2)	0.3592(1)	38(1)
S(11)	1.0417(4)	0.2344(2)	0.3955(2)	38(1)
S(12)	0.7506(4)	0.3371(3)	0.5614(1)	73(1)
S(13)	1.1281(14)	0.2338(9)	0.3739(6)	36(2)
S(14)	0.9841(10)	0.2827(8)	0.4802(5)	40(2)
S(15)	0.6013(14)	0.2898(11)	0.5806(5)	61(3)
S(16)	0.7131(3)	0.0647(2)	0.4866(1)	70(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{BiAs}_2\text{S}_8$ and $\text{Cs}_3\text{BiAs}_2\text{S}_8$

Atom	x	y	z	Ueq ^a
$\text{Rb}_3\text{BiAs}_2\text{S}_8$				
Bi(1)	0.5939(1)	0.1823(1)	0.4475(1)	24(1)
As(1)	0.6175(2)	0.2500	0.5896(1)	38(1)
As(2)	0.8440(1)	0.2500	0.3440(1)	21(1)
Rb(1)	1.2564(2)	0.2500	0.3154(1)	47(1)
Rb(2)	0.9809(2)	-0.2500	0.4282(1)	49(1)
Rb(3)	0.3633(2)	0.2500	0.7159(1)	34(1)
S(1)	0.6858(4)	0.2500	0.6698(2)	36(1)
S(2)	0.8748(4)	0.2500	0.4324(2)	41(1)
S(3)	0.9334(3)	-0.0005(4)	0.3103(1)	46(1)
S(4)	0.6875(3)	-0.0008(5)	0.5473(1)	51(1)
S(5)	0.6124(4)	0.2500	0.3372(2)	46(1)
S(6)	0.6163(5)	-0.1803(7)	0.4196(2)	26(1)
$\text{Cs}_3\text{BiAs}_2\text{S}_8$				
Bi(1)	-0.0871(1)	-0.1812(1)	0.9467(1)	24(1)
Cs(1)	0.2561(1)	-0.2500	0.8172(1)	47(1)
Cs(2)	0.5326(1)	-0.7500	0.9325(1)	46(1)
Cs(3)	0.3846(1)	0.2500	0.7185(1)	30(1)

As(1)	0.1268(1)	-0.7500	0.9152(1)	58(1)
As(2)	0.1725(1)	-0.2500	0.6566(1)	21(1)
S(1)	0.0851(2)	-0.0035(4)	0.6889(1)	38(1)
S(2)	-0.1022(3)	-0.2500	0.8367(1)	36(1)
S(3)	-0.3573(3)	-0.2500	0.9301(1)	41(1)
S(4)	-0.1006(4)	0.1736(6)	0.9196(2)	27(1)
S(5)	0.2073(3)	-0.7500	0.8382(1)	39(1)
S(6)	0.1865(3)	-0.9970(5)	0.9576(1)	62(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 6. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_9\text{BiAs}_4\text{S}_{16}$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$

Atom	x	y	z	Ueq ^a
$\text{K}_9\text{BiAs}_4\text{S}_{16}$				
Bi(1)	0.0042(3)	0.5252(3)	0.7779(1)	21(1)
As(1)	0.1231(1)	0.2915(2)	0.9916(2)	22(1)
As(2)	0.1365(1)	0.7276(2)	0.5241(2)	20(1)
K(1)	0.0757(2)	0.1442(4)	0.5035(4)	37(1)
K(2)	0	0.5000	0.2695(5)	34(1)
K(3)	0.2685(3)	-0.0180(6)	0.7390(4)	53(1)
K(4)	0.0869(2)	0.8745(4)	1.0196(4)	42(1)
K(5)	0.2482(2)	-0.0024(5)	0.2520(3)	44(1)
S(1)	0.1026(2)	0.4973(5)	0.5613(4)	34(1)
S(2)	0.1071(2)	0.5294(4)	0.9828(5)	34(1)
S(3)	0.0843(3)	0.8096(5)	0.3446(4)	37(1)
S(4)	0.2509(3)	0.7300(5)	0.4994(6)	33(1)
S(5)	0.0821(3)	0.1979(5)	1.1756(4)	40(1)
S(6)	0.2335(3)	0.2350(5)	0.9721(5)	46(1)
S(7)	0.0546(3)	0.2106(7)	0.8295(5)	60(2)
S(8)	0.1027(3)	0.8597(6)	0.6923(5)	51(2)

Rb ₉ BiAs ₄ S ₁₆				
Bi(1)	-0.0037(3)	0.0218(3)	0.2765(1)	25(1)
Rb(1)	0.0896(1)	0.6255(1)	0.5142(1)	35(1)
Rb(2)	0.2515(1)	0.0001(1)	0.2489(1)	36(1)
Rb(3)	0.2280(1)	0.0121(2)	0.7608(1)	45(1)
Rb(4)	0	0	0.7676(1)	30(1)
Rb(5)	0.0746(1)	0.3484(1)	0.0001(1)	33(1)
As(1)	0.1363(1)	-0.2330(1)	0.0233(1)	20(1)
As(2)	0.1214(1)	0.2064(1)	0.4886(1)	20(1)
S(1)	0.1062(2)	-0.0253(3)	0.4783(3)	32(1)
S(2)	0.2506(2)	0.2633(3)	-0.0025(3)	30(1)
S(3)	0.0799(2)	0.2968(3)	0.6665(3)	33(1)
S(4)	0.0880(2)	0.6908(3)	-0.1555(2)	30(1)
S(5)	0.1012(2)	-0.0101(3)	0.0612(3)	36(1)
S(6)	0.2311(2)	0.2620(3)	0.4738(3)	43(1)
S(7)	0.0548(2)	0.2831(4)	0.3264(3)	60(1)
S(8)	0.1010(2)	0.6386(4)	0.1854(3)	51(1)

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

Table 7. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{K}_6\text{InAs}_3\text{S}_{13}$, $\text{Rb}_6\text{InAs}_3\text{S}_{13}$ and $\text{Cs}_6\text{InAs}_3\text{S}_{13}$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{K}_6\text{InAs}_3\text{S}_{13}$						
In(1)	13(1)	12(1)	18(1)	-7(1)	3(1)	-3(1)
As(1)	14(1)	11(1)	16(1)	-6(1)	4(1)	-4(1)
As(2)	16(1)	16(1)	20(1)	-10(1)	6(1)	-8(1)
As(3)	36(1)	58(1)	23(1)	-23(1)	12(1)	-34(1)
K(1)	24(1)	28(1)	31(1)	-18(1)	10(1)	-14(1)
K(2)	32(1)	25(1)	25(1)	-10(1)	2(1)	-11(1)
K(3)	34(1)	18(1)	21(1)	-10(1)	-2(1)	-1(1)
K(4)	26(1)	20(1)	37(1)	-7(1)	12(1)	-10(1)
K(5)	25(1)	31(1)	24(1)	-13(1)	3(1)	-4(1)
K(6)	41(1)	32(1)	45(1)	-23(1)	27(1)	-20(1)
S(1)	21(1)	19(1)	18(1)	-7(1)	8(1)	-2(1)
S(2)	21(1)	30(1)	21(1)	-15(1)	5(1)	-10(1)
S(3)	26(1)	15(1)	19(1)	-7(1)	4(1)	-5(1)
S(4)	16(1)	18(1)	25(1)	-6(1)	-2(1)	-6(1)
S(5)	16(1)	17(1)	20(1)	-11(1)	7(1)	-8(1)
S(6)	19(1)	12(1)	21(1)	-4(1)	8(1)	-3(1)
S(7)	15(1)	23(1)	28(1)	-13(1)	2(1)	-7(1)
S(8)	20(1)	17(1)	22(1)	-12(1)	6(1)	-6(1)

S(9)	22(1)	13(1)	35(1)	-13(1)	8(1)	-8(1)
S(10)	19(1)	37(1)	32(1)	-25(1)	9(1)	-12(1)
S(11)	18(2)	22(2)	28(2)	-15(2)	2(2)	-6(2)
S(12)	25(1)	24(1)	31(1)	-18(1)	2(1)	0(1)
S(13)	48(2)	32(2)	30(2)	-15(2)	11(2)	-29(2)
S(14)	21(5)	28(5)	19(5)	-10(4)	1(4)	-7(4)
S(15)	50(7)	23(6)	30(5)	-5(4)	0(5)	-31(6)
S(16)	22(5)	18(6)	22(6)	-7(5)	-8(4)	-5(5)

Rb₆InAs₃S₁₃

In(1)	14(1)	11(1)	14(1)	-5(1)	1(1)	-4(1)
As(1)	14(1)	14(1)	12(1)	-5(1)	4(1)	-5(1)
As(2)	17(1)	14(1)	14(1)	-6(1)	2(1)	-8(1)
As(3)	30(1)	61(1)	18(1)	-21(1)	10(1)	-32(1)
Rb(1)	37(1)	16(1)	15(1)	-8(1)	-2(1)	-3(1)
Rb(2)	24(1)	25(1)	28(1)	-17(1)	8(1)	-14(1)
Rb(3)	31(1)	24(1)	20(1)	-8(1)	2(1)	-14(1)
Rb(4)	24(1)	31(1)	20(1)	-10(1)	1(1)	-6(1)
Rb(5)	25(1)	19(1)	38(1)	-8(1)	13(1)	-10(1)
Rb(6)	47(1)	31(1)	44(1)	-21(1)	30(1)	-24(1)
S(1)	17(2)	24(3)	17(3)	-9(2)	3(2)	-11(2)
S(2)	18(2)	11(2)	19(3)	-7(2)	-1(2)	-2(2)
S(3)	18(2)	26(3)	15(2)	-11(2)	4(2)	-11(2)

S(4)	16(2)	14(2)	16(2)	-7(2)	0(2)	-6(2)
S(5)	16(2)	14(2)	14(2)	-2(2)	4(2)	-1(2)
S(6)	21(3)	21(3)	24(3)	-5(2)	-3(2)	-6(2)
S(7)	20(3)	8(2)	16(2)	-1(2)	5(2)	-3(2)
S(8)	21(3)	15(2)	20(3)	-6(2)	2(2)	-10(2)
S(9)	23(3)	31(3)	18(3)	-17(2)	8(2)	-12(2)
S(10)	25(3)	13(2)	22(3)	-6(2)	7(2)	-8(2)
S(11)	24(3)	23(3)	36(3)	-21(2)	4(2)	1(2)
S(12)	16(4)	18(5)	17(5)	-10(4)	-1(3)	-5(3)
S(13)	44(6)	28(5)	25(5)	-9(4)	4(4)	-27(5)
S(14)	31(9)	35(9)	19(9)	-21(7)	6(7)	-18(7)
S(15)	47(12)	38(12)	14(8)	-6(8)	8(8)	-42(10)
S(16)	33(10)	31(11)	9(9)	-3(8)	-6(8)	-19(9)

$\text{Cs}_6\text{InAs}_3\text{S}_{13}$

Cs(1)	38(1)	35(1)	41(1)	-9(1)	-16(1)	-1(1)
Cs(2)	37(1)	40(1)	47(1)	-1(1)	-1(1)	3(1)
Cs(3)	31(1)	77(1)	44(1)	-17(1)	-7(1)	-13(1)
Cs(4)	59(1)	40(1)	53(1)	-4(1)	-18(1)	-12(1)
Cs(5)	63(1)	64(1)	52(1)	-15(1)	-26(1)	-10(1)
Cs(6)	78(2)	69(1)	40(1)	-9(1)	8(1)	-6(1)
Cs(7)	87(3)	139(3)	56(1)	-45(2)	-3(2)	-21(3)
In(1)	36(1)	26(1)	27(1)	-3(1)	-8(1)	-7(1)

As(1)	26(1)	24(1)	29(1)	-4(1)	-7(1)	-6(1)
As(2)	26(1)	27(1)	31(1)	-5(1)	-9(1)	-2(1)
As(3)	59(1)	42(1)	34(1)	-8(1)	-24(1)	1(1)
S(1)	30(1)	44(1)	34(1)	-12(1)	-12(1)	2(1)
S(2)	38(1)	33(1)	34(1)	-3(1)	-17(1)	-9(1)
S(3)	37(1)	35(1)	40(1)	-11(1)	-5(1)	-13(1)
S(4)	38(1)	34(1)	41(1)	2(1)	-4(1)	-14(1)
S(5)	32(1)	29(1)	31(1)	-6(1)	-14(1)	-5(1)
S(6)	38(1)	39(1)	37(1)	-1(1)	-1(1)	-4(1)
S(7)	36(1)	32(1)	46(1)	-13(1)	-16(1)	-3(1)
S(8)	41(1)	27(1)	44(1)	-2(1)	-8(1)	-3(1)
S(9)	36(1)	36(1)	47(1)	-15(1)	-4(1)	0(1)
S(10)	35(1)	48(1)	28(1)	1(1)	-7(1)	-8(1)
S(11)	35(1)	36(1)	42(1)	4(1)	-15(1)	-5(1)
S(12)	124(3)	61(2)	33(1)	-18(1)	-25(2)	10(2)
S(13)	28(5)	41(5)	32(4)	0(3)	-4(4)	0(4)
S(14)	37(5)	53(5)	32(4)	-3(4)	-11(3)	-9(4)
S(15)	66(7)	91(8)	26(4)	-17(4)	-5(4)	-6(6)
S(16)	95(2)	66(1)	55(1)	23(1)	-30(1)	-47(1)

* The anisotropic displacement factor exponent takes the form:

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

Table 8. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{BiAs}_2\text{S}_8$ and $\text{Cs}_3\text{BiAs}_2\text{S}_8$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{Rb}_3\text{BiAs}_2\text{S}_8$						
Bi(1)	25(1)	27(1)	21(1)	0(1)	2(1)	-2(1)
As(1)	21(1)	78(1)	16(1)	0	0(1)	0
As(2)	21(1)	21(1)	20(1)	0	2(1)	0
Rb(1)	33(1)	42(1)	66(1)	0	-6(1)	0
Rb(2)	39(1)	49(1)	60(1)	0	-13(1)	0
Rb(3)	33(1)	44(1)	25(1)	0	6(1)	0
S(1)	31(2)	55(3)	22(2)	0	-10(2)	0
S(2)	23(2)	79(3)	22(2)	0	-3(2)	0
S(3)	48(2)	27(2)	62(2)	-14(2)	21(2)	0(1)
S(4)	53(2)	60(2)	41(2)	-14(2)	10(2)	-28(2)
S(5)	24(2)	81(3)	32(2)	0	-4(2)	0
S(6)	22(2)	26(3)	31(3)	-9(2)	-5(2)	2(2)
$\text{Cs}_3\text{BiAs}_2\text{S}_8$						
Bi(1)	24(1)	24(1)	24(1)	1(1)	-2(1)	-2(1)
Cs(1)	28(1)	46(1)	67(1)	0	5(1)	0
Cs(2)	34(1)	53(1)	53(1)	0	8(1)	0
Cs(3)	28(1)	38(1)	25(1)	0	1(1)	0

As(1)	20(1)	136(2)	17(1)	0	1(1)	0
As(2)	19(1)	22(1)	23(1)	0	1(1)	0
S(1)	36(1)	26(1)	52(2)	-10(1)	12(1)	4(1)
S(2)	20(1)	51(2)	36(2)	0	2(1)	0
S(3)	21(2)	80(3)	22(2)	0	0(1)	0
S(4)	23(2)	26(2)	32(2)	7(2)	2(2)	2(2)
S(5)	30(2)	63(3)	24(2)	0	9(1)	0
S(6)	59(2)	89(3)	37(2)	5(2)	-2(1)	-42(2)

* The anisotropic displacement factor exponent takes the form:

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

Table 9. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{K}_9\text{BiAs}_4\text{S}_{16}$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{K}_9\text{BiAs}_4\text{S}_{16}$						
Bi(1)	25(1)	15(2)	22(1)	-1(1)	-1(1)	12(2)
As(1)	25(1)	21(1)	21(1)	-1(1)	2(1)	-1(1)
As(2)	16(1)	24(1)	21(1)	3(1)	2(1)	2(1)
K(1)	46(3)	31(2)	32(2)	2(2)	-1(2)	-2(2)
K(2)	36(4)	29(3)	38(3)	0	0	5(3)
K(3)	65(4)	50(3)	44(2)	6(2)	-22(2)	-6(3)
K(4)	58(4)	35(2)	33(2)	2(2)	-7(2)	2(2)
K(5)	49(4)	46(3)	37(2)	-10(2)	-6(2)	2(3)
S(1)	28(4)	27(2)	46(2)	3(2)	2(2)	-7(2)
S(2)	41(4)	19(2)	43(2)	1(2)	-4(2)	5(2)
S(3)	41(4)	43(3)	26(2)	7(2)	-7(2)	1(3)
S(4)	15(3)	39(2)	46(2)	6(2)	6(2)	-2(2)
S(5)	54(4)	37(3)	28(2)	9(2)	15(2)	6(3)
S(6)	35(4)	49(3)	55(3)	13(3)	12(3)	18(2)
S(7)	79(5)	73(4)	28(2)	-21(3)	6(3)	-47(4)
S(8)	64(5)	65(3)	26(3)	-9(2)	7(2)	30(3)

Rb₉BiAs₄S₁₆

Bi(1)	32(1)	23(2)	20(1)	-3(1)	1(1)	-15(1)
Rb(1)	47(1)	26(1)	30(1)	2(1)	-5(1)	0(1)
Rb(2)	41(1)	37(1)	28(1)	-7(1)	-1(1)	-2(1)
Rb(3)	62(1)	38(1)	35(1)	3(1)	-14(1)	-10(1)
Rb(4)	32(1)	26(1)	31(1)	0	0	-3(1)
Rb(5)	37(1)	32(1)	30(1)	0(1)	-1(1)	1(1)
As(1)	19(1)	21(1)	18(1)	-3(1)	0(1)	-1(1)
As(2)	26(1)	16(1)	18(1)	2(1)	3(1)	1(1)
S(1)	42(2)	18(1)	35(1)	-1(1)	-2(1)	-8(1)
S(2)	21(1)	33(1)	35(1)	3(1)	1(1)	-1(1)
S(3)	50(2)	27(2)	22(1)	-3(1)	11(1)	-2(1)
S(4)	35(2)	36(2)	20(1)	-5(1)	-8(1)	0(1)
S(5)	38(2)	25(1)	46(2)	-8(1)	-3(1)	14(1)
S(6)	34(2)	43(2)	50(2)	-13(2)	16(2)	-20(1)
S(7)	81(3)	71(3)	27(2)	17(2)	4(2)	47(2)
S(8)	62(2)	69(2)	22(2)	9(2)	7(2)	-28(2)

* The anisotropic displacement factor exponent takes the form:

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

C. Results and Discussion

C.1 Synthesis

The alkali metal indium thioarsenate system produced $A_6\text{InAs}_3\text{S}_{13}$ as the only crystalline phase. It was obtained from nearly all our reactions that involved changing the flux basicity, reaction temperature and reaction profile. A number of other $A_2\text{S}/\text{In}/\text{As}_2\text{S}_3/\text{s}$ ratios only yielded glassy products. We also attempted direct syntheses of $A_3\text{InAs}_2\text{S}_8$, $A_6\text{InAs}_3\text{S}_{12}$, $A_3\text{In}_2\text{As}_3\text{S}_{12}$ ($A = \text{K}, \text{Rb}, \text{Cs}$) but all of these reactions yielded glassy products. We sought to crystallize the glasses by subjecting them to a differential thermal analysis treatment, however the glasses did not transform through the entire range of the DTA (1000°C). We tried to prepare $M_3\text{InAs}_2\text{S}_8$, $M_6\text{InAs}_3\text{S}_{12}$ ($M = \text{Ag}, \text{Cu}$) but ended up with AgInS_2 , AgAsS_2 , Cu_3AsS_4 and CuInS_2 . Additionally all the ratios that produced the title compounds also gave AlnS_2 or Aln_5S_8 . Hence characterization of these materials was difficult.

The reactions of Bi in potassium, rubidium and cesium thioarsenate fluxes always yielded a mixture of products that included $A_3\text{BiAs}_2\text{S}_8$ and $A_9\text{BiAs}_4\text{S}_{16}$. We have evidence for $\text{K}_3\text{BiAs}_2\text{S}_8$ and $\text{Cs}_9\text{BiAs}_4\text{S}_{16}$ from EDS and cell parameters, but we haven't been able to solve their structures due to bad crystal quality. Reaction parameters were changed by adding more $A_2\text{S}$, changing As_2S_3 with metallic As and varying the metal content. However all the reactions produced $A_3\text{BiAs}_2\text{S}_8$ or $A_9\text{BiAs}_4\text{S}_{16}$ along with Bi_2S_3 and/or ABiS_2 . It seems that $A_9\text{BiAs}_4\text{S}_{16}$ is very stable under these conditions, since it was found in nearly every reaction. Attempts to obtain pure phases were made by reacting stoichiometric amounts of the elements, but these too gave a mixture of products.

Finally, the reactions of In and Bi in sodium thioarsenate fluxes resulted in phase separation giving Na_3AsS_4 , NaAsS_2 , NaInS_2 and Bi_2S_3 .

The solubility of the molecular compounds in water was determined. While $\text{A}_6\text{InAs}_3\text{S}_{13}$ dissolve in water, they decompose within a few minutes to give a white powdery precipitate. $\text{A}_9\text{BiAs}_4\text{S}_{16}$ dissolve in water to generate a reddish-brown solution, which remains stable for more than a day. $\text{K}_6\text{InAs}_3\text{S}_{13}$ is extremely air-sensitive whereas $\text{Rb}_6\text{InAs}_3\text{S}_{13}$ and $\text{Cs}_6\text{InAs}_3\text{S}_{13}$ are stable over several months. $\text{K}_9\text{BiAs}_4\text{S}_{16}$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ remain stable under ambient conditions but they absorb moisture on grinding.

C.2 Structure description of $\text{A}_6\text{InAs}_3\text{S}_{13}$

Since all the three compounds are isostructural, we will focus on the description of $\text{Cs}_6\text{InAs}_3\text{S}_{13}$. This compound is composed of $[\text{In}(\text{AsS}_4)_2(\text{AsS}_5)]^{6-}$ clusters that co-crystallize with $[\text{In}(\text{AsS}_4)(\text{AsS}_5)_2]^{6-}$ anions, with the former being the major anion (70%). Hence we will refer to this compound as $\text{Cs}_6\text{InAs}_3\text{S}_{13}$. Figure 1 shows the two components of this molecule. As we can see, the In is coordinated octahedrally by two tetrahedral AsS_4^{3-} anions and one AsS_5^{3-} anion. Each anion uses two of its sulfur atoms to coordinate to the metal. In the case of the AsS_5 unit, it uses the disulfide arm and one terminal sulfide to bind to the metal. The AsS_5 anion is the distinct feature of this compound. This ligand has not been observed previously in thioarsenate chemistry. The selenophosphate analog, PSe_5^{3-} , of this anion has been reported.³⁶ In has a distorted geometry with In-S bond lengths in the range 2.574(2) Å to 2.722(2) Å. As-S distances lie between 1.979(8) Å to 2.350(9) Å, while the S-S distance is 2.060(2) Å. There are 6

crystallographically unique Cs atoms. Considering the Cs-S cutoff bond length as 3.9 Å, Cs1, Cs2, Cs5 and Cs6/Cs7 are seven-coordinate with distances ranging from 2.705(12) Å to 3.874(15) Å, Cs3 and Cs4 sit in 8- coordinate sites with distances in the range 3.397(9) Å to 3.879(2) Å. S-In-S bond angles vary between 73.2(2) to 169.29(5). As(1)S₄ and As(2)S₄ tetrahedra show a small deviation from ideal tetrahedral angles. As(3)S₄/As(3)S₅ tetrahedron however shows a large deviation due to the disorder. Selected bond distances and angles for Cs₆InAs₃S₁₃, Cs₃BiAs₂S₈ and Rb₉BiAs₄S₁₆ are listed in Tables 10 and 11.

The compound Rb₈Cd₂As₄S₁₈, which was obtained from the reaction of Cd in Rb thioarsenate flux, consists of two co-crystallized anions [Cd₂(AsS₄)₄]⁸⁻ and [Cd₂(AsS₄)₂(AsS₅)₂]⁸⁻ with the latter being the major component.^{37a} Another compound that contains two different clusters in the lattice is Cs₆Mo₄S_{23.6}, which is made up of [Mo₄S₄(S₃)₆]⁶⁻ and [Mo₄S₄(S₄)₆]⁶⁻ anions.^{37b} A compound very similar to this complex is [In(en)₂(AsSe₄)]₂.en, which consists of octahedral In complexed by two ethylene diamine ligands and one pyramidal AsSe₄³⁻ ligand, in a bidentate fashion.³⁸ The co-crystallization of InAs₃S₁₃⁶⁻ and InAs₃S₁₄⁶⁻ implies that both the anions lie close to each other in terms of stability and it might be possible to make them independent of each other by slightly changing conditions.

C.3 Structure description of A₃BiAs₂S₈

Figure 2 displays the structure of Cs₃BiAs₂S₈. This compound consists of one-dimensional chains running down the c- axis. Figure 2b shows the chain, which is made up of 5- coordinate Bi that is arranged in a zigzag fashion along the chain. The

stereochemical expression of the Bi $6s^2$ lone pair is evident in the structure. Each Bi is coordinated by three tetrahedral AsS_4^{3-} anions, two of which coordinate using an edge and one coordinates in a corner-sharing fashion. There are two different kinds of AsS_4 ligands. $\text{As}(1)\text{S}_4$ coordinates to two Bi atoms by using an edge and corner. This ligand also serves to propagate the chain. $\text{As}(2)\text{S}_4$ is a terminal ligand and uses an edge to bind to a Bi atom.

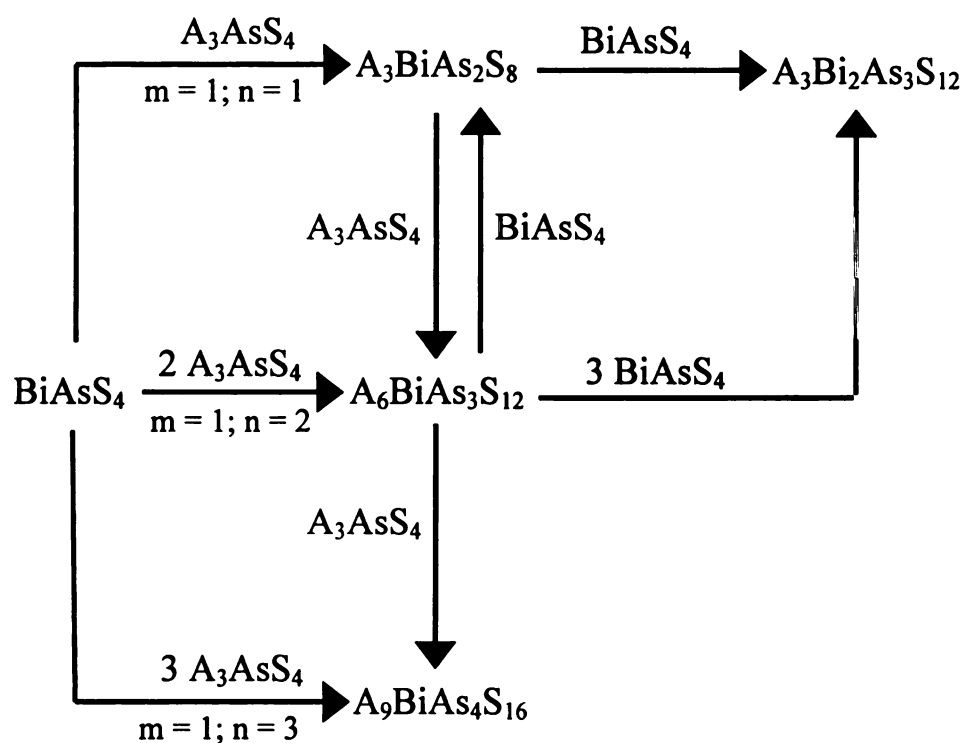
Bi-S distances range from 2.632(4) Å to 2.968(3) Å. There are 2 long Bi-S lengths at distances of 3.452(2) Å and 3.517(2) Å (not shown in Table 10). These are shown as dashed lines in Figure 2c. As-S distances vary between 2.104(4) Å to 2.267(4) Å. Cs1 is 5- coordinate, Cs2 sits in a nine coordinate site while Cs3 is surrounded by 10 S atoms. The minimum and maximum Cs-S bond lengths are 3.434(4) Å and 3.874(4) Å.

The structure of $\text{A}_3\text{BiAs}_2\text{S}_8$ is similar to $\text{A}_3\text{BiP}_2\text{S}_8$ except that $\text{A}_3\text{BiP}_2\text{S}_8$ crystallizes in the non-centrosymmetric space group $\text{P}2_12_12_1$ and does not exhibit Bi disorder. These chains are also very similar to $\text{K}_3\text{LaP}_2\text{S}_8$,³⁹ except that the La is 9- coordinated by 4 PS_4^{3-} units in edge and face- sharing modes.

Based on the formation of $\text{A}_3\text{BiAs}_2\text{S}_8$ and $\text{A}_9\text{BiAs}_4\text{S}_{16}$, a series of Bi compounds can be predicted, similar to the series of Pb compounds, according to the general formula $(\text{A}_3\text{AsS}_4)_n(\text{BiAsS}_4)_m$. This is shown in scheme 1. In the thiophosphate chemistry, we were able to prepare $\text{Cs}_3\text{Bi}_2(\text{PS}_4)_3$ while in the thioarsenate chemistry we were successful in isolating the end member of the series, $\text{A}_9\text{BiAs}_4\text{S}_{16}$, which is the next topic of discussion. Though BiPS_4 exists, several attempts to prepare BiAsS_4 proved futile.

C.4 Structure description of $A_9BiAs_4S_{16}$

This compound is the end member of the series depicted in scheme 1. We will discuss the structural details of $Rb_9BiAs_4S_{16}$. This compound consists of molecular anions $[Bi(AsS_4)_4]^{9-}$, that are packed as shown in Figure 3a. The individual molecule is shown



Scheme 1

in Figure 3b. As seen from this figure, Bi sits in a distorted octahedral geometry ligated by 4 AsS_4^{3-} anions. The Bi site is modeled as a split site. There are two kinds of AsS_4 ligands. One type coordinates to the metal using two sulfur atoms while the second type is monodentate and uses one sulfur atom to bind to the metal.

This compound is very similar to the molecular anion $[\text{Ce}(\text{PSe}_4)_4]^{9-}$.⁴⁰ The significant difference between the title compound and the above compound is the coordination geometry of the metal atom. Ce occupies a dodecahedral geometry compared to the octahedral coordination of Bi. Another very related compound is $\text{K}_{9-x}\text{La}_{1+x/3}(\text{PS}_4)_4$ which contains alternating rows of $[\text{La}(\text{PS}_4)_4]^{9-}$ clusters and chains of $[\text{La}_{0.67}(\text{PS}_4)_2]^{4-}$.³⁹ The La atoms in these clusters sit in an 8- coordinate square anti-prismatic site.

Bi-S distances are similar to the one reported above and range between 2.729(6) Å to 3.052(6) Å. As-S bond lengths are 2.142(3) Å to 2.219(3) Å. The five crystallographically unique Rb atoms are coordinated by 8, 7, 6, 8 and 7 sulfur atoms respectively. The cutoff Rb-S distance was taken as 3.8 Å.

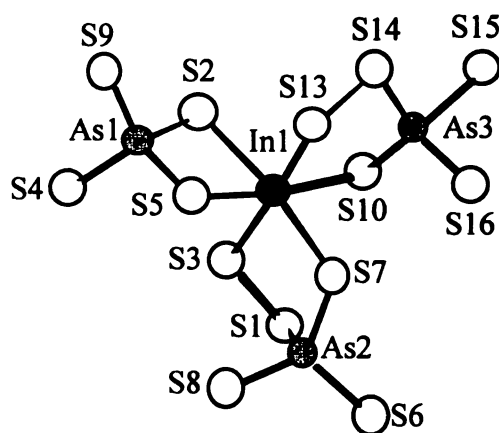
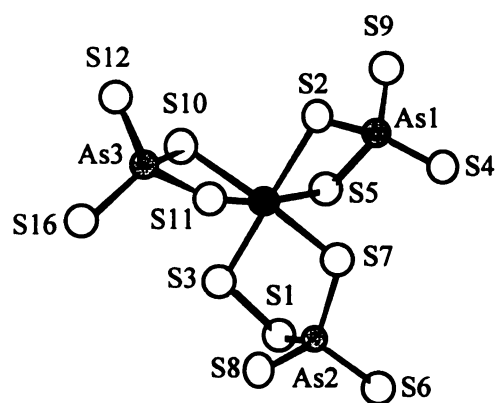


Figure 1. The two co-crystallized anions in the $\text{Cs}_6\text{InAs}_3\text{S}_{13}$ lattice, $[\text{In}(\text{AsS}_4)_2(\text{AsS}_5)]^{6-}$ and $[\text{In}(\text{AsS}_4)(\text{AsS}_5)_2]^{6-}$

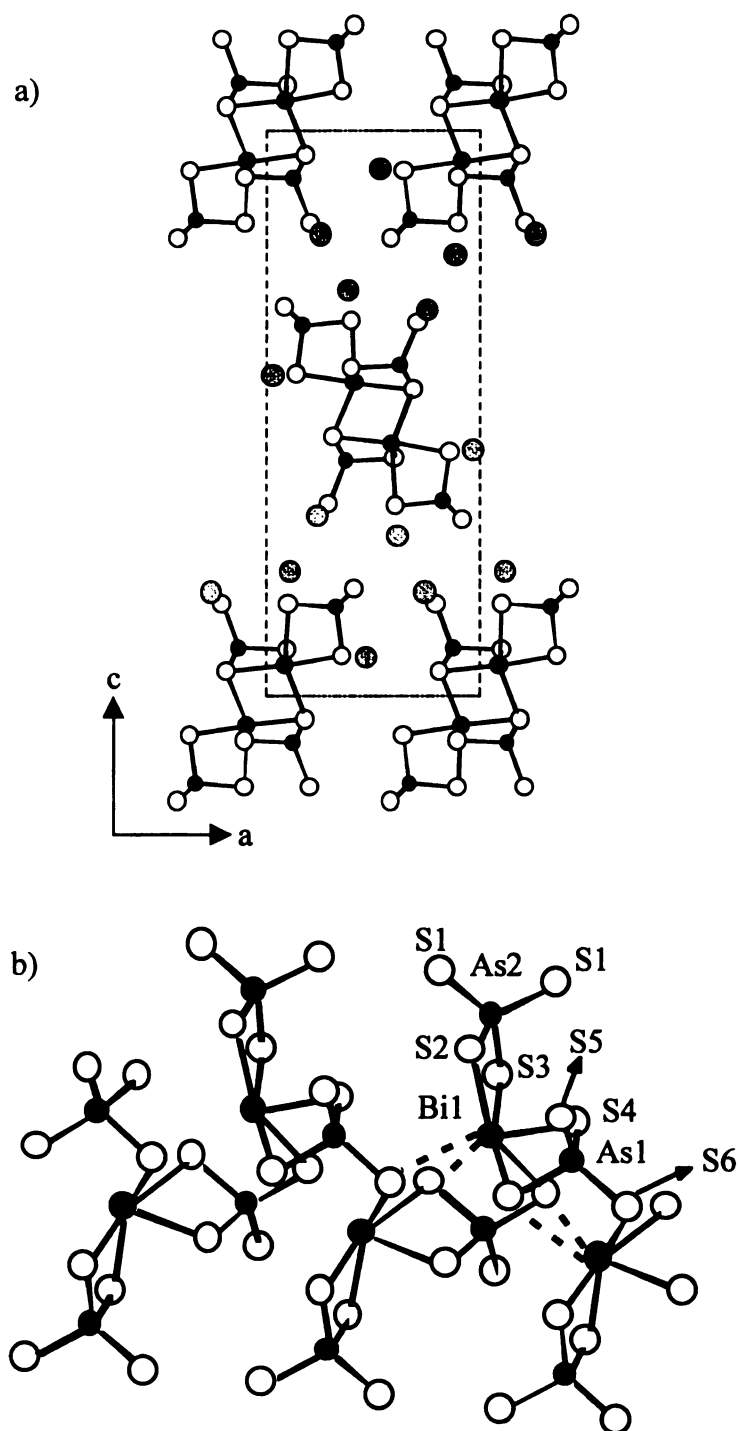


Figure 2. a) The unit cell of $\text{Cs}_3\text{BiAs}_2\text{S}_8$ looking down the b - axis b) A single chain showing the orientation of the $6s^2$ lone pair and coordination geometry around Bi

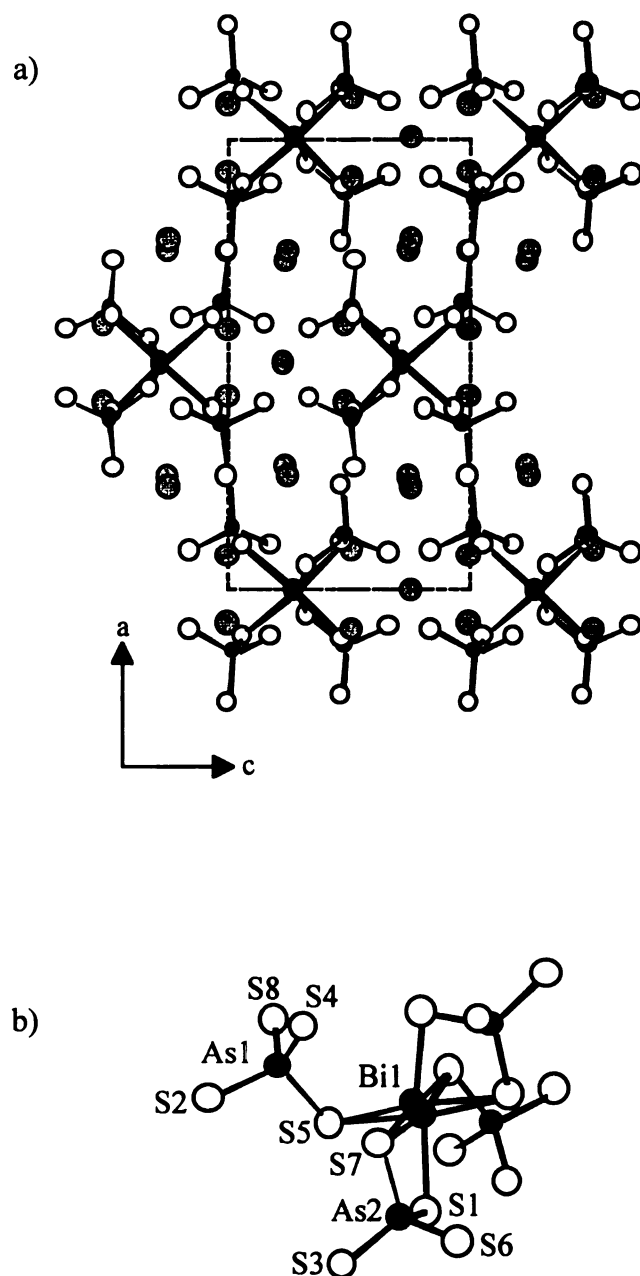


Figure 3. a) View down the b- axis of $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$. B) A single cluster anion, $[\text{Bi}(\text{AsS}_4)_4]^{9-}$ showing the octahedral geometry of Bi. The split site is due to the stereochemically active lone pair on Bi.

Table 10. Selected bond lengths for Cs₆InAs₃S₁₃, Cs₃BiAs₂S₈ and Rb₉BiAs₄S₁₆

Cs ₆ InAs ₃ S ₁₃					
Cs(1)-S(1)	3.4364(18)	Cs(4)-S(11)	3.637(3)	Cs(7)-S(13)	3.567(10)
Cs(1)-S(5)	3.4812(17)	Cs(4)-S(16)	3.665(3)	Cs(7)-S(11)	3.700(5)
Cs(1)-S(6)	3.551(2)	Cs(4)-S(13)	3.697(10)	Cs(7)-S(14)	3.874(15)
Cs(1)-S(7)	3.624(2)	Cs(4)-S(3)	3.709(2)	In(1)-S(11)	2.574(2)
Cs(1)-S(4)	3.628(2)	Cs(4)-S(9)	3.741(2)	In(1)-S(3)	2.5928(17)
Cs(1)-S(5)	3.6299(19)	Cs(5)-S(13)	3.290(11)	In(1)-S(5)	2.6073(16)
Cs(1)-S(6)	3.641(2)	Cs(5)-S(8)	3.448(2)	In(1)-S(2)	2.6143(18)
Cs(2)-S(8)	3.489(2)	Cs(5)-S(16)	3.459(2)	In(1)-S(13)	2.639(9)
Cs(2)-S(4)	3.5980(19)	Cs(5)-S(16)	3.585(2)	In(1)-S(10)	2.6748(18)
Cs(2)-S(6)	3.623(2)	Cs(5)-S(10)	3.642(2)	In(1)-S(7)	2.722(2)
Cs(2)-S(9)	3.648(2)	Cs(5)-S(9)	3.682(2)	As(1)-S(4)	2.1312(17)
Cs(2)-S(1)	3.6602(19)	Cs(5)-S(7)	3.7357(18)	As(1)-S(9)	2.1423(18)
Cs(2)-S(4)	3.744(2)	Cs(6)-Cs(7)	0.723(8)	As(1)-S(2)	2.1906(16)
Cs(2)-S(6)	3.846(2)	Cs(6)-S(15)	2.705(12)	As(1)-S(5)	2.2052(16)
Cs(3)-S(15)	3.397(9)	Cs(6)-S(14)	3.370(9)	As(2)-S(8)	2.1096(18)
Cs(3)-S(9)	3.527(2)	Cs(6)-S(12)	3.479(4)	As(2)-S(6)	2.1314(18)
Cs(3)-S(5)	3.594(2)	Cs(6)-S(9)	3.557(3)	As(2)-S(7)	2.1789(18)
Cs(3)-S(2)	3.599(2)	Cs(6)-S(2)	3.659(3)	As(3)-S(14)	1.979(8)
Cs(3)-S(12)	3.616(3)	Cs(6)-S(10)	3.746(3)	As(3)-S(16)	2.097(2)
Cs(3)-S(4)	3.617(2)	Cs(6)-S(12)	3.852(6)	As(3)-S(12)	2.110(3)

Cs(3)-S(6)	3.665(2)	Cs(7)-S(14)	2.850(10)	As(3)-S(10)	2.1843(17)
Cs(3)-S(7)	3.879(2)	Cs(7)-S(12)	3.130(10)	As(3)-S(11)	2.265(3)
Cs(4)-S(14)	3.522(8)	Cs(7)-S(2)	3.346(6)	As(3)-S(15)	2.350(9)
Cs(4)-S(8)	3.558(2)	Cs(7)-S(15)	3.413(16)	S(1)-S(3)	2.060(2)
Cs(4)-S(12)	3.569(3)				

Cs₃BiAs₂S₈

Bi(1)-Bi(1)	0.9835(13)	Cs(2)-S(4)	2 x 3.602(4)	Cs(3)-S(4)	2 x 3.550(4)
Bi(1)-S(4)	2.632(4)	Cs(2)-S(3)	3.874(4)	Cs(3)-S(2)	2 x 3.8420(17)
Bi(1)-S(3)	2.690(3)	Cs(2)-S(1)	2 x 3.610(3)	As(1)-S(5)	2.104(4)
Bi(1)-S(2)	2.837(4)	Cs(2)-S(3)	2 x 3.7312(14)	As(1)-S(6)	2 x 2.147(4)
Bi(1)-S(6)	2.905(4)	Cs(2)-S(6)	2 x 3.836(3)	As(1)-S(4)	2.267(4)
Bi(1)-S(6)	2.968(3)	Cs(3)-S(5)	3.434(4)	As(2)-S(1)	2 x 2.119(2)
Cs(1)-S(2)	3.498(3)	Cs(3)-S(5)	3.485(3)	As(2)-S(2)	2.185(3)
Cs(1)-S(1)	2 x 3.639(3)	Cs(3)-S(1)	2 x 3.497(3)	As(2)-S(3)	2.220(4)
Cs(1)-S(5)	2 x 3.6459(13)	Cs(3)-S(1)	2 x 3.543(2)		

Rb₉BiAs₄S₁₆

Bi(1)-Bi(1)	0.431(5)	Rb(2)-S(6)	3.368(3)	Rb(5)-S(8)	3.337(4)
Bi(1)-S(7)	2.729(6)	Rb(2)-S(5)	3.418(3)	Rb(5)-S(7)	3.384(3)
Bi(1)-S(1)	2.815(5)	Rb(2)-S(2)	3.543(3)	Rb(5)-S(2)	3.416(3)
Bi(1)-S(5)	2.858(5)	Rb(2)-S(6)	3.601(3)	Rb(5)-S(3)	3.417(3)
Bi(1)-S(1)	2.946(5)	Rb(2)-S(1)	3.605(3)	Rb(5)-S(5)	3.446(3)

Bi(1)-S(5)	2.963(5)	Rb(2)-S(4)	3.640(3)	Rb(5)-S(4)	3.471(3)
Bi(1)-S(7)	3.052(6)	Rb(3)-S(2)	3.385(3)	Rb(5)-S(4)	3.578(3)
Rb(1)-S(1)	3.301(3)	Rb(3)-S(2)	3.403(3)	As(1)-S(8)	2.142(3)
Rb(1)-S(8)	3.342(3)	Rb(3)-S(6)	3.422(3)	As(1)-S(2)	2.147(3)
Rb(1)-S(4)	3.403(3)	Rb(3)-S(8)	3.480(4)	As(1)-S(4)	2.150(3)
Rb(1)-S(7)	3.434(4)	Rb(3)-S(1)	3.690(3)	As(1)-S(5)	2.219(3)
Rb(1)-S(3)	3.444(3)	Rb(3)-S(6)	3.732(4)	As(2)-S(6)	2.140(3)
Rb(1)-S(6)	3.619(4)	Rb(4)-S(3)	2 x 3.321(3)	As(2)-S(3)	2.141(3)
Rb(1)-S(3)	3.626(4)	Rb(4)-S(4)	2 x 3.425(3)	As(2)-S(1)	2.188(3)
Rb(1)-S(7)	3.782(4)	Rb(4)-S(5)	2 x 3.538(3)	As(2)-S(7)	2.190(3)
Rb(2)-S(2)	3.338(3)	Rb(4)-S(1)	2 x 3.560(3)		

Table 11. Selected bond angles for Cs₆InAs₃S₁₃, Cs₃BiAs₂S₈ and Rb₉BiAs₄S₁₆

Cs ₆ InAs ₃ S ₁₃			
S(11)-In(1)-S(3)	99.72(7)	S(9)-As(1)-S(2)	110.14(7)
S(11)-In(1)-S(5)	167.75(7)	S(4)-As(1)-S(5)	112.09(7)
S(3)-In(1)-S(5)	89.67(6)	S(9)-As(1)-S(5)	111.35(7)
S(11)-In(1)-S(2)	90.62(7)	S(2)-As(1)-S(5)	100.26(6)
S(3)-In(1)-S(2)	169.29(5)	S(8)-As(2)-S(6)	113.41(7)
S(5)-In(1)-S(2)	80.50(5)	S(8)-As(2)-S(7)	114.69(7)
S(3)-In(1)-S(13)	101.1(2)	S(6)-As(2)-S(7)	113.05(7)
S(5)-In(1)-S(13)	166.2(2)	S(8)-As(2)-S(1)	109.68(7)
S(2)-In(1)-S(13)	88.1(2)	S(6)-As(2)-S(1)	101.64(7)
S(11)-In(1)-S(10)	79.31(8)	S(7)-As(2)-S(1)	102.90(6)
S(3)-In(1)-S(10)	87.10(6)	S(14)-As(3)-S(16)	122.8(3)
S(5)-In(1)-S(10)	93.43(5)	S(16)-As(3)-S(12)	116.05(12)
S(2)-In(1)-S(10)	97.64(6)	S(14)-As(3)-S(10)	118.0(2)
S(13)-In(1)-S(10)	95.8(2)	S(16)-As(3)-S(10)	113.20(8)
S(11)-In(1)-S(7)	89.59(8)	S(12)-As(3)-S(10)	111.48(10)
S(3)-In(1)-S(7)	91.54(5)	S(16)-As(3)-S(11)	108.12(10)
S(5)-In(1)-S(7)	98.07(5)	S(12)-As(3)-S(11)	108.53(13)
S(2)-In(1)-S(7)	85.70(5)	S(10)-As(3)-S(11)	97.71(8)
S(13)-In(1)-S(7)	73.2(2)	S(14)-As(3)-S(15)	100.7(4)
S(10)-In(1)-S(7)	168.41(5)	S(16)-As(3)-S(15)	88.9(3)

S(4)-As(1)-S(9)	111.91(7)	S(10)-As(3)-S(15)	105.0(3)
S(4)-As(1)-S(2)	110.52(7)		

Cs₃BiAs₂S₈

S(4)-Bi(1)-S(3)	95.03(9)	S(5)-As(1)-S(6)	2 x 111.47(11)
S(4)-Bi(1)-S(2)	84.75(10)	S(6)-As(1)-S(6)	110.70(17)
S(3)-Bi(1)-S(2)	76.43(9)	S(5)-As(1)-S(4)	113.88(16)
S(4)-Bi(1)-S(6)	77.18(12)	S(6)-As(1)-S(4)	2 x 92.14(14)
S(3)-Bi(1)-S(6)	83.66(9)	S(6)-As(1)-S(4)	2 x 115.72(15)
S(2)-Bi(1)-S(6)	151.76(9)	S(5)-As(1)-S(4)	113.88(16)
S(4)-Bi(1)-S(6)	68.92(12)	S(1)-As(2)-S(1)	112.56(15)
S(3)-Bi(1)-S(6)	163.90(9)	S(1)-As(2)-S(2)	2 x 111.55(9)
S(2)-Bi(1)-S(6)	102.40(8)	S(1)-As(2)-S(3)	2 x 109.36(9)
S(6)-Bi(1)-S(6)	91.23(9)	S(2)-As(2)-S(3)	101.92(13)

Rb₉BiAs₄S₁₆

S(7)-Bi(1)-S(1)	97.66(11)	S(5)-Bi(1)-S(7)	103.85(11)
S(7)-Bi(1)-S(5)	115.89(12)	S(8)-As(1)-S(2)	112.02(14)
S(1)-Bi(1)-S(5)	96.48(19)	S(8)-As(1)-S(4)	109.24(13)
S(7)-Bi(1)-S(1)	73.74(14)	S(2)-As(1)-S(4)	109.48(12)
S(1)-Bi(1)-S(1)	88.93(12)	S(8)-As(1)-S(5)	107.54(14)
S(5)-Bi(1)-S(1)	168.00(12)	S(2)-As(1)-S(5)	109.18(11)
S(7)-Bi(1)-S(5)	87.46(17)	S(4)-As(1)-S(5)	109.34(12)

S(1)-Bi(1)-S(5)	174.76(15)	S(6)-As(2)-S(3)	108.51(13)
S(5)-Bi(1)-S(5)	82.18(11)	S(6)-As(2)-S(1)	111.37(12)
S(1)-Bi(1)-S(5)	91.46(17)	S(3)-As(2)-S(1)	112.54(12)
S(7)-Bi(1)-S(7)	159.03(13)	S(6)-As(2)-S(7)	115.01(15)
S(1)-Bi(1)-S(7)	70.94(13)	S(3)-As(2)-S(7)	107.04(12)
S(5)-Bi(1)-S(7)	83.52(15)	S(1)-As(2)-S(7)	102.29(14)
S(1)-Bi(1)-S(7)	88.17(10)		

C.5 Spectroscopy

Diffuse reflectance spectra of $\text{Cs}_6\text{InAs}_3\text{S}_{13}$, $\text{Cs}_3\text{BiAs}_2\text{S}_8$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ indicated that these compounds were semiconductors with sharp absorptions at 2.64 eV, 2.34 eV and 1.98 eV, which correspond well with their observed colors of light-yellow, golden-yellow and red respectively, Figure 4. Though $\text{Cs}_3\text{BiAs}_2\text{S}_8$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ had impurities (Bi_2S_3 mainly), we could identify their absorption because of a big difference in the colors of the two phases (~ 1.2 eV for Bi_2S_3). In the case of the molecular phases, these gaps are more appropriately described as HOMO-LUMO transitions, rather than as band gaps.

Since $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ was soluble in water to give a reddish-brown solution, we decided to conduct some solution UV-Vis spectroscopy to ascertain if the anions stay intact in water. The spectrum of the solution showed a moderate absorption at 650nm (1.91 eV) which is very close to the absorbance of the solid, which indicates that the cluster remains stable in water.

The Far-IR spectra of $\text{Cs}_6\text{InAs}_3\text{S}_{13}$ and $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ are shown in Figure 5. The spectrum of $\text{Cs}_6\text{InAs}_3\text{S}_{13}$ shows a number of strong vibrational frequencies. Of these the peaks appearing at 384, 402, 427 and 451 cm^{-1} can be attributed to As-S stretching.⁴¹ The strong peaks below 350 cm^{-1} can be due to Bi-S or As-S vibrations. The strong peak at 469 cm^{-1} and the very weak peak at 502 cm^{-1} are due to the S-S asymmetric and symmetric stretching modes respectively in the AsS_5 ligand.⁴²

The spectra of $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ shows diagnostic peaks at 406, 431 and 443 cm^{-1} due to the stretching vibrations of the As-S bonds. Peaks at the same range have also been observed

for APbAsS_4 and $\text{A}_4\text{PbAs}_2\text{S}_8$ ($\text{A} = \text{Rb}, \text{Cs}$). The peaks below 400 cm^{-1} cannot be definitely assigned due to the presence of Bi_2S_3 impurity in the sample.

D. Conclusion

The reactions of In and Bi in alkali polythioarsenate fluxes yielded the molecular $\text{A}_6\text{InAs}_3\text{S}_{13}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), $\text{A}_9\text{BiAs}_4\text{S}_{16}$ ($\text{A} = \text{K}, \text{Rb}$) and the one-dimensional $\text{A}_3\text{BiAs}_2\text{S}_8$ ($\text{A} = \text{Rb}, \text{Cs}$). $\text{A}_6\text{InAs}_3\text{S}_{13}$ represents the first example where a tetrahedral AsS_5^{3-} ligand has been observed in a solid state compound. $\text{A}_3\text{BiAs}_2\text{S}_8$ and $\text{A}_9\text{BiAs}_4\text{S}_{16}$ belong to the general series of compounds $(\text{A}_3\text{AsS}_4)_n(\text{BiAsS}_4)_m$. The isolation of molecular anions with high charge was facilitated by the use of a flux. $\text{A}_6\text{InAs}_3\text{S}_{13}$ decomposes on dissolution in water however $\text{A}_9\text{BiAs}_4\text{S}_{16}$ remains stable suggesting that it probably can be synthesized via solution chemistry. This stability can also render the anion available for further chemistry in solution. A difficult problem in these systems has been to optimize the synthesis to obtain pure compounds. Further studies are therefore required to delineate the conditions in which these compounds can be obtained as single phases. Based on our observations, it does seem that the metal has a definite role to play in the determination of the ligands that are isolated in the product. To confirm this hypothesis, extensive investigations involving gradual change of the reaction parameters and metals are warranted.

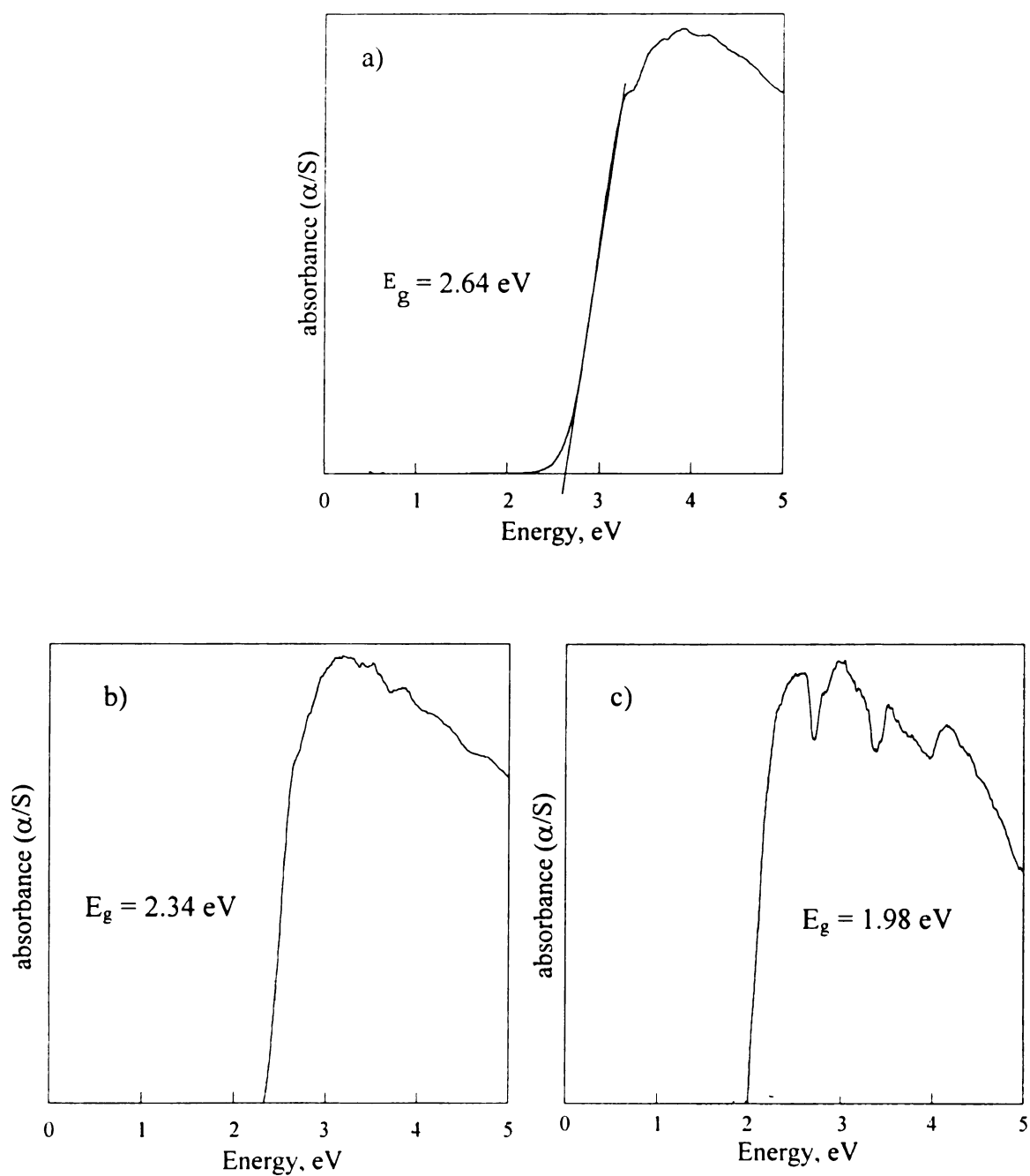


Figure 4. Optical absorption spectra of a) $\text{Cs}_6\text{InAs}_3\text{S}_{13}$ b) $\text{Cs}_3\text{BiAs}_2\text{S}_8$ and c) $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$ showing sharp absorption with onsets at 2.64 eV, 2.34 eV and 1.98 eV corresponding to their light-yellow, golden-yellow and red colors

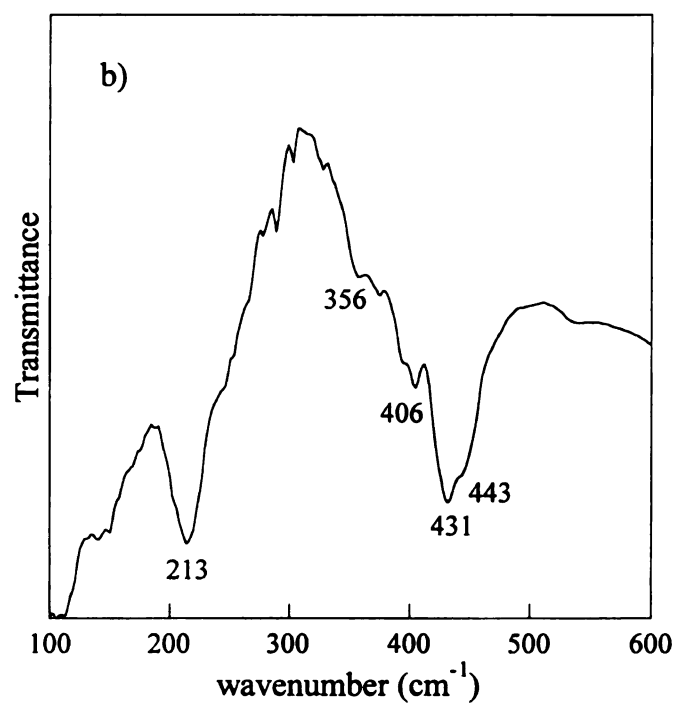
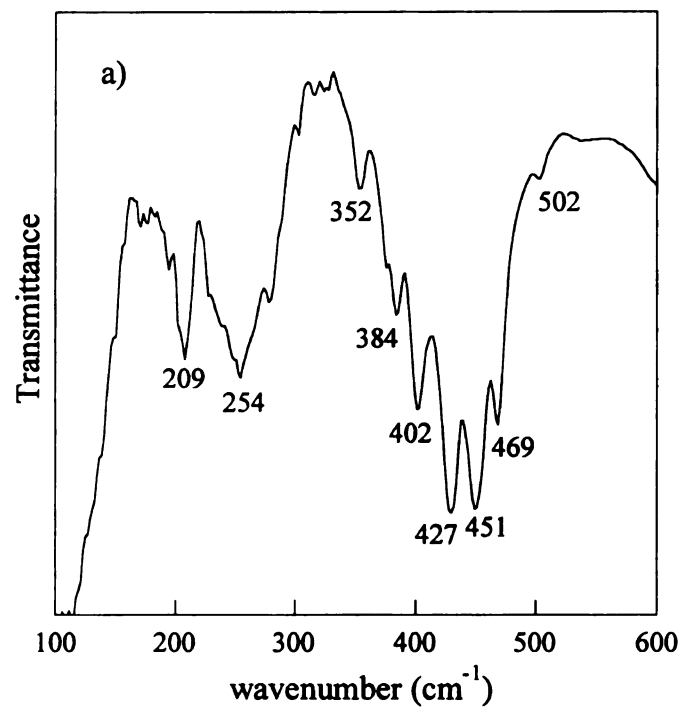


Figure 5. Far-IR spectra of a) $\text{Cs}_6\text{InAs}_3\text{S}_{13}$, the peak at 469 cm^{-1} is due to S-S stretching
b) $\text{Rb}_9\text{BiAs}_4\text{S}_{16}$, the peaks above 400 cm^{-1} are due to As-S stretching.

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Chapter 7

$[\text{Mn}_2(\text{AsS}_4)_4]^{8-}$ and $[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]^{8-}$: Discrete Clusters with High Negative Charge from Alkali Polythioarsenate Fluxes

Abstract

The reaction of Mn and Cd in alkali polythioarsenate fluxes afforded four new compounds featuring molecular anions. $\text{K}_8[\text{Mn}_2(\text{AsS}_4)_4]$ (**I**) crystallizes in the monoclinic space group $\text{P}2/n$ with $a = 9.1818(8) \text{ \AA}$, $b = 8.5867(8) \text{ \AA}$ and $c = 20.3802(19) \text{ \AA}$, $\beta = 95.095(2)^\circ$. $\text{Rb}_8[\text{Mn}_2(\text{AsS}_4)_4]$ (**II**) and $\text{Cs}_8[\text{Mn}_2(\text{AsS}_4)_4]$ (**III**) both crystallize in the triclinic space group $\text{P}-1$ with $a = 9.079(3) \text{ \AA}$, $b = 9.197(3) \text{ \AA}$, $c = 11.219(4) \text{ \AA}$, $\alpha = 105.958(7)^\circ$, $\beta = 103.950(5)^\circ$ and $\gamma = 92.612(6)^\circ$ for **II** and $a = 9.420(5) \text{ \AA}$, $b = 9.559(5) \text{ \AA}$, $c = 11.496(7) \text{ \AA}$, $\alpha = 105.606(14)^\circ$, $\beta = 102.999(12)^\circ$ and $\gamma = 92.423(14)^\circ$ for **III**. The discrete dimeric $[\text{Mn}_2(\text{AsS}_4)_4]^{8-}$ clusters in these compounds are composed of two octahedral Mn^{2+} ions bridged by two $[\text{AsS}_4]^{3-}$ units and chelated each by a $[\text{AsS}_4]^{3-}$ unit. $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]$ (**IV**) crystallizes in $\text{P}-1$ with $a = 9.122(2) \text{ \AA}$, $b = 9.285(2) \text{ \AA}$, $c = 12.400(3) \text{ \AA}$, $\alpha = 111.700(6)^\circ$, $\beta = 108.744^\circ$, $\gamma = 90.163(5)^\circ$. Owing to the bigger size of Cd than Mn, the Cd centers in this compound are bridged by $[\text{AsS}_5]^{3-}$ units. The $[\text{Cd}_2(\text{AsS}_4)_4]^{8-}$ cluster is a minor component cocrystallized in the lattice. These compounds are yellow in color and soluble in water.

A. Introduction

Traditionally "all-inorganic" cluster compounds have been prepared in solution near room temperature using standard precipitation techniques and aided by the use of organic counter-ions.¹ Inorganic clusters have often been thought of as thermally too sensitive to be stable at high temperatures and highly charged clusters have been exceedingly difficult to deal with in water or organic solvents. The development of low temperature techniques including the solventothermal method and the molten alkali flux method has made it easier to isolate compounds with discrete clusters. Although primarily designed for extended solids, the molten alkali polychalcogenide flux method² can be a promising synthetic technique for molecular chalcogenides as well. For example, alkali polychalcophosphate fluxes have yielded several such compounds including $\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]^3$, $\text{Rb}_8[\text{M}_4(\text{Se}_2)_2(\text{PSe}_4)_4]$ ($\text{M} = \text{Cd}, \text{Hg}$)⁴, $\text{Cs}_5[\text{In}(\text{P}_2\text{Se}_6)_2]^5$, $\text{K}_9[\text{Ce}(\text{PS}_4)_4]^6$, $\text{Rb}_9[\text{Ce}(\text{PSe}_4)_4]^7$, $\text{A}_5[\text{Sn}(\text{PSe}_5)_3]$ ($\text{A} = \text{K}, \text{Rb}$)⁸, $\text{A}_6[\text{Sn}_2\text{Se}_4(\text{PSe}_5)_2]$ ($\text{A} = \text{Rb}, \text{Cs}$)⁸, $\text{A}_5[\text{An}(\text{PS}_4)_3]$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$; $\text{An} = \text{U}, \text{Th}$)⁹, $\text{Cs}_{10}[\text{Pd}(\text{PSe}_4)_4]^{10}$, $\text{K}_4[\text{Pd}(\text{PS}_4)_2]^{10}$, $\text{Cs}_4[\text{Pd}(\text{PSe}_4)_2]^{10}$. Molecular salts are best obtained under highly basic flux conditions.² It is noteworthy that access to these highly charged anions would be extremely difficult using "wet" chemistry.

Since the broad synthetic scope of polychalcophosphate fluxes¹¹ in discovering new materials has been established, we decided to investigate how the corresponding chalcoarsenate fluxes might behave. Our initial experiments with main group metals, in alkali thioarsenate flux yielded us $\text{Cs}_2\text{SnAs}_2\text{Q}_9$ ($\text{Q} = \text{S}, \text{Se}$)¹² and $\text{A}_6[\text{InAs}_3\text{S}_{13}]^{13}$ ($\text{A} = \text{K}, \text{Cs}$) which contain discrete molecular complexes of $[\text{Sn}(\text{AsS}_4)(\text{AsS}_5)]^{2-}$ and $[\text{In}(\text{AsS}_4)_2(\text{AsS}_5)]^{6-}$ respectively.

We report here that the reactivity of Mn and Cd in alkali polythioarsenate fluxes (i.e. molten $AAsS_x$ (A =alkali)) affords salts containing the highly charged molecular thioarsenate complexes $[Mn_2(AsS_4)_4]^{8-}$ and $[Cd_2(AsS_4)_2(AsS_5)_2]^{8-}$. It is interesting that these salts are subsequently soluble in water. In addition, the cadmium complex presents a rare example of a sulfur-coordinated Cd^{2+} with a full octahedral geometry.

B. Experimental Section

B.1 Reagents

The following reagents were used as obtained: Rb, Cs metals (analytical reagent, Johnson Matthey / AESAR Group, Seabrook, NH), K metal (analytical reagent, Aldrich Chemical Company, Milwaukee, WI), S (99.9%, Strem Chemicals, Newburyport, MA), Cd, Mn (Johnson Matthey / AESAR Group, Seabrook, NH), As_2S_3 (99.9%; Strem Chemicals, Newburyport, MA). K_2S , Rb_2S and Cs_2S were made by the reaction of the alkali metal and sulfur in liquid ammonia using a modified literature procedure.¹⁴

B.2 Physical Measurements

Powder X-ray Diffraction

A calibrated CPS 120 INEL X-ray powder diffractometer equipped with a position-sensitive detector, operating at 40kV/25mA with a flat geometry and employing Cu $K\alpha$ radiation, was used to obtain diffractograms. Observed powder patterns were compared with powder patterns calculated using the Cerius² software package.

Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS), to analyze the composition of the compounds, was done on a JEOL JSM-35C Scanning Electron Microscope (SEM) equipped with a Tracor Northern detector. Data were acquired with an accelerating voltage of 20kV and accumulation time of 45s.

UV/Vis/near IR and Infrared Spectroscopy.

Optical diffuse reflectance measurements were made at room temperature using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer operating in the 200-2500 nm region using a procedure described elsewhere in detail.¹⁵

FT-IR spectra were recorded as solids in a CsI matrix. The samples were ground with dry CsI into a fine powder and pressed into translucent pellets. The spectra were recorded in the far-IR region ($600\text{-}100\text{cm}^{-1}$, 4cm^{-1} resolution) using a Nicolet 740 FT-IR spectrometer equipped with a TGS/PE detector and a silicon beam splitter.

Magnetic Susceptibility Measurements

Magnetization measurements as a function of applied magnetic field and temperature were made on a MPMS Quantum Design SQUID susceptometer in the temperature range of 2 to 300 K and magnetic fields of 0 to ± 55 kG. The samples consisted of a few (5 or 6) large single crystals.

Differential Thermal Analysis

Thermal studies were performed on Shimadzu DTA-50 thermal analyzer. Typically samples were heated to 600°C at the rate of $10^{\circ}\text{C}/\text{min}$, held there for a minute, followed by cooling to 100°C at the rate of $-10^{\circ}\text{C}/\text{min}$. Residues of the DTA experiments were

examined by powder X-ray diffraction. Multiple heating/cooling cycles were run to ascertain the reproducibility of the results.

B.3 Synthesis

$K_8[Mn_2(AsS_4)_4]$ (I) was prepared by reacting a mixture of K_2S (0.055g, 0.5 mmol), Mn (0.014g, 0.25mmol), As_2S_3 (0.062g, 0.25mmol) and S (0.08g, 2.5mmol) in the ratio 2/1/1/10. All manipulations were done in a glove box under nitrogen atmosphere. The reactants were loaded in fused silica tube and sealed under vacuum ($<10^{-4}$ Torr). The tube was then inserted in a furnace and heated to 500°C in 10 h. It was isothermed at this temperature for 60 h before cooling down to 250°C at the rate of 5°C/h, followed by rapid quenching to room temperature. Isolation of the product using N_2 -bubbled N, N - Dimethyl Formamide revealed large golden yellow crystals (~70% yield based on Mn) and green micro-crystals. Energy Dispersive Spectroscopy revealed an average composition of “ $K_{6.4}Mn_3As_4S_{14.4}$ ” and “ $K_2Mn_{2.3}As_4S_{4.7}$ ” for the golden yellow crystals and the green micro-crystals respectively. The powder diffraction pattern of the yellow crystals compared very well to the simulated pattern obtained from single crystal refinement.

$Rb_8[Mn_2(AsS_4)_4]$ (II) was synthesized from a $Rb_2S/Mn/As_2S_3/S$ ratio of 3/1/1/10 using the same heating profile as above. The product consisted of bright yellow, colorless and black crystals. Electron microscopy analysis on several of the yellow crystals gave an average composition of “ $Rb_{10.2}Mn_2As_4S_{13.6}$ ”. The colorless and the black crystals were Rb_3AsS_4 and MnS respectively.

$Cs_8[Mn_2(AsS_4)_4]$ (III) was obtained from a reaction of $Cs_2S/Mn/As_2S_3/S$ in the ratio 2/1/1/10. The method used was identical as mentioned above and the product consisted of yellow, colorless and black crystals. Elemental analysis using EDS on the yellow crystals confirmed the presence of all four elements with an average composition of “ $Cs_{7.9}Mn_{1.5}As_{4.3}S_{15.9}$ ”.

$Rb_8[Cd_2(AsS_4)_2(AsS_5)_2]$ (IV) was the product of the reaction of $Rb_2S/Cd/As_2S_3/S$ in the ratio 2/1/1/10. The synthetic conditions remained the same as above and along with the title compound were obtained colorless crystals of Rb_3AsS_4 and Rb_2S . The impurities were a minor part of the product as determined from powder diffraction pattern. EDS measurements on the yellow crystals gave an average value of “ $Rb_{9.6}Cd_2As_{4.6}S_{19.6}$ ”.

B.4 Single Crystal X-ray Crystallography

A Bruker SMART Platform CCD diffractometer, operating at 50kV/40mA and employing graphite monochromatized Mo $K\alpha$ radiation was used to collect crystal diffraction data. A full sphere of data was collected for all the compounds with scan widths of 0.3° in ω and an exposure time of at least 30s per frame. Data was collected using the SMART program and integrated with the program SAINT using the orientation matrix obtained from SMART. An empirical absorption correction was done with the program SADABS and all refinements were carried out with the SHELXTL¹⁶ package of crystallographic programs. Based on systematic absences and intensity statistics, the space group was determined to be $P2_1/n$ for I, $P-1$ for II, III and IV. Refinement of I, II and III was straightforward to give final $R1/wR2$ values of 1.88/4.39, 2.27/5.41 and 4.28/12.24 respectively. For IV, after the initial round of least squares, one Cd, four Rb,

two As and nine S atoms were found with $R1/wR2 = 8.85/20.66$. At this point, a high electron density peak (assigned As22) was observed at a distance of 0.72 Å from As2. Two more peaks, one close to the disulfide arm at 0.72 Å from S7 and 1.65 Å from S3 (assigned S10), and one 1.22 Å away from S9 (assigned S99), were observed. S10 and S99 were respectively 2.09 Å and 2.13 Å away from As22. Therefore a disordered model was considered and structure refinement led to an occupancy of 85% for the $[\text{AsS}_5]^{3-}$ ligand and 15% for the $[\text{AsS}_4]^{3-}$ ligand. Anisotropic refinement gave final $R1/wR2$ values of 5.01/11.19. Crystallographic refinement details, fractional atomic coordinates with isotropic temperature factors and anisotropic displacement parameters for all compounds are given in Tables 1, 2 and 3. Selected distances and angles for $\text{K}_8[\text{Mn}_2(\text{AsS}_4)_4]$ and $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]$ are given in Tables 4 and 5.

C. Results and Discussion

C.1 Synthesis

The synthesis of $\text{K}_8[\text{Mn}_2(\text{AsS}_4)_4]$ was achieved by reaction of a mixture of a 2:1:1:10 ratio of $\text{K}_2\text{S}/\text{Mn}/\text{As}_2\text{S}_3/\text{S}$ at 500°C. The compound forms as large golden yellow crystals. The product was contaminated with green micro-crystals of another quaternary phase of approximate composition “ $\text{K}_2\text{Mn}_{2.3}\text{AsS}_{4.7}$ ” (based on EDS). The reaction involved the oxidative dissolution of the metal in the basic melt and the subsequent coordination of the divalent metal cations with the present $[\text{AsS}_x]^{3-}$ anions. Reaction parameters were varied through the addition of K_2S and As_2S_3 . Increasing the basicity of the flux, by adding K_2S , led to the formation of K_3AsS_4 along with the title compound. Our attempts to obtain pure $\text{Rb}_8[\text{Mn}_2(\text{AsS}_4)_4]$ and $\text{Cs}_8[\text{Mn}_2(\text{AsS}_4)_4]$ were unsuccessful as the compounds always

formed with some amount of A_3AsS_4 and MnS . This effect is more pronounced on increasing the flux basicity by adding more alkali sulfide. Increasing the fraction of As_2S_3 always led to glassy products. No other phases were detected in any of the reactions.

The reactivity of Zn in potassium and rubidium thioarsenate fluxes was also explored. Using the same reaction conditions as above, we obtained A_3AsS_4 and ZnS . Further work needs to be done in order to establish an optimal synthetic ratio for isolating the Zn analogs of these clusters.

$Rb_8[Cd_2(AsS_4)_2(AsS_5)_2]$ was isolated from a reaction of $Rb_2S/Cd/As_2S_3/S$ ratio of 2/1/1/10. This system was more prone to give Rb_3AsS_4 and CdS on increasing the basicity of the reaction (i.e. increasing the fraction of Rb_2S). As with the Mn chemistry above, increasing the fraction of As_2S_3 yielded glassy phases.

The cluster compounds reported here are soluble in water but insoluble in ethanol and DMF. The aqueous solution of the $A_8Mn_2As_4S_{16}$ is initially yellow-brown in color but rapidly becomes colorless. This discoloration is so rapid that no absorption is observed in the UV-Vis spectrum. After about an hour, the solution becomes milky. For the $Rb_8Cd_2As_4S_{18}$ compound, a yellow precipitate is observed after about half a day. The powder pattern of this yellow precipitate shows that it is CdS . These observations indicate that the clusters do not remain intact in solution and precludes their formation by wet chemistry. The clusters were found to be stable in air for at least a month.

Table 1. Crystallographic refinement details of $\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Rb}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Cs}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ and $\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$

empirical formula	$\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$	$\text{Rb}_8\text{Mn}_2\text{As}_4\text{S}_{16}$	$\text{Cs}_8\text{Mn}_2\text{As}_4\text{S}_{16}$	$\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$
space Group	$P2/n$	$P-1$	$P-1$	$P-1$
a, Å	9.1818 (8)	9.079 (3)	9.420 (5)	9.122 (2)
b, Å	8.5867 (8)	9.197 (3)	9.559 (5)	9.285 (2)
c, Å	20.3802 (19)	11.219 (4)	11.496 (7)	12.400 (3)
α , deg	90	105.958 (7)	105.606 (14)	111.700 (6)
β , deg	95.095(2)	103.950 (5)	102.999 (12)	108.744 (5)
γ , deg	90	92.612 (6)	92.423 (14)	90.163 (5)
Z, V	4, 1600.5(3)	2, 867.8 (5)	2, 965.5 (9)	2, 915.2 (4)
ρ_{calcd} , g/cm ³	2.563	3.074	3.415	3.239
T, K	173	293	293	173
λ , Å	0.71073	0.71073	0.71073	0.71073
μ , mm ⁻¹	6.977	16.620	12.353	16.349
Total reflections	16097	8668	9201	9225
Total unique	3900	3921	4210	4291
R(int)	0.0275	0.0198	0.0266	0.0502
No. of parameters	137	145	136	173
Refinement method	Full-matrix least-squares on F^2			
R1 ^a	0.0188	0.0227	0.0428	0.0501
wR2 ^b	0.0439	0.0541	0.1224	0.1119
GOF on F^2	1.039	1.000	1.053	1.042

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

Table 2. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Rb}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Cs}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ and $\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$.

Atom	x	y	z	Ueq ^a
$\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$				
As(1)	-0.0034(1)	0.3349(1)	0.6138(1)	12(1)
As(2)	-0.4502(1)	0.1907(1)	0.3747(1)	12(1)
Mn(1)	-0.1690(1)	0.3701(1)	0.4582(1)	14(1)
K(1)	-0.1058(1)	0.3837(1)	0.8652(1)	22(1)
K(2)	-0.2500	-0.1191(1)	0.2500	30(1)
K(3)	-0.8699(1)	0.1049(1)	0.3349(1)	27(1)
K(4)	0.2867(1)	1146(1)	5155(1)	21(1)
K(5)	-0.2500	0.4114(1)	0.2500	26(1)
S(1)	-0.583(1)	0.1610(1)	0.5389(1)	15(1)
S(2)	-0.4491(1)	0.3393(1)	0.4614(1)	14(1)
S(3)	-0.5567(1)	0.3064(1)	0.2908(1)	23(1)
S(4)	0.2284(1)	0.3880(1)	0.6182(1)	16(1)
S(5)	-0.05614(1)	-0.0240(1)	0.3903(1)	24(1)
S(6)	-0.2166(1)	0.1507(1)	0.3664(1)	15(1)
S(7)	-0.1080(1)	0.5467(1)	0.5713(1)	15(1)
S(8)	-0.0708(1)	0.2647(1)	0.7067(1)	20(1)

Rb₈Mn₂As₄S₁₆

As(1)	0.1316(1)	0.3130(1)	0.2444(1)	20(1)
As(2)	0.5478(1)	0.8874(1)	0.2716(1)	20(1)
Rb(1)	0.5657(1)	0.4804(1)	0.2474(1)	31(1)
Rb(2)	-0.1020(1)	0.2608(1)	0.4813(1)	38(1)
Rb(3)	-0.2631(1)	0.0179(1)	0.0398(1)	34(1)
Rb(4)	0.1082(5)	0.6838(5)	0.1300(4)	65(1)
Rb(5)	0.1186(4)	0.6828(5)	0.1170(4)	34(1)
Mn(1)	0.3489(1)	0.1381(1)	0.4268(1)	24(1)
S(1)	0.5281(1)	1.1202(1)	0.2721(1)	25(1)
S(2)	0.3975(1)	0.8325(1)	0.3829(1)	24(1)
S(3)	0.3061(1)	0.4153(1)	0.4240(1)	28(1)
S(4)	0.4858(1)	0.7387(1)	0.0809(1)	36(1)
S(5)	0.0932(1)	0.0764(1)	0.2447(1)	29(1)
S(6)	0.2134(1)	0.3316(1)	0.0851(1)	28(1)
S(7)	-0.0745(1)	0.4199(1)	0.2406(1)	38(1)
S(8)	0.7719(1)	0.8666(1)	0.3840(1)	32(1)

Cs₈MnAs₄S₁₆

Cs(1)	0.0722(1)	0.4763(1)	0.7494(1)	33(1)
Cs(2)	0.2410(1)	0.0227(1)	0.5451(1)	34(1)
Cs(3)	0.4013(1)	0.2589(1)	0.9876(1)	38(1)
Cs(4)	-0.6145(1)	0.3151(1)	0.3761(1)	45(1)

Mn(1)	0.1509(1)	0.8618(1)	1.0727(1)	11(1)
As(1)	0.0470(1)	0.8878(1)	0.7744(1)	22(1)
As(2)	-0.3643(1)	0.3088(1)	0.7449(1)	23(1)
S(1)	0.0237(2)	0.1128(2)	0.7733(2)	28(1)
S(2)	0.3975(2)	-0.0804(2)	0.2519(2)	31(1)
S(3)	-0.2817(2)	0.3288(3)	0.5903(2)	30(1)
S(4)	0.2015(3)	0.5917(2)	1.0784(2)	31(1)
S(5)	-0.0068(3)	0.7446(3)	0.5885(2)	37(1)
S(6)	-0.0961(2)	0.8342(3)	0.8857(2)	29(1)
S(7)	0.2646(3)	0.8675(3)	0.8816(2)	34(1)
S(8)	0.4328(3)	0.4092(3)	0.7375(3)	36(1)

$\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$

Cd(1)	0.3520(1)	0.3068(1)	0.4365(1)	18(1)
Rb(1)	-0.1068(1)	0.2218(1)	0.4734(1)	19(1)
Rb(2)	0.4705(1)	0.1904(1)	0.7446(1)	20(1)
Rb(3)	-0.2316(1)	-0.0634(1)	-0.0023(1)	23(1)
Rb(4)	0.0466(1)	0.5106(1)	0.8377(1)	29(1)
As(1)	0.1044(1)	-0.388(1)	0.2686(1)	11(1)
As(2)	0.5734(2)	0.3607(2)	1.2344(2)	12(1)
As(22)	0.5628(14)	0.4050(13)	1.2725(12)	20(2)
S(1)	0.1424(3)	-0.2010(2)	0.1077(2)	20(1)
S(2)	0.3116(2)	0.0155(2)	0.4330(2)	15(1)

S(4)	0.0684(2)	0.1873(2)	0.2553(2)	17(1)
S(5)	-0.0980(2)	-0.1370(2)	0.2843(2)	19(1)
S(6)	0.2384(3)	0.4602(3)	0.6210(2)	24(1)
S(3)	0.6447(3)	0.5242(3)	0.7932(2)	14(1)
S(7)	0.3479(4)	0.5671(4)	0.3844(3)	14(1)
S(8)	0.5242(2)	0.1819(2)	0.2917(2)	17(1)
S(9)	0.5972(3)	0.2775(3)	1.0586(2)	20(1)
S(99)	0.5340(30)	0.3840(20)	1.0920(20)	61(7)
S(10)	0.3970(30)	0.5460(20)	0.3580(17)	23(4)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Rb}_8\text{Mn}_2\text{As}_4\text{S}_{16}$, $\text{Cs}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ and $\text{Rb}_8\text{Cd}_2\text{As}_4\text{S}_{18}$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$						
As(1)	12(1)	13(1)	11(1)	0(1)	0(1)	-1(1)
As(2)	11(1)	12(1)	13(1)	-3(1)	-1(1)	0(1)
Mn(1)	14(1)	15(1)	13(1)	1(1)	-2(1)	-2(1)
K(1)	20(1)	16(1)	29(1)	0(1)	3(1)	-1(1)
K(2)	34(1)	22(1)	31(1)	0	-15(1)	0
K(3)	21(1)	29(1)	28(1)	8(1)	-5(1)	-1(1)
K(4)	18(1)	26(1)	20(1)	-2(1)	2(1)	-1(1)
K(5)	38(1)	24(1)	16(1)	0	8(1)	0
S(1)	17(1)	14(1)	14(1)	-1(1)	-2(1)	-2(1)
S(2)	14(1)	17(1)	12(1)	-3(1)	1(1)	-1(1)
S(3)	25(1)	26(1)	15(1)	-2(1)	-7(1)	7(1)
S(4)	11(1)	17(1)	19(1)	0(1)	-2(1)	-1(1)
S(5)	17(1)	14(1)	39(1)	-2(1)	-1(1)	-4(1)
S(6)	13(1)	18(1)	16(1)	-2(1)	1(1)	1(1)
S(7)	16(1)	15(1)	15(1)	1(1)	0(1)	2(1)
S(8)	26(1)	24(1)	11(1)	2(1)	4(1)	2(1)

Rb₈Mn₂As₄S₁₆

As(1)	18(1)	20(1)	22(1)	7(1)	3(1)	3(1)
As(2)	25(1)	19(1)	19(1)	7(1)	7(1)	4(1)
Rb(1)	28(1)	26(1)	38(1)	11(1)	4(1)	4(1)
Rb(2)	36(1)	37(1)	39(1)	10(1)	10(1)	5(1)
Rb(3)	32(1)	35(1)	35(1)	10(1)	7(1)	6(1)
Rb(4)	72(2)	29(1)	64(2)	17(1)	-38(1)	-12(1)
Rb(5)	28(1)	33(1)	34(1)	9(1)	-3(1)	1(1)
Mn(1)	26(1)	26(1)	21(1)	9(1)	4(1)	7(1)
S(1)	32(1)	20(1)	28(1)	12(1)	10(1)	6(1)
S(2)	24(1)	27(1)	20(1)	8(1)	4(1)	-3(1)
S(3)	34(1)	22(1)	21(1)	4(1)	0(1)	3(1)
S(4)	58(1)	29(1)	21(1)	3(1)	12(1)	6(1)
S(5)	27(1)	21(1)	35(1)	10(1)	-1(1)	-2(1)
S(6)	31(1)	33(1)	22(1)	10(1)	6(1)	4(1)
S(7)	25(1)	42(1)	54(1)	22(1)	14(1)	16(1)
S(8)	26(1)	38(1)	36(1)	18(1)	9(1)	10(1)

Cs₈Mn₂As₄S₁₆

Cs(1)	29(1)	28(1)	40(1)	9(1)	4(1)	4(1)
Cs(2)	33(1)	34(1)	35(1)	6(1)	9(1)	4(1)
Cs(3)	36(1)	39(1)	38(1)	8(1)	11(1)	5(1)
Cs(4)	44(1)	34(1)	44(1)	11(1)	-12(1)	-4(1)

Mn(1)	12(1)	15(1)	6(1)	3(1)	1(1)	7(1)
As(1)	26(1)	21(1)	21(1)	6(1)	7(1)	3(1)
As(2)	21(1)	22(1)	24(1)	5(1)	4(1)	4(1)
S(1)	34(1)	22(1)	30(1)	11(1)	12(1)	7(1)
S(2)	29(1)	23(1)	37(1)	7(1)	2(1)	0(1)
S(3)	31(1)	34(1)	24(1)	7(1)	7(1)	5(1)
S(4)	37(1)	27(1)	24(1)	2(1)	1(1)	2(1)
S(5)	57(2)	29(1)	23(1)	4(1)	12(1)	6(1)
S(6)	28(1)	34(1)	23(1)	6(1)	6(1)	-5(1)
S(7)	26(1)	37(1)	39(1)	13(1)	6(1)	9(1)
S(8)	26(1)	38(1)	49(1)	15(1)	14(1)	13(1)

Rb₈Cd₂As₄S₁₈

Cd(1)	23(1)	13(1)	14(1)	2(1)	6(1)	-5(1)
Rb(1)	20(1)	18(1)	15(1)	4(1)	5(1)	1(1)
Rb(2)	20(1)	17(1)	23(1)	9(1)	7(1)	2(1)
Rb(3)	23(1)	22(1)	18(1)	7(1)	-1(1)	-4(1)
Rb(4)	39(1)	17(1)	21(1)	0(1)	9(1)	-2(1)
As(1)	13(1)	9(1)	10(1)	2(1)	3(1)	0(1)
As(2)	14(1)	8(1)	11(1)	1(1)	4(1)	-1(1)
As(22)	33(4)	3(4)	23(6)	8(4)	4(4)	-5(3)
S(1)	25(1)	19(1)	11(1)	0(1)	6(1)	2(1)
S(2)	16(1)	14(1)	10(1)	3(1)	0(1)	-2(1)

S(4)	21(1)	12(1)	18(1)	8(1)	4(1)	1(1)
S(5)	17(1)	18(1)	20(1)	6(1)	6(1)	-3(1)
S(6)	24(1)	17(1)	24(1)	-3(1)	12(1)	-8(1)
S(3)	17(1)	12(1)	11(1)	4(1)	3(1)	2(1)
S(7)	19(2)	10(1)	12(2)	-1(1)	9(1)	1(1)
S(8)	20(1)	10(1)	20(1)	6(1)	5(1)	0(1)
S(9)	25(1)	21(1)	9(1)	0(1)	8(1)	-2(1)
S(99)	120(20)	25(10)	39(12)	5(8)	39(13)	-17(11)
S(10)	43(12)	14(7)	9(8)	-2(6)	12(7)	9(7)

* The anisotropic displacement factor exponent takes the form:

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

The thermal response of **I** and **II** was measured using a Differential Thermal Analyzer. The data revealed that **I** and **II** melt incongruently at 480°C and 520°C respectively. The powder X-ray diffraction pattern of the residue taken after DTA showed the presence of MnS and amorphous $K(Rb)_xAs_yS_z$ along with the parent compound.

C.2 Structure description of $K_8[Mn_2(AsS_4)_4]$

The structure of $A_8[Mn_2(AsS_4)_4]$ contains the discrete molecular $[Mn_2(AsS_4)_4]^{8-}$ clusters and charge-compensating A^+ cations. We will discuss the structural details of $K_8[Mn_2(AsS_4)_4]$. The clusters are centrosymmetric and consist of octahedrally coordinated Mn^{2+} ions linked by tetrahedral $[AsS_4]^{3-}$ units, Figure 1. Each Mn center is connected to three $[AsS_4]^{3-}$ ligands and each ligand uses two of its S atoms to bind the metal. There are two different kinds of $[AsS_4]^{3-}$ ligands, terminal and bridging. The terminal $[AsS_4]^{3-}$ ligand uses two of its sulfur arms to chelate to a single Mn atom. The bridging $[AsS_4]^{3-}$ ligand uses three of its sulfur atoms, two binding to two Mn atoms and the third S atom forming a bridge between the metals. The fourth S atom remains non-bonding. Alternatively, two MnS_6 octahedra edge share with four AsS_4 tetrahedra to form the binuclear cluster.

The intra-core Mn-Mn distance is 4.070(1) Å. Mn-S distances range from 2.5812(6) Å to 2.7739(6) Å. (Table 2) As-S distances are normal between 2.1306(6) Å and 2.1984(5) Å for the terminal unit and 2.1378(6) Å to 2.1936(6) Å for the bridging ligand. MnS_6 is a distorted octahedron with S-Mn-S bond angles varying from 79.174(18)° to 167.96(2)°. The $[AsS_4]^{3-}$ tetrahedra are also distorted from ideal tetrahedral geometry with S-As-S

bond angles between $103.12(2)^\circ$ and $115.64(2)^\circ$ for bridging AsS_4 and between $102.70(2)^\circ$ and $113.08(2)^\circ$ for the terminal ligand. (Table 3)

There are 5 crystallographically unique K^+ ions. K1 sits in a nine coordinate pocket created by 8 S atoms and an As atom with distances between $3.1142(8) \text{ \AA}$ and $3.6755(6) \text{ \AA}$. K2 is coordinated to 6 S in the range $3.2489(7) \text{ \AA}$ to $3.5346(7) \text{ \AA}$. K3 is coordinated to 7 S atoms with bond distances ranging from $3.1167(7) \text{ \AA}$ to $3.5654(8) \text{ \AA}$. K4 is connected to 8 S atoms and an As atom at distances $3.1292(8) \text{ \AA}$ - $3.7104(7) \text{ \AA}$. K5 is hepta-coordinated by 6 S atoms and an As atom ranging from $3.1385(7) \text{ \AA}$ to $3.7765(5) \text{ \AA}$. Figure 2 shows the coordination environments of the K cations.

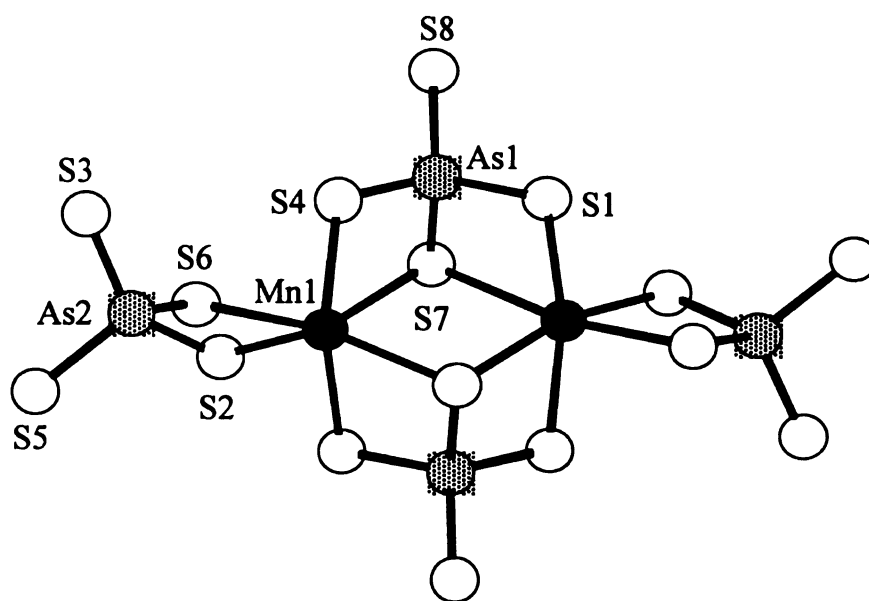


Figure 1. The molecular anion $[\text{Mn}_2(\text{AsS}_4)_4]^{8-}$. The black circles are Mn, the white circles are S and the grey circles are As.

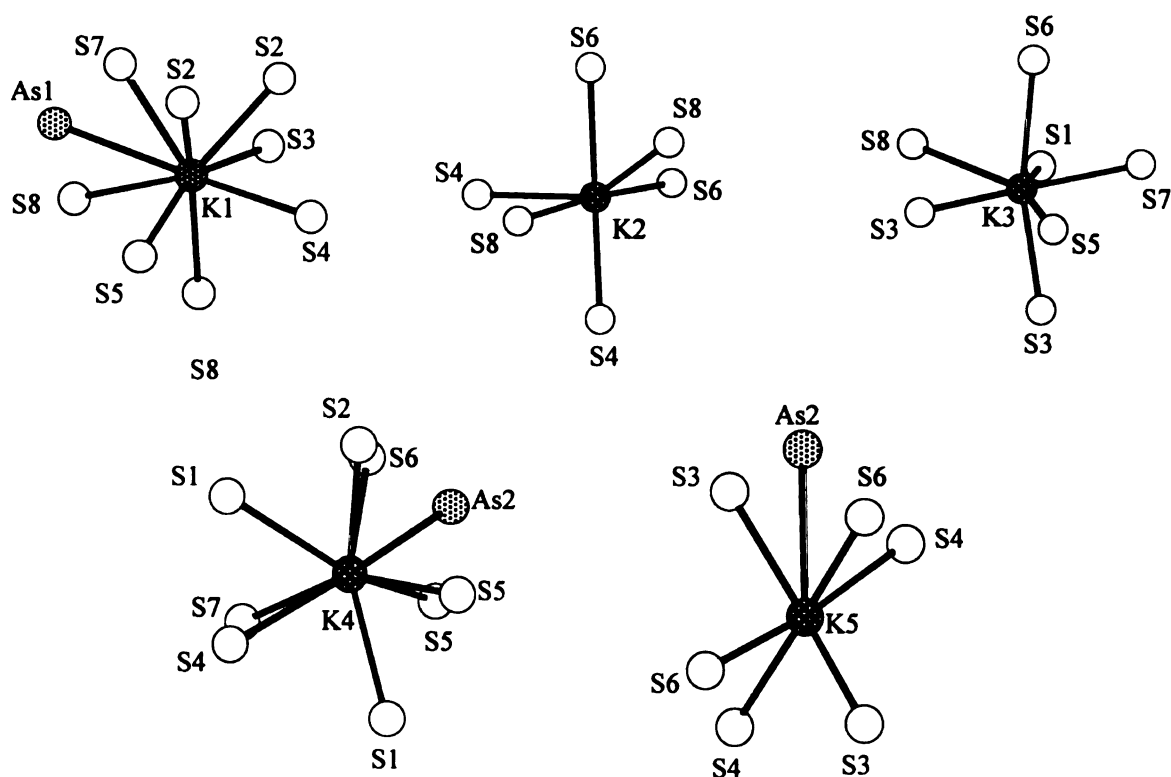


Figure 2. Coordination environments of the five crystallographically unique K^+ ions.

Table 4. Selected bond distances for $K_8Mn_2As_4S_{16}$, and $Rb_8Cd_2As_4S_{18}$.

$K_8Mn_2As_4S_{16}$					
As(1) - S(8)	2.1306(6)	K(1) - S(2)	3.3272(7)	K(3) - S(5)	3.1548(8)
As(1) - S(1)	2.1626(5)	K(1) - S(2)	3.5447(8)	K(3) - S(6)	3.3263(8)
As(1) - S(4)	2.1715(6)	K(1) - S(3)	3.1142(8)	K(3) - S(7)	3.5654(8)
As(1) - S(7)	2.1984(5)	K(1) - S(4)	3.4509(7)	K(3) - S(8)	3.3175(8)
As(2) - S(3)	2.1378(6)	K(1) - S(5)	3.1515(8)	K(4) - S(1)	3.2697(8)
As(2) - S(5)	2.1443(6)	K(1) - S(7)	3.3381(7)	K(4) - S(1)	3.2883(7)
As(2) - S(2)	2.1793(5)	K(1) - S(8)	3.3526(8)	K(4) - S(2)	3.3613(7)
As(2) - S(6)	2.1936(6)	K(1) - S(8)	3.4300(8)	K(4) - S(4)	3.2210(7)
Mn(1) - S(1)	2.5812(6)	K(1) - As(1)	3.6755(6)	K(4) - S(5)	3.2417(8)
Mn(1) - S(2)	2.5920(6)	K(2) - S(4)	2 x 3.5346(7)	K(4) - S(5)	3.1292(8)
Mn(1) - S(4)	2.6238(6)	K(2) - S(6)	2 x 3.3112(8)	K(4) - S(6)	3.4158(7)
Mn(1) - S(6)	2.6635(6)	K(2) - S(8)	2 x 3.2489(7)	K(4) - S(7)	3.7104(7)
Mn(1) - S(7)	2.7591(6)	K(3) - S(1)	3.5442(7)	K(4) - As(2)	3.6785(6)
Mn(1) - S(7)	2.7739(6)	K(3) - S(3)	3.1167(7)	K(5) - S(3)	2 x 3.1385(7)
Mn(1) - Mn(1)	4.070(1)	K(3) - S(3)	3.5402(8)	K(5) - S(4)	2 x 3.1828(7)
		K(5) - As(2)	3.7765(5)	K(5) - S(6)	2 x 3.2566(7)
$Rb_8Cd_2As_4S_{18}$					
As(1) - S(1)	2.143(2)	Rb(1) - S(2)	3.599(2)	Rb(3) - S(1)	3.382(2)
As(1) - S(5)	2.152(2)	Rb(1) - S(4)	3.479(2)	Rb(3) - S(1)	3.667(2)
As(1) - S(2)	2.177(2)	Rb(1) - S(5)	3.359(2)	Rb(3) - S(3)	3.650(3)

As(1) - S(4)	2.183(2)	Rb(1) - S(5)	3.309(2)	Rb(3) - S(4)	3.705(2)
As(2) - As(22)	0.536(13)	Rb(1) - S(6)	3.380(2)	Rb(3) - S(4)	3.458(2)
As(2) - S(99)	1.79(2)	Rb(1) - S(6)	3.634(3)	Rb(3) - S(5)	3.688(2)
As(2) - S(9)	2.111(3)	Rb(1) - S(7)	3.428(4)	Rb(3) - S(8)	3.482(2)
As(2) - S(8)	2.130(3)	Rb(1) - S(8)	3.324(2)	Rb(3) - S(9)	3.606(3)
As(2) - S(6)	2.174(3)	Rb(1) - As(1)	3.8262(12)	Rb(3) - S(9)	3.471(3)
As(2) - S(3)	2.250(3)	Rb(1) - As(2)	4.031(2)	Rb(3) - S(99)	3.64(2)
As(22) - S(6)	1.956(11)	Rb(1) - As(22)	4.065(11)	Rb(3) - As(1)	3.6801(13)
As(22) - S(3)	2.023(12)	Rb(2) - S(1)	3.397(2)	Rb(3) - As(2)	3.733(2)
As(22) - S(99)	2.11(2)	Rb(2) - S(2)	3.379(2)	Rb(4) - S(1)	3.259(2)
As(22) - S(8)	2.210(10)	Rb(2) - S(2)	3.489(2)	Rb(4) - S(1)	3.722(2)
As(22) - S(10)	2.27(3)	Rb(2) - S(3)	3.235(2)	Rb(4) - S(3)	3.537(3)
Cd(1) - S(10)	2.70(2)	Rb(2) - S(5)	3.317(2)	Rb(4) - S(4)	3.455(2)
Cd(1) - S(8)	2.705(2)	Rb(2) - S(6)	3.727(3)	Rb(4) - S(5)	3.335(2)
Cd(1) - S(2)	2.711(2)	Rb(2) - S(7)	3.836(3)	Rb(4) - S(6)	3.550(2)
Cd(1) - S(4)	2.716(2)	Rb(2) - S(8)	3.319(2)	Rb(4) - S(7)	3.634(4)
Cd(1) - S(7)	2.720(3)	Rb(2) - S(9)	3.453(3)	Rb(4) - S(9)	3.389(3)
Cd(1) - S(6)	2.732(2)	Rb(2) - S(99)	3.72(2)	Rb(4) - S(99)	3.68(3)
Cd(1) - S(10)	2.811(19)	Rb(2) - S(99)	3.84(2)	Rb(4) - S(10)	3.91(2)
Cd(1) - S(7)	2.819(3)	Rb(2) - S(10)	3.51(2)	Rb(4) - As(2)	4.123(2)
Cd(1) - Cd(1)	3.960(1)	S(3) - S(7)	2.071(4)		

Table 5. Selected bond angles for $K_8Mn_2As_4S_{16}$, and $Rb_8Cd_2As_4S_{18}$.

$K_8Mn_2As_4S_{16}$			
S(8) - As(1) - S(1)	111.38(2)	S(1) - Mn(1) - S(7)	79.174(18)
S(8) - As(1) - S(4)	112.56(2)	S(4) - Mn(1) - S(7)	79.224(17)
S(1) - As(1) - S(4)	109.90(2)	S(6) - Mn(1) - S(7)	97.290(18)
S(8) - As(1) - S(7)	115.64(2)	S(1) - Mn(1) - S(2)	104.37(2)
S(1) - As(1) - S(7)	103.12(2)	S(1) - Mn(1) - S(4)	167.96(2)
S(4) - As(1) - S(7)	103.58(2)	S(2) - Mn(1) - S(7)	99.327(18)
S(5) - As(2) - S(6)	111.00(2)	S(2) - Mn(1) - S(4)	86.625(18)
S(2) - As(2) - S(6)	102.70(2)	S(4) - Mn(1) - S(7)	94.387(19)
S(3) - As(2) - S(5)	109.14(2)	S(6) - Mn(1) - S(7)	168.10(2)
S(3) - As(2) - S(2)	110.19(2)	S(2) - Mn(1) - S(6)	81.041(17)
S(5) - As(2) - S(2)	110.60(2)	S(1) - Mn(1) - S(6)	89.19(2)
S(3) - As(2) - S(6)	113.08(2)	S(7) - Mn(1) - S(7)	85.296(18)
S(1) - Mn(1) - S(7)	90.038(19)	S(4) - Mn(1) - S(6)	97.51(2)
S(2) - Mn(1) - S(7)	165.44(2)		
$Rb_8Cd_2As_4S_{18}$			
S(2) - As(1) - S(4)	103.95(8)	S(8) - Cd(1) - S(7)	81.37(9)
S(1) - As(1) - S(5)	108.08(9)	S(10) - Cd(1) - S(8)	94.1(5)
S(1) - As(1) - S(2)	111.02(9)	S(2) - Cd(1) - S(7)	102.93(8)
S(5) - As(1) - S(2)	112.61(9)	S(10) - Cd(1) - S(2)	103.7(4)

S(1) - As(1) - S(4)	111.09(9)	S(4) - Cd(1) - S(7)	177.09(9)
S(5) - As(1) - S(4)	110.08(8)	S(8) - Cd(1) - S(2)	85.00(6)
S(10) - As(22) - S(9)	139.7(7)	S(7) - Cd(1) - S(7)	88.78(10)
S(3) - As(22) - S(8)	110.0(5)	S(10) - Cd(1) - S(4)	169.5(5)
S(6) - As(22) - S(10)	100.5(7)	S(6) - Cd(1) - S(7)	86.48(9)
S(8) - As(22) - S(10)	101.6(7)	S(8) - Cd(1) - S(4)	96.30(7)
S(99) - As(22) - S(8)	115.2(7)	S(10) - Cd(1) - S(7)	84.9(4)
S(6) - As(22) - S(99)	105.8(8)	S(2) - Cd(1) - S(4)	78.52(6)
S(3) - As(22) - S(99)	73.0(9)	S(10) - Cd(1) - S(7)	89.2(4)
S(6) - As(22) - S(8)	117.5(5)	S(8) - Cd(1) - S(7)	90.63(9)
S(99) - As(22) - S(10)	115.7(10)	S(2) - Cd(1) - S(7)	166.70(9)
S(6) - As(22) - S(9)	103.5(5)	S(4) - Cd(1) - S(7)	89.51(8)
S(3) - As(22) - S(9)	95.0(5)	S(10) - Cd(1) - S(6)	73.7(5)
S(8) - As(22) - S(9)	95.4(5)	S(8) - Cd(1) - S(6)	167.85(7)
S(99) - As(2) - S(8)	136.9(6)	S(2) - Cd(1) - S(6)	97.81(7)
S(6) - As(2) - S(3)	106.76(12)	S(4) - Cd(1) - S(6)	95.84(7)
S(9) - As(2) - S(8)	114.47(13)	S(7) - Cd(1) - S(6)	89.09(9)
S(99) - As(2) - S(6)	109.5(7)	S(10) - Cd(1) - S(10)	88.1(6)
S(9) - As(2) - S(6)	114.28(12)	S(8) - Cd(1) - S(10)	77.9(4)
S(8) - As(2) - S(6)	111.76(13)	S(2) - Cd(1) - S(10)	160.0(4)
S(99) - As(2) - S(3)	74.0(9)	S(4) - Cd(1) - S(10)	92.9(4)
S(9) - As(2) - S(3)	103.67(13)	S(6) - Cd(1) - S(10)	101.1(4)
S(8) - As(2) - S(3)	104.73(11)		

In the case of the Rb and Cs analogs the structure of the core remains the same however the octahedral angles in the MnS_6 and AsS_4 groups are more distorted presumably due to the slightly different packing forces arising from the presence of the bigger alkali metals. This also leads to a lowering of symmetry in the overall structure from monoclinic $P2/n$ for $\text{K}_8\text{Mn}_2\text{As}_4\text{S}_{16}$ to $P-1$ for the Rb and Cs phases. Mn-Mn distance within the core increases to 4.176(1) Å and 4.327(1) Å for the Rb and Cs compounds, respectively.

C.3 Structure description of $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]$

The structure of $\text{Rb}_8(\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2)$ presents an interesting case of ligand size adjustment to counter the size of the transition metal. The structure of this compound is similar to the Mn phase and consists of $[\text{Cd}_2(\text{AsS}_5)_2(\text{AsS}_4)_2]^{8-}$ clusters. (Figure 3) The interesting aspect in this structure is the presence of the tetrahedral $[\text{AsS}_5]^{3-}$ ligand which is derived from the $[\text{AsS}_4]^{3-}$ tetrahedron by substituting a terminal S atom with a disulfide S_2^{2-} unit. The presence of the larger Cd^{2+} ion in place of a Mn^{2+} probably puts a strain on the bridging $[\text{AsS}_4]^{3-}$ ligand causing the system to release this strain by taking in an additional S atom from the flux to form $[\text{AsS}_5]^{3-}$ and the ensuing molecular $[\text{Cd}_2(\text{AsS}_5)_2(\text{AsS}_4)_2]^{8-}$ unit. Thus this cluster is composed of two Cd atoms coordinated to two $[\text{AsS}_4]^{3-}$ units and bridged by two $[\text{AsS}_5]^{3-}$ units. This is by no means to say that $[\text{Cd}_2(\text{AsS}_4)_4]^{8-}$ doesn't exist. The refinement of this structure showed that the $[\text{Cd}_2(\text{AsS}_5)_2(\text{AsS}_4)_2]^{8-}$ anion is disordered with $[\text{Cd}_2(\text{AsS}_4)_4]^{8-}$ (15%) though the percentage of the former (85%) is much greater. Our attempts to isolate pure $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_4]$ were however unsuccessful.

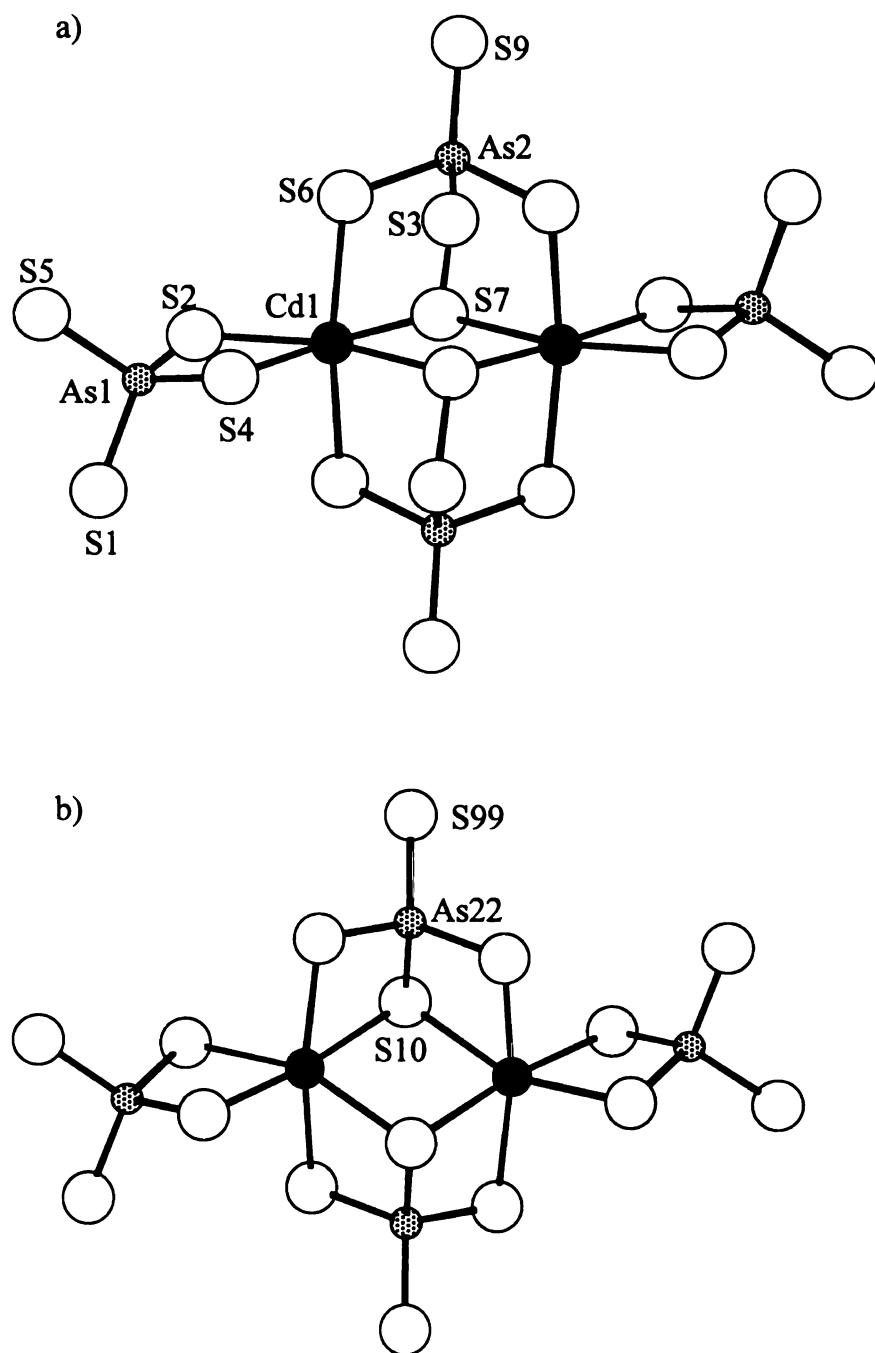


Figure 3. a) The molecular $[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]^{8-}$ anion. b) The co-crystallized $[\text{Cd}_2(\text{AsS}_4)_4]^{8-}$ anion.

The octahedral geometry of Cd^{2+} ions observed in $[\text{Cd}_2(\text{AsS}_5)_2(\text{AsS}_4)_2]^{8-}$ is indeed unusual for a sulfur based coordination environment. In the vast majority of cases this metal ion prefers the standard tetrahedral geometry.¹⁷

In this structure, Cd-S bond distances range from 2.705(2) Å to 2.819(3) Å. As-S distances vary from 2.112(3) Å to 2.250(3) Å for AsS_5 and 2.143(2) Å to 2.183(2) Å for AsS_4 . (Table 2) S-S distance is normal at 2.071(4) Å. Cd-Cd distance within the core is 3.960(1) Å. The formation of the AsS_5 ligand reduces the distortion of the CdS_6 octahedra with S-Cd-S bond angles being closer to 90° and 180°. S-As-S bond angles are slightly distorted ranging from 103.95(8)° to 112.61(9)°. (Table 3)

The Mn and Cd clusters are reminiscent of the clusters encountered in $\text{K}_6\text{Cr}_2(\text{PS}_4)_4$ ³ which also consists of a binuclear Cr center that is bonded by 4 PS_4 units in an identical fashion as described above. The one-dimensional compound $\text{K}_3\text{Cr}_2\text{P}_3\text{S}_{12}$ ¹⁸ has the same core that shares edges with another core through the terminal PS_4 tetrahedron. It is interesting to note that $\text{K}_6\text{Cr}_2\text{P}_4\text{S}_{16}$ can be conceptually obtained from $\text{K}_3\text{Cr}_2\text{P}_3\text{S}_{12}$ by addition of one equivalent of K_3PS_4 . A dimeric core can be seen in $\text{A}_5\text{An}(\text{PS}_4)_3$ (An = U, Th).⁸ However in these compounds, there are two terminal $[\text{PS}_4]^{3-}$ units per metal ion. This structural motif seems to be very stable and is observed in the chains of $\text{A}_3\text{RE}(\text{PSe}_4)_2$ ¹⁹ and $\text{K}_3\text{Pu}(\text{PS}_4)_2$ ²⁰ and the layers of $\text{Cs}_3\text{Bi}_2(\text{PS}_4)_3$.²¹

C.4 Spectroscopy

Large crystals of $\text{K}_8[\text{Mn}_2(\text{AsS}_4)_4]$, $\text{Rb}_8[\text{Mn}_2(\text{AsS}_4)_4]$, $\text{Cs}_8[\text{Mn}_2(\text{AsS}_4)_4]$ and $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]$ were hand-picked and ground to powder for diffuse reflectance spectroscopic examination. All compounds are yellow in color with energy gaps

commencing at 2.25eV for **I**, 2.33eV for **II**, 2.26eV for **III** and 2.67eV for **IV**. (Figure 4) Since these are molecular complexes, it is less meaningful to talk about band gaps, rather it is very likely that the energy gap arises from "localized" energy levels and can be assigned to S→M charge transfer transitions.

Infrared spectra for **I** and **IV** are shown in Figure 5. **I** shows frequencies at 426(m-s), 413(m), 384(m) cm^{-1} which can be assigned to As-S stretching. These frequencies are analogous to those observed in the clusters of $[\text{Pt}_3(\text{AsS}_4)_3]^{3-}$ and other reports.²² There are several weak peaks below 300cm^{-1} , which are contributed by Mn-S stretching modes. **IV** displays peaks at 468(s), 431, 411, 385, 362, 243 cm^{-1} . The peaks at 431, 411 and 385 cm^{-1} are due to As-S stretching while below that are due to Cd-S vibrations. The peak at 468 cm^{-1} is attributed to S-S stretching.

C.5 Magnetism

$\text{K}_8[\text{Mn}_2(\text{AsS}_4)_4]$ is paramagnetic, nearly obeying the Curie-Weiss law over the temperature range 20-300K. Figure 6a shows the plot of the reciprocal molar susceptibility ($1/\chi_m$) against temperature. The estimated μ_{eff} value of 5.4 BM confirms the Mn^{2+} nature of the metal even though it is slightly lower than the ideal 5.9 calculated for high-spin Mn^{2+} ions. Figure 6b shows the dependence of χ_m in the range 0-50K. As seen in the figure, the susceptibility shows a maximum indicating antiferromagnetic coupling. The maximum is observed at $\sim 6\text{K}$ with a Weiss constant, $\theta \sim -19\text{ K}$ suggesting that the antiferromagnetic interactions are weak in nature and this is in accordance with the long intra-core Mn-Mn distance of $4.070(1)\text{\AA}$.

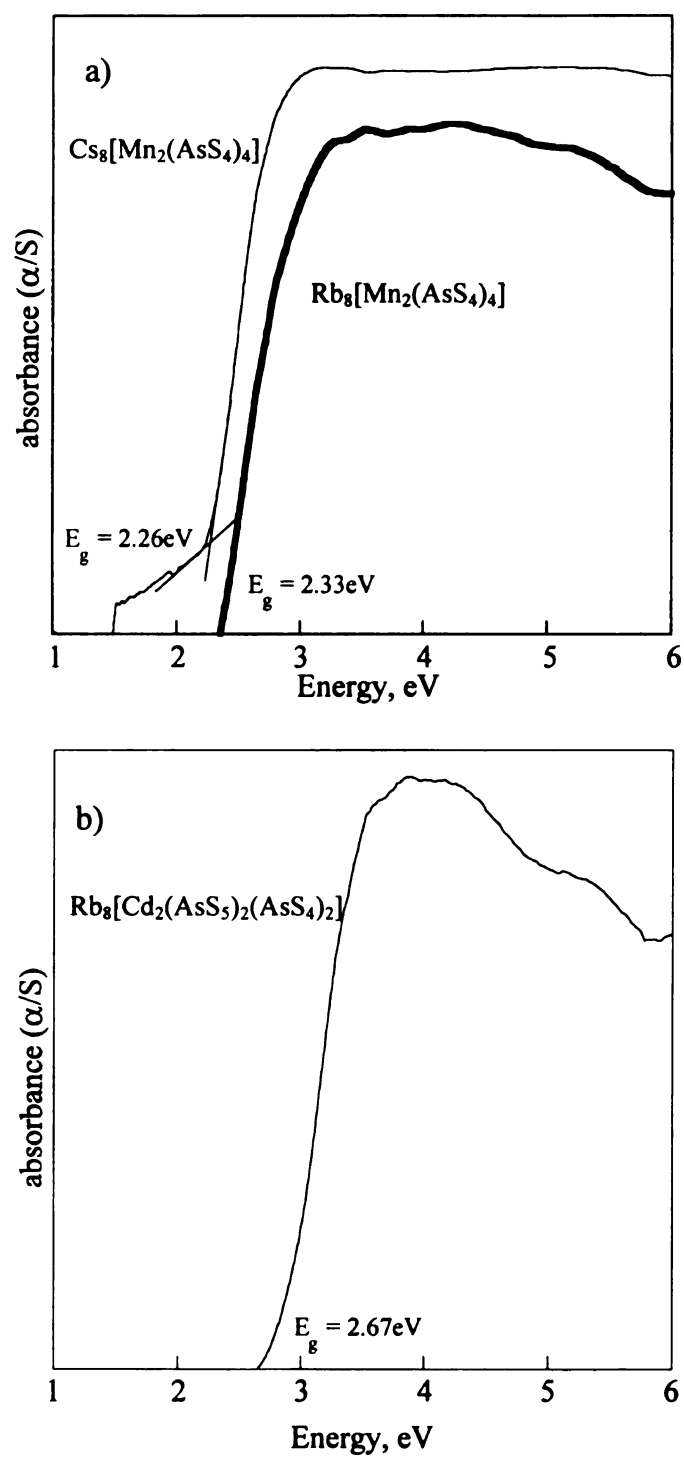


Figure 4. a) Optical absorption spectra of $\text{Cs}_8[\text{Mn}_2(\text{AsS}_4)_4]$ and $\text{Rb}_8[\text{Mn}_2(\text{AsS}_4)_4]$ showing energy gaps at 2.26 and 2.33 eV respectively. b) Optical absorption spectra of $\text{Rb}_8[\text{Cd}_2(\text{AsS}_4)_2(\text{AsS}_5)_2]$ with an onset at 2.67 eV.

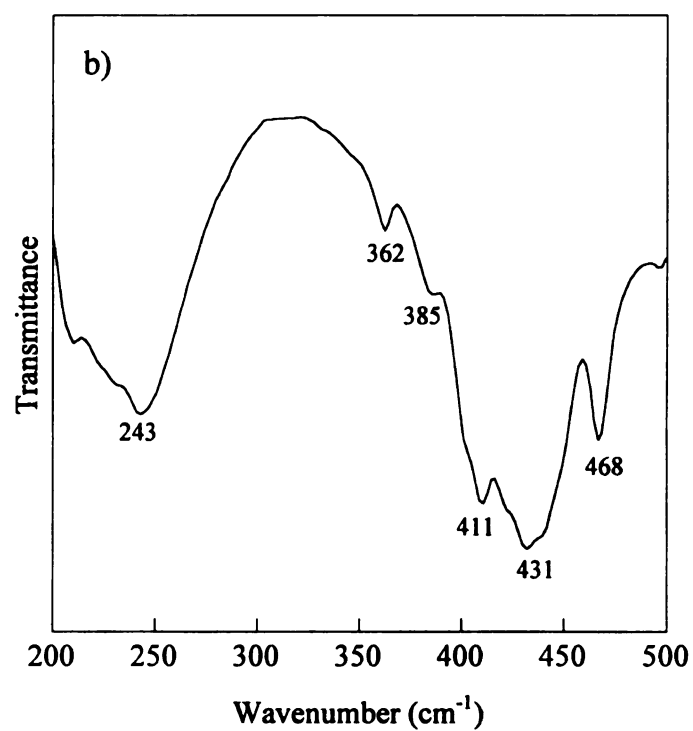
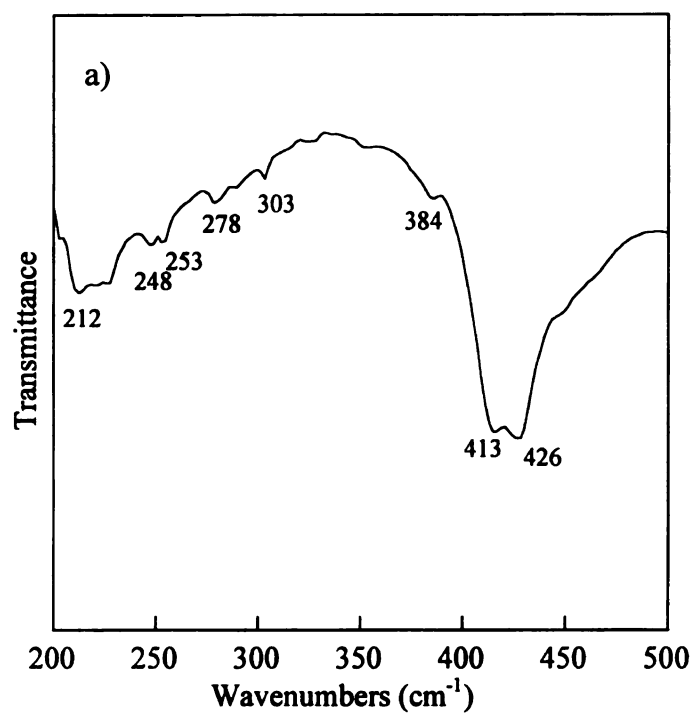


Figure 5. a) Far IR spectrum of $K_8[Mn_2(AsS_4)_4]$ b) Far IR spectrum of $Rb_8[Cd_2(AsS_4)_2(AsS_5)_2]$. The peak at 468 cm^{-1} is attributed to S-S stretching.

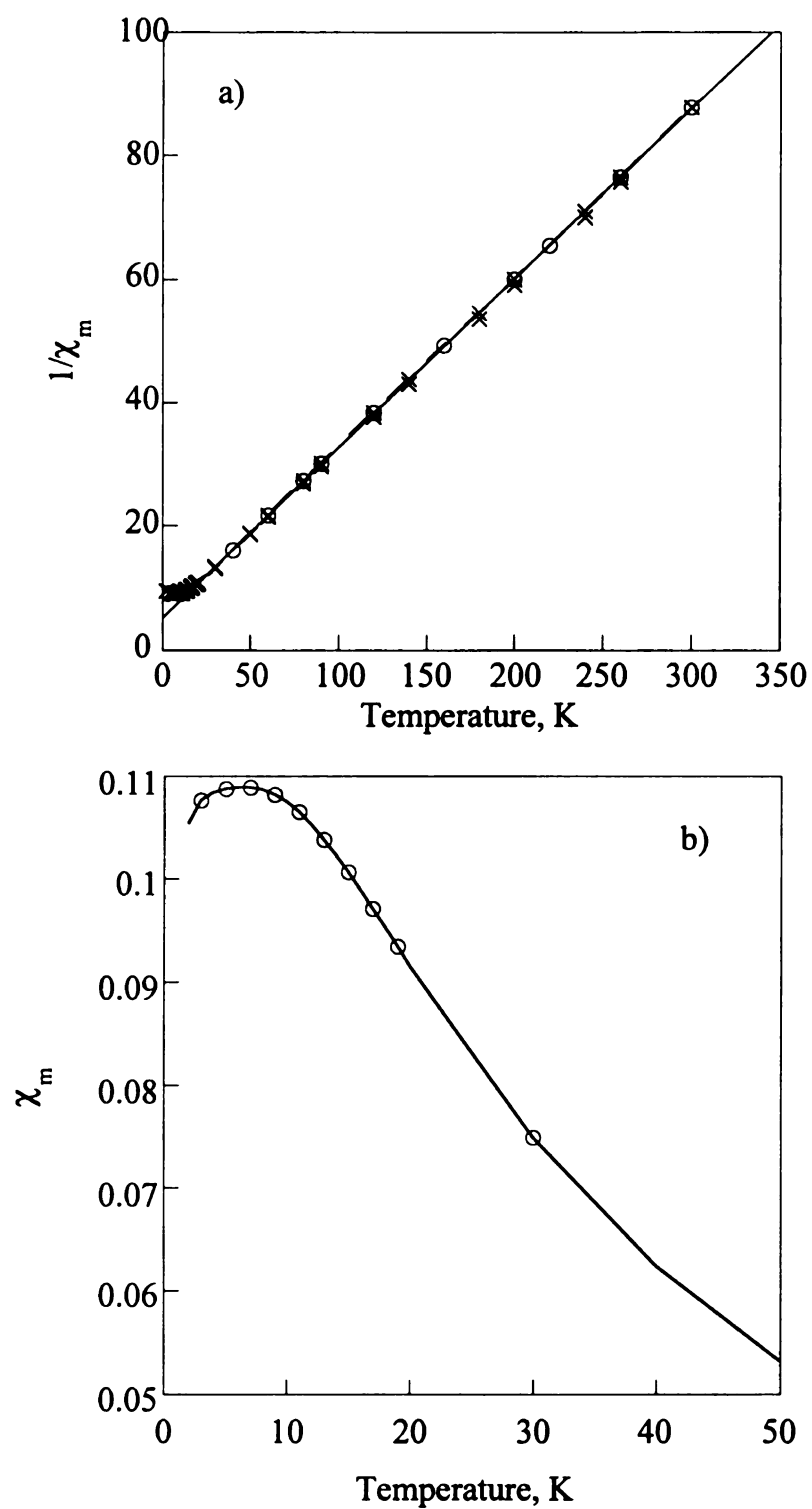


Figure 6. a) Plot of inverse molar susceptibility against temperature for $K_8[Mn_2(AsS_4)_4]$ showing a nearly Curie-Weiss behavior till 20K. b) Plot of molar susceptibility against temperature from 0-50K. The susceptibility reaches a maximum at 6K.

D. Concluding Remarks

Discrete molecules such as the anionic clusters $[\text{Mn}_2(\text{AsS}_4)_4]^{8-}$ and $[\text{Cd}(\text{AsS}_4)_2(\text{AsS}_5)_2]^{8-}$ form under essentially solution conditions inside a molten flux, and crystallize as their alkali salts. Such outcomes in metal reactivity stress the utility of a flux approach in preparing not only complex solid state compounds but, in many cases, also phases with discrete molecular species. The high negative charge of these clusters would have made it more difficult for them to be obtained via conventional solution techniques. The alkali thioarsenate flux is equally promising as its thiophosphate counterpart in exploring complex chalcogenides and further investigation is called for in order to realize the full potential of these fluxes.

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Chapter 8

Cs₁₀Cu₂As₄S₁₉, Cs₂MAsS₅ (M = Cu, Ag) and Cs₂AuAsS₄: Low Dimensional Coinage

Metal Compounds from Cesium Thioarsenate Fluxes

Abstract

The reactions of Cu, Ag and Au in cesium polythioarsenate fluxes yielded Cs₁₀[{Cu₂(AsS₅)₃}(AsS₄)], Cs₂MAsS₅ (M = Cu, Ag) and Cs₂AuAsS₄. Cs₁₀Cu₂As₄S₁₉ (I) crystallizes as yellow rods in space group *P2₁/c* with *a* = 15.967(4) Å, *b* = 9.581(3) Å, *c* = 29.636(8) Å, *β* = 97.233(4)°. Cs₂MAsS₅ (II and III) crystallizes in space group *I4/m* with *a* = 16.710(3) Å, *c* = 7.4313(18) Å for M = Cu (orange rods) and *a* = 17.211(5) Å, *c* = 7.397(3) Å for M = Ag (yellow needles). Cs₂AuAsS₄ (IV) crystallizes as bright yellow needles in space group *Pbcm* with *a* = 6.9320(14) Å, *b* = 20.272(4) Å, *c* = 7.1037(15) Å. The structure of Cs₁₀Cu₂As₄S₁₉ comprises of two co-crystallized anions, [Cu₂(AsS₅)₃]⁷⁻ and AsS₄³⁻. Cs₂MAsS₅ consist of the tetranuclear cluster anion [M₄(AsS₅)₄]⁸⁻ whereas Cs₂AuAsS₄ consists of chains formed by AsS₄³⁻ ligands coordinating to Au. The first three compounds have the tetrahedral AsS₅³⁻ building block whereas the Au compound features the tetrahedral AsS₄³⁻ anion. These compounds are semiconductors with energy gaps of 2.1, 2.41 and 2.54 eV for Cs₂CuAsS₅, Cs₂AgAsS₅ and Cs₂AuAsS₄ respectively. Cs₂CuAsS₅ and Cs₂AgAsS₅ decompose on dissolution in water.

A. Introduction

Coinage metal (Cu, Ag, Au) chalcogenides are among the most widely compounds. According to the ICSD, there are over a thousand binary, ternary and quaternary chalcogenides of the Group 11 metals.¹ The affinity of these metals for S, Se and Te is not surprising considering that the name "chalcogen" comes from Greek and means "copper-forming". Among the preparative techniques, the solvothermal method² and the molten flux method³ have been particularly successful in isolating a wide variety of compounds with diverse structural features. The structures differ in the coordination modes of the ligands and the geometry around the metal atom. Another important parameter aiding the structural diversity is the tendency of these metals to show mixed valency. Thus Au^{+1} strictly prefers a linear geometry whereas Au^{3+} likes to be square planar.⁴ Cu and Ag occur mostly in linear,⁵ trigonal planar⁶ and tetrahedral geometries.⁷ We have isolated a number of coinage metal- containing chalcogenides and chalcophosphates by utilizing the polychalcogenide and polychalcophosphate fluxes.⁸ Some of these compounds include KCuS_4 ,⁹ CsCuS_6 ,¹⁰ A_2AuPS_4 , AAuP_2S_7 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$),¹¹ AuCuSe_4 ,¹² $\text{A}(\text{AgTeS}_3)$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$),¹³ $\text{A}_3\text{Cu}_8\text{Te}_{10}$ ($\text{A} = \text{Rb}, \text{Cs}$),¹⁴ CsCuCeS_3 ,¹⁵ $\text{K}_2\text{Ag}_3\text{CeTe}_4$,¹⁶ $\text{K}_2\text{Au}_4\text{CdS}_4$ etc.¹⁷ Naturally we were interested in exploring how these metals performed in polythioarsenate fluxes. There are very few known quaternary thioarsenates of Cu, Ag and Au. These are KCu_2AsS_3 , KCu_4AsS_4 ,¹⁸ $\text{Cs}_2\text{AgAsS}_4$,¹⁹ $\text{KAg}_3\text{As}_2\text{S}_5$,²⁰ KAg_2AsS_4 ,²¹ $[\text{Fe}(\text{NH}_3)_6]\text{AgAsS}_4$,²² $(\text{NH}_4)\text{Ag}_2\text{AsS}_4$,²³ and K_2AuAsS_4 .²⁴ Of these, K_2AuAsS_4 is the only compound that has been synthesized by a solid state reaction. The other compounds have been prepared using the solvothermal technique. It is therefore clear the wide scope that the alkali polythioarsenate fluxes hold in discovering

new Group 11 thioarsenates. The syntheses and characterization of $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$, Cs_2MAsS_5 ($\text{M} = \text{Cu}, \text{Ag}$) and $\text{Cs}_2\text{AuAsS}_4$ are described in this chapter. These compounds are predecessors to what will likely develop into a substantial subclass of thioarsenates.

B. Experimental Section

B.1 Reagents

All manipulations were done in a nitrogen-filled dri-vac glove box. Reagents: Ag (99.99 %; Liberty Coins, Lansing, MI), Cu (Fisher Scientific Company, Fair Lawn, NJ), Au(325 mesh, 99.9%, Cerac, Milwaukee, WI), As_2S_3 (99.9 %; Strem Chemicals, Newburyport, MA), As (99.9%; Aldrich Chemical Co, Milwaukee, WI), S (99.9 %; Strem Chemicals, Newburyport, MA). N,N-dimethylformamide (Spectrum Chemicals, ACS reagent grade); diethyl ether (CCI, ACS grade). Cs_2S was prepared by dissolving the alkali metal in liquid NH_3 and reacting it with a stoichiometric amount of sulfur according to a modified literature procedure.²⁵

B.2 Physical Measurements

Powder X-ray Diffraction

X-ray powder diffraction patterns were recorded on a CPS 120 INEL diffractometer (Cu $\text{K}\alpha$ radiation) operating at 40kV/20mA and equipped with a position sensitive detector and a flat sample geometry.

Energy Dispersive Spectroscopy

Semiquantitative microprobe analyses on the compounds were done with a JEOL JSM-6400V scanning electron microscope equipped with a Tracor Noran Energy Dispersive

Spectroscopy detector. Elemental compositions were obtained from an average of three readings. Acquisition times were 30s or 45s per reading.

Diffuse Reflectance Spectroscopy

Solid state diffuse reflectance spectra were measured using a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as reference. Finely ground sample was spread on a sample holder preloaded with the reference. Energy gap was determined from a plot of absorbance vs energy by converting reflectance to absorbance using the Kubelka-Munk function.²⁶

Infrared Spectroscopy

Far IR spectra of the compounds were recorded as CsI pellets on a Nicolet 740 FT-IR spectrometer with a TSG/PE detector and silicon beam splitter. The spectra were obtained in the 600-100cm⁻¹ range with 4cm⁻¹ resolution.

Differential Thermal Analysis

The thermal behavior of the compounds was investigated by differential thermal analysis using a Shimadzu DTA-50 thermal analyzer. Typically a sample (~20 mg) of ground crystalline material was sealed in a silica ampule under vacuum. A similar ampoule of equal mass filled with Al₂O₃ was sealed and placed on the reference side of the detector. The sample was heated to the desired temperature at 10°C/min, and after 1-3 min it was cooled at a rate of -10°C/min to 50°C. Residues of the DTA experiments were examined by X-ray powder diffraction. Reproducibility of the results was checked by running multiple heating/ cooling cycles.

B.3 Synthesis

Cs₁₀Cu₂As₄S₁₉ (I) and **Cs₂CuAsS₅ (II)** were synthesized as yellow and red rods, respectively, from a reaction of Cs₂S/Cu/As₂S₃/S in the ratio 4/2/1/10. The reagents were loaded in a fused-silica tube inside a N₂- filled glove box. The tube was sealed under vacuum ($<10^{-4}$ Torr) and placed in a computer-controlled furnace. The tube was heated to 600°C and held at that temperature for 96h. This was followed by cooling to 200°C at the rate of 5°C/h followed by fast cooling to room temperature. The excess of flux was washed with degassed N,N- dimethylformamide to reveal red rods, yellow rods and colorless crystals. The yellow rods were a minor phase (<20%) whereas the red rods were the major phase (~ 50%). Energy dispersive spectroscopy measurements on several of the yellow crystals revealed an average composition of "Cs₁₁CuAs_{5.4}S₁₉" and "Cs_{2.1}CuAsS_{5.1}" for the red rods. The colorless crystals were Cs₃AsS₄. The powder diffraction pattern of the product was compared with the theoretical powder patterns calculated from single crystal structures of Cs₁₀Cu₂As₄S₁₉, Cs₂CuAsS₅ and Cs₃AsS₄, which indicated that it was a mixed phase.

Cs₂AgAsS₅ (III) was obtained as almost single phase by heating a mixture of Cs₂S (0.179g, 0.6mmol), Ag(0.032g, 0.3mmol), As₂S₃(0.074g, 0.3mmol) and S(0.077g, 2.4mmol) at 500°C. The reaction was maintained at this temperature for 60h, followed by cooling to 250°C at the rate of 5°C/h and fast cooling to room temperature. After washing the flux with DMF, yellow needles of Cs₂AgAsS₅ were produced in nearly 80% yield. The powder pattern of the product matched very well with the simulated pattern obtained from single crystal refinement. EDS measurements on a few crystals gave an average composition of "Cs_{2.6}Ag_{0.9}As_{0.9}S_{4.7}".

Cs₂AuAsS₄ (IV) was synthesized as a single phase from a reaction of Cs₂S, Au, As₂S₃ and S in the ratio 2:1:1:10. The reactants were loaded in a fused-silica tube and heated according to the profile given for **III**. On washing the excess flux away, yellow needles were obtained as the only product in about 70% yield. The powder pattern of the product matched perfectly with the simulated pattern obtained from single crystal refinement. EDS analysis on the needles gave an average composition of "Cs₂AuAsS_{4.6}".

B.4 Single crystal X-ray crystallography

For Cs₁₀Cu₂As₄S₁₉, a yellow rod with dimensions of 0.02 x 0.02 x <0.02 mm₃ was glued to a glass capillary fixed to an aluminum pin and mounted on a goniometer head. A full sphere of data was collected on a Bruker SMART system operating at 293K and equipped with Mo K α radiation and CCD detector. The data was integrated using SAINT and an absorption correction was applied using SADABS. The structure was solved in the monoclinic space group *P*2₁/*c* using the SHELXTL package of programs.²⁷ All the atoms were found within the first 3 least-squares cycles. All atoms were refined anisotropically to give final R1/wR2 values of 0.0602/0.1227.

A red rod of Cs₂CuAsS₅ with dimensions 0.02 x 0.02 x 0.1 mm³ was used for data collection. Based on systematic absences and E²-1 statistics, the possible space groups were *I*-4 and *I*4/*m*. The CFOM (Combined Figure of Merit) value for the former was lower and hence it was chosen as the space group. The program PLATON²⁸ indicated a missed center of symmetry and suggested the space group *I*4/*m*. Hence the structure refinement was redone in the space group *I*4/*m*. One Cu, one As, two Cs and four S atoms were found of which the Cu, and two S atoms occupied general positions. At this

point, the isotropic displacement parameters for Cu1 and S4 were found to be very high. Therefore they were allowed to refine freely. They refined to 50% occupancy with a significant decrease in their thermal parameters. Cu1 generates another Cu at a distance of 0.82 Å. This distance precludes the two atoms to be present at the same time. There are two S1 atoms linked to As (S1a and S1b). Depending on which Cu is present, atom S4 is connected to either S1a or S1b with an occupancy of 100%. Hence S1 is both terminal and part of the disulfide arm of the AsS_5^{3-} anion. The average structure determined from X-ray diffraction however shows that S4 is attached to both S1a and S1b with 50% occupancy. All the atoms were anisotropically refined to give final R1/wR2 values of 0.0408/0.0740. $\text{Cs}_2\text{AgAsS}_5$ was solved and refined in the same manner. We probed for the existence of super-cells in both the compounds by taking zone photos with exposure times of 5 min. However no super-cell reflections were observed.

The structure solution of $\text{Cs}_2\text{AuAsS}_4$ was straight-forward. All the atoms were found in two rounds of least squares refinement. After anisotropic refinement of all atoms, the final R1/wR2 values were 0.0221/0.0463.

The crystallographic refinement data along with the fractional atomic coordinates and anisotropic displacement parameters for all the compounds are listed in Tables 1, 2 and 3.

Table 1. Crystallographic data and refinement details for Cs₁₀Cu₂As₄S₁₉, Cs₂CuAsS₅, Cs₂AgAsS₅, and Cs₂AuAsS₄

empirical formula	Cs ₁₀ Cu ₂ As ₄ S ₁₉	Cs ₂ CuAsS ₅	Cs ₂ AgAsS ₅	Cs ₂ AuAsS ₄
fw	2365	564.58	608.91	1002.02
space group	<i>P2₁/c</i>	<i>I4/m</i>	<i>I4/m</i>	<i>Pbcm</i>
<i>a</i> , Å	15.967(4)	16.710(3)	17.211(5)	6.9320(14)
<i>b</i> , Å	9.581(3)	16.710(3)	17.211(5)	20.272(4)
<i>c</i> , Å	29.636(8)	7.4313(18)	7.397 (3)	7.1037(15)
α , deg	90	90	90	90
β , deg	97.233(4)	90	90	90
γ , deg	90	90	90	90
<i>V</i> , Å ³	4498(2)	2075(7)	2191(14)	998.3(4)
<i>Z</i>	4	8	8	2
ρ_{calcd} , g/cm ³	3.493	3.614	3.692	3.334
μ , mm ⁻¹	12.731	13.116	12.268	16.856
<i>T</i> , K	293(2)	173(2)	293(2)	173(2)
λ , Å	0.71073	0.71073	0.71073	0.71073
Total reflections	41522	10825	10755	11159
Total unique	10309	1384	1392	1329
R(int)	0.1416	0.0653	0.0573	0.0387
No. of parameters	317	59	65	45
Goodnes of fit on F ²	0.855	1.144	1.306	1.090
Refinement method	Full-matrix least-squares on F ²			
R1 ^a	0.0602	0.0408	0.0658	0.0221
wR2 ^b	0.1227	0.0740	0.1548	0.0463

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

Table 2. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$, $\text{Cs}_2\text{CuAsS}_5$, $\text{Cs}_2\text{AgAsS}_5$, and $\text{Cs}_2\text{AuAsS}_4$.

Atom	x	y	z	Ueq ^a
$\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$				
Cs(1)	0.1585(1)	0.173(1)	0.1819(1)	34(1)
Cs(2)	0.3758(1)	0.128(1)	0.585(1)	32(1)
Cs(3)	0.5989(1)	0.392(1)	0.1888(1)	37(1)
Cs(4)	0.8562(1)	-0.5355(1)	0.0571(1)	39(1)
Cs(5)	0.5732(1)	-0.3477(1)	0.0411(1)	39(1)
Cs(6)	0.3818(1)	0.388(1)	0.3009(1)	39(1)
Cs(7)	-0.0683(1)	-0.0176(2)	0.0606(1)	42(1)
Cs(8)	0.3574(1)	0.3743(1)	0.1648(1)	36(1)
Cs(9)	0.0979(1)	-0.3530(1)	0.2605(1)	41(1)
Cs(10)	0.2041(1)	-0.3249(1)	0.0851(1)	43(1)
As(1)	0.3934(1)	-0.1991(2)	0.1890(1)	23(1)
As(2)	0.6133(1)	0.2361(2)	0.0639(1)	24(1)
As(3)	0.1678(1)	0.2257(2)	0.3141(1)	24(1)
As(4)	0.1422(1)	0.2433(2)	0.0537(1)	25(1)
Cu(1)	0.9718(2)	-0.5181(3)	0.1619(1)	35(1)
Cu(2)	0.7264(2)	-0.0524(3)	0.1056(1)	34(1)
S(1)	0.3699(3)	0.0201(5)	0.1764(2)	30(1)
S(2)	0.5080(3)	0.2804(6)	0.2545(2)	34(1)

S(3)	0.4324(3)	-0.2973(6)	0.1291(2)	36(1)
S(4)	0.2799(3)	-0.3001(5)	0.2065(2)	35(1)
S(5)	0.6061(3)	0.0085(5)	0.0638(2)	31(1)
S(6)	0.7072(3)	0.2924(5)	0.1243(2)	35(1)
S(7)	0.7981(3)	0.1400(6)	0.1293(2)	42(1)
S(8)	0.5015(3)	0.3317(6)	0.0808(2)	40(1)
S(9)	0.3480(3)	-0.3166(5)	-0.0028(2)	34(1)
S(10)	0.2196(3)	0.3278(6)	0.2613(2)	40(1)
S(11)	0.7553(3)	-0.2719(5)	0.1205(2)	39(1)
S(12)	0.1356(3)	0.0104(5)	0.2982(2)	36(1)
S(13)	-0.0446(3)	-0.1661(5)	0.1779(2)	34(1)
S(14)	0.0168(3)	-0.3080(6)	0.1412(2)	37(1)
S(15)	0.1348(3)	0.3354(5)	0.1235(2)	34(1)
S(16)	0.2571(3)	0.3403(5)	0.0406(2)	35(1)
S(17)	1.0325(3)	-0.6956(6)	0.0103(2)	41(1)
S(18)	0.0171(3)	0.2792(5)	0.1400(2)	34(1)
S(19)	0.1493(3)	0.0194(5)	0.0597(2)	33(1)

$\text{Cs}_2\text{CuAsS}_5$

Cs(1)	0.3589(1)	0.3252(1)	0	22(1)
Cs(2)	0.1049(1)	0.3893(1)	0	24(1)
As(1)	0.2617(1)	0.0931(1)	0	13(1)
Cu(1)	0.4338(1)	0.3727(1)	0.4449	20(1)
S(1)	0.5213(1)	0.2705(1)	0.2654	31(1)

S(2)	0.3127(1)	0.3020(1)	-0.5000	18(1)
S(3)	0.3879(1)	0.1129(1)	0	22(1)
S(4)	0.3924(2)	0.4868(2)	0.2993	13(1)

Cs₂AgAsS₅

Cs(1)	0.1806(1)	0.1424(1)	0	35(1)
Cs(2)	0.1161(1)	0.3974(1)	0	52(1)
Ag(1)	0.1250(5)	0.0600(5)	-0.5712(16)	39(3)
Ag(2)	0.1205(10)	0.0647(9)	-0.5000	37(6)
As(1)	0.0955(1)	0.2629(1)	-0.5000	22(1)
S(1)	0.0277(3)	0.2345(3)	-0.2590(7)	42(1)
S(2)	0.1988(3)	0.1943(3)	-0.5000	28(1)
S(3)	0.3878(4)	0.1151(4)	0	45(2)
S(4)	0.1161(5)	-0.0146(5)	-0.7418(13)	28(2)

Cs₂AuAsS₄

Cs(1)	0.7070(1)	0.0142	0.2500	16(1)
Cs(2)	-0.1025(1)	0.3345	0.2500	24(1)
Au(1)	0.3923(1)	0.2500	0	16(1)
As(1)	0.2236(1)	0.1131	0.2500	12(1)
S(1)	-0.0457(3)	0.1622	0.2500	20(1)
S(2)	-0.2046(3)	0.5078	0.2500	15(1)
S(3)	0.3916(2)	0.3626	0.0039	19(1)

^a Ueq is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$, $\text{Cs}_2\text{CuAsS}_5$, $\text{Cs}_2\text{AgAsS}_5$, and $\text{Cs}_2\text{AuAsS}_4$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$						
Cs(1)	31(1)	36(1)	36(1)	5(1)	6(1)	4(1)
Cs(2)	31(1)	34(1)	32(1)	-1(1)	6(1)	0(1)
Cs(3)	37(1)	40(1)	37(1)	2(1)	14(1)	0(1)
Cs(4)	36(1)	43(1)	36(1)	2(1)	2(1)	2(1)
Cs(5)	42(1)	28(1)	44(1)	-1(1)	-4(1)	-2(1)
Cs(6)	37(1)	38(1)	43(1)	2(1)	13(1)	2(1)
Cs(7)	38(1)	50(1)	37(1)	-5(1)	9(1)	0(1)
Cs(8)	37(1)	28(1)	43(1)	1(1)	0(1)	1(1)
Cs(9)	43(1)	40(1)	37(1)	8(1)	0(1)	-1(1)
Cs(10)	51(1)	32(1)	48(1)	3(1)	15(1)	3(1)
As(1)	24(1)	21(1)	24(1)	1(1)	4(1)	0(1)
As(2)	25(1)	22(1)	24(1)	1(1)	4(1)	0(1)
As(3)	21(1)	22(1)	28(1)	0(1)	2(1)	-2(1)
As(4)	27(1)	22(1)	28(1)	2(1)	7(1)	3(1)
Cu(1)	36(2)	35(2)	33(1)	-6(1)	2(1)	11(1)
Cu(2)	34(1)	36(2)	33(1)	3(1)	4(1)	9(1)
S(1)	32(3)	22(3)	35(3)	6(2)	3(2)	4(2)
S(2)	30(3)	42(3)	28(3)	-1(2)	-3(2)	-2(2)

S(3)	44(3)	37(3)	29(3)	-3(2)	13(2)	-2(3)
S(4)	28(3)	35(3)	45(3)	8(3)	14(2)	-1(2)
S(5)	32(3)	25(3)	33(3)	0(2)	-4(2)	-2(2)
S(6)	45(3)	30(3)	31(3)	-1(2)	2(2)	1(3)
S(7)	30(3)	47(4)	47(3)	-9(3)	-5(3)	2(3)
S(8)	38(3)	35(3)	50(3)	4(3)	19(3)	5(3)
S(9)	38(3)	38(3)	28(3)	3(2)	10(2)	-3(2)
S(10)	43(3)	33(3)	48(3)	5(3)	19(3)	-4(3)
S(11)	44(3)	28(3)	40(3)	-4(2)	-16(3)	3(2)
S(12)	44(3)	30(3)	37(3)	-12(2)	14(2)	-9(2)
S(13)	28(3)	34(3)	43(3)	2(2)	9(2)	-5(2)
S(14)	30(3)	42(3)	42(3)	-4(3)	18(2)	-4(2)
S(15)	34(3)	35(3)	34(3)	-5(2)	11(2)	-3(2)
S(16)	32(3)	29(3)	47(3)	0(3)	16(3)	-3(2)
S(17)	34(3)	46(4)	44(3)	14(3)	5(3)	11(3)
S(18)	31(3)	29(3)	47(3)	-1(2)	18(2)	0(2)
S(19)	35(3)	25(3)	39(3)	3(2)	2(2)	6(2)

$\text{Cs}_2\text{CuAsS}_5$

Cs(1)	14(1)	27(1)	26(1)	0	0	-1(1)
Cs(2)	18(1)	23(1)	31(1)	0	0	-1(1)
As(1)	9(1)	11(1)	18(1)	0	0	0(1)
Cu(1)	16(1)	21(1)	24(1)	4	-7	1(1)
S(1)	48(1)	17(1)	27(1)	-2	-24	2(1)

S(2)	12(1)	10(1)	32(1)	0	0	1(1)
S(3)	12(1)	21(1)	34(1)	0	0	-2(1)
S(4)	14(1)	13(1)	12(2)	1	2	-2(1)

Cs₂AgAsS₅

Cs(1)	32(1)	28(1)	46(1)	0	0	-3(1)
Cs(2)	52(1)	34(1)	70(2)	0	0	-6(1)
Ag(1)	52(4)	42(3)	23(8)	12(4)	-7(4)	11(3)
Ag(2)	45(5)	29(4)	37(18)	0	0	0(3)
As(1)	20(1)	21(1)	26(1)	0	0	0(1)
S(1)	48(3)	34(2)	42(3)	-1(2)	22(2)	-3(2)
S(2)	23(3)	25(3)	38(4)	0	0	3(2)
S(3)	33(3)	22(3)	82(6)	0	0	-2(3)
S(4)	28(4)	26(4)	29(5)	0(3)	-1(4)	-1(3)

Cs₂AuAsS₄

Au(1)	18(1)	11(1)	17(1)	3(1)	0	0
Cs(1)	16(1)	16(1)	17(1)	0	0	-1(1)
Cs(2)	36(1)	18(1)	19(1)	0	0	4(1)
As(1)	17(1)	9(1)	10(1)	0	0	1(1)
S(1)	18(1)	17(1)	24(1)	0	0	6(1)
S(2)	19(1)	9(1)	18(1)	0	0	-1(1)
S(3)	29(1)	12(1)	15(1)	2(1)	-6(1)	-1(1)

* The anisotropic displacement factor exponent takes the form:

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

C. Results and Discussion

C.1 Synthesis

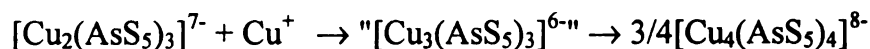
$\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ was first obtained from a reaction of $\text{Cs}_2\text{S}/\text{Cu}/\text{As}_2\text{S}_3/\text{S}$ in the ratio 4/1/1/10 as the minor product, the major product being $\text{Cs}_2\text{CuAsS}_5$. A direct combination of the reactants to produce $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ gave a mixture of this compound with $\text{Cs}_2\text{CuAsS}_5$. $\text{Cs}_2\text{CuAsS}_5$ is a molecular based salt with $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ clusters. $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ is a mixed salt with co-crystallized anions $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ and AsS_4^{3-} . We also observed a new phase (EDS: $\sim\text{Cs}_4\text{CuAs}_2\text{S}_6$) on changing the amount of Cs_2S to 2 equivalents. This was obtained as a pure phase but we were unable to solve the structure. Other ratios of Cs_2S usually gave $\text{Cs}_2\text{CuAsS}_5$ along with Cu_3AsS_4 and Cs_3AsS_4 .

In the case of $\text{Cs}_2\text{AgAsS}_5$, a pure phase was obtained from a reaction of 2/1/1/8 of $\text{Cs}_2\text{S}/\text{Ag}/\text{As}_2\text{S}_3/\text{S}$. Changing the reaction parameters like the flux basicity, the amount of metal or the amount of As_2S_3 usually led to the formation of $\text{Cs}_2\text{AgAsS}_5$ and/or glassy matrices. Similar behavior was observed in the reactions with Au. Pure $\text{Cs}_2\text{AuAsS}_4$ was obtained from a ratio of 2/1/1/10 of $\text{Cs}_2\text{S}/\text{Au}/\text{As}_2\text{S}_3/\text{S}$. Increasing the amount of Cs_2S usually gave the $\text{Cs}_2\text{AuAsS}_4$ along with Cs_3AsS_4 or $\text{Cs}_4\text{As}_2\text{S}_{10}$.

The reactions of Cu, Ag and Au in corresponding potassium and rubidium fluxes produced mostly Cu_3AsS_4 , KAg_2AsS_4 , $\text{RbAg}_2\text{AsS}_4$, K_2AuAsS_4 and A_3AsS_4 .

$\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$, $\text{Cs}_2\text{CuAsS}_5$, $\text{Cs}_2\text{AgAsS}_5$ and $\text{Cs}_2\text{AuAsS}_4$ are stable in air and insoluble in DMF and ethanol. However $\text{Cs}_2\text{CuAsS}_5$ (along with $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$) and $\text{Cs}_2\text{AgAsS}_5$ dissolve in water and form a clear, pale yellow solution after a few minutes, which turns milky in about half an hour. This indicates that the clusters decompose in water.

The $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ and $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ clusters differ only by a Cu atom and it would be expected that the latter might form in regions of slightly higher Cu^+ concentrations:



C.2 Structure description of $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$

The unit cell of $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ is shown in Figure 1a. The structure contains two co-crystallized anions, $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ and AsS_4^{3-} , charge balanced by Cs^+ cations. Figure 1b shows a clearer view of the disposition of the two anions in the unit cell. The two anions are shown in Figure 1c. The $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ anion is a very unusual species and consists of two Cu^+ ions coordinated by three tetrahedral AsS_5^{3-} ligands in a trigonal planar geometry. The AsS_5^{3-} anion is derived from the tetrahedral AsS_4^{3-} unit by substituting a terminal sulfur atom with a disulfide arm. Each Cu^+ ion is linked to two AsS_5^{3-} ligands. One of these ligands is terminal, while the other serves to bridge the two Cu cations. The bridging AsS_5^{3-} ligand uses an edge to bind to Cu(1) and a corner to link to Cu(2). The terminal AsS_5^{3-} ligand attached to Cu(1) uses its disulfide end to coordinate in a monodentate fashion to complete the trigonal planar geometry. The terminal AsS_5^{3-} ligand on Cu(2) uses its disulfide arm and a monosulfide end to coordinate in a bidentate chelating mode.

The co-crystallized anion in this lattice is the tetrahedral AsS_4^{3-} unit. It is surprising that this anion chose to crystallize along with the other anion rather than find a cation like Cs^+ or Cu^+ to form the well-known Cs_3AsS_4 or Cu_3AsS_4 . A possible explanation for this behavior could be that $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ is an intermediate compound that crystallizes first.

In our reactions, $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ always forms with $\text{Cs}_2\text{CuAsS}_5$, which is probably a thermodynamically more stable compound.

The Cu-S bond lengths in $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ are normal at 2.199(6) Å, 2.221(6) Å, 2.248(6) Å for Cu(1) and 2.187(6) Å, 2.228(5) Å and 2.236(6) Å for Cu(2). As-S distances range from 2.157(5) Å to 2.175(5) Å for As(1), 2.121(6) Å to 2.251(5) Å for As(2), 2.102(5) Å to 2.262(5) Å for As(3) and 2.122(5) Å to 2.264(5) Å for As(4). The S-S bond lengths are 2.064(7) Å, 2.072(7) Å and 2.050(8) Å. There are Cs-Cu distances comparable to Cs-S distances. S-Cu-S angles are distorted from the ideal trigonal planar angle of 120°. S-As-S angles deviate slightly from the tetrahedral angle of 109°. A list of selected bond distances and angles for **I**, **II**, and **IV** is given in Tables 4 and 5.

A compound, similar to the $[\text{Cu}_2(\text{AsS}_5)_3]^{7-}$ anion, and consisting of five member rings containing Cu is $(\text{Ph}_4\text{P})_4[\text{Cu}_2\text{Se}_{14}]$.²⁹ This compound has a tetra-selenide ligand, Se_4^{2-} that ligates to the Cu^+ ion in a bidentate fashion. This creates a five-member ring. Two such rings are bridged together by a hexaselenide ligand, Se_6^{2-} .

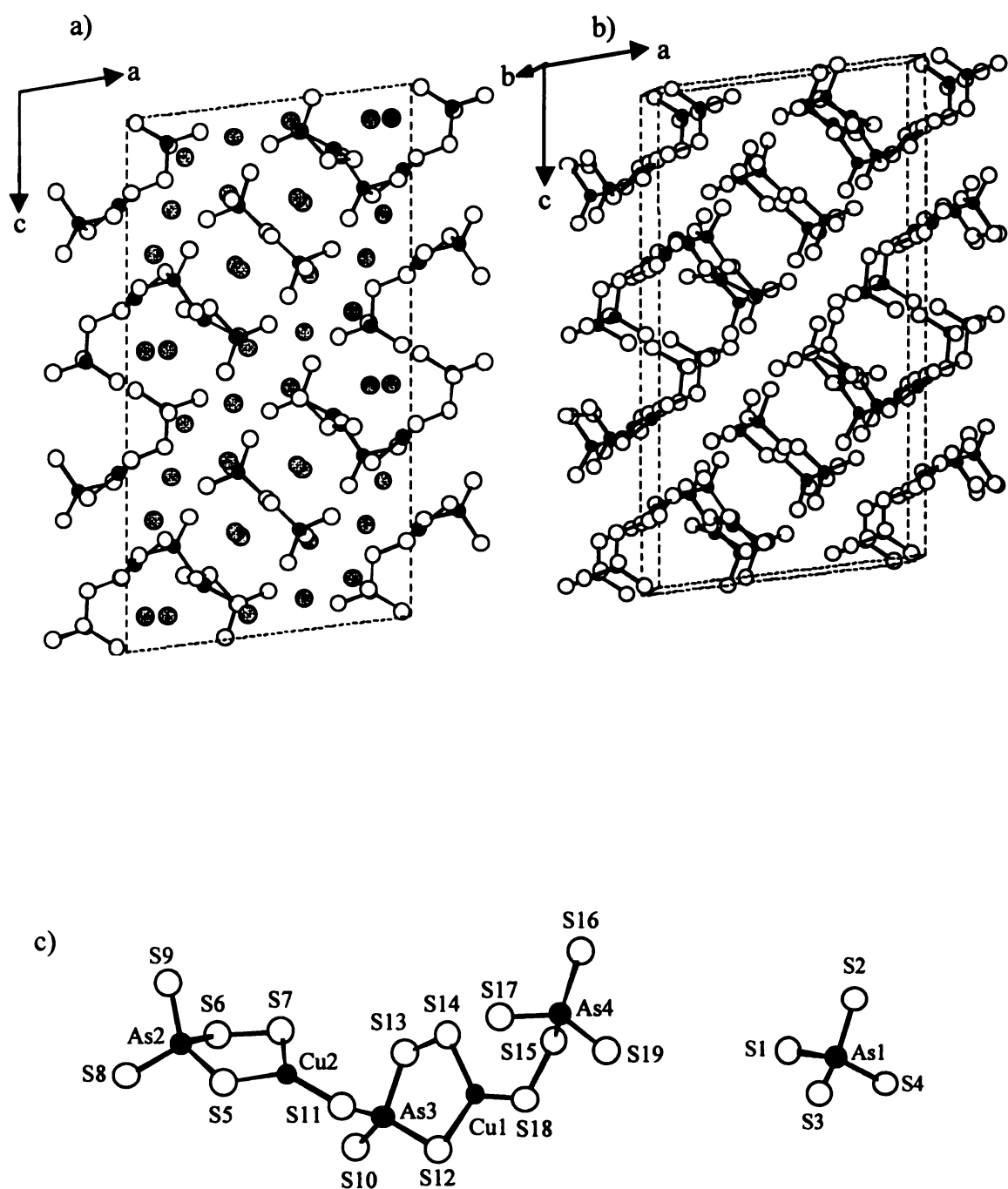


Figure 1. a) The unit cell of $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ b) The unit cell showing a clear view of the two co-crystallized anions $\text{Cu}_2\text{As}_3\text{S}_{15}^{7-}$ and AsS_4^{3-} . Cs^+ ions have been removed for clarity. b) The $\text{Cu}_2(\text{AsS}_5)_3^{7-}$ and the AsS_4^{3-} anions.

Table 4. Selected bond distances for Cs₁₀Cu₂As₄S₁₉, Cs₂CuAsS₅ and Cs₂AuAsS₄.

Cs ₁₀ Cu ₂ As ₄ S ₁₉					
Cu(1)-S(18)	2.199(6)	Cs(2)-S(16)	3.669(5)	Cs(6)-S(10)	3.872(6)
Cu(1)-S(12)	2.221(6)	Cs(2)-S(8)	3.670(6)	Cs(7)-S(7)	3.474(6)
Cu(1)-S(14)	2.248(6)	Cs(2)-S(5)	3.675(5)	Cs(7)-S(19)	3.495(5)
Cu(2)-S(11)	2.187(6)	Cs(2)-S(3)	3.681(5)	Cs(7)-S(17)	3.548(6)
Cu(2)-S(5)	2.228(5)	Cs(3)-S(2)	3.459(5)	Cs(7)-S(19)	3.636(5)
Cu(2)-S(7)	2.236(6)	Cs(3)-Cu(2)	3.499(3)	Cs(7)-Cu(2)	3.707(3)
As(1)-S(2)	2.157(5)	Cs(3)-S(2)	3.551(5)	Cs(7)-S(13)	3.731(5)
As(1)-S(1)	2.158(5)	Cs(3)-S(1)	3.634(5)	Cs(7)-S(14)	3.804(6)
As(1)-S(3)	2.168(5)	Cs(3)-S(6)	3.655(5)	Cs(7)-S(17)	3.865(6)
As(1)-S(4)	2.175(5)	Cs(3)-S(10)	3.689(6)	Cs(8)-S(1)	3.414(5)
As(2)-S(8)	2.121(6)	Cs(3)-S(5)	3.732(5)	Cs(8)-S(2)	3.472(5)
As(2)-S(9)	2.131(5)	Cs(3)-S(4)	3.773(5)	Cs(8)-S(3)	3.573(5)
As(2)-S(5)	2.184(5)	Cs(4)-Cu(1)	3.412(3)	Cs(8)-S(8)	3.619(5)
As(2)-S(6)	2.251(5)	Cs(4)-S(17)	3.596(6)	Cs(8)-S(15)	3.629(5)
As(3)-S(10)	2.102(5)	Cs(4)-S(17)	3.630(6)	Cs(8)-S(4)	3.631(6)
As(3)-S(11)	2.160(5)	Cs(4)-S(11)	3.643(6)	Cs(8)-S(16)	3.838(5)
As(3)-S(12)	2.163(5)	Cs(4)-S(6)	3.680(5)	Cs(8)-S(10)	3.847(5)
As(3)-S(13)	2.262(5)	Cs(4)-S(16)	3.720(5)	Cs(9)-S(7)	3.474(5)
As(4)-S(17)	2.122(5)	Cs(4)-S(9)	3.729(5)	Cs(9)-S(4)	3.526(5)
As(4)-S(16)	2.136(5)	Cs(4)-S(18)	3.768(5)	Cs(9)-S(13)	3.602(5)
As(4)-S(19)	2.154(5)	Cs(5)-S(5)	3.505(5)	Cs(9)-S(10)	3.622(6)

As(4)-S(15)	2.264(5)	Cs(5)-S(8)	3.531(6)	Cs(9)-S(14)	3.635(5)
Cs(1)-S(1)	3.399(5)	Cs(5)-S(11)	3.576(5)	Cs(9)-S(13)	3.668(5)
Cs(1)-S(18)	3.497(5)	Cs(5)-S(8)	3.663(6)	Cs(9)-S(12)	3.683(5)
Cs(1)-S(15)	3.502(5)	Cs(5)-S(9)	3.680(5)	Cs(9)-Cu(1)	3.689(3)
Cs(1)-S(12)	3.513(5)	Cs(5)-S(3)	3.684(5)	Cs(9)-S(18)	3.878(5)
Cs(1)-S(19)	3.605(5)	Cs(5)-S(9)	3.685(5)	Cs(10)-S(19)	3.472(5)
Cs(1)-S(4)	3.630(5)	Cs(5)-S(16)	3.855(5)	Cs(10)-S(14)	3.604(5)
Cs(1)-S(13)	3.678(5)	Cs(6)-S(2)	3.465(6)	Cs(10)-S(16)	3.610(5)
Cs(1)-S(10)	3.842(6)	Cs(6)-S(2)	3.558(5)	Cs(10)-S(4)	3.656(5)
Cs(2)-S(1)	3.508(5)	Cs(6)-S(6)	3.646(5)	Cs(10)-S(15)	3.664(5)
Cs(2)-S(19)	3.622(5)	Cs(6)-S(1)	3.677(5)	Cs(10)-S(9)	3.685(5)
Cs(2)-S(9)	3.640(5)	Cs(6)-S(3)	3.745(6)	Cs(10)-S(3)	3.723(6)
Cs(2)-S(5)	3.661(5)	Cs(6)-S(11)	3.845(6)		

Cs₂CuAsS₅

Cu(1)-Cu(1)	0.820(3)	As(1)-S(2)	2.148(2)	Cs(1)-Cu(1)	2 x 3.6229(16)
Cu(1)-S(4)	2.298(3)	As(1)-S(3)	2.135(2)	Cs(2)-S(3)	3.639(2)
Cu(1)-S(4)	2.342(3)	Cs(1)-S(1)	2 x 3.4779(18)	Cs(2)-S(1)	2 x 3.711(2)
Cu(1)-S(2)	2.378(3)	Cs(1)-S(4)	2 x 3.543(3)	Cs(2)-S(3)	2 x 3.7178(9)
Cu(1)-S(1)	2.615(2)	Cs(1)-S(1)	2 x 3.556(2)	Cs(2)-S(3)	3.725(2)
Cu(1)-S(4)	2.780(3)	Cs(1)-S(2)	3.570(2)	Cs(2)-S(1)	2 x 3.824(2)
S(1)-S(4)	2.058(3)	Cs(1)-S(3)	3.582(2)	Cs(2)-S(2)	3.481(2)
As(1)-S(1)	2 x 2.1839(18)	Cs(1)-S(4)	2 x 3.585(3)		

$\text{Cs}_2\text{AuAsS}_4$

Au(1)-S(3)	2 x 2.2818(14)	Cs(1)-S(2)	3.485(2)	Cs(2)-S(2)	3.5850(19)
As(1)-S(1)	2.116(2)	Cs(1)-S(2)	3.452(2)	Cs(2)-S(1)	3.514(2)
As(1)-S(2)	2.1381(19)	Cs(1)-S(2)	2 x 3.6319(8)	Cs(2)-S(1)	2 x 3.5743(8)
As(1)-S(3)	2 x 2.2026(14)	Cs(1)-S(3)	2 x 3.6025(15)	Cs(2)-S(3)	2 x 3.8876(16)
Cs(1)-S(1)	3.456(2)	Cs(1)-S(3)	2 x 3.7781(15)		

C.3 Structure description of Cs_2MAsS_5 ($\text{M} = \text{Cu}, \text{Ag}$)

$\text{Cs}_2\text{CuAsS}_5$ and $\text{Cs}_2\text{AgAsS}_5$ are isostructural. Therefore we will only discuss the structural details of $\text{Cs}_2\text{CuAsS}_5$. Figure 2a shows the unit cell of this compound. As we can see, the compound consists of discrete, molecular tetrameric $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ anions which sit on the crystallographic $4/m$ site. The four metal centers define a perfect square with sides of 3.390(1) Å. Within each tetramer, Cu is tetrahedral and coordinated by two AsS_5^{3-} ligands. Figure 2b shows an individual cluster. Each AsS_5^{3-} ligand uses two of its monosulfide arms to coordinate to two adjacent Cu atoms. The terminal sulfur atom of the disulfide arm forms a direct bridge between the same pair of Cu atoms. The remaining sulfur atom in the AsS_5^{3-} ligand is terminal and non-bonding.

Cu occupies a distorted tetrahedral site with Cu-S bond lengths ranging from 2.298(3) Å to 2.780(3) Å, Table 4. S-Cu-S angles vary between $100.91(10)^\circ$ to $118.94(16)^\circ$, Table 5. The tetrahedral As consists of As-S bond distances in the range 2.135(2) to 2.1839(18) Å. S-As-S angles vary from $105.97(12)^\circ$ to $116.48(9)^\circ$. S-S distance is 2.058(3) Å. Cs-Cu bond lengths that are similar to Cs-S distances are observed.

The $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ cluster is structurally related to that of another tetranuclear cluster anion, $[\text{Hg}_4(\text{Se}_2)_2(\text{PSe}_4)_4]^{8-}$.³⁰ This compound crystallizes in $P4_2/n$, which is a non-isomorphic sub group of $I4/m$. The compound consists of tetrahedral Hg^{2+} ions that are coordinated and bridged by tetrahedral PSe_4^{3-} ligands. In addition, the Hg atoms are also bridged by Se_2^{2-} dumbbells. The structure of this compound is shown in figure 2c. The non-bonding Se atoms on the PSe_4^{3-} ligand interact with the diselenide ligand. In $\text{Cs}_2\text{CuAsS}_5$, the disulfide ligand that connects two trans-metal atoms is absent, instead it is present as one of the arms of the thioarsenate ligand and bridges two cis-metal atoms.

The structure of the $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ cluster can be derived from the structure of the $[\text{Hg}_4(\text{Se}_2)_2(\text{PSe}_4)_4]^{8-}$ cluster. The transformation involves the reductive cleavage, by $4e^-$, of the diselenide bonds followed by oxidative coupling of the resulting 4 Se^{2-} ions to one of the terminal Se atoms on the PSe_4^{3-} ligand. Since the reduction of two diselenide bonds requires $4e^-$ whereas the coupling of 4 Se^{2-} ions involves $8e^-$, there is a net gain of $4e^-$. This difference is accounted for by reducing the charge on the cation by substituting Hg^{2+} with Cu^+ . A schematic representation of this transformation is shown in Figure 3.

C.4 Structure description of $\text{Cs}_2\text{AuAsS}_4$

The structure of $\text{Cs}_2\text{AuAsS}_4$ is very simple and shown in Figure 4. The compound consists of one dimensional $[\text{Au}(\text{AsS}_4)]^{2-}$ chains propagating down the c- axis. The chains are composed of a linear Au^+ coordinated by two AsS_4^{3-} ligands. Each AsS_4 unit ligates to two Au atoms. The linear coordination of Au^+ prevents the anion in this compound to adopt the cluster structure of the Cu and Ag analogs.

This compound is isostructural to its thiophosphate counterpart, Cs_2AuPS_4 ¹¹ and similar but not isostructural to K_2AuAsS_4 ²⁴. Au-S distance of 2.2818(14) Å compare well with the above mentioned compounds. As-S bond lengths vary from 2.116(2) to 2.2026(14). The distance between two Au atoms in a chain is 3.552(1) Å ruling out any significant Au---Au interactions. Cs(1) is surrounded by 9 S atoms at distances ranging from 3.456(2) to 3.7781(15) Å while Cs(2) interacts with 6 S atoms at distances between 3.514(2) to 3.8876(16) Å. Au is linear with S-Au-S bond angle of 179.77(7)°. Similarly, S-As-S angles deviate very slightly from the tetrahedral angle.

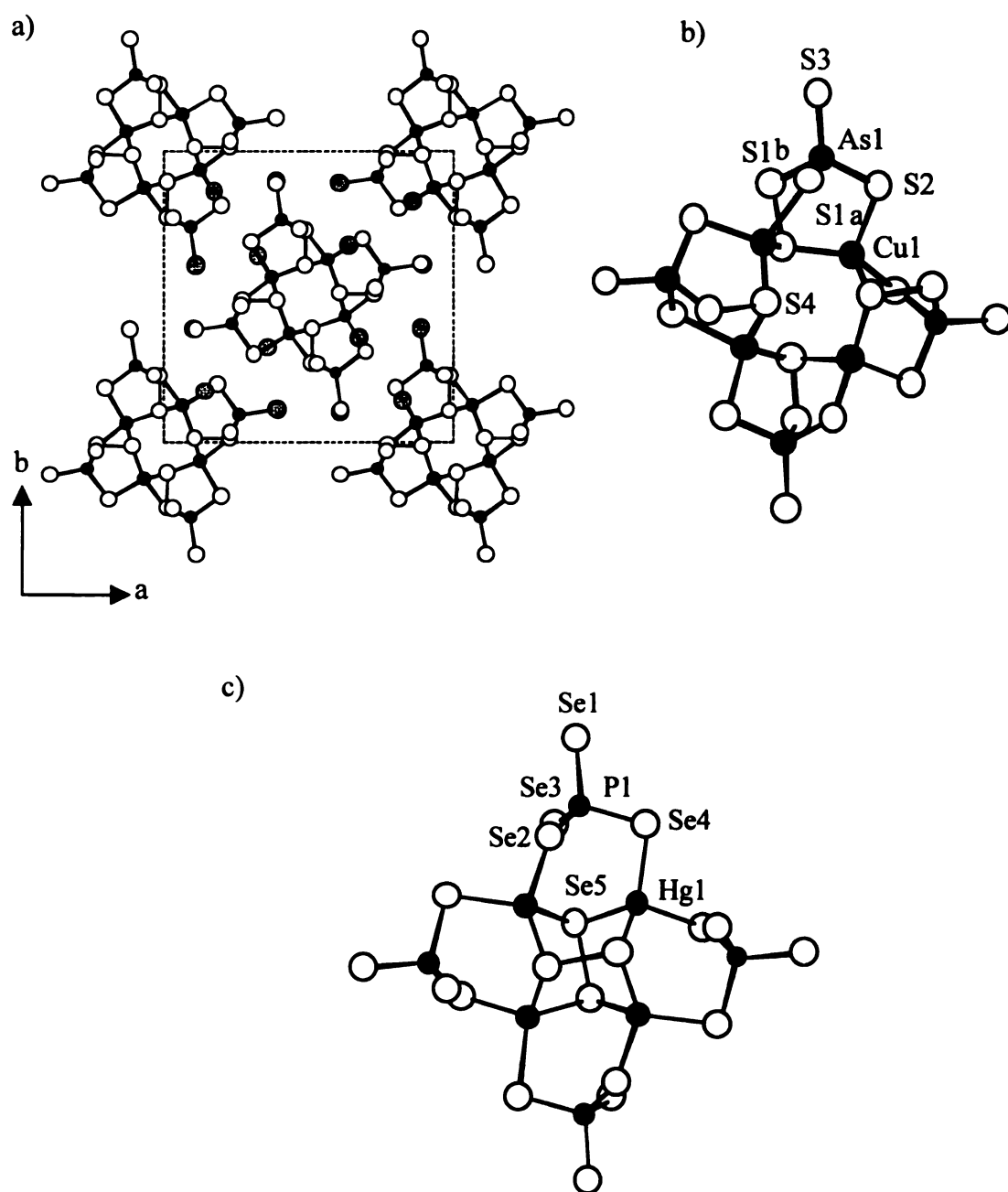


Figure 2. a) The unit cell of $\text{Cs}_2\text{CuAsS}_5$. b) The single tetrameric cluster anion $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ c) The $[\text{Hg}_4(\text{PSe}_4)_4(\text{Se}_2)_2]^{8-}$ cluster.

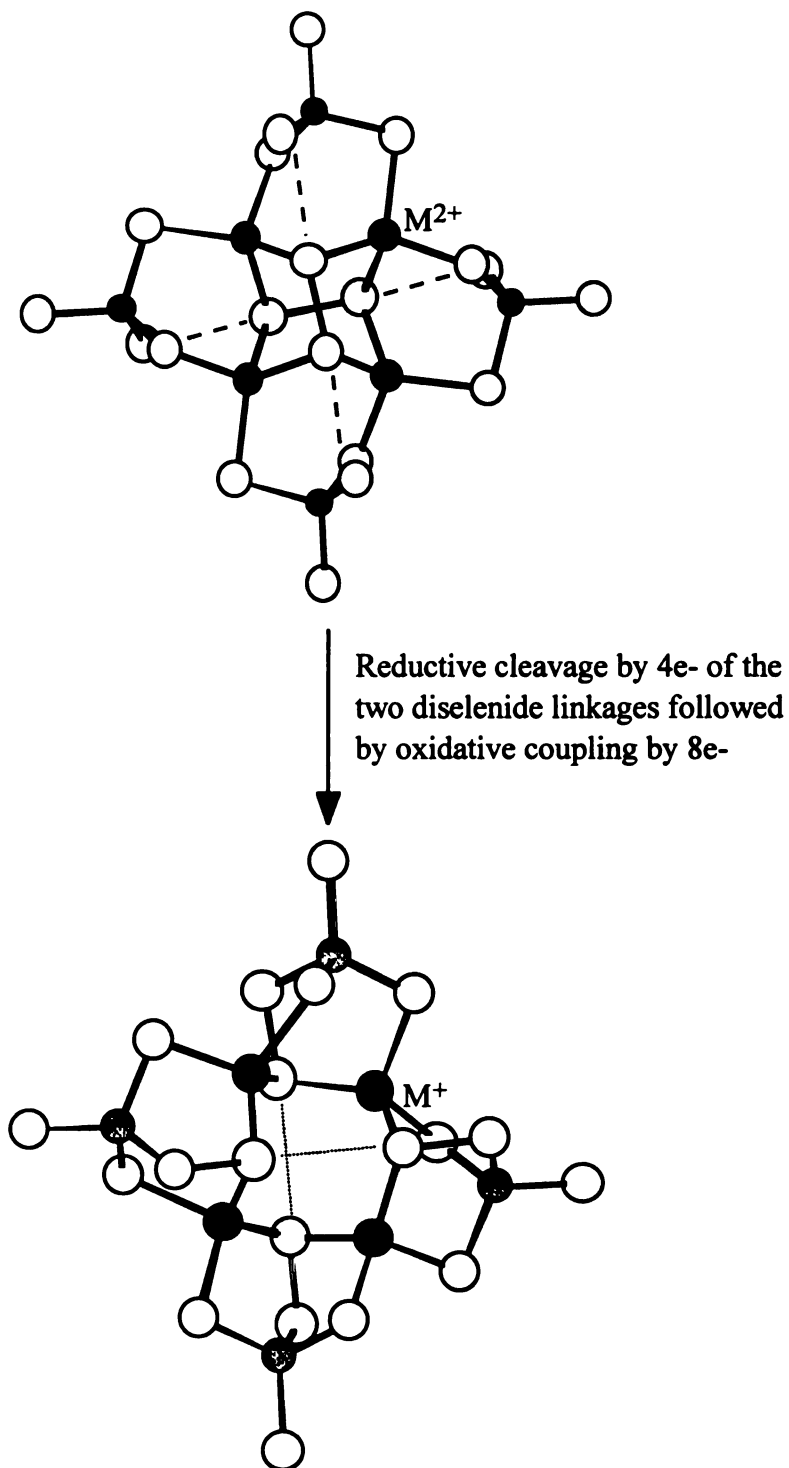


Figure 3. Schematic representation of the transformation of $[\text{Hg}_4(\text{Se}_2)(\text{PSe}_4)_4]^{8-}$ cluster to $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ cluster. The dotted lines indicate the breaking of the Se-Se bond in the former cluster followed by the formation of the diselenide bond in the thioarsenate ligand in the latter compound.

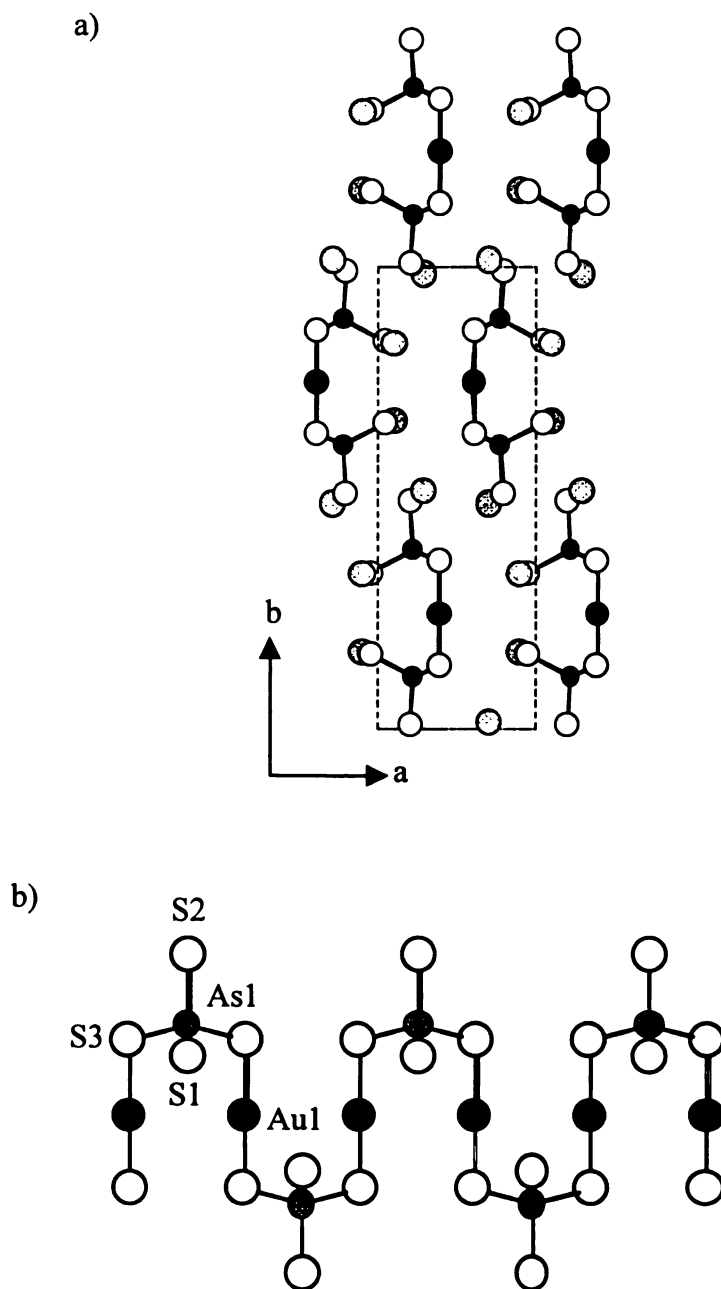


Figure 4. a) The unit cell of $\text{Cs}_2\text{AuAsS}_4$ looking down the c -axis. b) A single chain of $[\text{AuAsS}_4]^{2-}$ running along the c -axis.

Table 5. Selected bond angles for Cs₁₀Cu₂As₄S₁₉, Cs₂CuAsS₅ and Cs₂AuAsS₄.

Cs ₁₀ Cu ₂ As ₄ S ₁₉			
S(18)-Cu(1)-S(12)	124.8(2)	S(8)-As(2)-S(6)	101.9(2)
S(18)-Cu(1)-S(14)	125.6(2)	S(9)-As(2)-S(6)	110.7(2)
S(12)-Cu(1)-S(14)	109.3(2)	S(5)-As(2)-S(6)	105.71(19)
S(11)-Cu(2)-S(5)	120.6(2)	S(10)-As(3)-S(11)	115.5(2)
S(11)-Cu(2)-S(7)	130.0(2)	S(10)-As(3)-S(12)	112.7(2)
S(5)-Cu(2)-S(7)	109.3(2)	S(11)-As(3)-S(12)	107.3(2)
S(2)-As(1)-S(1)	108.5(2)	S(10)-As(3)-S(13)	107.1(2)
S(2)-As(1)-S(3)	109.8(2)	S(11)-As(3)-S(13)	107.7(2)
S(1)-As(1)-S(3)	110.0(2)	S(12)-As(3)-S(13)	105.9(2)
S(2)-As(1)-S(4)	108.9(2)	S(17)-As(4)-S(16)	115.6(2)
S(1)-As(1)-S(4)	110.0(2)	S(17)-As(4)-S(19)	110.8(2)
S(3)-As(1)-S(4)	109.6(2)	S(16)-As(4)-S(19)	114.2(2)
S(8)-As(2)-S(9)	112.7(2)	S(17)-As(4)-S(15)	108.2(2)
S(8)-As(2)-S(5)	112.7(2)	S(16)-As(4)-S(15)	98.1(2)
S(9)-As(2)-S(5)	112.3(2)	S(19)-As(4)-S(15)	108.7(2)
Cs ₂ CuAsS ₅			
S(4)-Cu(1)-S(2)	114.32(9)	S(3)-As(1)-S(2)	116.48(9)
S(4)-Cu(1)-S(4)	115.83(14)	S(3)-As(1)-S(1)	109.15(6)
S(4)-Cu(1)-S(1)	118.04(10)	S(2)-As(1)-S(1)	107.79(7)
S(4)-Cu(1)-S(1)	100.91(10)	S(3)-As(1)-S(1)	109.15(6)

S(2)-Cu(1)-S(1)	103.83(8)	S(2)-As(1)-S(1)	107.79(7)
S(4)-Cu(1)-S(4)	118.94(16)	S(1)-As(1)-S(1)	105.97(12)
S(4)-Cu(1)-S(2)	103.75(10)		

Cs₂AuAsS₄

S(3)-Au(1)-S(3)	179.77(7)	S(2)-As(1)-S(3)	2 x 104.85(5)
S(1)-As(1)-S(2)	114.55(8)	S(3)-As(1)-S(3)	109.92(8)
S(1)-As(1)-S(3)	2 x 111.15(5)		

C.5 Spectroscopy

Diffuse reflectance spectra in the UV/Vis/near-IR region of $\text{Cs}_2\text{CuAsS}_5$, $\text{Cs}_2\text{AgAsS}_5$ and $\text{Cs}_2\text{AuAsS}_4$ are shown in Figure 5. The spectra show sharp absorption onsets at 2.1, 2.41 and 2.54 eV respectively corresponding to their orange and yellow colors. In the case of $\text{Cs}_2\text{CuAsS}_5$ and $\text{Cs}_2\text{AgAsS}_5$, since there are no strong inter-cluster forces, the absorption must be intra-cluster in nature and as such an appropriate description would be a HOMO-LUMO type of transition.

Far-IR spectra of the three compounds are shown in Figure 6. The spectra of $\text{Cs}_2\text{CuAsS}_5$ and $\text{Cs}_2\text{AgAsS}_5$ are very similar. The peaks occurring between $380\text{--}450\text{ cm}^{-1}$ are attributed to As-S stretching vibrations.³¹ The weak peak at 470 cm^{-1} in figure 5a and the strong peak at 488 cm^{-1} in figure 5b are due to S-S asymmetric stretching.³² Noticeably this peak is absent in the spectrum of $\text{Cs}_2\text{AuAsS}_4$ corresponding to the lack of S-S bond in this structure. Also, we can correlate the peaks due to As-S stretching in this compound to the other two. Similar frequencies are observed for the compounds APbAsS_4 and $\text{A}_4\text{PbAs}_2\text{S}_8$, both of which feature the tetrahedral AsS_4^{3-} ligand.³³ Table 6 lists the peaks observed for the three compounds. The vibrations below 380 cm^{-1} can be assigned to M-S stretching or As-S bending modes.

Table 6. Comparison of IR frequencies of $\text{Cs}_2\text{CuAsS}_5$, $\text{Cs}_2\text{AgAsS}_5$ and $\text{Cs}_2\text{AuAsS}_4$.

Compound	IR frequency (cm^{-1} , w = weak; m = medium; s = strong)
$\text{Cs}_2\text{CuAsS}_5$	188(s), 211(s), 359(m), 414 (m-s), 430(m-s), 451(m), 470(w-m)
$\text{Cs}_2\text{AgAsS}_5$	184(s), 198(s), 227(s), 357(s), 395(s), 435(m-s), 450(m-s), 488(s)
$\text{Cs}_2\text{AuAsS}_4$	194(s), 208(m), 253(m-s), 310(m-s), 356(s), 386(s), 422(s), 433(s), 450(s)

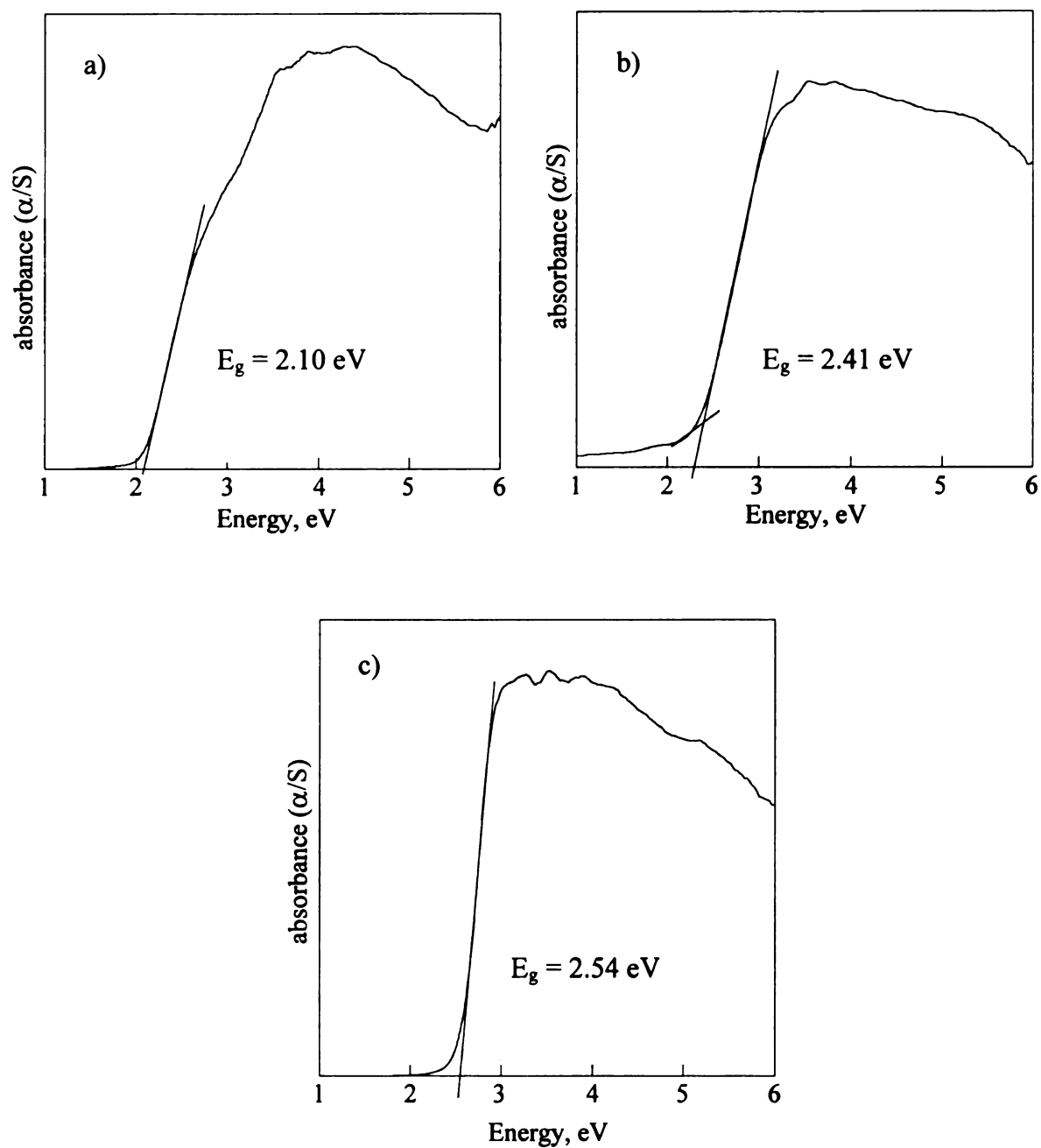


Figure 5. Diffuse reflectance spectra of a) $\text{Cs}_2\text{CuAsS}_5$ showing a sharp absorption at 2.10 eV b) $\text{Cs}_2\text{AgAsS}_5$ showing an absorption at 2.41 eV. The molecular nature of these clusters implies that the absorption is HOMO-LUMO transition. c) $\text{Cs}_2\text{AuAsS}_4$ displays a steep slope at 2.54 eV corresponding to its bright yellow color.

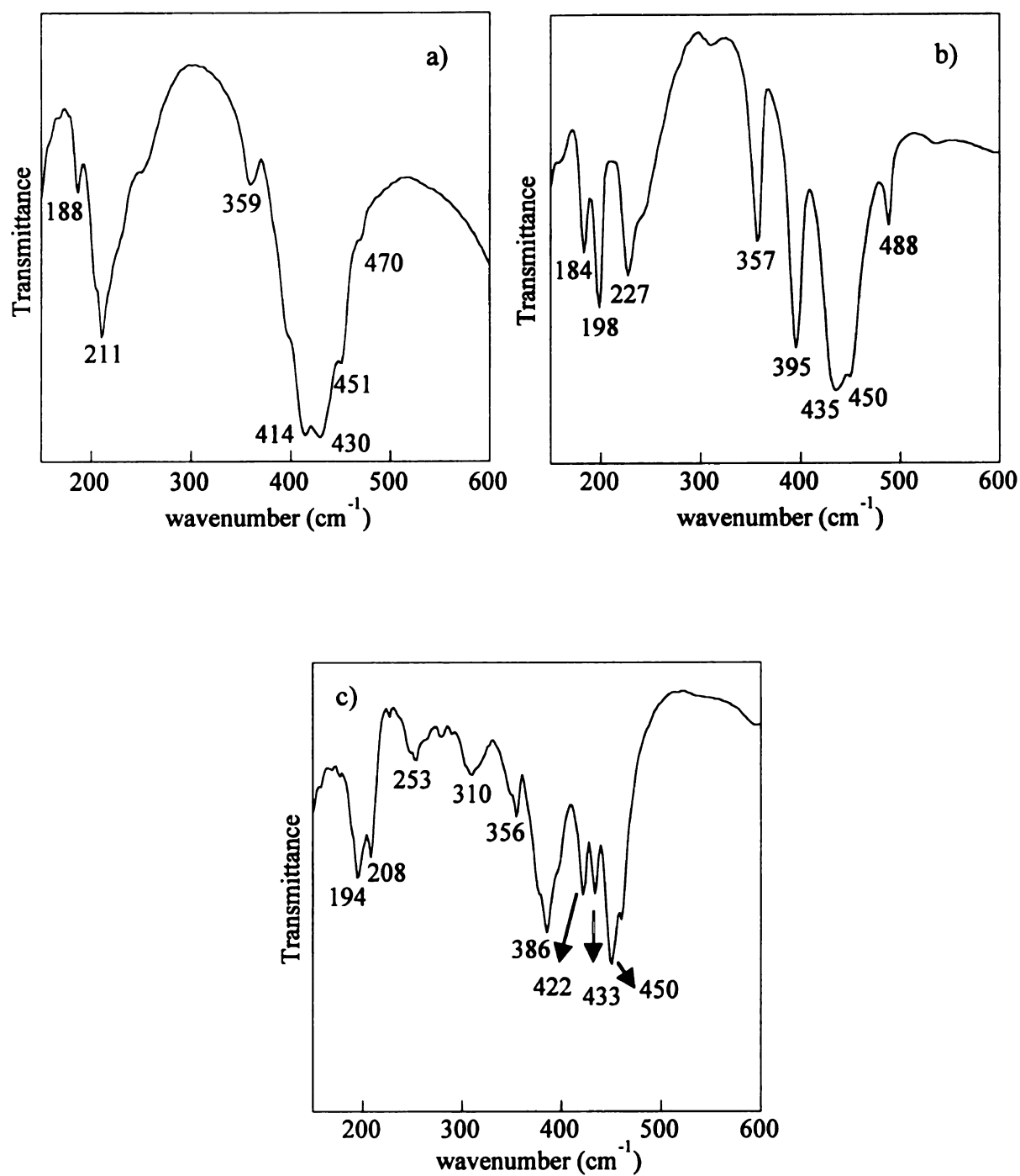
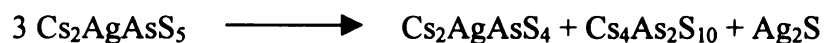


Figure 6. Far- IR spectra of a) $\text{Cs}_2\text{CuAsS}_5$, b) $\text{Cs}_2\text{AgAsS}_5$ and c) $\text{Cs}_2\text{AuAsS}_4$. The peak at 470 cm^{-1} for II and 488 cm^{-1} for III are due to S-S asymmetric stretching. The peaks between 400 and 450 cm^{-1} are due to As-S stretching.

C.6 Differential Thermal Analysis

$\text{Cs}_2\text{AuAsS}_4$ melts at $\sim 470^\circ\text{C}$ and recrystallizes upon cooling at 430°C . Figure 7 displays the differential thermal analysis plot showing the two events. The first cycle shows an endothermic melting peak at 474°C and an exothermic recrystallization peak at 430°C . In the second cycle, the melting point shifts slightly to 467°C while the recrystallization temperature remains the same. This shift in the melting peaks in the two cycles is due to the very fast heating rates ($10^\circ\text{C}/\text{min}$) used in the DTA. The powder pattern of the residue taken after the DTA matches the one taken before the start of the experiment indicating congruent melting.

We also measured the thermal behavior of $\text{Cs}_2\text{AgAsS}_5$. This compound decomposes at 346°C to give $\text{Cs}_2\text{AgAsS}_4$, $\text{Cs}_4\text{As}_2\text{S}_{10}$ and Ag_2S according to the following reaction:



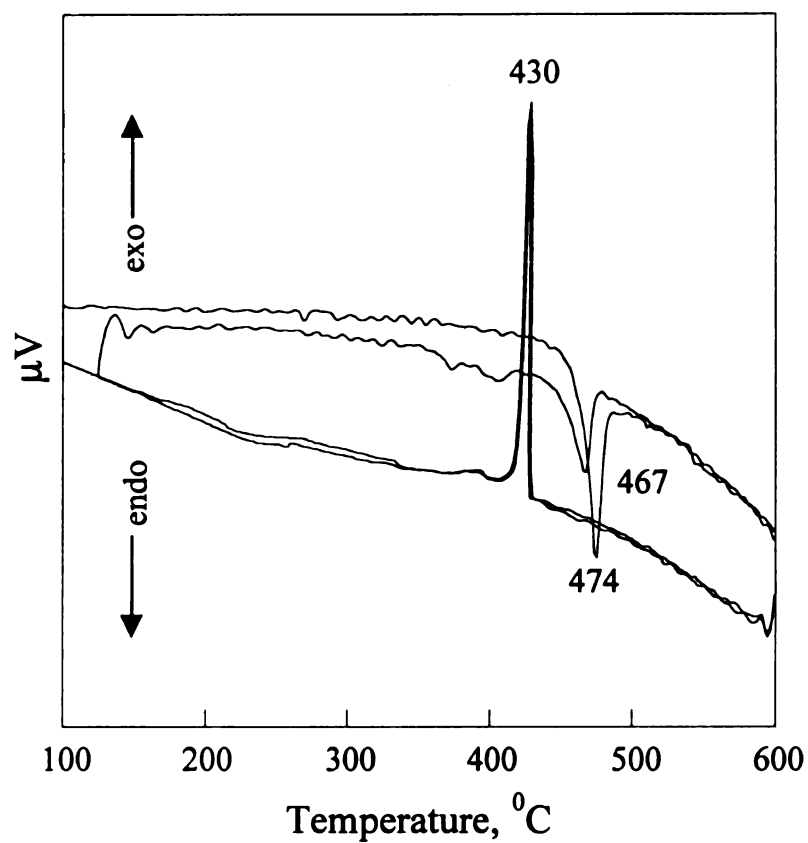


Figure 7. Differential Thermal Analysis of $\text{Cs}_2\text{AuAsS}_4$ showing a melting point at $\sim 470^\circ\text{C}$ and an exothermic crystallization peak at 430°C . The powder pattern of the product after the DTA matched the one before indicating a congruently melting compound.

D. Concluding Remarks

The reactions of main group metals In, Sn, Pb and Bi in thioarsenate fluxes have shown that the basicity of the metal was an important parameter in determining the oxidation state of As and the presence of disulfide linkages in the resulting thioarsenate ligands. In general, we observed that for a given flux, as the size of the metal increases the tendency to form As^{5+} increases and the tendency to form S-S bonds decreases. Thus the very acidic Sn^{4+} promotes the formation of As^{3+} and S-S linkages in its compounds while the basic Bi^{3+} forms compounds containing the tetrahedral AsS_4^{3-} anion. This observation holds true in the chemistry of coinage metals in cesium thioarsenate fluxes. As we go from Cu to Au, the thioarsenate ligand changes from the AsS_5^{3-} anion, which contains a disulfide arm, to the AsS_4^{3-} ligand. This understanding of the flux chemistry is a step ahead in the rational design of new compounds by using molten fluxes. $\text{Cs}_{10}\text{Cu}_2\text{As}_4\text{S}_{19}$ is an intermediate product leading to the more stable $\text{Cs}_2\text{CuAsS}_5$. It may be possible to obtain the Au compounds with Au in +3 oxidation state by utilizing a highly acidic flux. It might also be possible to connect the $[\text{Cu}_4(\text{AsS}_5)_4]^{8-}$ clusters in a three-dimensional network by the use of smaller alkali cations like Na^+ and Li^+ . Further work is therefore needed to explore these possibilities.

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APPENDIX

During the course of discovering new quaternary thioarsenates and their analogs, we isolated $\text{Cs}_4\text{As}_2\text{S}_{10}$, $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ and $\text{A}_3\text{CeAs}_2\text{S}_8$ ($\text{A} = \text{Rb}, \text{Cs}$). $\text{Cs}_4\text{As}_2\text{S}_{10}$ and $\text{A}_3\text{CeAs}_2\text{S}_8$ were obtained from thioarsenate fluxes while $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ was obtained while attempting to prepare $\text{Tl}_2\text{SnSb}_2\text{Se}_6$. These compounds could not be included in the main body of the dissertation since they did not fit in the flow. Hence the syntheses, structures and properties of these compounds are included in the appendix.

Synthesis and Structure of $\text{Cs}_4\text{As}_2\text{S}_{10}$

$\text{Cs}_4\text{As}_2\text{S}_{10}$ was initially obtained from a reaction of Cs_2S , Sn , As_2S_3 and S in the ratio 2/1/1/10 at 500°C . The compound was isolated as yellow plates. A pure synthesis can be achieved by reacting a stoichiometric amount of the starting materials, Cs_2S , As and S . $\text{Cs}_4\text{As}_2\text{S}_{10}$ crystallizes in the monoclinic space group $P2_1/c$ and is isostructural to $\text{Cs}_4\text{P}_2\text{S}_{10}$.¹ The structure of this compound is shown in Figure A-1. Table A-1 gives complete single crystal refinement details. Tables A-2, A-3, A-4 and A-5 list the fractional atomic coordinates, the anisotropic displacement parameters, selected bond distances and bond angles, respectively.

¹ Aitken, J. A.; Canlas, C.; Weliky, D. P.; Kanatzidis, M. G. *Inorg. Chem.* **2001**, *40*, 6496.

Table A-1. Crystallographic refinement details for Cs₄As₂S₁₀.

empirical formula	Cs ₄ As ₂ S ₁₀
fw	501.04
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	17.669(4)
<i>b</i> , Å	7.1936(15)
<i>c</i> , Å	24.171(5)
α , deg	90
β , deg	94.256(4)
γ , deg	90
<i>V</i> , Å ³	3063.6(11)
<i>Z</i>	12
ρ_{calcd} , g/cm ³	3.259
μ , mm ⁻¹	11.296
<i>T</i> , K	173(2)
λ , Å	0.71073
θ range, deg	1.69-28.30
Refinement method	Full-matrix least-squares on <i>F</i> ²
<i>R</i> 1 ^a	0.0493
<i>wR</i> 2 ^b	0.0919

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

Table A-2. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_4\text{As}_2\text{S}_{10}$.

Atom	x	y	z	Ueq
Cs(1)	0.4076(1)	0.7155(1)	0.0381(1)	26(1)
Cs(2)	0.2594(1)	0.2955(1)	0.1361(1)	36(1)
Cs(3)	0.1508(1)	0.8431(1)	-0.0007(1)	36(1)
Cs(4)	0.1003(1)	-0.2000(1)	0.2156(1)	37(1)
Cs(5)	0.1499(1)	0.3258(1)	0.3549(1)	36(1)
Cs(6)	0.4553(1)	0.5774(2)	0.3339(1)	52(1)
As(1)	0.6673(1)	0.7785(2)	0.0269(1)	20(1)
As(2)	0.3318(1)	0.7399(2)	0.2006(1)	21(1)
As(3)	-0.0055(1)	0.7353(2)	-0.1359(1)	38(1)
S(1)	0.3136(2)	0.9706(4)	-0.0718(1)	26(1)
S(2)	0.4378(2)	0.6253(5)	0.1817(1)	35(1)
S(3)	0.2755(2)	0.5942(4)	0.2612(1)	32(1)
S(4)	0.2586(2)	0.8109(4)	0.1297(1)	24(1)
S(5)	0.2296(2)	0.3518(4)	-0.0097(1)	32(1)
S(6)	0.6052(2)	0.5784(4)	0.0840(1)	30(1)
S(7)	0.4193(2)	1.2133(4)	0.0397(1)	27(1)
S(8)	0.3812(2)	0.0050(4)	0.2435(1)	32(1)
S(9)	0.3125(2)	-0.0481(4)	0.3648(1)	30(1)
S(10)	0.0765(2)	0.2949(5)	0.2116(2)	44(1)

S(11)	0.1099(2)	0.6662(5)	-0.1388(1)	40(1)
S(12)	0.3007(2)	0.1028(4)	0.2922(1)	39(1)
S(13)	0.0178(2)	1.0119(5)	0.0922(1)	43(1)
S(14)	-0.0629(3)	0.5041(8)	-0.0894(2)	107(2)
S(15)	0.0212(7)	0.4118(12)	-0.0310(6)	48(4)
S(16)	-0.0462(6)	0.5922(14)	-0.0053(9)	71(5)

Table A-3. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_4\text{As}_2\text{S}_{10}$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	33(1)	22(1)	24(1)	1(1)	5(1)	3(1)
Cs(2)	57(1)	21(1)	30(1)	0(1)	11(1)	1(1)
Cs(3)	33(1)	44(1)	31(1)	5(1)	5(1)	-8(1)
Cs(4)	32(1)	35(1)	45(1)	7(1)	11(1)	7(1)
Cs(5)	34(1)	35(1)	38(1)	-5(1)	-3(1)	8(1)
Cs(6)	34(1)	94(1)	28(1)	8(1)	6(1)	28(1)
As(1)	23(1)	20(1)	18(1)	-1(1)	3(1)	0(1)
As(2)	22(1)	21(1)	20(1)	2(1)	2(1)	1(1)
As(3)	27(1)	35(1)	51(1)	-1(1)	7(1)	-4(1)
S(1)	30(2)	23(2)	26(2)	-6(1)	3(1)	-3(1)
S(2)	33(2)	48(2)	24(2)	-2(2)	5(1)	14(2)
S(3)	28(2)	39(2)	29(2)	12(2)	2(1)	-9(1)
S(4)	26(2)	24(2)	22(2)	3(1)	1(1)	3(1)
S(5)	30(2)	32(2)	35(2)	2(1)	10(1)	7(1)
S(6)	28(2)	32(2)	29(2)	3(1)	1(1)	-2(1)
S(7)	33(2)	24(2)	22(2)	3(1)	-3(1)	-4(1)
S(8)	37(2)	38(2)	23(2)	-4(1)	4(2)	-13(2)
S(9)	38(2)	27(2)	25(2)	1(1)	7(1)	1(1)
S(10)	35(2)	37(2)	59(2)	-10(2)	-3(2)	-7(2)
S(11)	34(2)	41(2)	44(2)	-9(2)	2(2)	10(2)
S(12)	60(2)	32(2)	25(2)	3(1)	5(2)	20(2)

S(13)	44(2)	43(2)	44(2)	-8(2)	12(2)	11(2)
S(14)	112(4)	103(4)	104(4)	33(3)	-3(3)	-74(3)
S(15)	58(7)	39(5)	48(8)	0(4)	9(6)	1(4)
S(16)	47(6)	70(7)	96(14)	56(7)	-10(7)	-9(5)

* The anisotropic displacement factor exponent takes the form:

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

Table A-4. Selected bond distances for Cs₄As₂S₁₀.

As(1)-S(5)	2.116(3)	Cs(2)-S(3)	3.703(3)	Cs(4)-S(10)	3.586(4)
As(1)-S(1)	2.120(3)	Cs(2)-S(4)	3.711(3)	Cs(4)-S(4)	3.606(3)
As(1)-S(7)	2.137(3)	Cs(2)-As(2)	3.7399(14)	Cs(4)-S(10)	3.658(4)
As(1)-S(6)	2.326(3)	Cs(2)-S(10)	3.829(4)	Cs(4)-S(10)	3.696(4)
As(2)-S(3)	2.110(3)	Cs(2)-S(7)	3.839(3)	Cs(4)-S(14)	3.772(6)
As(2)-S(2)	2.126(3)	Cs(2)-S(14)	3.851(6)	Cs(5)-S(12)	3.546(3)
As(2)-S(4)	2.131(3)	Cs(2)-S(8)	3.861(3)	Cs(5)-S(13)	3.573(4)
As(2)-S(8)	2.312(3)	Cs(3)-S(4)	3.568(3)	Cs(5)-S(1)	3.592(3)
As(3)-S(11)	2.105(3)	Cs(3)-S(1)	3.577(3)	Cs(5)-S(10)	3.613(3)
As(3)-S(13)	2.122(4)	Cs(3)-S(13)	3.582(3)	Cs(5)-S(11)	3.614(3)
As(3)-S(10)	2.152(4)	Cs(3)-S(11)	3.595(3)	Cs(5)-S(5)	3.694(3)
As(3)-S(14)	2.287(5)	Cs(3)-S(16)	3.645(10)	Cs(5)-S(11)	3.728(4)
Cs(1)-S(2)	3.531(3)	Cs(3)-S(15)	3.679(9)	Cs(5)-S(3)	3.812(3)
Cs(1)-S(1)	3.539(3)	Cs(3)-S(13)	3.725(4)	Cs(5)-S(9)	3.930(3)
Cs(1)-S(7)	3.587(3)	Cs(3)-S(14)	3.727(5)	Cs(6)-S(3)	3.517(3)
Cs(1)-S(7)	3.619(3)	Cs(3)-S(5)	3.811(3)	Cs(6)-S(1)	3.525(3)
Cs(1)-S(6)	3.625(3)	Cs(3)-S(15)	3.893(9)	Cs(6)-S(8)	3.595(3)
Cs(1)-S(4)	3.628(3)	Cs(3)-S(16)	3.916(11)	Cs(6)-S(2)	3.686(3)
Cs(1)-S(6)	3.718(3)	Cs(3)-S(5)	3.927(3)	Cs(6)-S(7)	3.768(3)
Cs(1)-S(7)	3.743(3)	Cs(4)-S(11)	3.519(3)	Cs(6)-S(2)	3.794(4)
Cs(2)-S(4)	3.490(3)	Cs(4)-S(3)	3.533(3)	Cs(6)-S(9)	3.802(3)
Cs(2)-S(5)	3.547(3)	Cs(4)-S(13)	3.563(4)	Cs(6)-As(2)	3.9333(14)

Table A-5. Selected bond angles for Cs₄As₂S₁₀.

S(5)-As(1)-S(1)	111.80(13)	S(3)-As(2)-S(8)	106.23(12)
S(5)-As(1)-S(7)	116.33(13)	S(2)-As(2)-S(8)	96.15(13)
S(1)-As(1)-S(7)	116.04(12)	S(4)-As(2)-S(8)	110.49(12)
S(5)-As(1)-S(6)	107.06(12)	S(11)-As(3)-S(13)	110.74(14)
S(1)-As(1)-S(6)	106.65(12)	S(11)-As(3)-S(10)	116.92(14)
S(7)-As(1)-S(6)	96.94(11)	S(13)-As(3)-S(10)	115.78(14)
S(3)-As(2)-S(2)	115.15(13)	S(11)-As(3)-S(14)	108.1(2)
S(3)-As(2)-S(4)	112.80(12)	S(13)-As(3)-S(14)	108.2(2)
S(2)-As(2)-S(4)	114.35(12)	S(10)-As(3)-S(14)	95.34(17)

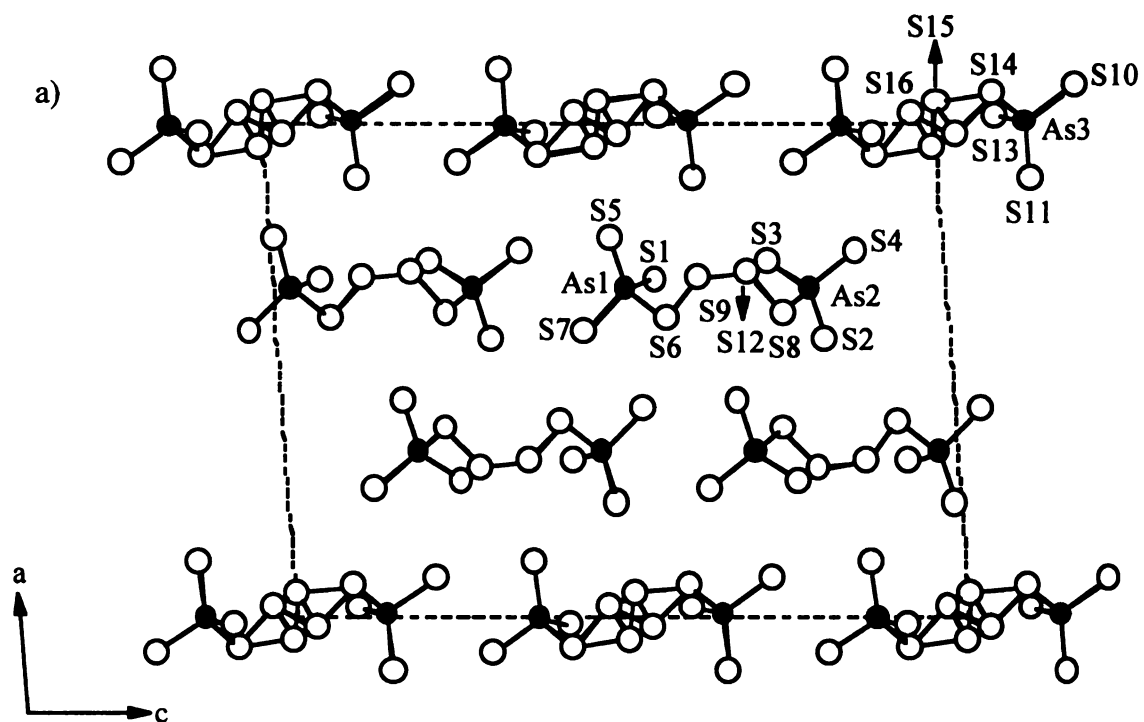


Figure A-1. Unit cell view of $\text{Cs}_4\text{As}_2\text{S}_{10}$ down the b -axis. Cs atoms have been removed for clarity. The figure shows two crystallographically distinct $\text{As}_2\text{S}_{10}^{4-}$ anions.

Synthesis and Structure of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$

$\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ was achieved by heating Tl, Sn, Sb_2Se_3 and Se in the stoichiometric ratio at 500°C. The reactants were loaded in a fused silica tube in a nitrogen atmosphere and tube sealed under vacuum. The tube was then heated to 500°C in 10h, held at that temperature for 60h and cooled down to 250°C at the rate of 5°C/h followed by rapid cooling to room temperature. The compound was obtained as black plates and the powder pattern of the product showed 100% phase purity.

Intensity statistics and systematic absence conditions pointed to the monoclinic space group, $C2/m$. Sb and Sn are indistinguishable by X-ray, therefore assignment of atoms in $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ were made on the basis of coordination geometry and charge-balancing requirements. All atoms were refined anisotropically to give final R1/wR2 value of 5.72/12.90. Crystal refinement details are given in Table A-6. Fractional atomic coordinates and anisotropic displacement parameters are listed in Tables A-7 and A-8. Selected bond distances and angles are given in Tables A-9 and A-10.

The structure of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ consists of two different kinds of layers, Figure A-2a. The first layer is the SnSe_2 structure type and consists of octahedral Sn and Sb bonded to Se atoms. This layer can be formulated as $(\text{Sn}_5\text{Sb}_2\text{Se}_{14})^{2-}$, Figure A-2b. The second layer is similar to the structure of SnSe with two Sn atoms removed periodically and replaced by Tl atoms slightly above and below the layer. This layer can be written as $(\text{Sb}_6\text{Se}_{10})^{2-}$ and consists of only Sb bonded to 5 Se atoms in a square pyramidal geometry, Figure A-2c. The layers are arranged in an ABABA fashion.

The DTA and diffuse reflectance spectrum of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ are shown in Figure A-3. The compound melts at 433°C and recrystallizes at 372°C. There are two additional small

peaks, labelled m and n, in the DTA plot, which maybe due to the presence of a little amount of impurities. The powder pattern of the product after the DTA matches the one taken before showing that the compound does not decompose on heating. The diffuse reflectance spectrum shows an energy gap of 0.64 eV, Figure A-3b.

Given the low band gap of the compound, we performed Seebeck measurement. The sample was in the form of a pressed pellet. Figure A-4 shows the plot of the Seebeck coefficient against temperature. The compound has a room temperature Seebeck Coefficient of $\sim -400 \mu\text{V/K}$. The negative sign indicates that it is an n-type semiconductor.

Table A-6. Crystallographic refinement details for $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

Formula	$\text{Tl}_8\text{Sn}_{18}\text{Sb}_8\text{Se}_{48}$
Space Group	$C2/m$
a, Å	42.95 (3)
b, Å	3.967 (2)
c, Å	13.369 (8)
α , deg	90
β , deg	98.813 (11)
γ , deg	90
Z, V	6, 2251 (2)
D, mg/m ³	5.510
Temp, K	293
λ , Å	0.71073
μ , mm ⁻¹	41.109
F(000)	3108
θ_{max} , deg	28.21
Total reflections	5347
Total unique reflections	2768
No. of parameters	125
Refinement Method	Full-matrix least-squares on F^2
Final R indices($I > 2s(I)$)	R1 = 0.0572, wR2 = 0.1290
R indices (all data)	R1 = 0.1179, wR2 = 0.1551
Goodness of fit on F^2	0.954

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

Table A-7. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

Atom	x	y	z	Ueq
Tl(1)	0.2923(1)	-0.5000	0.4084(1)	36(1)
Tl(2)	-0.0024(1)	-2.5000	0.1464(1)	36(1)
Sn(1)	0.3591(1)	0	0.1954(2)	19(1)
Sn(2)	0.5000	-1.0000	0.5000	21(1)
Sn(3)	0.2876(1)	-0.5000	0.0567(2)	20(1)
Sb(1)	0.1895(1)	-1.5000	0.2935(2)	23(1)
Sb(2)	0.0885(1)	-2.5000	0.0879(2)	24(1)
Sb(3)	0.1109(1)	-2.0000	0.3635(2)	28(1)
Sb(4)	0.4307(1)	-0.5000	0.3380(2)	21(1)
Se(1)	0.3670(1)	-0.5000	0.3401(2)	20(1)
Se(2)	0.1372(1)	-2.0000	0.2009(2)	22(1)
Se(3)	0.4341(1)	-1.0000	0.4822(2)	24(1)
Se(4)	0.0697(1)	-2.5000	0.2648(2)	21(1)
Se(5)	0.2969(1)	0	0.2046(2)	22(1)
Se(6)	0.2292(1)	-1.0000	0.3720(3)	28(1)
Se(7)	0.3517(1)	-0.5000	0.0496(2)	26(1)
Se(8)	0.5048(1)	-1.5000	0.6526(2)	25(1)
Se(9)	0.3422(1)	-1.0000	0.5534(2)	22(1)
Se(10)	0.0458(1)	-3.0000	0.0285(2)	25(1)
Se(11)	0.4229(1)	0	0.1917(2)	24(1)

Se(12)	0.2753(1)	-1.0000	-0.0858(2)	27(1)

Table A-8. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	30(1)	32(1)	45(1)	0	3(1)	0
Tl(2)	28(1)	40(1)	39(1)	0	5(1)	0
Sn(1)	13(1)	16(1)	29(1)	0	-1(1)	0
Sn(2)	15(2)	17(2)	30(2)	0	-3(1)	0
Sn(3)	14(1)	16(1)	28(1)	0	-3(1)	0
Sb(1)	19(1)	21(1)	31(1)	0	7(1)	0
Sb(2)	21(1)	21(1)	30(1)	0	5(1)	0
Sb(3)	32(1)	23(1)	30(1)	0	12(1)	0
Sb(4)	13(1)	19(1)	29(1)	0	-1(1)	0
Se(1)	17(2)	21(2)	23(2)	0	3(1)	0
Se(2)	22(2)	19(2)	27(2)	0	7(1)	0
Se(3)	22(2)	28(2)	24(2)	0	6(1)	0
Se(4)	16(2)	22(2)	24(2)	0	2(1)	0
Se(5)	14(2)	27(2)	26(2)	0	4(1)	0
Se(6)	14(2)	23(2)	45(2)	0	0(1)	0
Se(7)	23(2)	28(2)	26(2)	0	5(1)	0
Se(8)	26(2)	23(2)	27(2)	0	8(1)	0
Se(9)	17(2)	19(2)	30(2)	0	2(1)	0
Se(10)	19(2)	20(2)	33(2)	0	-3(1)	0
Se(11)	18(2)	28(2)	27(2)	0	5(1)	0

Se(12) 25(2) 31(2) 27(2) 0 8(1) 0

* The anisotropic displacement factor exponent takes the form:

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

Table A-9. Selected bond distances for $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

$\text{Tl}(1)\text{-Se}(6)$	3.210(4)	$\text{Sb}(1)\text{-Se}(9)$	2.625(4)
$\text{Tl}(2)\text{-Se}(4)$	3.255(4)	$\text{Sb}(1)\text{-Se}(6)$	2 x 2.720(3)
$\text{Sn}(1)\text{-Se}(5)$	2.695(4)	$\text{Sb}(1)\text{-Se}(2)$	2 x 3.108(2)
$\text{Sn}(1)\text{-Se}(11)$	2.746(4)	$\text{Sb}(2)\text{-Se}(4)$	2.613(4)
$\text{Sn}(1)\text{-Se}(1)$	2 x 2.755(3)	$\text{Sb}(2)\text{-Se}(10)$	2 x 2.735(3)
$\text{Sn}(1)\text{-Se}(7)$	2 x 2.766(3)	$\text{Sb}(2)\text{-Se}(2)$	2 x 3.102(2)
$\text{Sn}(2)\text{-Se}(3)$	2 x 2.804(4)	$\text{Sb}(3)\text{-Se}(2)$	2.600(4)
$\text{Sn}(2)\text{-Se}(8)$	4 x 2.830(2)	$\text{Sb}(3)\text{-Se}(4)$	2 x 2.844(3)
$\text{Sn}(3)\text{-Se}(12)$	2 x 2.745(3)	$\text{Sb}(3)\text{-Se}(9)$	2 x 2.924(3)
$\text{Sn}(3)\text{-Se}(7)$	2.770(4)	$\text{Sb}(4)\text{-Se}(1)$	2.741(4)
$\text{Sn}(3)\text{-Se}(5)$	2 x 2.786(3)	$\text{Sb}(4)\text{-Se}(8)$	2.751(4)
$\text{Sn}(3)\text{-Se}(12)$	2.788(4)	$\text{Sb}(4)\text{-Se}(3)$	2 x 2.754(3)
		$\text{Sb}(4)\text{-Se}(11)$	2 x 2.770(3)

Table A-10. Selected bond angles for $\text{Ti}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$.

Se(5)-Sn(1)-Se(11)	178.47(12)	Se(3)-Sn(2)-Se(3)	180.0
Se(5)-Sn(1)-Se(1)	2 x 89.09(10)	Se(3)-Sn(2)-Se(8)	4 x 91.30(8)
Se(11)-Sn(1)-Se(1)	2 x 89.84(9)	Se(3)-Sn(2)-Se(8)	4 x 88.70(8)
Se(1)-Sn(1)-Se(1)	92.12(11)	Se(8)-Sn(2)-Se(8)	2 x 88.99(10)
Se(5)-Sn(1)-Se(7)	2 x 91.38(9)	Se(8)-Sn(2)-Se(8)	2 x 179.996(1)
Se(11)-Sn(1)-Se(7)	2 x 89.69(10)	Se(8)-Sn(2)-Se(8)	2 x 91.01(10)
Se(1)-Sn(1)-Se(7)	2 x 179.47(13)	Se(9)-Sb(1)-Se(6)	2 x 93.89(11)
Se(1)-Sn(1)-Se(7)	2 x 88.11(8)	Se(6)-Sb(1)-Se(6)	93.65(12)
Se(7)-Sn(1)-Se(7)	91.65(12)	Se(4)-Sb(2)-Se(10)	2 x 88.67(10)
Se(12)-Sn(3)-Se(12)	92.53(12)	Se(10)-Sb(2)-Se(10)	92.96(12)
Se(12)-Sn(3)-Se(7)	2 x 93.60(10)	Se(2)-Sb(3)-Se(4)	2 x 86.03(10)
Se(12)-Sn(3)-Se(5)	2 x 176.83(13)	Se(4)-Sb(3)-Se(4)	88.45(11)
Se(12)-Sn(3)-Se(5)	2 x 88.25(8)	Se(2)-Sb(3)-Se(9)	2 x 87.41(10)
Se(7)-Sn(3)-Se(5)	2 x 89.41(9)	Se(4)-Sb(3)-Se(9)	2 x 92.68(7)
Se(5)-Sn(3)-Se(5)	90.81(11)	Se(4)-Sb(3)-Se(9)	2 x 173.25(12)
Se(12)-Sn(3)-Se(12)	2 x 90.54(10)	Se(9)-Sb(3)-Se(9)	85.42(11)
Se(7)-Sn(3)-Se(12)	174.01(12)	Se(8)-Sb(4)-Se(11)	2 x 92.57(10)
Se(5)-Sn(3)-Se(12)	2 x 86.39(10)	Se(1)-Sb(4)-Se(11)	2 x 89.63(9)
Se(1)-Sb(4)-Se(8)	176.84(12)	Se(3)-Sb(4)-Se(11)	2 x 88.06(8)
Se(1)-Sb(4)-Se(3)	2 x 86.46(9)	Se(3)-Sb(4)-Se(11)	2 x 176.07(12)
Se(8)-Sb(4)-Se(3)	2 x 91.35(9)	Se(11)-Sb(4)-Se(11)	91.48(12)
Se(3)-Sb(4)-Se(3)	92.13(12)		

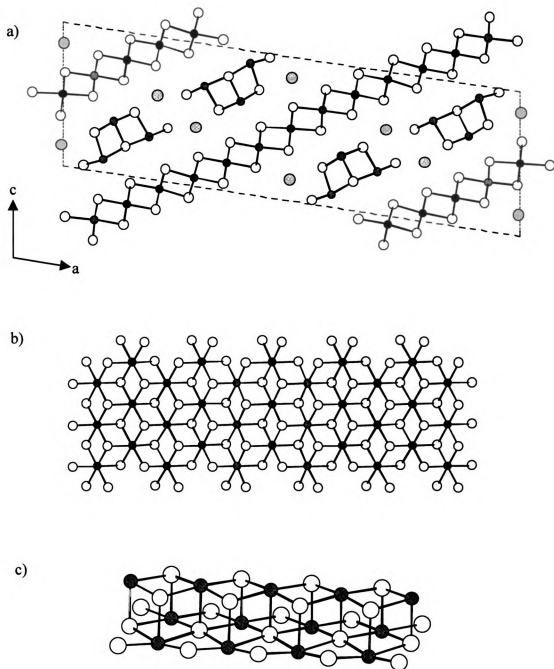


Figure A-2. a) Unit cell view down the b -axis of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ showing the two different kinds of layers constituting the cell. b) The $(\text{Sn}_5\text{Sb}_2\text{Se}_{14})^{2-}$ layer c) The $(\text{Sb}_6\text{Se}_{10})^{2-}$ layer. The large light gray circles are Tl, small dark gray circles are Sb, black circles are Sn and open circles are Se.

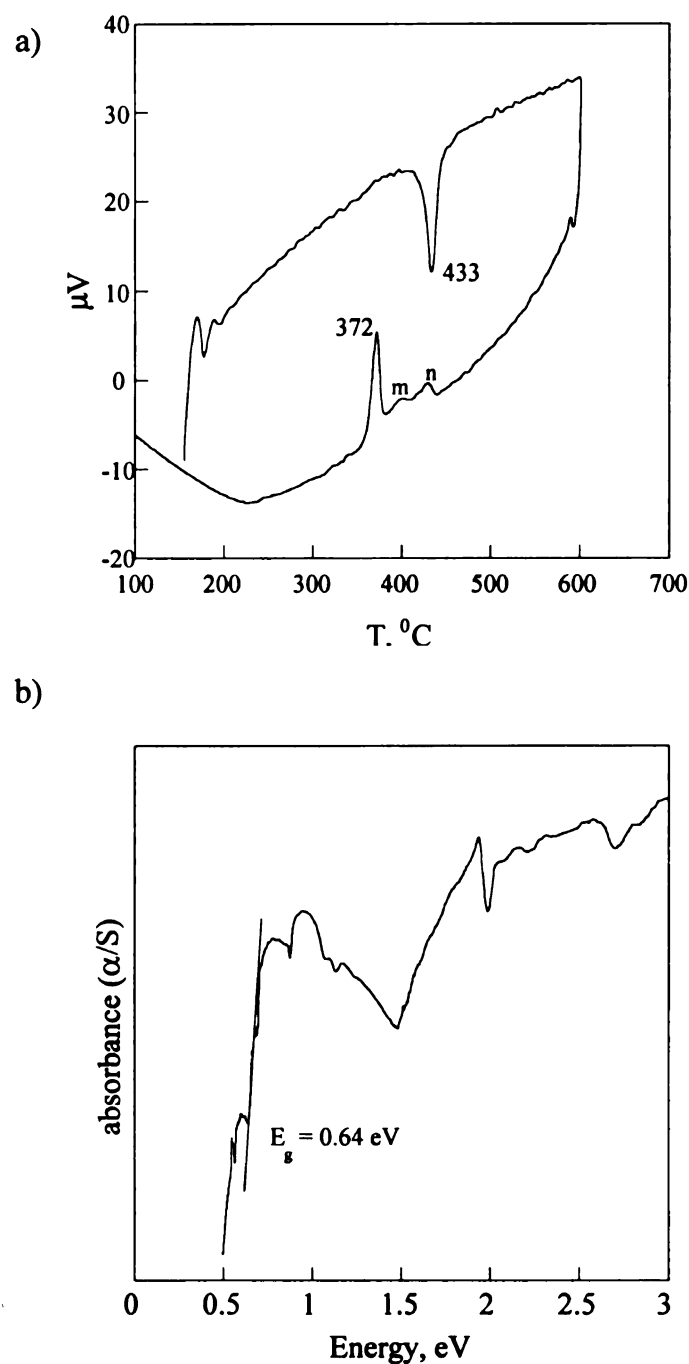


Figure A-3. a) Differential Thermal Analysis of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ showing a melting point of 433 $^{\circ}\text{C}$ and a recrystallization point of 372 $^{\circ}\text{C}$. The peaks labeled m and n are due to minor impurities. b) The diffuse reflectance spectrum showing a narrow band gap of 0.64 eV.

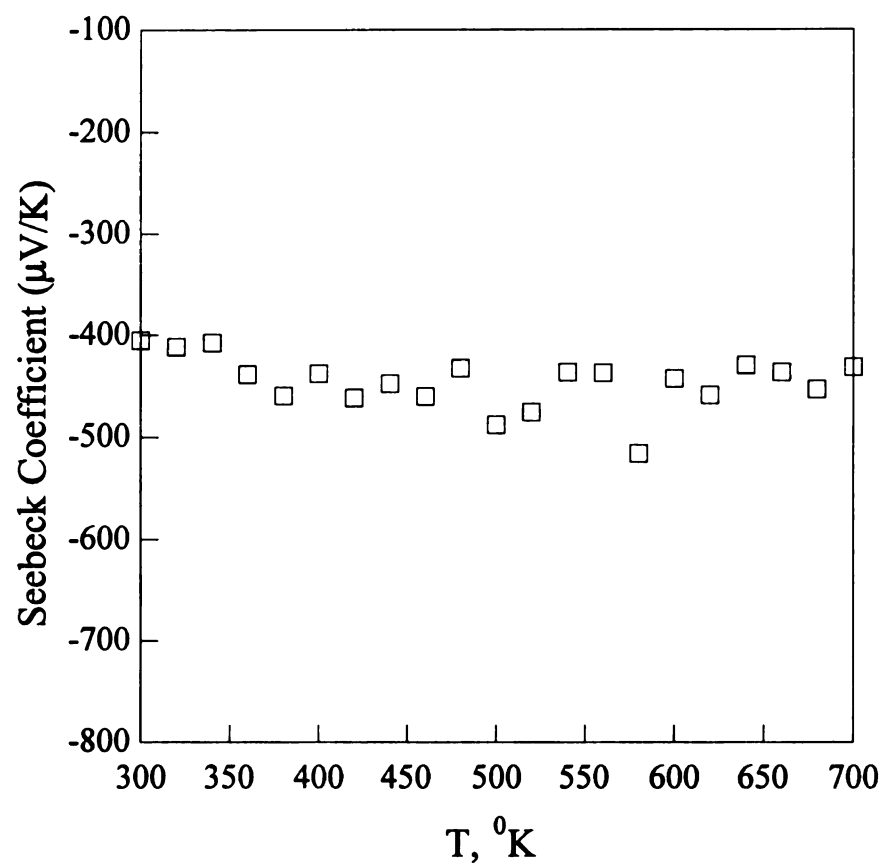


Figure A-4. A plot of the Seebeck coefficient of $\text{Tl}_8\text{Sn}_{10}\text{Sb}_{16}\text{Se}_{48}$ against temperature shows that it is a n-type semiconductor with a room temperature value of $\sim 400 \mu\text{V/K}$.

Synthesis and Structure of $A_3CeAs_2S_8$ ($A = Rb, Cs$)

Orange needles of $Rb_3CeAs_2S_8$ were obtained from a reaction of $Rb_2S/Ce/As_2S_3/S$ in the ratio 4/1/2/10 at 500°C. The reaction mixture was loaded in a fused silica tube in a N_2 filled glove box. The tube was sealed under vacuum ($<10^{-4}$ Torr) and heated in a computer-controlled furnace at 500°C for 60h. The tube was cooled to 250°C at the rate of 5°C/h and then fast-cooled to room temperature. The excess of flux was washed away with DMF, previously degassed with N_2 , to reveal orange needles and transparent yellow crystals. Semiquantitative analysis using EDS gave an average reading of " $Rb_{3.2}CeAs_2S_8$ " for the orange needles and " $Rb_{10.9}CeAs_{4.5}S_{18}$ " for the yellow crystals.

$Cs_3CeAs_2S_8$ was obtained as yellow crystals on heating a reaction mixture containing Cs_2S , Ce , As_2S_3 and S in the ratio 2:1:1.5:10 at 500°C using the same heating profile and isolation procedure as above. EDS on several crystals gave an average composition of " $Cs_{2.6}Ce_{0.8}As_2S_{7.9}$ ". Relevant single-crystal refinement details for $A_3CeAs_2S_8$ are given in Table A-11. Fractional atomic coordinates and anisotropic displacement parameters are listed in Tables A-12 and A-13. Selected bond distances and angles are given in Tables A-14 and A-15.

The structure of $A_3CeAs_2S_8$ is shown in Figure A-5. The unit cell consists of $[CeAs_2S_8]^-$ chains running down the b -axis. A single chain is shown in Figure A-5b. The chain is made up of CeS_8 bicapped trigonal prisms fused together by means of tetrahedral AsS_4^{3-} ligands. There are two kinds of AsS_4^{3-} ligands. The first type is terminal and uses three S atoms to bind to one Ce atom. The other type serves to bridge two Ce atoms and form the chain.

Table A-11. Crystallographic refinement details for Rb₃CeAs₂S₈ and Cs₃CeAs₂S₈.

Formula	Rb ₃ CeAs ₂ S ₈	Cs ₃ CeAs ₂ S ₈
Space Group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> , Å	9.901 (3)	10.059 (3)
<i>b</i> , Å	6.893 (2)	7.001 (2)
<i>c</i> , Å	11.620 (3)	11.875 (4)
α , deg	90	90
β , deg	90.807 (5)	90.223 (6)
γ , deg	90	90
<i>Z</i> , V	2, 793 (2)	2, 836.3 (5)
<i>D</i> , mg/m ³	3.363	3.753
Temp, K	293	293
λ , Å	0.71073	0.71073
μ , mm ⁻¹	17.175	14.047
<i>F</i> (000)	726	834
$\theta_{\max}$, deg	23.29	28.30
Total reflections	5569	8763
Total unique reflections	2213	2150
No. of parameters	127	82
Refinement Method	Full-matrix least-squares on <i>F</i> ²	
Final <i>R</i> indices(<i>I</i> >2 <i>s</i> (<i>I</i>))	<i>R</i> 1 = 0.0197, w <i>R</i> 2 = 0.0390	<i>R</i> 1 = 0.0302, w <i>R</i> 2 = 0.0604
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0245, w <i>R</i> 2 = 0.0403	<i>R</i> 1 = 0.0473, w <i>R</i> 2 = 0.0639
Goodness of fit on <i>F</i> ²	1.029	0.975

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

Table A-12. Fractional Atomic Coordinates and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{CeAs}_2\text{S}_8$ and $\text{Cs}_3\text{CeAs}_2\text{S}_8$.

Atom	x	y	z	Ueq
$\text{Rb}_3\text{CeAs}_2\text{S}_8$				
Ce(1)	0.8850(1)	0.1444(1)	0.6516(1)	18(1)
Rb(1)	0.5989(1)	0.1259(2)	1.1532(1)	28(1)
Rb(2)	0.3649(1)	0.1311(2)	0.5874(1)	49(1)
Rb(3)	0.8447(1)	0.6268(2)	0.9360(1)	40(1)
As(1)	0.9082(1)	0.1080(1)	0.13371(1)	17(1)
As(2)	0.6253(1)	0.1247(2)	0.8180(1)	19(1)
S(1)	0.6491(3)	0.3797(3)	0.7093(3)	28(1)
S(2)	0.4329(2)	0.1182(4)	0.8958(1)	30(1)
S(3)	0.7267(1)	0.1284(4)	0.4365(1)	26(1)
S(4)	0.6562(3)	-0.1216(3)	0.7050(3)	27(1)
S(5)	1.0993(2)	0.3577(3)	0.7729(2)	26(1)
S(6)	0.8051(2)	0.1300(4)	0.9246(1)	29(1)
S(7)	1.0677(2)	-0.1349(3)	0.7652(2)	30(1)
S(8)	1.0703(2)	0.0483(3)	0.4602(2)	22(1)
$\text{Cs}_3\text{CeAs}_2\text{S}_8$				
Ce(1)	0.1086(1)	0.2500	0.8487(1)	15(1)
Cs(1)	-0.4006(1)	-0.2500	0.6567(1)	15(1)
Cs(2)	0.1506(1)	-0.2500	0.5571(1)	20(1)
Cs(3)	-0.3714(1)	0.2500	0.9196(1)	22(1)

As(1)	0.3658(1)	0.2500	0.6847(1)	10(1)
As(2)	0.0927(1)	0.2500	1.1575(1)	18(1)
S(1)	0.1883(2)	0.2500	0.5813(2)	16(1)
S(2)	-0.4436(2)	0.2500	0.6080(2)	16(1)
S(3)	0.2689(2)	0.2500	1.0552(2)	14(1)
S(4)	0.3366(2)	0.0023	0.7930(1)	16(1)
S(5)	-0.0869(2)	0.0009	0.7383(1)	32(1)
S(6)	-0.0675(3)	0.1642	1.0404(2)	13(1)

Table A-13. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Rb}_3\text{CeAs}_2\text{S}_8$ and $\text{Cs}_3\text{CeAs}_2\text{S}_8$.

	U11	U22	U33	U23	U13	U12
$\text{Rb}_3\text{CeAs}_2\text{S}_8$						
Ce(1)	15(1)	20(1)	20(1)	1(1)	1(1)	-1(1)
Rb(1)	28(1)	31(1)	27(1)	1(1)	1(1)	2(1)
Rb(2)	39(1)	40(1)	68(1)	-5(1)	-25(1)	2(1)
Rb(3)	40(1)	31(1)	50(1)	-2(1)	14(1)	-2(1)
As(1)	15(1)	16(1)	20(1)	-1(1)	0(1)	0(1)
As(2)	18(1)	18(1)	23(1)	1(1)	5(1)	0(1)
S(1)	32(2)	19(1)	35(2)	3(1)	11(1)	3(1)
S(2)	19(1)	36(1)	34(1)	-1(1)	9(1)	1(1)
S(3)	13(1)	38(1)	25(1)	-2(2)	1(1)	-1(1)
S(4)	29(2)	20(1)	32(2)	-7(1)	6(1)	-5(1)
S(5)	32(1)	21(1)	27(1)	6(1)	-9(1)	-7(1)
S(6)	21(1)	32(1)	36(1)	-2(2)	-3(1)	0(1)
S(7)	39(2)	22(1)	28(1)	-5(1)	-6(1)	8(1)
S(8)	15(1)	29(1)	22(1)	-3(1)	-2(1)	2(1)
$\text{Cs}_3\text{CeAs}_2\text{S}_8$						
Ce(1)	10(1)	25(1)	10(1)	0	1(1)	0
Cs(1)	16(1)	16(1)	13(1)	0	0(1)	0
Cs(2)	22(1)	15(1)	23(1)	0	5(1)	0

Cs(3)	20(1)	19(1)	28(1)	0	-9(1)	0
As(1)	11(1)	10(1)	11(1)	0	3(1)	0
As(2)	10(1)	36(1)	9(1)	0	0(1)	0
S(1)	16(1)	12(1)	19(1)	0	-3(1)	0
S(2)	11(1)	17(1)	20(1)	0	5(1)	0
S(3)	11(1)	18(1)	14(1)	0	-1(1)	0
S(4)	20(1)	11(1)	17(1)	2	3(1)	1
S(5)	51(1)	28(1)	18(1)	-6	9(1)	-27
S(6)	13(1)	14(1)	12(1)	4	-2(1)	-2

* The anisotropic displacement factor exponent takes the form:

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

Table A-14. Selected bond distances for Rb₃CeAs₂S₈ and Cs₃CeAs₂S₈.

Rb ₃ CeAs ₂ S ₈					
Ce(1)-S(5)	2.927(3)	Rb(1)-S(2)	3.559(3)	Rb(3)-S(6)	3.493(3)
Ce(1)-S(1)	2.929(3)	Rb(1)-S(5)	3.607(3)	Rb(3)-S(1)	3.667(3)
Ce(1)-S(3)	2.9331(17)	Rb(1)-S(7)	3.798(3)	Rb(3)-S(5)	3.677(3)
Ce(1)-S(7)	2.942(2)	Rb(2)-S(8)	3.301(2)	Rb(3)-S(4)	3.683(3)
Ce(1)-S(8)	2.9771(18)	Rb(2)-S(3)	3.556(3)	Rb(3)-S(5)	3.772(3)
Ce(1)-S(4)	2.987(3)	Rb(2)-S(1)	3.570(3)	Rb(3)-S(6)	3.8065(19)
Ce(1)-S(8)	3.106(2)	Rb(2)-S(3)	3.591(3)	As(1)-S(5)	2.148(3)
Ce(1)-As(2)	3.2420(9)	Rb(2)-S(4)	3.620(3)	As(1)-S(7)	2.150(3)
Ce(1)-S(6)	3.2820(18)	Rb(2)-S(2)	3.638(2)	As(1)-S(3)	2.1538(15)
Rb(1)-S(6)	3.3735(17)	Rb(2)-S(5)	3.763(3)	As(1)-S(8)	2.174(2)
Rb(1)-S(2)	3.3931(19)	Rb(2)-S(4)	3.804(3)	As(2)-S(2)	2.1206(16)
Rb(1)-S(1)	3.401(3)	Rb(2)-S(1)	3.859(3)	As(2)-S(6)	2.1542(17)
Rb(1)-S(2)	3.454(3)	Rb(3)-S(2)	3.3954(17)	As(2)-S(4)	2.170(3)
Rb(1)-S(4)	3.498(3)	Rb(3)-S(7)	3.411(3)	As(2)-S(1)	2.180(3)
Rb(1)-S(3)	3.5099(18)	Rb(3)-S(6)	3.449(3)		
Cs ₃ CeAs ₂ S ₈					
Ce(1)-S(3)	2.930(2)	Cs(1)-S(3)	3.663(2)	Cs(3)-S(4)	2 x 3.7227(18)
Ce(1)-S(5)	2 x 2.934(2)	Cs(1)-S(5)	2 x 3.736(2)	Cs(3)-S(2)	3.768(3)
Ce(1)-S(6)	2 x 2.951(3)	Cs(2)-S(1)	2 x 3.533(2)	Cs(3)-S(4)	2 x 3.858(2)
Ce(1)-S(4)	2 x 2.953(2)	Cs(2)-S(2)	3.546(2)	As(1)-S(2)	2.126(2)
Ce(1)-S(6)	2 x 3.212(3)	Cs(2)-S(5)	2 x 3.669(2)	As(1)-S(1)	2.163(2)

Ce(1)-S(1)	3.279(2)	Cs(2)-S(1)	3.779(2)	As(1)-S(4)	2 x 2.1791(16)
Cs(1)-S(2)	3.507(2)	Cs(2)-S(4)	2 x 3.798(2)	As(2)-S(5)	2.1496(19)
Cs(1)-S(1)	3.549(2)	Cs(2)-S(5)	2 x 3.967(2)	As(2)-S(3)	2.153(2)
Cs(1)-S(4)	2 x 3.572(2)	Cs(3)-S(6)	2 x 3.425(3)	As(2)-S(6)	2 x 2.208(3)
Cs(1)-S(2)	2 x 3.574(1)	Cs(3)-S(3)	2 x 3.661(1)		

Table A-15. Selected bond angles for $\text{Rb}_3\text{CeAs}_2\text{S}_8$ and $\text{Cs}_3\text{CeAs}_2\text{S}_8$.

$\text{Rb}_3\text{CeAs}_2\text{S}_8$			
S(5)-As(1)-S(7)	109.64(8)	S(3)-Ce(1)-S(7)	132.50(8)
S(5)-As(1)-S(3)	110.46(11)	S(5)-Ce(1)-S(8)	91.22(7)
S(7)-As(1)-S(3)	110.05(11)	S(1)-Ce(1)-S(8)	142.75(7)
S(5)-As(1)-S(8)	105.00(9)	S(3)-Ce(1)-S(8)	71.51(5)
S(7)-As(1)-S(8)	115.66(9)	S(7)-Ce(1)-S(8)	78.94(6)
S(3)-As(1)-S(8)	105.86(7)	S(5)-Ce(1)-S(4)	139.04(8)
S(2)-As(2)-S(6)	119.69(7)	S(1)-Ce(1)-S(4)	71.50(5)
S(2)-As(2)-S(4)	112.11(11)	S(3)-Ce(1)-S(4)	75.89(7)
S(6)-As(2)-S(4)	103.83(11)	S(7)-Ce(1)-S(4)	88.18(8)
S(2)-As(2)-S(1)	111.66(11)	S(8)-Ce(1)-S(4)	119.72(6)
S(6)-As(2)-S(1)	102.96(11)	S(5)-Ce(1)-S(8)	69.19(6)
S(4)-As(2)-S(1)	105.24(7)	S(1)-Ce(1)-S(8)	73.64(6)
S(5)-Ce(1)-S(1)	100.76(8)	S(3)-Ce(1)-S(8)	75.82(7)
S(5)-Ce(1)-S(3)	143.55(7)	S(7)-Ce(1)-S(8)	133.15(6)
S(1)-Ce(1)-S(3)	78.33(7)	S(8)-Ce(1)-S(8)	78.13(3)
S(5)-Ce(1)-S(7)	71.06(6)	S(4)-Ce(1)-S(8)	138.59(6)
S(1)-Ce(1)-S(7)	138.31(8)		
$\text{Cs}_3\text{CeAs}_2\text{S}_8$			
S(3)-Ce(1)-S(5)	2 x 137.73(4)	S(4)-Ce(1)-S(6)	2 x 70.31(6)
S(5)-Ce(1)-S(5)	72.95(8)	S(6)-Ce(1)-S(6)	129.05(10)
S(3)-Ce(1)-S(6)	2 x 71.62(7)	S(3)-Ce(1)-S(1)	132.43(6)

S(5)-Ce(1)-S(6)	2 x 93.60(7)	S(5)-Ce(1)-S(1)	2 x 74.52(5)
S(5)-Ce(1)-S(6)	2 x 79.67(7)	S(6)-Ce(1)-S(1)	2 x 153.76(7)
S(3)-Ce(1)-S(4)	2 x 76.23(5)	S(4)-Ce(1)-S(1)	2 x 65.77(4)
S(5)-Ce(1)-S(4)	2 x 140.23(5)	S(6)-Ce(1)-S(1)	2 x 115.43(5)
S(5)-Ce(1)-S(4)	2 x 94.04(5)	S(2)-As(1)-S(1)	120.01(9)
S(6)-Ce(1)-S(4)	2 x 121.50(7)	S(2)-As(1)-S(4)	2 x 112.12(6)
S(6)-Ce(1)-S(4)	2 x 139.60(7)	S(1)-As(1)-S(4)	2 x 102.84(6)
S(4)-Ce(1)-S(4)	71.92(6)	S(4)-As(1)-S(4)	105.46(9)
S(3)-Ce(1)-S(6)	2 x 74.23(5)	S(5)-As(2)-S(5)	109.60(10)
S(5)-Ce(1)-S(6)	2 x 63.87(6)	S(5)-As(2)-S(3)	2 x 110.42(6)
S(5)-Ce(1)-S(6)	2 x 129.27(7)	S(5)-As(2)-S(6)	96.84(9)
S(6)-Ce(1)-S(6)	2 x 77.83(5)	S(5)-As(2)-S(6)	124.32(10)
S(6)-Ce(1)-S(6)	2 x 54.66(10)	S(3)-As(2)-S(6)	2 x 104.19(10)
S(4)-Ce(1)-S(6)	2 x 136.33(6)	S(5)-As(2)-S(6)	124.32(10)
		S(5)-As(2)-S(6)	96.84(9)

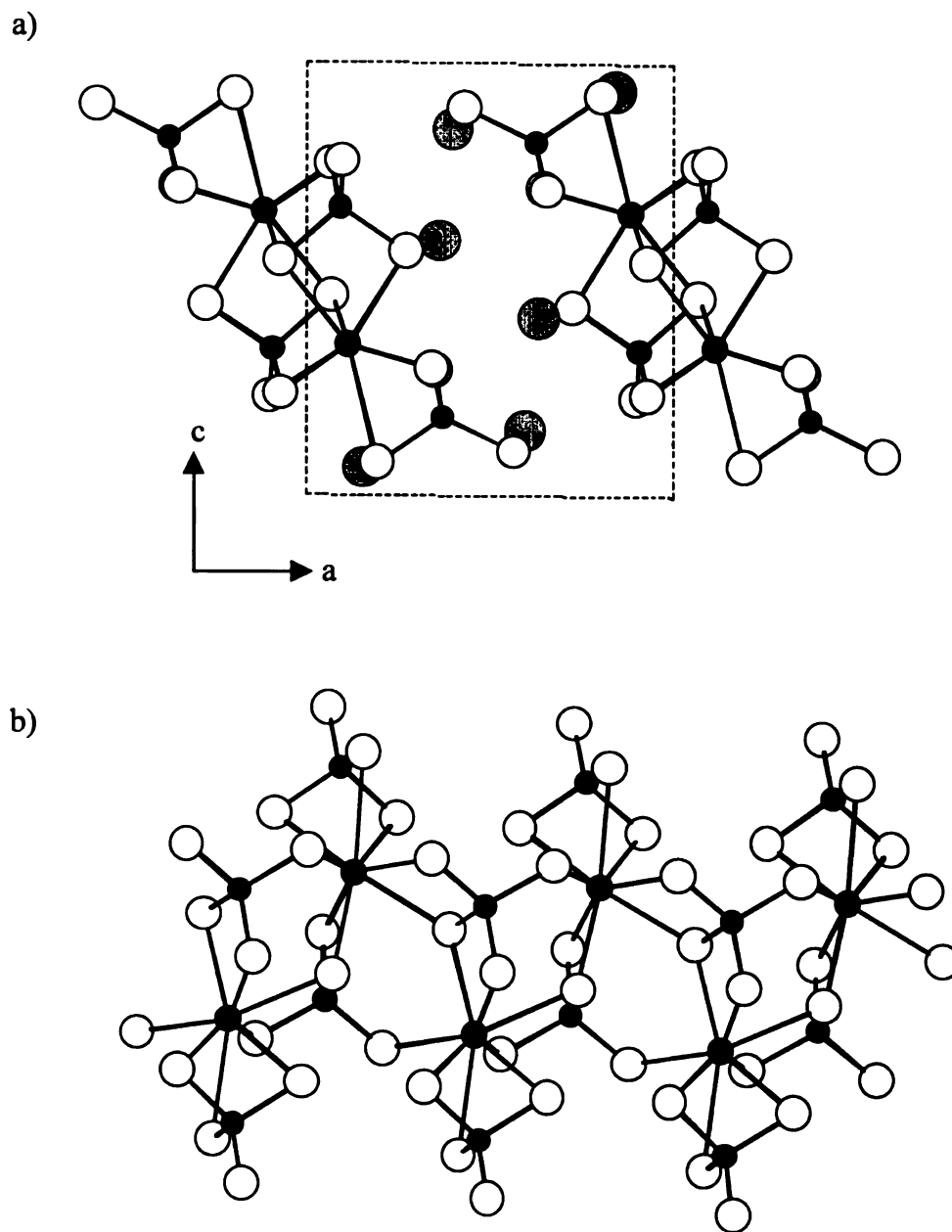


Figure A-5. a) Unit cell of $\text{Rb}_3\text{CeAs}_2\text{S}_8$ looking down the b -axis. The large light gray circles are Rb, the small dark gray circles are As, the black circles are Ce and the open circles are S. b) The $[\text{CeAs}_2\text{S}_8]^-$ chain showing the bicapped trigonal prismatic Ce coordinated by two different kinds of AsS_4^{3-} ligands.

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