行政院國家科學委員會補助專題研究計畫 ■ 成果報告 □期中進度報告

新穎三元及四元含硫、硒、碲之金屬固態化合物之合成與鑑定

Systematic Investigations of Ternary and Quaternary Metal Chalcogenides

計畫類別：■ 個別型計畫 □ 整合型計畫
計畫編號：NSC 94 - 2113 - M - 009 - 012 -
執行期間： 94 年 8 月 1 日至 95 年 12 月 31 日

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行政院國家科學委員會補助專題研究計畫
結案報告

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（一）中英文摘要

中文摘要

本計畫是 95 年國科會個別型計畫之結果摘要。這一年主要的工作在進行新穎固態化合物之合成、結構與物理性質測量。主要的研究工作為合成具有已知構造單元之新固態化合物。主要的研究成果為成功的合成並結構鑑定數個新穎固態化合物 $Sr_3GeSb_2Se_8$，$MPb_4In_8X_{17}$ (M = Cr, Mn, Fe, Cu, Ag, Au; X = S, Se)，與 $Sn_{3-x}Bi_{2+x}Se_6$ (0<x<0.62)。物理性質的測量顯示這些化合物均為半導體。

關鍵字: 固態化學，晶體結構，含第六族元素之固態化合物

Abstract

A new quaternary alkaline-earth selenide $Sr_3GeSb_2Se_8$ has been synthesized at 750 °C from pure elements in a stoichiometric ratio under vacuum. The product as synthesized is characterized by single-crystal X-ray diffraction, diffuse reflectance spectroscopy, and thermoanalysis. The title compound crystallizes in the orthorhombic space group *Pnma* with a = 12.633(4) Å, b = 4.301(1) Å, c =28.693(7) Å, V = 1558.8(8) Å^3, Z = 4, R_1 /wR_2 = 0.0582/0.1221, GOF = 1.077. The structure of $Sr_3GeSb_2Se_8$ features a novel structural type that consists of one-dimensional chains of vertex-sharing tetrahedra ${}^{1}_{\infty}[\mathrm{MSe}_3]$ (M=Ge/Sb) and fused-double chains of edge-shared square pyramids ${}^{1}_{\infty}[\mathrm{M}_2\mathrm{Se}_5]$, which are held together by Sr^{2+} ions. A band gap 0.75 eV for $Sr_3GeSb_2Se_8$ was derived from its diffuse reflectance spectrum.

Keyword: Solid state chemistry, crystal structure, chalcogenides

（二）計畫緣由與目的

Multinary chalcogenides exhibit varied structural types that have attracted intensive research for their prospective thermoelectric applications [1-6]. Much attention has been devoted to the synthesis of metal chalcogenides, such as $CsBi_4Te_6$[7] and $AgPb_mSbTe_{2+m}$[8,9], that might produce compounds with a narrow band gap for a large figure of merit ($ZT = \sigma S^2 / \kappa$; Z = figure of merit; T = temperature; S = Seebeck coefficient; σ = electrical conductivity; κ = thermal conductivity). For the reported chalcogenides, almost all main-group metals cooperate with elements of group 16 (S, Se, Te) and alkali, alkaline-earth metals or rare-earth elements to form multinary chalcogenides. [10] Among these compounds, only a few ternary selenides Sr-Ge-X and Sr-Sb-X (X = S, Se, Te) have been structurally characterized, such as $Sr_2Ge_2Se_5$ [11], $Sr_2Ge_2X_4$ (X = S, Se) [12,13], $Sr_3Sb_4S_9$ [14], and $Sr_6Sb_6S_{17}$ [15]. Only one multinary clalcogenide $Ba_4LaGe_3SbSe_{13}$ [16] containing Ge, Sb and Se, appears to have been reported. Our exploratory research has focused on chalcogenides of the form A_e-M_1-M_2-X (alkaline-earth element A_e; M_1 = Ge, Sn; M_2 = Sb, Bi; X = S, Se, Te) system. On extending the project to the Sr-Ge-Sb-Se system, we synthesized a new quaternary chalcogenide $Sr_3GeSb_2Se_8$ having one-dimensional chains of corner-sharing tetrahedra and fused square-pyramidal double chains. Here we report the synthesis, structure and characterization of $Sr_3GeSb_2Se_8$.

（三）現階段進度與結果

A) Experimental

Synthesis

$Sr_3GeSb_2Se_8$ was synthesized by a solid-state method. The initial reagents were strontium (Sr, 99.0%, Alfa Aesar), germanium (Ge, 99.999%, Alfa Aesar), antimony (Sb, 99.5%, Alfa Aesar), and selenium (Se, 99.999%, Alfa Aesar). In a typical reaction, these pure elements in stoichiometric proportions were mixed in an Ar-filled glove box (total mass ~ 0.5 g), placed in a silica tube, sealed under dynamic vacuum, and heated slowly to 750 °C within 72 h. This temperature was maintained for three days, followed by slow cooling to 550 °C over seven days, and finally to about 23 °C on simply terminating the power. Initial reactions were intended to synthesize '$Sr_3Ge_2Sb_2X_9$' (X = S, Se, Te). Based on the powder X-ray diffraction experiment, the S and Te reactions yield mixtures of Sr_2GeS_4, SrS for '$Sr_3Ge_2Sb_2X_9$' and SrTe, Sb_2Te_3, Te for '$Sr_3Ge_2Sb_2Te_9$' reactions. From the '$Sr_3Ge_2Sb_2Se_9$' reaction, the products contain a dark brown product with irregularly shaped crystals. As confirmed by single-crystal diffraction, we succeeded in preparing $Sr_3GeSb_2Se_8$ in quantitative yields using the elements in a stoichiometric ratio and the same heating profile as described above. Analysis of $Sr_3Ge_2Sb_2Se_9$ crystals with energy-dispersive spectra (SEM/EDX, Hitachi H-7500 Scanning Electron Microscope) showed the presence of Sr, Ge, Sb and Se. $Sr_3GeSb_2Se_8$ is sensitive to air and moisture such that it gradually decomposes to form a red amorphous powder in air in seven days.

Single-crystal X-ray diffraction (XRD)

A single crystal of compound $Sr_3GeSb_2Se_8$ (0.1 x 0.1 x 0.1 mm^3) was mounted on a glass fiber with epoxy glue; intensity data were collected on a diffractometer (Bruker APEX CCD equipped with graphite-monochromated Mo–Kα radiation, λ = 0.71073 Å) at 25(2) °C. The distance from the crystal to the detector was 5.0 cm. Data were collected in scans 0.3° in ϖ within groups of 600 frames each at ϕ settings 0° and 60°. The duration of exposure was 60 s/frame. The values of 2θ varied between 3.50° and 56.58°. Diffraction signals obtained from all frames of reciprocal-space images were used to determine the unit-cell parameters. The data were integrated using the Siemens SAINT program and were corrected for Lorentz and polarization effects. [17] Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements of numerous reflections. The structural model was obtained with the direct method and refined with full-matrix least-square refinement based on F^2 using the SHELXTL package. [18]

Structure Determination

A dark brown crystal of $Sr_3GeSb_2Se_8$ revealed an orthorhomic unit cell (a = 12.633(4) Å, b = 4.301(1) Å, c =28.693(7) Å, V = 1558.8(8) Å^3), and systematic absences indicated space group *Pnma* (No. 62). Using direct methods, a structural model was built with six unique sites for metal atoms (Sr, Ge and Sb) and eight unique sites for Se atoms. The crystal structure was initially refined in a model of $Sr_3GeSb_2Se_8$ with fully occupied sites of Sr (Sr(1)-Sr(3)), Ge (M(1)), Sb (M(2), M(3)) and Se (Se(1)-Se(8)). The isotropic displacement parameters (U_{iso}) of M(1)-M(3) sites exhibited unreasonable values, which indicated that M(1)-M(3) sites had partial or mixed occupancy by Ge or Sb cations. A subsequent refinement indicated that the M(1) site is occupied 65%/35% by Ge/Sb, whereas the M(2) and M(3) sites contain 6%/94% and 24%/76% of Ge/Sb, respectively. This result yielded a charge-balanced formula $Sr_3GeSb_2Se_8$. Final structural refinements yielded *R1/wR2* to be 0.0582/0.1221. All atomic positions were refined with anisotropic displacement parameters. Tables 1-3 summarize the crystallographic data, atomic coordinates and interatomic distances of $Sr_3GeSb_2Se_8$. Further details of the crystal-structure investigation can be obtained from the the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-XXXXXX.

Characterization

X-ray powder-diffraction data of the products were measured about 23 °C on a Bragg–Brentano-type powder diffractometer (Bruker D8 Advance, operated at 40 kV and 40 mA, Cu Kα, λ = 1.5418 Å). For phase identification, XRD data were collected in a 2θ range from 5° to 60° with a step interval 0.02°. Diffuse reflectance measurements were performed near 25 °C with a UV-visible spectrophotometer (Jasco V-570); an integrating sphere was used to measure the diffuse reflectance spectra over the range 200-2000 nm. Samples as ground powder were pressed onto a thin glass slide holder; a $BaSO_4$ plate served as reference. Thermogravimetric (TGA) analyses were performed on a thermogravimetric analyzer (Perkin-Elmer pyres). The sample was heated to 920 °C under a constant flow of N_2 with a heating rate 5 °C min^{-1}. Measurements of electrical resistivity were performed with the standard four-probe method on cold pressed bars (1x1x5 mm^3). The sample was annealed at 500 °C for 6 h before the measurement. For several samples, the electrical conductivity was so poor that the electrical resistance exceeded the limit (~ 10^3 MΩ) of the instrument.

B) Results and Discussion:

Structure Description

$Sr_3GeSb_2Se_8$ crystallizes in a new structural type with orthorhombic space group *Pnma*, with fourteen independent positions, three for Sr, three for mixed occupancy of Sb and Ge, and eight for Se atoms. The crystal structure of $Sr_3GeSb_2Se_8$ viewed along [0 1 0] is shown in Fig. 1. The major structural feature of this compound is the presence of alternative stacks of corner-shared tetrahedra and chains of edge-shared square pyramids, which are separated by Sr^{2+} ions. The Sr atoms are connected to seven or eight selenium atoms in a polyhedron close to a monocapped (Sr(2)) or bicapped (Sr(1), Sr(3)) trigonal prism with Sr–Se distances ranging between 3.1421(17) and 3.645(3) Å. The coordination environment of Sr^{2+} atoms is common in similar chalcogenides containing the Sr^{2+} cation, such as $Sr_2Ge_2Se_4$ [12], $Sr_3Sb_4S_9$ [14], and $Sr_6Sb_6S_{17}$ [15]. The M(1)-M(3) sites form a one-dimensional structure composed of corner-sharing tetrahedral chains $^1_\infty[MSe_3]$ (M(1)) and chains of edge-sharing double square-pyramids $^1_\infty[M_2Se_5]$ (M(2), M(3)), which are shown in Figure 2. For a $^1_\infty[MSe_3]$ unit, each central metal atom forms severely distorted tetrahedral units (bond angles between 93.89(9)° and 119.26(12)°) with four M-Se bonds of length 2.429(3), 2.427(2) and 2.492(2) (x2) Å, which share corners to form an infinite chain parallel to the *b* axis (Fig. 2a). These Se(3) atoms are shared between two MSe_4 tetrahedra. The M–Se distance is greater than for regular Ge-Se (~2.35 Å) but smaller than for Sb-Se (~2.6-2.8 Å) distances, indicating that the M(1) site has a mixed occupancy. The $^1_\infty[MSe_3]$ chain is rare in antimony chalcogenides, but similar corner-sharing $GeSe_4$ one-dimensional chains are found in A_2GeX_3 (A = Na, K, Rb, Cs; X = S, Se) [19-22]. Regarding the $^1_\infty[M_2Se_5]$ unit, the M(2) and M(3) sites form distorted square-pyramidal units with four selenium atoms that share edges to form a ribbon shape with fused square-pyramidal units parallel to the *b* axis (Fig. 2b). The distortion of the square-pyramidal unit is caused mainly by three short and two long M–Se bonds in each polyhedron. The M(2) atoms comprise three short bonds to Se between 2.611(2) and 2.774(1) Å and two longer ones at 3.020(2) Å, whereas M(3) exhibits three short M-Se bonds at 2.642(2)-2.864(2) and two longer ones at 2.917(2) Å. As M(2) and M(3) sites are rich (> 75%) in Sb, these M-Se bonds compare satisfactorily with the Sb-Se distances in Sb_2Se_3. The chains of fused double square pyramids form a pair that are related to each other via an *a*-glide plane parallel to the *a*-axis. Similar edge-sharing double chains were found in some multinary chalcogenides, such as $K_2Pr_{2-x}Sb_{4+x}Se_{12}$ [23], and $La_7Sb_9S_{24}$ [24]. Combining the Sr^{2+}, Ge-Se and Sb-Se anionic units, we express the charge-balanced formula as $[Sr^{2+}]_3[Ge^{4+}][Sb^{3+}]_2[Se^{2-}]_8$, which is consistent with the refined formula $Sr_3Ge_{0.95}Sb_{2.05}Se_8$.

Characterization

To determine the optical bandgap, the UV-vis diffuse reflectance spectrum of ground crystals of $Sr_3GeSb_2Se_8$ was measured between 200 and 2000 nm (6.2-0.62 eV); cf. Fig. 3. $Sr_3GeSb_2Se_8$ is expected to be a semiconductor because the charge of cations and anions is balanced. Those measurements of optical diffuse reflectance reveal that the band gap is near 0.75 eV. Thermogravimetric (TGA) measurements obtained on heating polycrystalline samples reveal a distinct decrease of mass near 700°C, attributed to decomposition of $Sr_3GeSb_2Se_8$ about that temperature (Fig. 4). Powder X-ray experiments indicate that the residues contain SrSe and an amorphous phase.

C) Conclusions

We have synthesized a new quaternary selenide $Sr_3GeSb_2Se_8$ that exhibits unique one-dimensional chains of vertex-sharing tetrahedra ${}_{\infty}^{1}[MSe_3]$(M=Ge/Sb) and fused double chains of edge-sharing square pyramids ${}_{\infty}^{1}[M_2Se_5]$. $Sr_3GeSb_2Se_8$ is an electron-precise compound with a measured band gap 0.75 eV.

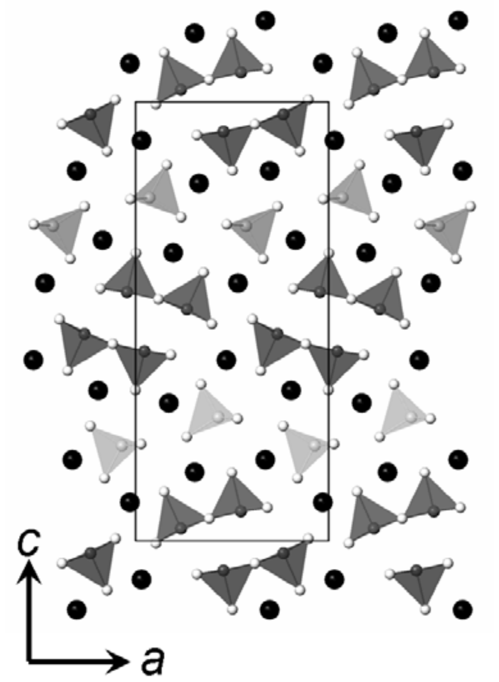

Fig. 1. a) Polyhedral representation of $Sr_3GeSb_2Se_8$ viewed along the crystallographic *b*-axis [010], showing 1D chains of ${}^{1}_{\infty}[\mathrm{MSe}_3]$(gray polyhedra) and ${}^{1}_{\infty}[\mathrm{M}_2\mathrm{Se}_5]$(dark gray polyhedra). Big black and small white circles denote Sr^{2+} and Se^{2-} atoms, respectively.

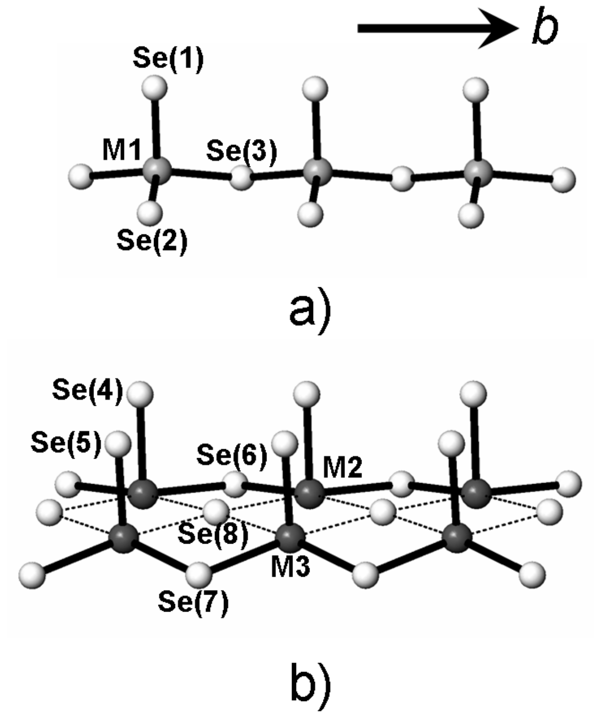

Fig. 2. (a) and (b) show ${}^{1}_{\infty}[\mathrm{MSe}_3]$and ${}^{1}_{\infty}[\mathrm{M}_2\mathrm{Se}_5]$ chains along the [010] direction. Solid and dashed lines indicate M-Se distances < 2.87 and < 3.02 Å, respectively.

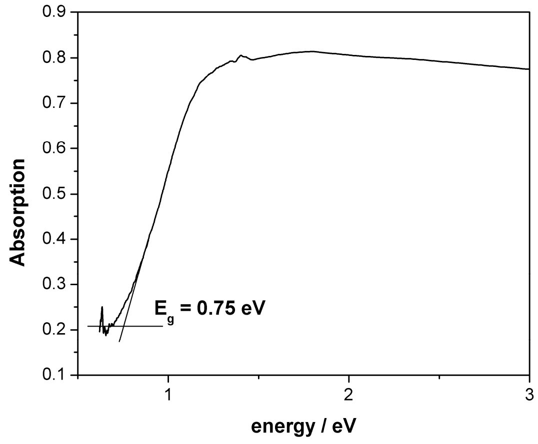

Fig. 3. TGA curve of $Sr_3GeSb_2Se_8$ (N_2 flow, heating rate = 5 °C/min).

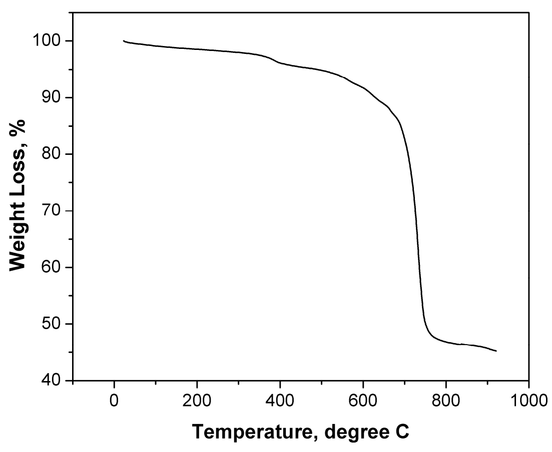

Fig. 4. Diffuse reflectance spectrum of $Sr_3GeSb_2Se_8$.

Table 1. Crystallographic Data for $Sr_3GeSb_2Se_8$

Empirical formula	$Sr_3GeSb_2Se_8$
Refined formula	$Sr_3Ge_{0.95(5)}Sb_{2.05(5)}Se_8$
Crystal size / mm^3	0.1×0.1×0.1
Formula mass / g mol^{-1}	1210.63
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	*orthorhombic*
Space group	*Pnma* (No. 62)
a/Å	12.633 (4)
b/Å	4.301(2)
c/Å	28.683(7)
V, $Å^3$	1558.8 (8)
Z	4
Calc. density / g cm^{-3}	5.158
Absorption coefficient / mm^{-1}	34.153
Transmission range	0.5046 - 1
Independent reflections	2188 [R(int) = 0.0497]
GOF on F^2	1.076
R1/*wR2* [$I>2\sigma(I)$]	0.0518/0.1241
$\Delta\rho$ (e/$Å^3$)	6.412 and -4.210

Table 2. Atomic Positional Coordinates, Isotropic Displacement Parameters / 10^{-3} Å^2, and Site Occupancies for $Sr_3GeSb_2Se_8$.

Atoms	*x*	*y*	*z*	U(eq)	Occ.
Sr(1)	0.8284(1)	0.7500	0.3147(1)	19(1)	
Sr(2)	0.11944(1)	0.7500	0.3433(1)	20(1)	
Sr(3)	0.15301(1)	0.7500	0.4123(1)	28(1)	
M(1)	0.10716(2)	0.2500	0.2178(1)	41(1)	Ge 0.65(2) Sb 0.35(2)
M(2)	0.9547(1)	0.2500	0.4328(1)	30(1)	Ge 0.06(2) Sb 0.94(2)
M(3)	0.12656(1)	0.2500	0.4719(1)	31(1)	Ge 0.24(2) Sb 0.76(2)
Se(1)	0.6612(1)	0.2500	0.3571(1)	21(1)	
Se(2)	0.7351(1)	0.2500	0.2378(1)	21(1)	
Se(3)	0.9722(2)	0.7500	0.2213(1)	88(1)	
Se(4)	0.0015(1)	0.2500	0.3441(1)	18(1)	
Se(5)	0.3520(1)	0.2500	0.3881(1)	19(1)	
Se(6)	0.8173(1)	0.7500	0.4245(1)	27(1)	
Se(7)	0.3950(2)	0.7500	0.5052(1)	36(1)	
Se(8)	0.8816(1)	0.2500	0.5508(1)	36(1)	

Table 3. Selected Interatomic Distances / Å for $Sr_3GeSb_2Se_8$.

Sr(1)-Se(1) x 2	3.250(2)	M(1)-Se(1)	2.429(3)
Sr(1)-Se(2) x 2	3.298(2)	M(1)-Se(2)	2.427(2)
Sr(1)-Se(3)	3.236(3)	M(1)-Se(3) x 2	2.492(2)
Sr(1)-Se(4) x 2	3.182(2)		
Sr(1)-Se(6)	3.154(2)		
		M(2)-Se(4)	2.611(2)
Sr(2)-Se(2) x 2	3.208(2)	M(2)-Se(6) x 2	2.774(1)
Sr(2)-Se(4) x 2	3.250(2)	M(2)-Se(8) x 2	3.020(2)
Sr(2)-Se(5) x 2	3.200(2)		
Sr(2)-Se(8)	3.187(2)	M(3)-Se(5)	2.642(2)
		M(3)-Se(7) x 2	2.864(2)
Sr(3)-Se(1) x 2	3.142(2)	M(3)-Se(8) x 2	2.917(2)
Sr(3)-Se(5) x 2	3.188(2)		
Sr(3)-Se(6)	3.645(3)		
Sr(3)-Se(7) x 2	3.337(2)		
Sr(3)-Se(7)	3.166(3)		

（四）計畫成果自評

This project was focused on the synthesis of new chalcogenides and a manuscript for $Sr_3GeSb_2Se_8$ was prepared. In addition, two series of chalcogenide compounds were synthesized and their preliminary results are summarized below. (1) The Effect of Transition Metal on the Synthesis of Quaternary Sulfides $MPb_4In_8X_{17}$ (M = Cr, Mn, Fe, Cu, Ag, Au; X = S, Se, **Figure 5)**[25]: The first representing compound is $TPb_4In_8S_{17}$ (T = Cu-Au). their structures are built from slabs of ${}^{2}_{\infty}[InS_2]$ and ${}^{2}_{\infty}[MPb_2In_3S_6]$. The transition metal is essential to the synthesis of these quaternary compounds. The EDS analysis on a single crystal has also confirmed the existence of transition metal. The compound crystallized in the monoclinic system, space group $P2_1/m$. Measurements on the title compounds as single crystals clearly show that the transition metals atoms occupy preferentially on different distorted octahedral sites depending on the d electron configuration. We propose that a transition metal with filled d orbitals would occupy preferentially a position with little M-S contact to avoid M-S antibonding interactions: the off-center octahedral sites fulfill this requirement (see M9 and M11 sites in **Figure 5)**. On the other hand, early transition metals prefer to occupy other octahedral sites; theoretical investigation is underway to understand the site preference of transition-metal and In atoms. Analogues with varied transition metals were also been synthesized and characterized. These compounds are semiconductors with electrical conductivity in the range $10^{-6} - 10^{-5}\ \Omega^{-1}cm^{-1}$ at room temperature. Measurements of optical diffuse reflectance on sulfide compounds revealed band gaps near 1.3 eV. (2) Experimental and Theoretical Investigation of the Ternary Chalcogenide $Sn_{3-x}Bi_{2+x}Se_6$ ($0<x<0.62$, **Figure 6.)**[26, 27]: A series of new ternary chalcogenides $Sn_{3-x}Bi_{2+x}Se_6$ ($0<x<0.62$) were synthesized and the crystal structure crystallizes in the orthorhombic space group *Pnma* (No.62). $Sn_{3-x}Bi_{2+x}Se_6$ is isostructure to the mineral of $Pb_3Bi_2S_6$. The structure is made up by slabs of the galena structure, which are juxtaposed and related to each other by (100) mirrors plane. The structure can be described as a polysynthetic twinning of the galena structure. The crystal structure exhibits Sn/Bi mixed occupancied sites, and experiments indicated phase width in $Sn_{3-x}Bi_{2+x}Se_6$ ($0<x<0.62$). The average thermopower of $Sn_{2.38}Bi_{2.62}Se_6$ and $Sn_3Bi_2Se_6$ over temperature range between 300 and 500K are -53(8)μV/K and 87(9)μV/K, respectively , which showed n-type and p-type semiconducting properties,. The relative Mulliken population analyses revealed positively and negatively polarized sites for Sn/Bi and Se sites and the proposed phase width from the calculations is in consistent with the experimental data. Detail characterizations including the purification of these phases, physical property measurement and detail theoretical studies could be done soon. During this project year, two posters were presented by graduate students in the 2005 annual Chinese Chemical Society meeting and the 2006 Meeting of the American Crystallographic Association. The manuscripts for these results are in progress.

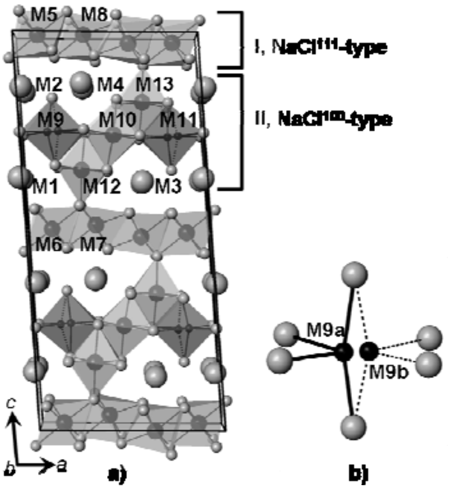

Figure 5. Three-dimensional structure of $CuPb_8In_{17}S_{34}$ projected along [010]; big gray circles: Pb; small gray circles: S; black circles inside the gray octahedral: In; small black circles inside the dark gray octahedral: 75% In/25% Cu. b) Coordination environment of the M9 site.

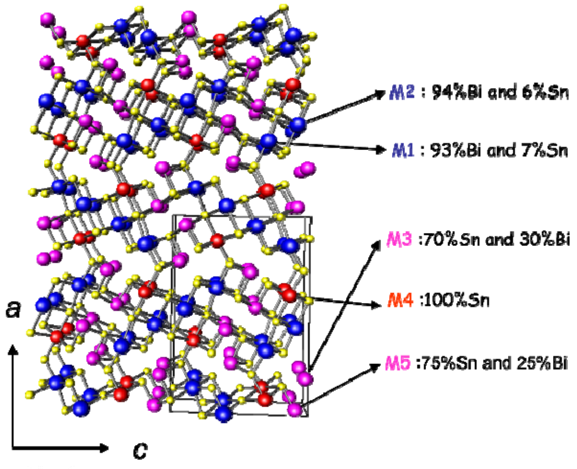

Figure 6. Perspect representation of $Sn_{3-x}Bi_{2+x}Se_6$ and viewed along b axis. Yellow: Se; Red: Sn; Blue , Pink: Sn/Bi.

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