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New quinternary selenides: Syntheses, characterizations, and electronic structure calculations

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Five quinternary selenides, $Sr_{2.63}Y_{0.37}Ge_{0.63}Sb_{2.37}Se_8$ (**I**), $Sr_{2.63}La_{0.37}Ge_{0.63}Sb_{2.37}Se_8$ (**II**), $Sr_{2.71}La_{0.29}Sn_{0.77}Bi_{2.23}Se_8$ (**III**), $Ba_{2.67}La_{0.33}Sn_{0.67}Sb_{2.33}Se_8$ (**IV**), and $Ba_{2.67}La_{0.33}Sn_{0.67}Bi_{2.33}Se_8$ (**V**), were synthesized by solid-state reaction in fused silica tubes. These compounds are isostructural and crystallize in the $Sr_3GeSb_2Se_8$ structural-type, which belongs to the orthorhombic space group *Pnma* (no. 62). Three structural units, ${}^{1}_{\infty}[MSe_3]$, ${}^{1}_{\infty}[M_4Se_{10}]$ (M=*Tt*, *Pn*) and M' (M'=groups **II** and **III** element), comprise the entire one-dimensional structure, separated by M'. Measurements of electronic resistivity and diffused reflectance suggest that **IV** and **V** have semiconducting properties. Electronic structure calculations confirm the site preferences of Sr/La element discovered by crystal structure refinement.

1. Introduction

Multinary chalcogenides play an increasingly important role in solid-state physics, chemistry, and materials science. Among these materials, chalcogenides containing alkali, alkaline earth, and rare earth elements have received attention for their diverse structures and applications in thermoelectric (TE) devices [1–5] and nonlinear optics [6–8]. These materials' chemical and physical properties can be manipulated by modifying the cation and chalcogen anion substitutions. Chalcogenides incorporating group **1**, **2**, or rare earth elements usually provide rich coordination environments for the main group elements, and have low structural dimensionalities. These features generally reduce thermal conductivity, and may enhance thermoelectric properties [3]. Combining the chalcogenides with other p-block elements, such as Ge, Sn, or Pb from group 14, or the elements Sb or Bi from group 15, results in the formation of various anionic frameworks that can function as building blocks in the formation of new structures with different coordination numbers [9–15].

Many quinternary chalcogenides have been studied during the past decade. The first published example was $K_{0.5}Ba_{0.5}DyCu_{1.5}Te_3$ [16]. The complex $A_{5-x}K_{1+x}Sn[Zn_4Sn_4S_{17}]$ (A=K^+, Rb^+, Cs^+; x=0, 4, 5)[17] exhibits a chalcogen-based open framework with interesting ion-exchange properties. Quinternary minerals with complex components have been studied, including angelaite [18], billingsleyite [19], watlinsonite [20], and cosalite [21]. Unlike other quinternary systems, $KCaEr_2CuS_5$ [22] is the first reported quinternary sulfide that does not exhibit substitutional disorder.

Our group has studied a number of multinary metal selenides representative of several different systems, including *Tr*–*Tt*–*Pn*–Se [23], *TM*–*Tr*–*Tt*–Se [24], and *Ae*–*Tt*–*Pn*–Se systems [25] (*Ae*=alkaline earth elements; *TM*=transition metal; *Tr*=In; *Tt*=Sn, Pb; *Pn*=Sb, Bi). Our studies of these systems revealed a charge-balanced system $Ae_3SnPn_2Se_8$ (*Ae*=Sr, Ba, *Pn*=Sb, Bi) [26] featuring tetrahedrally coordinated Bi atoms. We investigated an *A*–*M*–*Q* (*A*=alkali, alkaline earth, or rare earth metal; *M*=group 3–5 p-block metal; *Q*=S, Se, Te) series analogous to this system, and report the synthesis of five quinternary selenides. We present their syntheses, structures, physical properties, and calculations of their electronic structures. Sr and La metal sites exhibit substitutional disorder in *M*1–3 sites, with site preferences determined by single-crystal X-ray diffraction. These measurements are further supported by electronic structure calculations.

2. Experimental

2.1. Synthesis

All compound preparations were performed in a glove box under a dry nitrogen atmosphere. Chemicals were used as obtained (from Alfa Aesar)—Ba chunks, 99.00%; Sr chunks, 99.00%; Ge powder, 99.50%; Sn powder, 99.80%; Sb powder, 99.90%; Bi powder, 99.50%; Se powder, 99.95%; Y chunks, 99.00%; La chunks, 99.00%. All reactions were

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conducted using reagents in their elemental forms, in fused silica tubes placed in a temperature-controlled furnace.

In attempts to synthesize analogous compounds to $Sr_8YGe_2Bi_7Se_{24}$ [26], we combined pure elements in the appropriate stoichiometric ratios by weight (total mass approximately 0.5 g) under a dry nitrogen atmosphere following the general formula $Ae_8MTt_2Pn_7Se_{24}$ (Ae=Sr, Ba; M=Y, La; Tt=Ge, Sn; Pn=Sb, Bi). Reaction mixtures were heated to 1023 K over one day, maintained at that temperature for one day, slowly cooled to 673 K over a day, and finally cooled to room temperature (approximately 300 K) by terminating the power. The products were polycrystalline ingots that exhibited a metallic luster. Those were powdered before characterization by powder X-ray diffraction. The powder X-ray diffraction patterns for reaction mixtures $Sr_8YGe_2Sb_7Se_{24}$, $Sr_8LaGe_2Sb_7Se_{24}$, $Sr_8LaSn_2Bi_7Se_{24}$, $Ba_8LaSn_2Sb_7Se_{24}$, and $Ba_8LaSn_2Bi_7Se_{24}$ showed peaks corresponding to the $Sr_3GeSb_2Se_8$ [25] structure. After structural determination from single-crystal X-ray diffraction data, we obtained refined formulas for these new compounds, which are $Sr_{2.63}Y_{0.37}Ge_{0.63}Sb_{2.37}Se_8$ (**I**), $Sr_{2.63}La_{0.37}Ge_{0.63}Sb_{2.37}Se_8$ (**II**), $Sr_{2.71}La_{0.29}Sn_{0.77}Bi_{2.23}Se_8$ (**III**), $Ba_{2.67}La_{0.33}Sn_{0.67}Sb_{2.33}Se_8$ (**IV**), and $Ba_{2.67}La_{0.33}Sn_{0.67}Bi_{2.33}Se_8$ (**V**). Subsequent attempts to synthesize pure phases of compounds **I**–**V** were conducted using the mentioned reaction conditions. Powder X-ray diffraction measurements showed that samples **IV** and **V** were in good agreement with their calculated patterns, indicating pure phases for these compounds (Figs S4 and S5). However, the compositions of **I**, **II**, and **III** respectively produce a minor phase of Sb_2Se_3, Sb_2Se_3, and Bi_2Se_3 (Figs. S1–3).

3. Characterization

Powder X-ray diffraction was performed by a Bruker D8 Advance diffractometer (operated at 40 kV and 40 mA, with Cu $K\alpha$ radiation, λ=1.5418 Å). The data were collected over a 2θ range of 5–60° in 0.016° steps, with an exposure time of 0.1 s per step. Diffuse reflectance measurements were conducted using a UV–visible spectrophotometer (Jasco V-670). Ground powder samples were placed into a thin glass slide holder, and a $BaSO_4$ plate served as a reference. An integrating sphere was used to measure the diffuse reflectance spectra over the range 200–2000 nm. The band gap was determined by extrapolating the linear regions of each $(\alpha/s)^2$ versus energy plot to $(\alpha/s)^2$ to zero. Differential thermal analysis (DTA) data were obtained on a thermal analyzer (NETZSCH STA 409PC). A small quartz tube with an inner diameter (i.d.)=3 mm was filled with roughly 50 mg of the sample, sealed under vacuum, and placed into the analyzer. DTA data were collected by heating to 1073 K and cooling to 673 K at a rate of 10 K/min under a constant flow of nitrogen gas. Electrical resistivity measurements were performed using the standard four-probe method on a cold pressed bar ($1 \times 1 \times 5$ mm^3). Each sample bar was annealed at 673 K for one week before measurement.

3.1. Single-crystal X-ray diffraction

Single crystals were obtained from the crushed reaction products and mounted on the ends of glass fibers for single-crystal X-ray diffraction studies. Intensity data were collected on a diffractometer (Bruker APEX CCD equipped with graphite-monochromated Mo–$K\alpha$ radiation, λ=0.71073 Å) at 293(2) K. Crystals were positioned 5.0 cm from the detector. Data were collected by scans of 0.3° in ω in groups of 600 frames at φ settings of 0° and 60°. The 2θ values varied between 2.74° and 56.56°. Diffraction signals obtained from 80 frames of reciprocal-space images were used to determine unit-cell parameters. The APEX 2 program package, including SAINT and SHELXTL, was used for structure determination and refinement [27]. Absorption corrections were based on fitting a function to the empirical transmission surface, as sampled by multiple equivalent measurements of numerous reflections.

3.2. Calculation of electronic structure

The calculation of electronic structure was performed by self-consistent tight-binding first principle LMTO (linear muffin tin orbitals) calculations using the atomic spheres approximation (ASA) [28–32]. We applied density functional theory using local density approximation (LDA) in the LMTO approximation. To study the influence of M (M=Y, La) substitution and preference to the refined crystal structure, three models were constructed to represent different conditions of occupation for La and Sr atoms. Those models were based on the refined crystal structure of $Sr_{2.67}La_{0.33}Sn_{0.67}Bi_{2.33}Se_8$ and its b-axis was extended to a triple cell with the $Pna2_1$ space group. The general formula is $Sr_8LaSn_2Bi_7Se_{24}$. All independent crystallographic sites were triplicated and categorized as a, b, and c sites. For example, in a triple cell, the $M1$ site in the origin cell is split into three sites, named $M1a$,

Table 1
Crystal data and structure refinement for compounds **I**–**V.**

	I	**II**	**III**	**IV**	**V**
Refined composition	$Sr_{2.63}Y_{0.37}Ge_{0.63}Sb_{2.37}Se_8$	$Sr_{2.63}La_{0.37}Ge_{0.63}Sb_{2.37}Se_8$	$Sr_{2.71}La_{0.29}Sn_{0.77}Bi_{2.23}Se_8$	$Sr_{2.67}La_{0.33}Sn_{0.67}Sb_{2.23}Se_8$	$Ba_{2.66}La_{0.33}Sn_{0.67}Bi_{2.33}Se_8$
Temperature	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group, Z	*Pnma* (62), 4	*Pnma* (62), 4	*Pnma* (62), 4	*Pnma* (62), 4	*Pnma* (62), 4
a/Å	12.594(3)	12.537(3)	13.047(4)	12.630(3)	13.062(3)
b/Å	4.3323(9)	4.348(1)	4.262(1)	4.626(1)	4.4596(9)
c/Å	28.862(6)	28.812(6)	29.220(9)	29.628(8)	29.892(6)
V/Å^3	1574.7(6)	1570.7(6)	1624.7(8)	1731.1(8)	1735(1)
θ_{min}, θ_{max}/deg	1.41/25.02	1.41/25.02	1.71/25.02	1.37/25.03	1.36/25.03
Independent reflections (R_{int})	1587 (0.0476)	1581 (0.0353)	1637 (0.0595),	1746 (0.0341),	1759 (0.0467)
observed reflections	13602	13638	13211	14988	15229
$d_{calcd.}$/mg m^{-3}	3.883	3.946	5.177	4.050	4.609
Absorption coefficient/mm^{-1}	25.378	25.194	40.682	21.074	35.897
Goodness-of-fit on F^2	1.110	1.102	1.066	1.106	1.040
R_1, wR_2 ($I > 2s(I)$)	0.0364, 0.0792	0.0376, 0.0884	0.0279, 0.0591	0.0467, 0.1140	0.0393, 0.0870
R_1, wR_2 (all data)[a]	0.0474, 0.0841	0.0422, 0.0908	0.0368, 0.0625	0.0503, 0.1164	0.0454, 0.0907
Largest diff. peak and hole/eÅ^{-3}	3.316, −3.196	3.110, −3.157	1.826, −3.057	4.234, −5.375	5.5058, −3.350

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$ $wR_2 = \{\sum(w(F_0{}^2 - F_c{}^2)^2)/\sum(w(F_0{}^2)^2)\}^{1/2}$