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Synthesis and characterization of quaternary selenides $Sn_2Pb_5Bi_4Se_{13}$ and $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$

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ABSTRACT

Quaternary selenides $Sn_2Pb_5Bi_4Se_{13}$ and $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$ were synthesized from the elements in sealed silica tubes; their crystal structures were determined by single-crystal and powder X-ray diffraction. Both compounds crystallize in monoclinic space group $C2/m$ (No.12), with lattice parameters of $Sn_2Pb_5Bi_4Se_{13}$: $a = 14.001(6)$ Å, $b = 4.234(2)$ Å, $c = 23.471(8)$ Å, $V = 1376.2(1)$ Å^3, $R_1/wR_2 = 0.0584/0.1477$, and GOF = 1.023; $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$: $a = 13.872(3)$ Å, $b = 4.2021(8)$ (4) Å, $c = 26.855(5)$ Å, $V = 1557.1(5)$ Å^3, $R_1/wR_2 = 0.0506/0.1227$, and GOF = 1.425. These compounds exhibit tropochemical cell-twinning of NaCl-type structures with lillianite homologous series L(4, 5) and L(4, 7) for $Sn_2Pb_5Bi_4Se_{13}$ and $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$, respectively. Measurements of electrical conductivity indicate that these materials are semiconductors with narrow band gaps; $Sn_2Pb_5Bi_4Se_{13}$ is n-type, whereas $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$ is a p-type semiconductor with Seebeck coefficients −80(5) and 178(7) μV/K at 300 K, respectively.

1. Introduction

Seeking new materials for thermoelectric applications has become a research goal for scientists in recent decades. Among them, multinary chalcogenides possess complicated structural types and varied physical properties, which have been a subject of intensive investigation. The thermoelectric property is assessed according to the figure of merit $ZT = S^2\sigma/\kappa$ with Seebeck coefficient S, electrical conductivity σ, and thermal conductivity κ [1]. It has been shown that thermoelectric materials (TE) with a large figure of merit are semiconductors having complicated compositions and crystal structures; calculations reveal that the ideal band gaps should lie in a range 0.16–0.26 eV (6–10 $k_\beta T$) at 300 K [2]. Alloy $Bi_{2-x}Sb_xTe_{3-y}Se_y$ is used commercially for cooling applications near 300 K with optimized $ZT \sim 1$ [1]. Two newly reported materials, $CsBi_4Te_6$ [3] and $AgPb_mSbTe_{2+m}$ [4], show thermoelectric figure of merit $ZT \sim 0.8$ at 225 K and 2.2 at 800 K, respectively.

Synthetic approaches to discover new TE materials have focused on chalcogenides containing heavy main-group metals such as tin, lead or bismuth as constituent elements [5,6]. In seeking chalcogenides for thermoelectric applications, our research has focused on the systems Sn–Pb–Bi–X (X = S, Se, Te). The only compound structurally characterized is the quaternary sulfide $Pb_5Sn_3Bi_4S_{17}$ [7]. In the case of chalcogenides containing group 14 (Sn, Pb), 15 (Sb, Bi) and 16 (Se, Te) elements, no quaternary phase has been reported. Here we describe the synthesis, crystal structures, calculations of electronic structure and physical properties of compounds $Sn_2Pb_5Bi_4Se_{13}$ and $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$.

2. Experiments

2.1. Synthesis

All compounds were performed in a glove box under a dry nitrogen atmosphere. Chemicals were used as obtained (from Alfa Aesar) – Bi, 99.95%, powder; Sn, 99.5%, powder; Pb, 99.9%, powder; Se, 99.95%, powder. The total masses of samples (all elements combined) were about 0.5 g. All reactants in evacuated fused-silica tubes were placed in a resistance furnace with controlled temperature.

2.1.1. $Sn_2Pb_5Bi_4Se_{13}$

$Sn_2Pb_5Bi_4Se_{13}$ was initially observed from a reaction intended to synthesize '$Sn_{0.8}Pb_{2.2}Bi_2Se_6$'. The reaction mixture was heated slowly to 1073 K over 12 h. This temperature was maintained for 18 h, followed by slow cooling to 773 K over 12 h, and finally to about 300 K on simply terminating the power. The product, observed under an optical microscope, contained a molten part and cuboid-shaped crystals. Measurements of powder X-ray diffraction of the product of the '$Sn_{0.8}Pb_{2.2}Bi_2Se_6$' reaction revealed mixtures of

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$Pb_2Bi_2Se_5$ [8], $Sn_3Bi_9Se_{13}$ [9] and an unknown phase. Some cuboid-shaped crystals were chosen for measurements with single-crystal X-ray diffraction; the crystal structure was determined with a refined composition near $Sn_2Pb_5Bi_4Se_{13}$. Reactions with varied ratios Sn/Pb in $Sn_xPb_{7-x}Bi_4Se_{13}$ ($x = 0$, 2, 4, 6, 7) were utilized to probe the possible phase width with the same heating conditions as specified above. The products of each reaction displayed silvery, brittle ingots that were sensitive to neither air nor moisture. Chemical analyses by powder X-ray diffraction and energy-dispersive spectra (EDX) revealed a pure phase from reaction of '$Sn_2Pb_5Bi_4Se_{13}$'. The products from the other reactions comprised mixtures of $SnSe_2$ [10], PbSe [11], Bi_2Se_3 [12] and $Sn_{0.57}Bi_{0.28}Se$ [13]. Attempts to synthesize a quaternary phase $Sn_2Pb_5M_4X_{13}$ (M = Sb, Bi; X = S, Se) failed; the product yielded only known phases of $SnBi_2S_4$ [14], $Pb_2Bi_2S_5$ [15], PbSe [11], $PbSb_2Se_4$ [16] and a minor unknown phase.

2.1.2. $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$

$Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$ was initially observed from a reaction intended to synthesize '$Sn_{2.9}Pb_{0.1}Bi_2Se_6$', with heating conditions the same as specified above. The product contained a molten ingot with cuboid-shaped crystals. Measurements with powder X-ray diffraction indicated that this product contained mixtures of $(Sn_xPb_{1-x})_3Bi_2Se_6$ and an unknown phase. Measurements of single-crystal X-ray diffraction on a cuboid-shaped crystal revealed a quaternary phase with refined formula $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$. Reactions with varied ratios Sn/Pb in $Sn_{9-x}Pb_xBi_4Se_{15}$ ($x = 0, 0.35, 0.5, 1, 9$) were utilized to probe the possible phase width using the same heating conditions as specified above. The products from each reaction revealed silvery, brittle ingots that were stable in air. According to measurements of powder X-ray diffraction and energy-dispersive spectra (EDX), the pure phase was observed from only the reaction of '$Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$'. The products of other reactions contained mixtures of $Sn_{0.57}Bi_{0.28}Se$ [13], PbSe [11], Bi_2Se_3 [12] and $PbBi_2Se_4$ [17]. When other possible variations of $Sn_{8.65}Pb_{0.35}M_4X_{15}$ (M = Sb, Bi; X = S, Se) were tested, the products in each case contained mixtures of PbSe [11], $Sn_{17}Bi_6S_{29}$ [7], $Sn_4Sb_4Se_{10}$ [18] and $Sn_2Sb_2S_5$ [19].

Because the compound $Sn_2Pb_5Bi_4Se_{13}$ as-synthesized is near the reported phase of $KSn_5Bi_4Se_{13}$ [20], additional reactions were performed with various containers (graphite, alumina and tantalum) to avoid a possible contamination of alkali-metal cations (e.g. K^+, Na^+) from the silica tube; these containers were sealed inside silica tubes under vacuum and heated under the same conditions as specified above. Pure phases of the title compounds were observed; elemental analyses (EDX) show no signal from alkali metals (Na, K) in the products. Both compounds are stable in air under ambient conditions and the experimental X-ray powder-diffraction patterns agreed satisfactorily with patterns simulated based on single-crystal data, indicating the phase purity of the products as-synthesized (Fig. S1).

2.2. Single-crystal X-ray diffraction (XRD)

Single crystals of compounds $Sn_2Pb_5Bi_4Se_{13}$ ($0.08 \times 0.03 \times 0.03\ mm^3$) and $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$ ($0.08 \times 0.031 \times 0.03\ mm^3$) were mounted on glass fibers with epoxy glue; intensity data were collected on a diffractometer (Bruker APEX CCD) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The distance from the crystal to the detector was 5.038 cm. Data were collected with a scan 0.3° in groups of 600 frames each at ϕ settings 0°, 90°, 180° and 270°. The duration of exposure was 30 s for both samples; values of 2θ varied between 2.25° and 28.35°. Diffraction signals obtained from all frames of reciprocal space images were used to determine the parameters of the unit cell. The data were integrated (Siemens SAINT program) and corrected for Lorentz and polarization effects [21]. Absorption corrections were based on a function fitted to the empirical transmission surface as sampled by multiple equivalent measurements of numerous reflections. The structural model was obtained with direct methods and refined with full-matrix least-square refinement based on F^2 (SHELXTL package [22]). The atomic occupancy for each metal site was determined from the coordination environment compared with literature and a formula valence balance.

2.2.1. $Sn_2Pb_5Bi_4Se_{13}$

Several crystals from the crushed product were used for single-crystal X-ray diffraction, but the initial diffraction data to index these crystals indicated that many of them were twinned crystals with large standard deviations of the lattice parameters. The best crystal data for the structure determination were selected for a rod-shaped crystal that revealed a monoclinic unit cell ($a = 14.001(6)$ Å, $b = 4.234(2)$ Å and $c = 23.471(8)$ Å, $V = 1376.2(1)$ Å^3); systematic absences indicated space group $C2/m$ (No. 12). Thirteen independent crystallographic sites (M1–M6 and Se7–Se13) were located. The structural refinements displayed unreasonable thermal displacement parameters for sites M1–M6, indicative of positions with mixed occupancy of Bi/Sn or Pb/Sn. The basis of charge balance was used to determine the site preference for Pb or Bi; sites (M1–M3), (M4–M6) and Se7–Se13 were assigned as mixed occupancy of Bi/Sn, Pb/Sn, and 100% Se, respectively. During the latter stages of refinement, four large residues ($\sim$4–6 e/Å^3) appeared in the map of electron density at positions near M3 and M6 sites, which might be due to the contribution of twin components. These maxima were made to refine as partially occupied Sn, Pb or Bi atoms, but refined formula were not charge-balanced to justify the refinement. These maxima were therefore excluded as atoms in the final model because of their uncertainty. Attempts to collect data from the twin component and refine in a HKL5 format failed to improve the refinement with decreased residuals. Assuming Sn^{2+}, Pb^{2+}, Bi^{3+} and Se^{2-}, a charge-balanced formula $(Sn^{2+})_{2.07}(Pb^{2+})_{5.06}(Bi^{3+})_{3.87}(Se^{2-})_{13}$ was constructed. The final cycle of refinement included anisotropic displacement parameters and a secondary extinction correction performed on F_0^2 with 82 parameters and 1877 independent reflections. Final structural refinements produced $R1/wR2/\mathrm{GOF} = 0.058/0.147/1.023$.

2.2.2. $Sn_{8.65}Pb_{0.35}Bi_4Se_{15}$

X-ray measurements on a single crystal revealed a monoclinic unit cell with $a = 13.872(3)$ Å, $b = 4.2021(8)$ (4) Å, $c = 26.855(5)$ Å, $V = 1557.1(5)$ Å^3; systematic absences indicated space group $C2/m$ (No. 12). Fifteen crystallographic sites (M1–M2, Sn3, M4–M7, and Se8–Se15) were found. The cationic sites M1–M2 and M4–M7 have mixed occupancy by Bi/Sn and Pb/Sn atoms because of their atypical parameters for thermal displacement when refined with full occupancy by Sn, Pb or Bi. The refined electron density of site Sn3 is near 100% Sn within a standard deviation, and was so assigned. During the latter stages of refinement, a large maximum ($\sim$8 e/Å^3) appeared in the map of electron density at a position near M7 ($\sim$0.8 Å), which might be due to the contribution of twin components. This feature was made to refine as partially occupied Sn, Pb or Bi atoms, but the refined formulae were not charge-balanced, so this feature was excluded as an atom in the final model. Attempts to collect data from the twin component and refine in HKL5 format failed to improve the refinement with decreased residuals. Assuming Sn^{2+}/Pb^{2+}, Sn^{2+}/Bi^{3+} and Se^{2-}, a charge-balanced formula $(Sn^{2+}{}_{8.41}Pb^{2+}{}_{0.37})(Bi^{3+})_{4.22}(Se^{2-})_{15}$ was constructed that served to constrain the occupancies of the