

Effect of the Transition Metal on the Synthesis of Quaternary Sulfides MPb₈In₁₇S₃₄ (M = Cu, Ag, Au)

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Quaternary sulfides MPb₈In₁₇S₃₄ (M = Cu, Ag, Au) were synthesized at 1123 K from their elements in stoichiometric ratios. These compounds crystallize in monoclinic space group $P2_1/m$. The crystal structures feature combinations of ${}^2_{\infty}[\text{InS}_2]$ (NaCl¹¹¹-type) and ${}^2_{\infty}[\text{MPb}_2\text{In}_3\text{S}_6]$ (NaCl¹⁰⁰-type) slabs. These compounds are semiconductors with band gaps near 1.3 eV.

Among multinary chalcogenides with novel structures and properties,^{1,2} some are reported to possess thermoelectric properties that make them prospectively useful as devices for cooling and for generating electrical power.^{3–6} Most attention has been devoted to multinary systems containing alkali, alkaline-earth, and rare-earth elements;^{7–11} in contrast, little work has been done on chalcogenides lacking strongly reducing elements, and most reported compounds are sulfides obtained from minerals.^{12–15} Our work on a quaternary system $\text{M}_x\text{Pb}_y\text{In}_z\text{X}_u$ (M = transition metal; X = S, Se) has produced new sulfides in a series MPb₈In₁₇S₃₄ (M = Cu, Ag, Au). These compounds contain unit cells similar to a structurally unknown metastable phase “Pb₂In₆X₁₁” [or (PbX)₂(In₂X₃)₃; X = S, Se].^{16,17} Our experiments indicate

that the transition metal plays a critical role in stabilizing the metastable phase, and their distributions reveal a notable site preference. Here we report the synthesis and characterization of these quaternary compounds.

MPb₈In₁₇S₃₄ (M = Cu, Ag, Au) were synthesized from solid-state reactions of their elements in stoichiometric ratios.¹⁸ A transition metal in a small proportion (<4% by mass) is essential for the synthesis; otherwise, the major product is Pb_{3.4}In_{9.6}S₁₇ in its ternary orthorhombic phase.¹⁴ All compounds crystallize according to a new structural type with monoclinic space group $P2_1/m$ that contains one formula per unit cell.¹⁹ Measurements with X-rays on single crystals reveal 13 unique sites for metal atoms (M, Pb, and In) and 17 unique sites for S atoms. The following description focuses on the structure of CuPb₈In₁₇S₃₄. Figure 1a shows a [010] projection of the structure that comprises two distinct building units (I and II) derived from a structure of NaCl type;^{1,20} these labeled building units are expanded along the *b* axis. Region I is a slab of ${}^2_{\infty}[\text{InS}_2]$ (NaCl¹¹¹-type) containing three atomic layers: the top and bottom layers

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(18) Synthesis: All materials were handled in an Ar-filled glovebox in which the concentration of oxygen was less than 10 ppm. Initial materials included transition metals [Alfa Aesar, Cu (99.90%), Ag (99.50%), and Au (99.50%)], Pb powder (Alfa Aesar, 99.90%), In ingot (Alfa Aesar, 99.90%), and S powder (Alfa Aesar, 99.50%). Reactants in stoichiometric proportions were heated in an evacuated silica ampule ($P \sim 10^{-2}$ Pa) at 1123 K within 24 h, kept at 1123 K for 24 h, and then cooled slowly to 973 K at a rate 10 K/h; finally, the furnace was turned off to allow cooling to 295 K. All products exhibit a black color with bar-shaped crystals and are stable in air for at least 14 days. Powder X-ray experiments were performed with the synchrotron powder X-ray diffraction (NSRRC BL01C2 line, $\lambda = 0.620$ Å) and Bruker D8 powder X-ray diffractometers. Powder patterns of all sulfides show no additional diffraction from impurities. Semiquantitative analysis of the composition of compounds was performed with electron-dispersive X-rays using a scanning electron microscope (Hitachi SEM-S4700, Tokyo, Japan) on selected bar-shaped crystal samples. The transition metal and Pb, In, and S elements were detected without impurity. According to the TGA measurements (Perkin-Elmer TGA 7), these compounds decomposed at 1111, 1149, and 1102 K for copper, silver, and gold sulfides, respectively. The major product from the residuals of each compound was orthorhombic phase Pb_{3.6}In_{9.4}S₁₇.¹⁴ Attempts to synthesize analogues with hypothetical formulas “Pb₈In₁₈S₃₄”, “Pb₉In₁₇S₃₄”, and “MPb₈In₁₇Se₃₄” (M = Cu, Ag, Au) failed; the major products contain the orthorhombic phase Pb_{3.6}In_{9.4}X₁₇ and PbX (X = S, Se).^{14,26}

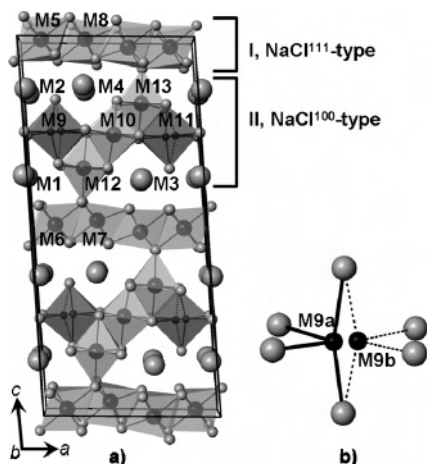


Figure 1. (a) Three-dimensional structure of $\text{CuPb}_8\text{In}_{17}\text{S}_{34}$ projected along [010]: big gray circles, Pb; small gray circles, S; black circles inside the gray octahedral, In; small black circles inside the dark gray octahedral, 75% In/25% Cu. (b) Coordination environment of the M9 site.

comprise S atoms that are nearly close-packed, whereas the central layer has atoms located in distorted octahedral sites. Region II is a slab of ${}^2_{\infty}[\text{CuPb}_2\text{In}_3\text{S}_6]$ (NaCl^{100} -type) that comprises interconnected metals (Cu, Pb, In) and S atoms in three layers, the arrangement of which is somewhat distorted from a structure of ideal NaCl type. Regions I and II stack to form a three-dimensional framework running along the c axis. Similar building slabs were observed in ternary sulfide $\text{In}_2\text{Sn}_3\text{S}_7$ that contains three and two atomic layers of NaCl^{111} - and NaCl^{100} -type units, respectively.²¹

A classification of metal sites is based on their coordination numbers. Metal sites M1–M4 of the first of three types are 100% Pb and are coordinated with eight S atoms in a bicapped trigonal prism ($d_{\text{M-S}} = 2.89\text{--}3.27$ Å). Metal sites M5–M8, M12, and M13 of the second type are 100% In; the coordination polyhedra around these sites are distorted octahedra with six S atoms ($d_{\text{M-S}} = 2.50\text{--}2.76$ Å). Metal sites M9–M11 of the third type contain refined electron density less or equal to that of an In atom. The coordination environments are six-coordinate with four short and two long M–S contacts ($d_{\text{M-S}} = 2.5(1) \times 4$ and $3.1(2) \times 2$ Å); these

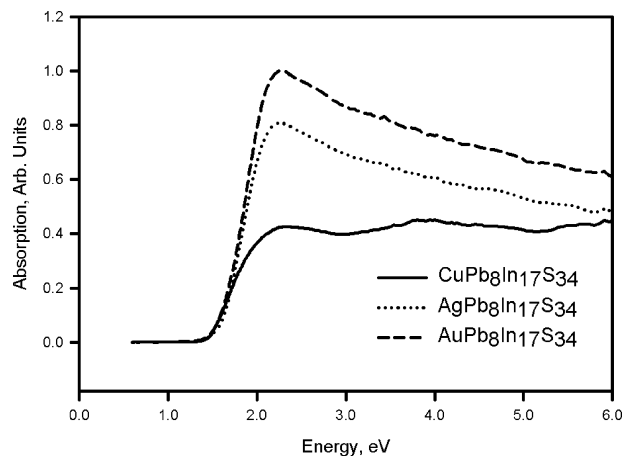


Figure 2. Diffuse-reflectance spectra of $\text{MPb}_8\text{In}_{17}\text{S}_{34}$ ($M = \text{Cu, Ag, Au}$). The solid, dotted, and dashed curves are for copper, silver, and gold sulfides, respectively.

positions are best described as distorted tetrahedral sites. Initial refinements of the crystal structure on these sites show large anisotropic thermal parameters along the a axis; the M9 and M11 sites were split into two dynamically distributed positions (M9a, M9b and M11a, M11b; see Figure 1b for the M9 site). The refined electron densities of the M9, M10, and M11 sites are 42.0(5), 49.0(4), and 43.3(6) e^-/site , respectively. If these sites are 100% occupied, the site compositions are near 75% In + 25% Cu for the M9 and M11 sites (44 e^-) and 100% In for the M10 sites (49 e^-). The Ag and Au phases reveal the same site compositions on the M9–M11 sites. These results yield a charge-balanced model $(\text{M}^{1+})(\text{Pb}^{2+})_8(\text{In}^{3+})_{17}(\text{S}^{2-})_{34}$ ($M = \text{Cu, Ag, Au}$).²²

Measurements on the title compounds as single crystals clearly show that Cu–Au atoms occupy preferentially the distorted tetrahedral sites M9 and M11. 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 (M9 and M11) fulfill this requirement.^{23,24} The reason that transition metals fail to occupy M10 or other octahedral sites is unclear; theoretical investigation is required to understand the site preference of transition-metal and In atoms.

$\text{MPb}_8\text{In}_{17}\text{S}_{34}$ ($M = \text{Cu, Ag, Au}$) are semiconductors with electrical conductivity in the range $10^{-6}\text{--}10^{-5} \Omega^{-1} \text{cm}^{-1}$ near 295 K. Measurements of the optical diffuse reflectance reveal that the band gaps are near 1.3 eV (Figure 2).²⁵

(19) Crystal data: (1) $\text{CuPb}_8\text{In}_{17}\text{S}_{34}$, monoclinic, $P2_1/m$ ($Z = 1$), $a = 12.664(3)$ Å, $b = 3.8816(10)$ Å, $c = 27.329(7)$ Å, $\beta = 94.377(6)^\circ$, $V = 1339.4(6)$ Å³, $R1/wR2 = 0.0544/0.1250$, $\text{GOF} = 1.073$. (2) $\text{AgPb}_8\text{In}_{17}\text{S}_{34}$, monoclinic, $P2_1/m$ ($Z = 1$); $a = 12.657(3)$ Å, $b = 3.8810(8)$ Å, $c = 27.459(6)$ Å, $\beta = 94.36(3)^\circ$, $V = 1344.9(5)$ Å³, $R1/wR2 = 0.0716/0.2098$, $\text{GOF} = 1.083$. (3) $\text{AuPb}_8\text{In}_{17}\text{S}_{34}$, monoclinic, $P2_1/m$ ($Z = 1$); $a = 12.701(3)$ Å, $b = 3.8794(9)$ Å, $c = 27.359(6)$ Å, $\beta = 94.347(4)^\circ$, $V = 1344.2(5)$ Å³, $R1/wR2 = 0.0426/0.1287$, $\text{GOF} = 1.093$. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 298(2) K with a Bruker APEX CCD diffractometer. All diffraction data were corrected for Lorentz and polarization effects; absorption corrections were based on fitting a function to an empirical transmission surface as sampled by multiple equivalent measurements.²⁷ The crystal structure was solved with direct methods (*SHELXTL*, version 6.10)²⁸ and subsequently refined through full-matrix least-squares calculations based on F^2 ; all independent atomic sites are assumed to be 100% Pb, In, S, and mixed occupied M/In ($M = \text{Cu, Ag, Au}$) atoms. The final refinement included anisotropic displacement parameters for all Pb, In, and S atoms. The mixed occupied sites M9 and M11 were refined isotropically with fixed 75% In and 25% M ($M = \text{Cu, Ag, Au}$).

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In summary, we report here the effect of transition metals on the formation of quaternary sulfides $MPb_8In_{17}S_{34}$ ($M = Cu, Ag, Au$). To enable an understanding of site preference and the effect on physical properties, analogues with varied transition metals should be synthesized and characterized; this related work is in progress.

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Supporting Information Available: Crystallographic data in CIF format and TGA curves for $MPb_8In_{17}S_{34}$ ($M = Cu, Ag, Au$). This material is available free of charge via Internet at <http://pubs.acs.org>.

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