LaPbCuS$_3$: Cu(I) Insertion into the α-La$_2$S$_3$ Framework

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The compound LaPbCuS$_3$, lanthanum lead copper sulfide, has been prepared and characterized from single crystal X-ray data. LaPbCuS$_3$ crystallizes in space group D_{2h}^{16}-$Pnma$ of the orthorhombic system, $a = 8.091(3)$, $b = 4.093(1)$, and $c = 15.996(5)$ Å, $V = 529.7$ Å^3 ($T = 293$ K), $Z = 4$, $M_r = 505.84$, $D_x = 6.341$ g/cm^3, $\lambda(\text{Mo}K\alpha_1) = 0.7093$ Å, $\mu = 448.8$ cm^{-1}, and $R(F_0) = 0.030$ and $R_w(F_0) = 0.042$ for 732 unique data with $F_0^2 > 3\sigma(F_0^2)$. The structure, which is related to that of α-La$_2$S$_3$, has 7-coordinate La and Pb atoms disordered unequally over two sites, with M–S bond lengths in the range from 2.864(3) to 3.168(3) Å. The Cu atoms are in tetrahedral sites that form corner-sharing chains along the b direction, with Cu–S distances ranging from 2.336(4) to 2.385(4) Å.   © 1992 Academic Press, Inc.

Introduction

Predictions about possible new structures of classical close-packed inorganic solids can often be made by considering the ways that corner-, edge-, and face-sharing octahedra and tetrahedra can be accommodated. In metal chalcogenides, however, the presence of more irregular polyhedra (e.g., capped trigonal prisms) introduces a level of complexity that makes it difficult to visualize possible substitution or insertion derivatives. Aikinite, BiPbCuS$_3$ (*1*), provides an example of cation insertion into a framework of capped trigonal prisms. BiPbCuS$_3$ may be thought of as a "stuffed derivative" (*2*) of Bi$_2$S$_3$ (which has the Sb$_2$S$_3$ or stibnite structure) with insertion of the Cu atom into a tetrahedral site among monocapped trigonal prisms.

α-La$_2$S$_3$ (*3*) has a structure that is similar to that of Sb$_2$S$_3$ and has La atoms in monocapped and bicapped trigonal-prismatic sites. Consequently, we envisioned a possi-

ble new structure in which a metal atom, for example Cu, would be in a tetrahedral site in α-La$_2$S$_3$. In this paper we present the synthesis and structure of the new quaternary chalcogenide, LaPbCuS$_3$. LaPbCuS$_3$ can be thought of as being derived from its parent compound, α-La$_2$S$_3$, by inserting a Cu(I) atom into a tetrahedral site in La$_2$S$_3$ coupled with partially substituting La(III) with Pb(II) to maintain charge balance.

Experimental

Synthesis. Single crystals of LaPbCuS$_3$ were isolated from the reaction of a mixture of La$_2$S$_3$ (Strem, 99.9%), Pb (Aldrich, 99.999%), Cu (Alfa, 99.5%), and S (Alfa, 99.999%) powders in a 1 : 4 : 6 : 9 ratio. The mixture of powders, 0.5 g total weight, was heated in an evacuated quartz tube at 773, 973, 1073, and 1273 K for 1 day each and then the furnace was shut off and allowed to cool. LaPbCuS$_3$ grew in ~10% yield as long deep-red transparent prisms; other

products from the reaction included PbS and La/Cu/S ternary compounds. EDAX microprobe analysis with an Hitachi S-570 SEM indicated the presence of La, Pb, Cu, and S in approximately a $1:1:1:3$ ratio.

Structure determination. A red elongated prism, $0.35 \times 0.04 \times 0.03$ mm, of $LaPbCuS_3$ was used for the collection of X-ray diffraction data. Preliminary cell constants were obtained with the use of Weissenberg photography. Overexposed photographs showed no evidence for a supercell. Refined unit cell parameters were determined from the least-squares analysis of 22 reflections in the range $30° \leq 2\theta(MoK\alpha_1) \leq 41°$ that had been automatically centered on a Picker FACS-1 diffractometer (4) at 293 K. Data were collected by the $\theta/2\theta$ technique with a scan range from $1.0°$ in 2θ below $K\alpha_1$ to $1.0°$ above $K\alpha_2$ at a scan rate of $2°/min$. Backgrounds were counted for 10 sec at each end of the scan range. Data were collected between $2° \leq 2\theta(MoK\alpha_1) \leq 65°$ (maximum $(\sin\theta)/\lambda = 0.758$ Å^{-1}) with Miller indices in the range $0 \leq h \leq 12$, $-6 \leq k \leq 6$, and $0 \leq l \leq 24$. Six representative standards were measured every 100 reflections during the course of data collection and showed no significant variation in intensity. Systematic absences $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$ lead to $Pn2_1a$ and $Pnma$ as possible space groups. A total of 2113 reflections was measured. Of these reflections, 1182 are unique in Laue group mmm. The 931 reflections observed twice (hkl, $h\bar{k}l$) afforded a merging R index of 6.6% before absorption correction and 5.0% after. We take this as ample evidence for the centrosymmetric space group $Pnma$. Of the 1182 unique reflections, 732 have $F_0^2 > 3\sigma(F_0^2)$. An analytical absorption correction (5) was applied. The dimensions (distance to faces from center) of the crystal were $0.176 \{010\}$, $0.013 \{101\}$, $0.014 \{10\bar{1}\}$, and $0.020 \{001\}$ mm, with a crystal volume of 2.8×10^{-4} mm^3. The transmission factors ranged from 0.206 to 0.388. The initial La, Pb, Cu, and S positions

in space group $Pnma$ were determined by direct methods with the program SHELXS-86 (6). Scattering factors and anomalous-dispersion terms were taken from the usual sources (7, 8). All calculations were done on a Stardent computer with programs standard in this laboratory (9). The crystal structure was standardized (10) according to the rules formulated by Parthé and Gelato (11). After the initial stages of refinement, disorder of the La and Pb sites was apparent from the thermal parameters. When the Pb and La site occupancies were fixed at 0.5 Pb and 0.5 La for each of the two sites, $R(F_0)$ was 0.054. With a total site occupancy constrained to be 1.0, the ratio of Pb to La was allowed to vary with the result of 0.642(8) Pb on the first site and 0.420(8) Pb on the second site with a final $R(F_0)$ of 0.049. Because these occupancies gave an overall ratio of La to Pb near $1:1$, the stoichiometry of the crystal was fixed at 1 La to 1 Pb. The final cycle of least-squares refinement on F_0^2 included anisotropic thermal parameters and resulted in values of $R(F_0)$ of 0.030 and $R_w(F_0)$ of 0.042 for data with $F_0^2 > 3\sigma(F_0^2)$, and $R(F_0^2)$ of 0.074 and $R_w(F_0^2)$ of 0.099 for 1182 data and 38 variables. There were no features greater than 3% the height of a Cu atom in the final difference electron density map. The error in the observation of unit weight is 1.21. The final positional and equivalent isotropic thermal parameters are given in Table I.[1] The occupancies of the disordered Pb/La sites are 0.657(1) Pb on the first metal site and therefore 0.343 on the second.

TABLE I

POSITIONAL PARAMETERS AND B_{eq} (Å^2) FOR LaPbCuS$_3$

Atom	x	y	z	B_{eq}^a (Å^2)
$M(1)^b$	0.08918(11)	$\frac{1}{4}$	0.78001(6)	1.49(2)
$M(2)$	0.25010(20)	$\frac{1}{4}$	0.03674(9)	1.21(3)
Cu	0.12122(24)	$\frac{1}{4}$	0.36696(11)	1.08(4)
S(1)	0.01243(43)	$\frac{1}{4}$	0.60007(19)	1.21(7)
S(2)	0.18064(41)	$\frac{1}{4}$	0.22092(20)	1.33(7)
S(3)	0.38093(42)	$\frac{1}{4}$	0.43046(21)	1.40(7)

^{a} $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$

^{b} $M(1)$ site is 0.657(1) Pb and 0.343 La; $M(2)$ site has reversed occupancies.

Results

The structure of LaPbCuS$_3$, shown in a labeled view in Fig. 1, is described in terms of bond distances and angles in Table II. As anticipated, the structure has the Cu atom in a tetrahedral site, with Cu–S bond lengths from 2.336(4) to 2.385(4) Å and S–Cu–S angles from 104.1(1)° to 119.1(2)°. The two La/Pb sites are each coordinated to seven S atoms in roughly a monocapped trigonal-prismatic arrangement, with M–S distances in the range from 2.864(3) to 3.168(3) Å (Fig. 2). The Cu–S tetrahedra share corners in

the b direction to form independent chains along b.

The structure of BiPbCuS$_3$ may be derived from that of Bi$_2$S$_3$ by inserting a Cu(I) atom into a tetrahedral site and substituting Pb(II) for Bi(III) for charge balance. The Bi$_2$S$_3$ framework is made up of two monocapped trigonal prisms, one of which has another very long Bi–S distance that could be considered a second cap. The Cu atom goes into a tetrahedral site that is located along the long Bi–S distance. Similarly, the LaPbCuS$_3$ structure can be derived from the α-La$_2$S$_3$ structure by inserting a Cu(I) atom into a tetrahedral site and then substituting Pb(II) for La(III) for charge balance (Fig. 3). LaPbCuS$_3$ and α-La$_2$S$_3$ crystallize in the same space group with similar axial lengths; the insertion of Cu into the α-La$_2$S$_3$ structure lengthens the a and c dimensions by 0.44 and 0.10 Å, respectively, while reducing the b dimension by 0.13 Å. In the α-La$_2$S$_3$ structure there are two potential sites for this tetrahedral insertion. The two S atoms that cap the 8-coordinate La site have approximately the same La–S bond lengths so that Cu insertion appears equally possible along either bond. However, only one of these two tetrahedral sites around the 8-coordinate La
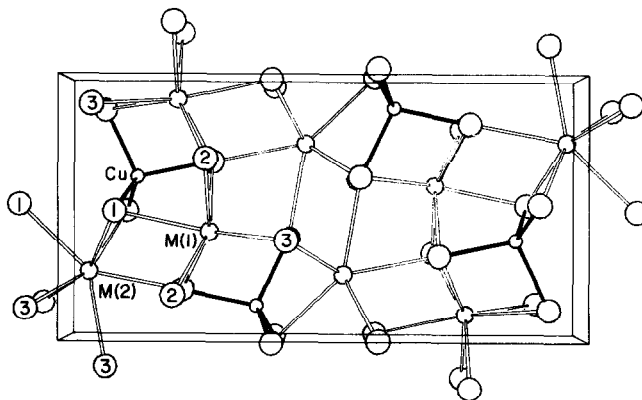

FIG. 1. A labeled view of LaPbCuS$_3$ down the b axis. The small circles are Cu, the medium circles are La/Pb, and the large circles are S. The Cu–S bonds are filled in.

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TABLE II

DISTANCES (Å) AND ANGLES (DEGREES) IN LaPbCuS₃

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M(1)–S(2)	2×	2.925(3)	M(2)–S(3)	2×	2.864(3)
M(1)–S(1)		2.945(3)	M(2)–S(1)	2×	2.986(3)
M(1)–S(2)	2×	2.994(3)	M(2)–S(2)		2.999(4)
M(1)–S(3)	2×	3.168(3)	M(2)–S(3)		3.036(4)
M(1)–Cu	2×	3.409(2)	M(2)–S(1)		3.050(4)
M(1)–Cu	2×	3.552(2)	M(2)–Cu		3.378(3)
S(3)–Cu–S(1)		108.29(10)	M(2)–Cu	2×	3.557(2)
S(3)–Cu–S(2)		104.14(14)	Cu–S(3)		2.336(4)
S(1)–Cu–S(1)		119.06(17)	Cu–S(1)	2×	2.374(2)
S(1)–Cu–S(2)		108.03(9)	Cu–S(2)		2.385(4)
S(2)–M(1)–S(2)		88.78(10)	S(3)–M(2)–S(3)		91.20(11)
S(2)–M(1)–S(1)		79.55(8)	S(3)–M(2)–S(1)		87.16(7)
S(2)–M(1)–S(2)		89.16(3)	S(3)–M(2)–S(1)		158.41(10)
S(2)–M(1)–S(2)		160.35(5)	S(3)–M(2)–S(2)		120.90(8)
S(2)–M(1)–S(3)		75.22(8)	S(3)–M(2)–S(3)		74.79(9)
S(2)–M(1)–S(3)		130.44(9)	S(3)–M(2)–S(1)		80.34(9)
S(1)–M(1)–S(2)		80.86(8)	S(1)–M(2)–S(1)		86.54(10)
S(1)–M(1)–S(3)		139.34(4)	S(1)–M(2)–S(2)		77.73(8)
S(2)–M(1)–S(2)		86.24(9)	S(1)–M(2)–S(3)		125.16(7)
S(2)–M(1)–S(3)		67.55(8)	S(1)–M(2)–S(1)		78.15(8)
S(2)–M(1)–S(3)		120.07(9)	S(2)–M(2)–S(3)		69.24(9)
S(3)–M(1)–S(3)		80.46(8)	S(2)–M(2)–S(1)		146.66(11)
			S(3)–M(2)–S(1)		144.11(10)

atom can be occupied at a time if face sharing of tetrahedra is to be avoided. In α-La₂S₃, there is both 7- and an 8-coordinate La site. When Cu is inserted into the framework, the 8-coordinate metal site is reduced to being 7-coordinate (Fig. 3). The La/Pb–S distances found in LaPbCuS₃, 2.864(3)–

3.168(3) Å, are comparable to the La–S distances found in α-La₂S₃, 2.91–3.16 Å.

In BiPbCuS₃ possible disordering of the Pb and Bi atoms, which have similar scattering factors, cannot be determined from the X-ray data. The Bi and Pb positions were assigned on the basis of the M–S bond
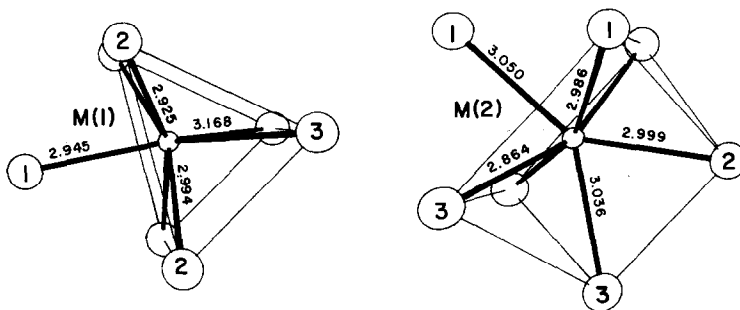

FIG. 2. The coordination geometries of M(1) (left) and M(2) (right). The solid lines show the trigonal prismatic arrangement of S atoms. Bond distances are in angstroms.

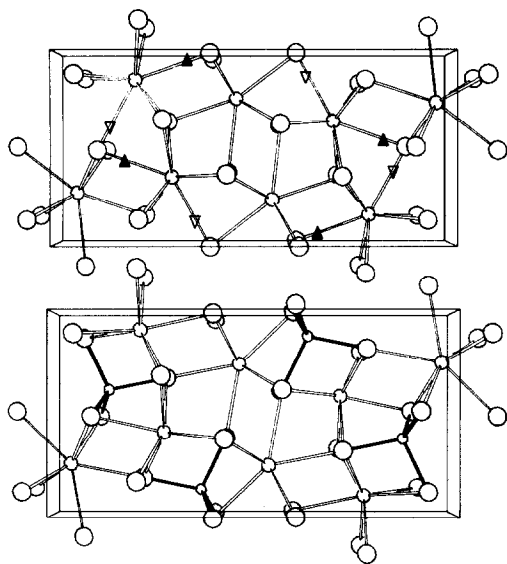FIG. 3. A comparison of the α-La₂S₃ (top) and LaPb-CuS₃ (bottom) structures. The potential sites for tetrahedral substitution into α-La₂S₃ are marked by a ▽ (occupied) or ▲ (unoccupied).

lengths. However, in LaPbCuS₃ disorder between La and Pb is observed and the ratio of Pb to La is approximately 2 : 1 on the first site and 1 : 2 on the second. If the two disordered metal sites had the same coordination environment, we would expect the ratio of La to Pb on each site to be 1 : 1. There must be some driving force away from an equal distribution. Both sites are 7-coordinate and the average M–S bond lengths are 3.017 and 2.969 Å, respectively, for the first and second metal sites. The difference in average bond lengths, 0.048 Å, is close to the expected difference, 0.040 Å, calculated from the ionic radii for 7-coordinate La(III) and Pb(II) (12) and the La to Pb ratio at the two sites. For the first site there are two short M–Cu distances of 3.409(2) Å and two longer distances of 3.552(2) Å. For the second site there are two M–Cu distances of 3.557(2) Å and one short distance of 3.378(3) Å. Perhaps the observed La to Pb ratios arise from electrostatics, with the two short

M–Cu distances of the first site favoring increased occupancy of the Pb(II) atom over the more highly charged La(III) atom. Electrostatics may also the reason why the particular tetrahedral site is filled by a Cu(I) atom. If instead the alternative tetrahedral site were filled, a much shorter and presumably less favorable M(2)–Cu distance would result.

LaPbCuS₃ has a deep-red color and consists formally of La(III), Pb(II), Cu(I), and S(−II). We thus expect it to be diamagnetic and a semiconductor with a band gap of ~1.5 eV.

Although LaPbCuS₃ is derived conceptually from the insertion of Cu(I) into α-La₂S₃ with concomitant partial substitution and disorder of Pb(II) for La(III), its successful synthesis is surprising in view of the stability of the various binaries and ternaries and the probable complexity of the quaternary phase diagram. Nevertheless, BiPbCuS₃ provides a similar example. Thus it may be that a number of other related compounds, e.g., Sn₂S₃ and U₂S₃, will prove amenable to Cu insertion.

Acknowledgments

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