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Structure Determination of $PbSb_2Se_4$

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Structure determination of $PbSb_2Se_4$ is reported, M_r = 766.5, orthorhombic space group *Pnnm*, a = 21.206(9)Å, b = 26.660(9)Å, c = 4.068(1) Å, V = 2300(1) Å^3, Z = 12, D_x = 6.641 g cm^{-1}, Mo$K\alpha$ radiation, λ = 0.7107 Å, μ = 477.8 cm^{-1}, F(000) = 3840, room temperature, R = 0.063, R_w = 0.069 for 1119 independent observed reflections. The crystal was prepared by annealing at 773 K for 2 weeks in vacuum-sealed ampoules. The structure of $PbSb_2Se_4$ is isotypic with $SnSb_2Se_4$. The cation distribution was determined by X-ray site-occupancy refinement and by bond-valence analysis. The distribution of cations in the tin analogue was also determined by the bond-valence analysis and is similar to that in $PbSb_2Se_4$.

INTRODUCTION

We undertook a study of the little known $PbSe–Sb_2Se_3$ system to compare the structural chemistry of the lead-antimony selenides with that of lead-antimony sulfides. Structure of only one intermediate compound, $Pb_4Sb_4Se_{10}$ (1) is known. Here we report the structure of $PbSb_2Se_4$.

EXPERIMENTAL

Single crystals of $PbSb_2Se_4$ were synthesized from elemental lead, antimony and selenium of "Specpure" grade supplied by Johnson Matthey plc. Ten samples were prepared by weighing the elements in proportions corresponding to compositions between PbSe and $PbSb_2Se_4$. The samples were sealed in evacuated silica ampoules, melted at 1127 K for 2 days, slowly cooled to 773 K (over 24 hr), annealed for 14 days, and quenched. Severe ingot separation occurred and needle-shaped crystals grew in various regions of the ampoules. The crystals from each region were examined separately by X-rays using a powder Guinier–Hägg camera. The crystal of $PbSb_2Se_4$ used in the structure determination was found in the sample with initial composition of 65 mole% PbSe and 35 mole% Sb_2Se_3.

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The crystal was mounted with the needle axis along the goniometer axis for intensity measurements using a Siemens R3m/V X-ray diffractometer. The peak widths were somewhat broad and required wide scan widths which caused some loss of accuracy in measuring the intensity of weak reflections proximate to the strong ones. The details of the measurements and of the structure solution and refinement are given in Table 1.

The observed systematic absences were consistent with space groups *Pnn*2 and *Pnnm* with E statistics supporting the centric group. The structure was solved by direct methods in *Pnnm*. Complex scattering factors for neutral atoms were taken from "International Tables for X-ray Crystallography" (2). Site occupancies for Pb and Sb as well as positional and thermal atomic displacement parameters were refined. Site occupations were fixed in the final cycles. However, the Pb/Sb sites exhibited large atomic displacement parameters, particularly in c direction. We therefore attempted to refine this structure in Pnnm with the metal atoms disordered about the mirror planes at z = 0 or $\frac{1}{2}$. With isotropic displacement parameters, the atoms remained disordered about the mirror plane, but with anisotropic refinement, they rapidly moved back to the mirror. Refinement in *Pnn*2 with isotropic displacement parameters produced a model with many atoms somewhat removed from z = 0 or $\frac{1}{2}$ but anisotropic refinement again returned the z coordinates to the mirror plane. We settle for the anisotropic refinement in *Pnnm* and list the final atomic coordinates in Table 2. The anisotropic displacement parameters and the interatomic distances are given in Tables 3 and 4.

Bond valences (s) were calculated using the interatomic distances (r) and the formula:

$$s = \exp(r_0 - r)/0.37, \quad (1)$$

where r_0 = 2.640 Å for Pb–Se bonds and r_0 = 2.620 Å for Sb–Se bonds. The value of r_0(Sb–Se) was chosen to bring the bond valence sums on the sites, $M(1)$, $M(5)$, and $M(6)$ close to 3.0. The value of r_0(Pb–Se) was then fitted to obtain the correct stoichiometry after summing

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TABLE 1
Structure Determination Summary

Crystal data	
Empirical formula	$PbSb_2Se_4$
Color; habit	Gray; needle
Crystal size (mm)	0.02{100} × 0.04{010} × 0.56{001}
Crystal system	Orthorhombic
Space group	*Pnnm*
Unit cell dimensions	a = 21.206(9) Å
	b = 26.660(9) Å
	c = 4.068(1) Å
Volume	2299.9(13) Å
Z	12
Formula weight	766.53
Density (calc)	6.641 g/cm^3
Absorption coefficient	477.84 cm^{-1}
F(000)	3840
Data collection	
Diffractometer used	Siemens R3m/V
Radiation	Mo$K\alpha$ (λ = 0.71073 Å)
Temperature	295 K
Monochromator	Highly oriented graphite crystal
2θ range	4.0 to 45.0°
Scan type	2θ–θ
Scan speed	Variable; 1.01 to 14.65°/min in ω
Scan range (ω)	1.00° plus $K\alpha$ separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	2 measured every 100 reflections
Index ranges	$0 \le h \le 22$, 0, $\le k \le 28$
	$0 \le l \le 4$
Reflections collected	1768
Independent reflections	1768
Observed reflections	1119 ($F > 6.0\sigma(F)$)
Absorption reflections	Face-indexed numerical
Min/max transmission	0.1799/0.4074
Solution and Refinement	
System used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Extinction correction	χ = 0.000153(12), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$x^{-1} = \sigma^2(F)$
Number of parameters refined	128
Final R indices (obs data)	R = 6.34%, wR = 6.85%
R indices (all data)	R = 8.91%, wR = 6.93%
Goodness-of-fit	4.22
Largest and mean Δ/σ	0.015, 0.001
Data-to-parameter ratio	8.7 : 1
Largest difference peak	3.37 eÅ^{-3}
Largest difference hole	−2.49 eÅ^{-3}

the occupations of the mixed sites. The occupations of the mixed sites were calculated using the method described by Skowron and Brown (3). The occupation numbers derived from the X-ray and bond-valence methods are given in Table 5. Table 6 shows the bond valence analysis. The

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters (Å^2)

	x	y	z	U_{eq} (Å^2)
M(1)	0.5892(2)	0.9898(2)	0.5	0.043(2)
M(2)	0.4250(2)	0.8740(2)	0.5	0.054(2)
M(3)	0.6072(2)	0.8527(2)	0.0	0.055(2)
M(4)	0.4517(2)	0.7411(1)	0.0	0.053(2)
M(5)	0.4139(2)	0.3720(2)	0.5	0.040(2)
M(6)	0.4320(2)	0.5427(2)	0.5	0.036(2)
M(7)	0.2634(3)	0.2829(2)	0.0	0.066(2)
M(8)	0.2839(2)	0.4666(1)	0.0	0.049(2)
M(9)	0.3111(2)	0.6398(2)	0.0	0.049(2)
Se(1)	0.6569(3)	0.0329(3)	0.0	0.036(3)
Se(2)	0.5124(3)	0.9243(3)	0.0	0.029(3)
Se(3)	0.3616(3)	0.8221(2)	0.0	0.030(3)
Se(4)	0.6660(3)	0.9124(2)	0.5	0.030(3)
Se(5)	0.5137(3)	0.8033(3)	0.5	0.031(3)
Se(6)	0.3486(3)	0.7095(3)	0.5	0.031(3)
Se(7)	0.4031(3)	0.3038(3)	0.0	0.029(3)
Se(8)	0.4167(3)	0.4618(2)	0.0	0.029(3)
Se(9)	0.4399(3)	0.6155(2)	0.0	0.028(3)
Se(10)	0.3030(3)	0.2200(3)	0.5	0.032(3)
Se(11)	0.2931(3)	0.3863(3)	0.5	0.029(3)
Se(12)	0.3104(3)	0.5500(2)	0.5	0.028(3)

Note. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

TABLE 3
Anisotropic Thermal Displacement Parameters (Å^2) for $PbSb_2Se_4$

	U_1	U_{22}	U_{33}	U_{12}
M(1)	0.034(3)	0.025(3)	0.070(5)	0.000(2)
M(2)	0.039(3)	0.031(3)	0.091(5)	0.001(2)
M(3)	0.042(3)	0.066(3)	0.057(3)	−0.003(2)
M(4)	0.059(3)	0.040(2)	0.060(4)	0.018(2)
M(5)	0.027(3)	0.031(3)	0.062(4)	0.001(2)
M(6)	0.022(3)	0.029(3)	0.057(4)	−0.003(2)
M(7)	0.089(4)	0.051(3)	0.057(4)	0.016(3)
M(8)	0.051(3)	0.036(2)	0.059(3)	−0.009(2)
M(9)	0.048(3)	0.042(3)	0.056(4)	−0.005(2)
Se(1)	0.021(5)	0.024(4)	0.061(7)	0.000(3)
Se(2)	0.028(5)	0.022(4)	0.036(6)	0.004(3)
Se(3)	0.024(5)	0.024(4)	0.042(6)	0.002(3)
Se(4)	0.025(7)	0.021(4)	0.044(6)	0.003(3)
Se(5)	0.028(5)	0.021(4)	0.041(6)	0.001(3)
Se(6)	0.022(4)	0.023(4)	0.047(6)	−0.001(3)
Se(7)	0.022(4)	0.019(4)	0.047(6)	−0.003(3)
Se(8)	0.022(5)	0.017(4)	0.048(6)	−0.001(3)
Se(9)	0.020(4)	0.012(4)	0.053(6)	−0.000(3)
Se(10)	0.028(5)	0.018(4)	0.049(6)	0.004(3)
Se(11)	0.024(7)	0.023(4)	0.042(6)	0.003(3)
Se(12)	0.021(4)	0.018(4)	0.043(5)	0.002(3)

TABLE 4
Interatomic Distances (Å) Less Than 3.6 Å in $PbSb_2Se_4$

M(1)–Se(4)	2.628(8)	*M*(6)–Se(12)	2.586(8)
Se(1) × 2	2.742(6)	Se(9) × 2	2.817(5)
Se(2) × 2	3.136(7)	Se(8) × 2	2.982(6)
Se(2) × 2	3.743(7)		
M(2)–Se(5)	2.660(9)	*M*(7)–Se(10) × 2	2.765(6)
Se(3) × 2	2.800(6)	Se(7)	3.015(9)
Se(2) × 2	3.068(7)	Se(6)	3.076(9)
Se(1) × 2	3.644(7)	Se(11) × 2	3.484(7)
		Se(3) × 2	3.501(7)
M(3)–Se(2)	2.772(8)	*M*(8)–Se(8)	2.819(8)
Se(4) × 2	2.868(6)	Se(11) × 2	2.959(6)
Se(5) × 2	3.132(6)	Se(12) × 2	3.067(6)
Se(10) × 2	3.397(7)	Se(1) × 2	3.375(7)
M(4)–Se(3)	2.883(8)	*M*(9)–Se(9)	2.806(8)
Se(5) × 2	2.935(6)	Se(6) × 2	2.867(6)
Se(6) × 2	3.103(6)	Se(12) × 2	3.142(6)
Se(7)	3.303(8)	Se(10)	3.230(8)
Se(9)	3.357(7)	Se(4)	3.379(9)
M(5)–Se(11)	2.589(9)		
Se(7) × 2	2.737(6)		
Se(8) × 2	3.142(6)		
Se(9) × 2	3.723(7)		

occupation numbers derived by the bond valence method were also used as fixed parameters in an X-ray refinement but resulted in significantly poorer agreement as judged using the Hamilton test (4).

DISCUSSION

The distribution of lead and antimony among the cation sites in $PbSb_2Se_4$ is complex but the overall stoichiometry of the crystal is essentially dictated by the oxydation states of the atoms. Deviations from the nomional lead to antimony ratio will imply either selenium vacancies or change of the oxidation states of the metals. Since there is no crystallographic indication in X-ray refinement nor in the bond valence analysis for such changes, we assume the nominal composition for the compound.

TABLE 5
Percentage of Sb on the Cation Sites in $PbSb_2Se_4$ and $SnSb_2Se_4$

	$PbSb_2Se_4$		$SnSb_2Se_4$
	X-ray	Bond-valence method[a]	Bond-valence method[b]
M(1)	92	100	100
M(2)	82	86	87
M(3)	42	53	59
M(4)	43	28	17
M(5)	95	100	100
M(6)	100	100	100
M(7)	56	45	77
M(8)	32	34	37
M(9)	58	50	41

[a] r_0(Pb–Se) = 2.640 Å, r_0(Sb–Se) = 2.620 Å, B = 0.37.
[b] r_0(Sn–Se) = 2.560 Å, r_0(Sb–Se) = 2.610 Å, B = 0.37.

The structure of $PbSb_2Se_4$ is shown in Fig. 1 projected along the short c axis. It is composed of ribbons, shaded in Fig. 2, made of four back-to-back square pyramids. Two ribbons hinge together at 120° angle by sharing selenium atoms. The hinging pairs are arranged such that a ribbon from each pair is parallel to a ribbon from another pair. Spaces between the ribbons, shaded coarsely in Fig. 2, are filled with an extra metal and extra selenium atoms resulting in trigonal bicapped coordination for the metal.

The four metal sites on the faces of the ribbons with which the hinging ribbons face other hinging ribbons, are 5-coordinated and these sites are occupied by mostly anti-

TABLE 6
Bond Valences in $PbSb_2S_4$ Weighted According to the X-ray Occupation Numbers

	M(1)	*M*(2)	*M*(3)	*M*(4)	*M*(5)	*M*(6)	*M*(7)	*M*(8)	*M*(9)	
% Sb	92	82	42	43	95	100	56	32	58	Σs
Se(1)	1.43	0.13						0.27		1.83
Se(2)	0.59	0.60	0.68							1.87
Se(3)		1.25		0.56			0.19			2.00
Se(4)	0.98		1.05						0.13	2.16
Se(5)		0.89	0.54	0.89						2.32
Se(6)				0.57			0.30		1.05	1.92
Se(7)				0.16	1.45		0.36			1.97
Se(8)					0.49	0.75		0.61		1.85
Se(9)				0.14	0.10	1.17			0.63	2.04
Se(10)			0.25				1.40		0.19	1.84
Se(11)					1.09		0.20	0.83		2.12
Se(12)						1.10		0.62	0.51	2.33
Σs	3.00	2.87	2.52	2.32	3.13	3.02	2.45	2.33	2.51	

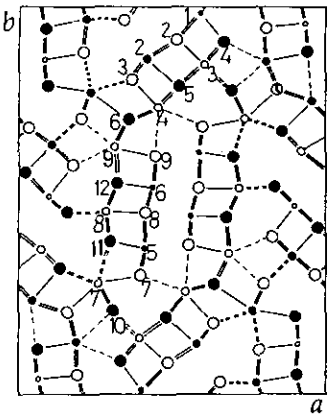

FIG. 1. The unit cell of $PbSb_2Se_4$ projected down [001]. In order of decreasing size the circles indicate Se, mixed sites, and Sb. Atoms close to $z = 0.0$ and 0.5 are indicated by open and full circles respectively. Bonds shorter than 3.2 Å are shown with full lines and those between 3.2 and 3.5 Å with broken lines.

mony. The sites on the other faces of the ribbons and those in the trigonal bicapped prisms, have higher coordination and mixed Pb/Sb occupation. Two of these sites are lead rich (~70%) and three have ~50% lead and 50% antimony.

$PbSb_2Se_4$ is isotypic with $SnSb_2S_4$ and $SnSb_2Se_4$ (5). The structure of the latter was solved using single crystal X-ray diffraction, but an assignment of cation distribution was not attempted since one cannot readily distinguish

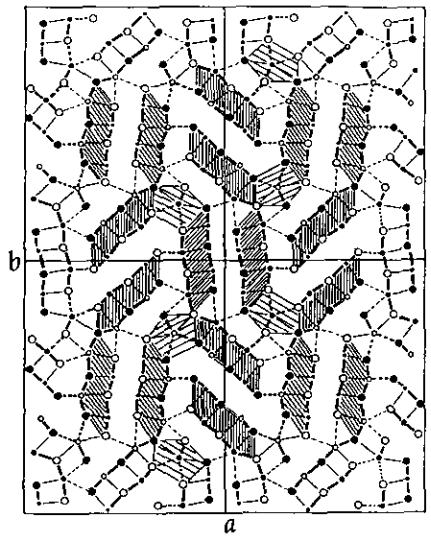

FIG. 2. Four unit cells of $PbSb_2Se_4$ projected down [001] with the ribbons and the trigonal prisms indicated by fine and coarse shading respectively.

TABLE 7
Bond-Valence Bond-Length Parameters (r_0) [Å] for Pb–Se, Sn–Se, and Sb–Se Bonds

	Brese and O'Keeffe (6)	Skowron and Brown (1)	This work
r_0(Pb–Se)	2.67	2.679	2.640[a]
r_0(Sn–Se)	2.59		2.560[b]
			2.570[c]
r_0(Sb–Se)	2.57	2.602	2.620[a]
			2.610[b]
			2.602[c]

[a] $PbSb_2Se_4$.
[b,c] $SnSb_2Se_4$.

tin and antimony in an X-ray diffraction experiment. We assigned the Sn/Sb distribution $SnSb_2S_4$ by the bond valence method using the interatomic distances reported in (5) and $r_0 = 2.560$ Å for the Sn–Se bonds and $r_0 = 2.610$ Å for the Sb–Se bonds. The resulting occupations are listed in Table 5 and show that the distribution of cations in the lead and tin analogues is very similar.

In Table 7 we compare the values of the bond parameters (r_0) for the bonds between Se and Pb, Sn, or Sb obtained from the above valence analyses of $PbSb_2Se_4$, $SnSb_2Se_4$ and $Pb_4Sb_4Se_{10}$ (1) with those given by Brese and O'Keeffe (6). We could obtain the electroneutral formula for $SnSb_2S_4$ using two sets of r_0 differing by ±0.01 Å, as listed in Table 7, with only small differences in the resulting site occupations. Brese and O'Keeffe estimate the accuracy of their r_0 values as ±0.02 Å. Our values of r_0 are different than those given in (6) by more than ±0.02 Å.

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