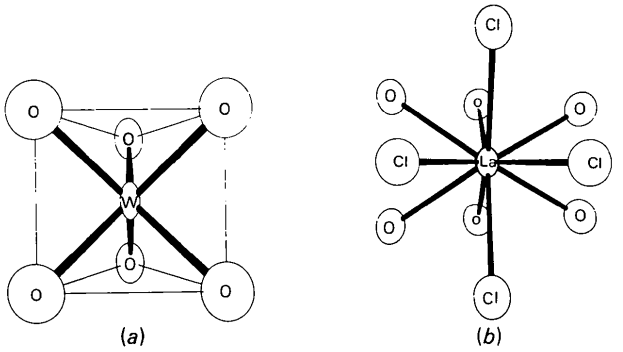

Fig. 2. Coordination about the (*a*) W and (*b*) La atoms in $LaWO_6Cl_3$.

Discussion. Table 1 lists the final refined atomic parameters, and Table 2 contains the pertinent bond lengths compared to those obtained previously. This refinement confirms the trigonal prismatic coordination of the WO_6 group in $La_3WO_6Cl_3$ as well as the other aspects of the structure.

Although the precision of the two structural refinements are comparable (Table 2), the W—O and La—Cl bond lengths determined from the neutron data are somewhat shorter. Computation of the bond lengths based on the cell dimensions determined from Guinier-camera data only decreases these distances by 0·001 Å. The La–O distances are in generally good agreement considering their associated e.s.d.

The WO_6 group and the coordination sphere of the La atom are shown in Fig. 2.

References

BRIXNER, L. H., CHEN, H. Y. & FORIS, C. M. (1982). *J. Solid State Chem.* **44**, 99–107.

FINGER, L. W. & PRINCE, E. (1975). *Natl Bur. Stand. US Tech. Note*, No. 854.

HOPPE, R. (1982). Private communication.

KOESTER, L. (1977). *Springer Tracts Mod. Phys.* **80**, 1–55.

PENSAK, D. A. & MCKINNEY, R. J. (1979). *Inorg. Chem.* **18**, 3407–3413.

PRINCE, E. (1980). *Natl Bur. Stand. US Tech. Note*, No. 1117, edited by F. SHORTEN.

PRINCE, E. & SANTORO, A. (1980). *Natl Bur. Stand. US Tech. Note*, No. 1117, edited by F. SHORTEN.

RIETVELD, H. M. (1969*a*). Research Report RCN 104. Reactor Centrum Nederland. (Unpublished.)

RIETVELD, H. M. (1969*b*). *J. Appl. Cryst.* **2**, 65–67.

VISSER, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.

Acta Cryst. (1983). C**39**, 1328–1329

Lead Indium Bismuth Chalcogenides. I. Structure of $Pb_{1.6}In_8Bi_4S_{19}$

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Abstract. $M_r = 2695{\cdot}2$, monoclinic, $C2/m$, $a = 29{\cdot}167\ (5)$, $b = 3{\cdot}872\ (2)$, $c = 15{\cdot}554\ (5)$ Å, $\beta = 121{\cdot}6\ (1)°$, $V = 1496{\cdot}1$ Å^3, $Z = 2$, $D_x = 5{\cdot}983$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 40{\cdot}24$ cm^{-1}, $F(000) = 2384$, room temperature; reflection condition hkl: $h + k = 2n$; final $R = 0{\cdot}062$ for 3560 independent reflections. The structure consists of distorted In—S octahedra, and mono- and bicapped triangular prisms of Bi—S as well as bicapped triangular prisms of Pb—S (site occupancy of Pb~0·8), all forming chains along y.

Introduction. The present paper is part of a series on the study of lead indium bismuth chalcogenides.

Experimental. Needle-shaped crystals up to 20 × 0·5 × 0·5 mm grown by chemical vapour transport with iodine in a two-zone furnace adjusted to 923–873 K; charge consisted of Pb+4In+2Bi+10S. Black crystals with high metallic lustre, elongated along y, pinacoids {100}, {001}, {20$\bar{1}$}, and {010}; D_m not measured; crystal 20 × 1500 × 20 μm, automatic four-circle diffractometer (Enraf–Nonius CAD-4), graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from refinement of 20 reflections, scan width 1·2°, ω–2θ scan mode, $2\theta < 70°$, h 0 to 46, k 0 to 6, $l \pm 21$; *SHELX* (Sheldrick, 1976) and XRAY systems (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); two standard reflections: no significant variation; 7296 total reflections, 3560 independent, 3038 with $I > 3\sigma(I)$; $R_{int} = 5{\cdot}0\%$; corrections for Lorentz–polarization, absorption (A^* 1·973 to 2·345), and extinction effects [$g = 2{\cdot}43\ (8) \times 10^{-4}$]. A starting set of heavy atoms was selected from an E map calculated with direct methods (*SHELX*); remaining atoms from successive Fourier syntheses; $\sum w(\Delta F^2)$ minimized, unit weights. Refinement of positional and

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anisotropic thermal parameters resulted in a final $R = 0{\cdot}068$ which dropped to $R = 0{\cdot}062$* when the partial-population parameter of Pb was refined to 0·8; $(\Delta/\rho)_{ave}$ 5×10^{-5}; final $\Delta\rho$ map: no significant peaks; scattering factors of neutral atoms (Cromer & Mann, 1968) were used and corrected for anomalous dispersion.

Discussion. The atomic coordinates are listed in Table 1, bond lengths in Table 2. A view of the structure is displayed in Fig. 1. All atoms lie on fourfold positions at the mirror planes at $y = 0$ and $\frac{1}{2}$ except S(1) which occupies the twofold position 000 and $\frac{1}{2}\frac{1}{2}0$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38704 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) ($y = 0$), *and isotropic thermal parameters* ($\times 10^2$) *with e.s.d.'s in parentheses*

	x	z	U_{eq} (Å^2)	Population parameter
Pb(1)	567 (1)	6345 (2)	6·0 (2)	0·806 (9)
In(1)	1084 (1)	1364 (2)	0·96 (4)	
In(2)	2457 (1)	5970 (2)	1·36 (5)	
In(3)	2921 (1)	2410 (2)	1·25 (5)	
In(4)	4855 (1)	1171 (2)	1·41 (5)	
Bi(1)	830 (1)	3870 (2)	3·76 (5)	
Bi(2)	1706 (1)	9406 (2)	2·83 (4)	
S(1)	0	0	1·5 (2)	
S(2)	219 (3)	7830 (5)	1·7 (2)	
S(3)	1660 (3)	6331 (5)	1·3 (2)	
S(4)	2102 (2)	2665 (5)	1·3 (2)	
S(5)	2514 (3)	9043 (5)	1·5 (2)	
S(6)	3092 (3)	5316 (5)	1·4 (2)	
S(7)	3712 (3)	2094 (5)	1·7 (2)	
S(8)	3876 (3)	9747 (5)	1·3 (2)	
S(9)	4125 (3)	7734 (5)	1·6 (2)	
S(10)	4575 (3)	5472 (5)	1·7 (2)	

Table 2. *Bond distances* (Å)

In(1)–S(8)	2·638 (2) 2×	Pb(1)–S(7)	2·952 (5) 2×
S(9)	2·642 (6) 2×	S(10)	3·139 (6) 2×
S(4)	2·572 (6)	S(4)	3·269 (7) 2×
S(1)	2·733 (4)	S(2)	2·972 (10)
		S(3)	3·200 (9)
In(2)–S(6)	2·638 (4) 2×		
S(4)	2·655 (4) 2×	Bi(1)–S(10)	2·729 (7) 2×
S(6)	2·536 (9)	S(9)	3·216 (7) 2×
S(3)	2·663 (8)	S(6)	3·327 (6) 2×
		S(2)	2·805 (7)
In(3)–S(3)	2·563 (4) 2×	S(3)	3·287 (7)
S(5)	2·730 (5) 2×		
S(7)	2·598 (9)	Bi(2)–S(7)	2·774 (5) 2×
S(4)	2·618 (8)	S(5)	3·000 (5) 2×
		S(8)	3·274 (7) 2×
In(4)–S(2)	2·561 (6) 2×	S(5)	2·694 (9)
S(1)	2·837 (2) 2×		
S(8)	2·535 (6)		
S(9)	2·538 (7)		

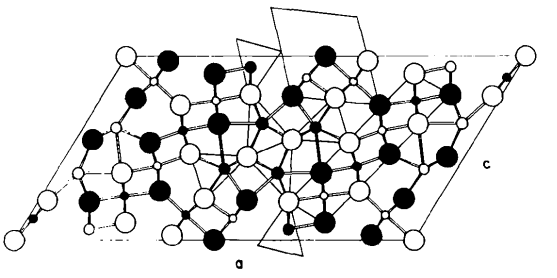

Fig. 1. Structure of $Pb_{1.6}In_8Bi_4S_{19}$ viewed along **b**; open circles are at $y = 0$, full circles at $y = \frac{1}{2}$ (small: In, medium: Pb and Bi, large: S). The arrangement of vane-like Pb–Bi–S units and In–S fourfold bands and columns is shown.

Pb(1) and Bi(1) are eightfold (bicapped triangular prisms), Bi(2) is sevenfold (monocapped triangular prism) coordinated; In(1–4) are surrounded by six S (distorted octahedra). The (mean) Pb–S distances range from 2·95 to 3·27, Bi–S from 2·69 to 2·81 and 3·00 to 3·33 respectively, and In–S from 2·53 to 2·84 Å. The monocapped Bi(2) prism has an eighth S atom [S(2)] at a rather large distance of 3·70 (1) Å. The distinction between Pb and Bi was made from their different bond distances in sulphosalts (Makovicky, 1981).

Two Pb–S prisms are face-shared forming a rhombic prism [Pb–Pb 3·73 (1) Å]; each of its four edges share a Bi–S prism in a vane-like arrangement. Two opposite Bi–S prisms of this unit are connected to the corresponding prisms of two adjacent units which are displaced by $b/2$; all are stacked in the y direction setting up infinite layers parallel to $(20\bar{1})$. These layers are linked by a fourfold band and a fourfold column of edge-shared In–S octahedra both running in the y direction and connected *via* common corners.

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References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

KELLER, E. (1980). *SCHAKAL. Ein Fortran-Programm zur graphischen Darstellung von Molekülmodellen.* Univ. Freiburg.

MAKOVICKY, E. (1981). *Fortschr. Mineral.* **59**, 137–190.

SHELDRICK, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.