SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1978). A**34**, 143–157.

Acta Cryst. (1982). B**38**, 3070–3071

The Structure of Antimony Bismuth Tin Sulphide $Bi_xSb_{2-x}Sn_2S_5$

BY V. KUPČIK AND M. WENDSCHUH

Mineralogisch-Kristallographisches Institut der Universität, Goldschmidtstrasse 1, *D*-3400 *Göttingen, Federal Republic of Germany*

(*Received* 19 *February* 1982; *accepted* 17 *June* 1982)

Abstract. $Bi_xSb_{2-x}Sn_2S_5$, orthorhombic, *Pmcn* or $P2_1cn$, $a = 3{\cdot}95\ (2)$, $b = 11{\cdot}26\ (4)$, $c = 19{\cdot}49\ (6)$ Å, $V = 866{\cdot}9$ Å^3, $Z = 4$. The crystal used was not analysed chemically but other samples from the same charge had $0{\cdot}4 > x > 0{\cdot}2$. The final R was 0·101 for 136 observed reflections [$R_w = 0{\cdot}082$ with $w = 1/\sigma(I)$]. The structure is built of ribbon-like [(Bi, Sb, Sn)$_8$S$_{10}$] sheets along [100].

Introduction. As part of an investigation of the Sn–Sb–Bi–S system the structure of the title compound was determined.

The synthetic crystals are elastic, flexible and opaque needles. The crystal used was approximately 150 μm long and 2–3 μm across.

428 reflections were recorded (Stoe four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $3° < 2\theta < 40°$, θ–θ scan, step width 0·02°, scan width 65 steps, Lorentz and polarization, but no absorption correction). Systematic extinctions indicated the space groups *Pmcn* or $P2_1cn$.

The structure was solved using Patterson and Fourier methods. The Patterson synthesis showed only maxima in $x = 0$ and $x = \frac{1}{2}$, *i.e.* the atoms are separated by $\frac{1}{2}$ in x. Therefore the centrosymmetric space group was assumed which has mirror planes at $x = \frac{1}{4}$ and $x = \frac{3}{4}$.

The metal atoms were located by means of the superposition method. Subsequent Fourier syntheses and structure factor calculations gave $R = 0{\cdot}30$. A difference synthesis allowed the positioning of the S atoms. The following least-squares refinement gave $R = 0{\cdot}101$ and $R_w = 0{\cdot}082$. Only reflections with $I/\sigma(I) > 1$ were used.

The calculations were performed on the Univac U1100 computer of GWD Göttingen with *ORFLS* (Busing, Martin & Levy, 1962) for the refinement and *GSFFR* (Ohmasa, undated) for Fourier and Patterson calculations.

Observed and calculated powder patterns showed close similarity with the powder patterns of $Sb_2Sn_2S_5$ (Wang & Eppelsheimer, 1976), which is probably

Table 1. *Atomic parameters of* $Bi_xSb_{2-x}Sn_2S_5$

	x	y	z	B (Å^2)	f.s.o.
$M(1)$	0·75	0·307 (1)	0·0217 (7)	0·9 (3)	1·05
$M(2)$	0·25	0·005 (1)	0·0933 (7)	1·4 (3)	1·14
$M(3)$	0·25	0·133 (1)	0·3732 (7)	1·1 (3)	1·08
$M(4)$	0·25	0·348 (1)	0·2016 (6)	1·1 (3)	1·21
S(1)	0·75	0·188 (6)	0·131 (3)	1·1	
S(2)	0·25	0·436 (5)	0·072 (3)	1·4	
S(3)	0·75	0·507 (5)	0·231 (3)	0·3	
S(4)	0·75	0·246 (5)	0·319 (3)	0·3	
S(5)	0·25	0·136 (7)	−0·020 (3)	1·0	

Table 2. *Distances* (Å) *and bond angles* (°) *with standard deviations*

$M(1)$–S(1)	2·52 (6)	$M(2)$–S(5)	2·68 (7)
–S(2)	2·66 (4) (2×)	–S(5)	2·91 (5) (2×)
–S(5)	2·86 (6) (2×)	–S(1)	2·96 (5) (2×)
S(2)	3·42 (6)	–S(3)	3·43 (6)
$M(3)$–S(3)	2·47 (6)	$M(4)$–S(2)	2·71 (6)
–S(4)	2·59 (4) (2×)	–S(3)	2·74 (4) (2×)
–S(2)	3·13 (6) (2×)	–S(1)	2·99 (5) (2×)
–S(5)	3·30 (7)	–S(4)	3·23 (5) (2×)

S(1)–$M(1)$–S(2)	88 (2)	S(5)–$M(2)$–S(1)	80 (2)
S(1)–$M(1)$–S(5)	84 (2)	S(5)–$M(2)$–S(5)	85 (2)
S(2)–$M(1)$–S(5)	88 (1)	S(1)–$M(2)$–S(1)	84 (1)
S(5)–$M(1)$–S(5)	87 (2)	S(1)–$M(2)$–S(5)	93 (1)
S(2)–$M(1)$–S(2)	96 (1)	S(5)–$M(2)$–S(5)	85 (2)
S(2)–$M(1)$–S(2)	75 (2)	S(3)–$M(2)$–S(1)	75 (2)
S(2)–$M(1)$–S(5)	114 (2)	S(3)–$M(2)$–S(5)	119 (2)
S(3)–$M(3)$–S(2)	83 (2)	S(2)–$M(4)$–S(3)	87 (2)
S(3)–$M(3)$–S(4)	87 (2)	S(2)–$M(4)$–S(1)	79 (2)
S(2)–$M(3)$–S(2)	78 (1)	S(3)–$M(4)$–S(3)	93 (1)
S(4)–$M(3)$–S(4)	99 (1)	S(1)–$M(4)$–S(1)	83 (1)
S(2)–$M(3)$–S(4)	91 (1)	S(3)–$M(4)$–S(1)	91 (1)
S(5)–$M(3)$–S(2)	110 (2)	S(2)–$M(4)$–S(4)	142 (2)
S(5)–$M(3)$–S(4)	82 (2)	S(4)–$M(4)$–S(4)	76 (1)

0567-7408/82/123070-02$01.00

© 1982 International Union of Crystallography

isostructural with $Pb_2Sb_2S_5$ (Wang, 1973). Neither of these structures is yet known. Therefore it is feasible that the structure type considered may occur in several sulphur salts.

Because of the similarity of the scattering factors of Sn and Sb the scattering factors of neutral Sn were used. With regard to the Bi content the formal site occupancy (f.s.o.) was assumed to be greater than one. The f.s.o. was obtained by integrating the electron density and was not refined.

Table 1 gives the final positional and thermal parameters with standard deviations and Table 2 the main interatomic distances and bond angles.*

Discussion. The coordination polyhedra of the metal atoms are slightly distorted square pyramids with M approximately at the centre of the base. Addition of one S atom to each pyramid results in an octahedral-like coordination for $M(1)$, $M(2)$ and $M(3)$, as shown in Fig. 1. $M(4)$ has one more S neighbour; therefore its coordination may be assumed to be 5 + 2.

A projection of the structure along $\mathbf{a}_0$ is shown in Fig. 2. Infinite chains along $\mathbf{a}_0$ (shaded) are formed by eight M–S pyramids (hatched) each. The chains are connected by longer M–S bonds.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38019 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

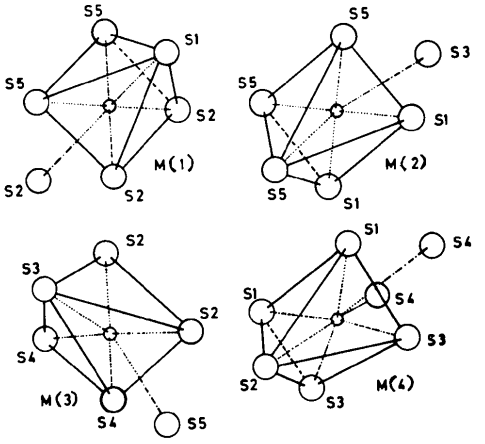

Fig. 1. Coordination polyhedra of M.

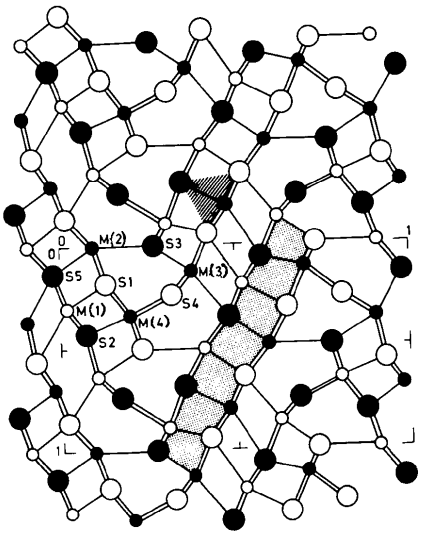

Fig. 2. The structure projected along $\mathbf{a}_0$. Filled circles: atoms at $x = \frac{1}{4}$. Open circles: atoms at $x = \frac{3}{4}$.

Because of the limited quality of the data and the correlation between thermal effects and site occupancy the data did not permit distinction between Sn, Sb and Bi. It is planned to obtain new data with synchrotron radiation and to solve the problem of the metal distribution using anomalous scattering (Kupčik, Pähler, Valena, Wendschuh & Wulf, 1982).

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

KUPČIK, V., PÄHLER, A., VALENA, I., WENDSCHUH, M. & WULF, R. (1982). *Fünfkreisdiffraktometer mit durchstimmbarer Wellenlänge für Synchrotronstrahlung*, in: *HASYLAB am Deutschen Elektronensynchrotron DESY* – Jahresbericht 1981, Hamburg.

WANG, N. (1973). *Neues Jahrb. Mineral. Monatsh.* **2**, 79–81.

WANG, N. & EPPELSHEIMER, D. (1976). *Chem. Erde*, **35**, 179–184.