

- CZAPLA, Z., LIS, T. & SOBCZYK, L. (1979). *Phys. Status Solidi A*, **51**, 609–612.
- CZAPLA, Z. & SOBCZYK, L. (1980). *Phys. Status Solidi A*, **58**, K161–K163.
- GESI, K. (1980). *J. Phys. Soc. Jpn.* **81**, 1399–1340.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KRUGLIK, A. I., MISOYUL, S. V. & ALEKSANDROV, K. S. (1980). *Dokl. Akad. Nauk SSSR*, **255**(2), 344–348.
- OLEJNIK, S., WAŚKOWSKA, A. & ŁUKASZEWICZ, K. (1979). Vth European Crystallographic Meeting, Copenhagen. Collected Abstracts.
- ROZIÈRE, J. (1979). Annex to the Annual Report ILL, Grenoble.
- STEWART, J. M. (1976). The XRAY system, version of 1976. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- SUZUKI, S., OSAKA, T. & MAKITA, Y. (1979). *J. Phys. Soc. Jpn.* **47**, 1741–1742.
- WAŚKOWSKA, A., OLEJNIK, S., ŁUKASZEWICZ, K. & CZAPLA, Z. (1980). *Cryst. Struct. Commun.* **9**, 663–689.
- WAŚKOWSKA, A., OLEJNIK, S., ŁUKASZEWICZ, K. & GŁOWIAK, T. (1978). *Acta Cryst.* **B34**, 3344–3346.

Acta Cryst. (1982). **B38**, 2020–2022

Crystal Growth and Structure of Diantimony(III) Zinc Oxide

BY E. GUTIÉRREZ PUEBLA, E. GUTIÉRREZ RÍOS, A. MONGE AND I. RASINES

Instituto de Química Inorgánica 'Elhuyar', Facultad de Ciencias Químicas, Madrid – 3, Spain

(Received 19 November 1981; accepted 15 February 1982)

Abstract. ZnSb₂O₄, tetragonal, space group $P4_2/mbc$, $a = b = 8.527$ (2), $c = 5.942$ (2) Å, $U = 432.1$ (2) Å³, $Z = 4$, $D_c = 5.73$ Mg m⁻³. Single crystals have been grown using Sb₂O₃ as flux. The structure proposed by Stahl [*Ark. Kemi, Mineral. Geol.* (1943). **17B** (5), 1–7] from powder data has been confirmed and refined to $R = 0.015$ for 168 independent reflections. It consists of chains of twisted and elongated ZnO₆ octahedra sharing opposite edges, these chains being linked by the Sb atoms, each with a pyramidal arrangement of three neighbouring O atoms.

Introduction. The crystal structure of ZnSb₂O₄ was studied by Stahl (1943) in a powdered sample. The atomic arrangement of Pb₃O₄ (space group $P4_2/mbc$) was assumed, Sb and Zn replacing Pb^{II} and Pb^{IV} respectively. The positions of the O atoms were fixed from the Zn–O distance, assumed to be 2.05 Å. The structure consists of ZnO₆ octahedra linked together by opposite edges, forming chains in the direction of the c axis, the chains being joined laterally by SbO₃ pyramids connected with each other (Wells, 1975). There are two Sb–O distances of 2.01 Å and one of 1.87 Å, and two O–Sb–O bond angles of 100.1° and one of 94.8°. More recently, single crystals of the isomorphous compound MgSb₂O₄ have been prepared from MgCl₂.KCl flux by Giroux-Maraine & Pérez (1975), who have established the atomic positions and isotropic temperature factors, refining the structure in

space group $P4_2/mbc$ to $R = 0.042$. Simultaneously Fischer & Pertlik (1975) refined the structure of the mineral schafarzikite, FeSb₂O₄ with small amounts of Mn, in the same space group to $R = 0.056$, with anisotropic temperature factors. As there are a good number of synthetic AB₂O₄ complex oxides isostructural with ZnSb₂O₄, the present paper reports the refinement of the structure of this compound using data from a synthetic crystal.

After several fruitless attempts, ZnSb₂O₄ crystals were grown from analytical-grade reagents by reaction of ZnO and a large excess of Sb₂O₃ in an evacuated and sealed quartz ampoule at 1023 K for 24 h, and then slowly decreasing the temperature to 873 K over a period of two days.

A colourless, approximately cubic crystal of 0.05 mm edge was examined at 291 K on a Nonius CAD-4F automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The unit-cell parameters were obtained by least-squares refinement of the setting angles of 24 reflections with $19^\circ < 2\theta < 48^\circ$.

Intensities were collected by ω - 2θ scans, with scan rates varying from 1.8 to 6.7° (2θ) min⁻¹ so that weaker reflections were measured more slowly. The scan width varied from 1.2° at low 2θ to 1.76° at higher angles. There was no appreciable drop in intensity of three standard reflections, checked every hour. 1566 reflections within half a sphere with $2^\circ <$

Table 1. Atomic coordinates ($\times 10^4$ for Zn and O; $\times 10^5$ for Sb) with e.s.d.'s in parentheses and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

		x	y	z	U_{eq}^*
Zn	4(d)	0	5000	2500	9
Sb	8(h)	32218 (5)	33622 (6)	0	9
O(1)	8(h)	963 (6)	3600 (6)	0	9
O(2)	8(g)	1804 (8)	6804 (8)	2500	15

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

$\theta < 25^\circ$ were measured, resulting in 208 unique reflections, 172 of which had $I > 2\sigma(I)$ and were considered as observed. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied [$\mu R = 0.9$, $\mu(\text{Mo } K\alpha) = 18.06 \text{ mm}^{-1}$]. The systematic absences were $0kl$ for k odd and hhl for l odd. The two possible space groups are the centrosymmetric $P4_2/mbc$ and the non-centrosymmetric $P4_2bc$. The centrosymmetric space group $P4_2/mbc$ was chosen from the statistical distribution of intensities. Confirmation was obtained in the course of the structure refinement. The scattering factors for neutral atoms and anomalous-dispersion corrections for Sb and Zn were taken from *International Tables for X-ray Crystallography* (1974). The Zn and Sb atoms were initially situated in the 4(d) and 8(h) positions determined by Stahl (1943), and the O atoms in 8(h) and 8(g) were located from a difference Fourier synthesis. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.018$. At this stage four reflections affected by extinction were omitted. No trend in ΔF vs F_o or $\sin \theta/\lambda$ was observed. Final $R = 0.015$ for 168 reflections. Atomic parameters are listed in Table 1.*

Discussion. As the melting point of Sb_2O_3 is 929 K at normal pressure, the reaction is thought to be between solid ZnO and liquid Sb_2O_3 , the excess of this acting as solvent for the complex oxide, which is crystallized by slow cooling.

It has been confirmed that the structure, illustrated in Figs. 1 and 2, consists of ZnO_6 octahedra sharing opposite edges, these chains being linked by the Sb atoms, each with a pyramidal arrangement of three neighbours. However, the coordination geometries of Zn and Sb are not regular (Table 2). Moreover, the ZnO_6 octahedra along the chain are twisted, as can be deduced from the torsion angle $\text{O}(1)\text{—Zn—O}(2)\text{—Zn}' = 165.43(11)^\circ$ [Zn' at $(x, y, -z)$].

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36742 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

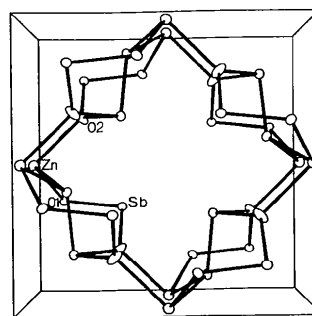


Fig. 1. View along the c axis of the unit cell of ZnSb_2O_4 . Only the atoms of one asymmetric unit are labelled.

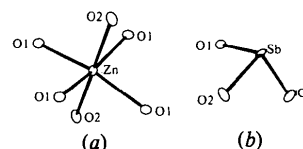


Fig. 2. Coordination polyhedra of (a) Zn and (b) Sb.

Table 2. Bond lengths (\AA) and angles ($^\circ$) for ZnSb_2O_4 with e.s.d.'s in parentheses

Zn—O(1)	2.075 (4)	Sb—O(1)	1.937 (5)
—O(2)	2.176 (5)	—O(2')	1.993 (5)

Relative position of the third atom

O(1)—Zn—O(2)	97.3 (2)	O(1)—Zn—O(1 ^{iv})	165.4 (2)
O(2)—Zn—O(2 ⁱⁱ)	180	O(1)—Sb—O(2 ⁱ)	93.4 (2)
O(1)—Zn—O(1 ⁱⁱ)	93.3 (1)	O(1)—Sb—O(2 ^v)	93.4 (2)
O(1)—Zn—O(1 ⁱⁱⁱ)	88.6 (1)	O(2 ⁱ)—Sb—O(2 ^v)	96.4 (1)

Symmetry code: (i) $1 - y, x, -\frac{1}{2} + z$; (ii) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$; (iii) $-x, 1 - y, -z$; (iv) $-\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, z$.

The sum of the radii of Zn and O (Shannon & Prewitt, 1969, 1970) agrees with the mean measured Zn—O distance, 2.11 \AA . As the mean Sb—O distance is 1.97 \AA , the Sb^{III} radius for pyramidal coordination can be estimated to be 0.61 \AA .

The cell volume per anion, ignoring the volumes of Zn and Sb, is 27.0 \AA^3 , approximately equal to those calculated from the unit-cell parameters (Svensson, 1974; Almin & Westgren, 1942) for orthorhombic and cubic Sb_2O_3 , 27.6 and 28.9 \AA^3 , respectively. According to Galy, Meunier, Andersson & Åström (1975), the volume of the Sb^{III} cation and its lone pair is the same as that of an anion. Taking this into account, and ignoring the volume of Zn, the volume per 'anion' is lowered to 18.0 \AA^3 , slightly higher than the corresponding values, 16.6 and 17.3 \AA^3 , for orthorhombic and cubic Sb_2O_3 .

This work has been possible thanks to the financial support of the Comisión Asesora de Investigación Científica y Técnica. We express our gratitude to Professors Dr G. Bombieri and A. del Pra, to Dr M. Martínez-Ripoll and Dr F. H. Cano for their helpful comments, and to the Junta de Energía Nuclear of Madrid, for permission to use its Univac 1100 computer.

References

- ALMIN, K. E. & WESTGREN, A. (1942). *Ark. Kemi, Mineral. Geol.* **15B** (22), 1–6.
- FISCHER, R. & PERTLIK, F. (1975). *Tschermaks Mineral. Petrogr. Mitt.* **22**, 236–241.
- GALY, J., MEUNIER, G., ANDERSSON, A. & ÅSTRÖM, A. (1975). *J. Solid State Chem.* **13**, 142–159.
- GIROUX-MARAINÉ, C. & PÉREZ, G. (1975). *Rev. Chim. Minér.* **12**, 427–432.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–929.
- SHANNON, R. D. & PREWITT, C. T. (1970). *Acta Cryst.* **B26**, 1046–1048.
- STAHL, S. (1943). *Ark. Kemi, Mineral. Geol.* **17B** (5), 1–7.
- SVENSSON, C. (1974). *Acta Cryst.* **B30**, 458–461.
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 712 and Fig. 12.15, p. 462. Oxford: Clarendon Press.

Acta Cryst. (1982). **B38**, 2022–2023

Structure of Tin(II) Tin(IV) Trisulphide, a Redetermination

BY R. KNIEP, D. MOOTZ, U. SEVERIN AND H. WUNDERLICH

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstr. 1, 4000 Düsseldorf, Federal Republic of Germany

(Received 1 December 1981; accepted 23 February 1982)

Abstract. Sn_2S_3 , orthorhombic, $Pnma$, $a = 8.878$ (2), $b = 3.751$ (1), $c = 14.020$ (3) Å, $Z = 4$, $D_m = 4.87$, $D_x = 4.75$ Mg m⁻³, $M_r = 333.6$, $\mu(\text{Mo } K\alpha) = 11.8$ mm⁻¹, final $R = 0.04$ for 1335 observed X-ray data. The crystal structure was redetermined using a crystal of improved quality and a diffractometer and applying corrections for absorption and extinction. The results of the previous determination with film data [Mootz & Puhl (1967). *Acta Cryst.* **23**, 471–476] were confirmed, but a higher accuracy and more reliable anisotropic thermal parameters were achieved.

Introduction. Needle-shaped crystals of Sn_2S_3 up to 10 mm long and 1–2 mm thick were obtained by heating a powdered mixture of the elements (54 at.% S; 46 at.% Sn) in a sealed tube of quartz glass (horizontal arrangement) from room temperature to 993 K within 24 h, followed by a period of constant temperature (993 K) for 2–3 days. Relative to the phase diagram Sn–S (Moh, 1969), the growth conditions lie within the two-phase region $\alpha\text{-SnS}_{(\text{solid})} + \beta\text{-Sn}_2\text{S}_{3(\text{solid})}$ (988–1011 K). High-temperature $\beta\text{-Sn}_2\text{S}_3$ cannot be quenched, but is transformed (988–983 K) to γ - and finally (948–934 K) to low-temperature $\delta\text{-Sn}_2\text{S}_3$ during cooling (Moh, 1969). In spite of these phase transformations (if really passed through) the crystals obtained were of good quality.

A needle-shaped crystal of approximately 0.45 × 0.08 × 0.03 mm was used for determination of lattice parameters (14 reflections with $34 \leq 2\theta \leq 54^\circ$, Mo $K\alpha$) and data collection. 1601 reflections, $2\theta \leq 80^\circ$ (Mo $K\alpha$), Syntex $P2_1$ diffractometer, crystal monochromator, ω -scan. 1335 reflections with $I > 1.96\sigma$, were classified observed. An absorption correction was made with the Gaussian grid method. The atomic coordinates of the previous determination (Mootz & Puhl, 1967) could be used as initial parameters for the refinement which converged (32 parameters) at $R = 0.040$ (0.042) and $R_w = 0.045$ (0.045) for the observed (all) reflections. The isotropic extinction coefficient (Larson, 1970) was 0.0096 (2), scattering factors were taken from Cromer & Mann (1968), and correction was made for anomalous dispersion. The weighting scheme $1/w = \sigma_F^2 + (0.02F)^2$ was employed. Calculations were made with the XRAY system (1972) on a Cyber 76 computer. The final parameters are given in Table 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36751 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.