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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

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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.

Table 1. Positional and thermal (\AA^2) parameters of Sn_2S_3 with e.s.d.'s in parenthesesThe exponent of the temperature factor is defined by $-\frac{1}{4}(B_{11}h^2a^{*2} + B_{12}hka^*b^* + \dots)$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{13}
Sn(1)	0.16494 (4)	0.25	0.05195 (3)	0.93 (1)	0.72 (1)	1.05 (1)	-0.18 (1)
Sn(2)	0.48509 (5)	0.75	0.16936 (4)	1.21 (1)	1.10 (1)	1.91 (2)	-0.33 (1)
S(1)	-0.01953 (15)	0.75	0.10640 (10)	0.96 (4)	0.90 (4)	0.84 (4)	0.00 (3)
S(2)	0.33879 (15)	0.75	-0.00476 (10)	0.91 (4)	0.94 (4)	1.09 (4)	0.07 (3)
S(3)	0.28631 (18)	0.25	0.21246 (11)	1.35 (4)	0.99 (4)	1.09 (4)	-0.21 (4)

Discussion. Since the first determination of its crystal structure (Mootz & Puhl, 1967) Sn_2S_3 has been studied under a variety of aspects, e.g. semiconductor properties (van Alpen, Fenner & Gmelin, 1975), effect of pressure on resistivity and Mössbauer spectra (Amthauer, Fenner, Hafner, Holzappel & Keller, 1979), and decomposition and thermodynamic functions (Wiedemeier, Csillag, Gaur & Wunderlich, 1980; Wiedemeier & Csillag, 1980). This enduring interest in the compound gave rise to the new structural study.

The new atomic coordinates confirm the features of a ribbon-type structure (Fig. 1) as established in the previous work (Mootz & Puhl, 1967) to within 0.024 \AA and 0.7° of bond lengths and bond angles, respectively, but with e.s.d.'s reduced to 15%. In addition, there is an improvement in the thermal parameters, which were determined in the anisotropic mode and, in view of the corrections for absorption and extinction applied to the data, now are of some physical relevance.

Sn_2S_3 as $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{S}_3$ is more or less isostructural (Mootz & Puhl, 1967) to several other ABX_3 compounds with NH_4CdCl_3 (Brasseur & Pauling, 1938) as the first reported representative. The following crystal structures of this type have been determined or redetermined recently: TlCdI_3 (Zandbergen, Verschoor & IJdo, 1979), PbZrS_3 (Lelieveld & IJdo, 1978), NH_4CdCl_3 (Rolies & De Ranter, 1978), RbCdCl_3 (Natarajan, Howard-Lock & Brown, 1978), RbCdBr_3

(Natarajan Iyer, Faggiani & Brown, 1977), RbPbI_3 (Haupt, Huber & Preut, 1974), and PbSnS_3 (Jumas, Ribes, Philippot & Maurin, 1972). Of these, PbSnS_3 was shown to form with Sn_2S_3 a continuous series of mixed crystals (Pütz, 1979).

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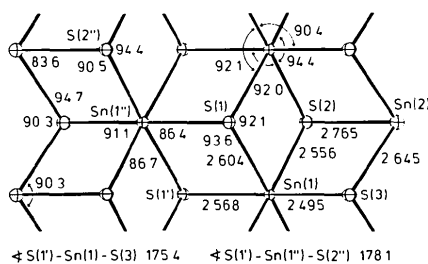


Fig. 1. A section of the ribbon-type crystal structure of Sn_2S_3 . The atoms are represented by thermal ellipsoids of 50% probability (ORTEP II, Johnson, 1976). Bond lengths (\AA) and bond angles ($^\circ$) are given, e.s.d.'s are 0.001–0.002 \AA and 0.04–0.05 $^\circ$. The shortest inter-ribbon distance is between an Sn(2) and an S(1) atom at 3.144 \AA . Symmetry code: (i) $-x, -\frac{1}{2} + y, -z$; (ii) $-x, \frac{1}{2} + y, -z$.