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Refinement of the Crystal Structure of Cubic Antimony Trioxide, Sb₂O₃

BY CHRISTER SVENSSON

Division of Inorganic Chemistry 2, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

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The structure of cubic Sb₂O₃, senarmontite, has been refined with X-ray data collected on a four-circle diffractometer. The space group is Fd3m and the lattice constant 11·1519 (2) Å. The final weighted R was 0.028 for 507 reflexions sampled in one octant of reciprocal space. Corrections for anomalous dispersion and isotropic secondary extinction were included. Sb is bonded to three O atoms at 1.977 (1) Å. The lone pair of electrons of Sb completes a tetrahedral arrangement. Apart from the usual description of the structure in terms of Sb₄O₆ units, the similarities to the pyrochlore structure are described.

Introduction

As part of a general study of the O coordination of Sb^{III} and in pursuit of accurate Sb^{III}–O distances for different coordination geometry, it was considered necessary to refine the crystal structures of the two polymorphs of Sb₂O₃. The refinement of the orthorhombic form has been published (Svensson, 1974). This communication describes a reinvestigation of the cubic form, the structure originally described by Bozorth (1923) and later confirmed by Almin & Westgren (1942).

Experimental

Crystals of cubic Sb₂O₃ were found among the main product of orthorhombic Sb₂O₃, prepared by sublimation in nitrogen at 600 °C, and were formed at temperatures below 570 °C. They were very fine, colourless octahedra. The symmetry of the atomic arrangement was checked from heavily exposed Weissenberg photographs. The following conditions limiting possible reflexions were found : hklh+k=2n, k+l=2n; 0kl k+l=4n; h0l h+l=4n; hk0 h+k=4n. These are consistent with space groups Fd3 (No. 203) and Fd3m(No. 227).

The crystal chosen for data collection was an octahedron truncated along (221). The distances from an origin in the crystal to the octahedral faces were approximately 0.072 mm, and to the (221) face 0.024 mm. An Enraf-Nonius CAD4 computer-controlled fourcircle diffractometer with graphite-monochromatized Mo K α radiation and a take-off angle of 3° was used. Least-squares analysis of 45 reflexions with θ values in the range 19 to 29° yielded the lattice parameter $a=11\cdot1519(2)$ Å at 22° C, λ (Mo K α_1)=0.70926 Å. This gives $V=1386\cdot9$ Å³, and with Z=16 the calculated density is 5.584 g cm⁻³. The cell dimension is in agreement with 11·1520(1) Å found by Ozolins & Ievins (1967) by extrapolation of powder data.

Intensities were collected by the $\omega - 2\theta$ scan with $\Delta \omega = 0.8^{\circ} + 0.5^{\circ} \tan \theta$. The background was measured by the moving-counter moving-crystal technique by

extending the scan interval 25% on each side. Double scans were made for each reflexion and a total net count of 10000 was pursued within 10 min. In this way 507 intensities in one octant of reciprocal space out to $\theta = 30^{\circ}$ were sampled. For 11 strong reflexions an attenuation filter was inserted in front of the detector. After every 20 measurements three standards were checked. Their intensities were constant throughout the experiment (total exposure time 53h). For all three standards $R(=\sum |I_o - I_m| / \sum I_o)$ was ≤ 0.006 , I_m being the arithmetic mean of the observations. No scaling was thus necessary. The reflexions were corrected for Lp and absorption effects. The polarization factor was $(\cos^2 2\theta + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m)$. The range of transmission factors was 0.20–0.31 ($\mu = 143$ cm⁻¹). One reflexion with negative intensity was given $F_o = 0$. All reflexions were used without averaging in the subsequent refinement.

The coordinates given by Almin & Westgren (1942), x(Sb) = 0.885 and x(O) = 0.175 in space group Fd3mwith origin at $\overline{4}3m$ and with Sb at the 32(e) and O at the 48(f) sites, were used as a starting point for the refinement. The calculations were based on the assumption of anisotropic thermal motion for both Sb and O. Scattering factors for neutral Sb and O from Doyle & Turner (1968) were used with the anomalous dispersion correction factors for Sb by Cromer & Liberman (1971). The secondary extinction coefficient g (Zachariasen, 1967) was refined. The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, where the weights were calculated from $w_i^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2 + 0.0003|F_o|^2 + 9$. In the last cycle the shifts for all parameters were less than 0.01 times the estimated standard deviations. The final agreement indices were R = 0.022, $R_w =$ 0.028, S = 1.04; $\{R = \sum (|F_o| - |F_c|) / \sum |F_o|, R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}, S = [\sum w_i(|F_o| - |F_c|)^2 / (m-n)]^{1/2} \}.$ The extinction coefficient was $2.90(13) \times 10^3$. The reflexion suffering most from secondary extinction, 222, had $|F_o|_{uncorr}^2 / |F_o|_{corr}^2 = 0.36$ and was presumably overcorrected. A final difference map showed residuals of $2 \cdot 1 e \text{ Å}^{-3}$ near the Sb position.

Space group Fd3 instead of Fd3m would reduce the point symmetry of both Sb and O but in terms of

independent parameters would mean only one more degree of freedom, viz. $\beta_{22} \neq \beta_{33}$ in the anisotropic temperature factor of O. A refinement in Fd3 did not produce any decrease in the R values or any significant changes of the structural model.

In the hope of increasing the crystal mosaicity and thereby decreasing primary extinction the crystal was subjected to thermal shock by bathing in liquid nitrogen. When the nitrogen had boiled off the crystal was remounted on the goniometer head and the same reflexions were measured under the conditions described

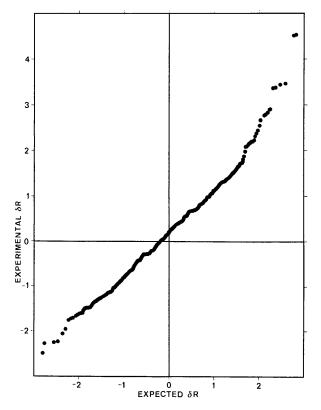


Fig. 1. δR normal probability plot (Abrahams, 1974) for the model according to Table 1. The ordered experimental values of $\delta R = (|F_c| - |F_c|)/\sigma(|F_o|)$ are plotted against the quantiles expected for a normal distribution. The plot includes 507 points. The slope and intercept of the least-squares line fitted to all the data are 1.01 and 0.20, respectively.

above, the only difference being a change in the azimuthal orientations. The intensities were then corrected as for the first data set. No reflexion had negative intensity. A refinement performed exactly as above resulted in R=0.021, $R_w=0.028$ and S=1.04. The extinction coefficient was $2.44(12) \times 10^3$. For the 222 reflexion $|F_o|_{uncorr}^2/|F_o|_{corr}^2$ was 0.40 and the subsequent difference map showed peaks of $1.7 \text{ e} \text{ Å}^{-3}$ near Sb. No positional or thermal parameter changed relative to the first refinement by more than twice its e.s.d. and the change of the extinction parameter between the two refinements is not significant. However, the δR plot (Abrahams, 1974) is noticeably more linear for the second data set.

Fig. 1 shows the δR plot for the last refinement. The central part of the plot is close to linear with a slope near unity, as expected for good-quality data. The displacement of the curve from the origin is probably due to the fact that small observed structure amplitudes more often than not are higher than the values calculated from the refined model. This seems to be a general problem at this installation, the cause of which has not yet been revealed. The rise of the curve for high values of δR is also mainly due to weak reflexions.

The final parameters from the last refinement are given in Table 1. Table 2 lists observed and calculated structure amplitudes. The calculated interatomic distances and angles (Table 3) were not corrected for thermal motion.

Table 1. Fractional coordinates and thermal parameters for cubic Sb₂O₃

The space group is Fd3m (No. 227) with origin at $\overline{4}3m$. The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$

- Sb in 32(e): x = 0.885271 (18) $\beta_{11} = \beta_{22} = \beta_{33} = 0.001576$ (26) $\beta_{12} = \beta_{13} = \beta_{23} = -0.000206$ (7) R.m.s. components: 0.0856 (12), 0.1060 (13), 0.1060 (7) Å
- O in 48(f): x = 0.18625 (19) $\beta_{11} = 0.00201$ (15), $\beta_{22} = \beta_{33} = 0.00203$ (9) $\beta_{12} = \beta_{13} = 0$, $\beta_{23} = 0.00054$ (12) R.m.s. components: 0.0968 (46), 0.1126 (43), 0.1271 (39) Å

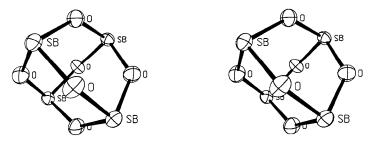


Fig. 2. A stereo view of an Sb_4O_6 unit in cubic Sb_2O_3 . The thermal vibration ellipsoids have been scaled to include 95% probability.

Table 2. Observed and calculated structure amplitudes for cubic Sb_2O_3

The columns list h, $|F_o|$ and $|F_c|$.

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Table 3. Interatomic distances and angles in cubic Sb₂O₃

All distances shorter than 4 Å are included. Atoms with the same superscript belong to the same Sb_4O_6 unit. The number of equivalent distances is shown. Standard deviations are given in parentheses.

(a) Distances (Å)		
Sb ¹ -Sb ¹ (3)	3.619 (1)	$Sb^{i}-O^{i}(3)$	3.813 (2)
-Sb ⁱⁱ (6)	3.949 (1)	$O^{i}-O^{i}(4)$	2.937 (3)
$-O^{1}(3)$	1.977 (1)	-O ⁱⁱ (4)	2.964 (1)
$-O^{11}(3)$	2.918 (2)		
(b) Angles (°)			
O ⁱ -Sb ⁱ -O ⁱ	95.9 (2)	O ⁱ –Sb ⁱ –O ⁱⁱ	71.6 (2)
O ⁱ -Sb ⁱ -O ⁱⁱ	160.8 (5)	Sb ¹ -O ¹ -Sb ¹	132.4 (2)
O ¹ -Sb ¹ -O ¹¹		$Sb^{i}-O^{i}-Sb^{i}$	

Discussion

Cubic Sb_2O_3 is isomorphous with cubic As_2O_3 (Bozorth, 1923) and has usually been described as composed of molecular units of Sb_4O_6 , Fig. 2. These were also found, by electron diffraction (Akishin & Spiridonov, 1961), to exist in the gas phase. In the crystals the O atoms of the Sb₄O₆ unit form by symmetry corners of an octahedron 2.937(3) Å on edge. Outside four of its faces there are Sb atoms, each bonded to three O atoms at 1.977(1) Å. Each O is shared between two Sb atoms. A tetrahedral arrangement around Sb is completed by its $5s^2$ lone pair of electrons. The angles O-Sb-O are $95.93(8)^\circ$. The Sb₄O₆ unit has T_d symmetry and could be described as a large tetrahedron with the four lone pairs as corners. These tetrahedra are arranged face to face in such a way that the O atoms of two adjacent faces are corners of a slightly distorted octahedron. The O...O distances between Sb₄O₆ units are 2.964(1) Å.

Though the molecular description of the crystal structure gives a neat correspondence with the conditions in the gas phase, it should be emphasized that cubic Sb_2O_3 has the same O arrangement as pyrochlore, $NaCaNb_2O_6F$ (Gaertner, 1930). The octahedra between the Sb_4O_6 units mentioned above correspond to the O octahedra enclosing Nb^V in pyrochlore. The cations and eight of the anions per unit cell, which are situated in the tunnels of pyrochlore, have no counterparts in cubic Sb_2O_3 . The Sb atoms and their lone pairs protrude into these regions, so that cubic Sb_2O_3 has no tunnels.

A cubic antimony oxide of formula $Sb_2O_{4\cdot35(5)}$ or Sb_6O_{13} with the pyrochlore structure has been described by Stewart, Knop, Ayasse & Woodhams (1972). It has the characteristic three-dimensional framework of Sb^v-O_6 octahedra while eight Sb^{III} and four O atoms partially occupy the (pyrochlore) sites in the tunnels. However, the Sb^{III} position at a centre of symmetry (actually $\overline{3}m$) seems questionable in view of the normally one-sided O coordination of Sb^{III} .

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