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## The Crystal Structure of Ferroelastic Antimony(III) Oxide Iodide $\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I

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Ferroelastic antimony(III) oxide iodide  $\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I is monoclinic, space group  $P2_1/c$ , with  $a = 6.772$  (3),  $b = 12.726$  (4),  $c = 13.392$  (5) Å,  $\beta = 120.1$  (1)°,  $Z = 4$ . The structure was solved from 1401 reflexions and refined to  $R = 3.7\%$ . It consists of pseudo-hexagonal sheets of  $\text{Sb}_2[\text{Sb}_3\text{O}_7]_2^+$  connected by intermediate iodine; the latter occupies the centre of a slightly distorted cubo-octahedron of antimony. The atomic displacements from plausible positions of space group  $P6_3/m$  of the high-temperature parent phase  $\beta$ -Sb<sub>5</sub>O<sub>7</sub>I which are considered responsible for the observed ferroelasticity are of the order of 0.2 Å.

### Introduction

Recently we reported the synthesis and crystal growth of a series of new antimony(III) oxide iodides of the compositions Sb<sub>3</sub>O<sub>4</sub>I, Sb<sub>8</sub>O<sub>11</sub>I<sub>2</sub>, and Sb<sub>5</sub>O<sub>7</sub>I (Krämer, Schuhmacher & Nitsche, 1973). In the course of further investigations it was found that Sb<sub>5</sub>O<sub>7</sub>I exists in (a) a low-temperature monoclinic (pseudo-hexagonal) phase,  $\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I, and (b) the hexagonal high-temperature phase,  $\beta$ -Sb<sub>5</sub>O<sub>7</sub>I.

The phase transition is reversible and takes place at a temperature of 208°C. Crystals of  $\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I show pure ferroelastic behaviour. They can exist in three different orientation states of mechanical strain which can be converted into each other by external stresses (Krämer, Nitsche & Schuhmacher, 1974).

Since the Sb<sub>5</sub>O<sub>7</sub>I phases represent a new structure type and in order to elucidate the ferroelastic behaviour, a crystal structure determination was performed.

### Experimental

X-ray powder data were obtained with a Philips diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å) with

As<sub>2</sub>O<sub>3</sub> (cubic,  $a = 11.0810$  Å) as a standard. Cell parameters were refined by least-squares calculations. A vapour-grown single-domain crystal was selected for Weissenberg and precession photographs. Intensities from the same crystal were measured on a computer-controlled automatic X-ray diffractometer (Enraf-Nonius CAD-4) by the  $\omega$ - $2\theta$  scan method. A Mo tube

Table 1. *Crystal data*

Formula	Sb <sub>5</sub> O <sub>7</sub> I
Formula weight	847.65
Habit	Flat pseudo-hexagonal prism
Colour	Transparent, colourless
Lattice parameters	$a = 6.772$ (3) Å $b = 12.726$ (4) $c = 13.392$ (5) $\beta = 120.1$ (1)° $V = 998.3$ Å <sup>3</sup> $Z = 4$
Density	$D_{\text{meas}} = 5.55$ g cm <sup>-3</sup> $D_{\text{calc}} = 5.64$
Reflexion conditions	$h0l: l = 2n; 0k0: k = 2n$
Space group	$P2_1/c$
Radiation	Mo $K\alpha$ , $\lambda = 0.71069$ Å
Linear absorption coefficient:	$\mu_{\text{Mo}} = 162.2$ cm <sup>-1</sup>
Crystal size:	$370 \times 70 \times 330$ $\mu\text{m}$

and a graphite monochromator were used to produce the Mo  $K\alpha$  radiation which was detected by a scintillation counter. The crystal data are given in Table 1.

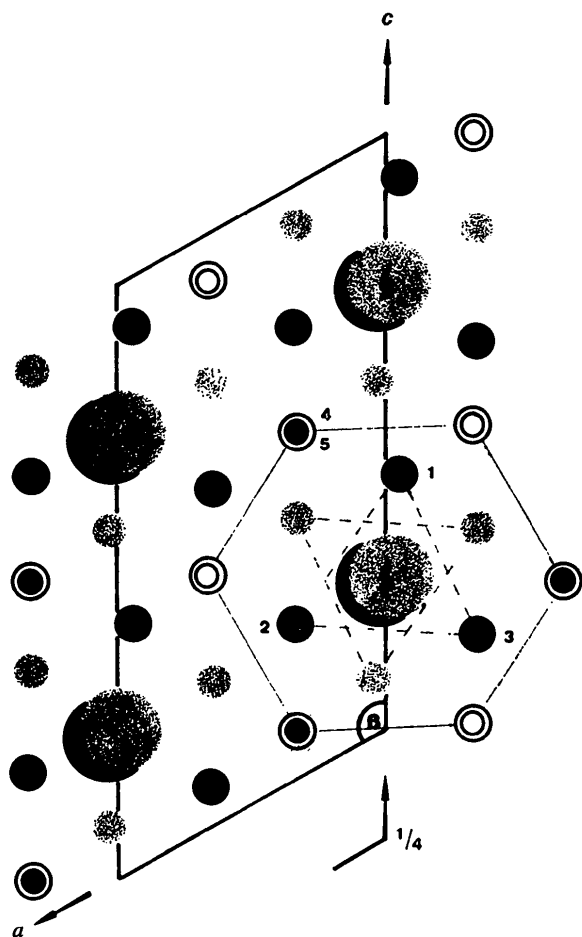


Fig. 1. Antimony and iodine viewed along  $b$ . The  $2_1$  screw axis runs parallel to  $b$  at  $z = \frac{1}{4}$ , the centre of symmetry is located at the origin. Small dots and circles represent Sb, the large dots are I. Approximate heights of Sb and I ( $y = \text{black/grey or white atoms}$ ): Sb(1), Sb(2), Sb(3):  $y \approx 0.25/0.75$ ; Sb(4):  $y \approx 0.05/0.55$ ; Sb(5):  $y \approx 0.45/0.95$ ; I:  $y \approx 0.00/0.50$ .

### Data reduction

All computations were performed with the 1970 version of the X-RAY system (Stewart, Kundell & Baldwin, 1970). 1401 independent reflexions were measured, 1152 of which had  $I \geq 3\sigma(I)$ , where  $\sigma^2$  is the variance of the observation. The intensities were corrected for absorption and Lorentz-polarization effects.

### Structure solution and refinement

From the calculation of the overall scale and temperature factors by a Wilson plot of the normalized structure factors, the structure was proved to be centrosymmetric. From an  $E$  map the relative arrangement of the six heavy atoms in the asymmetric unit (5 Sb and I) was established. Comparison of the  $E$  map with the Patterson map located the origin.

Subsequent difference maps yielded the seven oxygen positions. Least-squares refinement of the overall scale and isotropic temperature factors and the atomic parameters, minimizing the function  $\sum w||F_o| - |F_c||^2$ , where  $w = 1/\sigma^2$ , resulted in  $R = 0.138$ . In the course of the following isotropic extinction correction and anisotropic refinement of the temperature factors of antimony and iodine  $R$  converged to 0.037.\* Scattering factors for  $\text{Sb}^{3+}$  and  $\text{I}^-$  of Cromer & Waber (1965) and for  $\text{O}^{2-}$  of Baur (1956) were used and corrected for anomalous dispersion (Cromer & Liberman, 1970).

### Description of the structure

The atomic coordinates and thermal parameters are given in Table 2, interatomic distances in Table 3.

Each of the five antimony atoms has three oxygen neighbours which form a nearly equilateral triangle with antimony above the base; in these  $[\text{SbO}_3]^{3-}$  pyramids the mean Sb-O is 1.99 Å. Each of the three

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30663 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional coordinates and thermal parameters

Estimated standard deviations are in parentheses. Values are  $\times 10^4$ . The Debye-Waller term is defined as

$$T = \exp \left[ -2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 a_i a_j h_i h_j U^{ij} \right] \text{ for Sb and I, } T = \exp \left[ -2\pi^2 U^{11} (2 \sin \theta / \lambda)^2 \right] \text{ for O.}$$

	$x$	$y$	$z$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb(1)	-404 (2)	2379 (1)	4061 (1)	142 (8)	132 (9)	101 (10)	-3 (5)	58 (6)	4 (6)
Sb(2)	3494 (2)	2447 (1)	2619 (1)	107 (8)	173 (9)	132 (10)	21 (5)	47 (6)	25 (6)
Sb(3)	6757 (2)	2581 (1)	5684 (1)	120 (8)	148 (9)	80 (10)	-7 (5)	17 (6)	10 (6)
Sb(4)	3326 (2)	504 (1)	5758 (1)	140 (8)	80 (9)	173 (11)	2 (5)	61 (7)	-4 (6)
Sb(5)	3278 (2)	4477 (1)	5819 (1)	166 (8)	84 (9)	138 (11)	3 (5)	64 (7)	2 (6)
I	305 (3)	-48 (1)	2460 (2)	279 (9)	182 (10)	285 (12)	9 (7)	125 (8)	-11 (7)
	$x$	$y$	$z$	$U^{11}$	$x$	$y$	$z$	$U^{11}$	
O(1)	6649 (24)	2514 (12)	4147 (14)	111 (35)	O(5)	916 (29)	1661 (14)	389 (16)	237 (41)
O(2)	4736 (26)	1200 (13)	48 (15)	169 (34)	O(6)	4076 (29)	1659 (14)	4989 (16)	238 (41)
O(3)	258 (26)	1164 (13)	5074 (15)	163 (37)	O(7)	4617 (30)	3654 (15)	2175 (16)	270 (43)
O(4)	5153 (29)	1410 (15)	2213 (16)	241 (41)					

Table 3. *Interatomic distances in Å*

Standard deviations are given in parentheses.			
Sb(1)-O(3)	1.95 (2)	Sb(3)-O(2)	1.96 (2)
O(5)	1.96 (2)	O(6)	1.96 (2)
O(1)	2.06 (2)	O(1)	2.03 (2)
I	3.875 (3)	I	3.938 (3)
	3.923 (3)	I	3.942 (3)
Sb(2)	3.980 (6)	Sb(4)	3.553 (3)
Sb(3)	3.921 (9)	Sb(5)	3.439 (3)
Sb(4)	3.383 (7)		
Sb(5)	3.600 (7)	Sb(4)-O(7)	1.96 (2)
		O(3)	1.98 (2)
		O(6)	2.00 (2)
Sb(2)-O(7)	1.94 (2)	I	3.774 (11)
O(4)	1.98 (2)		3.881 (10)
O(1)	2.09 (2)		4.242 (7)
I	3.784 (3)		
	4.064 (4)	Sb(5)-O(2)	1.95 (2)
Sb(3)	3.949 (12)	O(4)	2.00 (2)
Sb(4)	3.569 (3)	O(5)	2.01 (2)
Sb(5)	3.387 (3)	I	3.725 (6)
			3.844 (11)
			4.176 (10)

antimony atoms Sb(1), Sb(2), Sb(3) is linked to two iodine atoms, each of the two others [Sb(4), Sb(5)] to three iodines. On the other hand (Fig. 1) iodine is surrounded by 12 antimony atoms: 2 × Sb(1), Sb(2), Sb(3), 3 × Sb(4) and 3 × Sb(5). In this cubo-octahedral configuration (Fig. 2) the mean Sb-I is 3.93 Å.

The mean Sb-Sb distances are 3.95 Å among Sb(1), Sb(2), Sb(3) and 3.49 Å for Sb(1), Sb(2), Sb(3) between Sb(4) and Sb(5). The [SbO<sub>3</sub>]<sup>3-</sup> pyramids built up by Sb(1), Sb(2), Sb(3) contain all the seven oxygen atoms; they are linked by O(1) in such a way that the [Sb<sub>3</sub>O<sub>7</sub>]<sup>5-</sup> building unit shown in Fig. 3 results. In this unit the oxygens are hexagonal-close-packed. Furthermore Sb(4) [Sb(5)] is bonded to three oxygens each of which belongs to the lower (higher) side of a different unit. By this means a connexion of the units to a pseudo-hexagonal sheet of Sb<sub>2</sub>[Sb<sub>3</sub>O<sub>7</sub>]<sub>2</sub><sup>±</sup> is obtained. The neighbouring sheet is rotated by 180° and moved by  $b/2$  along  $y$  (symmetry operation of the 2<sub>1</sub> screw); sheets are tied together by intermediate iodine. An idealized projection of the entire atomic arrangement is shown in Fig. 4.

Sb<sub>5</sub>O<sub>7</sub>I represents a new type of structure. However, a resemblance to symmetry-related apatite compounds, A<sub>5</sub>(BO<sub>4</sub>)<sub>3</sub>C (A: large bivalent cations, B: small trivalent ions, C: halogens or OH) of space group  $P6_3/m$  can be established: On substitution of the BO<sub>4</sub> groups by oxygen only a diminution of the unit cell results and hence cell parameters correspond in magnitude and the identical number of heavy atoms (5A; C/5Sb; I) in their geometrical arrangement.

### Discussion

$\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I transforms into hexagonal  $\beta$ -Sb<sub>5</sub>O<sub>7</sub>I [ $a = 6.80$  (4),  $c = 12.80$  (5) Å,  $Z = 2$ ; its space group  $P6_3/m$  is a supergroup of  $P2_1/c$ ]. If one superposes all the symmetry elements of space group  $P6_3/m$  on the struc-

ture of the low-temperature phase with the origin at  $z = \frac{1}{4}$  then all atoms lie very close to equipoints of this space group.

The hexagonal fractional coordinates  $X, Y, Z$  can be calculated from monoclinic  $x, y, z$  (Table 2) by the following transformation:  $X = x$ ;  $Y = 2z - 0.50$ ;  $Z = y$ .

The displacements of atoms of the  $\alpha$ -phase from ideal hexagonal positions are of the order of 0.2 Å. Some values and the corresponding equipoints of  $P6_3/m$  are given in Table 4.

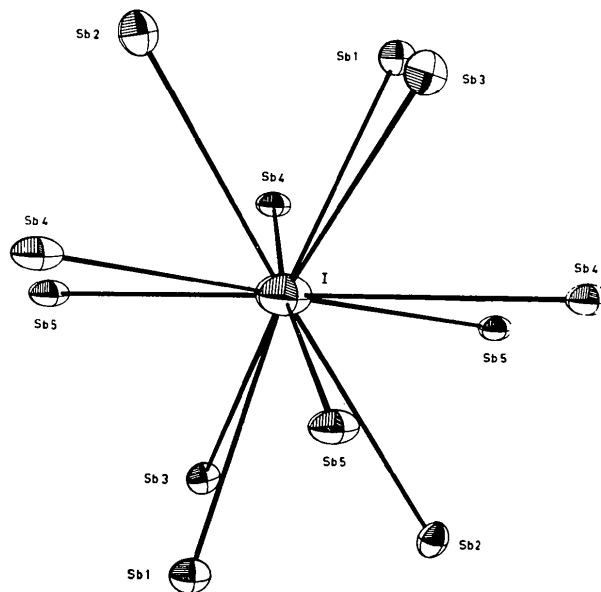


Fig. 2. A view of the slightly distorted antimony cubo-octahedron with iodine in the centre showing thermal vibration ellipsoids (drawn by program ORTEP: Johnson, 1965).

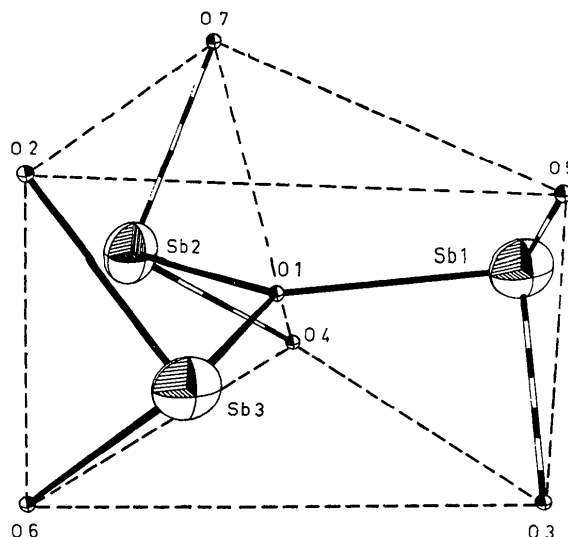


Fig. 3. [Sb<sub>3</sub>O<sub>7</sub>]<sup>5-</sup> building unit showing thermal vibration ellipsoids (drawn by program ORTEP: Johnson, 1965).

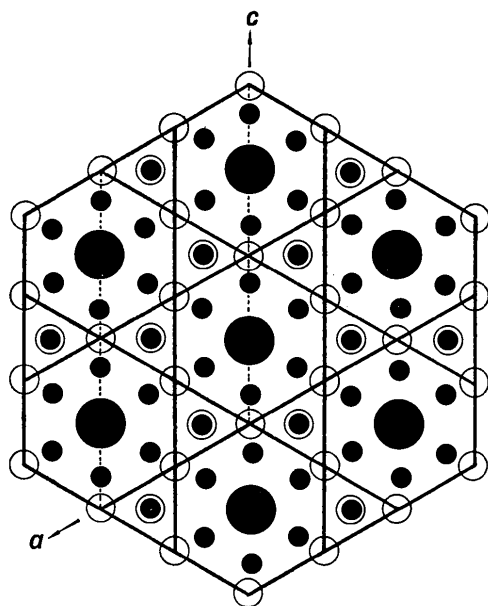


Fig. 4. Idealized projection on the (010) plane. Small dots represent Sb, large dots I, and circles O.

Table 4. Probably occupied equipoints of space group  $P6_3/m$  and magnitudes of displacements in Å

Atom	Equipoint	Displacement from mean position		
		X	Y	Z
Sb(1), Sb(2), Sb(3)	6(h)	0.07	0.07	0.15
Sb(4), Sb(5)	4(f)	0.1	0.1	0.06
I	2(b)	0.2	0.2	0.06
O(1)	2(d)			
O(2)–O(7)	12(i)			

A significant behaviour is shown by iodine (compare Fig. 1): It is bonded closer to one antimony [Sb(2)] than to the others and – influenced by the  $2_1$  screw – it

is alternately shifted in the  $x/-x$  direction. The approach of Sb(2) and I takes place parallel to the (001) plane which adjusts always perpendicular to the applied stress direction as microscopy and Laue photographs had shown. After stressing another pair of opposite prism faces  $[(100)/(\bar{1}00)$  or  $(\bar{1}02)/(10\bar{2})]$  the lattice is somewhat contracted in this direction, iodine is shifted parallel to this pair of planes and approaches just the antimony [Sb(1) or Sb(3) of the old arrangement] that is situated in the new (001) plane; accordingly the crystallographic orientation is changed.

Thus  $\alpha$ -Sb<sub>5</sub>O<sub>7</sub>I meets the requirements of ferroelasticity which were predicted by Aizu (1969).

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