

l'enchaînement de Sr(1)—Sr(1) se fait grâce à O(12)—O(12). Dans la direction *c*, Sr(2)—Sr(1) mettent en commun un sommet O(22). L'enchaînement est donc tridimensionnel.

Nous avons d'autre part essayé, mais sans résultat, de localiser les protons. A ce niveau, les synthèses de Fourier se sont révélées infructueuses.

Références

- LEHR, J. R., BROWN, E. H., FRAZIER, A. W., SMITH, J. P. & TASHER, R. D. (1967). *Crystallographic Properties of Fertilizer Compounds*. Tennessee Valley Authority, Tech. Eng. Bull. No. 6.
- PREWITT, C. T. (1966). *SFLS-5*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Acta Cryst. (1978), B34, 2695–2698

The Crystal Structure of the Ferroelastic/Ferroelectric 2MA Polytype of Antimony(III) Oxide Iodide, Sb₅O₇I

BY VOLKER KRÄMER

Kristallographisches Institut der Universität, Hebelstrasse 25, D-7800 Freiburg, Federal Republic of Germany

(Received 5 September 1977; accepted 5 April 1978)

The combined ferroelastic/ferroelectric polytype 2MA Sb₅O₇I is monoclinic, space group *Pc*, with $a = 6.759$ (3), $b = 12.718$ (6), $c = 13.405$ (6) Å, $\beta = 120.1$ (1)°, $Z = 4$. The structure was solved from 1704 reflections which were collected on a four-circle diffractometer. Atomic parameters were refined to a final $R = 0.032$. The structure consists of enantiomorphic Sb₂[Sb₃O₇]_∞⁺ layers alternately stacked in the *b* direction. Layers are connected by intermediate iodine; the latter is surrounded by twelve Sb atoms forming a slightly distorted hexagonal 'anti'-cuboctahedron. The occurrence of the h.c.p. coordination polyhedron is the essential difference between 2MA Sb₅O₇I and 2MC Sb₅O₇I (where a cuboctahedron has been found).

Introduction

Recently we reported the crystal growth and properties of the ferroelastic antimony(III) oxide iodide α -Sb₅O₇I (Krämer, Nitsche & Schuhmacher, 1974) as well as the determination of its crystal structure (Krämer, 1975). In the meantime, detailed optical and X-ray investigations of a great number of grown crystals have revealed that there exist at least nine polytypic modifications of Sb₅O₇I. Centrosymmetric polytypes show pure ferroelastic behaviour, while noncentrosymmetric polytypes show combined ferroelastic and ferroelectric behaviour. In order to discriminate between the various polytypes before accurate structural knowledge is gained we proposed a modified Ramsdell notation (Ramsdell, 1947) which contains additional information on whether the structure is centrosymmetric (*C*) or noncentrosymmetric (*A*) (Nitsche, Krämer, Schuhmacher & Bussmann, 1977). Accordingly, the former α -Sb₅O₇I becomes 2MC Sb₅O₇I.

This paper presents the results of the crystal structure analysis of 2MA Sb₅O₇I, which was performed to establish the main differences between the 2MA and 2MC polytypes as well as to discover the building principles of all Sb₅O₇I polytypes.

Experimental

The lattice parameters of 2MA Sb₅O₇I were refined by a least-squares procedure from X-ray powder data obtained with a Guinier–de Wolff camera (Cu *K* α radiation, $\lambda = 1.5418$ Å) with As₂O₃ (cubic, $a = 11.0180$ Å) as an internal standard.

Table 1. *Crystal data*

Formula	2MA Sb ₅ O ₇ I
Formula weight	847.65
Habit	Flat pseudo-hexagonal prism
Colour	Transparent, colourless
Lattice parameters	$a = 6.759$ (3) Å $b = 12.718$ (6) $c = 13.405$ (6) $\beta = 120.1$ (1)° $V = 998.0$ Å ³ $Z = 4$
Density	$D_{\text{pycn}} = 5.55$ g cm ⁻³ $D_{\text{calc}} = 5.64$
Reflection condition	$h0l: l = 2n$
Space group	<i>Pc</i>
Radiation	Mo <i>K</i> α , $\lambda = 0.71069$ Å
Linear absorption coefficient	$\mu_{\text{Mo}} = 162.2$ cm ⁻¹
Crystal size	460 × 100 × 430 μm

A vapour-grown single-domain crystal was selected for Weissenberg and precession photographs to find initial lattice parameters and possible space groups. X-ray intensities from this crystal were measured on an automatic four-circle diffractometer (Enraf-Nonius CAD-4) by the ω - 2θ scan method. Characteristic Mo $K\alpha$ radiation (Mo tube, graphite monochromator) was employed and detected by a scintillation counter. Crystal data are listed in Table 1.

Choice of the proper space group

Crystals of 2MA Sb₅O₇I are ferroelectric and show orthorhombic symmetry in single-crystal photographs. Together with the reflection conditions found, space group $P2nn$ was indicated with $a = 6.759$, $b = 12.718$, $c = 11.609$ Å. However, detailed piezoelectric measurements yield significant signals in all directions perpendicular to the b axis. Therefore, the glide plane perpendicular to (001) is not strictly realized, and the correct point-group symmetry is reduced to monoclinic m .

For reasons of direct structural comparisons between both polytypes [$2MA$ and $2MC(P2_1/c)$], space group Pc with the glide plane at height $y = \frac{1}{4}$ and the lattice parameters $a_{\text{mon}} = a_{\text{orth}}$, $b_{\text{mon}} = b_{\text{orth}}$, $c_{\text{mon}} = c_{\text{orth}}/\frac{1}{2}\sqrt{3}$, $\beta = 120.1^\circ$ were chosen.

It is interesting to note that *a priori* refinement in space group $P2nn$ converged at $R = 0.055$ (Krämer, 1976); *i.e.* the positions of all atoms in space group Pc do not vary significantly from the positions in $P2nn$ – as confirmed by the final lists of atomic coordinates.

Data reduction

All calculations were performed with computer programs from the XRAY system (Stewart, Kundell & Baldwin, 1970). 1704 independent reflections were collected, 1613 of which had $I \geq 3\sigma(I)$. Intensities were corrected for absorption effects by the program *ORABS*, which computes transmission factors and mean path lengths in the crystal by Gaussian integration.

Structure solution and refinement

The structure was easily solved by comparing the Patterson maps of $2MC$ and $2MA$ Sb₅O₇I, on the assumption that the latter has a similar but noncentrosymmetric arrangement of Sb atoms.

Several least-squares refinement cycles on all positional, isotropic extinction, and thermal parameters of O, and anisotropic thermal parameters of Sb and I resulted

in a final agreement index of $R = 0.032^*$ and an average shift/error of 2.7×10^{-2} . Scattering factors for Sb³⁺, I⁻ (Cromer & Waber, 1965), and O²⁻ (Baur, 1956) were used and corrected for anomalous dispersion (Cromer & Liberman, 1970).

Description of the structure

The atomic coordinates are listed in Table 2, interatomic distances in Table 3.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33543 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^4$)

Estimated standard deviations are in parentheses.

	x	y	z
Sb(1A)	-701 (7)	2345 (1)	4079 (3)
Sb(1B)	39 (7)	7548 (1)	4301 (3)
Sb(2A)	3206 (7)	2460 (2)	2652 (3)
Sb(2B)	2914 (7)	7541 (2)	2352 (4)
Sb(3A)	-3561 (7)	2451 (1)	700 (3)
Sb(3B)	-3859 (6)	7652 (1)	917 (3)
Sb(4A)	2931 (7)	551 (1)	802 (3)
Sb(5A)	3028 (7)	4520 (1)	807 (3)
Sb(4B)	-3664 (7)	5551 (1)	-800 (3)
Sb(5B)	-3581 (7)	9519 (1)	-805 (3)
I(1)	0	0	2500
I(2)	-654 (5)	4997 (2)	2504 (3)
O(1A)	6396 (41)	2484 (13)	4163 (22)
O(1B)	3073 (37)	7513 (11)	824 (20)
O(2A)	509 (49)	1678 (17)	432 (26)
O(3A)	-15 (42)	3858 (14)	125 (30)
O(2B)	-636 (37)	6243 (12)	-42 (19)
O(3B)	-1146 (50)	8429 (17)	-36 (24)
O(4A)	4378 (43)	1247 (14)	46 (22)
O(5A)	3742 (44)	3367 (15)	36 (22)
O(4B)	4873 (51)	6666 (17)	-354 (26)
O(5B)	4820 (48)	8871 (15)	-140 (24)
O(6A)	4744 (54)	1396 (18)	2204 (26)
O(7A)	4258 (47)	3665 (15)	2252 (22)
O(6B)	4894 (56)	6316 (17)	2802 (26)
O(7B)	5495 (59)	8567 (20)	2771 (28)

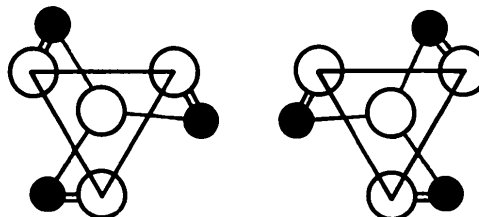


Fig. 1. Enantiomeric $[Sb_3O_7]^{5-}$ building units. $2MC$ Sb₅O₇I contains only one of these types, *e.g.* type *a* (right). In $2MA$ Sb₅O₇I succeeding layers are alternately built up from units of type *a* (right) and type *b* (left).

Table 3. *Interatomic distances* (Å)

Standard deviations are given in parentheses.

Sb(1 <i>A</i>)—O(1 <i>A</i>)	2.03 (3)	Sb(1 <i>B</i>)—O(1 <i>B</i>)	2.05 (2)
O(2 <i>A</i>)	2.00 (3)	O(2 <i>B</i>)	1.94 (2)
O(3 <i>A</i>)	1.97 (2)	O(3 <i>B</i>)	1.92 (3)
[O(5 <i>A</i>)	2.76 (3)]	[O(7 <i>B</i>)	3.00 (3)]
I(1)	2.821 (3)	I(1)	3.935 (3)
I(2)	3.988 (4)	I(2)	3.928 (4)
Sb(2 <i>A</i>)—O(1 <i>A</i>)	2.09 (2)	Sb(2 <i>B</i>)—O(1 <i>B</i>)	2.10 (3)
O(6 <i>A</i>)	1.98 (4)	O(6 <i>B</i>)	1.94 (3)
O(7 <i>A</i>)	1.88 (3)	O(7 <i>B</i>)	2.02 (3)
[O(2 <i>A</i>)	2.78 (3)]	[O(4 <i>B</i>)	2.86 (3)]
I(1)	3.754 (3)	I(1)	3.754 (4)
I(2)	4.092 (5)	I(2)	4.101 (5)
Sb(3 <i>A</i>)—O(1 <i>A</i>)	2.05 (3)	Sb(3 <i>B</i>)—O(1 <i>B</i>)	2.02 (3)
O(4 <i>A</i>)	1.96 (2)	O(4 <i>B</i>)	1.94 (3)
O(5 <i>A</i>)	1.96 (2)	O(5 <i>B</i>)	1.99 (2)
[O(6 <i>A</i>)	3.08 (4)]	[O(3 <i>B</i>)	2.88 (4)]
I(1)	3.940 (2)	I(1)	3.832 (2)
I(2)	3.930 (4)	I(2)	4.002 (3)
Sb(4 <i>A</i>)—O(2 <i>A</i>)	2.04 (3)	Sb(4 <i>B</i>)—O(2 <i>B</i>)	1.98 (2)
O(4 <i>A</i>)	1.94 (3)	O(4 <i>B</i>)	1.98 (3)
O(6 <i>A</i>)	1.97 (3)	O(7 <i>B</i>)	2.04 (3)
[O(5 <i>B</i>)	3.07 (3)]	[O(3 <i>A</i>)	3.03 (2)]
I(1)	3.756 (6)	I(1)	3.777 (4)
	4.199 (4)		4.178 (5)
I(2)	3.896 (5)	I(2)	3.902 (6)
Sb(5 <i>A</i>)—O(3 <i>A</i>)	1.97 (3)	Sb(5 <i>B</i>)—O(3 <i>B</i>)	2.00 (2)
O(5 <i>A</i>)	1.99 (3)	O(5 <i>B</i>)	1.90 (4)
O(7 <i>A</i>)	2.00 (3)	O(6 <i>B</i>)	1.94 (3)
[O(2 <i>B</i>)	3.07 (2)]	[O(4 <i>A</i>)	3.10 (3)]
I(1)	3.889 (4)	I(1)	3.890 (4)
I(2)	4.118 (5)	I(2)	3.731 (8)
	4.170 (7)		4.188 (5)

The structure of $2MA$ Sb_2O_7I is constructed in the same way as that of $2MC$ Sb_2O_7I : $[Sb_3O_7]^{5-}$ units (Fig. 1) are linked by pairs of Sb atoms [Sb(4*A*), Sb(5*A*)] to form an infinite pseudohexagonal $Sb_2[Sb_3O_7]_{\infty}^{+}$ layer (Fig. 2); the neighbouring layer is rotated by about 180° (rotation by 60 or 120° is also admissible), and moved by $b/2$ in the y direction, and connected by intermediate iodine. The only essential difference between $2MA$ and $2MC$ is that in $2MA$ each second layer contains the enantiomorphic Sb_3O_7 units shown in Fig. 1. Accordingly, atoms Sb(1*B*)–Sb(3*B*) of stacking unit b lie in nearly the same x and y positions as Sb(1*A*)–Sb(3*A*) of stacking unit a ; the O, I and remaining Sb [Sb(4*A*), Sb(5*A*), Sb(4*B*), Sb(5*B*)] positions are not altered with respect to $2MC$. Hence I is also twelfold coordinated by Sb, but the resulting coordination polyhedron is a slightly distorted hexagonal 'anti'-cuboctahedron (Nitsche *et al.*, 1977), as Fig. 3 indicates. An idealized projection of the entire atomic arrangement is shown in Fig. 4.

It can be clearly seen that all atomic distances are in good agreement with those found in $2MC$ Sb_2O_7I . The mean Sb–O bond length is 1.99 Å, and the mean Sb–I 3.93 Å. The Sb_3O_7 units are formed by (three) SbO_3

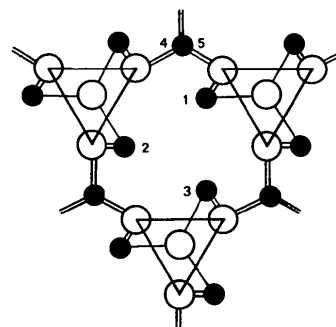


Fig. 2. Section of an $Sb_2[Sb_3O_7]_{\infty}^{+}$ layer projected onto (010). The $[Sb_3O_7]^{5-}$ units are of type a (cf. Fig. 1).

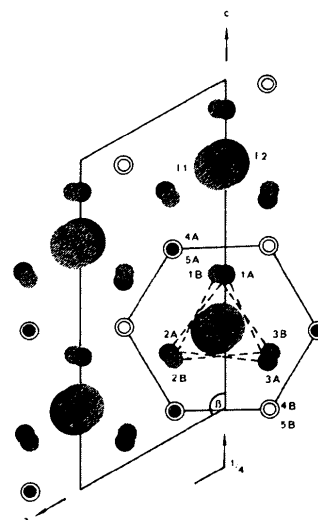


Fig. 3. Antimony (small filled and open circles) and iodine (large filled circles) viewed along b . Approximate heights: Sb(1*A*)–Sb(3*A*): $y \approx 0.25$; Sb(1*B*)–Sb(3*B*): $y \approx 0.75$; Sb(4*A*), Sb(5*A*): $y \approx 0.05/0.45$; Sb(4*B*), Sb(5*B*): $y \approx 0.55/0.95$; I(1), I(2): $y \approx 0.00/0.50$.

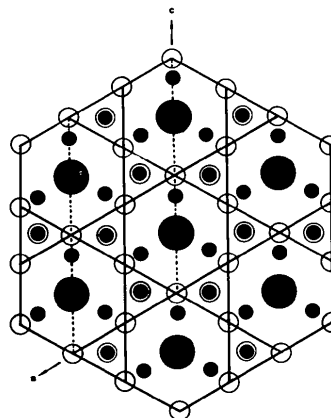


Fig. 4. Idealized projection of the entire framework onto (010). Small filled circles represent Sb, large ones I, and open circles O.

pyramids – as has been found in many other Sb–O compounds. When we consider the Sb–O bonds and the lone pair of electrons of an Sb atom [from the VSEPR model (Gillespie, 1970)], a ψ tetrahedron rather than a ψ trigonal bipyramid is obtained.* The fourth-nearest O atom which could possibly belong to the latter polyhedron has distances r such that $2.76 \leq r \leq 3.10 \text{ \AA}$ (see values in square brackets in Table 3). These rather large values are not concordant with an Sb–O bond distance (Bovin, 1976).

Conclusions

At 165°C a reversible phase transformation of 2MA Sb_5O_7I into the prototypic hexagonal polytype 2HA Sb_5O_7I takes place. For the 2HA polytype: $a = 6.78$, $c = 12.86 \text{ \AA}$, $Z = 2$, and the most probable space group is $P\bar{6}$. The lack of an inversion centre was confirmed by high-temperature SHG measurements (Häfele, 1976). The corresponding prototypic/ferroic transition is $6Fm$ (Aizu, 1969).

Each atom of the hexagonal prototype is assumed to lie at the centre of a triangle whose vertices correspond to the positions of this atom in the three stable orientation states of the ferroic phase. The displacements of atoms in the low-temperature phase from these idealized hexagonal positions, *i.e.* the central atom–vertex atom distances, are of the same kind and order of magnitude ($<0.25 \text{ \AA}$) as in 2MC Sb_5O_7I .

At the transition temperature T_c the double-refraction index undergoes a small but discrete jump down to zero. Furthermore, the cell volume of the prototypic phase reduces to half the volume of the ferroic phase. These facts indicate a first-order phase transformation. On the other hand, the atomic displacements exhibit three degrees of freedom; thus, ferro-

* ψ means that one vertex of the coordination polyhedron is occupied by an electron lone pair.

elastic 2MA Sb_5O_7I is also envisaged to be a three-dimensional improper ferroelectric material.

From the structures of the basic polytypes, 2MC and 2MA, we have deduced that all polytypes with higher stacking sequences consist of even-numbered multiples of both kinds of enantiomorphic stacking units (Nitsche *et al.*, 1977). To prove this assumption the crystal structure analyses of the two four-layered polytypes are in progress.

The author is indebted to Dr A. Haase for the intensity collection and to Dr I. R. Jahn for double-refraction measurements. Numerical computations were performed on the Univac 1106/II computer of the Rechenzentrum der Universität Freiburg. I gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft.

References

- AIZU, K. (1969). *J. Phys. Soc. Jpn.*, **27**, 387–396.
 BAUR, H. W. (1956). *Acta Cryst.* **9**, 515–519.
 BOVIN, J.-O. (1976). *Acta Cryst.* **B32**, 1771–1777.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 GILLESPIE, R. J. (1970). *J. Chem. Educ.* **47**, 18–23.
 HÄFELE, H. G. (1976). Private communication.
 KRÄMER, V. (1975). *Acta Cryst.* **B31**, 234–237.
 KRÄMER, V. (1976). Habilitationsschrift, Univ. Freiburg.
 KRÄMER, V., NITSCHKE, R. & SCHUHMACHER, M. (1974). *J. Cryst. Growth*, **24/25**, 179–182.
 NITSCHKE, R., KRÄMER, V., SCHUHMACHER, M. & BUSSMANN, A. (1977). *J. Cryst. Growth*, **42**, 549–559.
 RAMSDALL, L. S. (1947). *Am. Mineral.* **32**, 64–83.
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY system. Computer Science Center, Univ. of Maryland, College Park, Maryland.