

The Crystal Structure of L-SbOF

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Received May 8, 1972

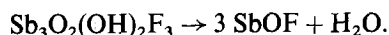
L-SbOF is orthorhombic, space group *Pnma*, with $a = 8.873$, $b = 4.099$ and $c = 5.483$ Å. Four anions are bonded to Sb^{3+} , all to one side, and such polyhedra form chains by edge sharing along c . Evidence is given for an ordered arrangement of fluorine and oxygen anions. The lone pair of electrons is described as taking a certain volume, the centre of which is derived. Relationships with other structures are discussed.

Introduction

Previously the existence of four different forms, of which one is a glass, of the oxide fluoride SbOF was briefly reported (1). The structure of one of them, which was made at the lowest temperature and consequently called L-SbOF, will be described here.

Experimental

Mixtures of SbF_3 and Sb_2O_3 of high purity in the molar ratio 1:1 were made in a dry box and placed in gold capsules, which were sealed by welding and heated at a temperature of 150–160°C overnight. When SbF_3 was heated in open air at a temperature around 100 C, a crystalline compound was formed rather quickly. This compound was analyzed chemically, as well as by a complete structure analysis by Aurivillius and Malmros (2), and found to have a composition of $\text{Sb}_3\text{O}_2(\text{OH})_2\text{F}_3$. This compound was heated in air, and gradually L-SbOF was formed in this way. Weight changes agreed with the following reaction:



Chemical analysis on fluorine for this material gave 12.2 wt % fluorine, while the calculated value is 12.1 % for the formula SbOF.

Rod-shaped, colorless crystals of SbOF were obtained by this sealed capsule method, and also during the thermal decomposition of $\text{Sb}_3\text{O}_2(\text{OH})_2\text{F}_3$. Single crystal studies showed the crystals to be of orthorhombic symmetry, and integrated data were collected with a Nonius

camera using Mo radiation. About 325 intensities were measured with a densitometer. Crystallographic constants are given in Table I, and the indexed Hagg–Guinier powder pattern in Table II. The following programs were used:

DRF: Data reduction and Fourier calculations; LALS: Full matrix, least squares calculations; DISTAN: Calculation of distances and angles (A. Zalkin, Berkeley, Ca.). (All programs modified for the UNIVAC 1108 Computer in Lund.)

Structure Determination

With the space group *Pnma*, and four formula units per cell, all atoms were assumed to be in $4(m)$. Antimony positions were derived from the Patterson function, and anion positions could easily be guessed. The parameters were then refined by electron density maps, and finally by least-squares calculations to an R factor of 6.6%.

So far, the anions were all treated as if they were oxygen atoms. In the structure, half the anions were engaged in polyhedral edge sharing and half were terminal. The latter were naturally assumed to be fluorines. Using Pauling's second rule (3) in calculating $\sum S_i$ (the sum of the strength of the electrostatic valence bonds) for the two crystallographically different anion positions, one position (the terminal) was also found to have a positive potential of 0.75, and the other position had a corresponding value of 2.25. Oxygen and fluorine were thus ordered according to this scheme, and a new least-squares

TABLE I
CRYSTALLOGRAPHIC CONSTANTS FOR L-SbOF

Symmetry: Orthorhombic
Unit cell dimensions (Å): $a = 8.873$, $b = 4.099$, $c = 5.483$
 $V = 119.4 \text{ \AA}^3$, $Z = 4$, space group $Pnma$, No. 62

TABLE II
POWDER PATTERN OF L-SbOF ($\text{CuK}\alpha_1$)

Int	$\sin^2 \theta_{\text{obs}}$	$h k l$	$\sin^2 \theta_{\text{calc}}$
w	.02720	1 0 1	.02727
m	.03006	2 0 0	.03014
st	.04979	2 0 1	.04988
st	.05509	0 1 1	.05505
m	.06548	2 1 0	.06545
w	.07894	0 0 2	.07894
m	.09513	2 1 1	.08519
m	.10910	2 0 2	.10908
m	.14018	4 0 1	.14029
m	.14127	0 2 0	.14127
w	.14443	2 1 2	.14440
w	.15596	4 1 0	.15588

treatment, using scattering factors for O^{2-} and F^- , resulted in a new R factor of 5.7%. (Atomic coordinates and temperature factors are given in Table III.)

Description of the Structure

In Fig. 1 the structure of L-SbOF is projected down the b -axis. Three oxygens and one fluorine are bonded to each antimony, all to one side, in such a way that the lone pair can be imagined to complete a trigonal bipyramid. Such SbO_3F

TABLE III
FRACTIONAL COORDINATES AND THERMAL PARAMETERS

	x	y	z	B
Sb	.0707(1)	.25	.2124(2)	
O	.054(2)	.75	.090(3)	1.7
F	.266(2)	.25	.047(3)	2.5

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	.0032(1)	.03(1)	.011(1)	.0	-.0008(4)	.0

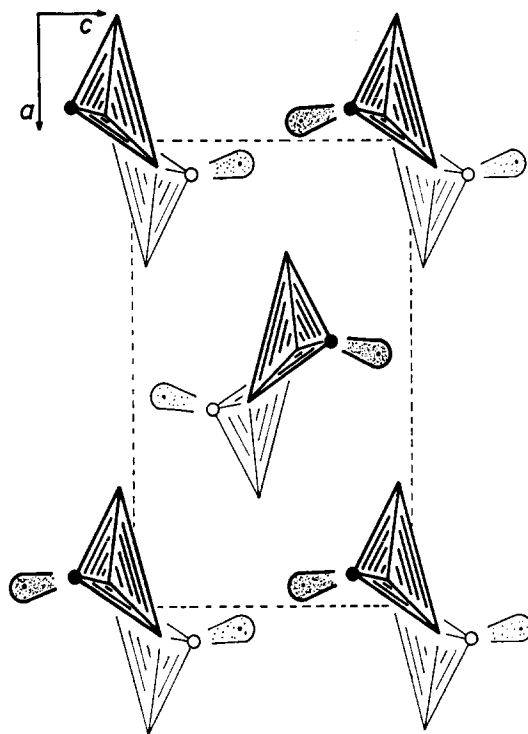


FIG. 1. The structure of L-SbOF projected down the b -axis. The heavier and lighter polyhedra and lone pairs are $b/2$ apart, as are the Sb atoms, marked with filled and open circles. All atoms are on $y = 1/4$ or $3/4$.

polyhedra share edges to form endless chains in the b -direction. Oxygens are in bridging and fluorines in terminal positions.

For some solid oxides, oxygen fluorides, or fluorides of Sb^{3+} , Bi^{3+} and Pb^{2+} , we have found that the volume of the lone pair and its cation is approximately the same size as that of each anion. The center of the volume of the lone pair could be localized to a position which is normally occupied by an anion or a large cation (4). The trigonal bipyramid, with an equatorial corner occupied by the lone pair, is very close to the regular one as it occurs in *hcp*. The calculated distances and angles within such a polyhedron agree very well with those actually observed (5), and the stereochemistry of this configuration seems then to be more a result of simple packing than anything else.

The agreement between theoretical and observed values for angles and distances is best when the AX_4 polyhedra join, or partly join, to other polyhedra with corner sharing. In L-SbOF, the polyhedra share edges, as demonstrated in

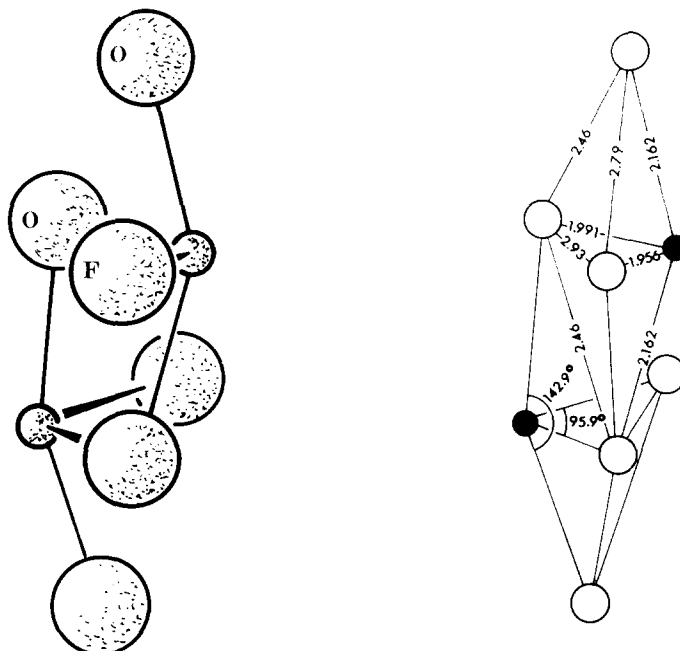


FIG. 2. Clinographic projection of part of the SbOF chain. In the right part the angles and distances are indicated. Nearest-neighbour distances for Sb: one Sb-F of 3.01(1) Å, and two Sb-F of 3.11(1) Å. The Sb-Sb distance across the shared edge is 3.347(3) Å; the Sb-Sb distance between two different chains is 3.965(3) Å; and the Sb-Sb distance across a shared corner is 4.099 Å.

Fig. 2, where the distances and angles are also given. The edge-sharing causes a distortion of the polyhedra, with an oxygen-oxygen distance of 2.46 Å, and also the anions are of two different kinds which brings in a second distortion. These distortions are thus due to electrostatic forces, but we do not correct for this; it is satisfactory enough to find that just by using average values, good agreement is still obtained.

Axial and equatorial angles and distances for antimony oxides or fluorides are given in Table

IV, and the calculated values from the model (5) are compared with the corresponding values observed for L-SbOF.

With the close-packed geometry of anions and the lone pair, the distance between the cation center and the center of the volume of the lone pair is calculated to be approximately 1.1 Å.

Some interesting relationships exist between L-SbOF and other structures. If alternate chains are translated $\frac{1}{2}c$, and the structure is allowed to shrink along a so that the chains can join up by

TABLE IV

AXIAL AND EQUATORIAL ANGLES AND DISTANCES FOR ANTIMONY OXIDES AND FLUORIDES^a

Distance or angle ^b	KSb ₂ F ₇ (6)	CsSb ₂ F ₇ (7)	Fluoride (calc) ^c	SbPO ₄ ·2H ₂ O (8)	SbNbO ₄ (9)	Oxide (calc) ^c	L-SbOF
d_1	1.92	1.94	1.91	1.97	2.02	2.00	1.97
d_2	2.07	2.11	2.14	2.22	2.23	2.27	2.16
β	90.4	90.5	91.3	94.4	92.1	93.6	95.9
α	155.2	151.6	150.2	156.0	150.7	153.4	142.9

^a References are italicized and in parentheses.

^b d_1 and β are equatorial distance and angle, respectively; d_2 and α are axial distance and angle, respectively.

^c Calculated values are according to the close-packed model given in ref. (5).

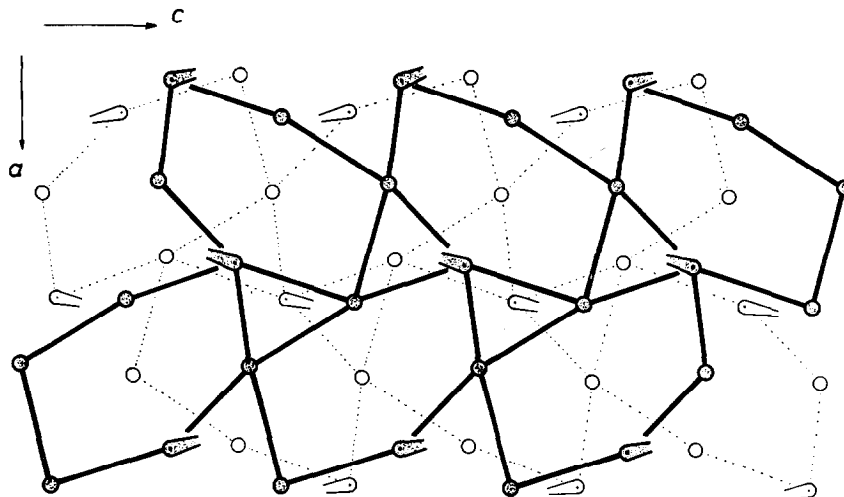


FIG. 3. Lone pair-anion net of L-SbOF. Dotted lines connect atoms and lone pairs on $y = 1/4$; heavy lines connect atoms and lone pairs on $y = 3/4$.

edge-sharing, the structure of yellow PbO is formed.

Lone pairs and oxygens in yellow PbO form a hexagonally close-packed net. This means that the lone pairs and anions in L-SbOF are partly hexagonally close-packed. As a whole, the net is drawn in Fig. 3. The packing is complex as in some alloys, and it is interesting to note that the Rh atoms in one section of the crystal structure of Rh_5Ge_3 (10) form the same net as that given in Fig. 3 for the anions and lone pairs in SbOF.

Acknowledgments

The authors are grateful to the Computer Division of the National Rationalization Agency for the use of the Univac 1108 Computer in Lund. This investigation forms a part of a research program sponsored by the Swedish Natural Science Research Council.

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