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Antimony oxofluorides – a synthesis concept that yields phase pure samples and single crystals[†]

The single crystals of the new isostructural compounds Sb_3O_4F and $Y_{0.5}Sb_{2.5}O_4F$ and the two previously

Sk Imran Ali and Mats Johnsson*

known compounds M-SbOF and α -Sb₃O₂F₅ were successfully grown by a hydrothermal technique at 230 °C. The new compound Sb₃O₄F crystallizes in the monoclinic space group $P2_1/c$; a = 5.6107(5) Å, b = 4.6847(5) Å, c = 20.2256(18) Å, $\beta = 94.145(8)^\circ$, z = 4. The replacing part of Sb with Y means a slight increase in the unit cell dimensions. The compounds M-SbOF and α -Sb₃O₂F₅ have not been grown as single crystals before and it can be concluded that hydrothermal synthesis has proved to be a suitable technique for growing single crystals of antimony oxofluorides because of the relatively low solubility of such compounds compared to other antimony oxohalides that most often have been synthesised at high temperatures by solid state reactions or gas–solid reactions.

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Introduction

There are several compounds described in the Sb³⁺–O–X (X = F, Cl, Br, I) system *e.g.* SbOCl, Sb₃O₄Cl, Sb₈O₁₁Cl₂ and Sb₈O₁₁Br₂, α - and β -Sb₃O₄I.¹⁻⁴ Five different oxofluorides have previously been reported, three of them are different forms of SbOF denoted as L-SbOF, M-SbOF and H-SbOF and the remaining two are α -Sb₃O₂F₅ and β -Sb₃O₂F₅.^{5,6} The hardness/ softness properties of the halide ions are reflected in how they are bonded in the different crystal structures. Fluoride ions form covalent bonds like oxygen to antimony and are integrated in the Sb–O–F framework while the other halide ions act more as counter ions and the structures become separated into oxide parts and halide parts.

The one-sided coordination around p-block cations having stereochemically active lone-pairs increases the chances to find compounds crystallizing in non-centrosymmetric space groups that thus can show non-linear optical properties, *e.g.* Te₂SeO₇, Na₂TeW₂O₉ and Bi₂TeO₅.^{7–9} Oxohalide glasses can also have non-linear optical properties.¹⁰ Further the lone-pairs open up crystal structures and when combining with transition metals it is very often so that the latter arrange in low dimensional arrangements especially in oxohalides like Cu₂Te₂O₅Cl₂ and CuNi₅(TeO₃)₄Cl₂ where the metal cations tend to both oxygen and halide ions while the lone-

Fax: +46-8-152187; Tel: +46-8-162169

pair element tends to bond only to oxygen.^{11,12} Several such compounds show *e.g.* magnetic frustration.

We have utilized hydrothermal reaction techniques to grow single crystals of oxofluoride compounds and to form monophasic synthesis products. The new compound Sb₃O₄F has been synthesized starting with Sb₂O₃ and SbF₃. The compound $Y_{0.5}Sb_{2.5}O_4F$ was obtained by introducing YF₃ in the reaction mixture. Two previously known compounds M-SbOF and α -Sb₃O₂F₅ were synthesized for the first time as single crystals; the synthesis products were found to be phase pure. The synthesis technique has proved to be suitable for synthesizing oxofluorides, however less suitable for oxohalides comprising Cl, Br, or I due to the higher solubility product of such compounds.

Experimental

Single crystals of Sb₃O₄F, Y_{0.5}Sb_{2.5}O₄F, M-SbOF and α -Sb₃O₂F₅ were synthesized by a hydrothermal technique. The compounds were found during investigations of the Sb–O–F and Y–Sb–O–F systems. All compounds were found from experiments using autoclaves equipped with 18 mL Teflon liners heated to 230 °C at a rate of 1.6 °C min⁻¹. The plateau temperature was maintained for four days and thereafter the temperature was lowered to 30 °C with the same rate as the heating. As starting materials the following chemicals were used: Sb₂O₃ (99.97%, Sigma-Aldrich), SbF₃ (99.8%, Sigma-Aldrich) and YF₃ (99.97%, Sigma-Aldrich).

 Sb_3O_4F crystals were obtained from a stoichiometric mixture of $Sb_2O_3:SbF_3 = 4:1$ in 1 mL deionized water. The starting amount was 1.00 mmol Sb_2O_3 . The experiment yielded

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Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden. E-mail: mats.johnsson@mmk.su.se;

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phase pure colourless Sb_3O_4F crystals. Crystals of $Y_{0.5}Sb_{2.5}O_4F$ and M-SbOF were found from a mixture of Sb_2O_3 : $YF_3 = 3:1$ in 1 mL deionized water and some few droplets of HF. The synthesis product was a mixture of yellowish crystals ($Y_{0.5}Sb_{2.5}O_4F$) and transparent colourless crystals (M-SbOF). Phase pure M-SbOF was synthesized from a stoichiometric mixture of $Sb_2O_3: SbF_3 = 1:1$ in 1 mL deionized water, and α -Sb_3O_2F_5 was obtained from an experiment starting with the same molar ratio $Sb_2O_3: SbF_3 = 1:1$, however in 1 mL deionized water plus some few droplets of HF. The weight in amounts is given in the ESI.[†]

Chemical compositions were obtained by EDS using a Hitachi M3000 Table top scanning electron microscope and a JEOL JSB-7000F. The EDS results for $Y_{0.5}Sb_{2.5}O_4F$ are shown in the ESI.[†]

Single crystal X-ray data were collected using a Bruker D8 Venture diffractometer equipped with a PHOTON 100 detector. Data integration, including the application of a correction for oblique incidence, was performed with the software package SAINT.¹³ Absorption correction was applied by the computer program SADABS.¹⁴ The crystal structures were solved using the program Superflip and refined by using the program JANA2006.^{15,16} All atoms are refined with anisotropic temperature displacement parameters. Crystallographic data for all compounds are shown in Table 1.

Further details on the crystal structural investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposit numbers CSD-431207 for Sb₃O₄F, CSD-431208 for $Y_{0.5}Sb_{2.5}O_4F,$ CSD-431209 for M-SbOF, and CSD-431210 for $\alpha\text{-}Sb_3O_2F_5.$

Powder X-ray data were collected on a Panalytical X'Pert PRO powder X-ray diffractometer in Bragg–Brentano geometry with Cu-Kα radiation. Rietveld refinement and the comparison of powder patterns against single crystal data were made by using the program Jana2006.

Thermogravimetric analyses (TG) were performed using a TA instruments Discovery equipment. The measurements were carried out in air with a heating rate of 5 °C min⁻¹ up to 700 °C, starting with an ~0.5 mg sample.

Results and discussion

It was found to be possible to synthesize the compounds Sb_3O_4F , $Y_{0.5}Sb_{2.5}O_4F$, α -Sb_3 O_2F_5 , and M-SbOF by hydrothermal synthesis. The two isostructural compounds Sb_3O_4F and $Y_{0.5}Sb_{2.5}O_4F$ are new while α -Sb_3 O_2F_5 and M-SbOF are known for a long time. α -Sb_3 O_2F_5 in the form of powder has previously been synthesised by reacting SbF₃ and NH₄F in water at room temperature and M-SbOF has previously been synthesized as powder by solid state reactions in gold tubes at 220–260 °C.^{6,17}

The crystal structure of Sb₃O₄F and Y_{0.5}Sb_{2.5}O₄F

The Sb_3O_4F crystal structure consists of three crystallographically independent Sb atoms having $[Sb(1)O_3]$, $[Sb(2)O_3F]$ and $[Sb(3)O_3]$ trigonal pyramidal and see-saw co-ordinations, see Fig. 1. If bond distances on the wedge to be included in the

Table 1	Crystallographic	data	for the	four	compounds	investigated

	Sb_3O_4F	$Y_{0.5}Sb_{2.5}O_4F$	M-SbOF	α -Sb ₃ O ₂ F ₅
Chemical formula	Sb ₃ O ₄ F	Y _{0.49} Sb _{2.51} O ₄ F	M-SbOF	α -Sb ₃ O ₂ F ₅
Formula weight/g mol ⁻¹	448.24	432.12	156.75	492.24
Temperature/K	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	Pbca	P2/c
a/Å	5.6107 (5)	5.6329 (3)	11.6718 (3)	13.2103 (8)
b/Å	4.6847 (5)	4.7150 (3)	5.5855 (7)	5.9519 (3)
C/Å	20.2256 (18)	20.3675 (12)	12.2688 (8)	9.0530 (5)
$\beta/^{\circ}$	94.145 (8)	94.304 (13)	90	107.865 (18)
$V/\text{\AA}^3$	530.2	539.4	799.8	677.5
$\rho/\mathrm{g~cm}^{-3}$	5.615	5.32	5.21	4.82
Z	4	4	16	4
Crystal size/mm ³	0.45 imes 0.3 imes 0.15	0.5 imes 0.2 imes 0.15	0.4 imes 0.4 imes 0.2	0.25 imes 0.2 imes 0.1
Radiation type	Μο-Κα	Мо-Ка	Мо-Ка	Μο-Κα
Wavelength/Å	0.71069	0.71069	0.71069	0.71069
Indices range	$-10 \le h \le 10$	$-9 \le h \le 9$	$-21 \le h \le 8$	$-20 \le h \le 21$
	$-8 \le k \le 8$	$-7 \le k \le 7$	$-10 \le k \le 6$	$-9 \le k \le 9$
	$-36 \le l \le 35$	$-33 \le l \le 33$	$-22 \le l \le 21$	$-14 \le l \le 14$
No. of reflections				
Measured/unique	16 860/3296	12 095/2615	9232/2499	11 126/2928
Observed $[I > 3 \sigma(I)]$	2785	2533	1894	1831
R _{int}	0.029	0.043	0.034	0.056
$(\sin \theta / \lambda)_{\rm max} / {\rm \AA}^{-1}$	0.90	0.84	0.90	0.80
$R_{\rm F}/{\rm w}R_{\rm F}$ [$F > 3\sigma(F)$]				
All reflections (%)	2.47/3.05	2.93/5.14	2.12/2.52	2.85/2.78
Goodness of fit (all)	3.81	2.65	1 1 2	1.06



Fig. 1 The asymmetric unit and selected equivalents of Sb₃O₄F. There are three crystallographic independent Sb atoms having [Sb(1)O₃], [Sb(2)O₃F] and [Sb(3)O₃] trigonal pyramidal and see-saw co-ordinations. Symmetry codes: (i) -1 + x, *y*, *z*; (ii) -x, -y, -z; (iii) -x, -0.5 + y, 0.5 - z.

primary coordination sphere are also included we end up with $[Sb(1)O_{3+1}F]$, $[Sb(2)O_{3+1}F]$ and $[Sb(3)O_3]$ co-ordinations. The long Sb(1)–O(2) and Sb(2)–O(4) bond distances are 2.586(2) Å and 2.679(2) Å respectively and the long Sb(1)–F distance is 2.630(2) Å. The operative definition of the outer primary coordination sphere according to Brown suggests this to be 2.76 Å for Sb–O and 2.67 Å for Sb–F.¹⁸ The Sb–O bond distances of ~2.0 Å in the [SbO₃] building blocks show very close proximity to the Sb–O distances in cubic Sb₂O₃, however the Sb–O–Sb angles differ slightly.¹⁹

The pairs of edge sharing $[Sb(2)O_3F]$ polyhedra are further bridged by two corner sharing $[Sb(1)O_3]$ units to make $[Sb_2O_3F]_n$ chains extending along [100], see Fig. 2a. The $[Sb(3)O_3]$ trigonal pyramids are corner sharing and make up $[Sb(3)O_2]_n$ chains extending along [010], see Fig. 2b. The two chain systems connect *via* Sb(1)-O(4)-Sb(3)-O(3)-Sb(3)-O(4)-Sb(1) to make up the three dimensional framework of Sb_3O_4F where the F atoms protrude into cavities in the structure and are thus not participating in building the framework, see



Fig. 2 (a) Pairs of edge sharing $[Sb(2)O_3F]$ polyhedra are bridged by corner sharing $Sb(1)O_3$ units to make $[Sb_2O_3F]_n$ chains extending along [100]. (b) The $[Sb(3)O_3]$ trigonal pyramids make up $[Sb(3)O_2]_n$ chains by corner sharing that extend along [010]. (c and d) The two chain systems connect and form the three dimensional network of Sb_3O_4F where the F atoms protrude into cavities in the structure. Grey atoms indicate Sb(1), brown Sb(2), blue Sb(3), and red O and green stands for F.

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Fig. 2c and d. The allocation of O and F was based on BVS calculations that show slight hyper-valence for Sb and O and hypo-valence for F indicating its more ionic nature (ESI[†]). It is not uncommon in oxohalides that halide ions show hypovalence.^{20,21} The lone electron pairs, E, on the three crystallographically different Sb³⁺ ions are stereochemically active and occupy space in the crystal structure and thus become responsible for the open framework that can be seen in Fig. 2c and d. For Sb(1) and Sb(3) the lone-pairs take apex positions in [SbO₃E] tetrahedra, and for Sb(2) it forms a [SbO₃FE] trigonal bipyramid where E sits at one of the corners of the base plane of the pyramid. The lone-pairs on Sb³⁺ point into the voids (channels) of the crystal structure as the F-atoms.

A phase pure sample of Sb_3O_4F could be obtained from a stoichiometric ratio of the starting materials, see Fig. 3.

 $Y_{0.5}Sb_{2.5}O_4F$ is isostructural to Sb_3O_4F and the presence of Y is responsible for the yellow colour as Sb_3O_4F is colourless. Y partly occupies all three Sb positions in the crystal structure. The insertion of Y is responsible for the 0.14 Å elongation of the *c*-axis and while the *a*- and *b*-axes are not significantly influenced. All Sb–O and Sb–F distances are slightly longer in $Y_{0.5}Sb_{2.5}O_4F$ compared to those in Sb_3O_4F , see the ESI.† When synthesizing $Y_{0.5}Sb_{2.5}O_4F$ the addition level of HF turned out to be very important in order to incorporate Y into the structure. Synthesis attempts were made with increased water content but it did not yield Y incorporated in $Sb^{3+}-O-F$ compounds.

M-SbOF and α-Sb₃O₂F₅

The compounds α -Sb₃O₂F₅ and M-SbOF were found while attempting to synthesize Y_{0.5}Sb_{2.5}O₄F. It was also possible to

synthesize both phase pure α -Sb₃O₂F₅ and M-SbOF from a mixture of SbF₃ and Sb₂O₃, *cf.* the Experimental section. The structure determination resulted in the same model as has previously been reported.^{6,17} However, the present data also allowed refining the ADPs, see Fig. 4a. The present model has a slightly smaller unit cell and small changes in bond distances compared to the older model. Bond-valence sum (BVS) calculations support that the valences are Sb³⁺, O²⁻ and F⁻ with slightly over-bonded antimony cations and oxygen anions and under-bonded fluorine atoms (see the ESI[†]).²² The compound M-SbOF has been described by Åström.¹⁷ The present structure determination also allows for anisotropic ADPs, see Fig. 4b.

Thermal gravimetry

The thermal decomposition of the compounds Sb_3O_4F , M-SbOF and α -Sb₃O₂F₅ is shown in Fig. 5. Based on the weight changes the new compound Sb₃O₄F decomposes in two steps to first give off SbF₃ (340–380 °C) and subsequently SbOF in the second step (450–550 °C), see reactions (1) and (2) below. Finally at 550–600 °C there is a slight weight increase when Sb₂O₃ partly oxidizes to Sb₂O₅, the latter step is in accordance with previous observations.²³

$$4Sb_3O_4F(s) \rightarrow 5Sb_2O_3(s) + L\text{-}SbOF(s) + SbF_3(g) \tag{1}$$

$$5Sb_2O_3(s) + L\text{-}SbOF(s) \rightarrow 5Sb_2O_3(s) + L\text{-}SbOF(g) \qquad (2)$$

$$Sb_2O_3(s) + O_2(g) \rightarrow Sb_2O_5(s)$$
 (3)

The compound M-SbOF decomposes (250-500 °C) in one step (4) with subsequent oxidation according to step (3).

Fig. 3 Comparison of the measured powder X-ray diffractogram and the calculated pattern for Sb_3O_4F based on the single crystal X-ray determination of the crystal structure ($R_p = 9.43$).



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Fig. 4 Crystal structures of (a) α-Sb₃O₂F₅ and (b) M-SbOF, projected along [010]. Grey atoms indicate Sb, red stands for O, and green stands for F.

$$3\text{M-SbOF}(s) \rightarrow \text{Sb}_2\text{O}_3(s) + \text{SbF}_3(g) \tag{4}$$

The compound $\alpha\text{-Sb}_3O_2F_5$ also decomposes (225–325 °C) in one step (5) with subsequent oxidation according to step (3).

$$3\alpha \text{-} Sb_3O_2F_5(s) \rightarrow 2Sb_2O_3(s) + 5SbF_3(g) \tag{5}$$

It can be concluded that $\rm Sb_3O_4F$ is thermally more stable than M-SbOF and $\alpha\text{-}\rm Sb_3O_2F_5.$

Comparison with other Sb-O-X compounds

Most compounds in the system Sb^{3+} –O–X (X = F, Cl, Br, I) are layered *e.g.* $Sb_4O_5(Cl, Br_2)$,^{24,25} Sb_5O_7I ,²⁶ $Sb_8O_{11}(Cl, Br, I)_2$,^{3,20} Sb_3O_4I ,² SbOCl,¹ and M-SbOF.¹⁷ Exceptions are $Sb_3O_4I^4$ that show ladders of $[Sb_3O_4]_n$ with I-atoms in between, the compounds α -Sb₃O₂F₅, L-SbOF⁵ and the present compound Sb₃O₄F that are 3D-frameworks. The compounds in the system Sb^{3+} –O–F have direct covalent bonds in between Sb³⁺ and F while when the halide ion is one of Cl, Br or I there is a separation into an oxide part consisting of a Sb–O framework made



Fig. 5 Thermal decomposition of the compounds Sb_3O_4F , M-SbOF and α -Sb₃ O_2F_5 , see the text for interpretation of the decomposition steps.



Fig. 6 (a) Sb_3O_4Cl consists of $[Sb_3O_4]_n$ layers parallel to [100] with Cl atoms situated in between the layers. (b) The compound α -Sb₃O₄I is composed of $[Sb_3O_4]_n$ tubes along [100] separated by I atoms.

up of $[SbO_3]$ and $[SbO_4]$ building blocks and a halide part where those ions take the role of counter ions in the crystal structures. However, there is one exception, SbOCl, where there is covalent Sb³⁺–Cl bonds and trigonal pyramidal $[SbO_2Cl]$ building blocks.

The oxohalides with the common formula Sb_3O_4X (X = Cl, I) have completely different crystal structures compared to the present compound Sb₃O₄F. Sb₃O₄Cl has a monoclinic structure that crystallizes in the space group P2/c.²⁷ It consists of $[Sb_3O_4]_n$ layers parallel to (100) with Cl atoms situated in between the layers, see Fig. 6a. BVS calculations show the ionic character of the Cl atoms ($V_i = 0.64$). Sb₃O₄I exists in two similar forms; orthorhombic α -phase (space group *Pbn2*₁) and monoclinic β -phase (space group $P2_1/c$). The structures are composed of $[Sb_3O_4]$ infinite Sb-O tubes along [100] that are separated by I atoms.⁴ The α -phase is shown in Fig. 6b. BVS calculation on I ($V_i = 0.80$) reveals a more covalent character for I than for Cl. The main difference between Sb₃O₄F and the Cl- and I analogues is that F is incorporated in the Sb-O-F network while for the other two the oxide part and the halide part of the crystal structures are separated.

Conclusions

The single crystals of Sb₃O₄F, Y_{0.5}Sb_{2.5}O₄F and the two previously known Sb–O–F compounds, 3M-SbOF and α -Sb₃O₂F₅, were successfully synthesized by hydrothermal methods at 230 °C. Depending on subtle differences in the synthesis method the different compounds were obtained. An interesting outcome of the work is the incorporation of yttrium in Sb₃O₄F to form Y_{0.5}Sb_{2.5}O₄F at such a low temperature used.

The new compound Sb₃O₄F is built from SbO₃ and SbO₃F polyhedra to form a three dimensional network. Incorporation of yttrium to form $Y_{0.5}Sb_{2.5}O_4F$ causes an elongation of the unit cell parameters. The three crystallographically different Sb sites in the crystal structure are all partially occupied by Y. The compounds M-SbOF and α -Sb₃O₂F₅ were previously synthesized by solid state reactions and in this work it was shown that they can form also by hydrothermal reactions. Accurate crystal structures of both compounds were determined from the single-crystal X-ray diffraction data. With respect to the previous structure refinement against powder X-ray diffraction the principal difference is the present refinement of anisotropic ADPs in the present study.

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