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

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The single crystals of the new isostructural compounds Sb$_3$O$_4$F and Y$_{0.5}$Sb$_2.5$O$_4$F and the two previously known compounds M-SbOF and α-Sb$_2$O$_2$F$_5$ were successfully grown by a hydrothermal technique at 230 °C. The new compound Sb$_3$O$_4$F crystallizes in the monoclinic space group P2$_1$/c; a = 5.6107(5) Å, b = 4.6847(5) Å, c = 20.2256(18) Å, β = 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-Sb$_2$O$_2$F$_5$ 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.

Introduction

There are several compounds described in the Sb$^{3+}$–O–X (X = F, Cl, Br, I) system e.g. SbOCl, Sb$_2$O$_3$Cl, Sb$_2$O$_4$Cl$_2$ and Sb$_2$O$_4$Br$_2$. α- and β-Sb$_2$O$_4$I$_4$. 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-Sb$_2$O$_2$F$_5$ and β-Sb$_2$O$_2$F$_5$. 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. Te$_2$SeO$_5$, Na$_2$TeW$_2$O$_9$ and Bi$_2$TeO$_5$. Oxohalide glasses can also have non-linear optical properties. 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 Cu$_2$Te$_2$O$_5$Cl$_2$ and CuNi$_2$(TeO$_3$)$_4$Cl$_2$ where the metal cations tend to bond to both oxygen and halide ions while the lone-pair element tends to bond only to oxygen. 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 Sb$_3$O$_4$F has been synthesized starting with Sb$_2$O$_3$ and SbF$_3$. The compound Y$_{0.5}$Sb$_2.5$O$_4$F was obtained by introducing YF$_3$ in the reaction mixture. Two previously known compounds M-SbOF and α-Sb$_2$O$_2$F$_5$ 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 Sb$_2$O$_3$F, Y$_{0.5}$Sb$_2.5$O$_4$F, M-SbOF and α-Sb$_2$O$_2$F$_5$ 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: Sb$_2$O$_3$ (99.97%, Sigma-Aldrich), SbF$_3$ (99.8%, Sigma-Aldrich) and YF$_3$ (99.97%, Sigma-Aldrich).

Sb$_2$O$_3$F crystals were obtained from a stoichiometric mixture of Sb$_2$O$_3$: SbF$_3$ = 4:1 in 1 mL deionized water. The starting amount was 1.00 mmol Sb$_2$O$_3$. The experiment yielded...
phase pure colourless Sb\textsubscript{3}O\textsubscript{4}F crystals. Crystals of Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F and M-SbOF were found from a mixture of Sb\textsubscript{2}O\textsubscript{3} : YF\textsubscript{3} = 3 : 1 in 1 mL deionized water and some few droplets of HF. The synthesis product was a mixture of yellowish crystals (Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F) and transparent colourless crystals (M-SbOF).

Phase pure M-SbOF was synthesized from a stoichiometric mixture of Sb\textsubscript{2}O\textsubscript{3} : SbF\textsubscript{3} = 1 : 1 in 1 mL deionized water, and α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3} was obtained from an experiment starting with the same molar ratio Sb\textsubscript{2}O\textsubscript{3} : SbF\textsubscript{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 JSM-7000F. The EDS results for Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F 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 Sb\textsubscript{3}O\textsubscript{4}F, CSD-431208 for Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F, CSD-431209 for M-SbOF, and CSD-431210 for α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3}.

Results and discussion

It was found to be possible to synthesize the compounds Sb\textsubscript{3}O\textsubscript{4}F, Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F, α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3}, and M-SbOF by hydrothermal synthesis. The two isostructural compounds Sb\textsubscript{3}O\textsubscript{4}F and Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F are new while α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3} and M-SbOF are known for a long time. α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3} in the form of powder has previously been synthesised by reacting SbF\textsubscript{3} and NH\textsubscript{4}F 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.5,17

The crystal structure of Sb\textsubscript{3}O\textsubscript{4}F and Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F

The Sb\textsubscript{3}O\textsubscript{4}F crystal structure consists of three crystallographically independent Sb atoms having [Sb(1)O\textsubscript{3}], [Sb(2)O\textsubscript{3}F] and [Sb(3)O\textsubscript{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

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<th>Chemical formula</th>
<th>Sb\textsubscript{3}O\textsubscript{4}F</th>
<th>Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F</th>
<th>M-SbOF</th>
<th>α-Sb\textsubscript{2}O\textsubscript{3}F\textsubscript{3}</th>
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primary coordination sphere are also included we end up with [Sb(1)O$_3$F], [Sb(2)O$_3$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.\textsuperscript{18} The Sb--O bond distances of $\sim$2.0 Å in the [SbO$_3$] building blocks show very close proximity to the Sb--O distances in cubic Sb$_2$O$_3$, however the Sb--O--Sb angles differ slightly.\textsuperscript{19}

The pairs of edge sharing [Sb(2)O$_3$F] polyhedra are further bridged by two corner sharing [Sb(1)O$_3$] units to make [Sb$_2$O$_3$F]$_n$ 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$_3$O$_4$F where the F atoms protrude into cavities in the structure and are thus not participating in building the framework, see

![Fig. 1](image1.png)

**Fig. 1** The asymmetric unit and selected equivalents of Sb$_3$O$_4$F. There are three crystallographic independent Sb atoms having [Sb(1)O$_3$], [Sb(2)O$_3$F] and [Sb(3)O$_3$] trigonal pyramidal and see-saw co-ordinations. Symmetry codes: (i) $-1+x,y,z$; (ii) $-x,-y,-z$; (iii) $-x,0.5+y,0.5-z$.

![Fig. 2](image2.png)

**Fig. 2** (a) Pairs of edge sharing [Sb(2)O$_3$F] polyhedra are bridged by corner sharing Sb(1)O$_3$ units to make [Sb$_2$O$_3$F]$_n$ chains extending along [100], see Fig. 2a. The [Sb(3)O$_3$] trigonal pyramids make up [Sb(3)O$_2$]$_n$ chains by corner sharing that extend 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$_3$O$_4$F where the F atoms protrude into cavities in the structure and are thus not participating in building the framework, see.
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 hypo-valence.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 Sb₃O₄F could be obtained from a stoichiometric ratio of the starting materials, see Fig. 3. Y₀.₅Sb₂.₅O₄F is isostructural to Sb₃O₄F and the presence of Y is responsible for the yellow colour as Sb₃O₄F 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 Y₀.₅Sb₂.₅O₄F compared to those in Sb₃O₄F, see the ESI†. When synthesizing Y₀.₅Sb₂.₅O₄F 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 Sb³⁺–O–F compounds.

M-SbOF and α-Sb₃O₂F₅

The compounds α-Sb₃O₂F₅ and M-SbOF were found while attempting to synthesize Y₀.₅Sb₂.₅O₄F. It was also possible to synthesize both phase pure α-Sb₂O₂F₅ 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 Sb₃O₄F, M-SbOF and α-Sb₃O₂F₅ is shown in Fig. 5. Based on the weight changes the new compound Sb₂O₃F 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

4Sb₃O₄F(s) → 5Sb₂O₃(s) + L-SbOF(s) + SbF₃(g)  (1)
5Sb₂O₃(s) + L-SbOF(s) → 5Sb₂O₅(s) + L-SbOF(g)  (2)
Sb₂O₃(s) + O₂(g) → Sb₂O₅(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 Sb₂O₄F based on the single crystal X-ray determination of the crystal structure (R_p = 9.43).
The compound $\alpha$-Sb$_3$O$_2$F$_5$ also decomposes (225–325 °C) in one step (5) with subsequent oxidation according to step (3).

$$3\alpha$-Sb$_3$O$_2$F$_5(s) \rightarrow 2$Sb$_2$O$_3(s) + 5$SbF$_3(g)$$ (5)

It can be concluded that Sb$_3$O$_4$F is thermally more stable than M-SbOF and $\alpha$-Sb$_3$O$_2$F$_5$.

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$_4$O$_6$(Cl, Br)$_2$, Sb$_2$O$_7$I, Sb$_2$O$_{11}$(Cl, Br, I)$_2$, Sb$_2$O$_4$I, SbOCl, and M-SbOF. Exceptions are Sb$_3$O$_4$I that show ladders of [Sb$_3$O$_4$]$_n$ with I-atoms in between, the compounds $\alpha$-Sb$_3$O$_2$F$_5$, L-SbOF$_5$ and the present compound Sb$_3$O$_4$F that are 3D-frameworks. The compounds in the system Sb$^{3+}$–O–F have direct covalent bonds in between Sb$^{3+}$ 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. 4 Crystal structures of (a) $\alpha$-Sb$_3$O$_2$F$_5$ and (b) M-SbOF, projected along [010]. Grey atoms indicate Sb, red stands for O, and green stands for F.](image)

![Fig. 5 Thermal decomposition of the compounds Sb$_2$O$_4$F, M-SbOF and $\alpha$-Sb$_3$O$_2$F$_5$, see the text for interpretation of the decomposition steps.](image)
The oxohalides with the common formula Sb\textsubscript{2}O\textsubscript{4}X (X = Cl, I) have completely different crystal structures compared to the present compound Sb\textsubscript{3}O\textsubscript{4}F. Sb\textsubscript{3}O\textsubscript{4}Cl has a monoclinic structure that crystallizes in the space group \textit{P}2/\textit{c}.\textsuperscript{27} It consists of [Sb\textsubscript{3}O\textsubscript{4}]\textsubscript{\textit{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 ($V_i = 0.64$). Sb\textsubscript{3}O\textsubscript{4}I exists in two similar forms; orthorhombic $\alpha$-phase (space group $Pbnm$) and monoclinic $\beta$-phase (space group $P2_1/c$). The structures are composed of [Sb\textsubscript{3}O\textsubscript{4}] infinite Sb–O tubes along [100] that are separated by I atoms.\textsuperscript{4} The $\alpha$-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 Sb\textsubscript{3}O\textsubscript{4}F 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 Sb\textsubscript{3}O\textsubscript{4}F, Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F and the two previously known Sb–O–F compounds, 3M-SbOF and $\alpha$-Sb\textsubscript{3}O\textsubscript{2}F\textsubscript{3}, 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 Sb\textsubscript{3}O\textsubscript{4}F to form Y\textsubscript{0.5}Sb\textsubscript{2.5}O\textsubscript{4}F at such a low temperature used.

References