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

Sk Imran Ali and Mats Johnsson*

The single crystals of the new isostructural compounds Sb₃O₄F and Y₀.5Sb₂.5O₄F and the two previously known compounds M-SbOF and α-Sb₂O₂F₅ were successfully grown by a hydrothermal technique at 230 °C. The new compound Sb₃O₄F crystallizes in the monoclinic space group P2₁/c; a = 5.6107(5) Å, b = 4.6847(5) Å, c = 20.2256(18) Å, β = 94.145(8)°, z = 4. The replacing part of Sb with Y means a slight increase in the unit cell dimensions. The compounds M-SbOF and α-Sb₂O₂F₅ 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 Sb₃⁺–O–X (X = F, Cl, Br, I) system e.g. SbOCl, Sb₂O₄Cl, Sb₂O₅Cl₂ and Sb₂O₅FBr₂, α- and β-Sb₂O₄F₁⁻⁴. 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-Sb₂O₂F₅ and β-Sb₂O₂F₅.⁵⁻⁶ 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., Te₂SeO₅, Na₂Te₂W₂O₉ 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 Cu₃Te₂O₅Cl₂ and CuNi₂(TeO₃)₄Cl₂ where the metal cations tend to bond to both oxygen and halide ions while the lone-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 oxofluorides compounds and to form monophasic synthesis products. The new compound Sb₂O₄F has been synthesized starting with Sb₂O₃ and SbF₃. The compound Y₀.5Sb₂.5O₄F was obtained by introducing YF₃ in the reaction mixture. Two previously known compounds M-SbOF and α-Sb₂O₂F₅ 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, Y₀.₅Sb₂.₅O₄F, M-SbOF and α-Sb₂O₂F₅ 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).

Sb₂O₄F crystals were obtained from a stoichiometric mixture of Sb₂O₃ : SbF₃ = 4 : 1 in 1 mL deionized water. The starting amount was 1.00 mmol Sb₂O₃. The experiment yielded
Observed No. of reflections

12168

Goodness of fit (all)

3.81

1.06

Table 1 Crystallographic data for the four compounds investigated

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Sb(_2)O(_4)F</th>
<th>Y(<em>{0.5})Sb(</em>{2.5})O(_4)F</th>
<th>M-SbOF</th>
<th>α-Sb(_2)O(_4)F</th>
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<tbody>
<tr>
<td>Formula weight/g mol(^{-1})</td>
<td>448.24</td>
<td>432.12</td>
<td>156.75</td>
<td>492.24</td>
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<td>293</td>
<td>293</td>
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<tr>
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<tr>
<td>a/Å</td>
<td>5.6107 (5)</td>
<td>5.6329 (3)</td>
<td>4.7150 (3)</td>
<td>5.6157 (5)</td>
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<tr>
<td>b/Å</td>
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<td>20.2256 (18)</td>
<td>20.3675 (12)</td>
<td>19.4145 (8)</td>
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<td>c/Å</td>
<td>94.145 (8)</td>
<td>94.304 (13)</td>
<td>93.040 (13)</td>
<td>53.94</td>
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<tr>
<td>β/°</td>
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<td>107.865 (18)</td>
<td>107.865 (18)</td>
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<td>4</td>
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<td>1894</td>
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<td>2.85/2.78</td>
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<tr>
<td>Goodness of fit (all)</td>
<td>3.81</td>
<td>2.65</td>
<td>1.12</td>
<td>1.06</td>
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primary coordination sphere are also included we end up with [Sb(1)O₃⁺₁F], [Sb(2)O₃⁺₁F] and [Sb(3)O₃] 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. 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.

The pairs of edge sharing [Sb(2)O₃F] polyhedra are further bridged by two corner sharing [Sb(1)O₃] units to make [Sb₂O₃F]ₙ chains extending along [100], see Fig. 2a. The [Sb(3)O₃] trigonal pyramids are corner sharing and make up [Sb(3)O₂]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 Sb₃O₄F where the F atoms protrude into cavities in the structure and are thus not participating in building the framework, see Fig. 1.
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 Sb$^{3+}$ 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 [SbO$_3$E] tetrahedra, and for Sb(2) it forms a [SbO$_3$FE] trigonal bipyramid where E sits at one of the corners of the base plane of the pyramid. The lone-pairs on Sb$^{3+}$ point into the voids (channels) of the crystal structure as the F-atoms.

A phase pure sample of Sb$_3$O$_4$F could be obtained from a stoichiometric ratio of the starting materials, see Fig. 3. Y$_{0.5}$Sb$_{2.5}$O$_4$F is isostructural to Sb$_3$O$_4$F and the presence of Y is responsible for the yellow colour as Sb$_3$O$_4$F 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$_4$F compared to those in Sb$_3$O$_4$F, see the ESI†. 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$_3$O$_4$F, M-SbOF and α-Sb$_3$O$_2$F$_5$ is shown in Fig. 5. Based on the weight changes the new compound Sb$_3$O$_4$F decomposes in two steps to first give off SbF$_3$ (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 Sb$_2$O$_3$ partly oxidizes to Sb$_2$O$_5$, the latter step is in accordance with previous observations.23

$$4\text{Sb}_3\text{O}_4\text{F}(s) \rightarrow 5\text{Sb}_2\text{O}_3(s) + \text{L-SbOF}(s) + \text{SbF}_3(g)$$ (1)

$$5\text{Sb}_2\text{O}_3(s) + \text{L-SbOF}(s) \rightarrow 5\text{Sb}_2\text{O}_5(s) + \text{L-SbOF}(g)$$ (2)

$$\text{Sb}_2\text{O}_3(s) + \text{O}_2(g) \rightarrow \text{Sb}_2\text{O}_5(s)$$ (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$_3$O$_4$F 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$_5$O$_5$(Cl, Br)$_3$, Sb$_5$O$_7$I, Sb$_8$O$_{11}$(Cl, Br, I)$_3$, Sb$_3$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
up of $[\text{SbO}_3]$ and $[\text{SbO}_4]$ building blocks and a halide part where those ions take the role of counter ions in the crystal structures. However, there is one exception, $\text{SbOCl}$, where there is covalent $\text{Sb}^{3+}$–$\text{Cl}$ bonds and trigonal pyramidal $[\text{SbO}_2\text{Cl}]$ building blocks.

The oxohalides with the common formula $\text{Sb}_3\text{O}_4X$ ($X = \text{Cl}, \text{I}$) have completely different crystal structures compared to the present compound $\text{Sb}_3\text{O}_4\text{F}$. $\text{Sb}_3\text{O}_4\text{Cl}$ has a monoclinic structure that crystallizes in the space group $P2_1/c$.\(^{27}\) It consists of $[\text{Sb}_3\text{O}_4]$ 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 ($V_I = 0.64$). $\text{Sb}_3\text{O}_4\text{I}$ 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 $[\text{Sb}_3\text{O}_4]$ infinite $\text{Sb}$–$\text{O}$ tubes along [100] that are separated by I atoms.\(^4\) 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 $\text{Sb}_3\text{O}_4\text{F}$ and the Cl- and I analogues is that F is incorporated in the $\text{Sb}$–$\text{O}$–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 $\text{Sb}_3\text{O}_4\text{F}$, $Y_{0.5}\text{Sb}_2.5\text{O}_4\text{F}$ and the two previously known $\text{Sb}$–$\text{O}$–$\text{F}$ compounds, $3\text{M}$-$\text{SbOF}$ and $\alpha$-$\text{Sb}_2\text{O}_2\text{F}_5$, 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 $\text{Sb}_3\text{O}_4\text{F}$ to form $Y_{0.5}\text{Sb}_2.5\text{O}_4\text{F}$ at such a low temperature used.

The new compound $\text{Sb}_3\text{O}_4\text{F}$ is built from $\text{SbO}_3$ and $\text{SbOF}_3$ polyhedra to form a three dimensional network. Incorporation of yttrium to form $Y_{0.5}\text{Sb}_2.5\text{O}_4\text{F}$ 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 $3\text{M}$-$\text{SbOF}$ and $\alpha$-$\text{Sb}_2\text{O}_2\text{F}_5$ 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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References