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Antimony Oxofluorides
–
a synthesis concept that yield phase pure samples and single crystals

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Abstract
Single crystals of the new isostructural compounds Sb_3O_4F and $Y_{0.5}Sb_{2.5}O_4F$ and the two previously known compounds M-SbOF and α-$Sb_3O_2F_5$ were successfully grown by a hydrothermal technique at 230°C. The new compound Sb_3O_4F crystallizes in the monoclinic space group $P2_1/c$; a = 5.6107(5) Å, b = 4.6847(5) Å, c = 20.55226(2) Å, β = 94.145°, z = 4. Replacing part of Sb with Y means a slight increase in the unit cell dimensions. The compounds M-SbOF and α-$Sb_3O_2F_5$ 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 product 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_3O_4Cl, $Sb_8O_{11}Cl_2$ and $Sb_8O_{11}Br_2$, α- and β-Sb_3O_4I.[1-4] Five different oxofluorides have previously been reported, three of them are different forms of SbOF denoted L-SbOF, M-SbOF and H-SbOF and the remaining two are α-$Sb_3O_2F_5$ and β-$Sb_3O_2F_5$.[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 becomes separated into oxide parts and halide parts.

The one-sided coordination around p-block cations having stereochemically active lone-pairs increase the chances to find compounds crystallizing in non-centrosymmetric space groups that thus can show non-linear optical properties *e.g.* Te_2SeO_7, $Na_2TeW_2O_9$ and Bi_2TeO_5.[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 $Cu_2Te_2O_5Cl_2$ and $CuNi_5(TeO_3)_4Cl_2$ where the metal cations tend to bond to both oxygen and halide ions while the lone-pair element tend 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 Sb_3O_4F has been synthesized starting with Sb_2O_3 and SbF_3. The compound $Y_{0.5}Sb_{2.5}O_4F$ was found by introducing YF_3 in the reaction mixture. Two previously known compounds M-SbOF and α-$Sb_3O_2F_5$ 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_3O_4F, $Y_{0.5}Sb_{2.5}O_4F$, M-SbOF and α-$Sb_3O_2F_5$ 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. 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_2O_3 (99.97%, Sigma-Aldrich), SbF_3 (99.8%, Sigma-Aldrich) and YF_3 (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 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 found from an experiment starting with 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 Supplementary materials.

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

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_3O_4F, CSD-431208 for $Y_{0.5}Sb_{2.5}O_4F$, CSD-431209 for M-SbOF, and CSD-431210 for α-$Sb_3O_2F_5$.

Powder X-ray data were collected on a Pananlytical 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.

Thermal gravimetric 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 up to 700°C, starting with ~0.5 mg sample.

Results and discussions

It was found possible to synthesize the compounds Sb_3O_4F, $Y_{0.5}Sb_{2.5}O_4F$, α-$Sb_3O_2F_5$, 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-$Sb_3O_2F_5$, and M-SbOF are known since before. α-$Sb_3O_2F_5$ in form of powder has previously been synthesised by reacting SbF_3 and NH_4F 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 Sb_3O_4F and $Y_{0.5}Sb_{2.5}O_4F$

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 Figure 1. If bond distances on the wedge to be included in the primary coordination sphere are also included we end up in [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 [SbO_3] building blocks show very close proximity to the Sb-O distances in cubic Sb_2O_3, however the Sb-O-Sb angles differ slightly.[19]

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 Figure 2a. The [Sb(3)O_3] trigonal pyramids are corner sharing and make up $[Sb(3)O_2]_n$ chains extending along [010], see Figure 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 Figures 2c-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 (supplementary materials). 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 Figure 2c-d. For Sb(1) and Sb(3) the lone-pairs take apex positions in $[SbO_3E]$ tetrahedra, for Sb(2) it forms a $[SbO_3FE]$ 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_3O_4F could be obtained from a stoichiometric ratio of the starting materials, see Figure 3.

$Y_{0.5}Sb_{2.5}O_4F$ is isostructural with 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 in Sb_3O_4F, see supplementary materials. 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-$Sb_3O_2F_5$

The compounds α-$Sb_3O_2F_5$ and M-SbOF were found while attempting to synthesize $Y_{0.5}Sb_{2.5}O_4F$. It was also possible to synthesize both phase pure α-$Sb_3O_2F_5$ and M-SbOF from a mixture of SbF_3 and Sb_2O_3, *c.f.* 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 Figure 4a. The present model has a slightly smaller unit cell and small changes in bond distances compared to the older model. Bond-valence sum calculations (BVS) support that the valences are Sb^{3+}, O^{2-} and F^- with slightly over-bonded antimony cations and oxygen anions and under-bonded fluorine atoms (see Supplementary information).[22] The compound M-SbOF has been described by Åström.[17] The present structure determination also allows for anisotropic ADPs, see Figure 4b.

Thermal gravimetry

The thermal decomposition of the compounds Sb_3O_4F, M-SbOF and α-$Sb_3O_2F_5$ are shown in Figure 5. Based on the weight changes the new compound Sb_3O_4F decompose 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_2O_3 partly oxidize to Sb_2O_5, the latter step is in accordance with previous observations.[23]

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

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

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

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

$3M\text{-}SbOF(s) \rightarrow Sb_2O_3(s) + SbF_3(g)$ (4)

The compound α-$Sb_3O_2F_5$ also decomposes (225-325°C) in one step (5) with subsequent oxidation according to step (3).

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

It can be concluded that Sb_3O_4F is thermally more stable than M-SbOF and α-$Sb_3O_2F_5$.

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-$Sb_3O_2F_5$, L-SbOF[5] and the present compound Sb_3O_4F 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 $[SbO_3]$ and $[SbO_4]$ building blocks and a halide part where those ions more take the role of counter ions in the crystal structures. However, there is one exception, SbOCl, where there is covalent Sb^{3+}-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 Sb_3O_4F. Sb_3O_4Cl 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 Figure 6a. BVS calculations show the ionic character of the Cl atoms (V_i = 0.64). Sb_3O_4I 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 Figure 6b. BVS calculation on I (V_i = 0.80) reveals a more covalent character for I than for Cl. The main difference in between Sb_3O_4F 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

Single crystals of Sb_3O_4F, $Y_{0.5}Sb_{2.5}O_4F$ and the two previously known Sb-O-F compounds, 3M-SbOF and α-$Sb_3O_2F_5$, 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 Sb_3O_4F to form $Y_{0.5}Sb_{2.5}O_4F$ at such a low temperature used.

The new compound Sb_3O_4F is built from SbO_3 and SbO_3F polyhedra to form a three dimensional network, Incorporation of yttrium to form $Y_{0.5}Sb_{2.5}O_4F$ cause 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-$Sb_3O_2F_5$ 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 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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Table

Table 1 Crystallographic data for the four compounds investigated.

	Sb_3O_4F	$Y_{0.5}Sb_{2.5}O_4F$	M-SbOF	α-$Sb_3O_2F_5$
chemical formula	Sb_3O_4F	$Y_{0.49}Sb_{2.51}O_4F$	M-SbOF	α- $Sb_3O_2F_5$
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	*P2₁/c*	*P2₁/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)
β /°	94.145 (8)	94.304 (13)	90	107.865 (18)
V /Å^3	530.2	539.4	799.8	677.5
ρ /g.cm^{-3}	5.615	5.32	5.21	4.82
Z	4	4	16	4
crystal size /mm^3	0.45×0.3×0.15	0.5×0.2×0.15	0.4×0.4×0.2	0.25×0.2×0.1
radiation type	Mo- Kα	Mo- Kα	Mo- Kα	Mo- Kα
wavelength /Å	0.71069	0.71069	0.71069	0.71069
indices range	-10 ≤ h ≤ 10 -8 ≤ k ≤ 8 -36 ≤ l ≤ 35	-9 ≤ h ≤ 9 -7 ≤ k ≤ 7 -33 ≤ l ≤ 33	-21 ≤ h ≤ 8 -10 ≤ k ≤ 6 -22 ≤ l ≤ 21	-20 ≤ h ≤ 21 -9 ≤ k ≤ 9 -14 ≤ l ≤ 14
No. of reflections				
Measured / unique	16860 / 3296	12095 / 2615	9232 / 2499	11126 / 2928
observed [I > 3 б(I)]	2785	2533	1894	1831
R_{int}	0.029	0.043	0.034	0.056
$(\sin\theta/\lambda)_{max}$ /Å^{-1}	0.90	0.84	0.90	0.80
R_F / wR_F [F>3б(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	1.12	1.06

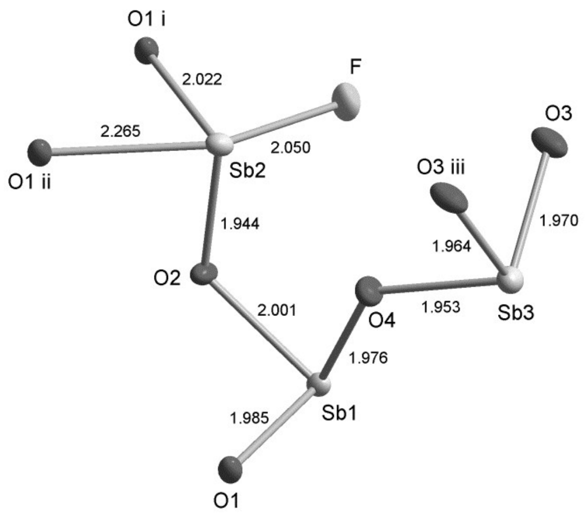


Fig. 1 The asymmetric unit and selected equivalents of Sb_3O_4F. There are three crystallographic independent Sb atoms having $[Sb(1)O_3]$, $[Sb(2)O_3F]$ and $[Sb(3)O_3]$ trigonal pyramidal and see-saw co-ordinations. Symmetry codes: (i) -1+x, y, z; (ii) –x, -y, -z; (iii) –x, -0.5+y, 0.5-z.

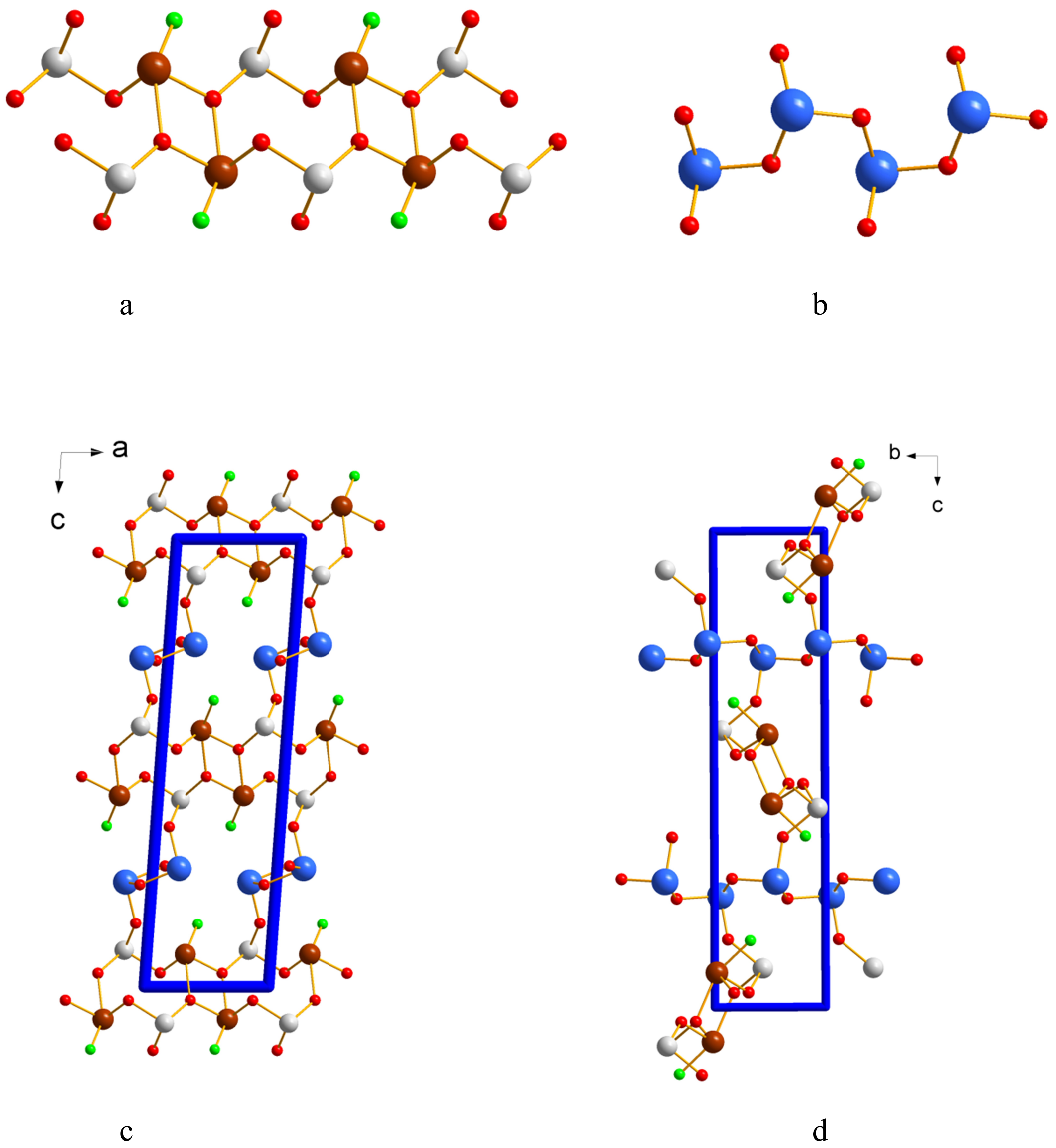


Fig. 2 **(a)** Pairs of edge sharing [Sb(2)O_3F] polyhedra are bridged by corner sharing Sb(1)O_3 units to make [Sb_2O_3F]$_n$ chains extending along [100]. **(b)** The [Sb(3)O_3] trigonal pyramids make up [Sb(3)O_2]$_n$ chains by corner sharing that extend along [010]. **(c-d)** The two chain systems 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), red O and green stands for F.

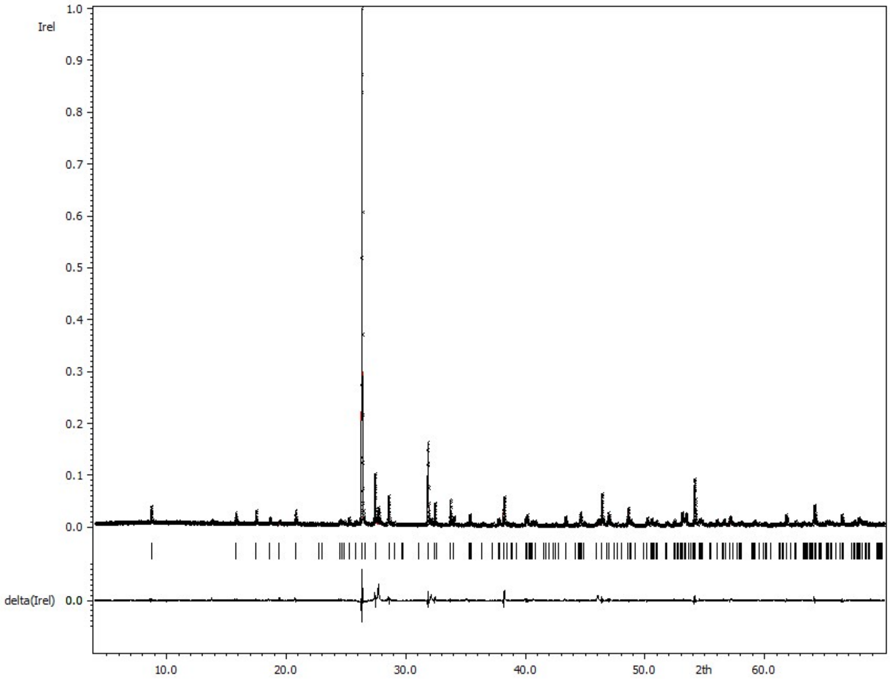
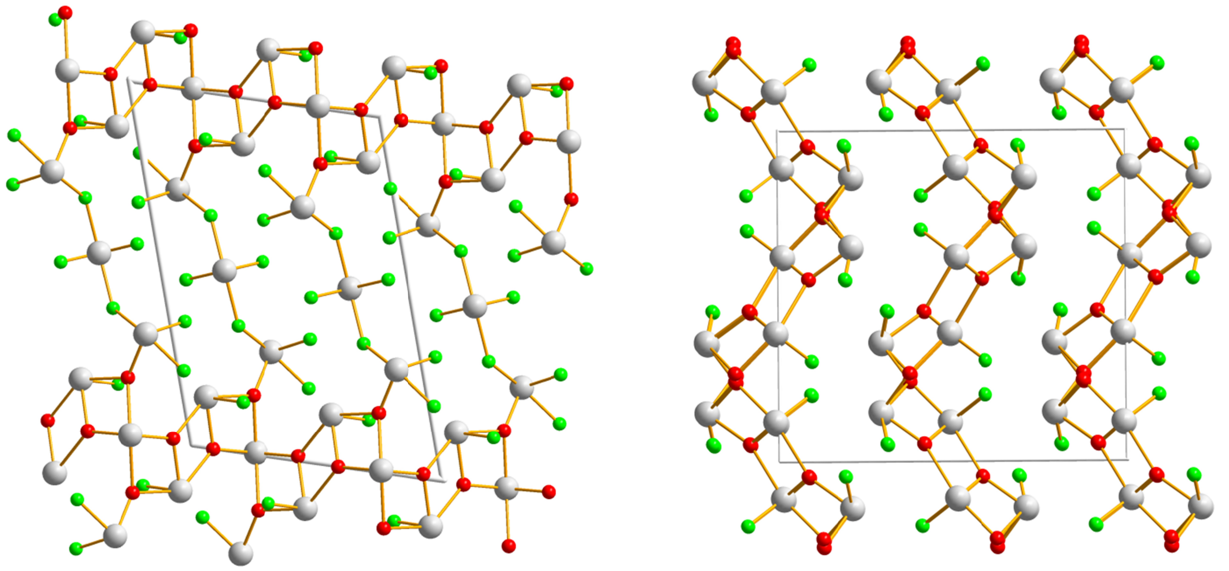


Fig. 3 Comparison of the measured powder X-ray diffractogram and the calculated pattern for Sb_3O_4F based on the single crystal X-ray determination of the crystal structure (Rp = 9.43)



a b

Fig. 4 Crystal structures of **(a)** α-$Sb_3O_2F_5$ and (b) M-SbOF, projected along [010]. Grey atoms indicate Sb, red O, green stands for F.

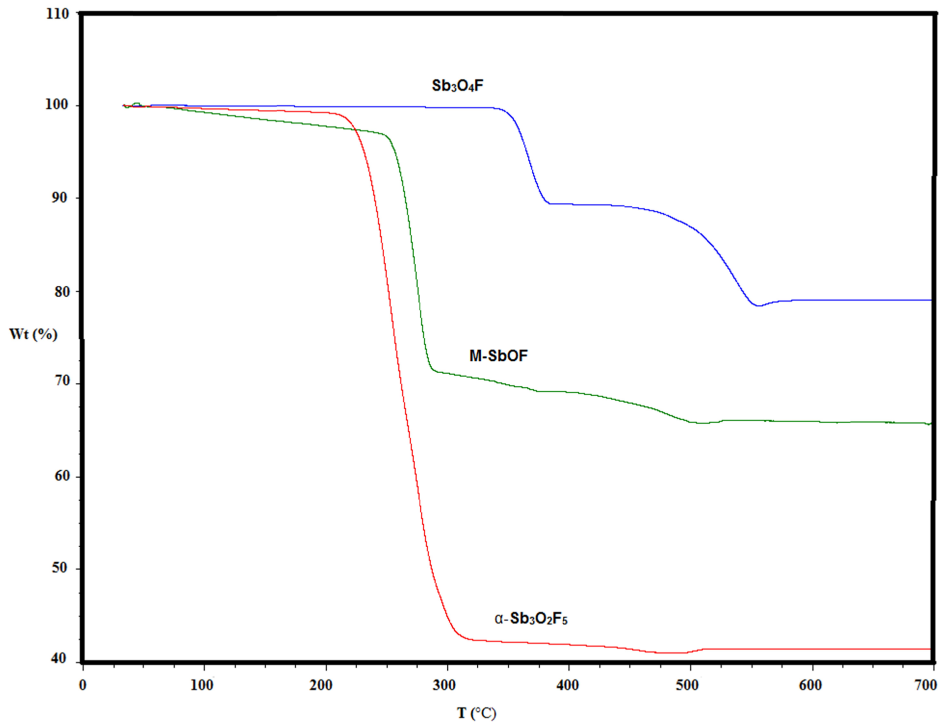
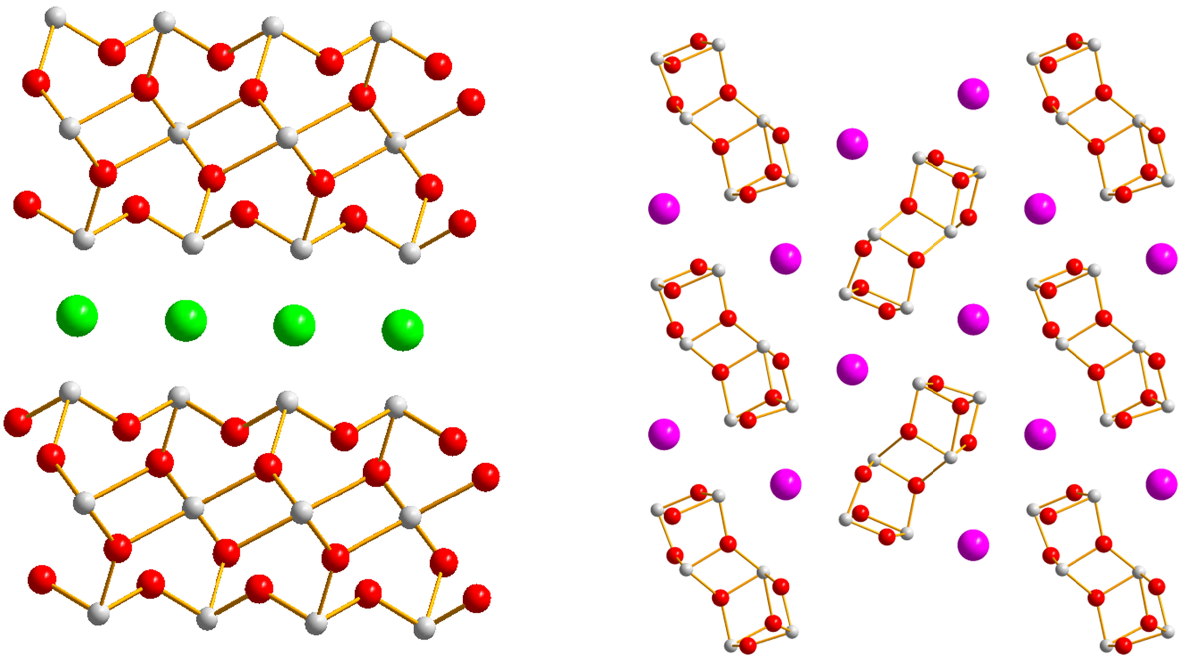


Fig. 5 Thermal decomposition of the compounds Sb_3O_4F, M-SbOF and α-$Sb_3O_2F_5$, see text for interpretation of the decomposition steps.



a b

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-Sb_3O_4I is composed of $[Sb_3O_4]_n$ tubes along [100] separated by I atoms.