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Synthesis and crystal structure of a series of incommensurately modulated composite oxohalide compounds

Iwan Zimmermann^a, Alexis Corgnet^a, Mats Johansson^{a*}, Sven Lidin^b

- a) Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
- b) Department of Chemistry, Division of Polymer & Materials Chemistry, Lund University, Box 124, SE-221 00 Lund, Sweden

* Corresponding author, Email: mats.johansson@mmk.su.se, tel: +46-8-162169, fax: +46-8-152187

Abstract

Transparent needle like single crystals of the isostructural compounds $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\delta \approx 0.2$ were obtained from chemical reactions in evacuated and sealed silica tubes. First the average structure was solved in $P2_1/n$ and then modulations were introduced but the model refined poorly and a lowering of the symmetry to the 3+1 dimensional space group $P2_1(\alpha 0 \gamma)0$ gave a much better fit to the data. This model used second order positional modulations for all atoms. While Sb, Cl (Br, I) and most O positions were well behaved there was a mismatch with Zn that was better described in a sub-cell, thus yielding a composite structure. The composite nature of the structure leads to a charge unbalance that is compensated for by oxygen vacancies.

Introduction

There is a rich structural variety among oxides and oxohalides containing antimony due to the flexibility of the coordination of Sb^{3+} . The stereochemically active lone-pair on Sb^{3+} causes an asymmetric coordination and the most common coordination polyhedra are $[\text{SbO}_3]$ trigonal pyramids and $[\text{SbO}_4]$ see-saws.

For ternary Sb-O-X ($X = \text{Cl, Br, I}$) compounds there is a tendency for the halide ion to take the role as a counter ion rather than forming covalent bonds to antimony. For quaternary compounds containing also a late transition metal it is most common that antimony only coordinate to oxygen and the transition metal bond to both oxygen and halide ions. This result in formation of non-bonding volumes in the crystal structure in between chalcogen/chalcophile and halogen/halophile parts were the terminal halogens and lone-pairs become roommates. The most reasonable explanation for this behavior is that they are excluded from the bonding subvolume of the structure rather than being attracted to each other. The flexibility in the coordination around Sb^{3+} and its preference to bond only to oxygen lead to several types of antimony oxide entities *e.g.* small cages resembling of cubic Sb_2O_3 in $\text{CuSb}_2\text{O}_3\text{Br}$,¹ bigger cages resembling zeolite β -cages in $\text{Cu}_{20}\text{Sb}_{35}\text{O}_{44}\text{Cl}_{37}$,² layers in $\text{CuSbTeO}_3\text{Cl}_2$ ³ and tubes in $\text{Sb}_8\text{O}_{11}\text{X}_2$.⁴⁻⁶ In this work we present the isostructural compounds $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$ ($X = \text{Cl, Br, I}$), $\delta \approx 0.2$ with a rather simple columnar average structure that, however, actually proved to be a composite structure where the Zn atoms are best described in a sub-cell. Composite structures are relatively rare and mainly observed among intermetallic and among sulfides and fluorides.⁷ The latter are, however, mostly layer misfit compounds and there is also one nice example of columnar misfit; the “Alchemists gold”, $\text{Hg}_{2.86}\text{AsF}_6$.⁸⁻⁹ Oxide based modulated composite structures have been found in several hexagonal perovskites and related materials such as *e.g.* $\text{Sr}_{1.2872}\text{NiO}_3$,¹⁰ $\text{Sr}_{1+x}(\text{Co}_x\text{Mn}_{1-x})\text{O}_3$,¹¹ $\text{Ba}_{1+x}[(\text{Cu}_x\text{Rh}_{1-x})\text{O}_3]$ ¹² and $\text{Sr}_{1+x}(\text{Cu}_x\text{Mn}_{1-x})\text{O}_3$.¹³ To the best of our knowledge the present compounds are the first oxohalides to show a composite structure.

Experimental

Transparent needle like single crystals of the compounds $[\text{Sb}_4\text{O}_{7+3\delta}\text{Cl}_4][\text{Zn}_3]_{1+\delta}$, $[\text{Sb}_4\text{O}_{7+3\delta}\text{Br}_4][\text{Zn}_3]_{1+\delta}$ and $[\text{Sb}_4\text{O}_{7+3\delta}\text{I}_4][\text{Zn}_3]_{1+\delta}$, $\delta \approx 0.2$ were obtained from chemical reactions in evacuated and sealed silica tubes. ZnO (ABCR), ZnCl_2 (Sigma -Aldrich), ZnBr_2 (Sigma -Aldrich), ZnI_2 (ABCR) and Sb_2O_3 (Sigma-Aldrich) were used as starting materials. For the

synthesis a 1:1:1 mixture of ZnX_2 ($X = \text{Cl, Br, or I}$), ZnO_2 and Sb_2O_3 was subsequently heat treated at $550\text{ }^\circ\text{C}$ for 60 h. Single crystals were separated manually from unreacted starting material and crystals of the previously described compound ZnSb_2O_4 ¹⁴ that was observed in minor amounts as by-product. Attempts to synthesize a corresponding oxofluoride phase starting with ZnF_2 as fluorine source failed.

Single crystal X-ray diffraction experiments were carried out on an Oxford Diffraction Xcalibur3 diffractometer equipped with a graphite monochromator. The data collection was at 293 K using $\text{MoK}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$. Data reduction was done with the software CrysAlis RED that also was employed for the analytical absorption correction. The crystal structures were solved by charge flipping implemented in SUPERFLIP¹⁵ and refined by full matrix least squares on F using the program JANA-2006,¹⁶ the W matrix was calculated according to van Smaalen.¹⁷⁻¹⁸

The structural drawings are made with the program DIAMOND.¹⁹ Powder patterns were collected on a Panalytical X'Pert PRO powder X-Ray diffractometer in Bragg-Brentano geometry with $\text{Cu-K}\alpha$ radiation. IR spectra were recorded on a Varian 670-IR FTIR spectrometer for the range $390\text{--}4000\text{ cm}^{-1}$ at ambient temperature. The spectrometer was equipped with an attenuated total reflection (ATR) detection device with a single reflection ATR diamond element. Thermogravimetric studies were performed in a Perkin-Elmer TGA7 unit in nitrogen using a heating rate of $5\text{ }^\circ\text{C}/\text{min}$.

Results

An inspection of reciprocal space images from compounds $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$ ($X = \text{Cl, Br, I}$), $\delta \approx 0.2$ clearly show that the structures are incommensurately modulated with a \mathbf{q} vector in the ac -plane of the fundamental monoclinic unit cell. The close to perfect orthorhombic pseudo symmetry of the fundamental unit cell and the presence of two (orthorhombically) symmetry-equivalent \mathbf{q} -vectors clearly indicates that pseudo merohedral twinning according to the orthorhombic-monoclinic symmetry lowering is to be expected. All structures contain a set of strong sub structure reflections and additionally a set of weaker satellites that appear to be incommensurate with the sub structure.

The crystallographic information of the three compounds is summarized in Table 1. The value of δ is given by the \mathbf{q} vector component along a^* . The patterns further share the special feature that 1st order satellites dominates for the $1kl$ reflections and the 2nd order satellites

dominates for the 2kl reflections as shown in Figure 1. This is a strong indication for composite behavior.

Structural solution using charge flipping in super space (superflip) of the compounds was relatively straight-forward. A first structural solution was carried out in the centro-symmetric space group $P2_1/n$, but this solution refined rather poorly. Lowering the symmetry to Pn did little to improve the situation while a model in the 3+1 dimensional space group $P2_1(\alpha 0 \gamma)0$ provided a much better fit to the data. This model used second order positional modulations for all atoms. The automatic procedure produced excellent starting positions and modulations for Sb and halides while the modulations for Zn turned out to be very large. Oxygen positions were only localized to some extent. The amplitude of the modulation of Zn positions was particularly large along the a direction and while this could be modeled as a saw-tooth type positional modulation, it was clear that a composite structure model would be more suitable, see Figure 2. After moving all Zn positions to the secondary unit cell, using the transformation matrix

$$W_2 = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

refining the structure as pseudo-merohedrally twinned proceeded without further complications. All oxygen positions were located and in the final model found to be best described in the primary unit cell

The compounds $[Sb_4O_{7+3\delta}X_4][Zn_3]_{1+\delta}$, ($X = Cl, Br, I$), $\delta \approx 0.2$ are isostructural, and may without loss of generality be described by the behavior of the iodide compound. The Br compound produced the crystals of relatively low quality, and for these, convergence was difficult to achieve. The problem was solved by restricting all oxygen thermal displacement parameters to be equal. The non-stoichiometry originates from the composite nature of the structures. The primary unit cell is the locus of the $Sb_4O_8I_4$ sub-structure while the secondary unit cell given by the relationship $a_2^* = a_1^* + q$, $b_2^* = b_1^*$, $c_2^* = c_1^*$ yielding $a = 3.4797 \text{ \AA}$, $b = 18.508 \text{ \AA}$, $c = 10.7768 \text{ \AA}$, $\beta = 97.915^\circ$ $q = (\alpha 0 \gamma)$, $\alpha = 0.1852$, $\gamma = 0.3451$ contains Zn only. This model refines very well yielding R1 values better than 6% for main reflections and better than 12% and 18% for 1st and 2nd order satellites respectively. The number of Sb positions in the primary cell is 4 while the number of Zn positions in the secondary cell is 3, but because of the metric relationship between the two unit cells, the relative amount Sb:Zn is not 4:3, but

4:3.682, *i.e.* since the Zn content refers to a smaller cell it must be multiplied by the ratio of the *a*-axes of the two cells, 4.271/3.4797. This still leaves the structure unbalanced with respect to charge. There are several possible remedies for this. The answer might be found in the partial replacement of O by OH, the oxidation of Sb(III) to Sb(V) or under-occupancy of either oxygen or iodine. Oxidation of Sb is unlikely given the absence of oxidizing agents in the synthesis and the local coordination of Sb that clearly indicates the trivalent state throughout the structure. Likewise, the absence of iodide should be very noticeable as negative residual electron density. The most likely charge compensation is therefore either partial occupancies on oxygen or/and presence of hydrogen in the structure. The latter can hardly constitute the sole contribution to charge balance since this would require a rather substantial moisture content in the reaction mixture. Given that the title compounds are the main product of the reaction, the required hydrogen content is $[\text{Sb}_4\text{O}_{7.38}(\text{OH})_{0.62}\text{I}_4][\text{Zn}_3]_{1.23}$, rather more than expected from contaminant water only. This leaves oxygen vacancies as the only plausible main contributor to balancing the charge of the non-stoichiometry.

It was found that bond valence sum calculations were quite a useful tool in this quest. While the BVS for all Sb positions vary, the BVS of Sb1 stands out as singular, reaching a maximum value well above four. A closer inspection reveals that the high value of this BVS is caused by a short Sb1-O5 distance over part of the range of the internal coordinate describing the propagation of the structure along the direction of the *q*-vector. Introducing occupational modulation on position O5 yields an improvement of the fit of the model to the data and reduces the offending BVS value to one more on par with those of the other Sb positions. The reduced occupancy of O5 also brings the compound closer to an over-all charge balance. A somewhat less problematic, but still high BVS is found for Sb3 and here the cause is a short distance to O6. Following the procedure for O5, an occupational modulation was introduced for O6 which led to further improvement and a change in composition to slightly below the ideal value $[\text{Sb}_4\text{O}_{7.69}\text{X}_4][\text{Zn}_3]_{1.23}$. In the final model the sum of the occupancies for positions O5 and O6 was set to 1.69 to avoid overcompensating for the Zn deficiency. Unsurprisingly, the agreement between model and data is quite insensitive to such small changes in oxygen content.

The structure is composed by columns centered by three Zn positions, the central one being coordinated exclusively by oxygen while the two outer ones also bind to Cl/Br/I. The oxygen atoms are further connected to Sb atoms belonging to Sb-O ladders. The structure looks rather simple when viewed along the **a** direction, see Figure 3. In a perpendicular view, the complexity becomes more pronounced. The mismatch between Zn and the rest of the

structure is most easily seen if the Sb-O ladders are removed from the column, see Figure 4. The coordination around the three Zn atoms are clarified with t-plots, see Figure 5, to show how the coordination number varies depending on the modulation. The composite nature of the structure leads to a charge unbalance that is compensated by oxygen vacancies, these are located in one of the Sb-O ladders, see Figure 6. The Sb-O ladders are strongly reminiscent of the ones in $\text{Sb}_8\text{O}_{11}\text{X}_2$.⁵⁻⁶ The electron density maps show that the atomic modulation functions capture the behavior of each atomic position well, see supporting information.

Almost phase pure material (see powder diffractogram in supporting information) could be synthesized for the iodine compound, which was used to collect an IR spectrum and to study the thermal decomposition. Figure 7a shows the transmission IR spectrum for $[\text{Sb}_4\text{O}_{7+3\delta}\text{I}_4][\text{Zn}_3]_{1+\delta}$ in the range 4000 to 400 cm^{-1} . Intense peaks are observed in the low energy region, which are most probably due to Sb-O and Zn-O vibrations. The absence of peaks in the high energy region confirms the absence of hydroxy groups which would give rise to strong signals. Thermogravimetry (TG) data of $[\text{Sb}_4\text{O}_{7+3\delta}\text{I}_4][\text{Zn}_3]_{1+\delta}$ was recorded from 30 – 900°C in nitrogen atmosphere with a heating rate of 5°C/min. The TG curve in Figure 7b shows that the compound is stable up to 400°C and decomposes shortly thereafter in a single step by releasing iodine as $\text{I}_2(\text{g})$. This is in good agreement with the total weight loss of about 37 %. A powder diffraction pattern of the decomposition product shows a mixture of the oxides ZnSb_2O_6 and $\text{Zn}_{2.33}\text{Sb}_{0.67}\text{O}_4$ which means that the antimony has been oxidized to Sb(V).

Conclusions

The new isostructural compounds $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$, (X = Cl, Br, I), $\delta \approx 0.2$ were synthesized via chemical reactions in evacuated and sealed silica tubes. The crystal structure was found to be incommensurately modulated and was refined in the monoclinic 3+1 dimensional space group $P2_1(\alpha 0 \gamma)0$ having a q vector in the ac plane. The close to perfect orthorhombic pseudo symmetry of the fundamental unit cell and the presence of two (orthorhombically) symmetry-equivalent q -vectors results in pseudo merohedral twinning. The structure consists of one dimensional columns having the Zn atoms in the center to which ladders of antimony oxide are attached. Domination of 1st order and 2nd order satellites for $1kl$ and $2kl$ reflections respectively strongly indicate a composite behavior and all Zn atoms were described in a 2nd composite unit cell. Overall charge balance was obtained by introducing

oxygen vacancies in the antimony ladders which is supported by bond valance sum calculations and by the IR measurements which do not show any signs of hydroxyl groups being present. From TG one can observe decomposition of the iodide phase in a single step above 400°C by releasing I₂(g) and oxidising antimony to Sb(V).

Acknowledgement

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Supporting Information

Further details on the crystal structural investigations can be obtained from the Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany (fax +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the following depository numbers: CSD-427521 for [Sb₄O_{7+3δ}Cl₄][Zn₃]_{1+δ}, CSD-427522 for [Sb₄O_{7+3δ}Br₄][Zn₃]_{1+δ}, and CSD-427523 for [Sb₄O_{7+3δ}I₄][Zn₃]_{1+δ}.

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Tables

Table 1 Crystallographic information for $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\delta \approx 0.2$

Compound	$[\text{Sb}_4\text{O}_{7+3\delta}\text{I}_4][\text{Zn}_3]_{1+\delta}$	$[\text{Sb}_4\text{O}_{7+3\delta}\text{Br}_4][\text{Zn}_3]_{1+\delta}$	$[\text{Sb}_4\text{O}_{7+3\delta}\text{Cl}_4][\text{Zn}_3]_{1+\delta}$
Space group	$P2_1(\alpha 0 \gamma)0$	$P2_1(\alpha 0 \gamma)0$	$P2_1(\alpha 0 \gamma)0$
Symmetry operators	x1, x2, x3, x4 -x1, x2+0.5, -x3, -x4	x1, x2, x3, x4 -x1, x2+0.5, -x3, -x4	x1, x2, x3, x4 -x1, x2+0.5, -x3, -x4
$a / \text{\AA}$	4.2710(8)	4.1307(13)	4.0634(6)
$b / \text{\AA}$	18.508(3)	17.9042(2)	17.163(2)
$c / \text{\AA}$	10.6741(14)	10.3021(10)	10.4699(13)
$\beta / ^\circ$	90.054(13)	90.331(6)	91.024(11)
q	$\begin{pmatrix} 0.2274(7) \\ 0 \\ 0.4236(15) \end{pmatrix}$	$\begin{pmatrix} 0.226(3) \\ 0 \\ 0.399(6) \end{pmatrix}$	$\begin{pmatrix} 0.2032(5) \\ 0 \\ 0.3602(12) \end{pmatrix}$
Crystal colour / habit	Colourless / needle	Colourless / needle	Colourless / needle
Crystal dimensions	0.32 x 0.04 x 0.03	0.21 x 0.03 x 0.02	0.20 x 0.04 x 0.02
No. of reflections all / [$I > 3\sigma(I)$]	16749 / 4073	26084 / 6011	22220 / 3537
Goodness of fit S	1.51	2.02	1.39
R factors [$I > 3\sigma(I)$]	$R_1=0.0729$ ($wR_2=0.0711$)	$R_1=0.0982$ ($wR_2=0.1015$)	$R_1=0.0714$ ($wR_2=0.0690$)
Equivalents	$R_{\text{int}}=0.0701$	$R_{\text{int}}=0.1192$	$R_{\text{int}}=0.1486$
Main reflections	$R=0.0556$ (2355)	$R=0.0808$ (3201)	$R=0.0592$ (2302)
1st order satellites	$R=0.1180$ (1610)	$R=0.1297$ (2316)	$R=0.1103$ (1003)
2nd order satellites	$R=0.1751$ (108)	$R=0.1920$ (494)	$R=0.1580$ (232)
Residual e^- density (min / max) / \AA^{-3}	4.23 / -4.84	13.86 / -9.56	9.13 / -9.04

Figures

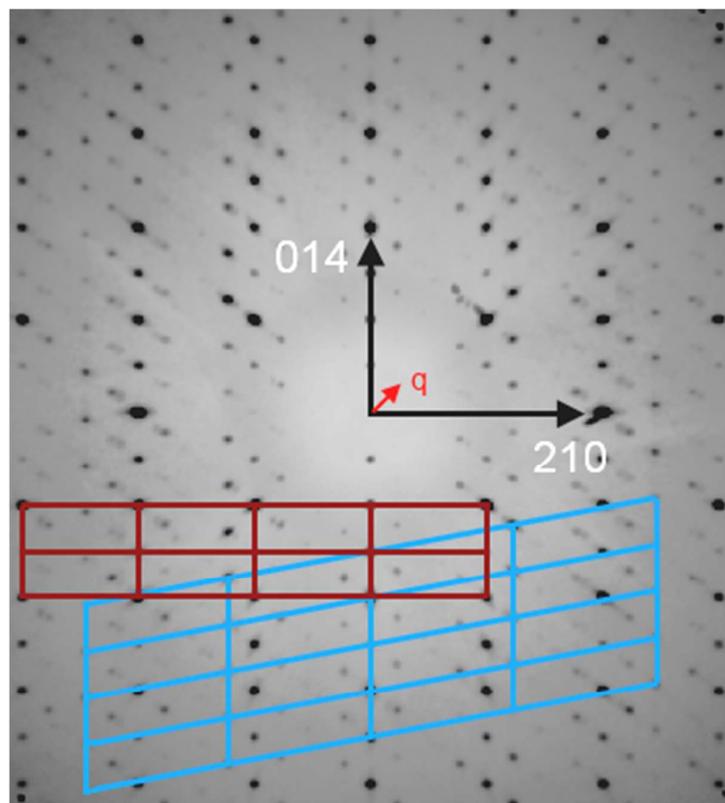


Figure 1 Reconstructed reciprocal lattice section hkl integrated from $k=0$ to $k=4$ of the iodide compound. Note the relative intensity of 1st order satellites for $1kl$ reflections and 2nd order satellites for $2kl$ reflections. Primary and secondary unit cell are indicated in red and blue respectively.

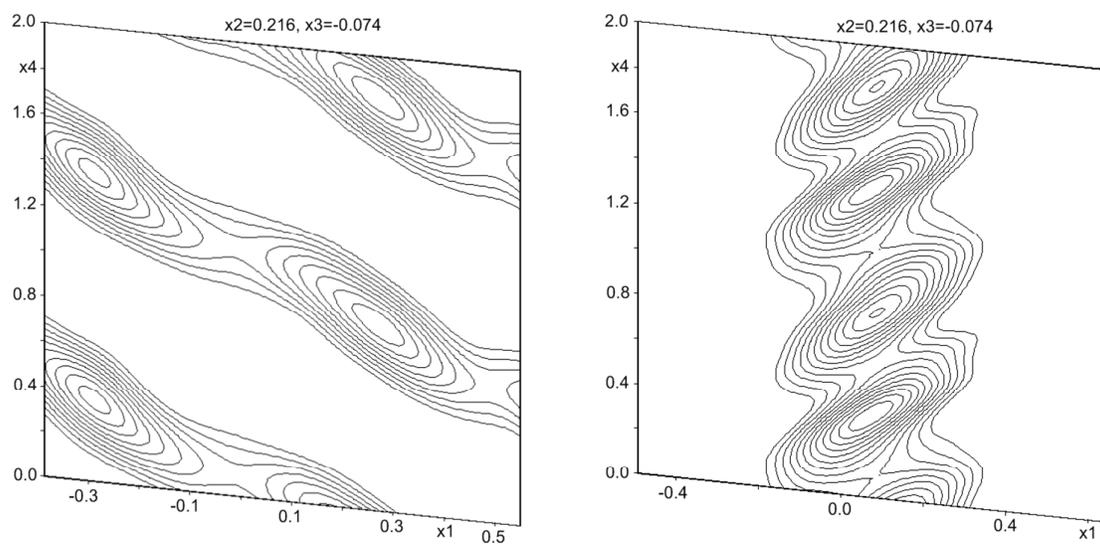


Figure 2 Electron density map of Zn1 in the primary unit cell (left) and the secondary unit cell (right).

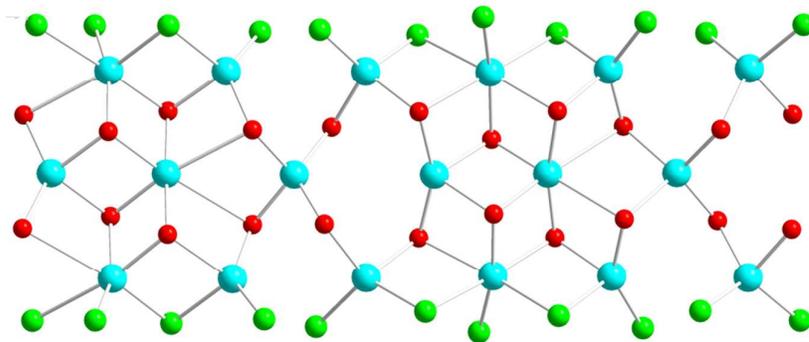


Figure 4 *Coeur-du-filé* of a single column of the structure, displaying the misfit between on one hand Zn(blue) and on the other hand oxygen (red) and I (green). The a direction is horizontal.

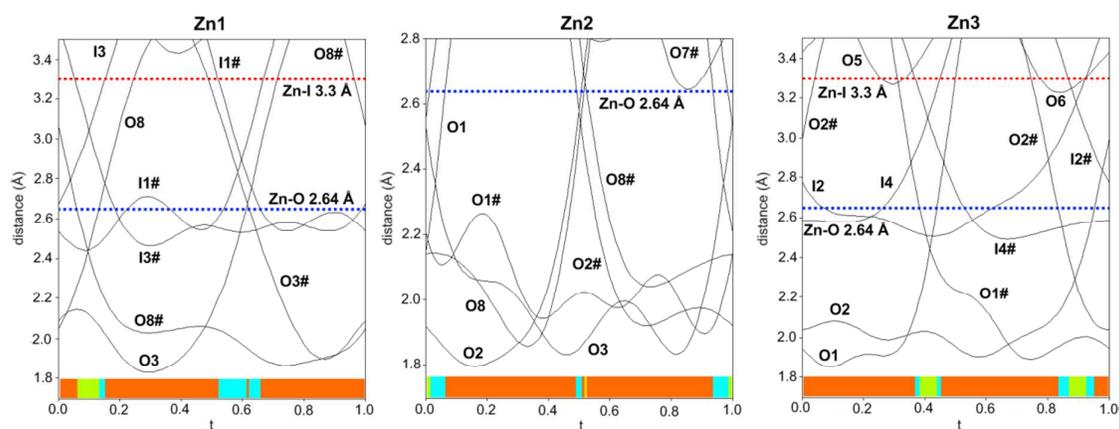


Figure 5 Variation in the coordination around the three crystallographic different Zn atoms in form of t-plots. The maximum Zn-O and Zn-I distances to be considered for covalent bonding are indicated with dotted lines. The coordination number is outlined with colored bars; yellow = 3-coordination, red = 4-coordination, blue = 5-coordination, green = 6-coordination. The # sign means symmetry equivalent atoms.

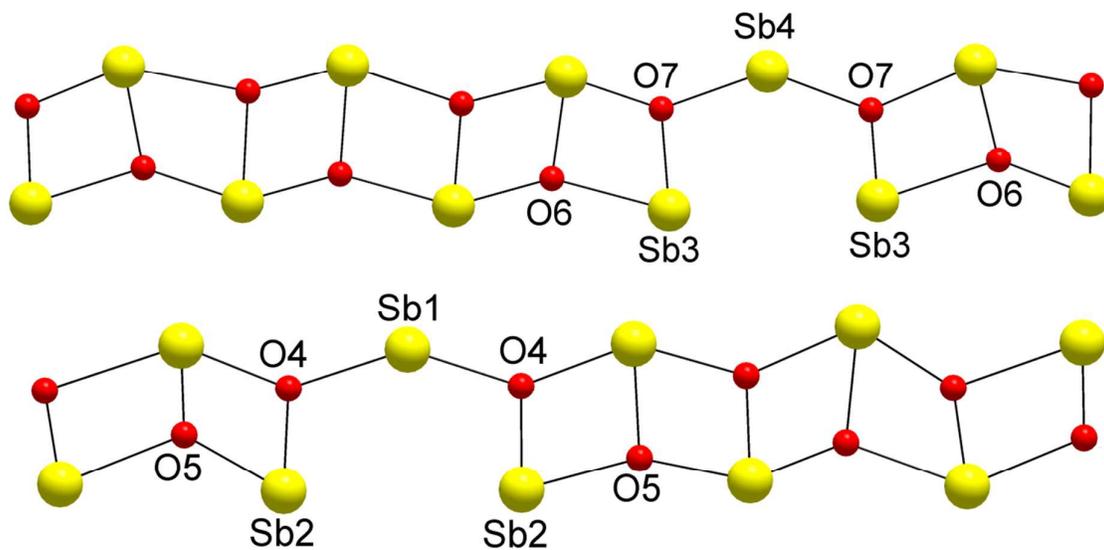


Figure 6 The two types of Sb-O ladders. Note that oxygen vacancies balance the charge deficiency. In one ladder there are O6 vacancies and in the other O5 vacancies.

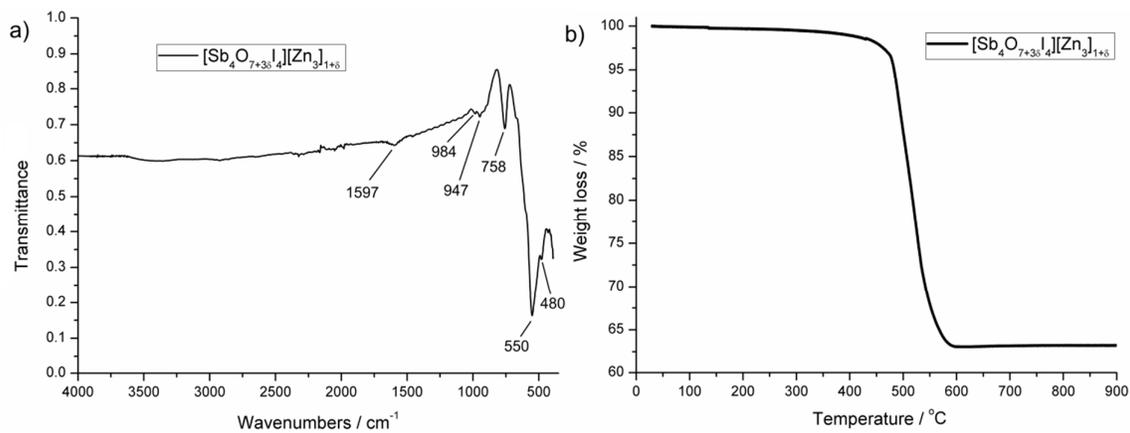
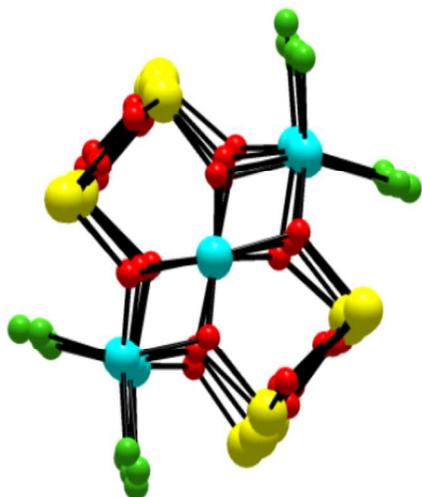


Figure 7 (a) FT-IR spectrum and (b) TG curve of $[\text{Sb}_4\text{O}_{7+3\delta}\text{L}_4][\text{Zn}_3]_{1+\delta}$.

Graphical abstract



The new isostructural oxohalides $[\text{Sb}_4\text{O}_{7+3\delta}\text{X}_4][\text{Zn}_3]_{1+\delta}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\delta \approx 0.2$ have a composite structure where the Zn atoms are best described in a second unit cell. The composite nature of the structure leads to a charge unbalance that is compensated for by oxygen vacancies.