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Synthesis, crystal structures and spectroscopic properties of pure $\text{YSb}_2\text{O}_4\text{Br}$ and $\text{YSb}_2\text{O}_4\text{Cl}$ as well as Eu^{3+} - and Tb^{3+} -doped samples†

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The quaternary halide-containing yttrium(III) oxidoantimonates(III) $\text{YSb}_2\text{O}_4\text{Cl}$ and $\text{YSb}_2\text{O}_4\text{Br}$ were synthesised through solid-state reactions from the binary components (Y_2O_3 , Sb_2O_3 and YX_3 , $\text{X} = \text{Cl}$ and Br) at 750 °C in evacuated fused silica ampoules with eutectic mixtures of NaX and CsX ($\text{X} = \text{Cl}$ and Br) as fluxing agents. $\text{YSb}_2\text{O}_4\text{Cl}$ crystallizes tetragonally in the non-centrosymmetric space group $P4_212$ with unit-cell parameters of $a = 773.56(4)$ pm and $c = 878.91(6)$ pm, whereas $\text{YSb}_2\text{O}_4\text{Br}$ is monoclinic (space group: $P2_1/c$) with $a = 896.54(6)$ pm, $b = 780.23(5)$ pm, $c = 779.61(5)$ pm and $\beta = 91.398(3)^\circ$, both for $Z = 4$. The two new $\text{YSb}_2\text{O}_4\text{X}$ compounds contain $[\text{YO}_8]^{13-}$ polyhedra, which are connected via four common edges to form $\frac{2}{\infty} \left\{ \left[\text{YO}_{8/2}^e \right]^{5-} \right\}$ layers ($d(\text{Y}^{3+} - \text{O}^{2-}) = 225\text{--}254$ pm) without any $\text{Y}^{3+} \cdots \text{X}^-$ bonds ($d(\text{Y}^{3+} \cdots \text{X}^-) > 400$ pm). Moreover, all oxygen atoms belong to ψ^1 -tetrahedral $[\text{SbO}_3]^{3-}$ units, which are either connected to four-membered rings $[\text{Sb}_4\text{O}_8]^{4-}$ in the chloride ($\text{Y}_2[\text{Sb}_4\text{O}_8]\text{Cl}_2$ for $Z = 2$) or endless chains in the bromide ($\text{Y}_{1/2}(\text{SbO}_2)\text{Br}_{1/2}$ for $Z = 8$) by common vertices. With distances of 307 pm in $\text{YSb}_2\text{O}_4\text{Cl}$ and 326 pm in $\text{YSb}_2\text{O}_4\text{Br}$ there are not even substantial bonding $\text{Sb}^{3+} \cdots \text{X}^-$ ($\text{X} = \text{Cl}$ and Br) interactions at work. Luminescence spectroscopy on samples doped with trivalent europium and terbium showed an energy transfer from the oxidoantimonate(III) moieties as the sensitizer in the host structure onto the lanthanoid activators.

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Introduction

In recent years, great attention has been paid to the structural diversity of rare-earth metal(III) oxidoarsenate(III) halides owing to the beneficial inorganic lone-pair antenna at the As^{3+} cations for luminescence applications.¹ Several representatives are known with the formula $\text{RE}_5\text{X}_3[\text{AsO}_3]_4$ ($\text{RE} = \text{La}\text{--}\text{Lu}$, $\text{X} = \text{F}\text{--}\text{Br}$), but all their different crystal structures have the motif of isolated ψ^1 -tetrahedral $[\text{AsO}_3]^{3-}$ anions in common. The fluoride derivatives ($\text{RE} = \text{Y}$, Ho , $\text{Tm}\text{--}\text{Lu}$)^{2,3} crystallize in the tetragonal space group $P4/ncc$ with separated $[\text{AsO}_3]^{3-}$ units that form a lone-pair channel along $[001]$, while the chloride derivatives crystallize monoclinically ($C2/c$ for $\text{La}\text{--}\text{Pr}$,^{4–6} $P2_1/c$ for $\text{Nd}^{5–7}$ and $\text{Sm}^{2,6}$) with a layered structure, in which the $[\text{AsO}_3]^{3-}$ units are linked to the chloride layers via weak secondary contacts. The three known bromide derivatives ($\text{RE} = \text{Pr}$, Sm , Eu)² crystallize again in the monoclinic system with space group $P2_1/c$ and

similar coordination features as the chloride derivatives. The motif of ψ^1 -tetrahedra $[\text{AsO}_3]^{3-}$ is also present in the oxide-halide representatives $\text{RE}_3\text{OCl}[\text{AsO}_3]_2$ and $\text{RE}_3\text{OBr}[\text{AsO}_3]_2$, which crystallize tetragonally in the space groups $P4_2/mnm$ ($\text{RE} = \text{La}$)^{8,9} or $P4_2nm$ ($\text{RE} = \text{Ce}\text{--}\text{Pr}$, $\text{Sm}\text{--}\text{Dy}$ with $\text{X} = \text{Cl}$,^{2,4,10} $\text{RE} = \text{Ce}$, Nd , Sm , Gd , Tb with $\text{X} = \text{Br}^2$). Like in the $\text{RE}_5\text{F}_3[\text{AsO}_3]_4$ cases ($\text{RE} = \text{Y}$, Ho , $\text{Tm}\text{--}\text{Lu}$), all $\text{RE}_3\text{OX}[\text{AsO}_3]_2$ representatives have a lone-pair tunnel structure of $[\text{AsO}_3]^{3-}$ units, but the rare-earth metal-oxygen linkage is different. Furthermore, there are $\text{RE}_5\text{O}_4\text{Cl}[\text{AsO}_3]_2$ members ($\text{RE} = \text{Nd}$, Pr)^{11,12} which crystallize monoclinically in $C2/m$. Not only compounds with isolated $[\text{AsO}_3]^{3-}$ anions were synthesised, but also with additional oxidoarsenate(III) units of the pyroanionic species $[\text{As}_2\text{O}_5]^{4-}$ in the triclinic $\text{RE}_3\text{X}_2[\text{As}_2\text{O}_5][\text{AsO}_3]$ examples ($\text{RE} = \text{Sm}\text{--}\text{Gd}$ with $\text{X} = \text{Cl}$,^{4,13} $\text{RE} = \text{Y}$, $\text{Ho}\text{--}\text{Yb}$ with $\text{X} = \text{Br}^{3,13}$). These also crystallize in a layered structure (space group: $P\bar{1}$), in which both the $[\text{AsO}_3]^{3-}$ and the $[\text{As}_2\text{O}_5]^{4-}$ anions are bound to the halide layers via weak secondary contacts.

The first rare-earth metal(III) oxidobismuthate(III) halide with the composition $\text{Nd}_{0.5}\text{Bi}_{2.5}\text{O}_4\text{Cl}^{14}$ was synthesised by Aurivillius. In this case, the rare-earth metal cation site is mixed with bismuth(III). Only ten years later, $\text{REBi}_2\text{O}_4\text{Cl}$ phases ($\text{RE} = \text{Y}$, La , Nd)¹⁵ were the first synthesised representatives without mixed

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occupation of the layers. Oppermann *et al.* extended the spectrum of these representatives at first with $\text{ErBi}_2\text{O}_4\text{I}^{16}$ considerably and found all except the cerium representatives with the composition $\text{REBi}_2\text{O}_4\text{X}$ ($\text{RE} = \text{La}, \text{Pr}-\text{Nd}, \text{Sm}-\text{Lu}$ for $\text{X} = \text{Cl}-\text{I}$).^{16,17} All these representatives crystallize in the tetragonal space group $P4/mmm$ and form layered structures, in which the rare-earth metal cations are surrounded cube-shaped by eight oxygen atoms $[\text{REO}_8]^{13-}$. These cubes are linked to each other *via* common edges. The Bi^{3+} cations form square ψ_{ax}^1 -pyramids $[\text{BiO}_4]^{5-}$ ($\text{ax} = \text{axial}$) with four oxygen, which are linked to each other *via* their corners to form layers as well.

The rare-earth metal(III) oxidoantimonate(III) halides have been neglected in previous research, except for $\text{La}_5\text{F}_3[\text{SbO}_3]_4$,¹⁸ which crystallizes analogously to the $\text{RE}_5\text{F}_3[\text{AsO}_3]_4$ series ($\text{RE} = \text{Y}, \text{Ho}, \text{Tm}-\text{Lu}$), and $\text{SmSb}_2\text{O}_4\text{Cl}^{19}$ postulated by Oppermann *et al.* to be the isotopic light homologue of $\text{SmBi}_2\text{O}_4\text{Cl}^{17}$ with layers of corner-linked $[\text{SbO}_4]^{4-}$ polyhedra (square ψ_{ax}^1 -pyramids)

with axial lone pairs. It was not until 20 years later that the true composition could be elucidated as $\text{Sm}_{1.3}\text{Sb}_{1.7}\text{O}_4\text{Cl}$,^{3,20} which crystallizes in principle analogously to the $\text{REBi}_2\text{O}_4\text{X}$ family in the tetragonal space group $P4/mmm$. Furthermore, the analogous bromide derivative $\text{Sm}_{1.5}\text{Sb}_{1.5}\text{O}_4\text{Br}^{3,20}$ was discovered, in which there is also a mixed occupation of the antimony position of the Sb^{3+} with Sm^{3+} cations just like in $\text{Sm}_{1.3}\text{Sb}_{1.7}\text{O}_4\text{Cl}$. In further studies, the derivatives of the other bromides with $\text{RE} = \text{Eu}-\text{Dy}^{3,21-23}$ with the compositions $\text{RESb}_2\text{O}_4\text{Br}$ were discovered. They crystallize in the monoclinic space group $P2_1/c$, but with a different linkage of the antimony–oxygen polyhedra. Here ψ^1 -tetrahedral $[\text{SbO}_3]^{3-}$ units with only three oxygen atoms are present, which are linked to each other *via* two corners to form

chains with the Niggli formula $\frac{1}{\infty} \left\{ \left[\text{SbO}_{2/2}^v \text{O}_{1/1}^t \right] \right\}$ ($v =$ vertex-sharing, $t =$ terminal), not showing any mixed occupation with RE^{3+} cations. Moreover, the luminescence of trivalent europium and terbium will be investigated and discussed. The oxidoantimonate(III) host structure promises to provide an energy transfer to enhance the luminescence of the $4f-4f$ activators. Trivalent antimony cations themselves show an efficient $5s-5p$ excitation that can be used as an antenna for lanthanoid activators²⁴⁻²⁶ and antimony(III) compounds have proven to transfer energy previously.^{27,28}

Results and discussion

The two rare-earth metal(III) oxidoantimonate(III) halides $\text{YSb}_2\text{O}_4\text{Cl}$ and $\text{YSb}_2\text{O}_4\text{Br}$ were formed from Y_2O_3 and Sb_2O_3 together with YX_3 ($\text{X} = \text{Cl}$ and Br) as colourless square platelets. $\text{YSb}_2\text{O}_4\text{Cl}$ crystallizes in the tetragonal space group $P4_212$, while $\text{YSb}_2\text{O}_4\text{Br}$ adopts the monoclinic space group $P2_1/c$, just like the already known $\text{RESb}_2\text{O}_4\text{Br}$ representatives with $\text{RE} = \text{Eu}-\text{Dy}$.^{3,21-23} The unit-cell parameters for $\text{YSb}_2\text{O}_4\text{Cl}$ are $a = 773.56(4)$ pm, $c = 878.91(6)$ pm ($c/a = 1.136$), while $a = 896.54(6)$ pm, $b = 780.23(5)$ pm, $c = 779.61(5)$ pm and $\beta = 91.398(3)^\circ$ apply for $\text{YSb}_2\text{O}_4\text{Br}$. The molar volumes of the bromides decrease from $\text{EuSb}_2\text{O}_4\text{Br}$ ($V_m = 84.36$ cm³ mol⁻¹) to

$\text{DySb}_2\text{O}_4\text{Br}$ ($V_m = 82.57$ cm³ mol⁻¹) as consequence of the lanthanoid contraction.²⁹ Despite being half as heavy the Y^{3+} cation can be classified by its ionic radius between Dy^{3+} and Ho^{3+} ,³⁰ which also holds here, indicated with the molar volume of 82.08 cm³ mol⁻¹ for $\text{YSb}_2\text{O}_4\text{Br}$. The molar volume of $\text{YSb}_2\text{O}_4\text{Cl}$ is with 79.19 cm³ mol⁻¹ considerably smaller as compared to the bromide derivative, due to the lighter and smaller halide anion.

While the monoclinic $\text{YSb}_2\text{O}_4\text{Br}$ shows two crystallographically distinct Y^{3+} positions, the tetragonal $\text{YSb}_2\text{O}_4\text{Cl}$ only comprises one Y^{3+} position. In both cases, however, the Y^{3+} cations are surrounded by eight oxygen atoms that arrange themselves to square hemiprisms $[\text{YO}_8]^{13-}$. The $[\text{YO}_8]^{13-}$ polyhedra are linked with four of their edges *via* the oxygen atoms to form two-dimensional infinite layers according to the Niggli formula $\frac{2}{\infty} \left\{ \left[\text{YO}_{8/2}^e \right]^{5-} \right\}$ ($e =$ edge-sharing, Fig. 1). These layers run parallel to the (001) plane in $\text{YSb}_2\text{O}_4\text{Cl}$ and to the (100) plane in $\text{YSb}_2\text{O}_4\text{Br}$. The distances between yttrium and the oxygen atoms range between 227 and 253 pm in $\text{YSb}_2\text{O}_4\text{Cl}$ or

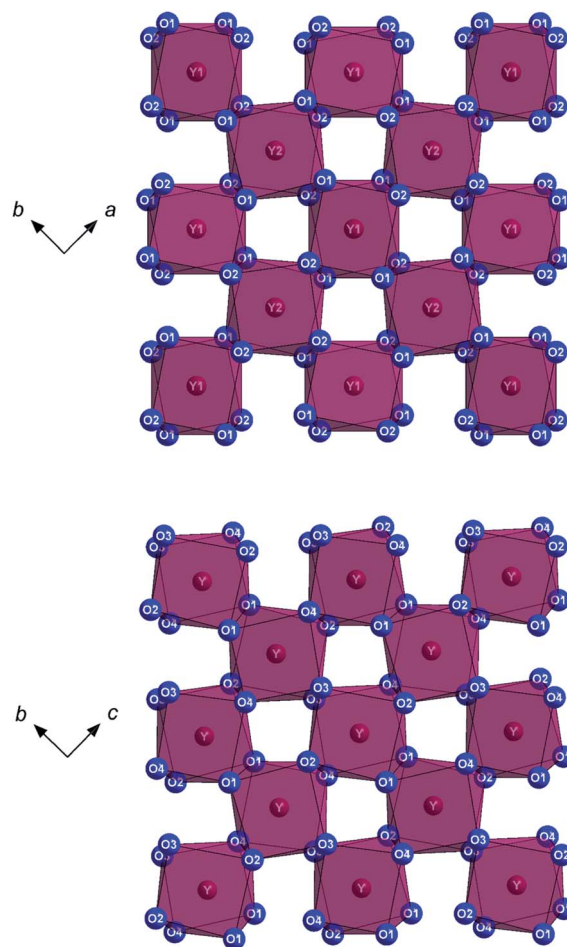


Fig. 1 Two-dimensional infinite layers $\frac{2}{\infty} \left\{ \left[\text{YO}_{8/2}^e \right]^{5-} \right\}$ of edge-linked square hemiprisms $[\text{YO}_8]^{13-}$ in the tetragonal crystal structure of $\text{YSb}_2\text{O}_4\text{Cl}$ (top) and in the monoclinic crystal structure of $\text{YSb}_2\text{O}_4\text{Br}$ (bottom).



225 and 253 pm in $\text{YSb}_2\text{O}_4\text{Br}$. These $\text{Y}^{3+}\text{--O}^{2-}$ distances are in similar intervals as in yttrium sesquioxide Y_2O_3 ($d(\text{Y}^{3+}\text{--O}^{2-}) = 225\text{--}234$ pm) with bixbyite-type structure,³¹ where Y^{3+} resides in sixfold oxygen coordination.

The antimony(III) cations occupy one crystallographic position in $\text{YSb}_2\text{O}_4\text{Cl}$, while there are two different of them in $\text{YSb}_2\text{O}_4\text{Br}$. Common for both structures, the Sb^{3+} cations form ψ^1 -tetrahedral $[\text{SbO}_3]^{3-}$ units with three oxygen atoms and the electron lone pair, but this is the only common feature, since in both structures they are linked differently to each other to achieve $\{[\text{SbO}_2]^{-}\}$ motifs. In $\text{YSb}_2\text{O}_4\text{Br}$, their arrangement is already known from the representatives $\text{RESb}_2\text{O}_4\text{Br}$ (RE = Eu–Dy),^{3,21–23} namely the linkage *via* two corners to form one-dimensional infinite chains according to the Niggli formula

$$\frac{1}{\infty} \left\{ \left[\text{SbO}_{\frac{2}{2}}^{\text{v}} \text{O}_{\frac{1}{1}}^{\text{t}} \right]^{-} \right\} \quad (\text{v} = \text{vertex-sharing, t} = \text{terminal};$$

Fig. 2). The bridging oxygen atoms show distances of 203–213 pm to the antimony(III) cations and are thus significantly longer than the terminal antimony–oxygen distances of 193–195 pm. Moreover, the terminal O1 atoms of $(\text{Sb1})^{3+}$ exhibit distances to the next $(\text{Sb2})^{3+}$ cation within the chain of $d(\text{Sb2}\cdots\text{O1}) = 317$ pm (Fig. 2, red), which is approximately the same as that of the terminal O2 atom of $(\text{Sb2})^{3+}$ to the next $(\text{Sb1})^{3+}$ cation, $d(\text{Sb1}\cdots\text{O2}) = 316$ pm, between the chains (Fig. 2, yellow). These meandering chains propagate along $[001]$ and lie parallel within the (100) plane.

The motif of chains occurs more frequently in crystal structures of ternary or quarternary antimony(III)–oxygen

compounds. However, Sb^{3+} has than a coordination number of four and forms square ψ^1 -pyramids $[\text{SbO}_4]^{5-}$ edge-linked according to $\frac{1}{\infty} \left\{ \left[\text{SbO}_{\frac{2}{2}}^{\text{e}} \text{O}_{\frac{2}{2}}^{\text{e}} \right]^{-} \right\}$. Examples of represen-

tatives for this behaviour are ASbO_2 (A = K–Cs),^{32,33} $\text{BaSb}_2\text{O}_4\text{Cl}$,³⁴ PbSbO_2Cl ³⁵ and ZnSbO_2I .³⁶ Oxygen antimony chains

$$\frac{1}{\infty} \left\{ \left[\text{SbO}_{\frac{2}{2}}^{\text{v}} \text{O}_{\frac{1}{1}}^{\text{t}} \right]^{-} \right\} \text{ similar as in } \text{YSb}_2\text{O}_4\text{Br} \text{ can be found}$$

in LiSbO_2 ,³⁷ but here they are twisted to spirals and not planar. In the $\text{YSb}_2\text{O}_4\text{Br}$ structure there are four crystallographic different oxygen atoms, whereas in $\text{YSb}_2\text{O}_4\text{Cl}$ we have only two different ones of them. Unlike the monoclinic compounds $\text{YSb}_2\text{O}_4\text{Br}$ and $\text{RESb}_2\text{O}_4\text{Br}$ (RE = Gd–Dy),^{3,21–23} in $\text{YSb}_2\text{O}_4\text{Cl}$ four ψ^1 -tetrahedra $[\text{SbO}_3]^{3-}$ form a closed ring according to $\{[\text{Sb}_4\text{O}_8]^{4-}\}$ by vertex-connections (Fig. 3). These rings lie within the (001) plane. The bridging oxygen atoms have distances of 204–210 pm to the Sb^{3+} cations. In contrast, the exo-standing terminal oxygen atoms show significantly shorter contacts of 194 pm just like it is the case for the monoclinic congeners. The terminal oxygen atoms O1 have a distance of $d(\text{Sb}\cdots\text{O1}) = 309$ pm to the next non-covalently bonded Sb^{3+} cation, which is a shorter secondary contact than in the monoclinic $\text{YSb}_2\text{O}_4\text{Br}$ representative. Discrete units of antimony and oxygen are relatively rare, but one example would be $\text{Na}_3[\text{SbO}_3]$,³⁸ where isolated ψ^1 -tetrahedral $[\text{SbO}_3]^{3-}$ anions ($d(\text{Sb--O}) = 189$ pm, $3\times$) are present with their full C_{3v} symmetry. The structural motif of separated $\frac{0}{\infty} \{[\text{Sb}_4\text{O}_8]^{4-}\}$ rings is also not novel, but found in valentinite ($\beta\text{-Sb}_2\text{O}_3$).³⁹ Here they are further connected, not isolated, and show a twisted configuration. The $\text{Sb}^{3+}\text{--O}^{2-}$ bond lengths in both compounds correspond well with typical antimony–oxygen distances in both crystalline forms of Sb_2O_3 (α :

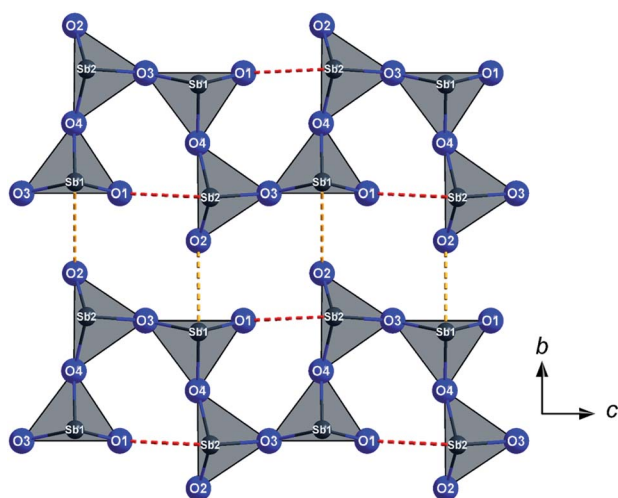


Fig. 2 One-dimensional infinite chains $\frac{1}{\infty} \left\{ \left[\text{SbO}_{\frac{2}{2}}^{\text{v}} \text{O}_{\frac{1}{1}}^{\text{t}} \right]^{-} \right\}$ of corner-linked ψ^1 -tetrahedra $[\text{SbO}_3]^{3-}$ in the monoclinic crystal structure of $\text{YSb}_2\text{O}_4\text{Br}$, which run parallel to the $[001]$ direction. The contacts of the terminal oxygen atoms to the next, not directly bonded Sb^{3+} cations are shown in red within the chains and in yellow between the chains.

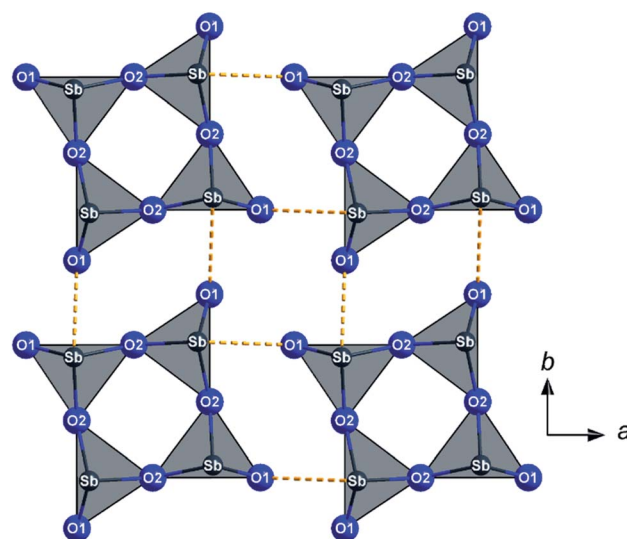


Fig. 3 Isolated rings $[\text{Sb}_4\text{O}_8]^{4-}$ of four cyclically vertex-linked ψ^1 -tetrahedra $[\text{SbO}_3]^{3-}$ in the tetragonal crystal structure of $\text{YSb}_2\text{O}_4\text{Cl}$ according to $\text{Y}_2[\text{Sb}_4\text{O}_8]\text{Cl}_2$. The contacts of the terminal oxygen atoms to the next, not directly bonded Sb^{3+} cations are shown in yellow.



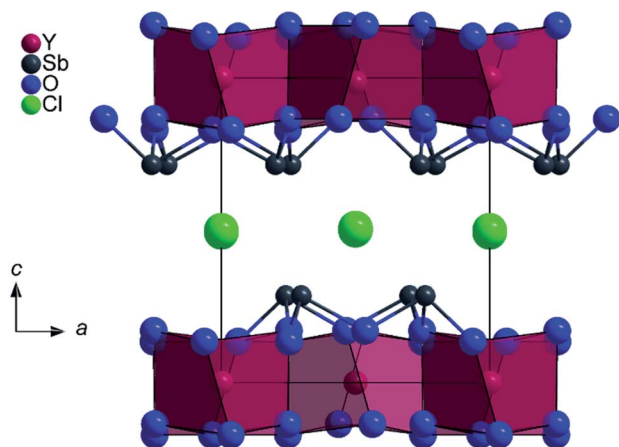


Fig. 4 Extended tetragonal unit cell of $\text{YSb}_2\text{O}_4\text{Cl}$ as viewed along [010].

senarmontite: $d(\text{Sb}-\text{O}) = 198 \text{ pm}$,⁴⁰ β : valentinite: $d(\text{Sb}-\text{O}) = 198\text{--}202 \text{ pm}$ ³⁹).

In $\text{YSb}_2\text{O}_4\text{Br}$ there is only one crystallographic position for the halide anion, whereas in $\text{YSb}_2\text{O}_4\text{Cl}$ two different ones of them are present. The halide anions show a minimum distance of $d(\text{Sb}\cdots\text{Cl}) = 307 \text{ pm}$ to the nearest Sb^{3+} cation in $\text{YSb}_2\text{O}_4\text{Cl}$ and of $d(\text{Sb}\cdots\text{Br}) = 326 \text{ pm}$ in $\text{YSb}_2\text{O}_4\text{Br}$. Their distances to the nearest Y^{3+} cation amount to $d(\text{Y}\cdots\text{Cl}) = 420 \text{ pm}$ for $\text{YSb}_2\text{O}_4\text{Cl}$ and $d(\text{Y}\cdots\text{Br}) = 427 \text{ pm}$ for $\text{YSb}_2\text{O}_4\text{Br}$. So at these distances, one can not speak of real coordination in either structure. Between each layer of Sb^{3+} cations there is a layer of halide anions, which in the case of $\text{YSb}_2\text{O}_4\text{Br}$ spreads out parallel to the (100) plane, but parallel to the (001) plane in the case of $\text{YSb}_2\text{O}_4\text{Cl}$. This halide layer has no contact or connection to any other layer, neither *via* $\text{X}^-\cdots\text{Sb}^{3+}$ nor *via* $\text{X}^-\cdots\text{Y}^{3+}$ bonds. However, the layer of Sb^{3+} cations enjoys linkage to the layer of Y^{3+} cations *via* all oxygen atoms according to $\infty \{[\text{YSb}_2\text{O}_4]^+\}$ in both yttrium(III) oxidoantimonate(III) halides $\text{YSb}_2\text{O}_4\text{X}$ ($\text{X} = \text{Cl}$ and Br).

Fig. 4 shows an extended unit cell of $\text{YSb}_2\text{O}_4\text{Br}$ with depicted coordination spheres of the Y^{3+} and Sb^{3+} cations. The same

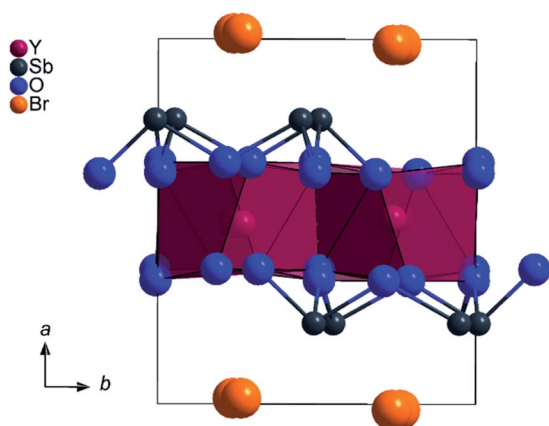


Fig. 5 Extended monoclinic unit cell of $\text{YSb}_2\text{O}_4\text{Br}$ as viewed along [001].

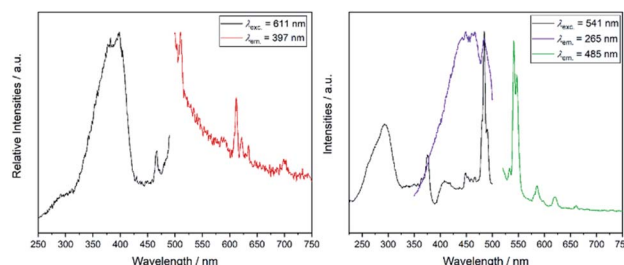


Fig. 6 Fluorescence spectra of $\text{YSb}_2\text{O}_4\text{Cl}$ doped with either Eu^{3+} (left) or Tb^{3+} (right). λ_{exc} describes the wavelength used to record the excitation spectrum, whereas λ_{em} represents the wavelength, at which the emission spectrum was recorded.

applies to Fig. 5, which shows the extended unit cell of $\text{YSb}_2\text{O}_4\text{Cl}$.

Since the yttrium cations are surrounded by oxidoantimonate layers, an energy transfer from these layers towards any cation doped on the yttrium site could be expected. This was verified *via* luminescence spectroscopy (Fig. 6 and 7), but apparently, the luminescence was quite different for all samples (Fig. 8).

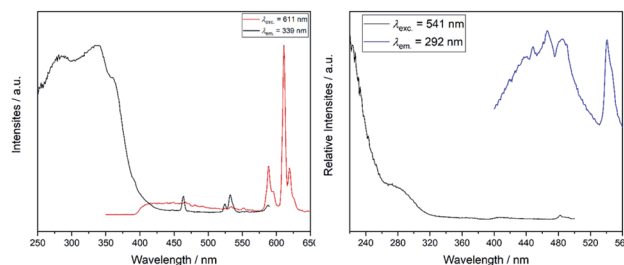


Fig. 7 Luminescence spectra of $\text{YSb}_2\text{O}_4\text{Br}$ doped with either Eu^{3+} (left) or Tb^{3+} (right). λ_{exc} describes the wavelength used to record the excitation spectrum, whereas λ_{em} represents the wavelength, at which the emission spectrum was recorded.

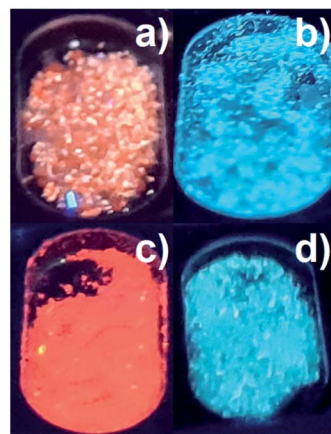


Fig. 8 Comparison of the visible luminescence of the four samples $\text{YSb}_2\text{O}_4\text{Cl}:\text{Eu}^{3+}$ (a), $\text{YSb}_2\text{O}_4\text{Cl}:\text{Tb}^{3+}$ (b), $\text{YSb}_2\text{O}_4\text{Br}:\text{Eu}^{3+}$ (c), and $\text{YSb}_2\text{O}_4\text{Br}:\text{Tb}^{3+}$ (d).

YSb₂O₄Cl:Eu³⁺ shows weak, orange-red luminescence. In the spectrum, the weak emission is represented by the low signal-to-noise-ratio. The excitation spectrum is dominated by the broad charge-transfer within the oxidoantimonate host structure peaking at 397 nm. Another band at 467 nm can be attributed to 4f–4f transitions of Eu³⁺. The emission spectrum features the main emission bands typical for trivalent europium. The band peaking at 612 nm, attributed to the emission ⁵D₀ → ⁷F₂, is much more intense than that for ⁵D₀ → ⁷F₁, normally located around 595 nm. This supports the experimentally obtained site symmetry of yttrium, as the comparably strong hypersensitive transition is a very good probe for the absence of a local inversion center.

The Tb³⁺-doped sample of YSb₂O₄Cl shows two different emissions (green and blue) that mix to give a turquoise colour impression. The broad emission in the blue regime with the maximum around 485 nm can be attributed to the emission of the host structure (³P_{1,2} → ¹S₀ transition of the Sb³⁺ lone-pair cation), which has been observed for LaOBr:Sb³⁺ (510 nm)³ and GdSb₂O₄Br (455 nm)²¹ as well and even matches with pure antimony(III) chlorides such as Cs₂NaSbCl₆⁴¹ upon excitation between 255 to 280 nm. Three sharp bands assigned to the 4f–4f transitions ⁵D₄ → ⁷F_J (J = 3, 4, 5) were also recorded. The excitation spectrum features two 4f–4f transitions with their respective maxima at 374 and 483 nm. The charge-transfer transition of the host structure is blue-shifted compared to the Eu³⁺-doped sample and peaks at 294 nm. In both spectra apparently an energy transfer between the host structure and the lanthanoid activator happens upon excitation to enhance the luminescence, but in the Tb³⁺-doped compound this transfer is obviously incomplete causing a characteristic turquoise emission colour.

The oxidoantimonate bromides show a similar luminescence, when doped with trivalent europium or terbium, but significantly more intense (“heavy-atom effect”).¹ YSb₂O₄Br:Eu³⁺ exhibits an excitation spectrum, in which the charge-transfer band of the oxidoantimonate host structure is even more dominating compared to any 4f–4f transition of Eu³⁺.

It is blue-shifted about 50 nm compared to the chloride. While the same bands were observed as in the oxidoantimonate chloride, their relative intensities are decidedly stronger.

The excitation band around 393 nm, normally the most prominent one, can be only seen as a slight shoulder. In the emission spectrum, the band attributed to the hypersensitive transition ⁵D₀ → ⁷F₂ is once again noticeably more intense as compared to the band of the ⁵D₀ → ⁷F₁ transition, since the yttrium cation occupies a site without inversion symmetry.

The emission spectrum of YSb₂O₄Br:Tb³⁺ consists of a very broad band, which we assign to the charge-transfer transition of the host structure. The sharp band of the ⁵D₄ → ⁷F₆ transition with a maximum around 540 nm is typically the most intense band in Tb³⁺ spectra, the other bands are not observed, due to restrictions on the recorded wavelength regime. Like in the case above, the excitation is blue-shifted and therefore not in the accessible region of the spectrum. Interestingly, the spectrum does not feature either the 4f–5d excitation or any of the typical 4f–4f transitions of Tb³⁺. This indicates that the Tb³⁺ cations are

Table 1 Crystallographic data for YSb₂O₄Cl and YSb₂O₄Br as well as their determination

	YSb ₂ O ₄ Cl	YSb ₂ O ₄ Br
Crystal system	Tetragonal	Monoclinic
Space group	<i>P</i> 4 ₂ /2 (no. 90)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
Lattice constants		
<i>a</i> /pm	773.56(4)	896.54(6)
<i>b</i> /pm	= <i>a</i> /pm	780.23(5)
<i>c</i> /pm	878.91(6)	779.61(5)
<i>β</i> /°	90	91.398(3)
Formula units, <i>Z</i>	4	4
X-ray density, <i>D_x</i> /g cm ^{−3}	5.454	5.803
Molar volume, <i>V_m</i> /cm ³ mol ^{−1}	79.185	82.083
Diffractionmeter	κ-CCD (Bruker-Nonius)	
Wavelength	λ = 71.07 pm (Mo-K _α)	
<i>F</i> (000)	760	832
<i>T_{max}</i> /°	27.48	27.39
<i>hkl</i> range (± <i>h</i> _{max} , ± <i>k</i> _{max} , ± <i>l</i> _{max})	10, 10, 11	11, 10, 10
Unique reflections	606	1220
Absorption coefficient, μ/mm ^{−1}	21.56	27.64
Absorption correction	Program X-SHAPE 2.21 ⁴⁵	
<i>R_{int}</i> / <i>R_σ</i>	0.098/0.047	0.132/0.104
<i>R₁</i> / <i>R₁</i> with <i>F_o</i> ≥ 4σ(<i>F_o</i>)	0.049/0.040	0.118/0.060
<i>wR₂</i> /goodness of fit (GooF)	0.085/1.090	0.129/0.986
Structure determination and refinement	Program SHELX-97 ^{43,44}	
Extinction coefficient, ε/10 ^{−6} pm ^{−3}	—	0.0008(2)
<i>ρ</i> _{max} /min/e [−] 10 ^{−6} pm ^{−3}	1.74/−1.71	2.16/−1.83
Batch scale factor (BASF) ^a	0.45(6)	—
CSD number	2044973	2044975

^a This value also represents the Flack-*x* parameter for non-centrosymmetric crystal structures, from which it is transferred into BASF after the TWIN refinement^{41–43} as inversion twin.

almost exclusively excited *via* the energy transfer from the oxidoantimonate(III) system (¹S₀ → ³P_{1,2} transition of the Sb³⁺ lone-pair cation and/or O^{2−} → Sb³⁺ charge-transfer excitation).

Table 1 lists the most important crystallographic data for YSb₂O₄Br and YSb₂O₄Cl, while Table 2 gives the atomic coordinates, Wyckoff positions and equivalent isotropic displacement parameters. Table 3 contains selected bond lengths and interatomic distances for YSb₂O₄Cl and YSb₂O₄Br.

Experimental section

Synthesis of YSb₂O₄Cl and YSb₂O₄Br

The yttrium(III) oxoantimonate(III) halides YSb₂O₄X (X = Cl and Br) were synthesised at elevated temperatures *via* solid-state reactions in evacuated silica ampoules (Quarz- und Glasbläserei Müller, Berlin-Adlershof; inner diameter: 10 mm, wall thickness: 1 mm, length: 40 mm). Yttrium oxide (Y₂O₃, ChemPur: 99.9%, 43.57 mg for the chloride, 39.51 mg for the bromide derivative), antimony sesquioxide (Sb₂O₃, ChemPur: 99.9%, 168.75 mg for the chloride, 153.00 mg for the bromide derivative) as well as yttrium chloride (YCl₃, ChemPur: 99.9%, 37.68 mg) and yttrium bromide (YBr₃, Aldrich: 99.9%, 57.49 mg) were used as reactants according to eqn (1). Eutectic mixtures of



Table 2 Atomic coordinates, Wyckoff positions and equivalent isotropic displacement parameters for tetragonal YSb₂O₄Cl (top) and monoclinic YSb₂O₄Br (bottom)

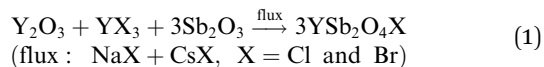
Atom	Wyckoff site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} /pm ²
Y1	2a	0	0	0	120(6)
Y2	2c	0	1/2	0.0153(4)	118(6)
Sb	8g	0.24016(8)	0.20182(8)	0.28547(9)	151(2)
O1	8g	0.0629(9)	0.2473(9)	0.1351(11)	165(17)
O2	8g	0.4648(9)	0.2483(9)	0.1705(11)	147(17)
Cl1	2b	0	0	1/2	265(19)
Cl2	2c	0	1/2	0.4929(9)	250(18)
Y	4e	0.4922(2)	0.2368(2)	0.5018(2)	232(5)
Sb1	4e	0.77879(14)	0.05212(15)	0.75550(15)	261(4)
Sb2	4e	0.22116(14)	0.00914(14)	0.79184(15)	240(4)
O1	4e	0.6339(15)	0.0071(13)	0.5739(14)	299(32)
O2	4e	0.3698(14)	0.1843(14)	0.7440(14)	285(29)
O3	4e	0.6613(13)	0.0069(13)	0.9704(13)	212(27)
O4	4e	0.6624(14)	0.2102(13)	0.2595(15)	281(30)
Br	4e	0.0153(2)	0.2371(2)	0.5044(2)	329(5)

sodium chloride (NaCl, Merck: 99.9%, 126 mg) and cesium chloride (CsCl, Aldrich: 99.9%, 674 mg) were used for YSb₂O₄Cl and those of sodium bromide (NaBr, Merck: 99.9%, 203 mg) and cesium bromide (CsBr, ChemPur: 99.9%, 597 mg) for YSb₂O₄Br to improve the reaction speed and the crystal growth

Table 3 Selected interatomic distances (*d*/pm) for tetragonal YSb₂O₄Cl (left) and monoclinic YSb₂O₄Br (right)

Distance	YSb ₂ O ₄ Cl	Distance	YSb ₂ O ₄ Br
Y1–O1	(4×) 230.3(10)	Y–O2	(1×) 224.5(12)
Y1–O2	(4×) 247.2(9)	Y–O1	(1×) 226.0(11)
Y2–O1	(4×) 227.3(9)	Y–O1'	(1×) 228.4(12)
Y2–O2	(4×) 253.6(9)	Y–O2	(1×) 234.9(11)
Y1...Sb	(4×) 349.06(8)	Y–O4	(1×) 246.6(12)
Y2...Sb	(4×) 366.9(2)	Y–O3	(1×) 252.5(11)
Sb–O1	(1×) 193.7(7)	Y–O4'	(1×) 252.7(12)
Sb–O2	(1×) 204.2(7)	Y–O3'	(1×) 252.9(10)
Sb–O2'	(1×) 209.6(7)	Y...Sb2	(1×) 351.0(2)
Cl1...Y1	(2×) 439.45(3)	Y...Sb1	(1×) 351.3(2)
Cl2...Y2	(1×) 419.8(9)	Y...Sb1'	(1×) 363.9(2)
Cl2...Y2'	(1×) 459.1(9)	Y...Sb2'	(1×) 367.5(2)
Cl1...Sb	(4×) 307.31(7)	Sb1–O1	(1×) 193.0(12)
Cl2...Sb	(4×) 320.5(5)	Sb1–O3	(1×) 203.1(10)
Cl2...Sb'	(4×) 347.8(4)	Sb1–O4	(1×) 212.9(11)
		Sb2–O2	(1×) 195.1(12)
		Sb2–O4	(1×) 204.9(11)
		Sb2–O3	(1×) 211.3(11)
		Br...Y	(1×) 427.6(3)
		Br...Y'	(1×) 468.9(3)
		Br...Sb1	(1×) 325.8(2)
		Br...Sb1'	(1×) 328.1(2)
		Br...Sb1''	(1×) 357.6(2)
		Br...Sb1'''	(1×) 357.6(2)
		Br...Sb2	(1×) 319.7(2)
		Br...Sb2'	(1×) 337.5(2)
		Br...Sb2''	(1×) 341.9(2)
		Br...Sb2'''	(1×) 364.4(2)

as fluxing agents. As doping material europium sesquioxide (Eu₂O₃, ChemPur: 99.9%, 1.7 mg) or terbium chloride (TbCl₃, Aldrich: 99.9%, 1.0 mg) were used for YSb₂O₄Cl and europium sesquioxide (Eu₂O₃: ChemPur: 99.9%, 1.5 mg) or terbium bromide (TbBr₃, Aldrich: 99.9%, 1.4 mg) for YSb₂O₄Br.



The reactants were weighed into glassy silica ampoules under inert gas (argon) inside a glove box (Glovebox System-technik, GS Mega E-line), sealed under dynamic vacuum and then subjected to a defined temperature program in a muffle furnace (Nabertherm, L 9/12). This was heated at a rate of 150 K h^{−1} to 750 °C, held there for two days, cooled with 5 K h^{−1} to 666 °C, held for another three days, cooled with 5 K h^{−1} to 530 °C, again held for two days, then cooled with 10 K h^{−1} to 480 °C and finally quenched to room temperature by cutting off the power to the closed furnace. The recovered product samples were washed with 500 ml demineralised water and then dried for 2 h in a drying oven at 120 °C. Under a stereomicroscope, colourless flat, square platelets were visible, clearly larger for YSb₂O₄Cl than for YSb₂O₄Br.

Single-crystal X-ray diffraction

Suitable crystals were selected from the samples for single-crystal X-ray diffraction experiments and fixed in glass capillaries (Hilgenberg, Malsfeld; outer diameter: 0.1 mm, wall thickness: 0.01 mm) with grease. The measurements were carried out with a κ-CCD four-circle diffractometer (Bruker-Nonius, Karlsruhe) at room temperature using Mo-K_α radiation. The program package Stoe X-Area 1.86 (2018) was used for data collection and integration. The crystal structures of YSb₂O₄Cl and YSb₂O₄Br were solved in the space groups *P*4₂/1 and *P*2₁/c, respectively, by direct methods and refined with the SHELX-97 program package.^{42–45}

Luminescence spectroscopy

The luminescence spectra of all samples were measured using a Horiba Fluoromax-4 spectrometer scanning from 220 to 800 nm at room temperature. Therefore, finely ground powder samples were filled into the sample holder and subsequently placed in the sample chamber. These measurements were conducted and evaluated with the program FluorEssence.⁴⁶ All excitation spectra were corrected to consider the xenon-lamp spectrum.

Conclusions

With YSb₂O₄Br another representative of the known series RESb₂O₄Br (RE = Eu–Dy) could be synthesised and structurally characterised. Thus it also shows the structural motif of ψ¹-tetrahedral [SbO₃]^{3−} groups linked to a meandering chain of the

formula $\frac{1}{\infty} \left\{ \left[\text{SbO}_{2/2} \text{O}_{1/1} \right] \right\}$ via common vertices. As first tetragonal representative of the rare-earth metal(III)



oxoantimonate(III) halides $\text{YSb}_2\text{O}_4\text{Cl}$ (space group: $P4_212$) was obtained. Although its structure shows many similarities to the monoclinic $\text{YSb}_2\text{O}_4\text{Br}$ (space group: $P2_1/c$) representative, it exhibits a different corner-linkage of the ψ^1 -tetrahedral $[\text{SbO}_3]^{3-}$ units resulting in closed $\infty \{[\text{Sb}_4\text{O}_8]^{4-}\}$ rings.

The luminescence spectra of samples doped with trivalent europium or terbium confirmed the lack of inversion symmetry around the yttrium cations in both structures, as well as an efficient energy transfer between the oxidoantimonate(III) layers and the lanthanoid(III)-activator cations.

Author contributions

The manuscript was written through contributions of all authors.

Conflicts of interest

There are no conflicts to declare.

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