TmSb$_2$O$_4$Br: The first tetragonal lanthanoid oxoantimonate bromide without mixed-cation occupation

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In the system of rare-earth metal oxoantimonate halides with the composition RESb$_2$O$_4$X there is a great structural diversity, although all these structures share some common features. For $X = \text{Br}$, compounds with the rare-earth metals RE = Y, Eu – Dy$^{[3]}$ are known so far, which crystallize in the monoclinic space group $P2_1/c$ and exhibit antimony-oxygen chains with vertex-connected $\psi^1$-tetrahedral [SbO$_3$]$^{5-}$ anions. The lattice parameters $a$ and $b$ become more and more similar with the heavier lanthanoids and furthermore the monoclinic angle $\beta$ successfully approaches 90°. Two different structure types are known for $X = \text{Cl}$ with an own one for $RE = \text{Sm}$ and Eu$^{[3]}$ in the centrosymmetric tetragonal space group $P4/nc$ showing a doubled lattice parameter $c$ as compared to the other tetragonal oxoantimonate(III) chlorides. These occur with a slightly different structure for $RE = Y$, Gd – Lu$^{[1,5]}$ in the non-centrosymmetric space group $P4_2/2$. Both tetragonal structures contain rings of antimony and oxygen instead of the antimony-oxygen chains. Furthermore, with Sm$_{1+x}$Sb$_2$O$_4$X ($X = \text{Cl}$ and Br$^{[6]}$) cation-disordered examples exist, which crystallize isotopically to SmBi$_2$O$_4$Cl$^{[7]}$ in the tetragonal space group $P4/mmm$, but exhibit a mixed occupation of samarium and antimony in the original bismuth layer. Almost colorless, platelet-shaped crystals of TmSb$_2$O$_4$Br were obtained by reacting thulium sesquioxide with antimony sesquioxide and thulium tribromide and a flux of rubidium bromide in evacuated glassy silica ampoules at 750 °C via solid-state synthesis within three days. TmSb$_2$O$_4$Br crystallizes isotopically to the chloride series RESb$_2$O$_4$Cl ($RE = Y$, Gd – Lu) in the tetragonal non-centrosymmetric space group $P4_2/2$ with $a = 772.89(2)$ pm and $c = 901.34(3)$ pm for $Z = 4$ (CSD-2219078). The crystal structure contains two positions for the Tm$^{3+}$ cations (Tm1 (2a): 0, 0, 0 and Tm2 (2c): 0, 1/2, 0.01376(13)), only one Sb$^{3+}$ site (Sb (8g): 0.23979(11), 0.20363(11), 0.27620(12)) and two O$^{2-}$ (O1 (8g): 0.0601(12), 0.2451(12), 0.1305(13) and O2 (8g): 0.4648(12), 0.2491(12), 0.1637(13)) as well as two Br$^-$ (Br1 (2b): 0, 0, 1/2 and Br2 (2c): 0, 1/2, 0.4863(4)) anions each positions. Around each Tm$^{3+}$ cation eight oxygen atoms form hemiprisms [TmO$_{13/2}$], which are linked by four edges to form layers 2D-$\{\text{TmO}_{13/2}\}$ parallel to the (001) plane (Figure 1, left). The Sb$^{3+}$ cations together with the three oxygen atoms each build $\psi^1$-tetrahedra [SbO$_3$]$^{5-}$. Out of the three oxygen atoms, two are connected to another Sb$^{3+}$ cations, while the third one maintains contact to only one of them. Four of these [SbO$_3$]$^{5-}$ units form 3D-$\{\text{SbO$_3$}^{5-}\}$ rings (Figure 1, mid), which also reside within the (001) plane. Between the layers with Sb$^{3+}$ cations nearly planar layers of Br$^-$ anions are intercalated almost free of bonds ($d(\text{Sb} \cdot \cdot \cdot \text{Br}) = 333 – 350$ pm). Therefore there is no real close connectivity to another differently charged layer, because two layers of Sb$^{3+}$ cations flank the layers with Tm$^{3+}$ cations via the oxygen atoms according to 2D-$\{\text{Tm}(\text{SbO$_3$})\text{Sb}\}$. Figure 1 (right) shows the complete unit cell of TmSb$_2$O$_4$Br as viewed along [010].

Figure 1. Infinite layers of edge-linked square hemiprisms [TmO$_{13/2}$] (left), an isolated ring [SbO$_3$]$^{5-}$ of four vertex-linked $\psi^1$-tetrahedra [SbO$_3$]$^{5-}$ (mid) and the extended tetragonal unit cell of TmSb$_2$O$_4$Br as viewed along [010] (right).