$SmBi_2O_4Cl$: The First Single-Crystal Study in the Systems $LnBi_2O_4X$

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A mixture of Bi_2O_3, Sm_2O_3 and $SmCl_3$ reacted at 800 °C in a eutectic mixture of NaCl and CsCl as flux in a fused silica ampoule resulted in yellow plates of the title compound. $SmBi_2O_4Cl$ crystallizes in the tetragonal space group *P*4/*mmm* with the lattice parameters *a* = 388.91(3) pm and *c* = 895.16(7) pm with *Z* = 4 and hitherto its structure was only known from X-ray powder diffraction data[1]. The corresponding antimonate(III) $SmSb_2O_4Cl$ with the real composition $Sm_{1,3}Sb_{1,7}O_4Cl$ offers a mixed occupation of the antimony position with samarium[2,3] for the same crystal structure. In contrast to this, $SmBi_2O_4Cl$ shows no mixed occupation, but one samarium and one bismuth position with regular occupation.

The structure features one crystallographic samarium (1*a*: 0, 0, 0), one bismuth (2*h*: $^1/_2$, $^1/_2$, 0.28294(9)), one oxygen (4*i*: 0, $^1/_2$, 0.1582(9)) and one chlorine position (1*b*: 0, 0, $^1/_2$) each. Sm^{3+} is coordinated by eight oxygen atoms (*d*(Sm–O) = 240.6(5) pm) forming a $[SmO_8]^{13-}$ cube. Each cube is connected via edges with four other cubes, resulting in a layer $^2_\infty\{[SmO^{e}_{8/2}]^{5-}\}$ parallel to the (001) plane (Figure 1). Bismuth is coordinated as ψ^1-square pyramid $[BiO_4]^{5-}$ by four oxygen atoms (*d*(Bi–O) = 224.2(4) pm), which are connected via four vertices to infinite layers $^2_\infty\{[BiO^{v}_{4/4}]^{+}\}$ sandwiching the $^2_\infty\{[SmO^{e}_{8/2}]^{5-}\}$ layers from both sides. The Cl^- anions are not efficiently connected to the Bi^{3+} cations (*d*(Cl···Bi) = 336.7(1)), but located in the gaps between the lone pairs at the Bi^{3+} centers.

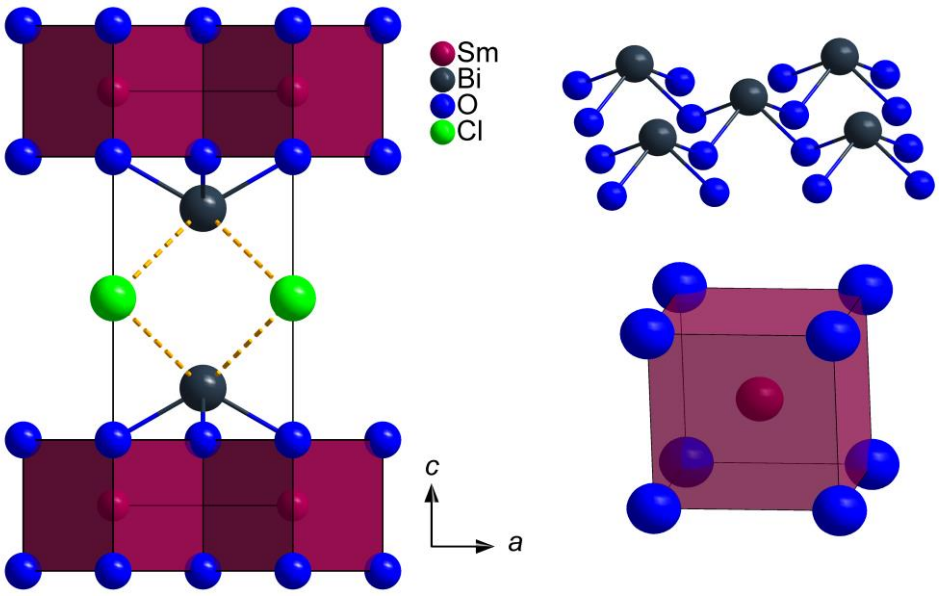

Figure 1. Extended unit cell of $SmBi_2O_4Cl$ as viewed along [010] (*left*), the $^2_\infty\{[BiO^{v}_{4/4}]^{+}\}$ layers (*right top*) and one $[SmO_8]^{13-}$ cube (*right bottom*).

[1] M. Schmidt, H. Oppermann, C. Henning, R. W. Henn, E. Gmelin, N. Söger, *Z. Anorg. Allg. Chem.* **2000**, *626*, 125.
[2] F. C. Goerigk, Th. Schleid, *Z. Anorg. Allg. Chem.* **2010**, *645*, 1079.
[3] F. C. Goerigk, *Doctoral Dissertation*, Univ. Stuttgart **2021**.