

SmBi₂O₄Cl: The First Single-Crystal Study in the Systems LnBi₂O₄X

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Introduction

The crystal structure of SmBi₂O₄Cl was first described by H. Oppermann and M. Schmidt in 2000. Back then, the crystal structure was only known from X-ray powder diffraction data^[1]. The pseudo-isotypical oxoantimonate(III) SmSb₂O₄Cl with the real composition Sm_{1.3}Sb_{1.7}O₄Cl offers a mixed occupation of the antimony position with samarium^[2,3] for the same crystal structure. In contrast to this, SmBi₂O₄Cl shows no mixed occupation, but one samarium and one bismuth position with regular occupation, as we will prove in the following.

Crystallographic Data for SmBi₂O₄Cl

| | |
|--|---|
| Crystal system, space group | tetragonal, <i>P4/mmm</i> |
| Lattice parameters | |
| <i>a</i> / pm | 388.91(3) |
| <i>c</i> / pm | 895.16(7) |
| Number of formula units (<i>Z</i>) | 4 |
| Calculated density (<i>D_x</i> in g/cm ³) | 8.190 |
| Molar volume (<i>V_m</i> in cm ³ /mol) | 81.53 |
| Diffractometer | <i>κ</i> -CCD (Bruker-Nonius) |
| Wavelength | Mo- <i>K_α</i> ; λ = 71.07 pm |
| Diffractometer limit (2θ _{max} in °) | 54.71 |
| Index range (± <i>h</i> _{max} , ± <i>k</i> _{max} , ± <i>l</i> _{max}) | 5, 5, 11 |
| Number of e ⁻ per unit cell (<i>F</i> (000)) | 277 |
| Absorption coefficient (μ in mm ⁻¹) | 75.93 |
| Number of collected / unique reflections | 2227 / 128 |
| Data set residuals (<i>R_{int}</i> / <i>R_σ</i>) | 0.077 / 0.024 |
| Structure residuals (<i>R₁</i> / <i>wR₂</i>) | 0.022 / 0.043 |
| Goodness of fit (GooF) | 1.131 |
| Residual electron density (max. / min. in 10 ⁶ pm ⁻³) | 1.48 / -1.57 |
| CSD number | 2127310 |

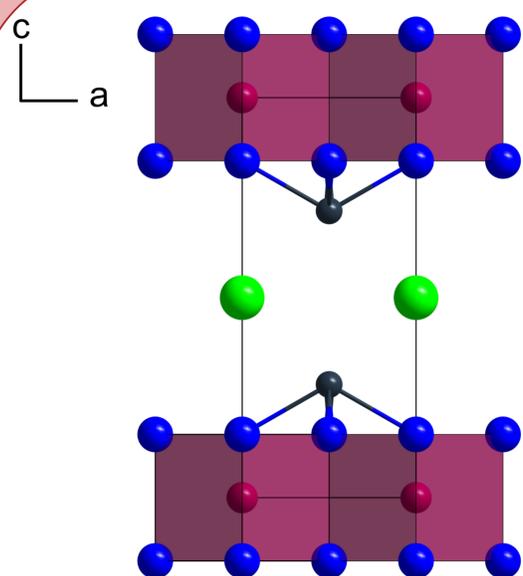


Figure 1. Extended unit cell of SmBi₂O₄Cl as viewed along [010] with emphasized [SmO₈]¹³⁻ polyhedra.

Crystal Structure

The structure features only one crystallographically unique samarium, bismuth, oxygen and chlorine position each. The Sm³⁺ cation is coordinated by eight oxygen atoms (*d*(Sm–O) = 240.6(5) pm) forming a [SmO₈]¹³⁻ cube. Each cube is connected via coplanar edges with four other cubes, resulting in a layer ²_∞{[SmO_{8/2}]⁵⁻} parallel to the *ab* plane (figure 2). Each Bi³⁺ cation is surrounded by four oxygen atoms (*d*(Bi–O) = 224.2(4) pm), resulting in a ψ^1 -square pyramid along with the stereochemically active lone-pair of electrons in apical position. These [BiO₄]⁵⁻ pyramids are connected via four vertices to layers ²_∞{[BiO_{4/4}]⁺}. A layer with chloride anions is located in between these ²_∞{[Bi₂SmO₄]⁺} triple layers with fluorite topology, and the chloride anions are not showing a direct bonding to neither the Bi³⁺ nor the Sm³⁺ cations (*d*(Cl··Bi) = 336.7(1) pm, *d*(Cl··Sm) = 447.6(3) pm), but are located in the gaps between the lone pairs at the Bi³⁺ centers.

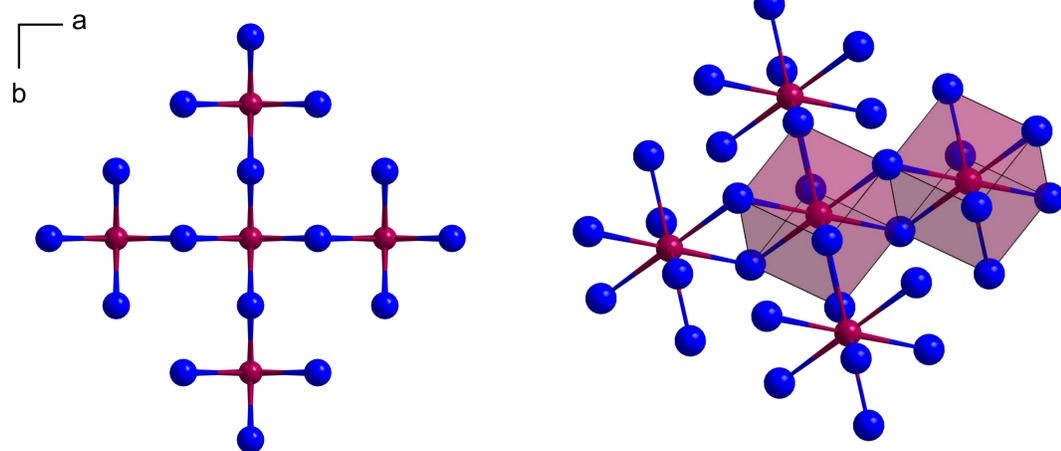


Figure 2. Samarium-oxygen layer as viewed along [001] (left) and its connectivity via four edges of the involved [SmO₈]¹³⁻ cubes each (right).

Experimental

A mixture of Bi₂O₃, Sm₂O₃ and SmCl₃ reacted at 800 °C in a eutectic mixture of NaCl and CsCl as flux in a fused silica ampoule resulting in yellow platelets of SmBi₂O₄Cl.

Table 2. Atomic coordinates and Wyckoff positions for SmBi₂O₄Cl.

| Atom | Site | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U_{eq}</i> |
|------|------|------------|------------|------------|-----------------------|
| Sm | 1a | 0 | 0 | 0 | 111(4) |
| Bi | 2h | 1/2 | 1/2 | 0.28294(9) | 123(4) |
| O | 4i | 0 | 1/2 | 0.1582(9) | 120(23) |
| Cl | 1b | 0 | 0 | 1/2 | 260(19) |

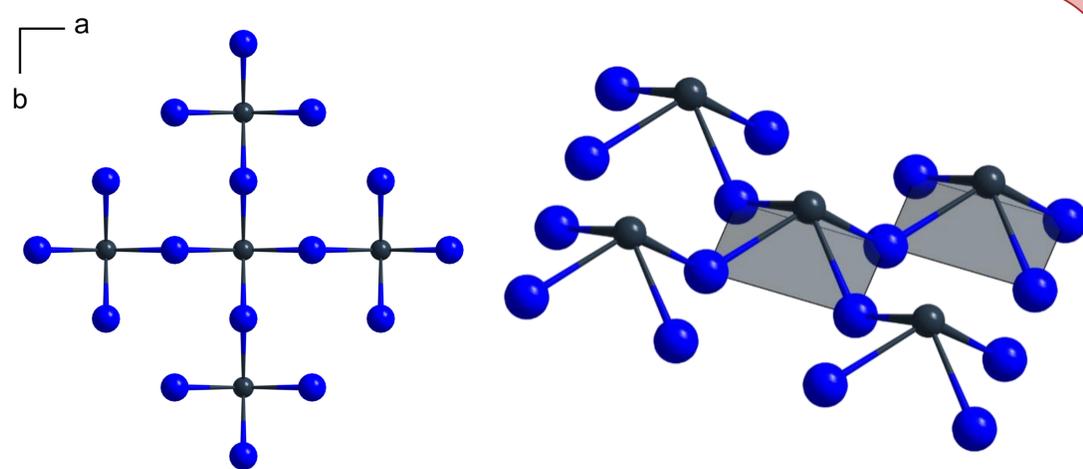


Figure 3. Layers of bismuth-oxygen polyhedra as viewed along [001] (left) and corner-sharing square [BiO₄]⁵⁻ pyramids with four more of these polyhedra (right).

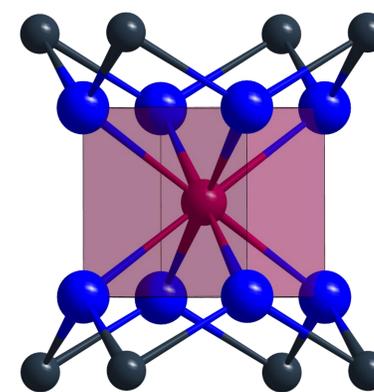


Figure 4. Samarium-oxygen polyhedra [SmO₈]¹³⁻ with highlighted connection to the Bi³⁺ cations, resulting in two dimensional layers perpendicular to the *c*-axis.

References

- [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**.

Legend for all figures

