High-pressure synthesis and crystal structure of the samarium meta-oxoborate $\gamma$-Sm(BO$_2$)$_3$

Abstract: $\gamma$-Sm(BO$_2$)$_3$ was obtained via a high-pressure/high-temperature approach in a multi-anvil apparatus at 10 GPa and 1673 K. It crystallizes in the orthorhombic space group Pca$_2_1$ (no. 29) with the lattice parameters $a = 18.3088(8)$, $b = 4.4181(2)$, and $c = 4.2551(2)$ Å. The compound was analysed by means of X-ray diffraction and vibrational spectroscopy. The structure is isotypic to that of the already known meta- and vibrational spectroscopy. The structure is isotypic to that of the already known meta-oxoborate $\gamma$-RE(BO$_2$)$_3$ ($\text{RE} = \text{La–Nd}$) and built up of a highly condensed borate framework containing three-, four-, six-, and ten-membered rings. Next to neodymium, samarium represents the second rare earth element that forms the $\alpha$-, $\beta$-, and $\gamma$-modification of the four known rare earth meta-oxoborate structure types.

Keywords: crystal structure; high-pressure chemistry; samarium borate; vibrational spectroscopy.

1 Introduction

High-pressure/high-temperature investigations into the broad field of rare earth borates have yielded various compositions hitherto unknown at ambient pressure conditions. New oxoborates with striking features like edge-sharing BO$_4$ tetrahedra as in $\text{RE}_2\text{B}_5\text{O}_{15}$ ($\text{RE} = \text{Dy, Ho}$) [1, 2] and $\alpha$-$\text{RE}_2\text{B}_6\text{O}_{12}$ ($\text{RE} = \text{Sm–Ho}$) [3–5], or $\text{RE}_2\text{B}_5\text{O}_{12}$ ($\text{RE} = \text{Sc, Er–Lu}$) [6, 7], which is analogous to the beryllio-silicate semenovite, have been found. But also in the extensively investigated family of meta-oxoborates with the composition $\text{RE}(\text{BO}_2)_3$ ($\text{RE} = \text{rare earth}$), discoveries are still made to date. Here, four modifications are known, designated with the Greek letters $\alpha$, $\beta$, $\gamma$, and $\delta$. The longest known $\alpha$-phase is well characterized, crystallizing in the monoclinic space group $C2/c$ and is built up of chains of planar BO$_3$ and tetrahedral BO$_4$ units (Figure 1, top). The first detailed description of the crystal structure of the $\beta$-modification (Figure 1, middle), more accurate $\beta$-$\text{Tb}(\text{BO}_2)_3$, was published in 2003 by Nikelski and Schleid [8]. Further isotypic compounds of the series $\beta$-$\text{RE}(\text{BO}_2)_3$ (RE = Y, Nd, Sm–Gd, Dy–Lu) [9–12] were synthesized under high-pressure conditions and $\beta$-$\text{Dy}(\text{BO}_2)_3$ additionally at ambient pressure conditions [13]. Investigations into the larger lanthanides led to another modification, designated as $\gamma$-phase (Figure 1, bottom), for $\gamma$-$\text{RE}(\text{BO}_2)_3$ ($\text{RE} = \text{La–Nd}$) under pressures of at least 7.5 GPa [14]. While the $\beta$-modification crystallizes in the orthorhombic space group $Pnma$, the $\gamma$-modification adopts the space group $Pca_2_1$. For lanthanum and cerium, yet another monoclinic modification was found, $\delta$-$\text{La}(\text{BO}_2)_3$ [15] and $\delta$-$\text{Ce}(\text{BO}_2)_3$ [16] at 5.5 and 3.5 GPa, respectively.

In contrast to the $\alpha$-phase, all three other modifications are built up exclusively of BO$_4$ tetrahedra, leading to complex borate frameworks with increasing condensation at higher pressures. This can be illustrated with the amount of threefold coordinated oxygen atoms within the structures, which concerns every sixth of the oxygen atoms in $\delta$-$\text{RE}(\text{BO}_2)_3$ ($\text{RE} = \text{La, Ce}$) and every third of the oxygen atoms in $\gamma$-$\text{RE}(\text{BO}_2)_3$ ($\text{RE} = \text{La–Nd}$).

In this work, we present $\gamma$-$\text{Sm}(\text{BO}_2)_3$, where samarium is now the fifth element of the lanthanoid series to exhibit this crystal structure and also only the second one to show the $\beta$- as well as the $\gamma$-modification. The various syntheses conditions are compared and the results of the single-crystal structure determination and the vibrational spectroscopic analysis are presented.

2 Results and discussion

2.1 Crystal structure

$\gamma$-$\text{Sm}(\text{BO}_2)_3$ crystallizes, like its isotypic compounds $\gamma$-$\text{RE}(\text{BO}_2)_3$ ($\text{RE} = \text{La–Nd}$), in the orthorhombic space group $Pca_2_1$ (no. 29). The unit cell comprises $Z = 4$ formula units and exhibits the lattice parameters $a = 18.3088(8)$, $b = 4.4181(2)$, and $c = 4.2551(2)$ Å and a volume of
Table 1: Crystal data and structure refinement of $\gamma$-Sm(BO$_2$)$_3$.

| Table 1: Crystal data and structure refinement of $\gamma$-Sm(BO$_2$)$_3$. |
|---|---|
| **Empirical formula** | $\gamma$-Sm(BO$_2$)$_3$ |
| **Molar mass, g mol$^{-1}$** | 278.78 |
| **Crystal system** | orthorhombic |
| **Space group** | Pca$_2_1$ (no. 29) |
| **Single-crystal data** | |
| $T$, K | 268(2) |
| Radiation; wavelength $\lambda$, pm | MoK$\alpha$; 71.07 |
| $a$, Å | 18.3088(8) |
| $b$, Å | 4.4181(2) |
| $c$, Å | 4.2551(2) |
| $V$, Å$^3$ | 344.20(3) |
| $Z$ | 4 |
| Calculated density, g cm$^{-3}$ | 5.38 |
| Absorption coeff., mm$^{-1}$ | 17.0 |
| $F(000)$, e | 500 |
| Crystal size, mm | 0.08 $\times$ 0.03 $\times$ 0.02 |
| $\theta$ range, deg | 3.3 $-$ 41.2 |
| Index ranges $hkl$ | $-32 \leq h \leq 33, -8 \leq k \leq 8, -7 \leq l \leq 7$ |
| Reflections collected | 17034 |
| Independent reflections | 2247 |
| $R_{int}/R_{B}$ | 0.0435 / 0.0250 |
| Completeness to $\theta = 25.2^\circ$, % | 100 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2247/1/87 |
| Goodness-of-fit on $F^2$ | 1.252 |
| Final $R_1$/$wR_2$ indices [$I > 2\sigma(I)$] | 0.0170/0.0378 |
| Final $R_1$/$wR_2$ indices (all data) | 0.0171/0.0378 |
| Largest diff. peak / hole, e Å$^{-3}$ | 3.62 $-$ 2.12 |
| Flack parameter | 0.066(6) |
| **Powder diffraction data** | |
| Radiation; wavelength $\lambda$, pm | MoK$\alpha$; 70.93 |
| $a$, Å | 18.3000(3) |
| $b$, Å | 4.41802(6) |
| $c$, Å | 4.25542(6) |
| $V$, Å$^3$ | 344.050(8) |
| $2\theta$ range, deg | 2.0 $-$ 42.0 |
| $2\theta$ step width, deg | 0.015 |
| $R_{exp}$, % | 2.66 |
| $R_{wp}$, % | 4.21 |
| $R_{B}$, % | 3.12 |

$V = 344.20(3)$ Å$^3$. Table 1 shows all relevant details of the single-crystal structure refinement.

The crystal structure of $\gamma$-Sm(BO$_2$)$_3$ is built up exclusively of BO$_4$ tetrahedra, which are connected by common corners to form a complex borate network. Alongside [001], the BO$_4$ tetrahedra are arranged in ten-membered rings (Figure 2), formed by alternating layers (blue polyhedra) and zig-zag chains of BO$_4$ tetrahedra (light blue polyhedra). The borate layers in the $bc$ plane are extremely condensed, with one third of the oxygen atoms being threefold coordinated. The BO$_4$ tetrahedra within these layers form three- and four-membered rings (Figure 3) with two of the three oxygen atoms in a three-membered ring being threefold coordinated and one of the oxygen atoms in a four-membered ring. Looking onto [010], six-membered rings are developed between the borate layers.

![Figure 1](image1.png)

**Figure 1:** Top: Crystal structure of $\alpha$-Sm(BO$_2$)$_3$ comprising chains of BO$_3$ groups and BO$_4$ tetrahedra. Middle: Corrugated layers in the structure of $\beta$-Sm(BO$_2$)$_3$. Bottom: Network of BO$_4$ tetrahedra in $\gamma$-Sm(BO$_2$)$_3$ forming six-membered rings.

![Figure 2](image2.png)

![Figure 3](image3.png)
and the connecting zig-zag chains (Figure 1, bottom). The B–O bond lengths in this structure range from 1.427(4) to 1.553(4) Å with the longest distances between the threefold coordinated oxygen atom O1 and the respective boron atoms (1.527(4) – 1.553(4) Å), which was found in the iso-
typic compounds γ-RE(BO2)3 (RE = La−Nd) as well [14]. The
average B–O distance of 1.476 Å is in good agreement with
the value of 1.48(4) reported by Zobetz [17]. The O–B–O
angles also lie within a rather wide range of 105.6(3) and
118.5(3)°, but the average value of 109.5° corresponds well
with the expected tetrahedral angle. All the bond lengths
and angles are listed in Table 2 and Table 3. The positional
parameters can be seen in Table 4.

The samarium cations in γ-Sm(BO2)3 are coordinated
by 8 + 2 oxygen atoms and are located in the six-
membered rings along [010]. The ten-membered rings
alongside [001] contain two Sm³⁺ cations each. The Sm–O
distances range from 2.342(6) to 2.838(3) Å, with two
additional oxygen atoms at slightly longer distances of
2.970(3) and 3.025(3) Å, that only coordinate weakly to the
rare earth cations, leading to the 8 + 2 coordination
(Figure 4).

This was confirmed by calculation of the bond valence
sums (ΣV) [18, 19] as well as the values based on the
CHARDI (ΣQ) [20] concept, which show only a small
contribution for these two oxygen atoms. The resulting
formal ionic charges correspond well with the expected
values of +3 for samarium and boron as well as –2 for
oxygen as shown in Table 5.

The newly presented meta-oxoborate γ-Sm(BO2)3 is
isotypic to the already known compounds γ-RE(BO2)3
(RE = La–Nd) and its lattice parameter fit well into this
series, which is shown in Table 6 and Figure 5. The
contraction of the structures due to the smaller radii for the
lanthanide cations going from the left to the right in the
periodic table (lanthanide contraction) is particularly

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**Table 2:** Interatomic B–O and Sm–O distances (Å) for γ-Sm(BO2)3
(standard deviations in parentheses).

|   | B1   |        | B2   |        |
|---|------|--------|------|--------|
| -02| 1.44(5) | B2   | -06  | 1.447(5) |
| -05| 1.45(4) | -03  | 1.451(7) |
| -04| 1.45(9) | -02  | 1.48(7) |
| -01| 1.54(8) | -03  | 1.488(5) |
| Ø  | 1.477 | Ø     | 1.468 |        |

|   | B3   |        | Sm1  | -05  | 2.34(2) |
|---|------|--------|------|------|--------|
| -04| 1.42(5) |      | -05  | 2.34(6) |
| -05| 1.43(2) | -04  | 2.37(4) |
| -01| 1.52(4) | -05  | 2.39(6) |
| -01| 1.55(3) | -01  | 2.42(0) |
| -05| 2.44(2) | -03  | 2.54(2) |
| -02| 2.78(3) | -04  | 2.83(8) |
| -04| 2.83(8) | -01  | 2.97(0) |
| -03| 3.02(5) |      |      |       |

Ø  | 1.485 | Ø     | 2.613 |        |
Table 3: Bond angles/deg for γ-Sm(BO$_3$)$_3$ (standard deviations in parentheses).

| Bond          | Angle (deg)   |
|---------------|--------------|
| O2–B1–O1     | 108.0 (3)    |
| O5–B1–O1     | 108.5 (3)    |
| O4–B1–O1     | 108.7 (2)    |
| O2–B1–O4     | 108.8 (3)    |
| O2–B1–O5     | 109.9 (3)    |
| O5–B1–O4     | 112.9 (3)    |
| Ø             | 109.5        |

Table 4: Atomic coordinates and equivalent isotropic displacement parameters $U_{eq}$ (Å$^2$) of γ-Sm(BO$_3$)$_3$. All atoms are located on Wyckoff positions 4a.

| Atom  | x   | y   | z   | $U_{eq}$ (Å$^2$) |
|-------|-----|-----|-----|------------------|
| Sm1   | 0.33892(2) | 0.69408(3) | 0.00019(8) | 0.00033(5) |
| B1    | 0.0738(2)  | 0.1739(7)   | 0.036(1)   | 0.0026(7)   |
| B2    | 0.2128(2)  | 0.1473(6)   | 0.003(2)   | 0.0025(3)   |
| B3    | 0.4983(2)  | 0.3227(7)   | 0.0613(8)  | 0.0027(3)   |
| O1    | 0.0153(2)  | 0.3681(6)   | 0.2041(5)  | 0.0030(3)   |
| O2    | 0.1450(2)  | 0.2701(6)   | 0.1470(6)  | 0.0030(3)   |
| O3    | 0.2772(2)  | 0.2560(6)   | 0.1843(5)  | 0.0030(3)   |
| O4    | 0.4307(2)  | 0.2305(6)   | 0.1984(6)  | 0.0035(3)   |
| O5    | 0.5618(2)  | 0.1413(6)   | 0.1169(6)  | 0.0033(3)   |
| O6    | 0.7091(2)  | 0.1798(4)   | 0.007(2)   | 0.0034(3)   |

Looking onto [010], the structure of γ-Sm(BO$_3$)$_3$ is very similar to that of the ambient pressure phase SrB$_4$O$_7$ [22–24] and its isotypic compounds PbB$_4$O$_7$ [23, 25] and EuB$_4$O$_7$ [26], as well as the high-pressure borates β-CaB$_4$O$_7$ [27] and β-HgB$_4$O$_7$ [28], exhibiting the same crystal structure. These compounds also feature borate layers in the bc plane that are condensed to form six-membered rings in [010]. In contrast to the γ-meta-oxoborates, these layers are not separated by zig-zag chains of BO$_4$ tetrahedra but are connected directly via a mirror plane (Figure 6). This symmetrical arrangement also leads to an increased cation coordination of CN = 15 by oxygen atoms.

2.2 X-ray powder diffraction

Figure 7 shows the Rietveld refinement plot of γ-Sm(BO$_3$)$_3$ derived from the structural model obtained through single-crystal X-ray diffraction.
crystal diffraction. No obvious side product can be found, but the halo at small 2θ angles indicates the presence of an amorphous phase, most likely excess B₂O₃. The signal at approximately 2θ = 8° stems from the grease that was used to prepare the sample. Further details on the Rietveld refinement can be found in Table 1.

### 2.3 Vibrational spectroscopy

Figure 8 depicts the infrared (IR) spectrum of a γ-Sm(BO₂)₃ powder sample in the range between 400 and 2500 cm⁻¹. In the upper range of the spectrum (2000–4000 cm⁻¹), no vibrational bands due to hydroxyl groups or water are visible. Between 900 and 1200 cm⁻¹, typical stretching vibrations of the BO₄ tetrahedra are present [29]. The absorption bands that appear at around 1300 cm⁻¹ and below 790 cm⁻¹ are in a range normally characteristic for BO₃ groups. Since γ-Sm(BO₂)₃ does not feature BO₃ groups, these bands could be attributed to O–B–Sm, B–O–B, O–B–

Table 5: Bond valence sums and charge distributions according to the bond-length/bond-strength (ΣV) as well as the CHARDI (ΣQ) concept, respectively.

|        | Sm1 | B1 | B2 | B3 | O1 | O2 | O3 | O4 | O5 | O6 |
|--------|-----|----|----|----|----|----|----|----|----|----|
| ΣV    | +2.94 | +3.01 | +3.07 | +2.97 | -1.95 | -2.14 | -1.87 | -1.94 | -1.89 | -2.12 |
| ΣQ    | +2.82 | +3.10 | +2.85 | +3.23 | -2.03 | -1.90 | -2.07 | -2.08 | -2.25 | -1.69 |

Table 6: Comparison of the lattice parameters (Å) and volumes (Å³) of γ-RE(BO₂)₃ (RE = La–Sm).

| Compound          | a       | b       | c       | V       | Reference |
|-------------------|---------|---------|---------|---------|-----------|
| γ-La(BO₂)₃        | 18.482(5) | 4.4781(7) | 4.308(2) | 356.55(9) | [14]      |
| γ-Ce(BO₂)₃        | 18.442(9) | 4.461(2)  | 4.294(2) | 353.3(2)  | [14]      |
| γ-Pr(BO₂)₃        | 18.381(6) | 4.4464(7) | 4.278(2) | 349.6(2)  | [14]      |
| γ-Nd(BO₂)₃        | 18.348(7) | 4.4394(8) | 4.272(2) | 348.0(2)  | [14]      |
| γ-Sm(BO₂)₃        | 18.3088(8) | 4.4181(2) | 4.2551(2) | 344.20(3) | this work |

**Figure 5:** Comparison of the cell parameters and cell volumes in the γ-RE(BO₂)₃ (RE = La–Sm) series.

**Figure 6:** Comparison of the crystal structures of γ-Sm(BO₂)₃ (top) and SrB₄O₇ (bottom).
O, and B–O bending and stretching vibrations, as confirmed by quantum-chemical calculations for β-ZnB₄O₇, a high-pressure compound that also features exclusively BO₄ tetrahedra, and β-CaB₄O₇, which is isotypic to the aforementioned SrB₄O₇ [30]. BO₄ bending vibrations are observed below ~900 cm⁻¹.

3 Conclusion

The new γ-meta-oxoborate γ-Sm(BO₂)₃ has been synthesized under high-pressure/high-temperature conditions of 10 GPa and 1673 K. It is isotypic to the already known series of γ-RE(BO₂)₃ (RE = La–Nd), which were all formed at not so extreme conditions of 7.5 GPa and 1273 K. Besides neodymium, samarium now represents only the second rare earth element that is able to develop the α-, β-, and γ-phase of the meta-oxoborate structure family.

The structure is built up of highly condensed BO₄ layers in the bc plane, which are connected via zig-zag chains of BO₄ tetrahedra. This borate network forms six-membered rings along [010] and ten-membered rings along [001], wherein one or two samarium cations are located, respectively. These Sm³⁺ cations are coordinated by 8 + 2 oxygen atoms.

These findings indicate that the use of higher pressure can be a successful route to further extend the already large meta-oxoborate structure family. Ongoing experiments suggest that also for Eu³⁺, which is even smaller than Sm³⁺, the γ-meta-oxoborate crystal structure can be formed at sufficiently high pressure.

4 Experimental section

4.1 Synthesis

A high-pressure/high-temperature experiment in a hydraulic 1000 t press with a modified Walker-type module (both Max Voggenreiter GmbH, Germany) was performed to obtain the title compound γ-Sm(BO₂)₃. A mixture of a stoichiometric ratio (1:6) of Sm₂O₃ (Smart Elements, Wien, Austria, 99.9%) and H₃BO₃ (Carl Roth, Karlsruhe, Germany, >99.8%) was ground together in an agate mortar filled into a Pt capsule, that was placed in an α-BN crucible, closed with a lid of the same material (both Henze Boron Nitride Products AG, Germany) and subsequently centered in a pressure transmitting octahedron (MgO, doped with 5% Cr₂O₃; Ceramic Substrates & Components Ltd, Newport, United Kingdom). The high-pressure/high-temperature experiment was carried out in an 18/11 assembly. A more detailed description of the experimental setup can be found in the literature [31–33].

The sample was compressed to 10 GPa in 270 min and then heated up to 1673 K in the following 15 min. This temperature was kept for the next 10 min, before it was lowered to room temperature in the following 25 min. Afterwards, the pressure was relieved in the following 810 min. The product was found to be light green crystal needles of γ-Sm(BO₂)₃.

4.2 X-ray diffraction measurements

The reaction product was characterized by powder diffraction analysis on a STOE Stadi P powder
diffractometer (STOE & Cie GmbH, Darmstadt, Germany), carried out on a flat sample in transmission geometry. The measurement was performed with Ge(111)-monochromatized MoKa radiation (λ = 70.93 pm) and detected with a Mythen 1 K detector (Dectris) in the 2θ range of 2–52° with a step size of 0.015°. The Rietveld refinement was performed employing the TOPAS 4.2 software [34].

For the single-crystal structure analyses, suitable crystals were separated under a polarization microscope and measured on a Bruker D8 Quest Kappa diffractometer equipped with an Incoatec microfocus X-ray tube, a multilayer optic to generate monochromatized MoKa radiation (λ = 0.7107 Å) and a Photon 100 CMOS detector. Reflections were measured in the range 3.3 ≤ θ ≤ 41.2° and the structure solution and parameter refinement were performed with Direct Methods using SHELXS/L-2017/1 [35, 36] implemented in the program WINGX-2013.3 [37]. All atoms except the boron atom B2 could be refined with anisotropic displacement parameters. The atomic coordinates were standardized employing STRUCTURE TIDY [38] as implemented in PLATON [39].

Further details of the crystal structure investigation may be obtained from The Cambridge Crystallographic Data Centre CCDC/FIZ Karlsruhe deposition service via www.ccdc.cam.ac.uk/structures on quoting the deposition number CCDC 1995888 for γ-Sm(BO$_2$)$_3$.

### 4.3 Vibrational spectroscopy

For further characterization of γ-Sm(BO$_2$)$_3$, an FTIR-ATR (Attenuated Total Reflection) spectrum of a powder sample was acquired with a Bruker ALPHA Platinum-ATR spectrometer (Bruker, Billerica, USA). The spectrometer is provided with a 2 × 2 mm diamond ATR-crystal and a DTGS detector. 320 scans of the powder sample were obtained in the spectral range of 400–4000 cm$^{-1}$ and afterwards corrected for atmospheric influences employing the OPUS 7.2 software [40].

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