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High-pressure synthesis and crystal structure of the samarium *meta*-oxoborate γ -Sm(BO₂)₃

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Abstract: γ -Sm(BO₂)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*2₁ (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*-oxoborates γ -RE(BO₂)₃ ($RE = \text{La–Nd}$) 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 α -, β -, and γ -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 BO₄ tetrahedra as in RE₄B₆O₁₅ ($RE = \text{Dy, Ho}$) [1, 2] and α -RE₂B₄O₉ ($RE = \text{Sm–Ho}$) [3–5], or RE₃B₅O₁₂ ($RE = \text{Sc, Er–Lu}$) [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 RE(BO₂)₃ ($RE = \text{rare earth}$), discoveries are still made to date. Here, four modifications are known, designated with the Greek letters α , β , γ , and δ . The longest known α -phase

is well characterized, crystallizing in the monoclinic space group *C2/c* and is built up of chains of planar BO₃ and tetrahedral BO₄ units (Figure 1, top). The first detailed description of the crystal structure of the β -modification (Figure 1, middle), more accurate β -Tb(BO₂)₃, was published in 2003 by Nikelski and Schleid [8]. Further isotypic compounds of the series β -RE(BO₂)₃ ($RE = \text{Y, Nd, Sm–Gd, Dy–Lu}$) [9–12] were synthesized under high-pressure conditions and β -Dy(BO₂)₃ additionally at ambient pressure conditions [13]. Investigations into the larger lanthanides led to another modification, designated as γ -phase (Figure 1, bottom), for γ -RE(BO₂)₃ ($RE = \text{La–Nd}$) under pressures of at least 7.5 GPa [14]. While the β -modification crystallizes in the orthorhombic space group *Pnma*, the γ -modification adopts the space group *Pca*2₁. For lanthanum and cerium, yet another monoclinic modification was found, δ -La(BO₂)₃ [15] and δ -Ce(BO₂)₃ [16] at 5.5 and 3.5 GPa, respectively.

In contrast to the α -phase, all three other modifications are built up exclusively of BO₄ 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 δ -RE(BO₂)₃ ($RE = \text{La, Ce}$) and every third of the oxygen atoms in γ -RE(BO₂)₃ ($RE = \text{La–Nd}$).

In this work, we present γ -Sm(BO₂)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 β - as well as the γ -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

γ -Sm(BO₂)₃ crystallizes, like its isotypic compounds γ -RE(BO₂)₃ ($RE = \text{La–Nd}$), in the orthorhombic space group *Pca*2₁ (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

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$V = 344.20(3) \text{ \AA}^3$. Table 1 shows all relevant details of the single-crystal structure refinement.

The crystal structure of γ -Sm(BO₂)₃ is built up exclusively of BO₄ tetrahedra, which are connected by common corners to form a complex borate network. Alongside [001],

Figure 1: Top: Crystal structure of α -Sm(BO₂)₃ comprising chains of BO₃ groups and BO₄ tetrahedra. Middle: Corrugated layers in the structure of β -Sm(BO₂)₃. Bottom: Network of BO₄ tetrahedra in γ -Sm(BO₂)₃ forming six-membered rings.

Table 1: Crystal data and structure refinement of γ -Sm(BO₂)₃.

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

the BO₄ tetrahedra are arranged in ten-membered rings (Figure 2), formed by alternating layers (blue polyhedra) and zig-zag chains of BO₄ 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 BO₄ 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 2: Crystal structure of γ -Sm(BO₂)₃ viewed along [001]. The borate layers (blue polyhedra) and zig-zag chains of BO₄ tetrahedra (light blue polyhedra) form ten-membered rings.

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 isotopic compounds γ -RE(BO₂)₃ (RE = La–Nd) as well [14]. The

Figure 3: One of the borate layers of γ -Sm(BO₂)₃ viewed parallel to the *bc* plane. The BO₄ tetrahedra form three- and four-membered rings. Threefold-coordinated oxygen atoms are shown in light blue.

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 isotopic 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

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

B1	–O2	1.449(5)	B2	–O6	1.447(3)
	–O5	1.452(4)		–O3	1.451(7)
	–O4	1.459(5)		–O2	1.487(5)
	–O1	1.548(4)		–O3	1.488(5)
∅		1.477	∅		1.468
B3	–O4	1.428(5)	Sm1	–O5	2.342(6)
	–O5	1.432(4)		–O4	2.374(3)
	–O1	1.527(4)		–O5	2.395(6)
	–O1	1.553(4)		–O1	2.420(3)
				–O5	2.442(2)
				–O3	2.548(2)
				–O2	2.780(3)
				–O4	2.838(3)
				–O1	2.970(3)
				–O3	3.025(3)
∅		1.485	∅		2.613

Table 3: Bond angles/deg for γ -Sm(BO₂)₃ (standard deviations in parentheses).

O2–B1–O1	108.0(3)	O3–B2–O3	106.1(2)	O4–B3–O1	105.6(3)
O5–B1–O1	108.5(3)	O6–B2–O2	108.7(3)	O5–B3–O1	105.6(3)
O4–B1–O1	108.7(2)	O2–B2–O3	109.3(4)	O4–B3–O1	107.3(3)
O2–B1–O4	108.8(3)	O6–B2–O3	110.3(5)	O1–B3–O1	107.9(2)
O2–B1–O5	109.9(3)	O6–B2–O3	110.7(3)	O5–B3–O1	111.4(3)
O5–B1–O4	112.9(3)	O3–B2–O2	111.7(3)	O4–B3–O5	118.5(3)
Ø	109.5	Ø	109.5	Ø	109.4

Table 4: Atomic coordinates and equivalent isotropic displacement parameters U_{eq} (Å²) of γ -Sm(BO₂)₃. All atoms are located on Wyckoff positions 4a.

Atom	x	y	z	U_{eq}
Sm1	0.33892(2)	0.69408(3)	0.00019(8)	0.00333(5)
B1	0.0738(2)	0.1739(7)	0.036(1)	0.0024(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(6)	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)

distinct for the a parameter. The crystal structure seems to be more compressible in this direction because of the looser connectivity between the layers and the chains of BO₄ tetrahedra compared to the shrinkage within the layers in the bc plane.

Samarium now represents the second lanthanide cation, the other being neodymium, to form the α -, β -, and γ -meta-oxoborate. The compound presented here was synthesized under quite extreme conditions of 10 GPa and 1673 K, while the β -compound γ -Sm(BO₂)₃ was first found at conditions of 7.5 GPa and 1323 K. Recent investigations in connection with the neighbouring phase β -Eu(BO₂)₃ have demonstrated that β -Sm(BO₂)₃ can already be formed at lower pressures of 4 GPa. This difference in the required pressure can also be observed for the compounds β - and γ -Nd(BO₂)₃. Here, the β -compound was found at 3.5 GPa and the γ -compound at 7.5 GPa.

This structure type has also been found for BiB₃O₆ prepared under high-pressure conditions of 5.5 GPa and 1093 K, designated as δ -BiB₃O₆. The two compounds differ mainly in the coordination of the cation [21]. Because of the sterically active lone pair of Bi³⁺, the cation is only seven-fold coordinated by oxygen atoms and the Bi–O distances are slightly shorter (2.26–2.73 Å) than in the γ -Sm(BO₂)₃ form presented here (Sm–O = 2.342–3.025 Å).

Looking onto [010], the structure of γ -Sm(BO₂)₃ is very similar to that of the ambient pressure phase SrB₄O₇ [22–24] and its isotypic compounds PbB₄O₇ [23, 25] and EuB₄O₇ [26], as well as the high-pressure borates β -CaB₄O₇ [27] and β -HgB₄O₇ [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 BO₄ 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(BO₂)₃ derived from the structural model obtained through single-

Figure 4: Coordination sphere of the Sm³⁺ cation in γ -Sm(BO₂)₃. Sm–O distances shown in Å.

Table 5: Bond valence sums and charge distributions according to the bond-length/bond-strength ($\sum V$) as well as the CHARDI ($\sum Q$) concept, respectively.

	Sm1	B1	B2	B3	O1	O2	O3	O4	O5	O6
$\sum V$	+2.94	+3.01	+3.07	+2.97	−1.95	−2.14	−1.87	−1.94	−1.89	−2.12
$\sum Q$	+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	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	Reference
γ -La(BO ₂) ₃	18.482(5)	4.4781(7)	4.308(2)	356.55(9)	[14]
γ -Ce(BO ₂) ₃	18.442(9)	4.461(2)	4.294(2)	353.3(2)	[14]
γ -Pr(BO ₂) ₃	18.381(6)	4.4464(7)	4.278(2)	349.6(2)	[14]
γ -Nd(BO ₂) ₃	18.348(7)	4.4394(8)	4.272(2)	348.0(2)	[14]
γ -Sm(BO ₂) ₃	18.3088(8)	4.4181(2)	4.2551(2)	344.20(3)	this work

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 $2\theta = 8^\circ$ 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–

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).

Figure 7: Rietveld refinement plot of γ -Sm(BO₂)₃.

Figure 8: IR spectrum of a γ -Sm(BO₂)₃ powder sample.

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 isotopic 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 isotopic 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 grinded together in an agate mortar under ambient conditions and 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 MoK α_1 radiation ($\lambda = 70.93$ 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 MoK α radiation ($\lambda = 0.7107$ Å) and a Photon 100 CMOS detector. Reflections were measured in the range $3.3 \leq \theta \leq 41.2^\circ$ 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(BO₂)₃.

4.3 Vibrational spectroscopy

For further characterization of γ -Sm(BO₂)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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