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β -Eu(BO₂)₃ – a new member of the β -RE(BO₂)₃ (RE=Y, Nd, Sm, Gd–Lu) structure family

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Abstract: The title compound β -Eu(BO₂)₃ was synthesized in a high-pressure/high-temperature experiment at 4 GPa and 1473 K. The europium borate crystallizes in the orthorhombic space group *Pnma* (no. 62) with the lattice parameters $a=16.071(2)$, $b=7.440(4)$, and $c=12.362(5)$ Å. The structure is isotypic to the already known *meta*-borates β -RE(BO₂)₃ (RE=Y, Nd, Sm, Gd, Dy–Lu) and is built up of approximately triangular ribbons of BO₄ tetrahedra. The compound was further characterized by X-ray powder diffraction, vibrational spectroscopy and shows a typical Eu³⁺ line emission upon excitation at 448 nm.

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

1 Introduction

In the past years, high-pressure investigations on rare earth borates led to a variety of new compositions that were not accessible under ambient pressure conditions. In the year 2002, the Huppertz group was able to synthesize the new compounds RE₄B₆O₁₅ (RE=Dy, Ho) with a molar ratio of metal to boron of 2:3 [1, 2]. Next to an unknown composition, Dy₄B₆O₁₅ was the first borate showing the structural feature of edge-sharing BO₄ tetrahedra. Further investigations into this system led to a variety of other compounds with previously unknown metal to boron ratios, like for example 1:2 in α -RE₂B₄O₉ (RE=Y, Sm–Ho) [3–5] and β -RE₂B₄O₉ (RE=Gd, Dy) [6, 7], or 3:5 in RE₃B₅O₁₂ (RE=Sc, Er–Lu) [8, 9]. Very recently, we were able to describe the hitherto unknown compound YB₇O₁₂, a highly condensed structure with an exceptionally low metal to boron ratio of 1:7 [10]. These examples impressively demonstrate the

potential of the high-pressure technique for the discovery of new compounds in the field of borates.

In addition, it was also possible to synthesize new modifications of already existing compositions. For example, in the field of rare earth *meta*-borates, four modifications of the composition RE(BO₂)₃ (RE=rare earth) are known to date, designated with the Greek letters α , β , γ , and δ . The monoclinic α -phase represents the longest known modification and is built up of chains of planar BO₃ and tetrahedral BO₄ units. For the β -modification, the first detailed description of the crystal structure was published by Nikelski and Schleid in 2003 [11], who synthesized the orthorhombic *meta*-borate β -Tb(BO₂)₃ in sealed platinum ampoules. Subsequently, the syntheses of the phases β -RE(BO₂)₃ (RE=Y, Nd, Sm, Gd, Dy–Lu) [12–14] were reported under high-pressure conditions. In 2008, Nikelski et al. [15] showed that the synthesis of β -Dy(BO₂)₃ was also possible under ambient pressure. For the larger lanthanides, two additional modifications were discovered under high-pressure conditions, e.g. at 7.5 GPa represented by γ -RE(BO₂)₃ (RE=La–Nd) [16] and at 5.5 and 3.5 GPa by δ -La(BO₂)₃ [17] and δ -Ce(BO₂)₃ [18], respectively.

To date, the ICSD (International Crystal Structure Database) lists six ternary europium borates that were obtained at ambient conditions, EuB₂O₄, EuB₄O₇, Eu₂B₂O₅ [19, 20], Eu₃(BO₂)₃ [21], EuBO₃ [22], and EuB₃O₆ [= α -Eu(BO₂)₃] [23], but only one high-pressure europium borate phase, α -Eu₂B₄O₉ [4], is known. Interestingly, no high-pressure *meta*-borate of europium has been described. In this work, we report the hitherto missing compound β -Eu(BO₂)₃ that completes the series of phases with the β -RE(BO₂)₃ structure type from neodymium to lutetium (without promethium). The new compound exhibits typical fluorescence bands of Eu³⁺ obtained upon excitation at 448 nm, which are presented below along with the results of the crystal structure determination and of vibrational spectroscopic investigations.

2 Results and discussion

2.1 Crystal structure

β -Eu(BO₂)₃ crystallizes in the orthorhombic space group *Pnma* (no. 62) like its isotypic compounds β -RE(BO₂)₃

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(RE = Y, Nd, Sm, Gd–Lu) [12–14]. The unit cell ($Z=16$) exhibits the lattice parameters $a=16.071(2)$, $b=7.440(4)$, and $c=12.362(5)$ Å and a volume of $V=1478.1(1)$ Å³. All relevant details of the structure refinement based on single-crystal data are listed in Table 1.

The anionic backbone of β -Eu(BO₂)₃ is built up exclusively of BO₄ tetrahedra. Three of them, namely those with the boron atoms B1, B2, and B3, are connected via the common oxygen atom O7 and form a “windmill-like” structural unit (Fig. 1, top). These “windmills” are linked by three [B₂O₇] groups developing the fundamental building block (FBB) that comprises 12 BO₄ tetrahedra (Fig. 1, bottom). Through the interconnection of the FBBs, infinite ribbons with an approximately triangular cross section are formed along [010] (Fig. 2). These ribbons are connected by the common oxygen atoms O15 to form corrugated layers parallel to the bc plane. The oxygen atom O14 constitutes the only oxygen atom that is coordinated to just one boron atom and represents the terminal corner of the triangular strand.

The B–O distances and O–B–O angles lie in the ranges 1.435(3)–1.531(2) Å and 103.5(2)–115.1(2)°, respectively (Tables 2 and 3). The corresponding average values of 1.474 Å

Table 1: Crystal data and structure refinement of β -Eu(BO₂)₃.

Empirical formula	β -Eu(BO ₂) ₃
Molar mass, g mol ⁻¹	280.39
Crystal system	Orthorhombic
Space group	$Pnma$ (no. 62)
Single-crystal data	
T , K	285(2)
Radiation/ λ , pm	MoK α /71.07
a , Å	16.071(2)
b , Å	7.440(4)
c , Å	12.362(5)
V , Å ³	1478.1(1)
Z	16
Calculated density, g cm ⁻³	5.04
Absorption coeff., mm ⁻¹	16.9
$F(000)$, e	2016
Crystal size, mm ³	0.120 × 0.030 × 0.020
θ range, deg	2.1–38.6
Index ranges	–27 ≤ h ≤ 28 –13 ≤ k ≤ 13 –21 ≤ l ≤ 21
Reflections collected	52777
Independent reflections/ R_{int}	4393/0.0352
Completeness to $\theta = 25.2^\circ$, %	100
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4393/197
Goodness-of-fit on F^2	1.457
Final $R1/wR2$ indices [$I > 2 \sigma(I)$]	0.0197/0.0483
Final $R1/wR2$ indices (all data)	0.0197/0.0483
Largest diff. peak/hole, e Å ⁻³	1.52/–4.04

Fig. 1: Top: “windmill-like” structural unit comprising three BO₄ tetrahedra that are connected via the common oxygen atom O7. Bottom: Connection of the “windmill-like” units through [B₂O₇] groups (light blue) to form infinite ribbons along [010]. Red spheres: boron; blue spheres: oxygen.

and 109.48° are similar to the those reported by Zobetz [1.476(35) Å/109.44(2.78)°] [24]. Interestingly, the two tetrahedra that exhibit both the lowest and the broadest spreading of their O–B–O angles are those which connect the triangular ribbons, B4O₄ and B6O₄, respectively.

The europium cations are located between the anionic BO layers (Fig. 3). The four crystallographically independent Eu³⁺ cations are each coordinated by eight oxygen atoms, forming irregularly shaped polyhedra (Fig. 4). The Eu–O distances range from 2.298 to 2.877 Å (see

Fig. 2: Triangular cross section of the fundamental building block (FBB) along [010]. Common oxygen atoms O15 form the link between two of these units at a time. Red spheres: boron; blue spheres: oxygen.

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

B1	–O8	1.455(3)	B2	–O2	1.451(2)	B3	–O13	1.435(3)
	–O1	1.459(2)		–O10	1.454(3)		–O12	1.445(2)
	–O9	1.472(3)		–O11	1.483(3)		–O3	1.486(2)
	–O7	1.507(2)		–O7	1.530(3)		–O7	1.531(2)
∅		1.473	∅		1.480	∅		1.474
B4	–O13	1.458(3)	B5	–O14	1.443(3)	B6	–O12	1.442(3)
	–O5	1.465(2)		–O10	1.444(3)		–O4	1.445(2)
	–O8	1.469(3)		–O6	1.511(2)		–O15	1.473(3)
	–O15	1.471(3)		–O9	1.517(3)		–O11	1.518(3)
∅		1.466	∅		1.479	∅		1.470

Table 4), which is in good agreement with the Sm–O and Gd–O distances in the isotopic compounds β -Sm(BO₂)₃ and β -Gd(BO₂)₃ (2.306–2.899 Å and 2.289–2.867 Å, respectively)

Table 3: Bond angles (deg) for β -Eu(BO₂)₃ (standard deviations in parentheses).

O8–B1–O9	106.4(2)	O10–B2–O7	107.1(2)	O12–B3–O3	106.6(2)
O8–B1–O1	107.0(2)	O10–B2–O11	107.4(2)	O13–B3–O7	107.6(2)
O1–B1–O9	109.6(2)	O2–B2–O11	107.9(2)	O13–B3–O12	108.9(2)
O9–B1–O7	110.5(2)	O2–B2–O10	110.3(2)	O12–B3–O7	109.3(2)
O1–B1–O7	111.1(2)	O11–B2–O7	111.3(2)	O13–B3–O3	111.4(2)
O8–B1–O7	112.1(2)	O2–B2–O7	112.7(2)	O3–B3–O7	113.1(2)
∅	109.5	∅	109.5	∅	109.5
O5–B4–O15	106.2(2)	O6–B5–O9	105.4(2)	O4–B6–O11	103.5(2)
O8–B4–O15	109.1(2)	O14–B5–O6	107.5(2)	O12–B6–O15	105.3(2)
O13–B4–O5	109.9(2)	O14–B5–O9	107.5(2)	O12–B6–O11	107.0(2)
O13–B4–O8	110.1(2)	O10–B5–O9	109.7(2)	O4–B6–O15	112.0(2)
O5–B4–O8	110.7(2)	O10–B5–O6	111.4(2)	O15–B6–O11	114.1(2)
O13–B4–O15	110.7(2)	O14–B5–O10	114.8(2)	O12–B6–O4	115.1(2)
∅	109.5	∅	109.4	∅	109.5

[14]. Also in comparison to another high-pressure europium-borate, α -Eu₂B₄O₉, which was synthesized at 10 GPa/1423 K and possesses Eu–O distances between 2.26 and 3.04 Å [4], the aforementioned Eu–O distances of β -Eu(BO₂)₃ lie within the same range.

The bond valence sums were calculated for all atoms in β -Eu(BO₂)₃ according to both, the bond-length/bond-strength (ΣV) [25, 26] as well as the CHARDI (ΣQ) [27] concept (Table 5). The formal ionic charges are in good agreement with the expected values within the limits of the concepts.

Table 6 and Fig. 5 allow a comparison of the lattice parameters and cell volumes of β -Eu(BO₂)₃ with those of the already known *meta*-borates β -RE(BO₂)₃ (RE=Y, Nd, Sm, Gd–Lu). The new europium compound fits well into this scheme. The positional parameters as well as the isotropic and anisotropic displacement parameters of the new phase are listed in Tables 7 and 8.

Interestingly, the title compound was synthesized at 4 GPa, while its neighbors β -Sm(BO₂)₃ and β -Gd(BO₂)₃ were obtained at 7.5 GPa. We tried to receive the latter two borates at the same conditions as the Eu compound, and this turned out to be possible. In contrast, when we tried to synthesize β -Eu(BO₂)₃ at 7.5 GPa, we only received the already known compounds EuB₄O₇ [19, 20] and α -Eu₂B₄O₉ [4].

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 1941204 for β -Eu(BO₂)₃.

2.2 X-ray powder diffraction

Figure 6 shows a comparison between the experimental X-ray powder diffraction pattern and the theoretical powder

Fig. 3: Layered structure of β -Eu(BO₂)₃ where the ribbons with approximately triangular cross section are interconnected *via* common vertices along [001]. The europium cations are located between the layers.

Fig. 4: Coordination spheres of the four crystallographically independent Eu³⁺ atoms in β -Eu(BO₂)₃.

pattern derived from the single-crystal data of β -Eu(BO₂)₃. Obviously the product was obtained phase-pure, as no side phase is visible in the experimental pattern.

2.3 Vibrational spectroscopy

The infrared (IR) spectrum of the β -Eu(BO₂)₃ powder sample in the range between 400 and 2500 cm⁻¹ is displayed in Fig. 7. Typical stretching vibrations of the BO₄ tetrahedra occur in the region between 900 and 1200 cm⁻¹

Table 4: Interatomic Eu–O distances (Å) for β -Eu(BO₂)₃ (standard deviations in parentheses).

Eu1	–O15	2.368(2)	2×	Eu2	–O12	2.338(2)	2×
	–O1	2.381(2)			–O5	2.416(2)	
	–O8	2.423(2)	2×		–O9	2.445(2)	2×
	–O9	2.548(2)	2×		–O14	2.475(2)	2×
	–O6	2.671(2)			–O3	2.584(2)	
∅		2.466		∅		2.440	
Eu3	–O13	2.304(2)	2×	Eu4	–O14	2.298(2)	2×
	–O6	2.378(2)			–O10	2.318(2)	2×
	–O11	2.468(2)	2×		–O4	2.341(2)	
	–O14	2.568(2)	2×		–O11	2.529(2)	2×
	–O2	2.649(2)			–O3	2.877(2)	
∅		2.463		∅		2.439	

[28]. The absorptions that appear between approximately 1300 and 1400 cm⁻¹, around 1200 cm⁻¹ and below 790 cm⁻¹ would be assigned to vibrations of BO₃ groups in standard cases. Since there are no BO₃ groups present in this compound, these vibrational bands may be due to O–B–Eu, B–O–B, O–B–O, and B–O bending and stretching vibrations, as was confirmed by quantum-chemical calculations for β -ZnB₄O₇ and β -CaB₄O₇, two high-pressure compounds that also only feature exclusively BO₄ tetrahedra connected via threefold coordinated oxygen atoms [29]. BO₄ bending vibrations are observed below ~900 cm⁻¹. In the upper range of the spectrum (2000–4000 cm⁻¹), no absorption bands due to hydroxyl groups or H₂O were visible.

2.4 Luminescence properties

The photoluminescence measurements were carried out on a polycrystalline sample. An emission spectrum was collected on excitation at 448 nm (Fig. 8). For orthorhombic structures, five groups of Eu³⁺ transitions are assigned to the ⁵D₀ → ⁷F_J (J=0–4) transitions as follows: a weak, single band at 579 nm is due to the ⁵D₀ → ⁷F₀ transition. The magnetic dipole transitions (⁵D₀ → ⁷F₁) in the region between 583 and 596 nm are less intense than the electric dipole transitions (⁵D₀ → ⁷F₂) between 614 and 624 nm [30]. This also confirms the presented crystal structure, in which no inversion center was found in the four crystallographic independent Eu³⁺ sites [31]. The ⁵D₀ → ⁷F₃ transitions may be attributed to the weak bands around 649 nm while the ⁵D₀ → ⁷F₄ transitions are visible in the region from 681 to 705 nm. Interestingly, no concentration quenching is observed in this compound, even though Eu³⁺ is the sole cationic species present. For the europium borates EuBO₃, EuB₂O₄, and EuB₄O₇ also no quenching effects were observed [20, 22].

Table 5: Charge distributions according to both the bond-length/bond-strength (ΣV) and the CHARDI (ΣQ) concept.

	Eu1	Eu2	Eu3	Eu4	B1	B2	B3	B4	B5	B6
ΣV	+2.89	+3.05	+3.02	+3.33	+3.04	+2.99	+3.04	+3.10	+3.00	+3.08
ΣQ	+2.93	+2.75	+2.78	+2.74	+3.21	+3.44	+3.35	+3.10	+2.68	+3.02
	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10
ΣV	−2.02	−1.82	−1.72	−2.13	−1.95	−2.01	−1.99	−1.96	−2.08	−2.14
ΣQ	−1.93	−1.82	−1.90	−2.06	−2.02	−2.18	−1.80	−1.95	−2.08	−2.07
	O11	O12	O13	O14	O15					
ΣV	−2.08	−2.14	−2.17	−1.98	−1.98					
ΣQ	−2.01	−1.99	−1.98	−2.20	−1.99					

Table 6: Comparison of the lattice parameters (Å) and volumes (Å³) of β -RE(BO₂)₃ (RE = Y, Nd, Sm–Lu).

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	Reference
β -Y(BO ₂) ₃	15.886(2)	7.3860(6)	12.2119(9)	1432.8(2)	[12]
β -Nd(BO ₂) ₃	16.162(3)	7.474(2)	12.442(3)	1502.8(5)	[14]
β -Sm(BO ₂) ₃	16.125(2)	7.4602(4)	12.4087(7)	1492.7(2)	[14]
β -Eu(BO ₂) ₃	16.071(2)	7.440(4)	12.362(5)	1478.1(1)	This work
β -Gd(BO ₂) ₃	16.028(2)	7.4270(4)	12.3217(7)	1466.8(2)	[14]
β -Tb(BO ₂) ₃	15.9897(9)	7.4139(4)	12.2958(7)	1457.6(2)	[11]
β -Dy(BO ₂) ₃	15.930(2)	7.402(2)	12.264(1)	1446(1)	[13, 15]
β -Ho(BO ₂) ₃	15.919(2)	7.395(2)	12.233(2)	1440(1)	[13]
β -Er(BO ₂) ₃	15.876(2)	7.380(2)	12.189(2)	1428(1)	[13]
β -Tm(BO ₂) ₃	15.816(2)	7.362(2)	12.162(2)	1416(1)	[13]
β -Yb(BO ₂) ₃	15.791(3)	7.352(2)	12.140(3)	1410(1)	[13]
β -Lu(BO ₂) ₃	15.767(2)	7.347(2)	12.115(2)	1403(1)	[13]

Fig. 5: Comparison of the cell parameters in the β -RE(BO₂)₃ (RE = Y, Nd, Sm–Lu) series.

3 Conclusion

In this work, we have presented a new member of the β -RE(BO₂)₃ (RE = Y, Nd, Sm, Gd–Lu) structure family. The hitherto missing β -Eu(BO₂)₃, synthesized at 4 GPa and

1473 K, completes the series of β -meta-borates from samarium to lutetium. The compound is built up of ribbons with triangular cross section along [010], which form corrugated layers parallel to the *bc* plane. Between those borate layers, the four crystallographically independent europium cations are located.

In contrast to the isotypic compounds β -Sm(BO₂)₃ and β -Gd(BO₂)₃ that were synthesized at 7.5 GPa, the europium meta-borate could not be obtained at higher pressures than the reported 4 GPa.

The compound has been characterized by single-crystal X-ray analyses and vibrational spectroscopy. In contrast to the aforementioned isotypic Sm³⁺ and Gd³⁺ analogues, β -Eu(BO₂)₃ exhibits a bright red emission.

4 Experimental section

4.1 Synthesis

For the synthesis of the title compound β -Eu(BO₂)₃, the starting materials Eu₂O₃ (Smart Elements, Wien, Austria,

Table 7: Wyckoff positions, atomic coordinates, and equivalent isotropic displacement parameters U_{eq} (Å²).

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Eu1	4c	0.54789(2)	1/4	0.58679(2)	0.00379(3)
Eu2	4c	0.87323(2)	1/4	0.22628(2)	0.00365(3)
Eu3	4c	0.82875(2)	3/4	0.43164(2)	0.00347(3)
Eu4	4c	0.37974(2)	1/4	−0.00582(2)	0.00334(3)
B1	8d	0.5584(2)	0.0732(3)	0.3450(2)	0.0034(3)
B2	8d	0.6102(2)	0.4229(3)	0.1445(2)	0.0034(3)
B3	8d	0.7174(2)	0.4292(3)	0.3135(2)	0.0037(3)
B4	8d	0.6542(2)	0.5757(3)	0.4817(2)	0.0035(3)
B5	8d	0.4701(2)	0.5615(3)	0.1794(2)	0.0035(3)
B6	8d	0.7568(2)	0.9310(3)	0.1292(2)	0.0035(3)
O1	4c	0.5479(2)	1/4	0.3942(2)	0.0050(3)
O2	4c	0.5786(2)	1/4	0.1089(2)	0.0044(3)
O3	4c	0.7451(2)	1/4	0.3525(2)	0.0043(3)
O4	4c	0.7248(2)	3/4	0.1376(2)	0.0046(3)
O5	4c	0.6611(2)	3/4	0.5360(2)	0.0040(3)
O6	4c	0.4381(2)	3/4	0.1980(2)	0.0051(3)
O7	8d	0.6296(8)	0.4270(2)	0.2656(2)	0.0029(2)
O8	8d	0.5715(9)	0.5539(2)	0.4329(2)	0.0044(2)
O9	8d	0.4807(9)	0.4809(2)	0.2912(2)	0.0044(2)
O10	8d	0.5492(9)	0.5630(2)	0.1239(2)	0.0037(2)
O11	8d	0.6851(9)	0.4653(2)	0.0792(2)	0.0038(2)
O12	8d	0.7759(9)	0.4835(2)	0.2309(2)	0.0049(2)
O13	8d	0.7185(9)	0.5597(2)	0.3989(2)	0.0038(2)
O14	8d	0.4052(1)	0.4621(2)	0.1252(2)	0.0048(2)
O15	8d	0.6655(9)	0.4385(2)	0.5661(2)	0.0038(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

Table 8: Anisotropic displacement parameters U_{ij} (Å²) (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu1	0.00233(5)	0.00454(6)	0.00449(5)	0	−0.00014(3)	0
Eu2	0.00319(5)	0.00453(5)	0.00322(5)	0	−0.00012(3)	0
Eu3	0.00251(5)	0.00383(5)	0.00409(5)	0	0.00017(3)	0
Eu4	0.00445(6)	0.00320(5)	0.00239(5)	0	−0.00026(3)	0
B1	0.0028(6)	0.0046(7)	0.0028(6)	−0.0003(5)	−0.0008(5)	0.0004(6)
B2	0.0027(6)	0.0042(7)	0.0032(6)	0.0001(5)	0.0003(5)	−0.0003(6)
B3	0.0030(7)	0.0050(7)	0.0031(6)	0.0003(6)	0.0000(5)	−0.0010(6)
B4	0.0037(7)	0.0038(7)	0.0029(6)	−0.0012(6)	−0.0002(5)	−0.0002(6)
B5	0.0024(6)	0.0046(7)	0.0033(6)	−0.0003(5)	−0.0010(5)	0.0002(6)
B6	0.0024(7)	0.0043(7)	0.0037(6)	0.0002(5)	−0.0004(5)	0.0000(6)
O1	0.0074(8)	0.0036(7)	0.0040(7)	0	0.0027(6)	0
O2	0.0043(7)	0.0030(7)	0.0058(7)	0	−0.0019(6)	0
O3	0.0053(7)	0.0025(7)	0.0052(7)	0	−0.0010(6)	0
O4	0.0033(7)	0.0034(7)	0.0071(8)	0	0.0000(6)	0
O5	0.0058(7)	0.0035(7)	0.0027(7)	0	−0.0002(6)	0
O6	0.0041(7)	0.0034(7)	0.0078(8)	0	0.0010(6)	0
O7	0.0011(5)	0.0059(5)	0.0017(4)	0.0001(4)	−0.0003(3)	−0.0001(4)
O8	0.0024(5)	0.0062(5)	0.0044(5)	−0.0024(4)	−0.0009(4)	0.0003(4)
O9	0.0021(5)	0.0082(5)	0.0029(5)	0.0012(4)	−0.0005(4)	0.0003(4)
O10	0.0026(5)	0.0043(5)	0.0043(5)	0.0011(4)	0.0016(4)	0.0014(4)
O11	0.0026(5)	0.0050(5)	0.0037(5)	−0.009(4)	0.0008(4)	−0.0008(4)
O12	0.0018(5)	0.0088(6)	0.0041(5)	0.0026(4)	0.0008(4)	0.0009(4)
O13	0.0020(5)	0.0050(5)	0.0044(5)	−0.0016(4)	0.0008(4)	−0.0007(4)
O14	0.0041(5)	0.0063(5)	0.0041(5)	−0.0012(4)	−0.0013(4)	−0.0010(4)
O15	0.0022(5)	0.0043(5)	0.0048(5)	0.0020(4)	−0.0019(4)	−0.0011(4)

99.99%) and B₂O₃ (Strem Chemicals, Newburyport, MA, USA, 99.9+ %) were grinded together in the stoichiometric ratio of 1:3 under ambient conditions. The homogenized mixture was filled into a Pt capsule, placed into a crucible and closed with a lid (both made of α -BN; Henze Boron Nitride Products AG, Germany). The high-pressure/high-temperature experiment was carried out in an 18/11 assembly. It was compressed by eight tungsten carbide cubes (Hawedia, Marklkofen, Germany) using a Walker-type module and a hydraulic 1000 t press (both Max Voggenreiter GmbH, Germany). A detailed description of this setup can be found in the literature [32–34].

A pressure of 4 GPa was built up within 110 min followed by heating the sample to 1473 K in the following 10 min. This temperature was kept for 10 min, before the sample was cooled to 773 K over the following 30 min. After quenching to room temperature, the 300 min decompression process started. The product was separated from its surroundings to reveal colorless crystals which were found to be β -Eu(BO₂)₃.

4.2 Single-crystal structure analysis

The intensity data of a single-crystal was collected at room temperature with a Bruker D8 Quest Kappa diffractometer equipped with a Photon 100 CMOS detector.

Fig. 6: Comparison of the experimental X-ray powder diffraction data (top) and the theoretical X-ray powder pattern simulated from the single-crystal data (bottom).

Fig. 7: IR spectrum of a β -Eu(BO₂)₃ powder sample.

Monochromatized MoK α radiation ($\lambda = 0.7107$ Å) was generated with an Incoatec microfocus X-ray tube and a multilayer optic. Reflections were measured in the range $2.1 \leq \theta \leq 38.6^\circ$ and a multiscan absorption correction of the intensity data was performed with SADABS-2014/5 [35]. For the structure solution and parameter refinement, the software SHELXS/L-2013 [36, 37] implemented in the program WINGX-2013.3 [38] was used.

4.3 X-ray powder diffraction

The powder diffraction pattern of the product was obtained in transmission geometry on a STOE Stadi P powder diffractometer (STOE & Cie GmbH, Darmstadt,

Fig. 8: Luminescence spectrum of β -Eu(BO₂)₃, obtained upon excitation at 448 nm.

Germany). The measurement was performed on a flat sample with Ge(111)-monochromatized MoK α radiation ($\lambda = 70.93$ pm) in the 2θ range of 2 – 52° with a step size of 0.015° . The reflections were detected with a Mythen 1 K detector (Dectris).

4.4 Vibrational spectroscopy

An FTIR-ATR (Attenuated Total Reflection) characterization of the β -Eu(BO₂)₃ powder sample was performed in the spectral range of 400 – 4000 cm^{−1} with a Bruker ALPHA Platinum-ATR spectrometer (Bruker, Billerica, MA, USA) provided with a 2×2 mm diamond ATR-crystal and a DTGS detector. Three hundred and twenty scans of the powder sample were acquired and afterwards corrected for atmospheric influences employing the OPUS 7.2 software [39].

4.5 Luminescence spectroscopy

The emission spectrum of the powder sample was collected using a setup equipped with an AvaSpec2048 spectrometer (AVANTES, Apeldoorn, Netherlands). As excitation source, a blue laser diode (THORLABS, Newton, NJ, USA) with 448 nm wavelength was used. Prior to the experiments, a tungsten-halogen calibration lamp was used for a spectral radiance calibration of the setup. The software AVA AvaSoft full version 7 was used for data handling. The excitation spectrum was measured in the range of 200 – 1100 nm and was background-corrected.

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