High-Pressure Synthesis, Crystal Structure, and Photoluminescence Properties of $\beta$-Y$_2$B$_4$O$_9$:Eu$^{3+}$

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Abstract: A high-pressure/high-temperature experiment at 7.5 GPa and 1673 K led to the formation of the new compound $\beta$-Y$_2$B$_4$O$_9$. In contrast to the already known polymorph $\alpha$-Y$_2$B$_4$O$_9$, which crystallizes in the space group $C2/c$, the reported structure could be solved via single-crystal X-ray diffraction in the triclinic space group $P\bar{1}$ (no. 2) and is isotypic to the already known lanthanide borates $\beta$-Dy$_2$B$_4$O$_9$ and $\beta$-Gd$_2$B$_4$O$_9$. Furthermore, the photoluminescence of an europium doped sample of $\beta$-Y$_2$B$_4$O$_9$:Eu$^{3+}$ (8%) was investigated.

Keywords: crystal structure; europium; high-pressure chemistry; photoluminescence; yttrium borate

1. Introduction

In the system Y–B–O, only two modifications of YBO$_3$ [1] (the low-temperature form $\pi$-YBO$_3$ and the high-temperature form $\mu$-YBO$_3$) and the compound Y$_{17.33}$(BO$_3$)$_4$(B$_2$O$_5$)$_2$O$_{16}$ [2] (revised formula of Y$_3$BO$_6$) were known until 2016. Through the implementation of high-pressure conditions as an additional reaction parameter, three new compositions $\beta$-Y(BO$_2$)$_3$ [3], $\alpha$-Y$_2$B$_4$O$_9$ [4], and YB$_7$O$_{12}$ [5] could be obtained by our group. As expected, all of the three latter compounds feature boron exclusively in a fourfold coordination by oxygen anions due to the applied high-pressure conditions. The anionic borate networks of these compounds are built up of corner-sharing and, in the case of $\alpha$-Y$_2$B$_4$O$_9$, also of edge-sharing BO$_4$ tetrahedra. Not only the coordination number of boron is often increased under high-pressure conditions, but also the oxygen atoms can exhibit an increased coordination number, e.g., coordinated by three boron atoms (O[3]), which is the case, for example, in the borates $\beta$-Y(BO$_2$)$_3$ and YB$_7$O$_{12}$.

In the following, we report on the high-pressure synthesis of $\beta$-Y$_2$B$_4$O$_9$, a hitherto missing polymorph of $\alpha$-Y$_2$B$_4$O$_9$. In contrast to the $\alpha$-modification, which was synthesized at 12.3 GPa, the $\beta$-phase was obtained at a lower pressure of 7.5 GPa and does still contain planar BO$_5$-groups and no edge-sharing BO$_4$ tetrahedra. Furthermore, $\beta$-Y$_2$B$_4$O$_9$ is isotypic to the already known compounds $\beta$-Dy$_2$B$_4$O$_9$ [6] and $\beta$-Gd$_2$B$_4$O$_9$ [7], which will be discussed in detail.

Rare earth borates have been known for their excellent properties as hosts for luminescent materials. They possess high quantum yields, an exceptional optical damage threshold, and a long lifetime, which makes them highly attractive for practical applications. The orthoborates (Y,Gd)BO$_3$:Eu$^{3+}$ and YBO$_3$:Tb$^{3+}$ are widely used, for example, in plasma display panels [8,9], but also co-doped inorganic phosphors like YBO$_3$:Eu$^{3+}$/Tb$^{3+}$ [10] or YAl$_3$(BO$_3$)$_2$:Eu$^{3+}$/Tb$^{3+}$ or Dy$^{3+}$/Tm$^{3+}$ [11,12] are applied. Research in this field is ongoing, as a recently published work on the complete solid
solution of $\alpha$-Y$_1$-Eu:B$_5$O$_9$ shows [13]. In connection with these findings, we also investigated the photoluminescence properties of a $\beta$-Y$_1$B$_5$O$_9$:Eu$^{3+}$ sample.

2. Results and Discussion

2.1. Crystal Structure

$\beta$-Y$_1$B$_5$O$_9$ crystallizes in the triclinic space group $P\bar{1}$ with the cell parameters $a = 6.1463(2)$, $b = 6.4053(2)$, $c = 7.4642(2)$ Å, $\alpha = 102.59(2)^\circ$, $\beta = 97.11(2)^\circ$, and $\gamma = 102.46(2)^\circ$. The unit cell ($V = 275.50(2)$ Å$^3$) comprises $Z = 2$ formula units. All the relevant data of the structure refinement are shown in Table 1.

The crystal structure is built up of bands of BO$_4$ tetrahedra, as well as planar BO$_3$-groups. The bands run alongside the crystallographic $a$-axis (see Figure 1). Three BO$_4$ tetrahedra form BO$_{3}$-rings, which are connected via two BO$_3$-groups to form “sechser”-rings alongside the ab plane. Additionally, the BO$_3$-rings are interconnected via two common corners to form four-membered rings (Figure 2). The B–O distances range from 1.421 to 1.555 Å within the BO$_4$ tetrahedra. The mean value of 1.474 Å corresponds very well with the average value of 1.476 Å reported by Zobetz [14]. The O–B–O angles lie in the rather wide range of 101.4–123.4°, which was also reported for the isotypic compounds $\beta$-Dy$_2$B$_4$O$_9$ [6] and $\beta$-Gd$_2$B$_4$O$_9$ [7]. The average value of 109.4° again is in good agreement with the reported value of 109.44° [14]. In the nearly planar BO$_3$-group ($\Sigma = 359.6^\circ$), the B–O bond lengths vary between 1.360 and 1.391 Å, while the O–B–O angles range from 114.9 to 122.7°. Both average values of 1.373 Å and 119.9° are in good agreement with the expected values, as the mean B–O distance for planar as well as non-planar BO$_3$-groups is 1.37 Å [15] and the perfect angle in a planar BO$_3$-group would be 120°. Similar results were found for $\beta$-Dy$_2$B$_4$O$_9$ [6] and $\beta$-Gd$_2$B$_4$O$_9$ [7] (1.376 Å/119.9°). The positional parameters, as well as the B–O distances and the O–B–O angles can be found in Tables 2–4.

![Figure 1. The interconnected BO$_4$ tetrahedra and BO$_3$ groups in $\beta$-Y$_1$B$_5$O$_9$ form bands along the $a$-axis.](image)

| Table 1. Crystal data and structure refinement of $\beta$-Y$_1$B$_5$O$_9$. |
|-----------------------------|-----------------------------|
| **Empirical Formula**       | $\beta$-Y$_1$B$_5$O$_9$     |
| Molar mass, g·mol$^{-1}$    | 365.06                      |
| Crystal system              | triclinic                   |
| Space group                 | $P\bar{1}$ (no. 2)          |
| **Single-crystal data**     |                             |
| T, K                        | 277(2)                      |
| Radiation                   | Mo K$_\alpha$ ($\lambda = 71.07$ pm) |
| $a$, Å                      | 6.1463(2)                   |
| $b$, Å                      | 6.4053(2)                   |
| $c$, Å                      | 7.4642(2)                   |
| $\alpha$, °                 | 102.59(2)                   |
| $\beta$, °                  | 97.11(2)                    |
Table 2. Atomic coordinates and equivalent isotropic displacement parameters \( U_{eq}/\text{Å}^2 \). \( U_{eq} \) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor (standard deviations in parentheses). All atoms are located on Wyckoff-site 2i.

| Atom | \( x \)         | \( y \)         | \( z \)         | \( U_{eq} \)       |
|------|----------------|----------------|----------------|-------------------|
| Y1   | 0.8881(1)     | 0.6775(1)     | 0.3598(1)     | 0.0022(1)         |
| Y2   | 0.5473(1)     | 0.0910(1)     | 0.2854(1)     | 0.0030(1)         |
| B1   | 0.7321(3)     | 0.3347(3)     | 0.9806(2)     | 0.0052(2)         |
| B2   | 0.6618(3)     | 0.6822(3)     | 0.9275(2)     | 0.0053(2)         |
| B3   | 0.6255(3)     | 0.3572(3)     | 0.6505(2)     | 0.0056(2)         |
| B4   | 0.0050(3)     | 0.8543(3)     | 0.8111(2)     | 0.0064(2)         |
| O1   | 0.5040(2)     | 0.7902(2)     | 0.0204(2)     | 0.0064(2)         |
| O2   | 0.4200(2)     | 0.1827(2)     | 0.5554(2)     | 0.0064(2)         |
| O3   | 0.2360(2)     | 0.7364(2)     | 0.2113(2)     | 0.0060(2)         |
| O4   | 0.7795(2)     | 0.4063(2)     | 0.5228(2)     | 0.0064(2)         |
| O5   | 0.1375(2)     | 0.7163(2)     | 0.8570(2)     | 0.0069(2)         |
| O6   | 0.5394(2)     | 0.5388(2)     | 0.7479(2)     | 0.0065(2)         |
| O7   | 0.7741(2)     | 0.5720(2)     | 0.0412(2)     | 0.0058(2)         |
| O8   | 0.8122(2)     | 0.8700(2)     | 0.8812(2)     | 0.0072(2)         |
| O9   | 0.0677(2)     | 0.9547(2)     | 0.6761(2)     | 0.0077(2)         |

Table 3. Interatomic B–O distances/Å for \( \beta\)-Y\(_2\)B\(_4\)O\(_9\) (standard deviations in parentheses).

| Bond   | Distance | Bond   | Distance |
|--------|----------|--------|----------|
| B1–O7  | 1.444(2) | B2–O7  | 1.421(2) |
| –O3    | 1.457(2) | –O6    | 1.457(2) |
| –O1    | 1.497(2) | –O1    | 1.466(2) |
| –O5    | 1.505(2) | –O8    | 1.483(2) |
| Ø      | 1.476    | Ø      | 1.457    |
| B3–O4  | 1.459(2) | B4–O9  | 1.360(2) |
| –O6    | 1.468(2) | –O8    | 1.367(2) |
| –O2    | 1.474(2) | –O5    | 1.391(2) |
| –O3    | 1.555(2) |
| Ø      | 1.489    | Ø      | 1.373    |

Table 4. Bond angles/° for \( \beta\)-Y\(_2\)B\(_4\)O\(_9\) (standard deviations in parentheses).

| Bond   | Angle | Bond   | Angle |
|--------|-------|--------|-------|
| O1–B1–O5 | 101.4(2) | O1–B2–O8 | 101.7(2) |
| O7–B1–O5 | 101.7(2) | O6–B2–O8 | 104.9(2) |
| O3–B1–O1 | 104.0(2) | O6–B2–O1 | 108.3(2) |
Figure 2. Crystal structure of $\beta$-Y$_2$B$_4$O$_9$ forming six-membered rings (one encircled in orange) and four-membered rings (one encircled in yellow and shown individually on the right).

The Y$^{3+}$ cations are located in the voids between the anionic borate bands. There are two crystallographically independent yttrium atoms in the structure: The first one is coordinated by nine oxygen atoms, the second one by ten oxygen atoms (see Figure 3). The Y–O distances lie in the range from 2.256 to 2.645 Å and are displayed in Table 5. This conforms to the reported values of $\beta$-Dy$_2$B$_4$O$_9$ (2.263–2.652 Å) and also to other high-pressure yttrium borates like $\beta$-Y(BO$_2$)$_3$ (2.383–2.419 Å) [3], $\alpha$-Y$_3$B$_6$O$_9$ (2.401–2.602 Å) [4], and YB$_7$O$_{12}$ (2.308–2.659 Å) [5].

Figure 3. Coordination spheres of the two crystallographically independent yttrium sites in the crystal structure of $\beta$-Y$_2$B$_4$O$_9$. 

| Bond            | Angle (°) |
|-----------------|-----------|
| O7–B1–O3        | 111.6(2)  |
| O7–B1–O1        | 114.9(2)  |
| O3–B1–O5        | 123.4(2)  |
| Ø               | 109.5     |
| O4–B3–O3        | 103.2(2)  |
| O6–B3–O2        | 104.3(2)  |
| O2–B3–O3        | 107.8(2)  |
| O4–B3–O2        | 112.0(2)  |
| O6–B3–O3        | 112.0(2)  |
| O4–B3–O6        | 117.4(2)  |
| Ø               | 109.5     |

Table 5: Bond Angles in $\beta$-Y$_2$B$_4$O$_9$.
Table 5. Interatomic Y–O distances/Å for $\beta$-Y$_2$B$_4$O$_9$ (standard deviations in parentheses).

| Bond | Distance | Bond | Distance |
|------|----------|------|----------|
| Y1   | O7       | Y2   | O2       |
|      | 2.299(2) |      | 2.256(2) |
| Y1   | O4       | Y2   | O1       |
|      | 2.338(2) |      | 2.384(2) |
| Y1   | O2       | Y2   | O4       |
|      | 2.359(2) |      | 2.414(2) |
| Y1   | O9       | Y2   | O9       |
|      | 2.359(2) |      | 2.436(2) |
| Y1   | O3       | Y2   | O3       |
|      | 2.523(2) |      | 2.538(2) |
| Y1   | O9       | Y2   | O6       |
|      | 2.573(2) |      | 2.541(2) |
| Y1   | O5       | Y2   | O5       |
|      | 2.625(2) |      | 2.563(2) |
| Ø    |          | Ø    |          |
|      | 2.457    |      | 2.457    |

The charge distributions and bond valences were calculated using both the bond-length/bond-strength (BLBS; $\Sigma V$) [16,17], and the CHARDI concept ($\Sigma Q$) [18]. The results are shown in Table 6 and they are in good agreement with the expected values of +3 for yttrium and boron and -2 for oxygen.

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-1955299 for $\beta$-Y$_2$B$_4$O$_9$. The cif- and checkcif-files are also available in the Supplementary Materials.

Table 6. Charge distributions according to both, the bond-length/bond-strength ($\Sigma V$) and the CHARDI ($\Sigma Q$) concept.

| Method | Y1 | Y2 | B1 | B2 | B3 | B4 |
|--------|----|----|----|----|----|----|
| $\Sigma V$ | +2.92 | +3.19 | +3.02 | +3.18 | +2.92 | +2.99 |
| $\Sigma Q$ | +2.97 | +3.01 | +3.00 | +2.97 | +3.03 | +3.03 |

| O1 | O2 | O3 | O4 | O5 | O6 | O7 | O8 | O9 |
|----|----|----|----|----|----|----|----|----|
| $\Sigma V$ | -2.09 | -2.09 | -1.90 | -1.95 | -2.07 | -1.97 | -2.16 | -2.03 | -1.94 |
| $\Sigma Q$ | -1.98 | -2.05 | -1.86 | -2.03 | -1.99 | -1.95 | -2.18 | -1.97 | -1.99 |

2.2. Elemental Analysis

The semiquantitative EDX measurements were performed to prove the presence of europium in the $\beta$-Y$_2$B$_4$O$_9$ host. Figure 4 shows the resulting EDX spectrum, which clearly confirms that europium is present in the structure. The measured and averaged values from the measurements can be seen in Table 7. Additionally, small amounts of silicon were detected in three of the measurements, which most likely originates from the agate mortar that was used to homogenize the sample, which is well known for hard borates.

Table 7. Measured composition (normalized to 100%) of $\beta$-Y$_2$B$_4$O$_9$:Eu$^{3+}$ (8%) (wt %). Accuracy for all measured values ± 3%.

| Element | Y  | B  | O  | Eu | Si |
|---------|----|----|----|----|----|
| M1      | 45.0 | 15.5 | 36.1 | 3.0 | 0.4 |
| M2      | 41.2 | 13.0 | 33.2 | 12.5 | 0.1 |
| M3      | 43.4 | 14.0 | 34.1 | 8.6 | 0.0 |
| M4      | 42.1 | 15.3 | 34.9 | 7.7 | 0.1 |
| M5      | 42.5 | 13.6 | 34.1 | 9.8 | 0.0 |

| average | 42.8(3) | 14.3(2) | 34.5(2) | 8.3(7) | 0.1 |
| expected | 46.1 | 11.7 | 38.9 | 3.3 |
Figure 4. (a) Crystal used for the EDX measurement (crosses indicate the measured positions); (b) EDX spectrum of $\beta$-Y$_2$B$_4$O$_9$:Eu$^{3+}$ (8%). The unindexed peak at ~0.3 keV originates from carbon used for the sputtering process.

### 2.3. Photoluminescence Properties

The emission spectrum of a $\beta$-Y$_2$B$_4$O$_9$:Eu$^{3+}$ (8%) single-crystal, obtained upon excitation by a blue laser diode ($\lambda_{exc} = 420$ nm) is shown in Figure 5. The Eu$^{3+}$ transitions can be assigned to the $^5D_0 \rightarrow ^7F_J$ ($J = 0–4$) transitions in the following way: the $^5D_0 \rightarrow ^7F_0$ transition corresponds to the single peak at 587 nm. The signals between 594 and 596 nm belong to the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$), while the strongest bands in the spectrum from 610 to 623 nm can be assigned to the electric dipole transition ($^5D_0 \rightarrow ^7F_2$). The $^5D_0 \rightarrow ^7F_3$ transitions occur as very weak signals in the range from 650 to 657 nm, and the signals between 684 and 705 nm belong to the $^5D_0 \rightarrow ^7F_4$ transitions [19]. The origin of the weak emission at 578–580 nm is the $^5D_0 \rightarrow ^7F_1$ transition, since 580 nm corresponds to an energy of 17.241 cm$^{-1}$. For the assignment of the transition, which matches the energy, the Dieke diagram was used [20].

As can be seen in Figure 5, the so-called hypersensitive $^5D_0 \rightarrow ^7F_2$ transition exhibits the strongest bands in the spectrum. For perfect inversion symmetry, e.g., for Eu$^{3+}$ located onto a regular octahedral site, the intensity of the $^5D_0 \rightarrow ^7F_2$ transition should be zero and thus the asymmetry ratio R should be zero too. However, since the $^5D_0 \rightarrow ^7F_2$ transition is hypersensitive, any tiny distortion of the inversion symmetry will result in an increase of its intensity and thus in the R value. It is not uncommon that the $^5D_0 \rightarrow ^7F_2$ transition is 10 times more intense than the $^5D_0 \rightarrow ^7F_1$ transition. However, the correlation is not simple and correlating the luminescence color or symmetry ratio with a particular site symmetry or deviation from inversion symmetry is rather difficult.

The factor R for the compound introduced in this paper has been calculated on the basis of the publication of K. Binnemans [19]. That leads to an integral of 9.4286 for the $^5D_0 \rightarrow ^7F_2$ transition (604–635 nm) and to an integral of 1.8115 for the $^5D_0 \rightarrow ^7F_1$ transition (589–604 nm). The R factor is calculated by $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ and leads to $R = 5.2$. 

3. Experimental Section

3.1. Synthesis

β-Y₂B₄O₉ was synthesized via a high-pressure/high-temperature experiment. For this synthesis, the starting materials Y₂O₃ (ChemPUR, Karlsruhe, Germany, 99.9%) and H₃BO₃ (Carl Roth, Karlsruhe, Germany, >99.8%) were ground together under ambient conditions in the stoichiometric ratio of 1:4.05, i.e., with a 5% excess of boric acid. The homogenized mixture was encapsulated in platinum foil, placed into a crucible made of α-BN and closed with a lid out of the same material (Henze Boron Nitride Products AG, Lauben, Germany). The crucible was placed into an 18/11 assembly, which was compressed and heated in a multianvil device based on a Walker-type module and a 1000 t downstroke press (both devices from Max Voggenreiter GmbH, Mainleus, Germany). A detailed description of the experimental setup can be found in the literature [21–23].

The sample was compressed to 7.5 GPa in 200 min, followed by a heating period of 10 min to 1673 K. This temperature was kept for 60 min, before the sample was slowly cooled down to room temperature in the following 240 min. Afterwards, the heating was switched off and the 600 min decompression process started. The recovered octahedral pressure medium was broken apart and the product carefully separated from the surrounding BN crucible and the platinum capsule. β-Y₂B₄O₉ could be obtained as colorless, irregular shaped crystals beside a significant amount of white microcrystalline powder.

The synthesis of the europium doped sample was carried out under the same conditions with Y₂O₃, Eu₂O₃ (Smart Elements, Wien, Austria, 99.99%) and H₃BO₃ in the stoichiometric ratio of 0.46:0.04:2 as starting materials.

The X-ray powder diffraction data revealed that the reaction product is composed of β-Y₂B₄O₉ (about 59%) and π-YBO₃ as the main side phase. Attempts to synthesize a pure sample of β-Y₂B₄O₉ were not successful, π-YBO₃ always occurs as the main side product in the X-ray powder pattern.

3.2. Single-Crystal Structure Analysis

The intensity data of a β-Y₂B₄O₉ single-crystal was collected using a Bruker D8 Quest Kappa diffractometer equipped with a Photon 100 CMOS detector. An Incoatec microfocus X-ray tube in multilayer optics generated the monochromatized Mo Kα radiation (λ = 0.7107 Å). A multiscan absorption correction of the intensity data with SADABS 2014/5 [24] was applied on the data. For the structure solution and parameter refinement, the software SHELXS/L-2013 [25,26], as implemented in the program WINGX-2013.3 [27], was employed. No systematic extinctions were observed, which led to the only possible space groups P1 and P1. During the refinement, the centrosymmetric space
group was found to be correct, which is in agreement with the results from the isotypic compounds β-Dy₂B₄O₉ and β-Gd₂B₄O₉. All atoms could be refined with anisotropic displacement parameters.

3.3. Energy-Dispersive X-ray Spectroscopy (EDX)

A semiquantitative EDX measurement was performed in high vacuum on a Jeol JSM-6010LA scanning electron microscope (SEM) (Bruker, Billerica, MA, USA). The crystal was attached to a carbon tape and coated with carbon. The measurement was carried out under an acceleration voltage of 15 kV, a working distance of 14 mm, and a measurement time of 60 s. Five different spots on the crystal were selected, the measured chemical composition was averaged and normalized to 100%.

3.4. Luminescence Spectroscopy

The emission spectrum of a β-Y₂B₄O₉ single-crystal was collected using a setup equipped with an AvaSpec2048 spectrometer (AVANTES, Apeldoorn, Netherlands). A blue laser diode (THORLABS, Newton, MA, USA) with 448 nm wavelength was used as excitation source. Prior to the experiments, a spectral radiance calibration of the setup was carried out using a tungsten-halogen calibration lamp. The software AVA AvaSoft full version 7 was employed for data handling. The emission spectrum was measured in the range of 200–1100 nm and was background-corrected.

4. Conclusions

The new compound β-Y₂B₄O₉, which is isotypic to β-Dy₂B₄O₉ and β-Gd₂B₄O₉, was synthesized under the high-pressure/high-temperature conditions of 7.5 GPa and 1673 K using a Walker-type multianvil press. The structure was characterized via single-crystal X-ray analysis and it is built up of BO₃ groups as well as BO₄ tetrahedra, forming three-, four-, and six-membered rings.

The experiments to substitute yttrium with europium were successful, as proven by the EDX measurements of a β-Y₂B₄O₉:Eu³⁺ (8%) crystal. Thus, the luminescence properties of the europium-substituted sample were investigated. The emission spectrum shows typical Eu³⁺ photoluminescence with the strongest peak originating from the 5D⁰ → 7F⁰ electric dipole transition.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, the CIF and the checkCIF output files.

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