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High-pressure/high-temperature synthesis of the first walstromite-analogue borate Tm₂CrB₃O₉

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Abstract: Tm₂CrB₃O₉ was obtained by high-pressure/high-temperature syntheses at 7.5 GPa and 850 °C. The compound crystallizes homeotypically to walstromite in the triclinic space group P\(\text{TI} (\text{no. 2})\) with the unit cell parameters \(a = 5.9118(4)\,\text Å, b = 5.9148(4)\,\text Å, c = 8.3575(6)\,\text Å, \alpha = 83.64(1)^{\circ}, \beta = 71.19(1)^{\circ}, \text{and} \gamma = 79.93(1)^{\circ} \rangle, \) and two formula units per cell. Single-crystal and powder diffraction data are accompanied by an infrared spectroscopic investigation and the structural features of this new compound are discussed in detail.

Keywords: borate; crystal structure; high-pressure; rare-earth; walstromite

1 Introduction

Walstromite was first described as BaCa₂Si₂O₇ by Alfs et al. as one of seven barium-containing minerals from Eastern Fresno County in California [1] and was found to be identical to a synthetic compound prepared in 1922 [2]. A structural characterization of synthetic walstromite was later carried out by Dent-Glasser and Glasser using photographic X-ray diffraction data [3]. The formal substitution of Ba by Ca leads to CaSiO₃-walstromite [4], which also occurs naturally in the form of the mineral breyite [5−7]. Furthermore, CaSiO₃-wollastonite-II, a high-pressure polymorph of wollastonite, was reported to display similar structural features as walstromite [8−11]. Structural differences between CaSiO₃-walstromite and CaSiO₃-wollastonite-II were discussed [9, 12, 13] until 2011 when Barkley et al. [11] pointed out that the crystal coordinates of walstromite, CaSiO₃-walstromite, and CaSiO₃-wollastonite-II can be transformed into each other by a linear transformation matrix and therefore all are isostructural. This also means that CaSiO₃-wollastonite-II are identical compounds [11]. In substance classes such as phosphates and germanates, walstromite-analogue crystal structures were previously described with the discoveries of Na₂KP₃O₉ [14] and BaSrGe₃O₉ [15], respectively. In this article, we report on the first borate Tm₂CrB₃O₉ within this structure family. Under ambient pressure, depending on the ionic radius of the lanthanoid, two structure types of lanthanoid chromium borates \(LnCr(BO₃)₂ (Ln = Ho–Lu) [16] \) and \(LnCr₂(BO₃)₄ (Ln = Eu, Gd) [17, 18] \) were previously described, while the new compound was obtained by high-pressure/high-temperature syntheses in a modified Walker-type multianvil device.

2 Experimental section

2.1 High-pressure/high-temperature synthesis

The title compound was first encountered during explorative syntheses in the system Tm₂O₃−Cr₂O₃−B₂O₃ at elevated pressures. Subsequently, a targeted synthesis of Tm₂CrB₃O₉ was carried out by mixing the starting materials Tm₂O₃ (0.17 mmol, ChemPur, 99.90 %), Cr(NO₃)₃·9H₂O (0.17 mmol; Sigma Aldrich; 99 %), and H₃BO₃ (0.52 mmol, Roth, >99.8 %) in the stoichiometric ratio 1:1:3. The sample was placed in a platinum capsule and centered in an 18/11 assembly of a modified Walker-type multianvil press (Max Vogenreiter GmbH, Mainleus, Germany) on which detailed information can be found in the literature [19−21]. The sample was compressed to 7.5 GPa within 196 min and subsequently heated to 850 °C within 10 min. The temperature was kept constant for 25 min before it was slowly decreased to 600 °C within 45 min, where the reaction was quenched. After the decompression phase of 588 min, a dark violet product was obtained. For structure determination, this product did not contain any sufficiently sized crystals. By applying the same pressure and temperature on a mixture of the starting materials in the molar ratio 1:1:7, red crystals of Tm₂CrB₃O₉ embedded in a dark-gray, unidentifiable matrix were obtained.

2.2 X-ray diffraction structure determination

Measurements were carried out on a Bruker D8 Quest equipped with a Photon III C14 area detector. The programs SMART (V8.40B) [22] and APEX4 (v2021.4.0) [23] were used for data collection and processing. A total of 18 tests and full measurements of different crystals of good optical quality were carried out. However, despite the good optical quality, all crystals displayed very strong signs of twinning, from which we deduce that intrinsic effects in Tm₂CrB₃O₉ lead to these results. Crystal structure determinations were therefore carried out on a non-merohedrally twinned crystal (BASF 0.3083). Three twin domains (second cell rotated 180.0° and third cell rotated 74.3° from the first domain) were identified.
in the data by the program cell_NOW [24]. A multi-scan absorption correction was carried out using the program TWINABS (2012/1) [25], and the structure was solved via SHELXT (2018/2) [26, 27] algorithms. 12150 reflections were found to only involve domain 1, 12441 reflections involved only domain 2, 21363 reflections were found to involve two domains, and 3 reflections were found to involve three domains. Of these, 2510, 2465, 3900, and 3 reflections, respectively, were considered to be unique. Due to the low number of reflections of the third domain, only domain one and two were considered in calculations of the structure refinements. During structure refinement, three reflections were omitted due to their high deviation. Structure refinements were calculated on the basis of a HKL2S data file using JANA2000 [28]. All atoms were refined anisotropically and the structural and refinement data are shown in Tables 1–4 below. Symmetry checks of the final structure solution using the adatoms- routine of PLATON [29–33] did not suggest any further change of the symmetry.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-2299369.

X-ray powder diffraction patterns (Figure 1) were collected on an STOE Stadi P Powder Diffractometer (STOE & CIE GmbH, Darmstadt, Germany) [34], equipped with a Ge(II) monochromator and an MYTHEN 1 K detector system (DeCTRIS Ltd., Baden Daettwil, Switzerland) [35]. The measurements were carried out overnight in transmission mode using a flat sample holder [36]. While the reflection positions show good congruency with the calculated positions, the relative intensities differ due to intrinsic effects of preferred orientations, which were found on several independent samples.

### 2.3 Infrared spectroscopy

Infrared spectra of the new compound were collected on a Bruker Alpha Platinum attenuated total reflection (ATR) spectrometer on the bulk material. The spectra were measured in the range of 4000 to 400 cm⁻¹, and the data was processed and corrected for atmospheric influences employing the opus 7.2 [37] software.

### 3 Results and discussion

#### 3.1 Crystal structure description

The compound Tm₂CrB₃O₉ crystallizes with two formula units per cell in the triclinic crystal system in the space group $P\overline{1}$ (no. 2) and displays unit cell parameters of $a = 5.9118(4)$ Å, $b = 5.9148(4)$ Å, $c = 8.3575(6)$ Å, $\alpha = 83.64(1)^\circ$, $\beta = 71.19(1)^\circ$, and $\gamma = 79.93(1)^\circ$. Three crystallographically different boron
 atoms, each tetrahedrally coordinated by oxygen atoms, are found in the crystal structure forming isolated three-membered rings, which can formally be described as [B\text{O}_4]\text{O}^– anions, as shown in Figure 2. Bond lengths within the [B\text{O}_4] tetrahedra are generally expected around 1.48(4) Å with O–B–O-angles around 109.4° [38]. In Tm\text{B}_2\text{O}_9, interatomic distances between 1.478(6) Å and 1.510(4) Å, between 1.453(6) Å and 1.556(4) Å, and from 1.435(6) Å to 1.527(4) Å are observed around the B1-, B2-, and B3-site respectively, which is reasonably close to the abovementioned values.

The chromium atoms are centered within an octahedron built up by six oxygen atoms. Within the [CrO\text{O}_4] octahedra, interatomic distances between 1.952(3) Å and 2.077(3) Å are observed, which matches with average Cr–O-distances in Tm\text{Cr}(\text{BO}_3)\text{O} (2.129 Å), \text{B}_2\text{O}_9\text{N} (1.9475 Å), and related compounds [16–18, 39, 40]. Furthermore, it is apparent from Table 4 that all bonding angles are in the expected range for a slightly distorted octahedron. Each corner of the [CrO\text{O}_4] octahedron is linked to one [B\text{O}_4]\text{O}^– anion and thus connects the isolated borate units within the crystal structure (Figure 3). Thereby, the O2 and O6 atoms of one [CrO\text{O}_4] octahedron belong to the same [B\text{O}_4]\text{O}^– anion.

Two crystallographically different thulium atoms are found in the voids within the crystal structure. For a graphical depiction of the respective coordination environments, see Figure 4. The Tm1-site is eight-fold coordinated by oxygen with interatomic distances between 2.171(3) Å and 2.607(3) Å. Around the Tm2-position, eight oxygen atoms are found at distances from 2.258(3) Å to 2.365(3) Å and two additional oxygen atoms are located at distances of 2.841(3) Å and 2.898(3) Å, leading to a ten-fold coordinated site. These values are reasonable, considering known thulium borates.
Table 4: Selected interatomic distances (Å) and bond angles (deg) (standard deviations in parentheses).

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance</th>
<th>Atoms</th>
<th>Distance</th>
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<tbody>
<tr>
<td>Tm1–O3</td>
<td>2.171(3)</td>
<td>Tm2–O7</td>
<td>2.258(3)</td>
</tr>
<tr>
<td>Tm1–O8d</td>
<td>2.319(3)</td>
<td>Tm2–O7d</td>
<td>2.293(3)</td>
</tr>
<tr>
<td>Tm1–O1</td>
<td>2.338(3)</td>
<td>Tm2–O6</td>
<td>2.300(3)</td>
</tr>
<tr>
<td>Tm1–O8</td>
<td>2.374(3)</td>
<td>Tm2–O3d</td>
<td>2.307(2)</td>
</tr>
<tr>
<td>Tm1–O2d</td>
<td>2.391(3)</td>
<td>Tm2–O9</td>
<td>2.321(4)</td>
</tr>
<tr>
<td>Tm1–O4</td>
<td>2.412(3)</td>
<td>Tm2–O5i</td>
<td>2.335(4)</td>
</tr>
<tr>
<td>Tm1–O6d</td>
<td>2.605(3)</td>
<td>Tm2–O2d</td>
<td>2.343(3)</td>
</tr>
<tr>
<td>Tm1–O1c</td>
<td>2.607(3)</td>
<td>Tm2–O3d</td>
<td>2.365(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tm2–O9g</td>
<td>2.841(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tm2–O5</td>
<td>2.898(3)</td>
</tr>
<tr>
<td>Average</td>
<td>2.402</td>
<td>Average</td>
<td>2.426</td>
</tr>
</tbody>
</table>

| B2–O3 | 1.453(6) | B3–O5 | 1.435(6) |
|       |          |       |          |
| B2–O7d | 1.462(5) | B3–O6 | 1.466(6) |
|       |          |       |          |
| B2–O5 | 1.481(5) | B3–O8h | 1.488(5) |
|       |          |       |          |
| B2–O9h | 1.546(4) | B3–O4 | 1.527(4) |
|       |          |       |          |
| Average | 1.486 | Average | 1.479 |

| O6–Cr1–O7 | 83.3(2) | O7–Cr1–O4 | 176.1(2) |
| O4h–Cr1–O4 | 83.3(2) | O2–Cr1–O4b | 175.7(2) |
| O8h–Cr1–O4h | 85.9(2) | O6–Cr1–O8b | 174.4(2) |
| O2–Cr1–O7 | 86.0(2) | Average | 175.4 |
| O6–Cr1–O4h | 89.1(2) |       |          |
| O8h–Cr1–O4h | 89.4(2) |       |          |
| O2–Cr1–O6 | 91.7(2) |       |          |
| O2–Cr1–O4 | 92.5(2) |       |          |
| O6–Cr1–O4 | 93.2(2) |       |          |
| O2–Cr1–O8h | 93.3(2) |       |          |
| O8h–Cr1–O7 | 94.5(2) |       |          |
| O4h–Cr1–O7 | 98.3(2) |       |          |
| Average | 90.0 |       |          |

| O2–B1–O9h | 107.7(3) | O3–B2–O7d | 110.0(3) |
| O2–B1–O1b | 114.2(4) | O3–B2–O5 | 108.9(3) |
| O2–B1–O4 | 105.9(3) | O3–B2–O9j | 108.2(3) |
| O9h–B1–O1b | 106.2(3) | O7h–B2–O5 | 113.9(3) |
| O9h–B1–O4 | 112.6(4) | O7h–B2–O9j | 112.3(3) |
| O1h–B1–O4 | 111.2(3) | O5–B2–O9j | 103.2(3) |
| Average | 109.5 | Average | 109.4 |

| O5–B3–O6 | 114.5(3) |       |          |
| O5–B3–O8h | 114.7(3) |       |          |
| O5–B3–O1 | 106.7(3) |       |          |
| O6–B3–O8h | 103.5(3) |       |          |
| O6–B3–O1 | 109.9(3) |       |          |
| O8h–B3–O1 | 107.4(3) |       |          |
| Average | 109.5 |       |          |

Symmetry operators for generating equivalent atoms:

- $^{a}x+1, -y, -z+1$;
- $^{b}-x, -y+1, -z+1$;
- $^{c}x, -y, -z+1$;
- $^{d}x+1, -y+1, -z$;
- $^{e}x+1, -y, -z$;
- $^{f}-x+1, -y+1, -z$;
- $^{g}-x+1, -y, -z+1$;
- $^{h}x, y, z+1$;
- $^{i}-x, y, z$;
- $^{j}x+2, -y+1, -z$;
- $^{k}-x+1, -y, -z+1$;
- $^{l}x, y, z-1$;
- $^{m}x-1, y, z$;

Figure 3: The chromium atoms are octahedrally coordinated. Each [CrO$_3$] octahedron is connected to a total of five [B$_3$O$_9$]$_2^+$ anions via corner-sharing.

Within the crystal structure, the isolated [B$_3$O$_9$]$_2^-$ anions are arranged in layers, in which the apices of two adjacent rings point in opposite directions. While the Tm1 atoms are located within these layers, the Tm2-site and the chromium atoms are found between two layers. In its unit cell, the resulting crystal structure is shown in Figure 5.

Calculations of the bond valence sums according to the bond-length/bond-strength (BLBS) [45] and charge distribution (CHARDD) [46] concept show good congruency with the expected values of +3 for thulium, chromium, and boron, and −2 for oxygen. The results of these calculations are provided in Table 5.

Tm$_2$CrB$_2$O$_9$ is an addition to the existing lanthanoid chromium borates LnCr(BO$_3$)$_2$ (Ln = Ho–Lu) [16] and

Figure 4: Graphical depiction of the coordination environments of the two crystallographically different thulium atoms.
LnCr$_3$(BO$_3$)$_4$ ($Ln$ = Eu, Gd) [17, 18], which were obtained under ambient pressure conditions. In these ambient pressure phases, the boron atoms are exclusively three-fold coordinated, while the crystal structure of the new high-pressure phase is exclusively built up by [BO$_4$] tetrahedra. This corresponds to the pressure-coordination rule [47], which can also be observed for the lanthanoid cations. In LnCr$_4$(BO$_3$)$_3$ ($Ln$ = Ho–Lu) [16] and LnCr$_3$(BO$_3$)$_4$ ($Ln$ = Eu, Gd) [17, 18], the lanthanoid atoms are six-fold coordinated in an octahedral or distorted trigonal prismatic geometry, while in Tm$_2$CrB$_3$O$_9$, the coordination numbers of the thulium atoms are considerably higher with C.N. 8 for the Tmt- and C.N. 10 for the Tm2-site. As expected, the increase of the coordination number is accompanied by an increase in interatomic distances [16–18, 47]. The chromium atoms are octahedrally coordinated in all compounds discussed [16–18]. During the investigation of the thermal behavior and stability of Tm$_2$CrB$_3$O$_9$ by powder X-ray diffraction, we have observed the formation of \( \pi \)-TmBO$_3$ [48, 49], after heating to temperatures around 900 °C and subsequent cooling. The formation of \( \pi \)-TmBO$_3$ [48, 49] was accompanied by a decrease of the reflection intensities assignable to the title compound, thus indicating its decomposition. However, at these temperatures, this reaction was very slow. We have therefore placed the quartz capillary in a high-frequency furnace and heated the sample up to 1200 °C. This resulted in a powder diffraction pattern which showed reflections of \( \pi \)-TmBO$_3$ [48, 49], and weaker ones that could be assigned to cristobalite (ICDD collection code: 00-039-1425). Notably, no chromium species could be identified, despite the green color of the resulting product. Likely, this is due to a reaction with the quartz glass at such high temperatures. Syntheses carried out under ambient pressure did not yield Tm$_2$CrB$_3$O$_9$. Although a detailed investigation was not yet possible, its status as a high-pressure phase seems likely, considering these observations.

### 3.2 Infrared spectroscopy

In Figure 6, the infrared spectrum of Tm$_2$CrB$_3$O$_9$ is shown. Notably, the absence of a broad absorption at wavenumbers around 3000 cm$^{-1}$ confirms a hydroxyl-free crystal structure.
for the title compound [50]. Stretching vibrations of [BO₄] tetrahedra are observed in the expected wavenumber range of 800–1100 cm⁻¹ [51], but are also preceded to contribute to signals at slightly higher wavenumbers by ab initio quantum chemical calculations [52]. Bending modes of [BO₄] tetrahedra and vibrations involving the chromium- and thulium-centered polyhedra are expected in the lower wavenumber range [50–54]. Therefore, it can be said that the infrared spectroscopic characteristics of the sample match with our expectations from the single-crystal structure solution.

4 Conclusions

Tm₂CrB₃O₉ is the first borate that exhibits a crystal structure analogous to walstromite. It was synthesized in a modified Walker-type high-pressure device at 7.5 GPa and 850 °C and forms red, strongly twinned crystals with a structure built up of isolated [B₂O₉]⁹⁻ anions. The structural model is further supported by an infrared spectroscopic investigation.

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Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Competing interests: The authors declare no conflicts of interest regarding this article.

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Data availability: Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fzinformationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-2299369.

References

35. B.-D. Dectris Ltd. TECHNICAL DOCUMENTATION; B.-D. Dectris Ltd: BadenDaettwil, Switzerland, 2015.

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