High-Pressure Synthesis and Crystal Structure of Ce$_4$B$_{14}$O$_{27}$

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of His 80th Birthday

Keywords: High-pressure chemistry; Multianvil; Cerium; Borates; Crystal structure

Abstract. Ce$_4$B$_{14}$O$_{27}$ was synthesized under conditions of 2.6 GPa and 750 °C in a Walker-type multianvil apparatus. The crystal structure was determined on the basis of single-crystal X-ray diffraction data, collected at room temperature, revealing that Ce$_4$B$_{14}$O$_{27}$ is isotypic to La$_4$B$_{14}$O$_{27}$. Ce$_4$B$_{14}$O$_{27}$ crystallizes monoclincally with four formula units in the space group $C2/c$ (No. 15) and the lattice parameters $a = 1117.8(2)$, $b = 640.9(2)$, $c = 2531.7(5)$ pm, and $\beta = 100.2(1)^\circ$. The three-dimensional boron-oxygen framework consists of [BO$_4$]$^{5-}$ tetrahedra and trigonal-planar [BO$_3$]$^{3-}$ groups. The structure contains two crystallographically different cerium ions. Furthermore, Raman spectroscopy was performed on single crystals of Ce$_4$B$_{14}$O$_{27}$.

Introduction

The structural chemistry of oxoborates exhibits a respectable diversity, which yields from the ability of the boron atom to form trigonal-planar [BO$_3$]$^{3-}$ groups and tetrahedral [BO$_4$]$^{5-}$ groups. These groups can occur isolated or linked to highly-condensed three-dimensional networks. In the majority of cases, the trigonal-planar [BO$_3$]$^{3-}$ groups disappear with increasing pressure, so in high-pressure oxoborates, the boron atoms favor the fourfold coordination forming [BO$_4$]$^{5-}$ groups. Above a pressure of 10 GPa, only a few compounds are known, which contain trigonal-planar [BO$_3$]$^{3-}$ groups, e.g. Ho$_3$O$_{12}$[BO$_3$]$_3$(BO$_2$)$_2$[1]. The linking of the tetrahedral [BO$_4$]$^{5-}$ groups follows normally via common corners. In the past, we observed that these boron–oxygen tetrahedra can share common edges to realize denser structures like the po-

Experimental Section

Synthesis: During our attempts, to synthesize a cerium fluoro- or fluoride borate under high-pressure/high-temperature conditions of 2.6 GPa and 750 °C, the new cerium oxoborate Ce$_4$B$_{14}$O$_{27}$ was synthesized, starting from a mixture of 79.2 mg CeO$_2$ (Auer-Remy, Hamburg, Germany, 99.9 %), 80.1 mg B$_2$O$_3$ (Strem Chemicals, Newburyport, USA, 99.94%), and 90.7 mg CeF$_3$ (Strem Chemicals, Newburyport, USA 99.94%). The starting materials were finely ground and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S100, Kempten, Germany). The crucible was placed into an 18/11-assembly and compressed by eight tungsten carbide cubes (TSM-10, Cezaritiz, Reutte, Austria). To apply the pressure, a 1000 t multianvil press with a Walker-type module (both devices from the company Voggenreiter, Innsbruck, Austria) was used. After pressurized, the system Ce$_2$O$_3$B$_2$O$_3$ was represented by four modifications of the ortho-oxoborate CeBO$_3$ (Ce$_2$O$_3$:B$_2$O$_3$ = 1:1; $\lambda$, $\nu$, $\pi$, and H-CeBO$_3$), and two new modifications of cerium meta-oxoborate. The monoclinic $\delta$-Ce(BO$_2$)$_3$ was synthesized at 3.5 GPa and 1050 °C, the synthesis of the orthorhombic $\gamma$-Ce(BO$_2$)$_3$, needed high-pressure/high-temperature conditions of 7.5 GPa and 1000 °C. Despite intensive search, no cerium-polyoxoborates with compositions like RE$_2$B$_{10}$O$_{24}$ ($RE =$ La, Pr$_1$,$^{[16,17]}$ RE$_2$B$_{10}$O$_{12}$ ($RE =$ Er–Lu$_3$)$^{[18]}$ or RE$_2$B$_{15}$O$_{35}$ ($RE =$ Dy, Ho)$^{[2–3]}$ could be synthesized. Now, the application of high-pressure/high-temperature conditions enabled the synthesis of a cerium-polyoxyborate with the composition Ce$_6$B$_{14}$O$_{27}$, which is isotypic to the recently discovered La$_4$B$_{14}$O$_{27}$.$^{[19]}$ In this paper, we describe the synthesis of Ce$_4$B$_{14}$O$_{27}$, the single-crystal structure determination, Raman spectroscopic investigations, and a comparison to the isotypic phase La$_4$B$_{14}$O$_{27}$. Starting research, the system Ce$_2$O$_3$B$_2$O$_3$ was represented by four modifications of the ortho-oxoborate CeBO$_3$ (Ce$_2$O$_3$:B$_2$O$_3$ = 1:1; $\lambda$, $\nu$, $\pi$, and H-CeBO$_3$), and two new modifications of cerium meta-oxoborate. The monoclinic $\delta$-Ce(BO$_2$)$_3$ was synthesized at 3.5 GPa and 1050 °C, the synthesis of the orthorhombic $\gamma$-Ce(BO$_2$)$_3$ needed high-pressure/high-temperature conditions of 7.5 GPa and 1000 °C. Despite intensive search, no cerium-polyoxoborates with compositions like RE$_2$B$_{10}$O$_{24}$ ($RE =$ La, Pr$_1$,$^{[16,17]}$ RE$_2$B$_{10}$O$_{12}$ ($RE =$ Er–Lu$_3$)$^{[18]}$ or RE$_2$B$_{15}$O$_{35}$ ($RE =$ Dy, Ho)$^{[2–3]}$ could be synthesized. Now, the application of high-pressure/high-temperature conditions enabled the synthesis of a cerium-polyoxyborate with the composition Ce$_6$B$_{14}$O$_{27}$, which is isotypic to the recently discovered La$_4$B$_{14}$O$_{27}$.$^{[19]}$ In this paper, we describe the synthesis of Ce$_4$B$_{14}$O$_{27}$, the single-crystal structure determination, Raman spectroscopic investigations, and a comparison to the isotypic phase La$_4$B$_{14}$O$_{27}$. Starting research, the system Ce$_2$O$_3$B$_2$O$_3$ was represented by four modifications of the ortho-oxoborate CeBO$_3$ (Ce$_2$O$_3$:B$_2$O$_3$ = 1:1; $\lambda$, $\nu$, $\pi$, and H-CeBO$_3$), and two new modifications of cerium meta-oxoborate. The monoclinic $\delta$-Ce(BO$_2$)$_3$ was synthesized at 3.5 GPa and 1050 °C, the synthesis of the orthorhombic $\gamma$-Ce(BO$_2$)$_3$ needed high-pressure/high-temperature conditions of 7.5 GPa and 1000 °C. Despite intensive search, no cerium-polyoxoborates with compositions like RE$_2$B$_{10}$O$_{24}$ ($RE =$ La, Pr$_1$,$^{[16,17]}$ RE$_2$B$_{10}$O$_{12}$ ($RE =$ Er–Lu$_3$)$^{[18]}$ or RE$_2$B$_{15}$O$_{35}$ ($RE =$ Dy, Ho)$^{[2–3]}$ could be synthesized. Now, the application of high-pressure/high-temperature conditions enabled the synthesis of a cerium-polyoxyborate with the composition Ce$_6$B$_{14}$O$_{27}$, which is isotypic to the recently discovered La$_4$B$_{14}$O$_{27}$.$^{[19]}$ In this paper, we describe the synthesis of Ce$_4$B$_{14}$O$_{27}$, the single-crystal structure determination, Raman spectroscopic investigations, and a comparison to the isotypic phase La$_4$B$_{14}$O$_{27}$.
Mainleus, Germany) was used. The assembly and its preparation are described in the literature.\textsuperscript{[20–24]}

The 18/11 assembly was compressed up to 2.6 GPa in 65 min and heated to 750 °C (cylindrical graphite furnace) in the following 10 min, kept there for 15 min, and cooled down to 450 °C in 25 min at constant pressure. After natural cooling down to room temperature by switching off the heating, a decompression period of 3.5 h was required. The recovered octahedral pressure medium (MgO, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) was broken apart and the sample was carefully separated from the surrounding graphite and boron nitride. The compound Ce₄B₁₄O₂₇ was found in the form of colorless air-resistant crystals.

Two corresponding experiments under ambient pressure conditions at 700 °C and 850 °C using CeO₂, B₂O₃, and CeF₃ (flux material) in a boron-nitride crucible did not lead to the desired polyborate Ce₄B₁₄O₂₇. Instead of, the syntheses led to the monoclinic boron nitride. The compound Ce₄B₁₄O₂₇ was found in the form of small single-crystals of Ce₄B₁₄O₂₇ were isolated by mechanical fragmentation. 

Figure 1 shows the experimental powder pattern that matches well with the theoretical pattern simulated from the single-crystal data. Small single-crystals of Ce₄B₁₄O₂₇ were isolated by mechanical fragmentation. The single crystal intensity data were collected at room temperature with a Nonius Kappa-CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 70.08 pm). A semiempirical absorption correction based on equivalent and redundant intensities (SCALEPACK)\textsuperscript{[23]} was applied to the intensity data. All relevant details of the data collection and evaluation are listed in Table 1. According to the systematic extinctions, the monoclinic space group C2/c (No. 15) was derived. Because of the fact that Ce₄B₁₄O₂₇ is isotypic to La₄B₁₄O₂₇ and CeF₃. Figure 1 shows the experimental powder pattern that matches well with the theoretical pattern simulated from the single-crystal data. Small single-crystals of Ce₄B₁₄O₂₇ were isolated by mechanical fragmentation. The single crystal intensity data were collected at room temperature with a Nonius Kappa-CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 70.08 pm). A semiempirical absorption correction based on equivalent and redundant intensities (SCALEPACK)\textsuperscript{[23]} was applied to the intensity data. All relevant details of the data collection and evaluation are listed in Table 1. According to the systematic extinctions, the monoclinic space group C2/c (No. 15) was derived. Because of the fact that Ce₄B₁₄O₂₇ is isotypic to La₄B₁₄O₂₇ and CeF₃. Figure 1 shows the experimental powder pattern that matches well with the theoretical pattern simulated from the single-crystal data. Small single-crystals of Ce₄B₁₄O₂₇ were isolated by mechanical fragmentation. 

Crystal Structure Analysis: The sample was characterized by powder X-ray diffraction, which was performed in transmission geometry on a flat sample of the reaction product, using a STOE STADI powder diffractometer with Ge(111)-monochromatized Mo-Kα radiation. The diffraction pattern showed reflections of Ce₄B₁₄O₂₇ and CeF₃. Instead of, the syntheses led to the monoclinic boron nitride. The compound Ce₄B₁₄O₂₇ was found in the form of colorless air-resistant crystals.

The structure of Ce₄B₁₄O₂₇ consists of a highly condensed boron-oxygen network and trivalent cerium ions. Figure 2 shows the structure along [010]. The boron-oxygen network is composed of linked trigonal [BO₃]³⁻ and tetrahedral [BO₄]⁴⁻ groups. Four of the seven crystallographically different boron atoms are coordinated by four oxygen ions [B₁–B₄; d(B–O) = 144.3(4)–149.4(4) pm, O-B-O = 133.9(4)–141.4(4)°], while the remaining boron atoms build up trigonal groups [B₅–B₇; d(B–O) = 133.9(4)–141.4(4) pm, O-B-O = 116.2(3)–122.5(3)°]. All cerium–oxygen distances and boron–oxygen distances are listed in Table 4. The mean values of the boron-oxygen distances (146.7–147.8 pm for tetrahedral coordinated boron atoms and 136.6–137.9 pm for trigonal-planar boron atoms) correspond well with the known average values for

| Table 1. Crystal data and structure refinement of Ce₄B₁₄O₂₇. |
|-----------------|-----------------|
| Empirical Formula | Ce₄B₁₄O₂₇       |
| Molar mass /g·mol⁻¹ | 1143.82         |
| Crystal system    | monoclinic      |
| Space group       | C2/c (No. 15)   |
| Single-crystal diffractometer | Bruker AXS / Nonius Kappa CCD |
| Radiation         | Mo-Kα (λ = 71.073 pm) |
| a /pm             | 1117.8(2)       |
| b /pm             | 640.9(2)        |
| c /pm             | 2531.7(5)       |
| β /°              | 100.2(1)        |
| Volume /Å³        | 1785.0(6)       |
| Formula units per cell | 4               |
| Temperature /K     | 293(2)          |
| Calculated density /g·cm⁻³ | 4.26          |
| Crystal size /mm² | 0.04 × 0.03 × 0.02 |
| Absorption coefficient /mm⁻¹ | 10.2      |
| F(000)            | 2072            |
| θ range /°        | 1.6–37.8        |
| Range in h k l    | −17 < h < 19    |
| −11 < k < 8      |
| −41 < l < 43     |
| Total no. reflections | 13907          |
| Independent reflections | 4768 (Rint = 0.0599) |
| Reflections with f > 2σ(f) | 3605 (Rwp = 0.0598) |
| Data / parameters | 4768 / 205      |
| Absorption correction | Multi-scan\textsuperscript{[23]} |
| Goodness-of-fit (R²) | 1.058          |
| Final R indices [I > 2σ(I)] | R₁ = 0.0360; wR₂ = 0.0600 |
| R indices (all data) | R₁ = 0.0613; wR₂ = 0.0660 |
| Largest differ. peak / deepest hole /eÅ⁻³ | 2.15 / −2.73 |

Results and Discussion

Crystal Structure of Ce₄B₁₄O₂₇

The structure of Ce₄B₁₄O₂₇ consists of a highly condensed boron-oxygen network and trivalent cerium ions. Figure 2 shows the structure along [010]. The boron-oxygen network is comprised of linked trigonal [BO₃]³⁻ and tetrahedral [BO₄]⁴⁻ groups. Four of the seven crystallographically distinct boron atoms are coordinated by four oxygen ions [B₁–B₄; d(B–O) = 144.3(4)–149.4(4) pm, O-B-O = 133.9(4)–141.4(4)°], while the remaining boron atoms build up trigonal groups [B₅–B₇; d(B–O) = 133.9(4)–141.4(4) pm, O-B-O = 116.2(3)–122.5(3)°]. All cerium–oxygen distances and boron–oxygen distances are listed in Table 4. The mean values of the boron-oxygen distances (146.7–147.8 pm for tetrahedral coordinated boron atoms and 136.6–137.9 pm for trigonal-planar boron atoms) correspond well with the known average values for

| Figure 1. Experimental powder pattern of Ce₄B₁₄O₂₇ (top) and the reflections of CeF₃ (top, lines) in comparison with the theoretical powder pattern of Ce₄B₁₄O₂₇ (bottom) based on single-crystal diffraction data. |  |
B–O distances in [BO$_4$]$_5^–$ (147.6 pm) and [BO$_3$]$_3^–$ (137.0 pm) groups \cite{29-31}. The oxygen–boron–oxygen angles of the trigonal [BO$_3$]$_3^–$ and tetrahedral [BO$_4$]$_5^–$ groups are listed in Table 5 and correspond well to the expected angles of tetrahedral- and trigonal groups. Three tetrahedral [BO$_4$]$_5^–$ groups (B1–B3) are condensed via shared corners to so called “dreier” rings.\cite{32}. These [B$_{14}$O$_{27}$]$^{6–}$ groups are linked via trigonal [BO$_3$]$_3^–$ groups (B7) to layers in the ab plane as shown in Figure 3. Two of these layers condense via the O(1) atom to a double layer (Figure 4). The resultant double tetrahedron [B$_1$]$_2$O$_{32}$$^{8–}$ is shown in Figure 5. These double layers are linked via stronds of condensed [B(4)O$_4$]$_5^–$ and [B(5,6)O$_4$]$_5^–$ groups to a three-dimensional network (Figure 6). The crystal structure of Ce$_4$B$_{14}$O$_{27}$ contains two crystallographically distinguishable rare-earth ions. The rare-earth ion Ce1 is surrounded by ten oxygen atoms between 238.4(2) and 285.9(2) pm with a mean value of 263.1 pm, whereas Ce2 is coordinated by eight oxygen atoms between 231.9(2) and 284.1(2) pm with a mean value of 252.6 pm. Figure 7 displays the coordination spheres of the cerium ions. For a more detailed description of the structure, the reader is referred to the description of the isotopic compound La$_4$B$_{14}$O$_{27}$. In this paper, we briefly compare Ce$_4$B$_{14}$O$_{27}$ to the isotypic phase La$_4$B$_{14}$O$_{27}$.

The MAPLE values (MAdelung Part of Lattice Energy)\cite{33-35} were calculated from the crystal structure to compare them with the MAPLE values received from the summation of the
Table 4. Cerium-oxygen and boron-oxygen distances /pm in Ce₄B₁₄O₂₇, calculated with the single-crystal lattice parameters.

| Distances          | Values (pm)        |
|--------------------|--------------------|
| Ce₁–O₁₃            | 238.4(2)           |
| Ce₁–O₁₅            | 244.5(2)           |
| Ce₁–O₁₈            | 255.0(2)           |
| Ce₁–O₁₄            | 257.4(2)           |
| Ce₁–O₁₃            | 261.7(2)           |
| Ce₁–O₁₂            | 261.8(2)           |
| Ce₁–O₁₀            | 267.5(2)           |
| Ce₂–O₁₄            | 231.9(2)           |
| Ce₂–O₁₃            | 248.0(2)           |
| Ce₂–O₁₀            | 251.7(2)           |
| Ce₂–O₁₁            | 253.2(2)           |
| B₁–O₁              | 145.4(3)           |
| B₂–O₂              | 147.9(4)           |
| B₂–O₁              | 148.5(4)           |
| B₁–O₂              | 149.4(4)           |
| B₂–O₃              | 147.8              |
| B₂–O₄              | 147.8              |
| B₂–O₅              | 144.0(4)           |
| B₂–O₆              | 145.4(4)           |
| B₂–O₇              | 147.4(4)           |
| B₂–O₈              | 147.4(4)           |
| B₂–O₉              | 147.4(4)           |
| B₂–O₁₀             | 147.4(4)           |
| B₂–O₁₁             | 147.4(4)           |
| B₂–O₁₂             | 147.4(4)           |
| Ø                  | 147.1              |

Table 5. Selected interatomic angles /° in Ce₄B₁₄O₂₇, calculated with the single-crystal lattice parameters.

| Angles             | Values (°)        |
|--------------------|------------------|
| O₁–B₁–O₂          | 105.5(2)         |
| O₁–B₁–O₃          | 116.4(3)         |
| O₂–B₁–O₃          | 108.2(3)         |
| O₁–B₁–O₄          | 109.9(2)         |
| O₂–B₁–O₄          | 113.8(2)         |
| O₃–B₁–O₄          | 104.3(2)         |
| Ø                  | 109.5             |
| O₅–B₃–O₉          | 112.9(3)         |
| O₅–B₃–O₈          | 110.9(3)         |
| O₉–B₄–O₁₀         | 112.6(3)         |
| O₅–B₃–O₂          | 110.5(3)         |
| O₉–B₃–O₂          | 103.5(3)         |
| O₈–B₃–O₂          | 106.0(2)         |
| Ø                  | 109.4             |
| O₁₄–B₅–O₇         | 117.1(3)         |
| O₁₄–B₅–O₁₀        | 121.8(3)         |
| Ø                  | 120.0             |
| O₆–B₇–O₃          | 117.8(3)         |
| O₆–B₇–O₈          | 120.3(3)         |
| Ø                  | 120.0             |

binary components A-type Ce₂O₃[36] and the high-pressure modification B₂O₃-II[37] The value of 182961 kJ·mol⁻¹ was obtained in comparison to 181866 kJ·mol⁻¹ (deviation = 0.6%), starting from the binary oxides [2 × Ce₂O₃ (14150 kJ·mol⁻¹) + 7 × B₂O₃-II (21938 kJ·mol⁻¹)].

Furthermore, the bond-valence sums of Ce₄B₁₄O₂₇ were calculated from the crystal structure for the rare-earth ions, using the bond length/bond-strength concept (ΣV)[38,39]. The calculation revealed values of: +2.95 (Ce₁) and +3.12 (Ce₂), which fit well for the formal ionic charges. For the boron ions, the values vary between +2.91 and +3.09. The oxygen ions show values of −1.90 to −2.15.

Figure 2. Crystal structure of Ce₄B₁₄O₂₇ along [010].

The comparison of the lattice parameters a, b, c, and β [a = 1117.8(2), b = 640.9(2), c = 2531.7(5), β = 100.2(1)° for Ce₄B₁₄O₂₇ and a = 1120.84(9), b = 641.98(6), c = 2537.2(2), β = 100.125(8)° for La₄B₁₄O₂₇] reveals the typical rise from cerium compounds to lanthanum compounds corresponding to...
the slightly larger size of La$^{3+}$ compared to Ce$^{3+}$. No greater deviations of the bond lengths and angles are observed. The coordination numbers of the rare-earth ions are equivalent.

**Physical Properties of Ce$_4$B$_{14}$O$_{27}$**

**Raman Spectroscopy**

Confocal Raman spectra of single crystals of Ce$_4$B$_{14}$O$_{27}$ were measured in the range of 100–6000 cm$^{-1}$ with a HORIBA LABRAM HR-800 Raman micro-spectrometer under a 100× objective (numerical aperture N.A. 0.9, Olympus, Hamburg, Germany). The crystal was excited by the 532.2 nm emission line of a 30 mW Nd:YAG laser (green). The laser focus on the sample surface was ca. 1 μm. The scattered light was dispersed by a grating with 1800 lines per mm and collected by a 1024/256 open electrode CCD detector. Third order polynomial background subtraction, normalization, and band fitting by Gauss-Lorentz functions were done by the LABSPEC 5 software (HORIBA).

Figure 8 shows the Raman spectrum of Ce$_4$B$_{14}$O$_{27}$ in the range of 100 to 4000 cm$^{-1}$.

LABRAM HR-800 Raman micro-spectrometer under a 100× objective (numerical aperture N.A. 0.9, Olympus, Hamburg, Germany). The crystal was excited by the 532.2 nm emission line of a 30 mW Nd:YAG laser (green). The laser focus on the sample surface was ca. 1 μm. The scattered light was dispersed by a grating with 1800 lines per mm and collected by a 1024/256 open electrode CCD detector. Third order polynomial background subtraction, normalization, and band fitting by Gauss-Lorentz functions were done by the LABSPEC 5 software (HORIBA).

Figure 8 shows the Raman spectrum of Ce$_4$B$_{14}$O$_{27}$ from 100 to 4000 cm$^{-1}$. In the range of 3000 to 3600 cm$^{-1}$, no O-H water bands could be detected. Bands around 900 cm$^{-1}$ in oxoborates are usually assigned to stretching modes of the [BO$_4$]$^{5-}$ groups. However, the trigonal [BO$_3$]$^{5-}$ groups are ex-
pected at wavenumbers above 1200 cm\(^{-1}\).\(^{5,40-43}\) The range between 100 and 1500 cm\(^{-1}\) is displayed in Figure 9 (top) and the range between 1500 and 3000 cm\(^{-1}\) in the bottom of Figure 9. Bands at wavenumbers smaller than 500 cm\(^{-1}\) can be assigned to Ce–O bonds, to lower wavenumbers shifted bending and stretching modes of the tetrahedral \([\text{BO}_4]^{5-}\) groups, whereas vibrational modes above 1200 cm\(^{-1}\) generally refer to trigonal \([\text{BO}_3]^{3-}\) groups leading to various modes and based on the deviation of the distances from the ideal B–O distance to a large shift of the bands.

Conclusions

With the successful synthesis of \(\text{Ce}_4\text{B}_{14}\text{O}_{27}\), a new cerium polyborate and furthermore the first isotypic compound to \(\text{La}_8\text{B}_{14}\text{O}_{27}\) was synthesized and characterized. In accordance with the relatively low applied pressure of 2.6 GPa, the boron oxygen network is built up by trigonal \([\text{BO}_3]^{3-}\) and tetrahedral \([\text{BO}_4]^{5-}\) groups. Four of the seven crystallographically different boron atoms are coordinated by four oxygen ions. The application of similar synthetic conditions to heavier rare-earth elements could lead to additional isotypic compounds and will be studied in the future.

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References

[1] S. A. Hering, A. Haberer, R. Kaindl, H. Huppertz, Solid State Sci. 2010, 12, 1993.
[2] H. Huppertz, B. von der Eltz, J. Am. Chem. Soc. 2002, 124, 9376.
[3] H. Huppertz, Z. Naturforsch. 2003, 58b, 278.
[4] H. Emme, H. Huppertz, Z. Anorg. Allg. Chem. 2002, 628, 2165.
[5] H. Emme, H. Huppertz, Chem. Eur. J. 2003, 9, 3623.
[6] H. Emme, H. Huppertz, Acta Crystallogr. Sect. A 2005, 61, 129.
[7] F. Goubin, Y. Montardi, P. Deniard, X. Rocquefelte, B. Brec, S. Jobic, J. Solid State Chem. 2004, 177, 89.
[8] J. Weidelt, H. U. Bambauer, Naturwissenschaften 1968, 55, 342.
[9] R. Böhlhoff, H. U. Bambauer, W. Hoffmann, Naturwissenschaften 1971, 133, 386.
[10] R. Böhlhoff, H. U. Bambauer, W. Hoffmann, Z. Kristallogr. 1970, 57, 129.
[11] J. Y. Henry, Mater. Res. Bull. 1976, 11, 577.
[12] A. Gerjounova, P. Held, P. Becker, L. Bohaty, Acta Crystallogr. Sect. E 2004, 60, 1134.
[13] L. Li, X. Jin, G. Li, Y. Wang, F. Liao, Chem. Mater. 2003, 15, 2253.
[14] A. Haberer, G. Heymann, H. Huppertz, Z. Naturforsch. 2007, 62b, 759.
[15] H. Emme, C. Despotopoulou, H. Huppertz, Z. Anorg. Allg. Chem. 2004, 630, 2450.
[16] A. Haberer, G. Heymann, H. Huppertz, J. Solid State Chem. 2007, 180, 1595.
[17] E. Hinteregger, G. Heymann, T. S. Hofer, H. Huppertz, Z. Naturforsch. 2012, 67b, 605.
[18] H. Emme, M. Valldor, R. Pöttgen, H. Huppertz, Chem. Mater. 2005, 17, 2707.
[19] T. Nikelski, M. C. Schäfer, Th. Schleid, Z. Anorg. Allg. Chem. 2008, 634, 49.
[20] N. Kawai, S. Endo, Rev. Sci. Instrum. 1970, 41, 1178.
[21] D. Walker, M. A. Carpenier, C. M. Hitch, Am. Mineral. 1990, 75, 1020.
[22] D. Walker, Am. Mineral. 1991, 76, 1092.
[23] D. C. Rubie, Phase Transitions 1999, 68, 431.
[24] H. Huppertz, Z. Kristallogr. 2004, 219, 330.
[25] Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307.
[26] G. M. Sheldrick, SHELXS-97 and SHELXL-97. Program Suite for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[27] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112.
[28] G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467.
[29] E. Zobetz, Z. Kristallogr. 1990, 191, 45.
[30] F. C. Hawthorne, P. C. Burns, J. D. Grice, Boron: Mineralogy, Petrology and Geochemistry (Ed.: E. S. Grew), Mineralogical Society of America, Washington, 1996.
[31] E. Zobetz, Z. Kristallogr. 1982, 160, 81.
[32] The naming of rings of structural elements was coined by F. Liebau, Structural Chemistry of Silicates, Springer, Berlin, Germany 1985 and is derived from german numbers, e.g. the term “dreier” ring is derived from the words “drei”, which means three. However, the term “dreier” ring does not mean a three-membered
ring, but rather a ring with three tetrahedral centers (B) and three electronegative atoms (O).

[33] R. Hoppe, *Angew. Chem.* 1966, 78, 52; *Angew. Chem. Int. Ed. Engl.* 1966, 5, 95.
[34] R. Hoppe, *Angew. Chem.* 1970, 82, 7; *Angew. Chem. Int. Ed. Engl.* 1970, 9, 25.
[35] R. Hübenthal, Maple, Program for the Calculation of MAPLE Values (version 4) University of Giessen, Gießen, Germany, 1993.
[36] N. Hirosaki, S. Ogata, C. Kocer, *J. Alloys Compd.* 2003, 351, 21.
[37] C. T. Prewitt, R. D. Shannon, *Acta Crystallogr. Sect. B* 1968, 24, 869.
[38] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* 1985, 41, 244.
[39] N. E. Brese, M. O’Keeffe, *Acta Crystallogr. Sect. B* 1991, 47, 192.
[40] H. Huppertz, *J. Solid State Chem.* 2004, 177, 3700.
[41] L. Jun, X. Shuping, G. Shiyang, *Spectrochim. Acta A* 1995, 51, 519.
[42] G. Chadeyron, M. El-Ghozzi, R. Mahiou, A. Arbus, J. C. Cousseins, *J. Solid State Chem.* 1997, 128, 261.
[43] J. C. Zhang, Y. H. Wang, X. Guo, *J. Lumin.* 2007, 122–123, 980.

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