

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

Ernst Hinteregger,<sup>[a]</sup> Lukas Perfler,<sup>[b]</sup> and Hubert Huppertz\*<sup>[a]</sup>

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

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

**Abstract.**  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  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  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  is isotopic to  $\text{La}_4\text{B}_{14}\text{O}_{27}$ .  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  crystallizes monoclinically 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  $[\text{BO}_4]^{5-}$  tetrahedra and trigonal-planar  $[\text{BO}_3]^{3-}$  groups. The structure contains two crystallographically different cerium ions. Furthermore, Raman spectroscopy was performed on single crystals of  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$ .

## Introduction

The structural chemistry of oxoborates exhibits a respectable diversity, which yields from the ability of the boron atom to form trigonal-planar  $[\text{BO}_3]^{3-}$  groups and tetrahedral  $[\text{BO}_4]^{5-}$  groups. These groups can occur isolated or linked to highly-condensed three-dimensional networks. In the majority of cases, the trigonal-planar  $[\text{BO}_3]^{3-}$  groups disappear with increasing pressure, so in high-pressure oxoborates, the boron atoms favor the fourfold coordination forming  $[\text{BO}_4]^{5-}$  groups. Above a pressure of 10 GPa, only a few compounds are known, which contain trigonal-planar  $[\text{BO}_3]^{3-}$  groups, e.g.  $\text{Ho}_3\text{O}_{27}(\text{BO}_3)_3(\text{BO}_4)_6$ .<sup>[1]</sup> The linking of the tetrahedral  $[\text{BO}_4]^{5-}$  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 polyborates  $\text{RE}_4\text{B}_6\text{O}_{15}$  ( $\text{RE} = \text{Dy}, \text{Ho}$ ),<sup>[2,3]</sup> and  $\alpha\text{-RE}_2\text{B}_4\text{O}_9$  ( $\text{RE} = \text{Sm-Ho}$ ).<sup>[4–6]</sup> Moreover, high-pressure/high-temperature syntheses led to increased coordination numbers (CN) of the rare-earth ions, and also the coordination numbers of the oxygen atoms could be partially enhanced from twofold ( $\text{O}^{2\text{I}}$ ) to threefold coordinated ( $\text{O}^{3\text{I}}$ ).

Recent studies into the chemistry of rare-earth oxoborates under high-pressure/high-temperature conditions reached to a large number of polymorphs and new compositions. Before we

started research, the system  $\text{Ce}_2\text{O}_3/\text{B}_2\text{O}_3$  was represented by four modifications of the *ortho*-oxoborate  $\text{CeBO}_3$  ( $\text{Ce}_2\text{O}_3:\text{B}_2\text{O}_3 = 1:1$ ;  $\lambda$ -,  $\nu$ -,  $\pi$ -, and  $\text{H-CeBO}_3$ ),<sup>[7–11]</sup> the *meta*-oxoborate  $\alpha\text{-Ce}(\text{BO}_2)_3$  ( $\text{Ce}_2\text{O}_3:\text{B}_2\text{O}_3 = 1:3$ ),<sup>[1,12]</sup> and  $\beta\text{-REB}_5\text{O}_9$ .<sup>[13]</sup> The application of high-pressure/high-temperature techniques allowed the synthesis of  $\delta\text{-Ce}(\text{BO}_2)_3$ <sup>[14]</sup> and  $\gamma\text{-Ce}(\text{BO}_2)_3$ .<sup>[15]</sup> Two new modifications of cerium *meta*-oxoborate. While the monoclinic  $\delta\text{-Ce}(\text{BO}_2)_3$  was synthesized at 3.5 GPa and 1050 °C, the synthesis of the orthorhombic  $\gamma\text{-Ce}(\text{BO}_2)_3$  needed high-pressure/high-temperature conditions of 7.5 GPa and 1000 °C. Despite intensive search, no cerium-polyoxoborates with compositions like  $\text{RE}_4\text{B}_{10}\text{O}_{21}$  ( $\text{RE} = \text{La}, \text{Pr}$ ),<sup>[16,17]</sup>  $\text{RE}_3\text{B}_5\text{O}_{12}$  ( $\text{RE} = \text{Er-Lu}$ ),<sup>[18]</sup> or  $\text{RE}_4\text{B}_6\text{O}_{15}$  ( $\text{RE} = \text{Dy}, \text{Ho}$ )<sup>[2,3]</sup> could be synthesized. Now, the application of high-pressure/high-temperature conditions enabled the synthesis of a cerium-polyoxoborate with the composition  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$ , which is isotopic to the recently discovered  $\text{La}_4\text{B}_{14}\text{O}_{27}$ .<sup>[19]</sup> In this paper, we describe the synthesis of  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$ , the single-crystal structure determination, Raman spectroscopic investigations, and a comparison to the isotopic phase  $\text{La}_4\text{B}_{14}\text{O}_{27}$ .

## Experimental Section

**Synthesis:** During our attempts, to synthesize a cerium fluorido- or fluoride borate under high-pressure/high-temperature conditions of 2.6 GPa and 750 °C, the new cerium oxoborate  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  was synthesized, starting from a mixture of 79.2 mg  $\text{CeO}_2$  (Auer-Remy, Hamburg, Germany, 99.9%), 80.1 mg  $\text{B}_2\text{O}_3$  (Strem Chemicals, Newburyport, USA, 99.9+%), and 90.7 mg  $\text{CeF}_3$  (Strem Chemicals, Newburyport, USA 99.9+%). 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, Ceratizit, Reutte, Austria). To apply the pressure, a 1000 t multianvil press with a Walker-type module (both devices from the company Voggenreiter,

\* Prof. Dr. H. Huppertz  
E-Mail: Hubert.Huppertz@uibk.ac.at

[a] Institut für Allgemeine, Anorganische und Theoretische Chemie  
Leopold-Franzens-Universität Innsbruck  
Innrain 80-82  
6020 Innsbruck, Austria

[b] Institut für Mineralogie und Petrographie  
Leopold-Franzens-Universität Innsbruck  
Innrain 52  
6020 Innsbruck, Austria

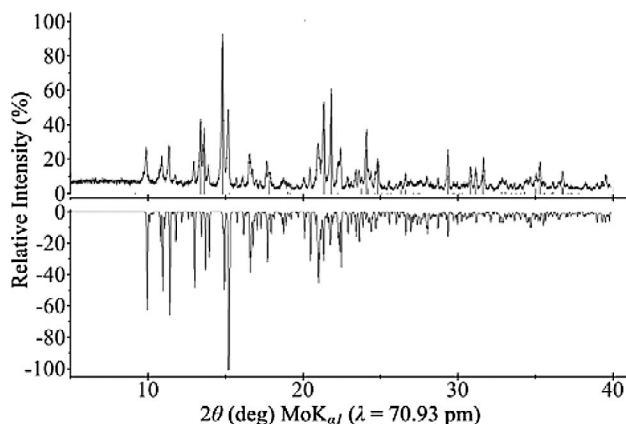
Re-use of this article is permitted in accordance with the Terms and Conditions set out at <http://zaac.wiley-vch.de/open>.

Mainleus, Germany) was used. The assembly and its preparation are described in the literature.<sup>[20–24]</sup>

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 Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> was found in the form of colorless air-resistant crystals.

Two corresponding experiments under ambient pressure conditions at 700 °C and 850 °C using CeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and CeF<sub>3</sub> (flux material) in a boron-nitride crucible did not lead to the desired polyborate Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub>. Instead of, the syntheses led to the monoclinic *meta*-borate  $\alpha$ -Ce(BO<sub>2</sub>)<sub>3</sub>.<sup>[1,12]</sup>

**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 P powder diffractometer with Ge(111)-monochromatized Mo-*K*<sub>α1</sub> ( $\lambda = 70.93$  pm) radiation. The diffraction pattern showed reflections of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> and CeF<sub>3</sub>. Figure 1 shows the experimental powder pattern that matches well with the theoretical pattern simulated from the single-crystal data. Small single-crystals of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> were isolated by mechanical fragmentation. The single crystal intensity data were collected at room temperature with a Nonius Kappa-CCD diffractometer with graphite-monochromatized Mo-*K*<sub>α</sub> radiation ( $\lambda = 71.073$  pm). A semiempirical absorption correction based on equivalent and redundant intensities (SCALEPACK)<sup>[25]</sup> 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 Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> is isotypic to La<sub>4</sub>B<sub>14</sub>O<sub>27</sub>,<sup>[16]</sup> the structural refinement was performed using the positional parameters of La<sub>4</sub>B<sub>14</sub>O<sub>27</sub> as starting values [SHELXL-97<sup>[26–28]</sup> (full-matrix least-squares on *F*<sup>2</sup>)]. In comparison with the structure data of *Schleid* et al., in which only the lanthanum atoms could be refined with anisotropic displacement parameters, an anisotropic refinement for all atoms of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> was possible. The final difference Fourier syntheses did not reveal any significant peaks in the refine-



**Figure 1.** Experimental powder pattern of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> (top) and the reflections of CeF<sub>3</sub> (top, lines) in comparison with the theoretical powder pattern of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> (bottom) based on single-crystal diffraction data.

**Table 1.** Crystal data and structure refinement of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub>.

Empirical Formula	Ce <sub>4</sub> B <sub>14</sub> O <sub>27</sub>
Molar mass /g·mol <sup>-1</sup>	1143.82
Crystal system	monoclinic
Space group	<i>C2/c</i> (No. 15)
Single-crystal diffractometer	Bruker AXS / Nonius Kappa CCD
Radiation	Mo- <i>K</i> <sub>α</sub> ( $\lambda = 71.073$ pm)
<i>a</i> /pm	1117.8(2)
<i>b</i> /pm	640.9(2)
<i>c</i> /pm	2531.7(5)
$\beta$ /°	100.2(1)
Volume /Å <sup>3</sup>	1785.0(6)
Formula units per cell	4
Temperature /K	293(2)
Calculated density /g·cm <sup>-3</sup>	4.26
Crystal size /mm <sup>3</sup>	0.04 × 0.03 × 0.02
Absorption coefficient /mm <sup>-1</sup>	10.2
<i>F</i> (000)	2072
$\theta$ range /°	1.6–37.8
Range in <i>h k l</i>	–17 < <i>h</i> < 19 –11 < <i>k</i> < 8 –41 < <i>l</i> < 43
Total no. reflections	13907
Independent reflections	4768 ( <i>R</i> <sub>int</sub> = 0.0509)
Reflections with <i>I</i> > 2σ( <i>I</i> )	3605 ( <i>R</i> <sub>σ</sub> = 0.0598)
Data / parameters	4768 / 205
Absorption correction	Multi-scan <sup>[23]</sup>
Goodness-of-fit ( <i>F</i> <sup>2</sup> )	1.058
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0360; <i>wR</i> <sub>2</sub> = 0.0600
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0613; <i>wR</i> <sub>2</sub> = 0.0660
Largest differ. peak / deepest hole /e·Å <sup>-3</sup>	2.15 / –2.73

ment. As positional parameters of La<sub>4</sub>B<sub>14</sub>O<sub>27</sub>, we used the standard setting as deposited at the FIZ Karlsruhe with the deposition number CSD-418109. Table 2, Table 3, Table 4, and Table 5 list the positional parameters, anisotropic displacement parameters, interatomic distances, and angles.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request-for-deposited-data.html>) on quoting the depository number CSD-425017.

## Results and Discussion

### Crystal Structure of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub>

The structure of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> consists of a highly condensed boron-oxygen network and trivalent cerium ions. Figure 2 shows the structure along [0 $\bar{1}$ 0]. The boron-oxygen network is composed of linked trigonal [BO<sub>3</sub>]<sup>3-</sup> and tetrahedral [BO<sub>4</sub>]<sup>5-</sup> 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,  $\angle$ 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,  $\angle$ 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 2.** Atomic coordinates and isotropic equivalent displacement parameters ( $U_{\text{eq}}/\text{\AA}^2$ ) for  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  and  $(\text{La}_4\text{B}_{14}\text{O}_{27})$ .  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckoff-Symbol	x	y	z	$U_{\text{eq}}$
Ce1	8f	0.17020(2)	0.08703(3)	0.184732(6)	0.00727(5)
(La1)		(0.1709)	(0.0835)	(0.1849)	(0.0057)
Ce2	8f	0.09943(2)	0.24975(3)	0.443926(7)	0.00805(5)
(La2)		(0.0985)	(0.2487)	(0.4441)	(0.0067)
B1	8f	0.0925(3)	0.2682(5)	0.2948(2)	0.0067(6)
(B1)		(0.0899)	(0.2667)	(0.2948)	(0.0072)
B2	8f	0.2822(3)	0.0764(6)	0.3244(2)	0.0071(6)
(B2)		(0.2807)	(0.0759)	(0.3245)	(0.0059)
B3	8f	0.4010(3)	0.4345(6)	0.1494(2)	0.0074(6)
(B3)		(0.4005)	(0.4340)	(0.1493)	(0.0053)
B4	8f	0.3948(3)	0.2377(6)	0.0549(2)	0.0078(6)
(B4)		(0.3951)	(0.2385)	(0.0545)	(0.0047)
B5	8f	0.3778(3)	0.1689(6)	0.4217(2)	0.0088(6)
(B5)		(0.3788)	(0.1682)	(0.4213)	(0.0082)
B6	8f	0.1678(3)	0.1430(6)	0.0469(2)	0.0075(6)
(B6)		(0.1686)	(0.1428)	(0.0461)	(0.0084)
B7	8f	0.5038(3)	0.1001(6)	0.1868(2)	0.0075(6)
(B7)		(0.5053)	(0.1010)	(0.1873)	(0.0051)
O1	4e	0	0.2029(5)	¼	0.0106(6)
(O1)		(0)	(0.2025)	(¼)	(0.0093)
O2	8f	0.0634(2)	0.1574(4)	0.34220(8)	0.0070(4)
(O2)		(0.0629)	(0.1544)	(0.3417)	(0.0053)
O3	8f	0.0991(2)	0.4951(4)	0.30690(9)	0.0078(4)
(O3)		(0.0985)	(0.4916)	(0.3067)	(0.0083)
O4	8f	0.2149(2)	0.2163(4)	0.28251(8)	0.0080(4)
(O4)		(0.2139)	(0.2143)	(0.2831)	(0.0054)
O5	8f	0.2909(2)	0.3928(3)	0.16986(9)	0.0084(4)
(O5)		(0.2902)	(0.3919)	(0.1699)	(0.0080)
O6	8f	0.1091(2)	0.4888(3)	0.19066(9)	0.0073(4)
(O6)		(0.1102)	(0.4881)	(0.1912)	(0.0070)
O7	8f	0.3071(2)	0.2091(4)	0.37269(8)	0.0094(4)
(O7)		(0.3071)	(0.2077)	(0.3725)	(0.0074)
O8	8f	0.5040(2)	0.3111(4)	0.17882(9)	0.0082(4)
(O8)		(0.5033)	(0.3083)	(0.1787)	(0.0066)
O9	8f	0.3863(2)	0.4085(4)	0.09132(8)	0.0089(4)
(O9)		(0.3865)	(0.4067)	(0.0919)	(0.0069)
O10	8f	0.5006(2)	0.1005(4)	0.07423(9)	0.0089(4)
(O10)		(0.5009)	(0.1023)	(0.0737)	(0.0076)
O11	8f	0.2906(2)	0.0967(4)	0.04966(9)	0.0101(4)
(O11)		(0.2907)	(0.0994)	(0.0489)	(0.0082)
O12	8f	0.4093(2)	0.3303(4)	0.00230(9)	0.0117(4)
(O12)		(0.4092)	(0.3334)	(0.0026)	(0.0080)
O13	8f	0.1151(2)	0.1508(4)	0.09082(9)	0.0114(4)
(O13)		(0.1169)	(0.1496)	(0.0902)	(0.0098)
O14	8f	0.3279(2)	0.2033(4)	0.46524(9)	0.0125(5)
(O14)		(0.3279)	(0.2055)	(0.4644)	(0.0084)

**Table 3.** Anisotropic displacement parameters ( $U_{ij}/\text{\AA}^2$ ) for  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  (space group  $C2/c$ ).

Atom	$U_{11}$	$U_{22}$	$U_{33}$
Ce1	0.00685(8)	0.00764(8)	0.00715(7)
Ce2	0.00801(8)	0.00791(8)	0.00758(8)
B1	0.005(2)	0.007(2)	0.009(2)
B2	0.006(2)	0.008(2)	0.007(2)
B3	0.008(2)	0.006(2)	0.008(2)
B4	0.008(2)	0.010(2)	0.005(2)
B5	0.011(2)	0.007(2)	0.008(2)
B6	0.009(2)	0.006(2)	0.008(2)
B7	0.009(2)	0.008(2)	0.006(2)
O1	0.013(2)	0.009(2)	0.009(2)
O2	0.008(2)	0.006(2)	0.0074(9)
O3	0.007(2)	0.0048(9)	0.011(2)
O4	0.008(2)	0.011(2)	0.0054(9)
O5	0.007(2)	0.006(2)	0.014(2)
O6	0.0043(9)	0.0065(9)	0.012(2)
O7	0.009(2)	0.012(2)	0.0068(9)
O8	0.007(2)	0.0058(9)	0.011(2)
O9	0.011(2)	0.008(2)	0.0074(9)
O10	0.0051(9)	0.010(2)	0.011(2)
O11	0.007(2)	0.008(2)	0.015(2)
O12	0.007(2)	0.020(2)	0.007(2)
O13	0.010(2)	0.017(2)	0.008(2)
O14	0.011(2)	0.019(2)	0.008(2)
	$U_{23}$	$U_{13}$	$U_{12}$
Ce1	0.00049(6)	0.00082(5)	-0.00081(6)
Ce2	-0.00119(6)	-0.00043(6)	0.00000(6)
B1	0.001(2)	0.001(2)	0.000(2)
B2	-0.001(2)	0.001(2)	0.002(2)
B3	-0.001(2)	0.002(2)	-0.001(2)
B4	-0.001(2)	-0.001(2)	-0.001(2)
B5	-0.000(2)	0.001(2)	0.002(2)
B6	0.002(2)	0.003(2)	0.000(2)
B7	0.001(2)	0.001(2)	0.000(2)
O1	0	0.000(2)	0
O2	0.0003(8)	0.0035(8)	0.0013(8)
O3	-0.0004(8)	0.0015(8)	-0.0002(8)
O4	0.0005(8)	0.0021(8)	0.0022(8)
O5	0.0000(8)	0.0056(8)	0.0016(8)
O6	0.0004(8)	0.0021(8)	0.0007(8)
O7	-0.0026(8)	-0.0003(8)	0.0014(8)
O8	0.0007(8)	0.0002(8)	0.0024(8)
O9	-0.0005(8)	0.0014(8)	0.0016(9)
O10	0.0010(8)	0.0002(8)	0.0013(8)
O11	-0.0010(8)	0.0008(8)	-0.0009(8)
O12	0.0040(9)	0.0000(8)	-0.0007(9)
O13	-0.0006(9)	0.0038(8)	0.0031(9)
O14	-0.0016(9)	0.0017(8)	0.0007(9)

B–O distances in  $[\text{BO}_4]^{5-}$  (147.6 pm) and  $[\text{BO}_3]^{3-}$  (137.0 pm) groups.<sup>[29–31]</sup> The oxygen–boron–oxygen angles of the trigonal  $[\text{BO}_3]^{3-}$  and tetrahedral  $[\text{BO}_4]^{5-}$  groups are listed in Table 5 and correspond well to the expected angles of tetrahedral- and trigonal groups. Three tetrahedral  $[\text{BO}_4]^{5-}$  groups (B1–B3) are condensed via shared corners to so called “dreier” rings.<sup>[32]</sup> These  $[\text{B}_3\text{O}_9]^{9-}$  groups are linked via trigonal  $[\text{BO}_3]^{3-}$  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  $[(\text{B}1)_2\text{O}_7]^{8-}$  is shown in Figure 5. These double layers are linked via strands of condensed  $[\text{B}(4)\text{O}_4]^{5-}$  and  $[\text{B}(5,6)\text{O}_3]^{3-}$  groups to a three-dimensional network (Figure 6). The crystal structure of  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$

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 isotypic compound  $\text{La}_4\text{B}_{14}\text{O}_{27}$ .<sup>[16]</sup> In this paper, we briefly compare  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  to the isotypic phase  $\text{La}_4\text{B}_{14}\text{O}_{27}$ .

The MAPLE values (*M*Adelung *P*art of *L*attice *E*nergy)<sup>[33–35]</sup> 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 Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub>, calculated with the single-crystal lattice parameters.

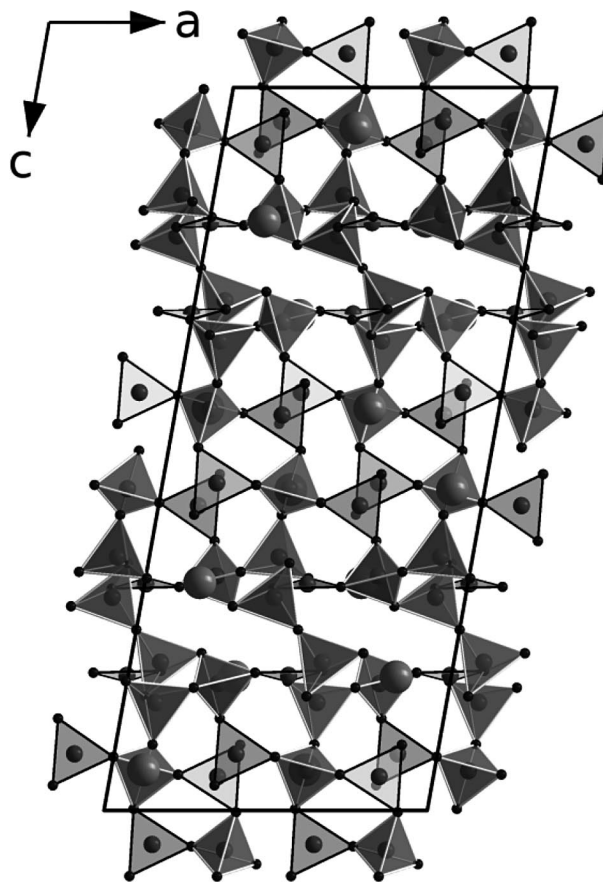
Ce1–O13	238.4(2)	Ce2–O14	231.9(2)	B1–O1	145.4(3)
Ce1–O5	244.5(2)	Ce2–O9	237.8(2)	B1–O2	147.9(4)
Ce1–O8	255.0(2)	Ce2–O13	248.6(2)	B1–O3	148.5(4)
Ce1–O4	257.4(2)	Ce2–O10	251.7(2)	B1–O4	149.4(4)
Ce1–O3	261.7(2)	Ce2–O11	253.2(2)	∅ =	147.8
Ce1–O2	261.8(2)	Ce2–O14	253.2(2)		
Ce1–O6	267.5(2)	Ce2–O2	260.3(2)	B2–O6	145.0(4)
Ce1–O4	275.8(2)	Ce2–O12	284.1(2)	B2–O5	145.4(4)
Ce1–O1	283.1(2)	∅ =	252.6	B2–O7	147.4(4)
Ce1–O7	285.9(2)			B2–O4	148.8(4)
∅ =	263.1			∅ =	146.7
B3–O5	144.3(4)	B4–O9	144.5(4)	B5–O14	133.9(4)
B3–O9	146.0(4)	B4–O11	146.1(4)	B5–O7	137.3(4)
B3–O8	148.4(4)	B4–O10	148.6(4)	B5–O10	141.4(4)
B3–O2	148.8(4)	B4–O12	149.3(4)	∅ =	137.5
∅ =	146.9	∅ =	147.1		
B6–O13	134.7(4)	B7–O6	136.5(4)		
B6–O11	139.4(4)	B7–O3	136.7(4)		
B6–O12	139.5(4)	B7–O8	136.7(4)		
∅ =	137.9	∅ =	136.6		

**Table 5.** Selected interatomic angles /° in Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub>, calculated with the single-crystal lattice parameters.

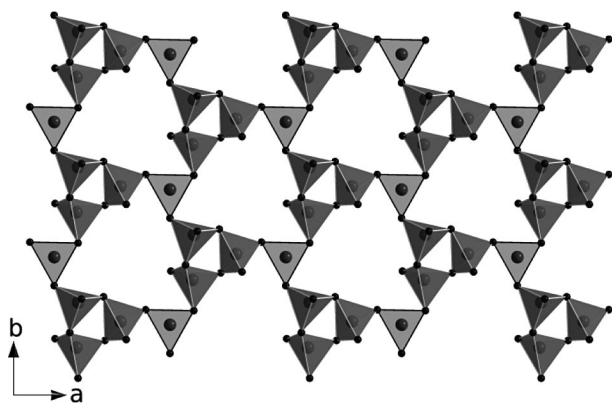
O1–B1–O2	105.5(2)	O6–B2–O5	103.0(3)
O1–B1–O3	116.4(3)	O6–B2–O7	113.4(3)
O2–B1–O3	108.2(3)	O5–B2–O7	114.3(3)
O1–B1–O4	108.9(2)	O6–B2–O4	112.8(3)
O2–B1–O4	113.8(2)	O5–B2–O4	109.7(2)
O3–B1–O4	104.3(2)	O7–B2–O2	104.0(3)
∅ =	109.5	∅ =	109.5
O5–B3–O9	112.9(3)	O9–B4–O11	112.7(3)
O5–B3–O8	110.9(3)	O9–B4–O10	112.1(2)
O9–B3–O8	112.6(3)	O11–B4–O10	103.8(3)
O5–B3–O2	110.5(3)	O9–B4–O12	107.3(3)
O9–B3–O2	103.5(3)	O11–B4–O12	112.1(2)
O8–B3–O2	106.0(2)	O10–B4–O12	108.9(3)
∅ =	109.4	∅ =	109.5
O14–B5–O7	117.1(3)	O13–B6–O11	122.5(3)
O14–B5–O10	121.8(3)	O13–B6–O12	116.2(3)
O7–B5–O10	121.1(3)	O11–B6–O12	121.2(3)
∅ =	120.0	∅ =	120.0
O6–B7–O3	117.8(3)		
O6–B7–O8	120.3(3)		
O3–B7–O8	121.8(3)		
∅ =	120.0		

binary components A-type Ce<sub>2</sub>O<sub>3</sub><sup>[36]</sup> and the high-pressure modification B<sub>2</sub>O<sub>3</sub>-II.<sup>[37]</sup> The value of 182961 kJ·mol<sup>-1</sup> was obtained in comparison to 181866 kJ·mol<sup>-1</sup> (deviation = 0.6%), starting from the binary oxides [2 × Ce<sub>2</sub>O<sub>3</sub> (14150 kJ·mol<sup>-1</sup>) + 7 × B<sub>2</sub>O<sub>3</sub>-II (21938 kJ·mol<sup>-1</sup>)].

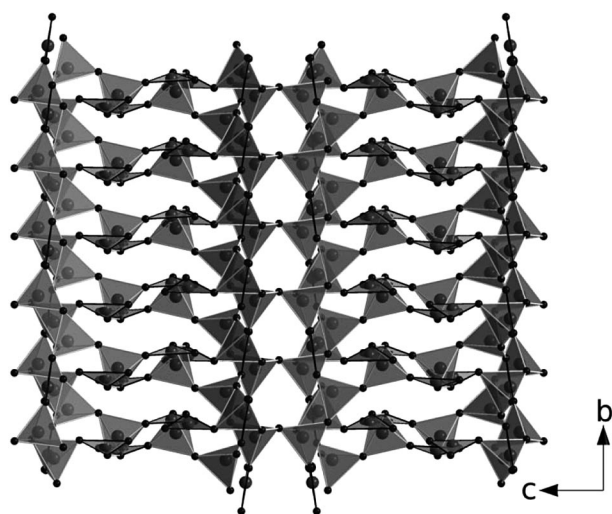
Furthermore, the bond-valence sums of Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> were calculated from the crystal structure for the rare-earth ions, using the bond length/bond-strength concept (ΣV).<sup>[38,39]</sup> The calculation revealed values of: +2.95 (Ce1) and +3.12 (Ce2), which fit well for 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 Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> along [010].

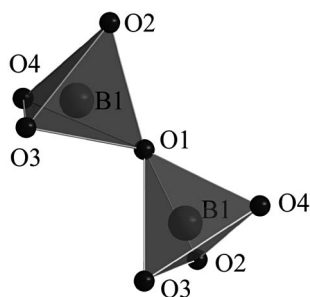
The comparison of the lattice parameters *a*, *b*, *c*, and β [*a* = 1117.8(2), *b* = 640.9(2), *c* = 2531.7(5), β = 100.2(1)° for Ce<sub>4</sub>B<sub>14</sub>O<sub>27</sub> and *a* = 1120.84(9), *b* = 641.98(6), *c* = 2537.2(2), β = 100.125(8)° for La<sub>4</sub>B<sub>14</sub>O<sub>27</sub>] reveals the typical rise from cerium compounds to lanthanum compounds corresponding to



**Figure 3.** A layer built up of so called "dreier" rings and trigonal  $[B(7)O_3]^{3-}$  groups.



**Figure 4.** Two layers which are condensed to a double layer.



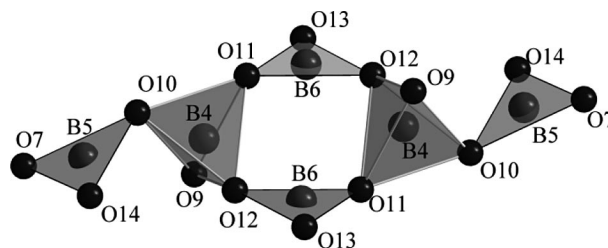
**Figure 5.** Linking  $[B_2O_7]^{8-}$  group.

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.

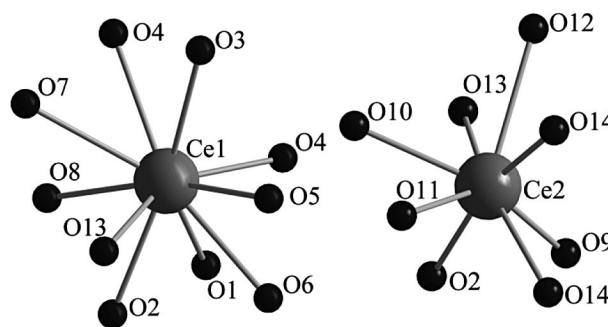
### Physical Properties of $Ce_4B_{14}O_{27}$

#### Raman Spectroscopy

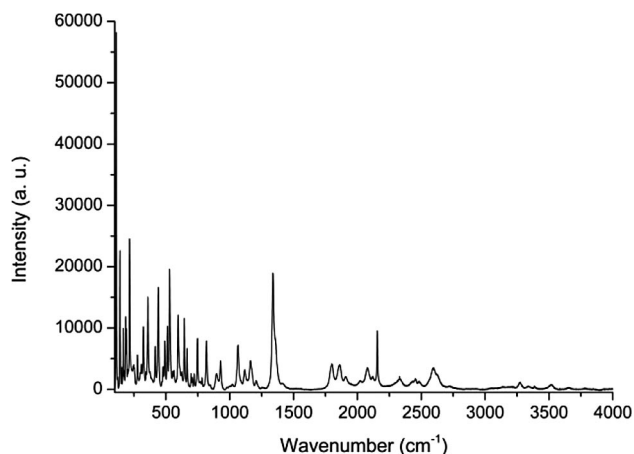
Confocal Raman spectra of single crystals of  $Ce_4B_{14}O_{27}$  were measured in the range of 100–6000  $cm^{-1}$  with a HORIBA



**Figure 6.** Condensed  $[B(4)O_4]^{5-}$  and  $[B(5,6)O_3]^{3-}$  groups, which link the double layers.



**Figure 7.** Coordination spheres of the  $Ce^{3+}$  ions in  $Ce_4B_{14}O_{27}$ .

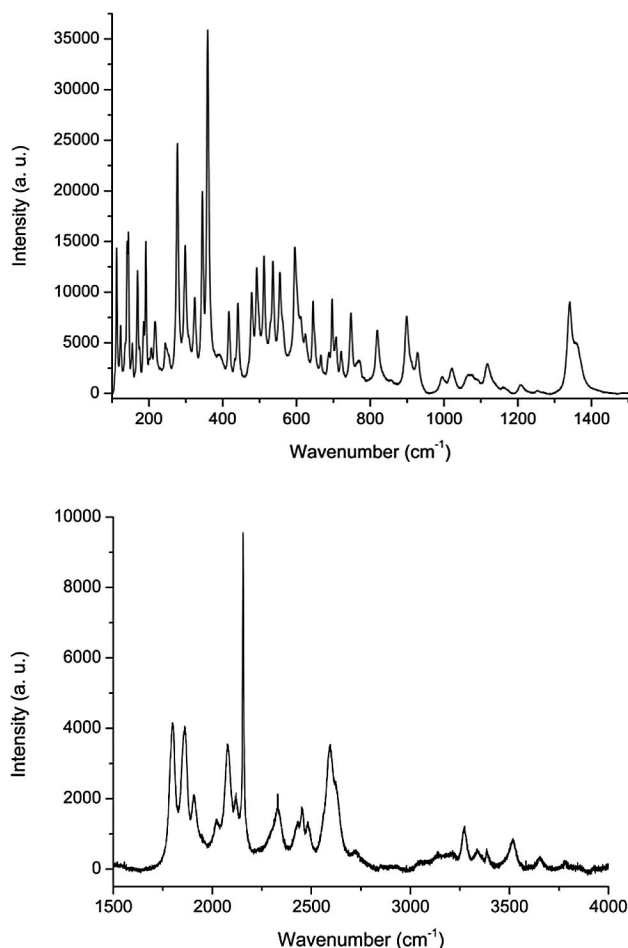


**Figure 8.** Raman spectrum of  $Ce_4B_{14}O_{27}$  in the range of 100 to 4000  $cm^{-1}$ .

LABRAM HR-800 Raman micro-spectrometer under a  $100\times$  objective (numerical aperture N.A. 0.9, Olympus, Hamburg, Germany). The crystal was excited by the 532.22 nm emission line of a 30 mW Nd:YAG laser (green). The laser focus on the sample surface was ca. 1  $\mu m$ . The scattered light was dispersed by a grating with 1800 lines per mm and collected by a  $1024\times 256$  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  $Ce_4B_{14}O_{27}$  from 100 to 4000  $cm^{-1}$ . In the range of 3000 to 3600  $cm^{-1}$ , no OH or 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  $[BO_3]^{3-}$  groups are ex-

pected at wavenumbers above  $1100\text{ cm}^{-1}$ .<sup>[5,40–43]</sup> The range between  $100$  and  $1500\text{ cm}^{-1}$  is displayed in Figure 9 (top) and the range between  $1500$  and  $3000\text{ cm}^{-1}$  in the bottom of Figure 9. Bands at wavenumbers smaller than  $500\text{ cm}^{-1}$  can be assigned to Ce–O bonds, to lower wavenumbers shifted bending and stretching modes of the tetrahedral  $[\text{BO}_4]^{5-}$  groups, as well as lattice vibrations. As expected, bands between  $800$  and  $1800\text{ cm}^{-1}$  are observed due to the presence of trigonal  $[\text{BO}_3]^{3-}$  and tetrahedral  $[\text{BO}_4]^{5-}$  groups, whereas vibrational modes above  $1200\text{ cm}^{-1}$  generally refer to trigonal  $[\text{BO}_3]^{3-}$  groups. The large variation of B–O distances inside the  $[\text{BO}_4]^{5-}$  and  $[\text{BO}_3]^{3-}$  groups leads to various modes and based on the deviation of the distances from the ideal B–O distance to a large shift of the bands.



**Figure 9.** Raman spectrum of the compound  $\text{Ce}_4\text{B}_{14}\text{O}_{27}$  between  $100$  and  $1500\text{ cm}^{-1}$  (top) and between  $1500$  and  $4000\text{ cm}^{-1}$  (bottom).

## 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  $\text{La}_4\text{B}_{14}\text{O}_{27}$  was synthesized and characterized. In accordance with the relatively low applied pressure of  $2.6\text{ GPa}$ , 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 dif-

ferent 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.

## Acknowledgements

We would like to thank *Dr. G. Heymann* for collecting the single-crystal data. The research was funded by the Austrian Science Fund (FWF): P 23212-N19.

## 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*, i29.
- [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. Goriounova, P. Held, P. Becker, L. Bohaty, *Acta Crystallogr. Sect. E* **2004**, *60*, i134.
- [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. Carpenter, 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.

Received: September 10, 2012  
Published Online: October 24, 2012