inorganic compounds

High-pressure syntheses of α-RE$_2$B$_4$O$_9$ (RE = Sm, Ho), with a structure type displaying edge-sharing BO$_4$ tetrahedra

Holger Emme and Hubert Huppertz*

Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstraße 5-13, D-81377 München, Germany
Correspondence e-mail: huh@cup.uni-muenchen.de

The compounds α-RE$_2$B$_4$O$_9$, with RE = Sm (disamarium tetraborate) and Ho (diholmium tetraborate), were synthesized under conditions of high pressure and high temperature in a Walker-type multianvil apparatus, at 7.5 GPa and 1323 K for α-Sm$_2$B$_4$O$_9$ and at 10 GPa and 1323 K for α-Ho$_2$B$_4$O$_9$. The crystal structures were determined from single-crystal X-ray diffraction data collected at room temperature. The structures are isotypic with the already known α-RE$_2$B$_4$O$_9$ (RE = Eu–Dy) phases, displaying the new structural motif of edge-sharing BO$_4$ tetrahedra next to the known motif of corner-sharing BO$_4$ tetrahedra. As the end members of this isotypic series, the two title compounds mark the borders of the stability field of the appearance of edge-sharing BO$_4$ tetrahedra.

Comment

Using extreme high-pressure/high-temperature conditions, we intended to provide new structural motifs and new compositions in oxoborate chemistry. Normal-pressure phases are dominated by trigonal BO$_3$ groups and additional BO$_4$ groups. Examples of normal-pressure phases exclusively built up by BO$_4$ tetrahedra are rare. In accordance with the pressure–coordination rule, it is possible to realise rare-earth oxoborate crystal structures based exclusively on BO$_4$ tetrahedra by the use of high pressure, for example, β-RE(BO$_2$)$_3$ (RE = Tb–Lu; Nikelski & Schleid, 2003; Emme, Nikelski *et al.*, 2004) and γ-RE(BO$_2$)$_3$ (RE = La–Nd; Emme *et al.*, 2004a,b). The first oxoborates exhibiting edge-sharing BO$_4$ tetrahedra beside corner-sharing BO$_4$ tetrahedra in their crystal structures, RE$_4$B$_6$O$_{15}$ (RE = Dy, Ho; von der Eltz & Huppertz, 2002; Huppertz, 2003) and α-RE$_2$B$_4$O$_9$ (RE = Eu–Dy; Emme & Huppertz, 2002, 2003), represent a breakthrough for high-pressure oxoborate chemistry. Recently, we have synthesized single crystals of the isotypic samarium and holmium compounds of α-RE$_2$B$_4$O$_9$, starting from the pure binary

oxides and using high-pressure/high-temperature conditions (7.5 GPa and 1323 K for Sm, and 10 GPa and 1323 K for Ho), and we present their crystal structures here.

As expected, the lattice parameters (see *Crystal data*) of the isotropic series decrease in a regular fashion from Sm to Ho, along with the size of the cations, including the data published previously by Emme & Huppertz (2003).

Fig. 1 gives a view of the crystal structure of α-RE$_2$B$_4$O$_9$ (RE = Sm and Ho) along [010]. The structure exhibits a complex network of linked BO$_4$ tetrahedra. In order to clarify the representation, the corner-sharing tetrahedra are drawn light and the edge-sharing tetrahedra are drawn black. More details concerning the complex linkage of the BO$_4$ tetrahedra
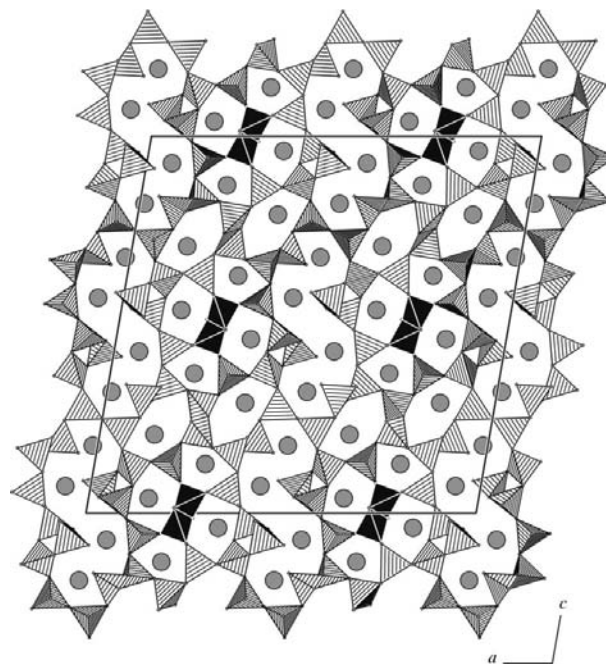

Figure 1
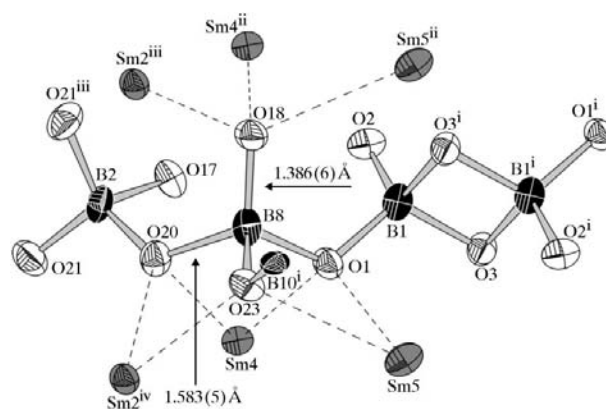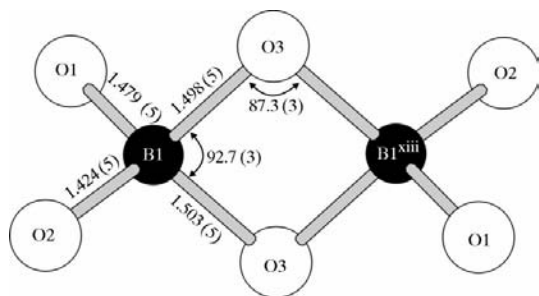The crystal structure of α-RE$_2$B$_4$O$_9$ (RE = Sm and Ho), viewed along [010].

Figure 2
The distortion of the B8O$_4$ tetrahedron in α-Sm$_2$B$_4$O$_9$ next to the two edge-sharing tetrahedra. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

Figure 3
Interatomic bond lengths (Å) and angles (°) inside the edge-sharing BO_4 tetrahedra of α-$Sm_2B_4O_9$. [Symmetry code: (i) $\frac{1}{2} - x$, $\frac{3}{2} - y$, $-z$.]

within the structure can be found in the previous publication of the isotypic compounds with RE = Eu–Dy (Emme & Huppertz, 2003).

The structural details of these two new compounds are of special interest for further theoretical investigations like density functional theory (DFT) calculations and the prediction of spectroscopic properties, as the samarium and holmium compounds mark the borders of the stability field of the isotypic series. Smaller ions (Er–Lu) lead to the new oxoborates $RE_3B_5O_{12}$ and larger ions to a new unknown phase. Therefore, new insights into the formation of edge-sharing BO_4 tetrahedra in oxoborate structures could be obtained.

The B—O bond lengths in α-$RE_2B_4O_9$ (RE = Sm, Ho) slightly exceed the typical B—O bond lengths in BO_4 tetrahedra (Zobetz, 1990), with values in the range 1.386 (6)–1.583 (5) Å in α-$Sm_2B_4O_9$ and 1.358 (14)–1.602 (13) Å in α-$Ho_2B_4O_9$, similar to the B—O bond lengths found in the isotypic compounds with RE = Eu–Dy. Both uncommon bond lengths appear in the B8 tetrahedron, which is directly linked to the edge-sharing tetrahedra (B1; Tables 1 and 2). A view of the displacement ellipsoids around B8 in α-$Sm_2B_4O_9$ shows no discrepancies in their dimensions (Fig. 2). The B—O bond lengths and angles in the edge-sharing BO_4 tetrahedra of α-$Sm_2B_4O_9$ are shown in Fig. 3. The B$\cdots$B distances in the edge-sharing tetrahedra are 2.071 (9) Å in α-$Sm_2B_4O_9$ and 2.04 (3) Å in α-$Ho_2B_4O_9$, which are in good agreement with the values observed for the isotypic compounds [2.04 (2) Å in α-$Gd_2B_4O_9$, 2.053 (9) Å in α-$Eu_2B_4O_9$, and 2.055 (9) Å in α-$Tb_2B_4O_9$]. The Sm—O and Ho—O distances are in the ranges 2.272 (3)–3.028 (3) and 2.212 (7)–3.084 (7) Å, respectively.

Experimental

The starting materials for the syntheses of α-$RE_2B_4O_9$ (RE = Sm and Ho) in this work were 2:1 molar mixtures of B_2O_3 (Strem Chemicals, Newburyport, USA, 99.9%) with the rare-earth oxides RE_2O_3 (RE = Sm and Ho; 99.9%). The compounds were compressed and heated *via* a multianvil assembly. Details concerning the construction of the assembly can be found in the literature (Huppertz, 2001, 2004; Walker *et al.*, 1990; Walker, 1991; Rubie, 1999). For the syntheses of α-$RE_2B_4O_9$ (RE = Sm and Ho), the 18/11 assemblies were compressed within 3 h to 7.5 GPa (for Sm) and within 4 h to 10 GPa (for Ho), and heated to 1323 K in the following 10 min. After maintaining this temperature for 10 min, the samples were cooled to room temperature over a period of a further 10 min. After decom-

pression, the experimental octahedra recovered from the assemblies were broken apart and the samples were carefully separated from the boron nitride crucibles. The compounds α-$RE_2B_4O_9$ (RE = Sm and Ho) were obtained as single-phase crystalline products (yield 75 mg per run). The substances are air- and water-resistant, and crystallize as long thin colourless (Sm) and pale-yellow (Ho) needles.

$Sm_2B_4O_9$

Crystal data

$Sm_2B_4O_9$	$D_x = 5.787$ Mg m^{-3}
$M_r = 487.94$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 8000
$a = 25.572$ (5) Å	reflections
$b = 4.4516$ (9) Å	$\theta = 3.4$–$32.1°$
$c = 24.967$ (5) Å	$\mu = 20.80$ mm^{-1}
$\beta = 99.85$ (3)°	$T = 293$ (2) K
$V = 2800.3$ (10) Å^3	Rod, colourless
$Z = 20$	$0.05 \times 0.05 \times 0.04$ mm

Data collection

Stoe IPDS diffractometer	2381 reflections with $I > 2\sigma(I)$
Profile data from φ scans	$R_{int} = 0.024$
Absorption correction: ψ scan	$\theta_{max} = 26.5°$
($XPREP$; Siemens, 1990–1996)	$h = -32 \rightarrow 32$
$T_{min} = 0.381$, $T_{max} = 0.435$	$k = -5 \rightarrow 4$
9846 measured reflections	$l = -31 \rightarrow 31$
2709 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.014$	$\Delta\rho_{max} = 0.80$ e Å^{-3}
$wR(F^2) = 0.029$	$\Delta\rho_{min} = -0.66$ e Å^{-3}
$S = 0.95$	Extinction correction: $SHELXL97$
2709 reflections	(Sheldrick, 1997)
340 parameters	Extinction coefficient: 0.000226 (7)
$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected interatomic distances (Å) for α-$Sm_2B_4O_9$.

B1—O2	1.424 (5)	B8—O18	1.386 (6)
B1—O1	1.479 (5)	B8—O23	1.496 (5)
B1—O3	1.498 (5)	B8—O1	1.546 (5)
B1—O3^i	1.503 (5)	B8—O20	1.583 (5)

Symmetry code: (i) $\frac{1}{2} - x$, $\frac{3}{2} - y$, $-z$.

$Ho_2B_4O_9$

Crystal data

$Ho_2B_4O_9$	$D_x = 6.389$ Mg m^{-3}
$M_r = 517.10$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 8000
$a = 25.090$ (5) Å	reflections
$b = 4.3941$ (9) Å	$\theta = 3.3$–$28.3°$
$c = 24.742$ (5) Å	$\mu = 29.26$ mm^{-1}
$\beta = 99.83$ (3)°	$T = 293$ (2) K
$V = 2687.7$ (10) Å^3	Rod, light yellow
$Z = 20$	$0.15 \times 0.12 \times 0.1$ mm

Data collection

Stoe IPDS diffractometer	2507 independent reflections
Profile data from φ scans	2169 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.068$
($HABITUS$; Herrendorf &	$\theta_{max} = 25.5°$
Bärnighausen, 1993–1997)	$h = -30 \rightarrow 30$
$T_{min} = 0.009$, $T_{max} = 0.050$	$k = -5 \rightarrow 5$
8632 measured reflections	$l = -29 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 2.26$ e Å^{-3}
2507 reflections	$\Delta\rho_{min} = -2.50$ e Å^{-3}
340 parameters	Extinction correction: *SHELXL97*
No H atoms present	(Sheldrick, 1997)
	Extinction coefficient: 0.00023 (2)

Table 2
Selected interatomic distances (Å) for α-Ho$_2$B$_4$O$_9$.

B1—O2	1.427 (14)	B8—O18	1.358 (14)
B1—O1	1.479 (14)	B8—O23	1.489 (13)
B1—O3	1.493 (13)	B8—O1	1.534 (13)
B1—O3^i	1.505 (15)	B8—O20	1.602 (13)

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

For both compounds, data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); publication software: *enCIFer* (Allen *et al.*, 2004) and *SHELXL97*.

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