

High-pressure synthesis of the new rare-earth oxoborate β -Gd₂B₄O₉

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β -Digadolinium tetraborate (β -Gd₂B₄O₉) was synthesized under high-pressure/high-temperature conditions in a Walker-type multi-anvil apparatus at 3 GPa and 1223 K from the pure binary oxides. Its crystal structure has been determined from single-crystal X-ray diffraction data collected at room temperature. The compound is isotypic with the known compound β -Dy₂B₄O₉, which was synthesized under extreme conditions by use of a flux.

Comment

High-pressure multi-anvil techniques have made it possible to extend substantially the structural and compositional diversity in oxoborate chemistry. Recently, we reported the syntheses and crystal structures of the new rare-earth oxoborates α -RE₂B₄O₉, with RE = Sm and Ho, displaying the new structural motif of edge-sharing BO₄ tetrahedra (Emme & Huppertz, 2005). These structures are isotypic with the compounds α -RE₂B₄O₉ (RE = Eu–Dy) synthesized by Emme & Huppertz (2002, 2003). They represent the first examples of 1:2 compounds in the RE₂O₃–B₂O₃ system. Huppertz *et al.* (2003) synthesized a new polymorph, β -Dy₂B₄O₉, exhibiting a new structure type built up from triangular BO₃ and tetrahedral BO₄ groups. This synthesis was carried out under extreme high-pressure/high-temperature conditions of 8 GPa and 1273 K using Dy₂O₃ and boron oxide in a B₂O₃/Na₂O₂ flux. At pressures of 8 GPa, borate structures built up exclusively of BO₄ tetrahedra are normally expected. The appearance of triangular BO₃ groups besides tetrahedral BO₄ groups in β -Dy₂B₄O₉ implied that the flux supports the formation of a structure which is normally expected at lower pressures. Systematic investigations of the 1:2 RE₂O₃–B₂O₃ system confirmed this suspicion. Ongoing experiments have shown that it is possible to synthesize β -Dy₂B₄O₉ in the lower pressure range of 4–6.3 GPa at 1223 K directly, starting with pure B₂O₃ and Dy₂O₃. Analogous experiments with Gd₂O₃ led to the isotypic gadolinium compound in the pressure range 3–5 GPa and at 1223 K. A detailed study concerning the formation ranges showed that, at lower pressures, the triclinic

phases ν -REBO₃ (RE = Gd or Dy) were formed (Emme & Huppertz, 2004). The normal-pressure phases π -REBO₃ occur below 2 GPa for RE = Gd and below 3 GPa for RE = Dy. Above 6.3 GPa (RE = Gd) and 7.5 GPa (RE = Dy), the experiments resulted in the formation of the α -phases.

The crystal structure of β -Gd₂B₄O₉ is built up of triangular BO₃ groups and BO₄ tetrahedra forming [100] ribbons (Fig. 1), with the Gd³⁺ cations positioned in the voids between the ribbons. The bond-valence sums for the two crystallographically independent Gd³⁺ cations are 3.02 for Gd1 and 3.31 for Gd2 (Bresle & O'Keeffe, 1991). Within the ribbons, the

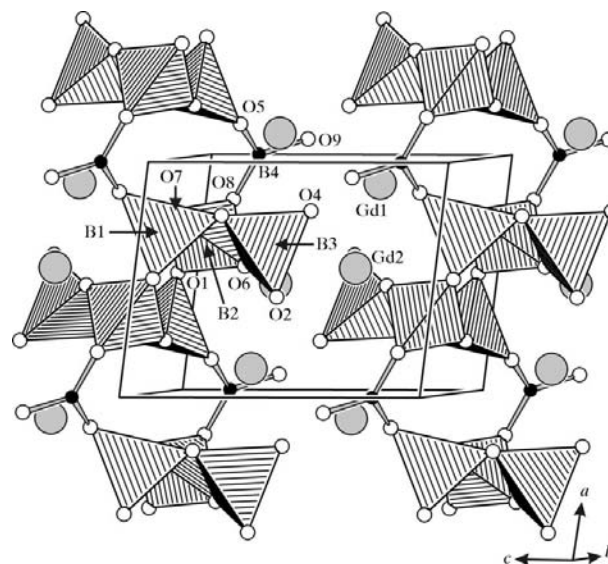


Figure 1
The crystal structure of β -Gd₂B₄O₉, viewed along [010].

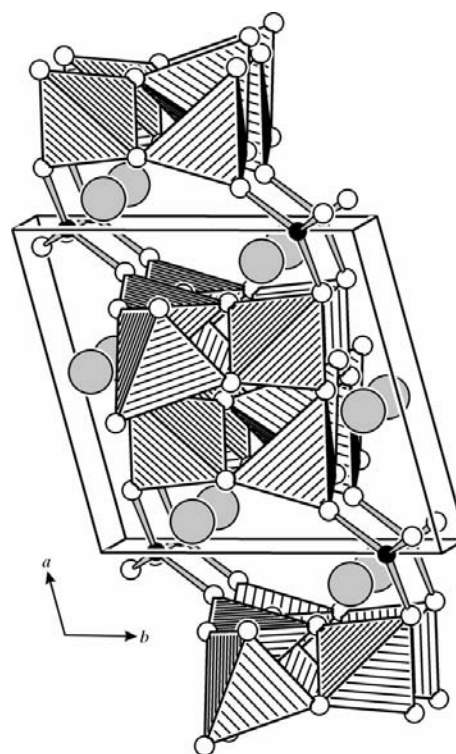


Figure 2
The crystal structure of β -Gd₂B₄O₉, viewed along [001].

BO₄ tetrahedra form three-membered B₃O₉ rings linked to each other *via* two triangular BO₃ groups, forming six-membered rings (Fig. 2). Additionally, each B₃O₉ ring is connected to the adjacent ring *via* two common corners, forming four-membered rings.

Experimental

The starting materials for the synthesis of β-Gd₂B₄O₉ in this work were a 2:1 molar mixture of B₂O₃ [from H₃BO₃ (99.8%, Merck, Darmstadt) fired at 873 K] and Gd₂O₃ (99.9%). The materials were compressed and heated *via* a multi-anvil assembly. Details concerning the construction of the assembly have been published previously (Huppertz, 2001, 2004; Walker *et al.*, 1990; Walker, 1991; Rubie, 1999). For the synthesis of β-Gd₂B₄O₉, the 18/11 assembly was compressed within 1 h to 3 GPa and heated to 1223 K in the following 10 min. After maintaining this temperature for 10 min, the sample was cooled to room temperature in another 10 min. After decompression, the sample assembly was broken apart and the sample was carefully separated from the surrounding boron nitride. β-Gd₂B₄O₉ was obtained as a single-phase crystalline product (yield 75 mg per run). It crystallizes as small colourless parallelepiped-like crystals which are stable in air and water.

Crystal data

Gd ₂ B ₄ O ₉	Z = 2
M _r = 501.74	D _x = 5.880 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
a = 6.1973 (10) Å	Cell parameters from 4198 reflections
b = 6.4757 (10) Å	θ = 3.1–37.8°
c = 7.5249 (10) Å	μ = 23.23 mm ⁻¹
α = 102.386 (10)°	T = 293 (2) K
β = 96.983 (10)°	Block, colourless
γ = 102.544 (10)°	0.05 × 0.04 × 0.02 mm
V = 283.41 (8) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	3007 independent reflections
φ and ω scans	2538 reflections with I > 2σ(I)
Absorption correction: numerical (HABITUS; Herrendorf & Bärnighausen, 1997)	R _{int} = 0.045
T _{min} = 0.365, T _{max} = 0.695	θ _{max} = 37.9°
10 001 measured reflections	h = -10 → 10
	k = -11 → 10
	l = -12 → 12

Refinement

Refinement on F ²	(Δ/σ) _{max} = 0.001
R[F ² > 2σ(F ²)] = 0.026	Δρ _{max} = 2.30 e Å ⁻³
wR(F ²) = 0.050	Δρ _{min} = -2.93 e Å ⁻³
S = 1.00	Extinction correction: SHELXL97 (Sheldrick, 1997)
3007 reflections	Extinction coefficient: 0.0185 (4)
137 parameters	
w = 1/[σ ² (F _o ²) + (0.009P) ²]	
where P = (F _o ² + 2F _c ²)/3	

The highest electron-density peak is 0.86 Å from atom B4 and the deepest hole is 0.58 Å from atom Gd2.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997);

Table 1

Selected geometric parameters (Å).

Gd1—O7 ⁱ	2.334 (2)	Gd2—O1 ⁱⁱⁱ	2.568 (2)
Gd1—O4 ⁱⁱ	2.366 (2)	Gd2—O6 ⁱⁱⁱ	2.631 (2)
Gd1—O2 ⁱⁱⁱ	2.383 (2)	B1—O7	1.442 (4)
Gd1—O4	2.395 (2)	B1—O3	1.456 (4)
Gd1—O9 ^{iv}	2.432 (2)	B1—O5 ^{vii}	1.503 (4)
Gd1—O3 ⁱⁱ	2.556 (2)	B1—O1 ^{viii}	1.518 (4)
Gd1—O9	2.602 (2)	B2—O7	1.417 (4)
Gd1—O6 ⁱⁱⁱ	2.656 (2)	B2—O6	1.452 (4)
Gd1—O5 ⁱⁱ	2.688 (2)	B2—O1	1.469 (4)
Gd2—O2	2.293 (2)	B2—O8	1.485 (4)
Gd2—O2 ^v	2.376 (2)	B3—O4	1.458 (4)
Gd2—O1 ^{vi}	2.433 (2)	B3—O6	1.467 (4)
Gd2—O4	2.453 (2)	B3—O2	1.475 (4)
Gd2—O9 ⁱⁱ	2.475 (2)	B3—O3	1.564 (4)
Gd2—O8 ⁱⁱⁱ	2.526 (2)	B4—O9	1.370 (4)
Gd2—O3 ^v	2.559 (2)	B4—O8	1.371 (4)
Gd2—O5 ⁱⁱ	2.560 (2)	B4—O5	1.389 (4)

Symmetry codes: (i) x, y, z - 1; (ii) -x + 2, -y + 1, -z + 1; (iii) -x + 1, -y + 1, -z + 1; (iv) -x + 2, -y + 2, -z + 1; (v) -x + 1, -y, -z + 1; (vi) x, y - 1, z - 1; (vii) -x + 2, -y + 1, -z + 2; (viii) -x + 1, -y + 1, -z + 2.

molecular graphics: DIAMOND (Brandenburg & Berndt, 1999); software used to prepare material for publication: enCIFer (Allen *et al.*, 2004) and SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1065). Services for accessing these data are described at the back of the journal.

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