High-pressure synthesis of ν-DyBO$_3$

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ν-Dysprosium borate (ν-DyBO$_3$) was synthesized under conditions of high temperature and pressure in a Walker-type multi-anvil apparatus at 3 GPa and 1323 K. The compound is isotypic with the already known ν-samarium and ν-europium orthoborates.

Comment

The rare earth (RE) orthoborates REBO$_3$ exhibit a complex polymorphism. According to the nomenclature of Meyer (1969, 1972; Meyer & Skokan, 1971), the first polymorphs were designated with the greek letters β, λ, μ, π and ν. Additionally, monoclinic phases H-REBO$_3$ (RE is La or Ce) were described by Böhlhoff et al. (1971) and Lemanceau et al. (1999). Depending on the cation size, rare earth orthoborates are related to the three crystalline forms of CaCO$_3$, i.e. aragonite (λ phase), vaterite (π and μ phases) and calcite (β

phase). Recently, the vaterite-type rare earth orthoborates have been well investigated by Ren et al. (1999) and Lin et al. (2004), who finally solved the long-debated structures of the π and μ phases by means of neutron diffraction. Additionally, Huppertz et al. (2002) were able to synthesize the high-pressure orthoborate phases χ-REBO$_3$ with RE = Dy and Er. These phases contain the new non-cyclic [B$_3$O$_9$]$^{9-}$ anion and represent intermediates between the low- (π) and high-temperature (μ) polymorphs. In 1972, Meyer reported the syntheses and lattice parameters of the triclinic rare earth orthoborates REBO$_3$ (RE = Pr–Dy), which were designated as ν phases. For RE = Pr–Eu, the syntheses were performed at ambient pressure, whereas for RE = Gd–Dy, high-pressure conditions (1–4.5 GPa) were applied. The structure solution and refinement of triclinic ν-SmBO$_3$ were first performed by Palkina et al. (1976) in the space group $P1$, but this was corrected afterwards to $P\bar{1}$. Corbel et al. (1999) confirmed the new space group in their characterization of ν-EuBO$_3$ and also briefly reported on the isotypic gadolinium compound. All three compounds were synthesized from the binary oxides with additional Na$_2$B$_4$O$_7$ as a flux.

In this work, we have been able to synthesize single crystals of the isotypic dysprosium compound, ν-DyBO$_3$, starting from the pure binary oxides using conditions of high temperature and pressure (3 GPa and 1323 K). The structure solution confirmed the $P\bar{1}$ model (Fig. 1) found by Palkina et al. (1976). The lattice parameters of ν-DyBO$_3$ agree well with the results published by Meyer (1972) [$a = 6.147$ (1), $b = 6.386$ (1) and $c = 6.391$ (1) Å, and $\alpha = 92.53$ (1), $\beta = 107.64$ (1) and $\gamma = 108.28$ (1)$^\circ$]. As expected, the lattice parameters decrease regularly from Pr to Dy, along with the size of the cations.

In the structure of ν-DyBO$_3$, the rare earth atoms occupy the centres of distorted DyO$_8$ triangulated dodecahedra (Fig. 2). Each dodecahedron shares edges with four others to build infinite double chains along the [110] direction (Fig. 3). The isolated threefold coordination of boron is regular, with B—O distances corresponding to the known average value of 1.370 Å for orthoborates (Table 1 and Fig. 4).

A calculation of the bond-valence sums (Brese & O'Keeffe, 1991) around atoms Dy1 and Dy2 led to values of 3.22 and
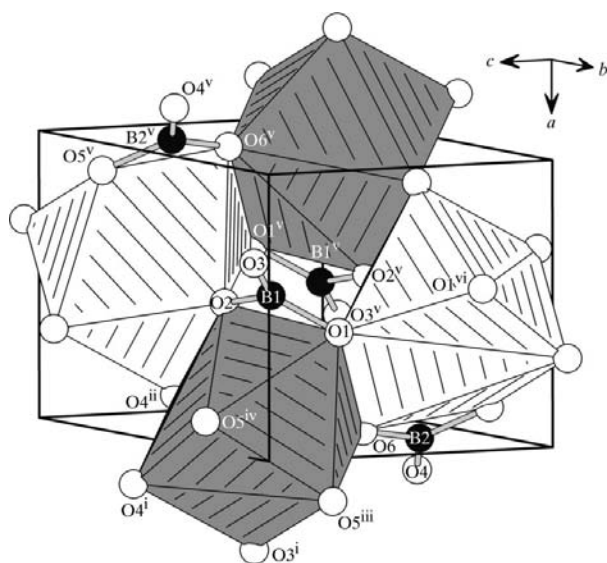

Figure 1
A schematic drawing of the unit cell of ν-DyBO$_3$. Shaded and unshaded polyhedra contain atoms Dy1 and Dy2, respectively. Symmetry codes are as given in Table 1.
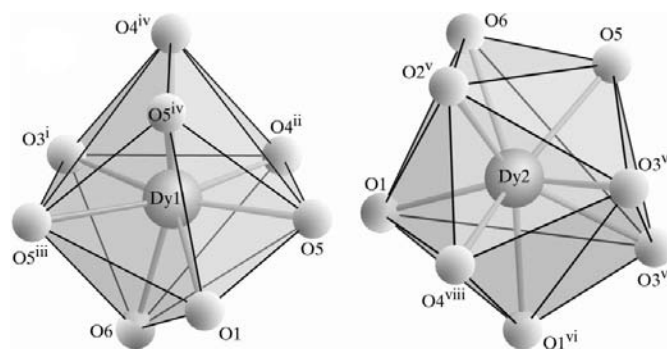

Figure 2
The coordination environments of Dy^{3+} (grey spheres) in the crystal structure of ν-DyBO$_3$. Symmetry codes are as given in Table 1.
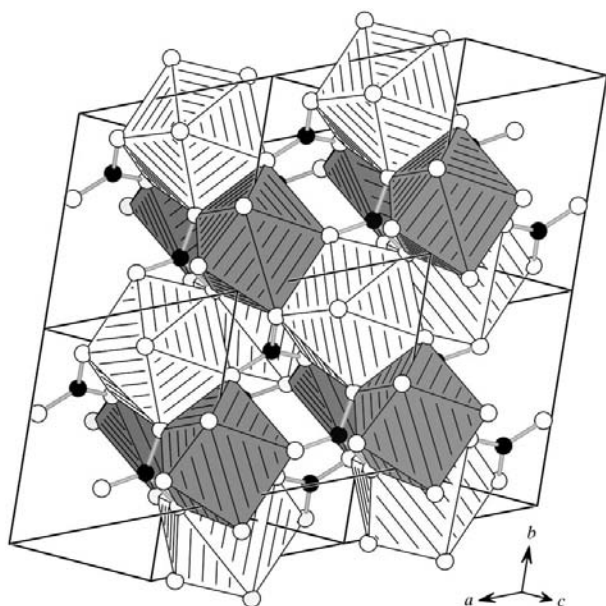
inorganic compounds

Figure 3
The crystal structure of ν-DyBO$_3$. Shaded and unshaded polyhedra contain atoms Dy1 and Dy2, respectively.
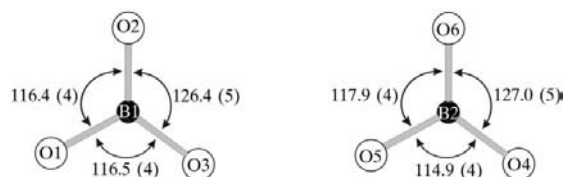

Figure 4
O—B—O angles (°) in the BO$_3$ groups of ν-DyBO$_3$ (s.u. values are given in parentheses).

3.00, respectively. These correspond to the values found for the six crystallographically different Dy atoms in χ-DyBO$_3$ (2.94–3.13).

In situ X-ray diffractometry showed that ν-DyBO$_3$ is stable up to a temperature of 1073 K, followed by a structural re-transformation into the high-temperature polymorph μ-DyBO$_3$. Subsequent cooling leads to a complete transformation into the room-temperature modification π-DyBO$_3$.

Experimental

The starting material for the synthesis of triclinic ν-DyBO$_3$ in this work was a 1:1 molar mixture of B$_2$O$_3$ [from H$_3$BO$_3$ (99.8%, Merck, Darmstadt), fired at 873 K] and the rare earth oxide Dy$_2$O$_3$ (99.9%). The compounds were compressed and heated *via* a multi-anvil assembly. Details of the assembly can be found elsewhere (Huppertz, 2001, 2004; Walker *et al.*, 1990; Walker, 1991; Rubie, 1999). For the synthesis of ν-DyBO$_3$, the 18/11 assembly was compressed within 1 h to 3 GPa and heated to 1323 K in the following 10 min. After holding this temperature for 10 min, the sample was cooled to room temperature over another 10 min period. After decompression, the octahedral sample assembly was broken apart and the sample was carefully separated from the surrounding boron nitride. ν-DyBO$_3$ was

obtained as a single-phase crystalline product (yield 75 mg per run). The compound is air and water resistant and crystallizes as long thin colourless needles.

Crystal data

DyBO$_3$	$Z = 4$
$M_r = 221.31$	$D_x = 6.557$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.1463$ (12) Å	Cell parameters from 3498
$b = 6.3856$ (13) Å	reflections
$c = 6.3894$ (13) Å	$\theta = 3.1$–37.8°
$\alpha = 92.52$ (3)°	$\mu = 33.01$ mm^{-1}
$\beta = 107.65$ (3)°	$T = 293$ (2) K
$\gamma = 108.29$ (3)°	Rod, colourless
$V = 224.20$ (10) Å^3	$0.03 \times 0.02 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	1623 independent reflections
	1446 reflections with $I > 2\sigma(I)$
φ or ω scans	$R_{int} = 0.046$
Absorption correction: ψ scan (*XPREP*; Siemens, 1996)	$\theta_{max} = 32.5°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.432$, $T_{max} = 0.760$	$k = -9 \rightarrow 9$
6397 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{max} = 2.53$ e Å^{-3}
$wR(F^2) = 0.051$	$\Delta\rho_{min} = -2.72$ e Å^{-3}
$S = 1.15$	Extinction correction: *SHELXL*97
1623 reflections	(Sheldrick, 1997)
92 parameters	Extinction coefficient: 0.0101 (5)
$w = 1/[\sigma^2(F_o^2) + (0.0081P)^2 + 0.5392P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Dy1—O6	2.227 (4)	Dy2—O1^{vi}	2.386 (3)
Dy1—O3^i	2.320 (3)	Dy2—O3^{vii}	2.409 (4)
Dy1—O4^{ii}	2.334 (4)	Dy2—O4^{viii}	2.446 (4)
Dy1—O2	2.341 (4)	Dy2—O3^{vi}	2.562 (4)
Dy1—O5^{iii}	2.393 (4)	Dy2—O6	2.635 (4)
Dy1—O5^{iv}	2.414 (3)	B1—O1	1.382 (7)
Dy1—O4^{iv}	2.480 (4)	B1—O2	1.347 (6)
Dy1—O1	2.578 (4)	B1—O3	1.386 (6)
Dy2—O2^v	2.234 (4)	B2—O4	1.388 (6)
Dy2—O1	2.329 (3)	B2—O5	1.405 (6)
Dy2—O5	2.342 (3)	B2—O6	1.330 (6)
O2—B1—O1	116.4 (4)	O6—B2—O4	127.0 (5)
O2—B1—O3	126.4 (5)	O6—B2—O5	117.9 (4)
O1—B1—O3	116.5 (4)	O4—B2—O5	114.9 (4)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1055). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Böhlhoff, R., Bambauer, H. U. & Hoffmann, W. (1971). *Z. Kristallogr.* **133**, 386–395.

Brandenburg, K. & Berndt, M. (1999). *DIAMOND.* Version 2.1c. Crystal Impact GbR, Bonn, Germany.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Corbel, G., Leblanc, M., Antic Fidancev, E., Lemaître-Blaize, M. & Krupa, J. C. (1999). *J. Alloys Compd*, **287**, 71–78.

Huppertz, H. (2001). *Z. Naturforsch. Teil B*, **56**, 697–703.

Huppertz, H. (2004). *Z. Kristallogr.* **219**, 330–338.

Huppertz, H., von der Eltz, B., Hoffmann, R.-D. & Piotrowski, H. (2002). *J. Solid State Chem.* **166**, 203–212.

Lemanceau, S., Bertrand-Chadeyron, G., Mahiou, R., El-Ghozzi, M., Cousseins, J. C., Conflant, P. & Vannier, R. N. (1999). *J. Solid State Chem.* **148**, 229–235.

Lin, J. H., Sheptyakov, D., Wang, Y. & Allenspach, P. (2004). *Chem. Mater.* **16**, 2418–2424.

Meyer, H. J. (1969). *Naturwissenschaften*, **56**, 458–459.

Meyer, H. J. (1972). *Naturwissenschaften*, **59**, 215.

Meyer, H. J. & Skokan, A. (1971). *Naturwissenschaften*, **58**, 566.

Nonius (1998). *COLLECT.* Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Palkina, K. K., Kuznetsov, V. G., Butman, L. A. & Dzhurinskii, B. F. (1976). *Russ. J. Coord. Chem.* **2**, 286–289.

Ren, M., Lin, J. H., Dong, Y., Yang, L. Q., Su, M. Z. & You, L. P. (1999). *Chem. Mater.* **11**, 1576–1580.

Rubie, D. C. (1999). *Phase Transitions*, **68**, 431–451.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1996). *XPREP.* Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Walker, D. (1991). *Am. Mineral.* **76**, 1092–1100.

Walker, D., Carpenter, M. A. & Hitch, C. M. (1990). *Am. Mineral.* **75**, 1020–1028.