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Multianvil High-Pressure Synthesis of $Dy_4B_6O_{15}$: The First Oxoborate with Edge-Sharing BO_4 Tetrahedra

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In the past decades oxoborates have developed into an important field of mineralogical and industrial interest. In particular the properties of the rare earth oxoborates, which exhibit high thermal stabilities and luminescence, have led to a variety of studies concerning high-temperature applications, optical glasses, phosphors, and NLO-materials.[1]

The structural chemistry of oxoborates is analoguous to that of silicates. The main difference is the possibility of boron to coordinate with oxygen not only in four-fold coordination (tetrahedral) but also in three-fold coordination (triangular). Until now it is not clear which one of the two coordination spheres is preferred under ambient conditions. For example, α-metaboric acid (α-HBO_2) exhibits only trigonal BO_3 groups, β-metaboric acid (β-HBO_2) has trigonal and tetrahedral coordinations, and γ-metaboric acid (γ-HBO_2) shows exclusively tetrahedral coordination of boron.[2] In analogy to the silicates the BO_3 and BO_4 groups can occur isolated or condensed in the form of groups, rings, chains, layers, or networks. Over the past decade Burns et al. developed a comprehensive description based on fundamental building blocks "FBB" to have a clearer nomenclature for more complicated polyanions.[3,4]

Primary high-pressure investigations on the rare-earth oxoborates *RE*BO_3 (*RE* = Pr, Nd, Sm−Dy, Yb) were performed by Meyer.[5] In these phases all boron atoms were still three-fold coordinated. Corresponding to the pressure−coordination rule[6] an increase of pressure can lead to a higher coordination number of the boron atom, e.g. in B_2O_3−I all boron atoms have the coordination number three, whereas in the high-pressure modification B_2O_3−II all boron atoms are coordinated tetrahedrally.[7] As a common feature of all nearly 500 structurally characterized oxoborates it can be pointed out that the BO_3 triangles and the BO_4 tetrahedra link to each other only via common corners (oxygen atoms) and not via edges or faces, to form rigid boron oxygen groups, that constitute the fundamental building blocks (FBB) of the structure. These distinguishing features were already postulated 1969 by Edwards and Ross.[3,4,8]

In this study we describe the synthesis and structure of a new oxoborate $Dy_4B_6O_{15}$, which differs structurally from all known oxoborates in a remarkable way: for the first time we observe that the exclusively appearing BO_4 tetrahedra can link together not only via common corners but also via common edges. Therefore, one of the main postulates of oxoborate chemistry, that BO_3 and BO_4 polyhedra only share corners, is no longer valid.

$Dy_4B_6O_{15}$ was synthesized starting from stoichiometric amounts of boron oxide B_2O_3 and dysprosium oxide Dy_2O_3 in a multianvil apparatus under a pressure of 8 GPa and a temperature of 1000 °C (Scheme 1). We used a modified Walker module and a 1000-t press.[9] As a pressure medium precast MgO octahedra (Ceramic Substrates & Components Ltd., Isle of Wight) with an edge length of 18 mm were used. Eight tungsten carbide cubes with a truncation of 11 mm separated by pyrophyllite gaskets compressed the octahedra. (18/11 assembly in conventionell terminology). The mixture was filled in a cylindrical boron nitride cylinder that was sealed by a boron nitride plate. The sample cylinder was placed at the center of a cylindrical resistance heater (graphite) that had a variable (stepped) wall thickness to minimize the thermal gradient along the sample. MgO rods filled the space on the top and bottom of the sample. A cylindrical zirconia sleeve surrounding the furnace provided thermal insulation. The assembly was positioned inside the octahedra and contacted with a molybdenum ring at the top and a molybdenum plate at the bottom. The experimental temperature was monitored using a Pt/$Pt_{87}Rh_{13}$ thermocouple that was inserted axially into the octahedral assembly, with the hot junction in contact with the boron nitride cylinder.

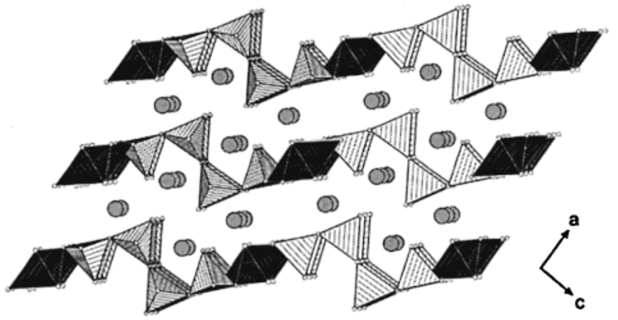

Figure 1. Crystal structure of $Dy_4B_6O_{15}$, viewed along [010]. The structure is built up from corrugated layers of corner-sharing (light) and edge-sharing (dark) BO_4 tetrahedra. The Dy^{3+} ions are positioned between the layers.

Scheme 1

$$2\,Dy_2O_3 + 3\,B_2O_3 \xrightarrow[1000\ °C]{8.0\ GPa} Dy_4B_6O_{15}$$

$Dy_4B_6O_{15}$ synthesized under these conditions is a colorless, nearly phase-pure, coarse crystalline solid (yield: 40 mg per run). Elemental analyses of dysprosium and boron by ICP on a Varian-Vista spectrometer revealed 68.7 wt % Dy and 6.6 wt % B (calcd: 68.1% Dy, 6.8% B). The absence of hydrogen (OH) was checked by IR spectroscopy. X-ray structure analysis on single crystals showed that the structure of $Dy_4B_6O_{15}$ is built up from corrugated layers of linked BO_4 tetrahedra (Figure 1).[10] The Dy^{3+} ions are positioned between the layers.

BO_4 tetrahedra inside the layers are linked via common corners as well as common edges (Figure 2). In detail the edge-sharing tetrahedra (dark polyhedra) form six-membered rings with two additional corner-sharing BO_4 tetrahedra (light polyhedra). The linkage of these rings by further corner-sharing BO_4 tetrahedra leads to 10-membered rings forming corrugated layers.

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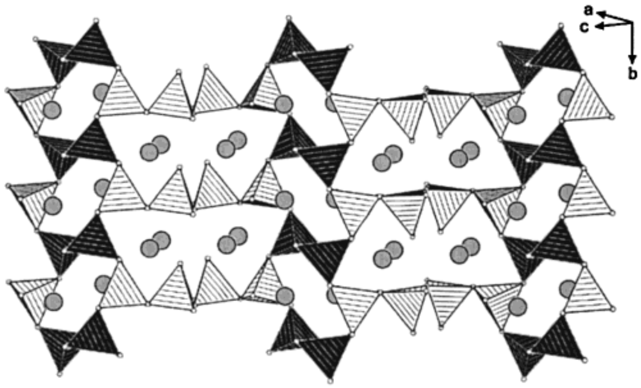

Figure 2. View on a corrugated layer of BO_4 tetrahedra in $Dy_4B_6O_{15}$. The linkage of the tetrahedra to rings is via common corners as well as via common edges.

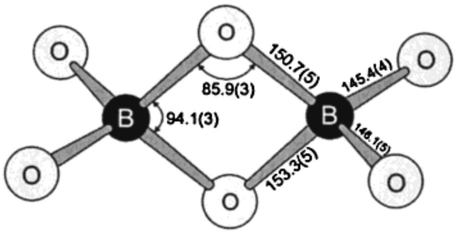

Figure 3. Interatomic distances in pm and angles in deg inside the edge-sharing BO_4 tetrahedra of $Dy_4B_6O_{15}$.

Ionic oxotetrahedra do not normally link together via common edges. In 1965 a work[11] about “fibrous SiO_2” was published describing edge-sharing SiO_4 tetrahedra. A verification of these results was not possible. In the higher homologues of the boron and silicon chalcogenides (B_2S_3,[12−14] SiS_2,[15] $SiSe_2$,[15] $SiTe_2$ [16]) the formation of B_2S_2, Si_2S_2, Si_2Se_2, and Si_2Te_2 rings is not uncommon. This is due to the lower ionicity and the remarkable larger distances inside the four-membered rings. Because of the fact, that oxosilicates do not exhibit edge-sharing SiO_4 tetrahedra, it is much more remarkable for boron as an element of the first short period to form edge-sharing BO_4 tetrahedra under these reaction conditions. One of the main reasons is the lower formal charge of boron (+3) in contrast to silicon (+4). Until now only five crystal structures containing four-membered B_2O_2 rings have been reported in molecular chemistry, but none of these examples shows boron exclusively coordinated by oxygen.[17,18]

The B−O bond lengths inside the corner-sharing BO_4 tetrahedra of $Dy_4B_6O_{15}$ vary between 143 and 152 pm. Inside the B_2O_2 ring of the edge-sharing tetrahedra the B−O distances are slightly longer (150.7(5) and 153.3(5) pm) (Figure 3). The average B−O distance of 147.9 pm in $Dy_4B_6O_{15}$ is in good agreement with the average B−O bond length of 147.6 pm in BO_4 tetrahedra.[19] The transannular B⋯B distance (207.2(8) pm) in the B_2O_2 ring is markedly shorter than in B_2S_3 (224 pm).[13] Both crystallographically different Dy^{3+} ions are coordinated from eight oxygen atoms in the range 224−265 pm. A classification of $Dy_4B_6O_{15}$ with the help of the “FBB”-concept after Burns et al.[4] will follow when the concept is extended by a descriptor for edge-sharing tetrahedra.

Raman- and IR-spectroscopic investigations were performed. A clear classification of the vibrational bands is an issue of great complexity because comparative data for edge-sharing BO_4 tetrahedra are not available. To investigate the metastable character of the high-pressure phase $Dy_4B_6O_{15}$ temperature-dependent X-ray powder diffraction measurements were performed on a STOE powder diffractometer Stadi P. Above 700 °C $Dy_4B_6O_{15}$ decomposes into the hexagonal phase π-$DyBO_3$ (room-temperature phase), μ-$DyBO_3$ (high-temperature phase), and B_2O_3. Further raising the temperature to 1100 °C leads to a complete transformation of π-$DyBO_3$ into the high-temperature phase. Experiments to synthesize $Dy_4B_6O_{15}$ under normal pressure resulted in a mixture of π-$DyBO_3$ and B_2O_3 as a byproduct.

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Supporting Information Available: Crystallographic data and further details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org or from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), e-mail: crysdata@fiz-karlsruhe.de, by quoting the registry number CSD-412041.

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(10) Crystal structure analysis of $Dy_4B_6O_{15}$: MW = 954.86 g/mol, colorless block, 0.03 × 0.05 × 0.06 mm^3, monoclinic, space group: $C2/c$, a = 1169.4(1) pm, b = 437.8(1) pm, c = 1893.0(1) pm, β = 96.66(1)°, V = 0.960(2) nm^3, $Z = 4$, $\rho_{calc} = 6.589$ g/cm^3, Enraf-Nonius Kappa CCD with rotating anode, Mo Kα-radiation (λ = 71.073 pm), graphite-monochromator, $F(000) = 1656$, μ = 30.8 mm^{-1}, T = 293(2) K, φ/ω-scan, 11351 measured reflections in the range $7° < 2\theta < 60°$, 1405 unique reflections with $I \geq 0\sigma(I)$, numerical absorption correction (HABITUS), transmissions ratio: 2.25 (max/min), $R_{int} = 0.0439$; the crystal structure was solved by direct methods (SHELXS-97) and anisotropically refined by a least squares procedure against F^2 with all data, 115 refined parameters, R1 = 0.0155 and wR2 = 0.0349 for $F_o^2 \geq 2\sigma(F_o^2)$; R1 = 0.0173 and wR2 = 0.0356 for all F_o^2, GOF = 1.098.
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