Preparative and structural extension of oxoborate chemistry through high-pressure/high-temperature syntheses

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Abstract

High-pressure/high-temperature conditions were used to synthesize the new rare earth oxoborates $Ln_4B_6O_{15}$ (Ln = Dy, Ho; 8.0 GPa, 1000 °C) and α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy; 10.0 GPa, 1150 °C) in a Walker-type multianvil apparatus. In addition to their new compositions, which were unattainable under normal pressure conditions, the structures exhibit the new structural motif of edge sharing BO_4 tetrahedra leading to a structural extension of oxoborate chemistry.

1. Introduction

For the class of oxoborates, the numbers of synthesis studies, structural characterizations, and materials processings have continuously increased during the past decade [1–4]. The structural chemistry of oxoborates exhibits a considerable diversity that results from the ability of boron to bind to three or four oxygen atoms forming BO_3 or BO_4 groups. These groups can occur isolated or linked to groups, chains, bands, sheets, or complex networks leading to a great structural diversity [5, 6]. In principle, the structural characteristics are analogues to those of the silicates with the triangular BO_3 group as an additional structural component. As a common feature 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 common edges or faces. This characteristic was already postulated in 1967 by Ross and Edwards and was still considered valid until a short while ago [7, 8].

In contrast to normal pressure investigations on borates, high-pressure investigations are rare. The major part of the results come from the area of geological research, investigating borate containing minerals. Following common belief, boron is mainly enriched in the continental crust of the Earth due to its high volatility, where it forms borates mainly in

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near-surface environments or borosilicates deep in the Earth. Thus, taking the thickness of the normal continental crust into account, boron bearing minerals should be restricted approximately to the upper 30 km of the globe, while mantle rocks are extremely poor in boron. Both points are caused and enhanced by the fact that, melting in the mantle, boron fractionates strongly into the liquid phase [9]. Therefore, studies on borates and borosilicates were limited to pressures below 1 GPa for a long time. The discovery of ultrahigh-pressure metamorphism of crustal rocks, occurring at depths of 100 km or more, led to considerable petrological and geochemical interest in the fate of boron in deeply subducted continental crusts [10]. Several studies were performed by Werding and Schreyer, collecting data in the pressure range from 3 to 5 GPa [11]. To investigate the synthesis and stability of boron bearing systems at elevated temperatures and pressures, they used hydrothermal bombs up to about 0.6 GPa, 650–800 °C; internally heated gas pressure vessels up to about 0.8 GPa, 1000 °C; and several types of piston–cylinder apparatus up to 6 GPa, 1100 °C. Due to the substantial experimental requirements, only a few experiments were performed at higher pressures (>6 GPa), with a multianvil apparatus at the Bayerisches Geoinstitut, Bayreuth, Germany [11]. In our group we were able to use a Walker multianvil device to perform experiments in oxoborate chemistry routinely up to a pressure of 15 GPa. Therefore, we expect new insights into the structural behaviour of these compounds at elevated pressures.

Corresponding to the pressure–coordination rule [12], an increase of pressure can lead to a higher coordination number of the boron atoms; e.g. in the normal pressure modification of boron oxide B_2O_3-I, all boron atoms have the coordination number three [13], whereas in the high-pressure modification B_2O_3-II, all boron atoms are coordinated tetrahedrally [14].

Recently, we found that the use of high pressure during the synthesis extends the compositional and structural scope. Known compositions in the system Ln_2O_3/B_2O_3 under ambient conditions are Ln_3BO_6 (3:1) (which can be regarded as orthoborates $((LnO)_3BO_3)$), the orthoborates $LnBO_3$ (1:1), and the metaborates LnB_3O_6 (1:3) $(Ln(BO_2)_3)$ [15, 16]. In the system Ln_2O_3/B_2O_3 we were able to realize the new compositions $Ln_4B_6O_{15}$ (Ln = Dy, Ho) [15, 17] and α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) [18, 19] under high-pressure/high-temperature conditions (>6 GPa). In contrast to all nearly 500 structurally characterized oxoborates, in which the linkage of BO_3 and BO_4 units occurs exclusively via corners, these new oxoborates are the first examples exhibiting edge sharing BO_4 tetrahedra next to corner sharing BO_4 tetrahedra. The experimental conditions and structural characteristics are presented in the following.

2. Experimental section

According to reaction (1) the starting materials for the syntheses of $Ln_4B_6O_{15}$ (Ln = Dy, Ho) were 3:2 molar mixtures of B_2O_3 (from H_3BO_3 (99.8%, Merck, Darmstadt) fired at 600 °C) with the rare earth oxides Dy_2O_3 and Ho_2O_3 (99.9%, Sigma-Aldrich, Taufkirchen):

$$2Ln_2O_3 + 3B_2O_3 \xrightarrow[1000\,°C]{8.0\ GPa} Ln_4B_6O_{15} \qquad (Ln = Dy, Ho). \qquad (1)$$

The materials for the syntheses of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Dy) were 1:2 molar mixtures of the rare earth oxides Ln_2O_3 (Ln = Eu, Gd, Dy) (99.9 %, Sigma-Aldrich, Taufkirchen) with B_2O_3 (reaction (2)):

$$Ln_2O_3 + 2B_2O_3 \xrightarrow[1150\,°C]{10.0\ GPa} \alpha\text{-}Ln_2B_4O_9 \qquad (Ln = Eu, Gd, Dy). \qquad (2)$$

For the synthesis of α-$Tb_2B_4O_9$ we used Tb_4O_7 and B_2O_3 according to reaction (3):

$$Tb_4O_7 + 4B_2O_3 \xrightarrow[1150\,°C]{10.0\ GPa} 2\alpha\text{-}Tb_2B_4O_9 + (1/2)O_2. \qquad (3)$$
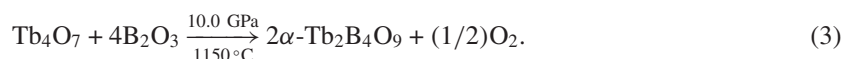
The mixtures were compressed via a multianvil assembly using conventional 18/11 and 14/8 assemblies with a modified Walker module and a 1000 ton press. As a pressure medium, precast MgO octahedra (Ceramic Substrates and Components Ltd, Isle of Wight) with edge lengths of 18 and 14 mm were used. Eight tungsten carbide cubes with the specific truncations of 11 or 8 mm, separated by pyrophyllite gaskets, compressed the octahedra. The samples were filled in cylindrical boron nitride crucibles that were sealed by boron nitride plates. The sample cylinders were placed at the centres of cylindrical resistance heaters (graphite), that had variable (stepped) wall thickness to minimize the thermal gradient along the sample. MgO rods filled the space at the top and bottom of the samples. A cylindrical zirconia sleeve, surrounding the furnace, provided thermal isolation. The assemblies were 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 assemblies, with the hot junction in contact with the boron nitride cylinder. More details concerning the construction of the assembly can be found in [20] and [21–23].

For the syntheses of $Ln_4B_6O_{15}$ (Ln = Dy, Ho), the assemblies were compressed in 3 h to 8 GPa and heated up to 1000 °C in the following 10 min. After holding this temperature for 10 min the samples were cooled down in another 10 min. For the syntheses of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) the assemblies were compressed in 3 h to 10 GPa and heated up to 1150 °C with the same temperature programme. After decompression, the recovered experimental octahedra were broken apart and the samples carefully separated from the surrounding BN. All compounds except α-$Eu_2B_4O_9$ were obtained as nearly single-phase, crystalline products. The powder pattern of α-$Eu_2B_4O_9$ exhibited an additional phase, which was identified as EuB_4O_7.

$Dy_4B_6O_{15}$ synthesized under these conditions is a colourless, nearly phase pure, coarse crystalline solid (yield: 40 mg per run). Elemental analyses of dysprosium and boron using ICP (inductively coupled plasma) on a VARIAN-VISTA spectrometer revealed 68.7 wt% Dy and 6.6 wt% B (calculated: 68.1% Dy, 6.8% B). The absence of hydrogen (OH) was checked by IR spectroscopy. $Ho_4B_6O_{15}$ was also obtained as a single-phase, crystalline product. The colour of $Ho_4B_6O_{15}$ depends on the light source. In daylight, $Ho_4B_6O_{15}$ has a light beige colour, while in the laboratory (neon lamps) it appears bright pink (Alexandrite effect) [24]. Quantitative analysis of α-$RE_2B_4O_9$ (RE = Gd, Tb) as regards the elements gadolinium, terbium, and boron using ICP on a VARIAN-VISTA spectrometer led to 62.7 wt% Gd (64.2%)/8.7% B (8.6%) in α-$Gd_2B_4O_9$ and 60.5 wt% Tb (62.9%)/8.6% B (8.6%) in α-$Tb_2B_4O_9$ (theoretical values in parentheses).

More information about the detailed syntheses can be found in [17–19].

3. Results and discussion

$Ln_4B_6O_{15}$ (Ln = Dy, Ho)

The structure solutions for the above mentioned compositions were performed using single crystals for all compounds. The structure of $Ln_4B_6O_{15}$ (Ln = Dy, Ho) is built up from corrugated layers of linked BO_4 tetrahedra (figure 1). The Ln^{3+} ions are positioned between the layers. The linkage of the BO_4 tetrahedra inside the layers is realized via common corners as well as common edges (figure 2, centre). In detail, two pairs of edge sharing tetrahedra (dark polyhedra) are linked via two additional corner sharing BO_4 tetrahedra (light polyhedra) to form six-membered rings. The linkage of these rings by further corner sharing BO_4 tetrahedra leads to rings consisting of ten BO_4 tetrahedra forming corrugated layers.
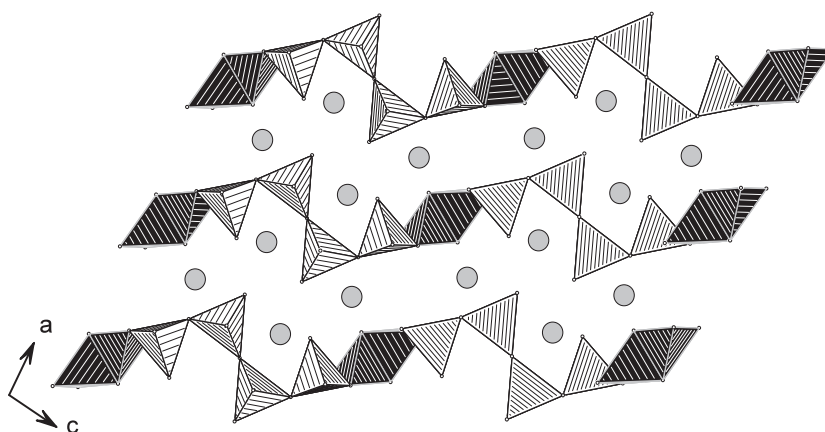
Figure 1. The crystal structure of $Ln_4B_6O_{15}$ (Ln = Dy, Ho); viewed along [010]. The structure is built up from corrugated layers of corner (light) and edge sharing (dark) BO_4 tetrahedra. The Ln^{3+} ions are positioned between the layers.

The use of hierarchical sequences for organizing crystal structures has long been recognized. Specifically for borate structures, there have been numerous classifications over the past decades reviewed by Christ and Clark [6]. Although the concepts were useful for small polyhedral boron units, they gave no indication about the topology or about the translation throughout the crystal structure. Units with identical numbers of $B\Phi_3$ triangles and $B\Phi_4$ tetrahedra (Φ: unspecified anion) always have identical descriptors, even where the structural arrangements are very different. The lack of topological characteristics of the linkage has been the main weakness of this notation. Therefore, a more detailed descriptor for fundamental borate building blocks that includes information on the connectivity of the BO_3 triangles and BO_4 tetrahedra was required. In the last decade, a new fundamental building block concept was introduced by Burns *et al* striking successfully a balance between the amount of information conveyed and the complexity of the descriptor [25, 26]. Although this method does not always result in a unique descriptor for the fundamental building block, considerably more information is included than in previous schemes. As the concept is based on the assumption that the polymerization of adjacent polyhedra involves only corner sharing, we had to expand this concept of fundamental building blocks by introducing a new descriptor '▱◺' for edge sharing BO_4 tetrahedra. Therefore the fundamental building block of $Ln_4B_6O_{15}$ (Ln = Dy, Ho) can be characterized by the descriptor 12▢ : 2 ▢▢◺◺4▢ ◺◺2▢ (figure 2, bottom). This cluster is repeated only by translation to give the corrugated layer of corner and edge sharing BO_4 tetrahedra (figure 2, centre). The top of figure 2 gives another possible choice for a fundamental building block describing the layer in $Ln_4B_6O_{15}$ (Ln = Dy, Ho): 12▢ : [<▢◺◺▢◺◺>] 2▢|▢|2▢|▢|. This formulation describes a six-membered ring built up by two pairs of edge sharing tetrahedra linked via two corner sharing BO_4 tetrahedra. This ring is decorated with six additional tetrahedra. In contrast to the former fundamental building block, this formulation captures more of the structural flavour of $Ln_4B_6O_{15}$ (Ln = Dy, Ho). A disadvantage of this description is that in addition to translation also rotation of the fundamental building block has to be performed to build up the layer.
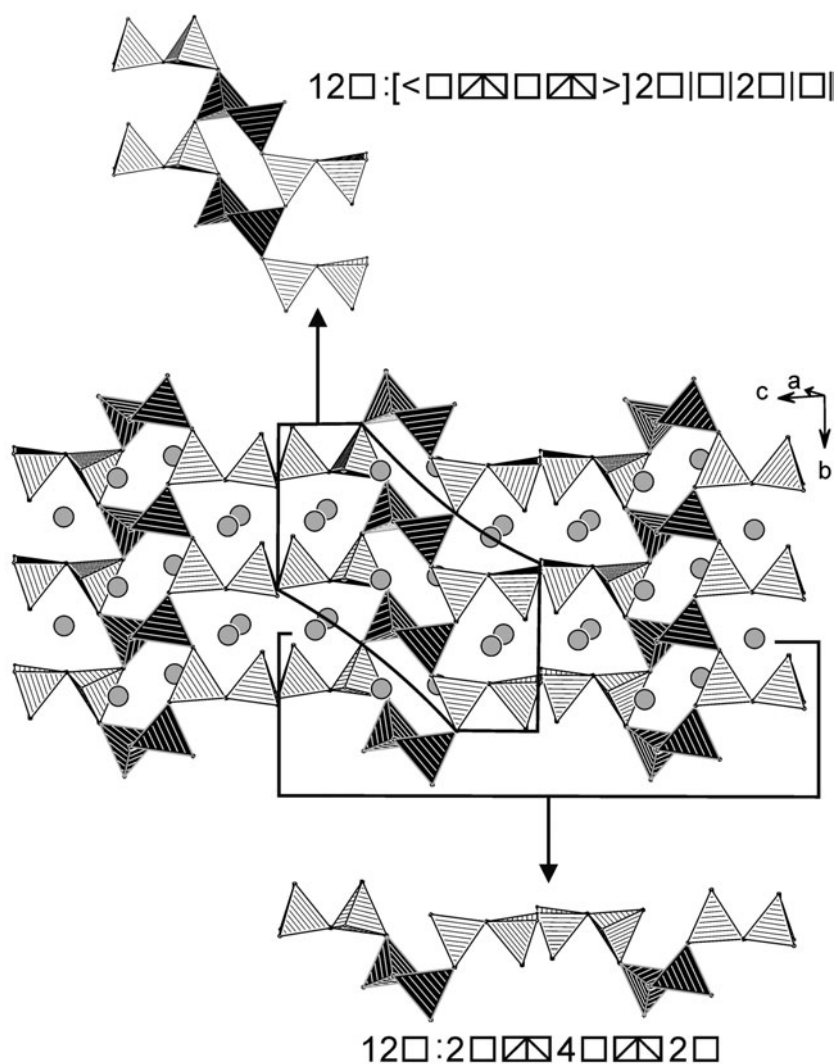
Figure 2. A view of a corrugated layer of BO_4 tetrahedra in $Ln_4B_6O_{15}$ (Ln = Dy, Ho). The linkage of the tetrahedra to rings is realized via common corners as well as via common edges.

α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy)

Figure 3 gives a view of the crystal structure of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) along [010]. The structure exhibits a complex network of linked BO_4 tetrahedra. After $Ln_4B_6O_{15}$ (Ln = Dy, Ho), this new structure of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) is the second example for an oxoborate wherein the linkage of BO_4 tetrahedra is realized via common corners as well as via common edges. For a clearer representation, the corner sharing tetrahedra are drawn as light polyhedra and the edge sharing tetrahedra as black polyhedra. Figure 4 represents the centrosymmetric fundamental building block consisting of 18 corner sharing and two edge sharing BO_4 tetrahedra. Using the new symbol for edge sharing tetrahedra, the fundamental building block of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) can be described with the descriptor 20 □ : [☒] =<4□☒>=<3□>□|-<5□>□|=<4□☒>=<3□>□|-<5□>□|. In detail,
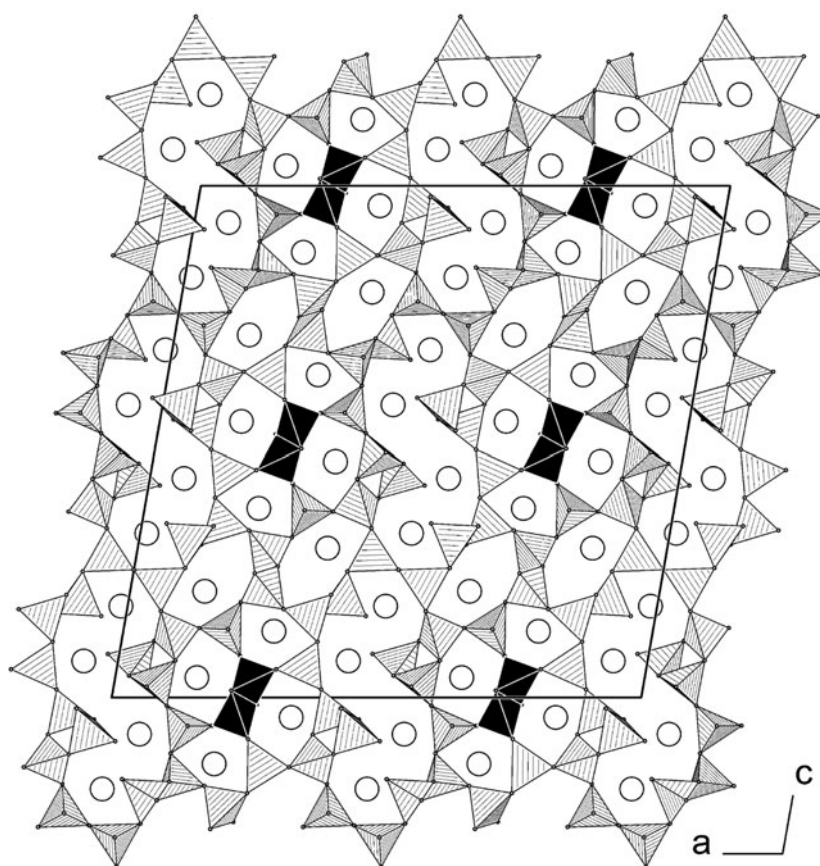
Figure 3. The crystal structure of α-Ln$_2$B$_4$O$_9$ (Ln = Eu, Gd, Tb, Dy); viewed along [010].

the edge sharing tetrahedra represent the centre of the FBB '[◰]'. On each of the two longer sides of this centre, a six-membered ring <4□◰> is built up by four additional corner sharing tetrahedra. On each of the shorter sides, one of the edge sharing tetrahedra builds up a five-membered ring with four additional corner sharing tetrahedra <5□>, from which two tetrahedra already belong to the six-membered rings on the longer sides. On the outer side of the six-membered rings, an additional three-membered ring <3□> is built up with the use of two common corner sharing tetrahedra. Both the six- and five-membered rings are additionally connected to a single outer tetrahedron □ in such a manner that the centrosymmetry of the fundamental building block is fulfilled.

The fundamental building blocks are linked together via the single outer tetrahedron and the one tetrahedron of the five-membered rings, which neither is linked with the single outer tetrahedron nor is part of one of the six-membered rings. By the linkage of the fundamental building blocks, further rings are formed between them. Additional seven-membered rings on the sides of the five-membered rings and additional fourteen-membered rings on the sides of the six-membered rings form a stretched 'S' (figure 3). These rings form planes, which are linked with the corresponding planes above and below. By the complex connection of these planes, even more rings are built up.
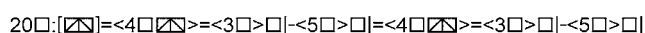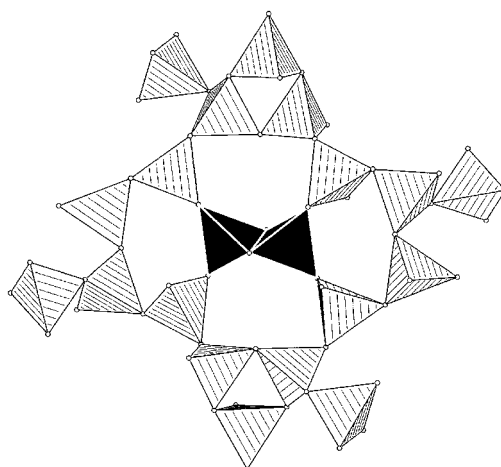
20□:[⊠]=<4□⊠>=<3□>□|-<5□>□|=<4□⊠>=<3□>□|-<5□>□|

Figure 4. The fundamental building block of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy).

Comparison of the edge sharing BO_4 tetrahedra

The B–O distances and angles in the edge sharing BO_4 tetrahedra of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb) in comparison to the data on $Ln_4B_6O_{15}$ (Ln = Dy, Ho) are of special interest. The B$\cdots$B distances in the edge sharing tetrahedra are 204(2) pm in α-$Gd_2B_4O_9$, 205.3(9) pm in α-$Eu_2B_4O_9$, and 205.9(9) pm in α-$Tb_2B_4O_9$. These are even shorter than in $Ln_4B_6O_{15}$ (Ln = Dy, Ho) (207.2(8) and 207(1) pm). The angles in the planar B_2O_2 ring exhibit average values of 86.5° and 93.5°. Conclusively, the bond distances and angles inside the edge sharing BO_4 tetrahedra of α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb) and $Ln_4B_6O_{15}$ (Ln = Dy, Ho) are similar.

4. Conclusion

By the high-pressure/high-temperature syntheses of the compounds $Ln_4B_6O_{15}$ (Ln = Dy, Ho) [17, 15] and α-$Ln_2B_4O_9$ (Ln = Eu, Gd, Tb, Dy) [18, 19] it was possible to realize edge sharing of BO_4 tetrahedra for the first time in the structural chemistry of oxoborates. Besides the new structural motif, these compounds exhibit new compositions, which had been unattainable under normal pressure conditions up to now.

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