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High-pressure synthesis of $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$)

<https://doi.org/10.1515/znb-2020-0180>

Received November 2, 2020; accepted November 20, 2020;

published online December 4, 2020

Abstract: The rare earth oxoborates $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$) were synthesized in a Walker-type multianvil apparatus at a pressure of 2.5 GPa and a temperature of 673 K. Single-crystal X-ray diffraction data provided the basis for the structure solution and refinement. The compounds crystallize in the monoclinic space group $C2$ (no. 5) and are composed of a layer-like structure containing *dreier* and *sechser* rings of corner sharing $[BO_4]^{5-}$ tetrahedra. The rare earth metal cations are coordinated between two adjacent *sechser* rings. Further characterization was performed utilizing IR spectroscopy.

Keywords: crystal structure; high-pressure; IR spectroscopy; powder X-ray diffraction; rare earth borate.

1 Introduction

The invention of Bridgman's anvil apparatus [1] marked the first step to the introduction of the “belt” by Hall [2] and therefore to high-pressure chemistry. The “belt” combines the possibility of high pressures with a significant amount of sample volume, establishing conditions up to 10 GPa at temperatures of more than 2000 °C for relatively long periods of time. Thereafter, multianvil devices were further developed yielding complex devices with ever increasing anvil quantities [3]. However, to keep costs low and enable high-pressure research with large volumes and high temperatures at a reasonable price, further development was directed at devices utilizing a uniaxial hydraulic press [3]. Considering the options of different high-pressure techniques to be used in solid state chemistry, an excellent compromise can be found in a multianvil module developed by Walker et al. [4, 5],

enabling us to combine the traditionally modifiable parameters of temperature and composition with pressure, thereby opening up a vast array of hitherto unseen possibilities. Depending on the assembly, the Walker-type module enables our group to work under extreme conditions (routinely up to 15 GPa and 1500 °C), which we have successfully employed to synthesize and characterize compounds in the field of solid state chemistry, especially in borate chemistry [3].

Borates generally comprise three- and four-fold oxygen coordinated boron atoms with diverse structural motifs ranging from isolated polyhedra to large borate clusters. In accordance with the general rule of thumb by Prewitt and Downs (“increasing pressure increases the coordination number”) [6, 7], the tetrahedrally coordinated $[BO_4]^{5-}$ group is more common in high-pressure borates than the trigonal-planar $[BO_3]^{3-}$ group. The discovery of $Dy_4B_6O_{15}$ [8] in 2002 revealed new structural variations with the first occurrence of edge-sharing tetrahedra in borate chemistry. This previously unknown structural motif has since been encountered several times in high-pressure borate chemistry [9, 10]. Additionally, the edge-sharing of borate tetrahedra was found under ambient pressure conditions in $KZnB_3O_6$ [11], $Li_4Na_2CsB_7O_{14}$ [12], β - CsB_9O_{14} [13], and α - $Ba_3(B_{10}O_{17}[OH]_2)$ [14]. The focus of interest subsequently shifted to incorporate transition metal cations, including among others the nickel borate γ - NiB_4O_7 [15] and the molybdenum borate $Mo_2B_4O_9$ [16] containing a tetrahedral Mo_4 cluster representing a combination of borate and metal-cluster chemistry. Furthermore, our group has supplemented the borate backbone with different anionic structural motifs yielding compounds like the borosulfate $CaB_2S_4O_{16}$ [17] and the borate nitrate $Lu_2B_2O_5(NO_3)_2 \cdot 2H_2O$ [18].

Having turned full circle, our group currently further expands the chemistry of the rare earth (RE) borates as recently exemplified by $La_3B_6O_{13}(OH)$ [19], the first acentric borate in the group of compounds exhibiting edge-sharing $[BO_4]^{5-}$ tetrahedra. Additionally, we have recently reported on the high-pressure rare earth metal borate $DyB_5O_8(OH)_2$ [20]. Subsequently, we tried to complement the family of compounds of the type $REB_5O_8(OH)_2$ by presenting the isotopic compounds incorporating the rare earth metals Ho, Er, and Tm. Here we report their characterization *via* single-crystal and powder X-ray diffraction, and by infrared spectroscopy.

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2 Experimental section

2.1 Synthesis

All three compounds $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$) were synthesized under high-pressure conditions utilizing a Walker-type multianvil module in a 1000 t downstroke press (both Max Voggenreiter GmbH, Mainleus, Germany) from a mixture of the rare earth metal oxides (RE_2O_3 ; $RE = Ho, Er, Tm$), boric acid H_3BO_3 , and diboron trioxide B_2O_3 . The total mass and the molar ratios are given in the following: $Ho_2O_3:H_3BO_3:B_2O_3 = 45.30\text{ mg (0.12 mmol):29.65 mg (0.48 mmol):25.04 mg (0.36 mmol)}$, $Er_2O_3:H_3BO_3:B_2O_3 = 45.61\text{ mg (0.12 mmol):29.49 mg (0.48 mmol):24.90 mg (0.36 mmol)}$, and $Tm_2O_3:H_3BO_3:B_2O_3 = 45.83\text{ mg (0.12 mmol):29.37 mg (0.48 mmol):24.80 mg (0.36 mmol)}$.

After grinding, the mixtures were placed in 18/11 assemblies and compressed by eight tungsten carbide cubes (Hawedia, Marklkofen, Germany). Further information concerning the high-pressure assembly and its preparation can be found in the literature [3–5]. The samples were then compressed in the multianvil apparatus to 2.5 GPa within 65 min, heated to 673 K in 5 min, kept at $T = 673\text{ K}$ for 30 min, and then cooled to room temperature in 60 min. However, in the case of $TmB_5O_8(OH)_2$ this procedure was not sufficient to yield single crystals of satisfactory size. The temperature was therefore increased to 723 K, kept at 723 K for 45 min, and then cooled to room temperature in 90 min, which yielded the desired single-crystal quality. After cooling, the decompression of the module was conducted over 180 min. Subsequently, the samples were separated from the surroundings and the final products were recovered as air stable crystals. Ambient pressure synthesis was attempted for all three title compounds, however these attempts were unsuccessful and resulted in yet unidentified phases.

2.2 X-ray structure determination

A STOE Stadi P diffractometer with monochromatized $MoK\alpha_1$ radiation ($\lambda = 70.93\text{ pm}$; curved Ge(111)) was used to characterize polycrystalline samples by powder X-ray diffraction. Diffraction intensities were measured with a Mythen2 1K microstrip detector with 1280 strips (Dectris, Baden-Daettwil, Switzerland).

The products were ground in an agate mortar, fixed between two polyacetate films and investigated by powder X-ray diffraction (Figure 1). For clarity, the powder diffraction data of all three compounds is compared in one single

Figure 1: Powder X-ray diffraction data of $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$) compared to the theoretical pattern of $DyB_5O_8(OH)_2$.

Figure for $HoB_5O_8(OH)_2$, $ErB_5O_8(OH)_2$, and $TmB_5O_8(OH)_2$ (top to bottom). Despite several attempts, we were thus far unable to obtain the title compounds as phase pure products. The diffraction patterns indicate significant amounts of impurities (marked by asterisks), likely a combination of an unidentified side phase, boric acid, and the corresponding rare earth metal oxide (starting materials).

Under a polarisation microscope, suitable single crystals were fixed on the tip of a MicroMount™ (MiTeGen, LLC, Ithaca, NY, USA) and placed inside the diffractometer. The intensity data was collected with a Bruker D8 Quest diffractometer (Bruker, Karlsruhe, Germany) equipped with a Photon 100 detector system and an Incoatec microfocus source generator (multi-layered optic, monochromatized $MoK\alpha$ radiation, $\lambda = 71.073\text{ pm}$). Concerning the ω and φ scans, the collection strategy was optimized using the APEX III [21] program package. Thus, complete data sets up to high angles with high redundancies were received. For data processing and data reduction, the program SAINT [22] was employed. Thereafter, multi-scan absorption corrections were applied with the program SADABS [23].

The structure solution and parameter refinement with anisotropic displacement parameters was done utilising the SHELXS/L-2013 [24, 25] software implemented in the program WINGX-2013.3 [26]. In the course of the structure determinations, the non-centrosymmetric monoclinic space group $C2$ was found to be correct, but only partial anisotropic refinement was possible for the oxygen and boron positions. Therefore, we have decided to utilize an anisotropic refinement only for the rare earth cations

(holmium, erbium, and thulium) and to stick with an isotropic refinement for the oxygen and boron positions.

Relevant details of the data collection and evaluation are listed in Table 1, the atomic coordinates and the isotropic displacement parameters are given in Table 2. Interatomic distances are shown in Table 3 and bond angles in Table 4.

CCDC 2033530 ($HoB_5O_8(OH)_2$), 2033529 ($ErB_5O_8(OH)_2$), and 2033532 ($TmB_5O_8(OH)_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3 Infrared spectroscopy

A Bruker Alpha Platinum spectrometer using the ATR method (attenuated total reflection) was used to record the IR data. The spectra were measured on the bulk phase in the range from 4000 to 400 cm^{-1} . The OPUS 7.2 [27] program

was used to correct for atmospheric influences and to process the IR data.

3 Results and discussion

3.1 Crystal structure

The title compounds $HoB_5O_8(OH)_2$, $ErB_5O_8(OH)_2$, and $TmB_5O_8(OH)_2$ crystallize in the monoclinic non-centrosymmetric space group C2 (no. 5), show exactly the same site symmetry, are clearly isotypic to each other, and complement the previously characterized compound $DyB_5O_8(OH)_2$ [20]. The change in the cell parameters with the exchange of the rare earth metal cation is shown in Figure 2. As expected, the progression to higher atomic numbers (and therefore smaller atomic radii) results in a contraction of the overall cell volume V . This however only corresponds to a decrease of the cell parameters a and b . Interestingly, the cell parameter c decreases from dysprosium to holmium, but shows a sharp increase towards the

Table 1: Crystal data and structure refinement of $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$) with standard deviations in parentheses; space group C2 (no. 5).

Empirical formula	$HoB_5O_8(OH)_2$	$ErB_5O_8(OH)_2$	$TmB_5O_8(OH)_2$
Molar mass/ $g\ mol^{-1}$	381.00	383.33	385.00
Single-crystal diffractometer	Bruker D8 Quest Photon 100		
Radiation; wavelength λ/pm	$MoK\alpha$; 71.073		
a/pm	792.33(3)	790.94(8)	789.26(7)
b/pm	439.49(2)	439.04(4)	437.80(3)
c/pm	933.10(3)	935.95(12)	937.26(7)
β/deg	113.825(1)	114.396(3)	114.730(6)
V/nm^3	0.29724(2)	0.29599(6)	0.29416(4)
Formula units per cell Z	2	2	2
Calculated density/ $g\ cm^{-3}$	4.23	4.28	4.32
Crystal size/ mm^3	$0.060 \times 0.030 \times 0.020$	$0.020 \times 0.020 \times 0.020$	$0.030 \times 0.030 \times 0.010$
Temperature/K	296(2)	183(2)	173(2)
Absorption coefficient/ mm^{-1}	13.4	14.2	15.1
$F(000)/e$	344	346	348
2θ range/deg	9.55–74.12	9.57–75.72	9.58–82.45
Range in hkl	$\pm 13, \pm 7, \pm 15$	$\pm 13, \pm 7, \pm 16$	$\pm 14, \pm 8, \pm 17$
Total no. of reflections	9121	4115	14529
Independent reflections; R_{int}	1517; 0.0298	1580; 0.0443	1978; 0.0434
Data; restraints; parameters	1517; 1; 36	1580; 1; 37	1978; 1; 37
Absorption correction	Multi-scan (Bruker SADABS 2016/2)		
Final R_1 ; wR_2 ($I > 2\sigma(I_0)$)	0.0132; 0.0310	0.0352; 0.0582	0.0205; 0.0448
Final R_1 ; wR_2 (all data)	0.0132; 0.0310	0.0368; 0.0594	0.0205; 0.0448
Flack x	–0.018(7)	–0.026(18)	–0.015(7)
Goodness-of-fit on F_o^2	1.133	1.152	1.161
Largest diff. peak; hole/ $e\ \text{\AA}^{-3}$	0.94; –1.00	3.27; –3.05	4.51; –2.44

Table 2: Atomic coordinates and equivalent isotropic displacement parameters U_{eq} (isotropic displacement parameters U_{iso} for B and O atoms; $U_{eq/iso}$ in $\text{\AA}^2$) for $REB_5O_8(OH)_2$ with $RE = Ho, Er, Tm$ (space group C2, no. 5). All atoms are on the Wyckoff positions 4c, except for B3 (2a), and Ho/Er/Tm (2b). All sites are fully occupied.

HoB₅O₈(OH)₂				
Atom	x	y	z	$U_{eq/iso}$
Ho1	0	0.25435(3)	1/2	0.00330(4)
B1	0.2056(3)	0.2328(11)	0.2708(3)	0.0037(4)
B2	0.5343(3)	0.254(3)	0.2700(3)	0.0038(3)
B3	0	0.000(1)	0	0.0043(6)
O1	0.0803(3)	0.4342(5)	0.3072(3)	0.0045(3)
O2	0.1526(3)	0.1894(4)	0.1019(3)	0.0047(3)
O3	0.3010(3)	0.4400(5)	0.6528(3)	0.0046(3)
O4	0.3981(3)	0.3370(5)	0.3393(3)	0.0043(3)
O5	0.4435(3)	0.3121(4)	0.1012(2)	0.0047(4)
ErB₅O₈(OH)₂				
Atom	x	y	z	$U_{eq/iso}$
Er1	0	0.2492(3)	1/2	0.00326(8)
B1	0.2045(12)	0.231(4)	0.2715(9)	0.0050(16)
B2	0.5346(10)	0.254(6)	0.2712(8)	0.0020(12)
B3	0	0.000(5)	0	0.0044(16)
O1	0.0799(9)	0.4276(13)	0.3082(7)	0.0032(10)
O2	0.1522(10)	0.1857(14)	0.1017(8)	0.0049(14)
O3	0.2997(8)	0.4349(13)	0.6522(7)	0.0027(10)
O4	0.3982(8)	0.3354(10)	0.3398(6)	0.0025(9)
O5	0.4424(10)	0.3079(14)	0.1011(8)	0.0034(13)
TmB₅O₈(OH)₂				
Atom	x	y	z	$U_{eq/iso}$
Tm1	0	0.2498(3)	1/2	0.00283(4)
B1	0.2020(8)	0.234(2)	0.2711(5)	0.0022(9)
B2	0.5295(8)	0.254(4)	0.2713(5)	0.0029(8)
B3	0	0.000(8)	0	0.0049(8)
O1	0.0766(6)	0.4293(9)	0.3093(5)	0.0031(5)
O2	0.1455(8)	0.1926(11)	0.1011(7)	0.0029(12)
O3	0.3008(6)	0.4358(8)	0.6526(5)	0.0030(5)
O4	0.3963(5)	0.3393(8)	0.3398(4)	0.0037(5)
O5	0.4366(9)	0.3139(12)	0.1019(7)	0.0042(12)

thulium compound. The monoclinic angle β steadily increases, however the same sharp increase is observed from holmium to erbium.

The fundamental building block is formed by three crystallographically different borate tetrahedra with B–O distances ranging from 142(2) to 149(2) pm and O–B–O angles ranging from 104.3(5) to 114(2)°, which both agree well with values presented in the literature [28]. The combination of fundamental building blocks yields a layer-like structure along the *ab* plane and a stacking along the *c* axis with alternating rare earth metal cation and borate

domains (Figure 3). Each borate layer is built up from two layers of *sechser* rings, expanding along the *ab* plane (Figure 3; right), which are interconnected by B3 tetrahedra, thereby forming *dreier* rings. The term *sechser* ring was coined by F. Liebau, is derived from the German word “*sechs*” and describes a ring with six tetrahedral centres [29]. The same is applicable for *dreier* rings, where “*drei*” is used to describe a three membered ring. The layer transition depicting the rare earth metal cation between two adjacent *sechser* rings is shown in Figure 4. In the case of the transition from Dy^{3+} to Tm^{3+} , the ionic radii decrease from 105.2 to 102 pm [30], which results in an overall smaller space requirement. While the borate layer thickness (Figure 3, orange arrow) remains virtually unchanged, the cation-cation distance (dark yellow arrow) decreases from 453.41(2) (Dy) to 451.3(1) pm (Tm). The overall layer thickness (measured as the distance from cation to cation through the layer, Figure 3, dark green arrow) decreases as well, from 883.01(7) (Dy) to 879.00(9) pm (Tm). Due to the contraction of the layer thickness, the monoclinic angle β and the *c* axis increase, while the *a* and *b* axes decrease, as well as the overall cell volume (see Figure 2). This modification of the cell parameters is presumably caused by the smaller space requirement of the cation and the decreasing RE–O distances.

At this point, it should be noted that identifying the position of hydrogen atoms *via* X-ray diffraction experiments can be difficult. Although the hydrogen atoms could be located in the structure of $DyB_5O_8(OH)_2$ (interconnecting the B1 and B2 tetrahedra and spanning along the *sechser* rings), this was not possible in the present cases. However, for charge equalization, one hydrogen position has to be added to the structure of all three compounds. Like for the isotypic compound $DyB_5O_8(OH)_2$, we suggest that the hydrogen atoms are situated between the O2 and the O5 oxygen atoms.

To verify the structure solution, the bond valence sums were calculated for all crystallographically different Ho/Er/Tm, B, and O atoms *via* the bond-length/bond-strength concept [31]. The results given in Table 5 agree well with the expected values, the only exceptions being the O2 and O5 oxygen atoms. However, this only further indicates the presence of a hydrogen atom bonded to one of these atoms. Inserting a hydrogen atom at a distance of approximately 84 pm (as found for $DyB_5O_8(OH)_2$) shifts the charge values towards the expected value of -2 . Pronounced OH bands in the infrared spectra shown in Figure 5 further indicate the presence of OH groups.

Table 3: Selected interatomic distances (pm) in $REB_5O_8(OH)_2$ with $RE = Ho, Er, Tm$ (standard deviations in parentheses).

$HoB_5O_8(OH)_2$		$ErB_5O_8(OH)_2$		$TmB_5O_8(OH)_2$	
Atoms	Distance	Atoms	Distance	Atoms	Distance
Ho1–O1	227.9(2)	Er1–O1	227.4(6)	Tm1–O1	225.5(4)
Ho1–O1	227.9(2)	Er1–O1	227.4(6)	Tm1–O1	225.5(4)
Ho1–O4	230.0(2)	Er1–O4	228.0(5)	Tm1–O4	226.4(3)
Ho1–O4	230.0(2)	Er1–O4	228.0(5)	Tm1–O4	226.4(3)
Ho1–O3	237.5(2)	Er1–O3	235.0(6)	Tm1–O3	234.6(4)
Ho1–O3	237.5(2)	Er1–O3	235.0(6)	Tm1–O3	234.6(4)
Ho1–O3	287.2(2)	Er1–O3	288.2(6)	Tm1–O3	287.9(4)
Ho1–O3	287.2(2)	Er1–O3	288.2(6)	Tm1–O3	287.9(4)
	$\bar{d} = 245.7$		$\bar{d} = 244.7$		$\bar{d} = 243.6$
B1–O1	146.9(4)	B1–O1	145(2)	B1–O1	146.1(8)
B1–O4	146.9(4)	B1–O4	147(2)	B1–O4	146.8(8)
B1–O2	147.0(3)	B1–O2	148(1)	B1–O2	147.5(7)
B1–O3	148.2(5)	B1–O3	149(2)	B1–O3	149(1)
	$\bar{d} = 147.3$		$\bar{d} = 147$		$\bar{d} = 147$
B2–O1	146(1)	B2–O3	145(2)	B2–O3	146(1)
B2–O3	146.0(7)	B2–O5	147(1)	B2–O5	146.7(8)
B2–O5	146.6(4)	B2–O1	148(3)	B2–O1	148(2)
B2–O4	151.0(4)	B2–O4	151(1)	B2–O4	149.0(8)
	$\bar{d} = 147$		$\bar{d} = 148$		$\bar{d} = 147$
B3–O5	145.5(3)	B3–O2	144(2)	B3–O2	142(2)
B3–O5	145.5(3)	B3–O2	144(2)	B3–O2	142(2)
B3–O2	145.9(3)	B3–O5	147(2)	B3–O5	149(2)
B3–O2	145.9(3)	B3–O5	147(2)	B3–O5	149(2)
	$\bar{d} = 145.7$		$\bar{d} = 146$		$\bar{d} = 146$

Table 4: Selected bond angles (deg) in $REB_5O_8(OH)_2$ with $RE = Ho, Er, Tm$ (standard deviations in parentheses).

$HoB_5O_8(OH)_2$		$ErB_5O_8(OH)_2$		$TmB_5O_8(OH)_2$	
Atoms	Bond angle	Atoms	Bond angle	Atoms	Bond angle
O1–B1–O4	113.1(3)	O1–B1–O4	114(1)	O1–B1–O4	113.5(6)
O1–B1–O2	113.5(2)	O1–B1–O2	114.7(8)	O1–B1–O2	114.0(5)
O4–B1–O2	107.7(2)	O4–B1–O2	106.8(7)	O4–B1–O2	107.4(5)
O1–B1–O3	104.7(2)	O1–B1–O3	104.6(7)	O1–B1–O3	104.3(5)
O4–B1–O3	107.1(2)	O4–B1–O3	106.8(8)	O4–B1–O3	106.7(4)
O2–B1–O3	110.6(3)	O2–B1–O3	110(2)	O2–B1–O3	110.6(7)
	$\emptyset = 109.5$		$\emptyset = 109$		$\emptyset = 109.4$
O1–B2–O3	109.6(3)	O3–B2–O5	113(2)	O3–B2–O5	111.9(8)
O1–B2–O5	113.0(5)	O3–B2–O1	109.5(8)	O3–B2–O1	108.7(6)
O3–B2–O5	112.6(5)	O5–B2–O1	112(2)	O5–B2–O1	113.2(9)
O1–B2–O4	106.6(4)	O3–B2–O4	109(2)	O3–B2–O4	108.7(8)
O3–B2–O4	107.7(5)	O5–B2–O4	107.5(8)	O5–B2–O4	107.3(6)
O5–B2–O4	107.0(3)	O1–B2–O4	106(1)	O1–B2–O4	106.8(7)
	$\emptyset = 109.4$		$\emptyset = 109$		$\emptyset = 109.4$
O5–B3–O5	110.8(3)	O2–B3–O2	111(2)	O2–B3–O2	107(2)
O5–B3–O2	110.8(1)	O2–B3–O5	110.7(2)	O2–B3–O5	110.9(3)
O5–B3–O2	107.0(2)	O2–B3–O5	107.2(2)	O2–B3–O5	106.9(2)
O5–B3–O2	107.0(2)	O2–B3–O5	107.2(2)	O2–B3–O5	106.9(2)
O5–B3–O2	110.8(1)	O2–B3–O5	110.7(2)	O2–B3–O5	110.9(3)
O2–B3–O2	110.5(3)	O5–B3–O5	110(2)	O5–B3–O5	114(2)
	$\emptyset = 109.5$		$\emptyset = 109$		$\emptyset = 109$

Figure 2: Progression of the cell parameters in $REB_5O_8(OH)_2$ ($RE = Dy, Ho, Er, Tm$).

3.2 Infrared spectroscopy

All three compounds show very similar infrared spectra. The distinct ν_{OH} band at approximately 3200 cm^{-1} [32] indicates the presence of hydroxide groups ($\nu(O-H)$). The absorption peaks in the region between 1100 and 800 cm^{-1} are those typical for tetrahedrally coordinated $[BO_4]^{5-}$ groups. The region below 900 cm^{-1} is generally attributed to vibrations of $[BO_3]^{3-}$ and $[BO_4]^{5-}$ groups [33, 34]. The broad peak at 1450 cm^{-1} is usually attributed to stretching vibrations of $[BO_3]^{3-}$ groups. However, no $[BO_3]^{3-}$ groups were found in the structure solution process and the bands are instead tentatively assigned to B–O–B, O–B–O, and B–O–RE ($RE = \text{rare earth metal ion}$) vibrations, as verified by *ab initio* quantum-chemical calculations for $\beta\text{-ZnB}_4\text{O}_7$ and $\beta\text{-CaB}_4\text{O}_7$ [35]. These findings are in good agreement with the observations for the isotopic compound $DyB_5O_8(OH)_2$ [20]. In general, the band positions vary only slightly among the four isotopic compounds.

Figure 4: Rare earth metal cation surrounded by borate *sechser* rings.

Table 5: Charge distribution in $REB_5O_8(OH)_2$ with $RE = Ho, Er, Tm$, calculated with the bond-length/bond-strength concept (ΣV) [31].

$HoB_5O_8(OH)_2$		$ErB_5O_8(OH)_2$		$TmB_5O_8(OH)_2$	
Atom	ΣV	Atom	ΣV	Atom	ΣV
Ho1	2.92	Er1	2.93	Tm1	2.95
B1	3.04	B1	3.03	B1	3.03
B2	3.04	B2	3.01	B2	3.04
B3	3.17	B3	3.18	B3	3.20
O1	2.06	O1	2.03	O1	2.04
O2	1.55	O2	1.57	O2	1.63
O3	1.91	O3	1.94	O3	1.90
O4	1.93	O4	1.94	O4	1.98
O5	1.57	O5	1.52	O5	1.50

Figure 3: Layer-like structure stacking along the c axis (left) and detail of the *sechser* rings expanding in the ab plane (right) in $REB_5O_8(OH)_2$ ($RE = Dy, Ho, Er, Tm$).

Figure 5: Infrared spectra of powder samples of $REB_5O_8(OH)_2$ ($RE = Ho, Er, Tm$) and of $DyB_5O_8(OH)_2$ reported previously [20].

4 Conclusion

The three isotopic compounds $HoB_5O_8(OH)_2$, $ErB_5O_8(OH)_2$, and $TmB_5O_8(OH)_2$ were synthesized via high-pressure/high-temperature syntheses, expanding the family $REB_5O_8(OH)_2$ ($RE = Dy-Tm$). Further characterization was done utilizing infrared spectroscopy. The crystal structure consists of three crystallographically different borate tetrahedra arranged in a *dreier* ring. Expanding and interconnecting these *dreier* rings yields the formation of *sechser* rings in the *ab* plane. The *sechser* rings are in turn interconnected via the *dreier* rings forming borate layers incorporating the *RE* cations.

Acknowledgments: The authors thank Assoz.-Prof. Dr. Gunter Heymann for the single-crystal X-ray measurements and Dr. Daniela Vitzthum for the helpful input regarding the structure solution process. Additionally, the authors thank Barbara Simic, BSc, for her efforts in synthesizing the presented compounds.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bridgman P. W. *Proc. Roy. Soc.* 1950, A203, 1–17.
2. Hall H. T. *Rev. Sci. Instrum.* 1960, 31, 125–131.

3. Huppertz H. *Z. Kristallogr.* 2004, 219, 330–338.
4. Walker D., Carpenter M., Hitch C. *Am. Mineral.* 1990, 75, 1020–1028.
5. Walker D. *Am. Mineral.* 1991, 76, 1092–1100.
6. Prewitt C. T., Downs R. T. *Rev. Mineral.* 1998, 37, 284–318.
7. Grochala W., Hoffmann R., Feng J., Ashcroft N. W. *Angew. Chem. Int. Ed.* 2007, 46, 3620–3642.
8. Huppertz H., von der Eltz B. *J. Am. Chem. Soc.* 2002, 124, 9376–9377.
9. Emme H., Huppertz H. *Chem. Eur. J.* 2003, 9, 3623–3633.
10. Huppertz H. *Z. Naturforsch.* 2003, 58b, 278–290.
11. Jin S., Cai G., Wang W., He M., Wang S., Chen X. *Angew. Chem. Int. Ed.* 2010, 122, 5087–5090.
12. Mutailipu M., Zhang M., Li H., Fan X., Yang Z., Jin S., Wang G., Pan S. *Chem. Commun.* 2019, 55, 1295–1298.
13. Han S., Huang C., Tudi A., Hu S., Yang Z., Pan S. *Chem. Eur. J.* 2019, 25, 11614–11619.
14. Jen I. H., Lee Y. C., Tsai C. E., Lii K. H. *Inorg. Chem.* 2019, 58, 4085–4088.
15. Schmitt M. K., Janka O., Niehaus O., Dresselhaus T., Pöttgen R., Pielhofer F., Weihrich R., Krzhizhanovskaya M., Filatov S., Bubnova R. *Inorg. Chem.* 2017, 56, 4217–4228.
16. Schmitt M. K., Janka O., Pöttgen R., Benndorf C., de Oliveira M. Jr., Eckert H., Pielhofer F., Tragl A. S., Weihrich R., Joachim B. *Angew. Chem. Int. Ed.* 2017, 56, 6449–6453.
17. Bruns J., Podewitz M., Schauperl M., Joachim B., Liedl K. R., Huppertz H. *Chem. Eur. J.* 2017, 23, 16773–16781.
18. Ortner T. S., Wurst K., Hejny C., Huppertz H. *J. Solid State Chem.* 2016, 233, 329–334.
19. Fuchs B., Heymann G., Wang X., Tudi A., Bayarjargal L., Siegel R., Schmutzler A., Senker J., Joachim-Mrosko B., Saxer A. *Chem. Eur. J.* 2020, 26, 6851–6861.
20. Zoller M., Heymann G., Saxer A., Huppertz H. *Eur. J. Inorg. Chem.* 2020, 2020, 370–376.
21. APEX III (version 2017 3-0); Bruker AXS GmbH: Karlsruhe (Germany), 2017.
22. SAINT (version 8.38A); Bruker AXS GmbH: Karlsruhe (Germany), 2016.
23. SADABS (version 2014/5); Bruker AXS Inc.: Madison, WI (USA), 2014.
24. Sheldrick G. *Acta Crystallogr.* 2008, A64, 112–122.
25. Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3–8.
26. Farrugia L. J. *Appl. Crystallogr.* 2012, 45, 849–854.
27. OPUS (version 7.2); Bruker Corporation: Billerica, MA (USA), 2012.
28. Zöbetsch E. *Z. Kristallogr.* 1990, 191, 45–58.
29. Liebau F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985.
30. Holleman A. F., Wiberg E., Wiberg N. *Lehrbuch der Anorganischen Chemie*, 102nd ed.; De Gruyter: Berlin, 2007.
31. Brown I., Altermatt D. *Acta Crystallogr.* 1985, B41, 244–247.
32. Nakamoto K., Margoshes M., Rundle R. *J. Am. Chem. Soc.* 1955, 77, 6480–6486.
33. Neumair S. C., Vanicek S., Kaindl R., Többsen D. M., Martineau C., Taulelle F., Senker J., Huppertz H. *Eur. J. Inorg. Chem.* 2011, 2011, 4147–4152.
34. Schmitt M. K., Janka O., Pöttgen R., Huppertz H. *Z. Anorg. Allg. Chem.* 2017, 643, 1344–1350.
35. Kaindl R., Sohr G., Huppertz H. *Spectrochim. Acta, Part A* 2013, 116, 408–417.