High-pressure Syntheses and Characterization of the Rare-earth Fluoride Borates $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho)

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The new rare-earth fluoride borates $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) were synthesized under high-pressure/high-temperature conditions of 1.5 GPa/1200 °C for $Tb_2(BO_3)F_3$ and 3.0 GPa/900 °C for $Dy_2(BO_3)F_3$ and $Ho_2(BO_3)F_3$ in a Walker-type multianvil apparatus from the corresponding rare-earth sesquioxides, rare-earth fluorides, and boron oxide. The single-crystal structure determinations revealed that the new compounds are isotypic to the known rare-earth fluoride borate $Gd_2(BO_3)F_3$. The new rare-earth fluoride borates crystallize in the monoclinic space group $P2_1/c$ ($Z = 8$) with the lattice parameters $a = 16.296(3)$, $b = 6.197(2)$, $c = 8.338(2)$ Å, $\beta = 93.58(3)°$ for $Tb_2(BO_3)F_3$, $a = 16.225(3)$, $b = 6.160(2)$, $c = 8.307(2)$ Å, $\beta = 93.64(3)°$ for $Dy_2(BO_3)F_3$, and $a = 16.189(3)$, $b = 6.124(2)$, $c = 8.282(2)$ Å, $\beta = 93.69(3)°$ for $Ho_2(BO_3)F_3$. The four crystallographically different rare-earth cations (CN = 9) are surrounded by oxygen and fluoride anions. All boron atoms form isolated trigonal-planar $[BO_3]^{3-}$ groups. The six crystallographically different fluoride anions are in a nearly planar coordination by three rare-earth cations.

Key words: High Pressure, Lanthanoides, Fluoride, Borate, Crystal Structure

Introduction

In 1998, Corbel *et al*. synthesized the first rare-earth fluoride borates $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd) [1]. These flux-supported solid-state syntheses led solely to a powder sample with low crystallinity. Therefore, Corbel *et al*. presented an *ab initio* structure determination of $Gd_3(BO_3)_2F_3$ based on powder X-ray diffraction data. Due to the weak scattering factor of boron, it was impossible to refine the boron atoms. Later work by Antic-Fidancev *et al*. led to the assumption of a disorder in the crystal structure [2]. The reason for this assumption was the observation of extremely broadened bands during luminescence measurements of the isotypic compound $Eu_3(BO_3)_2F_3$. Out of this observation, Antic-Fidancev *et al*. postulated a disorder model in which three fluoride anions were replaced by a $[BO_3]^{3-}$ group, and so the formula changed to $Eu_3F_{3-3x}(BO_3)_{2+x}$ with a small value for *x*. However, the authors could not explain how this exchange could be realized without any major effects to the crystal structure. A reliable way of substituting a $[BO_3]^{3-}$ group against three fluoride anions was recently described by Rashchenko *et al.* [3]. In 2002, Müller-Bunz *et al.* tried to reproduce the synthesis of $Gd_3(BO_3)_2F_3$ without success. All their attempts led to the rare-earth fluoride borate $Gd_2(BO_3)F_3$ [4], which is structurally related. Müller-Bunz *et al.* yielded single crystals with sufficient quality for a single-crystal structure determination. For the compound $Gd_2(BO_3)F_3$, an anionic disorder evoked by two possible positions of one boron atom between the RE–O/F polyhedra was proposed, leading to a $[BO_3]^{3-}$ or a $[BO_2F]^{2-}$ group. The close relationship of the crystal structures of $Gd_2(BO_3)F_3$ and $Gd_3(BO_3)_2F_3$ suggested the possibility of a similar disorder in the rare-earth fluoride borates $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd) [1]. In the past years, our group described a further related structure type for the compounds $RE_5(BO_3)_2F_9$ (RE = Tb, Ho, Er, Tm, Yb) using the multi-anvil high-pressure/high-

temperature technique [5 – 8]. In the following, we describe the syntheses and the single-crystal structure determinations of $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) and compare the new compounds to the isotypic phase $Gd_2(BO_3)F_3$.

Experimental Section

Syntheses

The syntheses of the compounds $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) took place under high-pressure/high-temperature conditions. The synthesis of $Tb_2(BO_3)F_3$ was carried out at 1.5 GPa and 1200 °C, while the isotypic compounds $Dy_2(BO_3)F_3$ and $Ho_2(BO_3)F_3$ were obtained at 3.0 GPa and 900 °C. Depending on the rare-earth fluoride borate, stoichiometric mixtures of rare-earth sesquioxides (Strem Chemicals, 99.9 %), B_2O_3 (Strem Chemicals, 99.9+ %), and the rare-earth(III) fluorides (Strem Chemicals, 99.9 %) with a molar ratio of 1 : 1 : 2 were finely ground and filled into boron nitride crucibles (Henze BNP GmbH, HeBoSint® S100, Kempten, Germany). These crucibles were placed into the center of an 18/11-assembly. All working steps were done inside of a glove box. The assemblies were compressed by eight tungsten carbide cubes (TSM-10 Ceratizit, Reutte, Austria). To apply the pressure, a 1000 t multianvil press with a Walker-type module (both devices from the company Voggenreiter, Mainleus, Germany) was used. The assembly and its preparation are described in refs. [9 – 13]. For the synthesis of $Tb_2(BO_3)F_3$, the 18/11 assembly was compressed up to 1.5 GPa in 50 min, then heated to 1200 °C (cylindrical graphite furnace) within 10 min, kept there for 15 min, and cooled down to 450 °C in 25 min at constant pressure. $Dy_2(BO_3)F_3$ and $Ho_2(BO_3)F_3$ were synthesized by compressing the 18/11-assembly up to 3.0 GPa in 80 min and heated to 900 °C (cylindrical graphite furnace) in the following 15 min, kept there for 20 min, and cooled down to 700 °C in 20 min at constant pressure. After natural cooling down to room temperature by switching off the heating, decompression periods of 2 h for $Tb_2(BO_3)F_3$, and 4.5 h for $Dy_2(BO_3)F_3$ and $Ho_2(BO_3)F_3$ were required. The recovered octahedral pressure media (MgO, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) were broken apart and the samples carefully separated from the surrounding graphite and boron nitride. While $Tb_2(BO_3)F_3$ and $Dy_2(BO_3)F_3$ were found in form of colorless, air-stable crystals, the compound $Ho_2(BO_3)F_3$ showed an intense alexandrite effect (daylight: yellow, incandescent light: pink).

All efforts to synthesize the new rare-earth fluoride borates $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) under ambient pressure conditions were unsuccessful. The high-temperature syntheses were performed in boron nitride crucibles placed into silica glass tubes. These assemblies were heated under ambient pressure conditions in a tube furnace from the company Carbolite.

Crystal structure analyses

The isotypic compounds $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) were identified by powder X-ray diffraction on flat samples of the reaction products using a Stoe Stadi P powder diffractometer with MoK_{α_1} radiation (transmission geometry, Ge monochromator, $\lambda = 70.93$ pm). The powder diffraction patterns showed reflections of the new rare-earth fluoride borates $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) and in all cases reflections of a side product. While the side products of the syntheses with dysprosium oxide and holmium oxide were identified by reflection patterns of the compounds $RE_5(BO_3)_2F_9$ ($RE =$ Dy, Ho) [5 – 8], the respective diffraction pattern of $Tb_5(BO_3)_2F_9$ showed a still unknown side product. Theoretical powder patterns were simulated from the single-crystal data matching well with the experimental powder patterns. Small single crystals of $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) were isolated by mechanical fragmentation. The single-crystal intensity data were collected at room temperature using a Nonius Kappa-CCD diffractometer with graphite-monochromatized MoK_α radiation ($\lambda = 71.073$ pm). A semiempirical absorption correction based on equivalent and redundant intensities (SCALEPACK [14]) was applied to the intensity data. All relevant details of the data collection and evaluation for $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) are listed in Table 1. According to the systematic extinctions, the monoclinic space group $P2_1/c$ was derived for the three isotypic compounds. Due to the fact that the compounds $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho) are isotypic to $Gd_2(BO_3)F_3$ [4], the structural refinement was performed using the positional parameters of $Gd_2(BO_3)F_3$ as starting values (SHELXL-97 [15, 16] (full-matrix least-squares on F^2)). All rare-earth atoms and most of the anions were refined with anisotropic displacement parameters. For one $[BO_3]^{3-}$ group and the corresponding fluoride anion, we found split positions. Due to the split positions, it was not possible to calculate the anisotropic displacement parameters for all atoms. The final difference Fourier syntheses did not reveal any significant peaks in all refinements. Tables 2 – 11 list the positional parameters, anisotropic displacement parameters, interatomic distances, and angles of all compounds.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-426477 ($Tb_2(BO_3)F_3$), CSD-426478 ($Dy_2(BO_3)F_3$), and CSD-426479 ($Ho_2(BO_3)F_3$).

Table 1. Crystal data and structure refinement of $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) (standard deviations in parentheses).

Empirical formula	$Tb_2(BO_3)F_3$	$Dy_2(BO_3)F_3$	$Ho_2(BO_3)F_3$
Molar mass, g mol^{-1}	433.65	440.81	445.67
Crystal system		monoclinic	
Space group		$P2_1/c$ (no. 14)	
Single crystal diffractometer		Enraf-Nonius Kappa-CCD	
Radiation; wavelength, pm		Mo K_α; 71.073 (graphite monochromator)	
Single-crystal data			
a, Å	16.296(3)	16.225(3)	16.189(3)
b, Å	6.197(2)	6.160(2)	6.124(2)
c, Å	8.338(2)	8.307(2)	8.282(2)
β, deg	93.58(3)	93.64(3)	93.69(3)
V, Å^3	840.3(3)	828.5(3)	819.4(3)
Formula units per cell, Z		8	
Calculated density, g cm^{-3}	6.86	7.07	7.23
Crystal size, mm^3	$0.04 \times 0.02 \times 0.02$	$0.07 \times 0.06 \times 0.04$	$0.06 \times 0.05 \times 0.03$
Temperature, K		293(2)	
Absorption coefficient, mm^{-1}	33.8	35.8	38.3
$F(000)$, e	1488	1504	1520
θ range, deg	1.3 – 30.0	1.3 – 30.0	1.3 – 35.0
Range in hkl	$\pm22, \pm8, \pm11$	$\pm22, \pm8, \pm11$	$-24 \leq h \leq 26$ ±9 $-12 \leq l \leq 13$
Total no. of reflections	9323	8170	10 574
Independent reflections / R_{int} / R_σ	2448 / 0.0383 / 0.0283	2421 / 0.0516 / 0.0364	3591 / 0.0948 / 0.0873
Reflections with $I > 2\,\sigma(I)$	2141	2113	2604
Data / ref. parameters	2448 / 172	2421 / 172	3591 / 162
Absorption correction		multi-scan [14]	
Goodness-of-fit on F^2	1.070	1.087	1.037
Final $R1$ / $wR2$ [$I > 2\,\sigma(I)$]	0.0214 / 0.0487	0.0261 / 0.0616	0.0472 / 0.1065
$R1$ / $wR2$ (all data)	0.0276 / 0.0508	0.0322 / 0.0636	0.0785 / 0.1149
Largest diff. peak / hole, e Å^{-3}	2.19 / -1.40	2.59 / -2.05	3.64 / -4.48

Results and Discussion

Crystal structures of $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho)

The new isotypic rare-earth fluoride borates $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) crystallize in the monoclinic space group $P2_1/c$ with eight formula units per cell. The lattice parameters are listed in Table 1. Fig. 1 gives a view of the crystal structure of $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) along the b axis built up of isolated trigonal $[BO_3]^{3-}$ groups, fluoride anions, and four crystallographically different nine-fold coordinated rare-earth cations. The structure can be described by alternating layers of the formal compositions "REBO$_3$" and "REF$_3$" in the bc plane, related to the structure types $RE_3(BO_3)_2F_3$ and $RE_5(BO_3)_2F_9$. Starting from $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd, Dy) [1, 2, 17] the compounds $RE_2(BO_3)F_3$ ($\equiv (RE_3(BO_3)_2F_3 \cdot$

REF$_3)/2$) (RE = Gd, Tb, Dy, Ho) [4] are formed by inserting a formal layer "REF$_3$" into the bc plane. By adding a further layer "REF$_3$" into the bc plane, the compounds $RE_5(BO_3)_2F_9$ ($\equiv RE_3(BO_3)_2F_3 \cdot 2REF_3$) ($RE$ = Dy–Yb) [5 – 8] are formed. The positional parameters, anisotropic displacement parameters, interatomic distances, and the oxygen-boron-oxygen angles are listed in Tables 2–11. For more information on the main structure, the reader is referred to the detailed description of the isotypic compound $Gd_2(BO_3)F_3$ [4] and the related structures $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd, Dy) [1, 2, 17] and $RE_5(BO_3)_2F_9$ (RE = Dy–Yb) [5 – 8]. In this paper, we took a closer look at the disorder in the crystal structure, and we briefly compare the isotypic phases $RE_2(BO_3)F_3$ (RE = Gd, Tb, Dy, Ho).

Fig. 2 shows the disorder of one borate and a fluoride anion. In addition to the disorder model of

Table 2. Atomic coordinates, equivalent isotropic displacement parameters U_{eq} (Å^2), and site occupancy factors (s. o. f.) of Tb$_2$(BO$_3$)F$_3$ (space group: $P2_1/c$) with standard deviations in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms on Wyckoff site 4e.

Atom	x	y	z	U_{eq}	s. o. f.
Tb1	0.43050(2)	0.13083(3)	0.33386(3)	0.00550(6)	
Tb2	0.05348(2)	0.64202(3)	0.19686(3)	0.00709(7)	
Tb3	0.67517(2)	0.13720(3)	0.05717(3)	0.00778(7)	
Tb4	0.19061(2)	0.13919(4)	0.32008(3)	0.00886(7)	
B1	0.3276(4)	0.3472(8)	0.1000(7)	0.011(2)	
B2	0.0500(6)	0.156(1)	0.037(2)	0.019(2)	0.67(2)
B3	0.125(2)	0.065(3)	0.018(2)	0.015(3)	0.33(2)
O1	0.3046(2)	0.3533(5)	0.2574(4)	0.0073(6)	
O2	0.3038(2)	0.0093(5)	0.4807(4)	0.0074(6)	
O3	0.3858(2)	0.1891(5)	0.0629(4)	0.0099(7)	
O4	0.0133(4)	0.812(2)	0.4262(7)	0.009(2)	0.67(2)
O5	0.0779(2)	0.0122(5)	0.1607(4)	0.0109(7)	
O6	0.0775(2)	0.3524(6)	0.3771(5)	0.0136(7)	
O7	0.2097(9)	0.084(2)	0.031(2)	0.012(3)	0.33(2)
F1	0.6478(2)	0.3302(4)	0.2827(3)	0.0098(5)	
F2	0.2284(4)	0.0681(9)	0.0443(7)	0.009(2)	0.67(2)
F3	0.5484(2)	0.3256(4)	0.0096(4)	0.0099(5)	
F4	0.8101(2)	0.2605(5)	0.1802(4)	0.0156(6)	
F5	0.1477(2)	0.4361(5)	0.0879(4)	0.0206(7)	
F6	0.4666(2)	0.4765(5)	0.2953(4)	0.0124(6)	
F7	0.0322(6)	0.849(2)	0.417(2)	0.006(2)	0.33(2)

Table 4. Atomic coordinates, equivalent isotropic displacement parameters U_{eq} (Å^2), and site occupancy factors (s. o. f.) of Ho$_2$(BO$_3$)F$_3$ (space group: $P2_1/c$) with standard deviations in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms on Wyckoff site 4e.

Atom	x	y	z	U_{eq}	s. o. f.
Ho1	0.43000(2)	0.12948(6)	0.33529(4)	0.0067(2)	
Ho2	0.05256(2)	0.64067(6)	0.19680(4)	0.0084(2)	
Ho3	0.67523(2)	0.13683(6)	0.05493(5)	0.0095(2)	
Ho4	0.19082(2)	0.13701(6)	0.32116(5)	0.0102 (2)	
B1	0.3280(6)	0.349(2)	0.103(2)	0.012(2)	
B2	0.050(2)	0.162(3)	0.037(2)	0.024(4)	0.67(3)
B3	0.127(2)	0.060(4)	0.024(3)	0.009(5)	0.33(3)
O1	0.3041(3)	0.3529(9)	0.2594(7)	0.009(2)	
O2	0.3042(3)	0.0065(9)	0.4819(7)	0.008(2)	
O3	0.3869(4)	0.185(2)	0.0619(7)	0.012(2)	
O4	0.0144(7)	0.808(2)	0.427(2)	0.013(3)	0.67(3)
O5	0.0775(3)	0.0109(9)	0.1606(7)	0.009(2)	
O6	0.0786(4)	0.354(2)	0.3769(8)	0.014(2)	
O7	0.218(2)	0.085(5)	0.043(4)	0.006(6)	0.33(3)
F1	0.6485(3)	0.3281(8)	0.2808(6)	0.012(2)	
F2	0.2272(8)	0.061(2)	0.044(2)	0.017(4)	0.67(3)
F3	0.5480(3)	0.3245(8)	0.0085(6)	0.0115(9)	
F4	0.8107(3)	0.2587(9)	0.1781(6)	0.014(2)	
F5	0.1479(3)	0.440(2)	0.0865(7)	0.022(2)	
F6	0.4683(3)	0.4738(9)	0.2940(7)	0.015(2)	
F7	0.028(2)	0.846(3)	0.416(2)	0.004(3)	0.33(3)

Table 3. Atomic coordinates, equivalent isotropic displacement parameters U_{eq} (Å^2), and site occupancy factors (s. o. f.) of Dy$_2$(BO$_3$)F$_3$ (space group: $P2_1/c$) with standard deviations in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms on Wyckoff site 4e.

Atom	x	y	z	U_{eq}	s. o. f.
Dy1	0.43021(2)	0.13028(4)	0.33483(3)	0.00494(8)	
Dy2	0.05314(2)	0.64155(4)	0.19700(3)	0.00635(8)	
Dy3	0.67545(2)	0.13714(4)	0.05596(3)	0.00719(8)	
Dy4	0.19067(2)	0.13767(4)	0.32089(3)	0.00825(8)	
B1	0.3282(4)	0.347(2)	0.1017(8)	0.010(2)	
B2	0.0490(7)	0.156(2)	0.039(2)	0.013(2)	0.65(2)
B3	0.123(2)	0.064(3)	0.022(3)	0.018(4)	0.35(2)
O1	0.3043(3)	0.3537(6)	0.2588(5)	0.0076(8)	
O2	0.3036(2)	0.0087(6)	0.4800(4)	0.0073(7)	
O3	0.3866(3)	0.1871(7)	0.0638(5)	0.0114(8)	
O4	0.0135(5)	0.813(2)	0.426(2)	0.010(2)	0.65(2)
O5	0.0777(3)	0.0113(7)	0.1606(5)	0.0094(8)	
O6	0.0779(3)	0.3537(6)	0.3769(5)	0.0117(9)	
O7	0.211(2)	0.086(3)	0.035(2)	0.011(4)	0.35(2)
F1	0.6482(2)	0.3291(5)	0.2822(4)	0.0099(7)	
F2	0.2278(5)	0.067(2)	0.0449(9)	0.011(2)	0.65(2)
F3	0.5489(2)	0.3252(5)	0.0090(4)	0.0092(6)	
F4	0.8108(2)	0.2587(6)	0.1794(4)	0.0139(7)	
F5	0.1481(2)	0.4385(7)	0.0876(5)	0.0206(8)	
F6	0.4676(2)	0.4750(5)	0.2941(4)	0.0108(7)	
F7	0.0287(8)	0.848(2)	0.419(2)	0.003(2)	0.35(2)

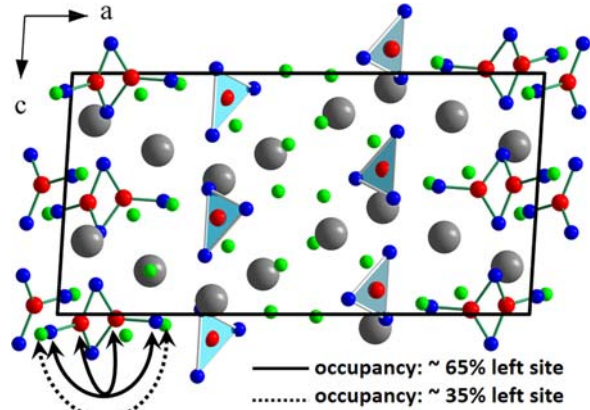— occupancy: ~ 65% left site
...... occupancy: ~ 35% left site

Fig. 1 (color online). Crystal structure of $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) (space group: $P2_1/c$) showing isolated [BO$_3$]$^{3-}$ groups and the disorder of one [BO$_3$]$^{3-}$ group.

Müller-Bunz *et al.* observed in several crystals, in which one oxygen position in the disordered trigonal-planar BO$_3$ anion is replaced by a fluoride anion, we also found a split position of the fluoride anion with the same ratio like the borate disorder. These re-

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	0.0061(2)	0.0055(2)	0.0049(2)	−0.00007(7)	0.00042(7)	0.00066(7)
Tb2	0.0089(2)	0.0057(2)	0.0067(2)	−0.00117(7)	0.00133(8)	0.00043(7)
Tb3	0.0136(2)	0.0052(2)	0.0044(2)	−0.00028(7)	−0.00023(8)	0.00165(7)
Tb4	0.0059(2)	0.0010(2)	0.0107(2)	−0.00067(8)	0.00037(9)	−0.00125(8)
B1	0.013(2)	0.008(2)	0.011(3)	0.002(2)	−0.001(2)	−0.003(2)
B2	0.018(4)	0.013(4)	0.024(5)	−0.001(3)	−0.003(4)	−0.004(3)
B3	0.006(7)	0.008(7)	0.03(2)	0.001(7)	0.006(7)	−0.004(5)
O1	0.007(2)	0.006(2)	0.009(2)	0.000(2)	−0.001(2)	−0.001(2)
O2	0.010(2)	0.005(2)	0.006(2)	0.000(2)	−0.001(2)	0.001(2)
O3	0.013(2)	0.009(2)	0.007(2)	−0.001(2)	0.000(2)	−0.002(2)
O5	0.014(2)	0.007(2)	0.011(2)	0.000(2)	−0.005(2)	−0.004(2)
O6	0.018(2)	0.013(2)	0.010(2)	0.000(2)	0.001(2)	0.007(2)
F1	0.017(2)	0.009(2)	0.004(2)	0.000(2)	0.001(2)	0.002(2)
F3	0.009(2)	0.010(2)	0.010(2)	−0.002(2)	−0.003(2)	−0.001(2)
F4	0.016(2)	0.011(2)	0.019(2)	0.001(2)	−0.001(2)	0.002(2)
F5	0.016(2)	0.024(2)	0.022(2)	−0.012(2)	0.006(2)	−0.001(2)
F6	0.014(2)	0.012(2)	0.011(2)	0.003(2)	0.000(2)	−0.003(2)

Table 5. Anisotropic displacement parameters of $Tb_2(BO_3)F_3$ (space group: $P2_1/c$) with standard deviations in parentheses. (No anisotropic displacement parameters for the atoms O4, O7, F2, and F7).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Dy1	0.0050(2)	0.0041(2)	0.0056(2)	−0.00005(8)	0.00011(9)	0.00054(8)
Dy2	0.0080(2)	0.0043(2)	0.0068(2)	−0.00109(8)	0.0009(2)	0.00031(8)
Dy3	0.0127(2)	0.0038(2)	0.0050(2)	−0.00036(8)	−0.00063(9)	0.00164(9)
Dy4	0.0044(2)	0.0088(2)	0.0114(2)	−0.00081(9)	0.0002(2)	−0.00137(9)
B1	0.011(3)	0.011(3)	0.010(3)	0.002(2)	−0.001(2)	−0.001(2)
B2	0.012(5)	0.006(4)	0.021(5)	0.000(3)	0.001(4)	−0.005(4)
B3	0.02(2)	0.011(9)	0.02(2)	−0.001(7)	0.001(8)	−0.010(8)
O1	0.010(2)	0.005(2)	0.008(2)	0.002(2)	0.002(2)	0.001(2)
O2	0.006(2)	0.008(2)	0.007(2)	−0.002(2)	−0.003(2)	0.000(2)
O3	0.018(2)	0.011(2)	0.005(2)	0.000(2)	−0.004(2)	−0.006(2)
O5	0.010(2)	0.009(2)	0.009(2)	0.001(2)	−0.003(2)	−0.003(2)
O6	0.015(2)	0.010(2)	0.010(2)	0.001(2)	−0.002(2)	0.009(2)
F1	0.017(2)	0.005(2)	0.008(2)	−0.001(2)	0.002(2)	0.000(2)
F3	0.009(2)	0.007(2)	0.011(2)	−0.002(2)	−0.003(2)	−0.002(2)
F4	0.009(2)	0.013(2)	0.019(2)	0.000(2)	−0.001(2)	0.003(3)
F5	0.015(2)	0.022(2)	0.026(2)	−0.012(2)	0.005(2)	−0.002(2)
F6	0.011(2)	0.009(2)	0.013(2)	0.001(2)	0.001(2)	−0.004(2)

Table 6. Anisotropic displacement parameters of $Dy_2(BO_3)F_3$ (space group: $P2_1/c$) with standard deviations in parentheses. (No anisotropic displacement parameters for the atoms O4, O7, F2, and F7).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ho1	0.0058(2)	0.0067(2)	0.0074(2)	0.0000(2)	−0.0010(2)	0.0006(2)
Ho2	0.0093(2)	0.0072(2)	0.0085(2)	−0.0011(2)	−0.0004(2)	0.0003(2)
Ho3	0.0150(2)	0.0065(2)	0.0066(2)	−0.0003(2)	−0.0017(2)	0.0021(2)
Ho4	0.0052(2)	0.0120(2)	0.0133(2)	−0.0011(2)	−0.0007(2)	−0.0012(2)
B1	0.013(4)	0.009(4)	0.013(4)	−0.001(3)	0.004(3)	0.002(3)
O1	0.007(2)	0.011(3)	0.008(3)	0.001(2)	−0.003(2)	0.0010(2)
O2	0.008(2)	0.005(2)	0.009(3)	0.000(2)	−0.001(2)	0.000(2)
O3	0.010(2)	0.018(3)	0.008(3)	0.002(2)	−0.001(2)	−0.002(2)
O5	0.005(2)	0.011(3)	0.011(3)	−0.001(2)	−0.002(2)	−0.001(2)
O6	0.014(3)	0.016(3)	0.011(3)	−0.001(2)	−0.001(2)	0.006(2)
F1	0.018(2)	0.008(2)	0.010(2)	0.003(2)	−0.001(2)	0.003(2)
F3	0.010(2)	0.012(2)	0.011(2)	−0.003(2)	−0.003(2)	−0.001(2)
F4	0.011(2)	0.012(3)	0.018(3)	−0.002(2)	−0.001(2)	0.003(2)
F5	0.015(2)	0.025(3)	0.025(3)	−0.013(2)	0.006(2)	−0.002(2)
F6	0.010(2)	0.017(3)	0.017(3)	0.006(2)	−0.003(2)	−0.007(2)

Table 7. Anisotropic displacement parameters of $Ho_2(BO_3)F_3$ (space group: $P2_1/c$) with standard deviations in parentheses. (No anisotropic displacement parameters for the atoms B2, B3, O4, O7, F2, and F7).

Tb1–F6	225.0(3)	Tb2–F5	223.3(3)	*Tb3–F2*	*222.9(6)*	Tb4–O5	233.6(3)
Tb1–F6′	226.1(3)	*Tb2–F7*	*228(2)*	Tb3–F1′	229.6(3)	Tb4–O6	234.0(4)
Tb1–F3	231.1(3)	*Tb2–O4*	*231.3(6)*	Tb3–F1	231.3(3)	Tb4–F4	234.7(3)
Tb1–O3	235.8(4)	*Tb2–O4′*	*232.8(6)*	Tb3–O1	235.2(3)	Tb4–O2	235.3(3)
Tb1–F3′	235.8(3)	*Tb2–F7′*	*234(2)*	Tb3–O2	235.5(3)	Tb4–O1	236.8(3)
Tb1–O3′	236.6(4)	Tb2–O5	235.1(3)	Tb3–F3	238.4(3)	Tb4–F5	242.6(3)
Tb1–F1	242.6(3)	Tb2–O6	235.8(4)	Tb3–O3	244.0(3)	*Tb4–F2*	*245.7(6)*
Tb1–O1	252.1(3)	*Tb2–F7″*	*244.7(9)*	*Tb3–O7*	*247(2)*	*Tb4–O7*	*246(2)*
Tb1–O2	257.7(3)	Tb2–F4	250.0(3)	Tb3–F4	248.7(3)	*Tb4–O7′*	*248(2)*
∅ = 238.1		*Tb2–O4″*	*250.6(6)*	Tb3–F6	286.3(3)	*Tb4–F2′*	*265.0(6)*
		Tb2–O6′	254.4(4)	∅ = 242.2		Tb4–F5′	273.0(4)
		Tb2–O5′	263.7(4)			∅ = 243.9	
		∅ = 241.6					

B1–O2	137.2(6)	*B2–O5*	*142(2)*	*B3–O7*	*139(2)*
B1–O1	138.7(7)	*B2–O6*	*144(2)*	*B3–O6*	*146(2)*
B1–O3	141.2(7)	*B2–O4*	*146(2)*	*B3–O5*	*149(2)*
∅ = 139.0		∅ = 144		∅ = 145	

Dy1–F6	224.0(3)	Dy2–F5	222.3(4)	*Dy3–F2*	*221.5(8)*	Dy4–O2	233.0(4)
Dy1–F6′	224.5(3)	*Dy2–F7*	*230(2)*	Dy3–F1	228.7(3)	Dy4–O5	233.0(4)
Dy1–F3	229.7(3)	*Dy2–O4*	*230.1(8)*	Dy3–F1′	229.8(3)	Dy4–O6	233.3(4)
Dy1–O3	234.3(4)	*Dy2–O4′*	*231.9(8)*	Dy3–O2	233.6(4)	Dy4–F4	233.5(4)
Dy1–F3′	235.0(4)	*Dy2–F7′*	*232(2)*	Dy3–O1	233.7(4)	Dy4–O1	235.7(4)
Dy1–O3′	235.7(4)	Dy2–O5	233.6(4)	Dy3–F3	236.8(4)	Dy4–F5	240.8(4)
Dy1–F1	241.8(3)	Dy2–O6	233.7(4)	Dy3–O3	242.2(4)	*Dy4–O7*	*244(2)*
Dy1–O1	251.1(4)	*Dy2–F7″*	*241(2)*	*Dy3–O7*	*246(2)*	*Dy4–F2*	*244.7(7)*
Dy1–O2	256.0(4)	Dy2–F4	248.3(3)	Dy3–F4	247.9(4)	*Dy4–O7′*	*247(2)*
∅ = 236.9		*Dy2–O4″*	*248.6(8)*	Dy3–F6	288.1(4)	*Dy4–F2′*	*264.7(8)*
		Dy2–O6′	253.7(5)	∅ = 241.2		Dy4–F5′	273.8(4)
		Dy2–O5′	262.0(4)			∅ = 242.9	
		∅ = 240.2					

B1–O1	138.5(8)	*B2–O5*	*140(2)*	*B3–O7*	*142(3)*
B1–O2	138.6(7)	*B2–O6*	*144(2)*	*B3–O5*	*144(2)*
B1–O3	141.2(8)	*B2–O4*	*146(2)*	*B3–O6*	*146(2)*
∅ = 139.0		∅ = 143		∅ = 144	

Ho1–F6	223.1(5)	Ho2–F5	221.6(6)	*Ho3–F2*	*221.5(8)*	Ho4–F4	231.7(5)
Ho1–F6′	223.5(5)	*Ho2–F7*	*226(2)*	Ho3–F1	228.7(3)	Ho4–O6	232.0(6)
Ho1–F3	228.7(5)	*Ho2–O4*	*229(2)*	Ho3–F1′	229.8(3)	Ho4–O5	232.8(5)
Ho1–F3′	233.1(5)	*Ho2–O4′*	*230(2)*	Ho3–O2	233.6(4)	Ho4–O2	233.8(5)
Ho1–O3	234.0(6)	Ho2–O5	232.6(6)	Ho3–O1	233.7(4)	Ho4–O1	234.4(6)
Ho1–O3′	235.0(6)	Ho2–O6	232.7(6)	Ho3–F3	236.8(4)	*Ho4–O7*	*239(3)*
Ho1–F1	240.7(5)	*Ho2–F7′*	*234.0(2)*	*Ho3–O7*	*242.2(4)*	Ho4–F5	239.4(6)
Ho1–O1	250.1(5)	*Ho2–F7″*	*238(2)*	Ho3–O3	246(2)	*Ho4–F2*	*245(2)*
Ho1–O2	255.1(6)	Ho2–F4	249.1(5)	Ho3–F4	247.9(4)	*Ho4–O7′*	*253(3)*
∅ = 235.9		*Ho2–O4″*	*250(2)*	Ho3–F6	288.7(4)	*Ho4–F2′*	*265(2)*
		Ho2–O6′	253.2(6)	∅ = 241.5		Ho4–F5′	274.3(7)
		Ho2–O5′	260.4(6)			∅ = 242.5	
		∅ = 239.4					

B1–O2	137(2)	*B2–O4*	*142(2)*	*B3–O5*	*146(3)*
B1–O1	138(2)	*B2–O5*	*143(2)*	*B3–O7*	*148(4)*
B1–O3	144(2)	*B2–O6*	*143(2)*	*B3–O6*	*150(3)*
∅ = 140		∅ = 143		∅ = 148	

$Tb_2(BO_3)F_3$	O2–B1–O1	126.0(5)	*O5–B2–O6*	*123.4(7)*	*O7–B3–O6*	*120(2)*
	O2–B1–O3	117.0(5)	*O5–B2–O4*	*117.6(8)*	*O7–B3–O5*	*121(2)*
	O1–B1–O3	116.8(4)	*O6–B2–O4*	*119.0(7)*	*O6–B3–O5*	*117(2)*
		∅ = 119.9		∅ = 120.0		∅ = 119
$Dy_2(BO_3)F_3$	O1–B1–O2	125.7(5)	*O5–B2–O4*	*119.0(8)*	*O7–B3–O5*	*122(2)*
	O1–B1–O3	117.5(5)	*O5–B2–O6*	*121.8(8)*	*O7–B3–O6*	*118(2)*
	O2–B1–O3	116.7(5)	*O4–B2–O6*	*119.1(9)*	*O5–B3–O6*	*119(2)*
		∅ = 120.0		∅ = 120.0		∅ = 120
$Ho_2(BO_3)F_3$	O2–B1–O1	126.4(8)	*O4–B2–O5*	*117(2)*	*O5–B3–O7*	*122(2)*
	O2–B1–O3	115.9(8)	*O4–B2–O6*	*121(2)*	*O5–B3–O6*	*115(2)*
	O1–B1–O3	117.7(8)	*O5–B2–O6*	*121(2)*	*O7–B3–O6*	*121(2)*
		∅ = 120.0		∅ = 120		∅ = 119

Table 11. Interatomic oxygen–boron–oxygen angles (deg) in $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) (space group: $P2_1/c$) calculated with the single-crystal lattice parameters (standard deviations in parentheses). Angles possessing disordered boron atoms are written in italics.

	$Gd_2(BO_3)F_3$	$Tb_2(BO_3)F_3$	$Dy_2(BO_3)F_3$	$Ho_2(BO_3)F_3$
Empirical formula				
Reference	[4]	[this work]	[this work]	[this work]
Molar mass, g mol^{-1}	430.31	433.65	440.81	445.67
Unit cell dimensions				
a, Å	16.372(1)	16.296(3)	16.225(3)	16.189(3)
b, Å	6.2478(4)	6.197(2)	6.160(2)	6.124(2)
c, Å	8.3804(6)	8.338(2)	8.307(2)	8.282(2)
β, deg	93.341(8)	93.58(3)	93.64(3)	93.69(3)
V, Å^3	855.77	840.3(3)	828.5(3)	819.4(3)
Coordination number (CN)				
$RE1$–$RE4$ (RE = Gd–Ho)	9	9	9	9
av. $RE1$–O/F (RE = Gd–Ho) distance, Å	2.395	2.381	2.369	2.359
av. $RE2$–O/F (RE = Gd–Ho) distance, Å	2.429	2.416	2.402	2.394
av. $RE3$–O/F (RE = Gd–Ho) distance, Å	2.428	2.422	2.412	2.415
av. $RE4$–O/F (RE = Gd–Ho) distance, Å	2.456	2.439	2.429	2.425
av. B–O distance in $[B(1)O_3]^{3-}$, Å	1.391	1.390	1.390	1.40
av. B–O distance in $[B(2)O_3]^{3-}$, Å	1.472	1.44	1.43	1.43
av. B–O distance in $[B(3)O_3]^{3-}$, Å	1.523[a]	1.45	1.44	1.48

Table 12. Comparison of the isotypic structures $RE_2(BO_3)F_3$ (RE = Gd, Tb, Dy, Ho) (space group: $P2_1/c$).

[a] Average B–O distance in the B(3)O$_2$F group of $Gd_2(BO_3)F_3$.

Fig. 2 (color online). Disordered $[BO_3]^{3-}$ group. In the crystal structure of $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) the $[B(2)O_3(5,6,4)]^{3-}$ and the atom F2 is represented by an occupation of 65 % for $Dy_2(BO_3)F_3$ and by 67 % for $Tb_2(BO_3)F_3$ and $Ho_2(BO_3)F_3$.

sults led to better values of the refined distances inside the borate group. Furthermore, the disorder model of Müller-Bunz et al. describes a rare-earth fluorido fluoride borate. This combination of ionic and covalently bonded fluorine in the System RE-B-O-F has not been confirmed up to now. The single-crystal data of the compounds $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) now revealed split positions of one boron, one oxygen, and one fluorine atom, leading to the atomic positions B2/B3, O4/O7, and F2/F7 (Fig. 2). This leads to the formation of the trigonal group B2 with the oxygen atoms O4/O5/O6 and the fluoride anion F2 or to the trigonal group B3 with the oxygen atoms O7/O5/O6 and the fluoride anion F7. This flip of the $[BO_3]^{3-}$ group is possible because the $[BO_3]^{3-}$ group has two almost identically options in the gap between the rare-earth oxygen/fluorine polyhedra (see Fig. 3). The ratio of B2/O4/F2 : B3/O7/F7 is nearly the same in all compounds resulting in values of 0.67(2) : 0.33(2) for $Tb_2(BO_3)F_3$, 0.65(2) : 0.35(2) for $Dy_2(BO_3)F_3$, and 0.67(3) : 0.33(3) for $Ho_2(BO_3)F_3$.

Table 13. Comparison of the pressure/temperature conditions for the syntheses of the cognate structures $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd, Dy) [1, 2, 17], $RE_2(BO_3)F_3$ (RE = Gd, Tb, Dy, Ho) [4, this work] and $RE_5(BO_3)_2F_9$ (RE = Tb, Ho, Er, Tm, Yb) [5 – 8].[a]

	$RE_3(BO_3)_2F_3$	$RE_2(BO_3)F_3$	$RE_5(BO_3)_2F_9$
Sm	a. p./900 °C		
Eu	a. p./900 °C		
Gd	a. p./850 °C	a. p./700 °C	
	3.0 GPa/900 °C		
Tb		1.5 GPa/1200 °C	
Dy	5.0 GPa/900 °C	3.0 GPa/900 °C	1.5 GPa/1250 °C
Ho		3.0 GPa/900 °C	2.5 GPa/1200 °C
Er			3.0 GPa/800 °C
Tm			5.0 GPa/900 °C
Yb			7.5 GPa/1100 °C

[a] a. p. – ambient pressure.
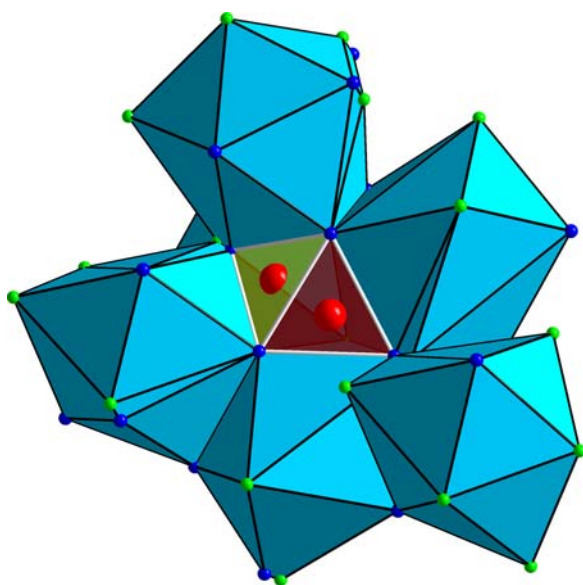
Fig. 3 (color online). The disordered $[BO_3]^{3-}$ group has two almost identical options in the gap between the rare-earth oxygen/fluoride polyhedra. Oxygen atoms are highlighted with blue spheres, fluoride anions with light-green spheres.

For comparison Table 12 lists data of the isotypic compounds $RE_2(BO_3)F_3$ (RE = Gd, Tb, Dy, Ho). The mean rare-earth oxygen/fluorine distances shrink from Gd₂(BO₃)F₃ (242.7 pm) *via* Tb₂(BO₃)F₃ (241.5 pm) and Dy₂(BO₃)F₃ (240.3 pm) to Ho₂(BO₃)F₃ (239.8 pm). The differences correspond to the decrease in the ionic radii of the ninefold coordinated rare-earth ions (Gd^{3+} = 124.7, Tb^{3+} = 123.5, Dy^{3+} = 122.3, and Ho^{3+} = 121.2 pm) [18],
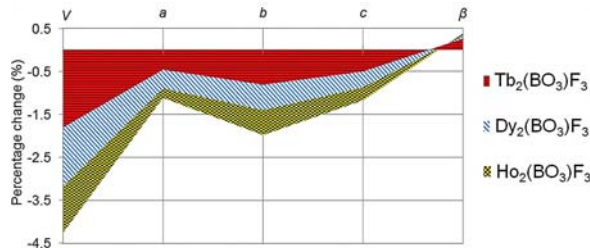

Fig. 4 (color online). Percentage change of the lattice parameters and volumes of the isotypic phases $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) relative to Gd₂(BO₃)F₃.

which is based on the lanthanoide contraction. The boron oxygen distances inside the not disordered, isolated trigonal $[B(1)O_3]^{3-}$ groups are 137.2(6) – 141.2(7) pm with a mean value of 139.1 pm for Dy₂(BO₃)F₃, between 138.5(8) and 141.2(8) pm with a mean value of 139.0 pm for Ho₂(BO₃)F₃, and 137(2) – 144(2) pm with a mean value of 140 pm for Tb₂(BO₃)F₃. These mean values of the boron oxygen distances, ranging usually around 137 pm [19 – 21], are slightly larger. The mean boron oxygen distances of the disordered $[BO_3]^{3-}$ group varies between 143 pm for the $[B(2)O_3]^{3-}$ group in Dy₂(BO₃)F₃ and Ho₂(BO₃)F₃, and 148 pm for the $[B(2)O_3]^{3-}$ group in Ho₂(BO₃)F₃. These values are much larger than normally accepted for boron oxygen distances in trigonal-planar BO₃ groups, which results from the described disorder, for which an anisotropic refinement of the atoms O4, O7, F2, and F7 of the disordered groups is impossible. Fig. 4 shows the deviation of the lattice parameters of the isotypic compounds $RE_2(BO_3)F_3$ (RE = Tb, Dy, Ho) relative to Gd₂(BO₃)F₃ [4]. Due to the fact that the size difference is marginal, no greater deviation of the bond lengths and angles are observed. A closer look at the lattice parameters *a*, *b*, and *c* reveals the anisotropy of the structure. The lattice parameters *b* shrink more than the lattice parameters *a* and *c*. This behavior was also observed in the related compounds $RE_5(BO_3)_2F_9$ (RE = Dy–Yb) [5 – 8].

Table 13 shows the comparison of the synthetic conditions of the related compounds $RE_3(BO_3)_2F_3$ (RE = Sm, Eu, Gd, Dy), $RE_2(BO_3)F_3$ (RE = Gd, Tb, Dy, Ho), and $RE_5(BO_3)_2F_9$ (RE = Dy–Yb). Interestingly, the necessary pressure conditions correlate with the atomic number of the rare-earth cation. Smaller cations require higher pressures. Furthermore, the formal adding of a "REF₃" layers is preferred under high-pressure conditions.

Conclusions

With the syntheses of the new rare-earth fluoride borates $RE_2(BO_3)F_3$ ($RE =$ Tb, Dy, Ho), we add three isotypic phases to the known compound $Gd_2(BO_3)F_3$. Furthermore, we could verify and even amend the disorder model postulated by Müller-Bunz *et al*. In accordance with the relatively mild applied pressure of 1.5 and 3.0 GPa, the structures consist exclusively of $[BO_3]^{3-}$ groups. To investigate the stability range of this structure type and related ones, *viz.* $RE_3(BO_3)_2F_3$ and $RE_5(BO_3)_2F_9$, additional experiments will be performed with the neighboring rare-earth cations.

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