High-pressure Syntheses, Crystal Structures, and Thermal Behaviour of β-$RE(BO_2)_3$ (RE = Nd, Sm, Gd)

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The compounds β-$RE(BO_2)_3$ [RE = Nd (neodymium *meta*-borate), Sm (samarium *meta*-borate) and Gd (gadolinium *meta*-borate)] were synthesized under high-pressure and high-temperature conditions in a Walker-type multianvil apparatus at 3.5 GPa (Nd), 7.5 GPa (Sm, Gd) and 1050 °C. The crystal structures were determined by single crystal X-ray diffraction data collected at r. t. (Sm, Gd) and at −73 °C (Nd), respectively. The structures are isotypic with the already known ambient-pressure phases β-$RE(BO_2)_3$ (RE = (Tb, Dy) and the high-pressure phases β-$RE(BO_2)_3$ (RE = Ho–Lu).

Key words: High-pressure Phases, Borates, Crystal Structure

Introduction

In recent years, a systematic investigation of rare earth *meta*-borates with the composition $RE(BO_2)_3$ under ambient- and high-pressure conditions led to the discovery of new modifications and the clarification of the stability ranges. Up to now, four modifications of rare earth *meta*-borates are known, designated chronologically as α-, β-, γ-, and δ-$RE(BO_2)_3$. The monoclinic phases α-$RE(BO_2)_3$ (RE = La [1, 2], Ce [3], Pr [4], Nd [5, 6], Sm [7], Eu [8], Gd [7], Tb [9]) crystallize in the space group *I*2/*a*. They are built up of chains of triangular $[BO_3]^{3-}$ and tetrahedral $[BO_4]^{5-}$ units, representing the longest known phases. In 2003, Nikelski and Schleid solved the structure of the second polymorph β-$RE(BO_2)_3$ (RE = Tb), built up exclusively of $[BO_4]^{5-}$ tetrahedra, forming corrugated layers [10]. This second modification was also observed with RE = Dy under ambient-pressure conditions. However, the synthesis of the β-modification with the smaller rare earth cations Ho–Lu required the use of high-pressure / high-temperature conditions (7.5 GPa, 1273 K) [11]. In 2004, we were able to realize a third modification γ-$RE(BO_2)_3$ with the larger rare earth cations La–Nd at 7.5 GPa and 1273 K, which exhibits a highly condensed network of $[BO_4]^{5-}$ tetrahedra [12]. Due to the remarkable difference between ambient-pressure conditions and 7.5 GPa, we investigated the pressure range below 7.5 GPa and discovered a fourth modification, δ-$RE(BO_2)_3$, at 5.5 GPa and 1323 K with the rare earth cations La^{3+} and Ce^{3+} [13, 14]. In accordance with the pressure coordination rule, δ-$RE(BO_2)_3$ consists exclusively of $[BO_4]^{5-}$ tetrahedra in contrast to the α-modification, which exhibits $[BO_3]^{3-}$ and $[BO_4]^{5-}$ units. In principle, compounds exhibiting $[BO_3]^{3-}$ groups can be transformed into more dense modifications with $[BO_4]^{5-}$ groups. Therefore, we tried to synthesize more dense modifications of α-$RE(BO_2)_3$ (RE = Nd, Sm, Gd) under high pressure. We succeeded in the transformation into the phases β-$RE(BO_2)_3$ (RE = Nd, Sm, and Gd), about which we report below.

Experimental Section

The starting materials for the syntheses of β-$RE(BO_2)_3$ (RE = Nd, Sm, Gd) were 3 : 1 molar mixtures of B_2O_3 (Strem Chemicals, Newburyport, USA; 99.9 %) with the rare earth oxides RE_2O_3 (RE = Nd, Sm, Gd; 99.9 %). The compounds were compressed and heated *via* a multianvil assembly. Details of the assembly can be found in the literature [15 – 18]. For the synthesis of β-$Nd(BO_2)_3$, an 18/11 assembly was compressed within 80 min to 3.5 GPa and heated to 1323 K in the following 25 min. Having maintained this temperature for 5 min, the sample was cooled to about 700 K during further 25 min. Afterwards, the sample was quenched to r. t. For the syntheses of β-$RE(BO_2)_3$ (RE = Sm, Gd), an 18/11 (Gd) and an 14/8 assembly (Sm) were compressed within 3 h (18/11) / 2 h (14/8) up to 7.5 GPa and heated up to 1323 K in the following 10 min. Having kept this temperature for 10 min, the samples were cooled down to r. t. within 10 min. After the de-

Table 1. Crystal data and structure refinement for β-$RE(BO_2)_3$ (RE = Nd, Sm, Gd), space group *Pnma*, $Z = 16$.

Empirical formula	β-$Nd(BO_2)_3$	β-$Sm(BO_2)_3$	β-$Gd(BO_2)_3$
Molar mass [g mol^{-1}]	272.67	278.78	285.68
Unit cell dimensions			
a [pm]	1616.2(3)	1612.5(2)	1602.8(2)
b [pm]	747.4(2)	746.02(4)	742.70(4)
c [pm]	1244.2(3)	1240.87(7)	1232.17(7)
V [nm^3]	1.5028(5)	1.4927(2)	1.4668(2)
Calculated density [g cm^{-3}]	4.82	4.96	5.18
Crystal size [μm^3]	$50 \times 35 \times 30$	$60 \times 40 \times 20$	$60 \times 50 \times 50$
Temperature [°C]	−73(2)	20(2)	20(2)
Detector distance [mm]	40	40	45
Exposure time [min]	14	10	15
ω range [°]; increment [°]	0 – 180; 1.2	0 – 180; 1.1	0 – 180; 1.2
Transm. ratio [max/min]	0.469 / 0.663	0.319 / 0.595	0.414 / 0.487
Absorption coefficient [mm^{-1}]	13.8	15.7	18.0
F(000)	1968	2000	2032
θ range [°]	3.2 to 31.0	3.4 to 30.0	3.0 to 31.6
Range in hkl	±23, ±10, ±18	±22, ±9, −17/+15	±23, ±10, −18/+17
Total no. reflections	16464	15072	16539
Independent reflections	2550 (R_{int} = 0.080)	2209 (R_{int} = 0.149)	2490 (R_{int} = 0.066)
Reflections with $I \geq 2\sigma(I)$	1897 (R_σ = 0.060)	1587 (R_σ = 0.089)	1813 (R_σ = 0.066)
Data/parameters	2550 / 167	2209 / 169	2490 / 196
Goodness-of-fit on F^2	0.927	0.855	0.796
Final R indices [$I \geq 2\sigma(I)$]	$R1$ = 0.042	$R1$ = 0.034	$R1$ = 0.020
	$wR2$ = 0.097	$wR2$ = 0.066	$wR2$ = 0.031
R indices (all data)	$R1$ = 0.063	$R1$ = 0.056	$R1$ = 0.041
	$wR2$ = 0.102	$wR2$ = 0.070	$wR2$ = 0.033
Largest diff. peak / hole [e Å^{-3}]	2.86 / −2.93	2.09 / −2.22	1.12 / −1.31

compression of the assemblies the recovered octahedral pressure media were broken apart. The samples were carefully separated from the surrounding boron nitride crucibles. The compounds β-$RE(BO_2)_3$ (RE = Nd, Sm, Gd) were gained as single-phase crystalline products [yield: *ca.* 75 mg (18/11) / *ca.* 40 mg (14/8) per run]. The substances are air- and water-resistant, crystallizing as thin colourless (Sm, Gd) and pale-pink (Nd) platelets.

Crystal structure analysis

Small, irregularly shaped single crystals of the compounds β-$RE(BO_2)_3$ (RE = Nd, Sm, Gd) were first examined through a Buerger camera, equipped with an image plate system (Fujifilm BAS-1800) in order to establish both the symmetry and the suitability for intensity data collection. The single crystal intensity data were collected at r. t. (Sm, Gd) and at −73 °C (Nd) by a Stoe IPDS-I diffractometer with graphite-monochromatized MoK_α radiation (λ = 71.073 pm). For β-$Nd(BO_2)_3$, an empirical absorption correction was applied on the basis of ψ-scan data. A numerical absorption correction (HABITUS [19]) was used for the data of β-$RE(BO_2)_3$ (RE = Sm and Gd). All relevant details of the data collections and evaluations are listed in Table 1. The atomic parameters of β-$Dy(BO_2)_3$ [11] were taken as starting values for all three *meta*-borates, and the structures were refined by full-matrix least-squares on F^2 using SHELXL-97 [20]. Anisotropic atomic displacement parame-

Table 2. Atomic coordinates and isotropic equivalent displacement parameters U_{eq} (Å^2) for β-$Nd(BO_2)_3$ (space group *Pnma*). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff-Position	x	y	z	U_{eq}
Nd1	4c	0.17059(4)	1/4	0.92991(5)	0.0061(2)
Nd2	4c	0.12034(4)	3/4	0.00416(5)	0.0071(2)
Nd3	4c	0.04745(4)	1/4	0.58560(5)	0.0064(2)
Nd4	4c	0.12564(4)	3/4	0.72233(5)	0.0070(2)
B1	8d	0.2831(6)	0.931(2)	0.8123(7)	0.008(2)
B2	8d	0.9403(5)	0.928(2)	0.6558(7)	0.005(2)
B3	8d	0.0273(6)	0.061(2)	0.8199(8)	0.008(2)
B4	8d	0.1554(5)	0.928(2)	0.4817(7)	0.005(2)
B5	8d	0.1105(5)	0.079(2)	0.1458(7)	0.007(2)
B6	8d	0.2568(5)	0.932(2)	0.1297(7)	0.005(2)
O1	4c	0.1616(6)	3/4	0.5321(7)	0.009(2)
O2	8d	0.2816(4)	0.0558(8)	0.8997(5)	0.006(2)
O3	8d	0.9270(4)	0.0496(8)	0.5665(5)	0.008(2)
O4	8d	0.0500(4)	0.9386(7)	0.1254(5)	0.005(2)
O5	8d	0.3701(4)	0.9274(7)	0.7665(5)	0.007(2)
O6	8d	0.1852(3)	0.0352(7)	0.0813(4)	0.005(2)
O7	4c	0.0596(5)	1/4	0.8012(7)	0.007(2)
O8	4c	0.2256(5)	3/4	0.1363(7)	0.009(2)
O9	8d	0.0930(4)	0.9636(7)	0.8723(5)	0.007(2)
O10	8d	0.1666(4)	0.0584(8)	0.5675(5)	0.007(2)
O11	4c	0.0796(5)	1/4	0.1105(6)	0.004(2)
O12	4c	0.2556(5)	3/4	0.8503(7)	0.006(2)
O13	4c	0.0471(6)	1/4	0.3911(8)	0.009(2)
O14	8d	0.0171(4)	0.9846(8)	0.7087(5)	0.007(2)
O15	8d	0.2249(4)	0.9861(9)	0.7323(5)	0.008(2)

Table 3. Atomic coordinates and isotropic equivalent displacement parameters U_{eq} (Å^2) for β-Sm$(BO_2)_3$ (space group *Pnma*). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff-Position	*x*	*y*	*z*	U_{eq}
Sm1	4*c*	0.17139(3)	1/4	0.93085(4)	0.0087(2)
Sm2	4*c*	0.12001(3)	3/4	0.00528(5)	0.0115(2)
Sm3	4*c*	0.04787(3)	1/4	0.58599(4)	0.0088(2)
Sm4	4*c*	0.12643(3)	3/4	0.72539(4)	0.0096(2)
B1	8*d*	0.2831(6)	0.929(2)	0.8130(7)	0.011(2)
B2	8*d*	0.9416(5)	0.929(2)	0.6557(7)	0.009(2)
B3	8*d*	0.0296(5)	0.060(2)	0.8207(7)	0.010(2)
B4	8*d*	0.1551(5)	0.921(2)	0.4808(7)	0.008(2)
B5	8*d*	0.1101(5)	0.078(2)	0.1445(7)	0.009(2)
B6	8*d*	0.2562(5)	0.932(2)	0.1288(7)	0.007(2)
O1	4*c*	0.1605(4)	3/4	0.5340(6)	0.007(2)
O2	8*d*	0.2821(3)	0.0590(8)	0.8989(4)	0.010(2)
O3	8*d*	0.9276(3)	0.0519(9)	0.5671(4)	0.010(2)
O4	8*d*	0.0491(3)	0.9363(8)	0.1239(4)	0.011(2)
O5	8*d*	0.3706(3)	0.9272(7)	0.7656(4)	0.008(2)
O6	8*d*	0.1849(3)	0.0341(8)	0.0801(4)	0.009(2)
O7	4*c*	0.0609(4)	1/4	0.8020(6)	0.009(2)
O8	4*c*	0.2246(4)	3/4	0.1383(6)	0.009(2)
O9	8*d*	0.0940(3)	0.9617(8)	0.8742(4)	0.010(2)
O10	8*d*	0.1665(3)	0.0600(8)	0.5662(4)	0.009(2)
O11	4*c*	0.0776(5)	1/4	0.1082(6)	0.010(2)
O12	4*c*	0.2562(5)	3/4	0.8528(6)	0.010(2)
O13	4*c*	0.0473(5)	1/4	0.3922(6)	0.010(2)
O14	8*d*	0.0189(3)	0.9834(8)	0.7078(4)	0.010(2)
O15	8*d*	0.2247(3)	0.9839(9)	0.7303(5)	0.011(2)

Table 4. Atomic coordinates and isotropic equivalent displacement parameters U_{eq} (Å^2) for β-Gd$(BO_2)_3$ (space group *Pnma*). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff-Position	*x*	*y*	*z*	U_{eq}
Gd1	4*c*	0.17134(2)	1/4	0.93258(2)	0.00408(7)
Gd2	4*c*	0.12070(2)	3/4	0.00677(2)	0.00421(7)
Gd3	4*c*	0.04789(2)	1/4	0.58769(2)	0.00432(7)
Gd4	4*c*	0.12680(2)	3/4	0.72781(2)	0.00431(7)
B1	8*d*	0.2825(3)	0.9301(8)	0.8136(4)	0.005(2)
B2	8*d*	0.9416(3)	0.9267(8)	0.6540(4)	0.004(2)
B3	8*d*	0.0311(3)	0.0608(8)	0.8217(4)	0.006(2)
B4	8*d*	0.1541(3)	0.9235(7)	0.4831(4)	0.006(2)
B5	8*d*	0.1100(3)	0.0767(7)	0.1439(4)	0.0045(9)
B6	8*d*	0.2575(3)	0.9304(8)	0.1297(4)	0.0045(9)
O1	4*c*	0.1607(2)	3/4	0.5376(3)	0.0037(9)
O2	8*d*	0.2819(2)	0.0622(5)	0.8992(5)	0.0047(7)
O3	8*d*	0.9292(2)	0.0537(5)	0.5663(2)	0.0035(6)
O4	8*d*	0.0492(2)	0.9358(4)	0.1238(2)	0.0041(6)
O5	8*d*	0.3705(2)	0.9259(4)	0.7655(2)	0.0029(6)
O6	8*d*	0.1853(2)	0.0350(5)	0.0789(2)	0.0036(6)
O7	4*c*	0.0627(3)	1/4	0.8015(3)	0.0061(9)
O8	4*c*	0.2249(2)	3/4	0.1391(3)	0.0038(9)
O9	8*d*	0.0948(2)	0.9605(5)	0.8756(2)	0.0050(6)
O10	8*d*	0.1655(2)	0.0625(4)	0.5661(2)	0.0037(6)
O11	4*c*	0.0791(2)	1/4	0.1079(3)	0.0038(9)
O12	4*c*	0.2553(3)	3/4	0.8535(3)	0.0060(9)
O13	4*c*	0.0484(3)	1/4	0.3952(3)	0.0048(9)
O14	8*d*	0.0197(2)	0.9793(5)	0.7088(2)	0.0039(7)
O15	8*d*	0.2240(2)	0.9828(5)	0.7314(2)	0.0048(7)

ters were used for all atoms except the boron atoms of β-Nd$(BO_2)_3$, which were refined isotropically. The final difference Fourier syntheses revealed no significant residual peaks in all refinements. The positional parameters are listed in Tables 2 – 4. Anisotropic displacement parameters, interatomic distances, and interatomic angles are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-417645 (β-Nd$(BO_2)_3$), CSD-417643 (β-Sm$(BO_2)_3$), and CSD-417644 (β-Gd$(BO_2)_3$).

Results and Discussion

Fig. 1 shows a view of the crystal structure of β-*RE*$(BO_2)_3$, which is composed of strongly corrugated layers of corner sharing $[BO_4]^{5-}$ tetrahedra. A detailed description of this structure type can be found in the references [10] and [11]. The characteristic aspects of the new compounds are briefly reported in the following.

The B–O bond lengths in β-*RE*$(BO_2)_3$ (*RE* = Nd, Sm, Gd) are in the range of 142.3(2) – 153.4(2) pm in β-Nd$(BO_2)_3$, 143.3(2) – 153.5(2) pm in β-Sm$(BO_2)_3$, and 142.8(6) – 153.1(5) pm in β-Gd$(BO_2)_3$, similar to

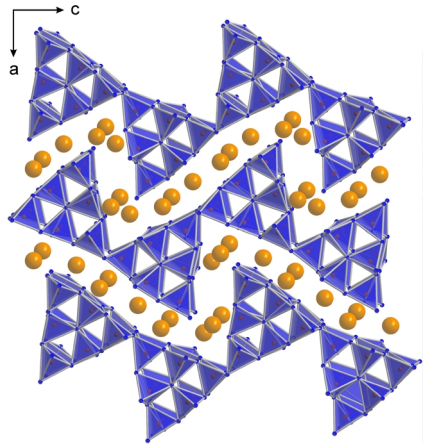

Fig. 1. Crystal structure of the *meta*-borates β-*RE*$(BO_2)_3$ (*RE* = Nd, Sm, Gd).

the B–O bond lengths found in the isotypic compounds with *RE* = Tb–Lu. The distances Nd–O, Sm–O, and Ho–O are in the ranges 233.1(6)–296.0(6), 230.6(6)–289.9(7), and 228.6(3)–286.7(4) pm, respectively. The B–O bond lengths of the three-coordinate O(5) atoms in the $[OB_3]^{7+}$ groups of the compounds vary in the

Table 5. Comparison of the lattice parameters (pm) and volumes (nm^3) of *RE*$(BO_2)_3$ (*RE* = Tb–Lu).

Compound	*a*	*b*	*c*	*V*
β-Nd$(BO_2)_3$ [*]	1616.2(3)	747.4(2)	1244.2(3)	1.503(1)
β-Sm$(BO_2)_3$ [*]	1612.5(2)	746.02(4)	1240.87(7)	1.492(1)
β-Gd$(BO_2)_3$ [*]	1602.9(2)	742.70(4)	1232.17(7)	1.467(1)
β-Tb$(BO_2)_3$ [10]	1598.97(9)	741.39(4)	1229.58(7)	1.458(1)
β-Dy$(BO_2)_3$ [11]	1592.4(1)	739.7(1)	1225.0(1)	1.443(1)
β-Ho$(BO_2)_3$ [11]	1590.0(4)	739.3(2)	1223.1(4)	1.438(1)
β-Er$(BO_2)_3$ [11]	1589.1(2)	737.6(1)	1219.1(1)	1.429(1)
β-Tm$(BO_2)_3$ [11]	1582.6(3)	736.8(3)	1216.4(3)	1.418(1)
β-Yb$(BO_2)_3$ [11]	1579.1(3)	735.2(2)	1214.0(3)	1.410(1)
β-Lu$(BO_2)_3$ [11]	1576.7(3)	734.9(2)	1211.7(3)	1.404(1)

* This work.

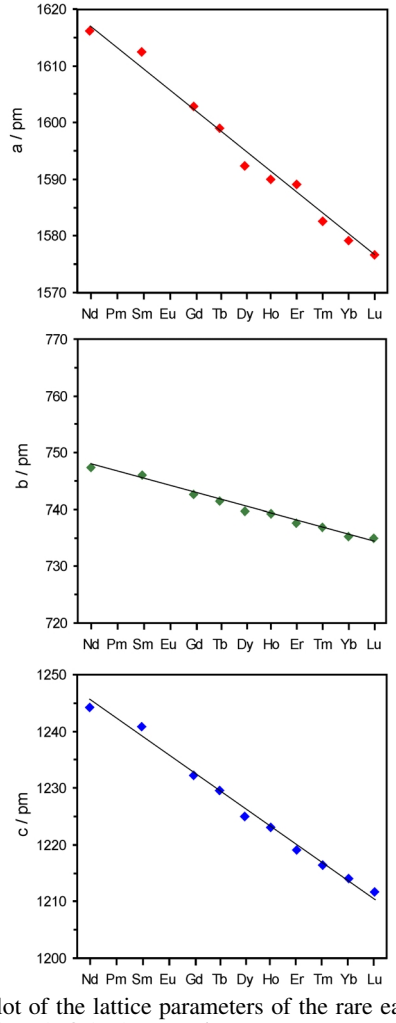

Fig. 2. Plot of the lattice parameters of the rare earth *meta*-borates β-*RE*$(BO_2)_3$ (*RE* = Nd–Lu, except Pm and Eu).

ranges 149.1(2)–153.4(2) pm in Nd$(BO_2)_3$, 150.4(2)–153.5(2) pm in Sm$(BO_2)_3$, and 151.0(2)–153.1(5) pm in Gd$(BO_2)_3$.

Table 5 and Fig. 2 present a survey of the lattice parameters of all known β-*RE*$(BO_2)_3$ phases (*RE* = Nd–Lu except Pm and Eu). The new *meta*-borates fit well into the scheme of the known compounds. Nd^{3+}, Sm^{3+}, and Gd^{3+} represent the largest rare earth ions in this series, and here we also observe the trend towards a much more slowly decreasing lattice parameter *b* in contrast to *a* and *c*, as we already noted for the compounds β-*RE*$(BO_2)_3$ (*RE* = Dy–Lu). This is caused by the ability to contract more strongly along the *a* and *c* direction in the crystal structure (Fig. 1), in contrast to *b* (layers of $[BO_4]^{5-}$ tetrahedra), in accordance with the shrinking radius of the RE^{3+} ions (lanthanoid contraction).

Fig. 3 illustrates the modifications of all rare earth *meta*-borates synthesized up to now. The scheme distinguishes between syntheses under ambient- (X) and high-pressure ($\varnothing$) conditions. Next to La$(BO_2)_3$, which can be synthesized in three different modifications (α, β, δ), Nd$(BO_2)_3$ is the second example, that can be synthesized in three different structures (α, β, γ), depending on the applied pressure. Up to now, it is not clear if the phases β-*RE*$(BO_2)_3$ (*RE* = Nd, Sm, Gd) can also be synthesized under ambient-pressure conditions, as it is possible for *RE* = Tb, Dy. However, high-pressure conditions favour the formation of the β-modifications due to the densification effect [21]. At pressures of 3.5 GPa (Nd) and 7.5 GPa (Sm, Gd) the compounds crystallize in the orthorhombic β-*RE*$(BO_2)_3$ structure, possessing a higher density than the corresponding α-phases. *E. g.*, α-Nd$(BO_2)_3$ has a density of 4.50 g cm^{-3} and the more dense modification β-Nd$(BO_2)_3$ presented here exhibits a value of 4.82 g cm^{-3}. In analogy, β-Sm$(BO_2)_3$ and β-Gd$(BO_2)_3$ possess values of 4.96 and 5.18 g cm^{-3}, which are higher than the densities of the α-modifications with 4.63 and 4.84 g cm^{-3}, respectively.

Thermal behaviour of β-Sm$(BO_2)_3$ and β-Gd$(BO_2)_3$

In situ X-ray powder diffraction experiments were performed on a STOE STADI P powder diffractometer (MoK_α radiation, λ = 71.073 pm) with a computer controlled STOE furnace: The sample was enclosed in a quartz capillary and heated from r. t. to 500 °C in 100 °C steps, and from 500 °C to 1100 °C in 50 °C steps. Afterwards, the sample was cooled down to 500 °C in 50 °C steps, and from 500 °C to r. t. in

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
α-$RE(BO_2)_3$	X	X	X	X		X	X	X	X						
β-$RE(BO_2)_3$				∅		∅		∅	X	X	∅	∅	∅	∅	∅
γ-$RE(BO_2)_3$	∅	∅	∅	∅											
	∅	∅													
δ-$RE(BO_2)_3$	∅														

X Ambient-pressure conditions; ∅ High-pressure conditions.

Fig. 3. Schematic view of the existing modifications of the rare earth *meta*-borates $RE(BO_2)_3$.

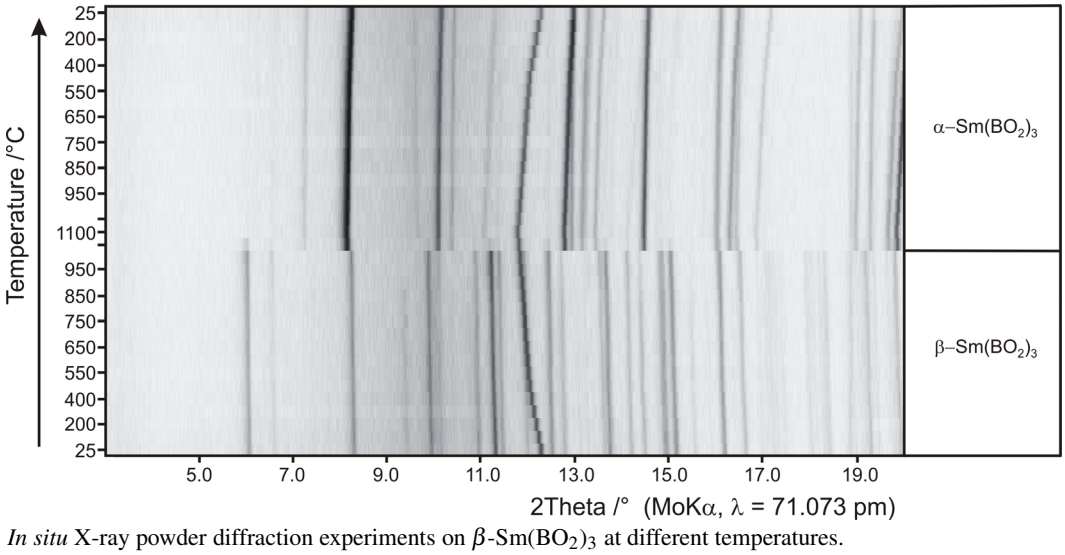

Fig. 4. *In situ* X-ray powder diffraction experiments on β-$Sm(BO_2)_3$ at different temperatures.

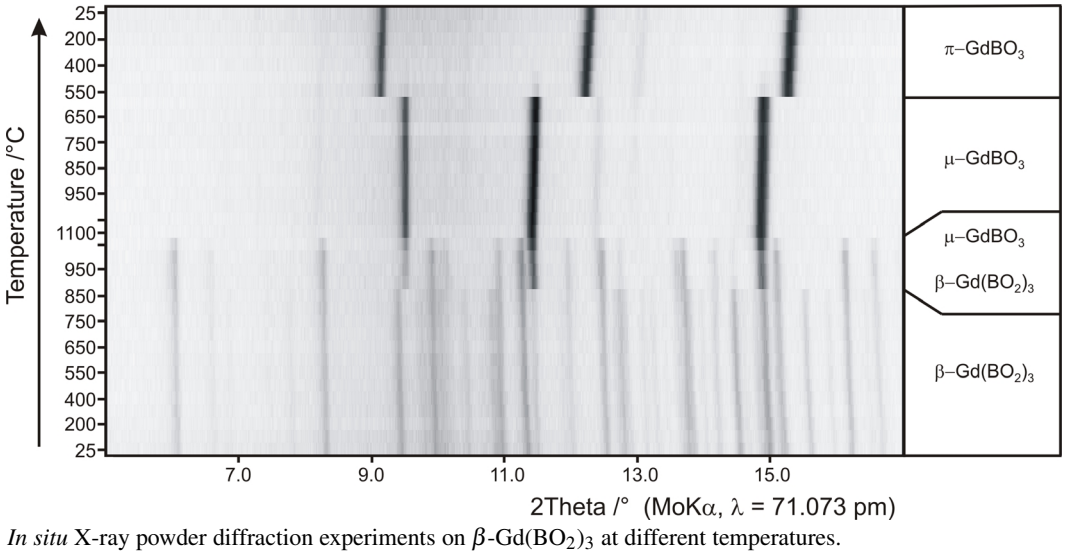

Fig. 5. *In situ* X-ray powder diffraction experiments on β-$Gd(BO_2)_3$ at different temperatures.

100 °C steps. After each heating step, diffraction patterns of β-$Sm(BO_2)_3$ and β-$Gd(BO_2)_3$ were recorded over the angular range $3° \leq 2\theta \leq 20°$ and $5° \leq 2\theta \leq 17°$, respectively. Fig. 4 [β-$Sm(BO_2)_3$] and Fig. 5 [β-$Gd(BO_2)_3$] illustrate the temperature programmed X-ray powder diffraction patterns of both compounds.

Interestingly, the thermal behaviour of β-$Sm(BO_2)_3$ and β-$Gd(BO_2)_3$ is different. For β-$Sm(BO_2)_3$, we observe a transformation of the high-pressure β-phase into the normal-pressure α-phase in the temperature range 1000 – 1050 °C. At r. t., α-$Sm(BO_2)_3$ is the only detectable phase. In contrast, β-$Gd(BO_2)_3$ starts to decompose at 900 °C into the high-temperature *ortho*-borate μ-$GdBO_3$ [22, 23] and presumably B_2O_3. The latter is not detectable in this measurement, because it is liquid at this temperature (melting point of B_2O_3: 475 °C). The decomposition process is complete at 1100 °C. Successive cooling to r. t. reveals the transformation of the high-temperature phase μ-$GdBO_3$ into the room-temperature phase π-$GdBO_3$ in the temperature range 600 – 500 °C. At r. t., boron oxide remains in an amorphous state.

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