Synthesis of Rare Earth Polyborates Using Molten Boric Acid as a Flux

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Hydrated rare earth hexaborates $H_3LnB_6O_{12}$ (Ln = Sm−Lu) have been synthesized by using molten boric acid as the reaction medium. $H_3LnB_6O_{12}$ decomposes at certain temperatures to form anhydrous pentaborates LnB_5O_9 (Ln = Sm−Er) or orthoborates $LnBO_3$ (Ln = Tm−Lu). The crystal structures of the hexaborates and pentaborates have been determined by single-crystal and powder diffraction techniques. The hydrated hexaborates $H_3LnB_6O_{12}$ crystallize in a trigonal structure in the space group *R*3*c*, which contain a six-membered ring B_6O_{15} as a fundamental fragment. Anhydrous pentaborates LnB_5O_9 crystallize in a tetragonal structure that is built up with B_4O_9 and BO_3. LnB_5O_9 decomposes at higher temperature to metaborates (Ln = Sm−Tb) and orthoborates (Ln = Dy−Er). A phase diagram is presented that shows the stable range of both $H_3LnB_6O_{12}$ and LnB_5O_9. The luminescent property of the europium-doped GdB_5O_9 was studied.

Introduction

Borates have long been the subject of interest over many decades, motivated by their extraordinary optical properties. Many borates are transparent in a wide spectrum with high nonlinear optical coefficients due to the strong covalent B−O bond and diverse structures. The syntheses of borates can be readily achieved either by high-temperature reaction or in aqueous solution. According to the Lux-Flood acid−base concept, anhydrous polyborates are less stable for the small-size and high-valence cations;[1] therefore, high-temperature syntheses often failed for some polyborate systems. Rare earth borates are one of the typical examples, wherein only three compounds were identified by high-temperature reaction in the Ln_2O_3−B_2O_3 (Ln = rare earth) system.[2] The oxyborates[3,4] and orthoborates[5,6] are stable at high temperature for all rare earths. The stability of the metaborates[7] declines with the decrease of the cation size to the point that the metaborates of heavy rare earths (Dy−Lu) are not present. Considering the diversity of the polyborate groups, more boron-rich rare earth polyborates may exist, but they may not be stable at high temperature. One possible approach for obtaining rare earth polyborates is to carry out the reaction at low temperature in a controlled manner.

Boric acid melts at about 171 °C and it does preserve most desirable requirements as a reaction medium for polyborates. Recently, we found that boric acid is indeed a suitable reaction medium, in which several novel rare earth polyborates were obtained.[8] Here in this report, we describe the syntheses and structure characterization of the hydrated rare earth hexaborates $H_3LnB_6O_{12}$ (Ln = Sm−Lu). Careful dehydration of $H_3LnB_6O_{12}$ at mild conditions resulted in boron-rich anhydrous pentaborates LnB_5O_9 (Ln = Sm−Er).

Experimental Section

General Procedure. $H_3LnB_6O_{12}$ (Ln = Sm−Lu) were synthesized by using H_3BO_3 (analytical grade) and Ln_2O_3 (99.99%) as the starting materials. DTA and TGA measurements were carried out on a Dupont 1090 instrument. IR spectra were recorded on a Nickel Magna-750 FT-IR spectrometer. Luminescent spectra under VUV excitation were recorded at Beijing Synchrotron Radiation Laboratory, using sodium salicylate as a standard. Powder X-ray diffraction patterns were recorded on a Rigaku D/max-2000 diffractometer with graphite monochromatized Cu Kα radiation at 50 kV, 120 mA.

Synthesis of Hydrated Hexaborates $H_3LnB_6O_{12}$ (Ln = Sm−Lu). H_3BO_3 and Ln_2O_3 in a mole ratio of 60:1 were mixed

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Table 1. Crystal Data and the Structure Refinement of $H_3GdB_6O_{12}$ and GdB_5O_9

formula	$H_3GdB_6O_{12}$	GdB_5O_9
formula mass	417.13	355.30
crystal system	trigonal	tetragonal
space group	*R*3*c*	$I4_1/acd$
a (Å)	8.405(1)	8.23813(6)
c (Å)	20.771(4)	33.6377(4)
V (Å^3)	1270.8(3)	2282.88(4)
Z	6	16
density (calc.) (g/cm^3)	3.27	4.135
diffraction technique	single-crystal diffraction	powder X-ray diffraction
reflections	3228 of which 1014 are unique	5399 profile data, 293 reflections
structure determination and refinement	direct method, SHELXL 97	direct method, EXTRA, Sirpow, and GSAS
R indices ($I > 2\sigma$)	R1 = 0.0260, wR2 = 0.0617	Rp = 0.0548, Rwp = 0.0782

Table 2. Atomic Coordinates and Isotropic Thermal Displacement Parameters in $H_3GdB_6O_{12}$

atom	site	*x*	*y*	*z*	*U*(eq)
Gd1	3a	1/3	2/3	0.0797(2)	0.009(1)
O1	18b	0.5279(6)	0.5290(6)	−0.0531(2)	0.012(1)
O2	18b	0.8644(5)	0.7727(7)	−0.1693(2)	0.013(1)
O3	18b	0.4923(5)	0.3999(4)	−0.1784(1)	0.013(1)
O4	18b	0.2416(3)	0.3227(4)	−0.1043(1)	0.011(1)
B1	18b	0.6284(6)	0.6664(7)	−0.0027(3)	0.011(1)
B2	18b	0.7571(6)	0.7646(6)	−0.2203(3)	0.012(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $H_3GdB_6O_{12}$

bond distance (Å)			bond angles (deg)	
Gd1−O2	3	2.387(5)	O3−B1−O1	112.5(4)
Gd1−O3	3	2.392(4)	O3−B1−O4	111.6(3)
Gd1−O4	3	2.470(3)	O1−B1−O4	111.5(4)
B1−O1		1.472(7)	O3−B1−O2	110.9(4)
B1−O2		1.509(5)	O1−B1−O2	108.0(4)
B1−O3		1.449(6)	O4−B1−O2	101.8(4)
B1−O4		1.479(5)	O1−B2−O4	122.9(5)
B2−O1		1.363(6)	O1−B2−O2	120.8(5)
B2−O2		1.370(7)	O4−B2−O2	116.4(4)
B2−O4		1.369(6)		

and charged into Teflon autoclaves. The reactions were carried out at 240 °C for about 5 days. The excess boric acid was removed by washing the products with distilled water, and the products were then dried at 80 °C for 10 h. Chemical analysis (ICP method) shows that the B:Ln ratio is approximately 6:1, and IR spectra indicate the presence of both BO_3 and BO_4 groups[9,10] in the products. Crystals used for single-crystal structure determination were obtained in a similar fashion. A small amount of water (H_2O:H_3BO_3:Ln_2O_3 = 60:60:1) was found to be helpful for obtaining single crystals.

Synthesis of Anhydrous Pentaborates LnB_5O_9 (Ln = Sm−Er). Anhydrous pentaborates LnB_5O_9 (Ln = Sm−Er) were obtained by heating $H_3LnB_6O_{12}$ at 650−700 °C for 5 days. Decomposition of the hydrated hexaborates of the heavy rare earth (Ln = Tm, Yb, and Lu) resulted in the orthoborates, instead of the pentaborates. IR spectroscopy confirms that the pentaborates contain both BO_3 and BO_4.[9,10]

X-ray Crystallographic Study. A crystal of $H_3GdB_6O_{12}$ of about 0.15 × 0.15 × 0.15 mm^3 was used for single-crystal diffraction data collection on a Rigaku R-AXIS RAPID image plate diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data set was collected up to 2θ = 54.7° and absorption correction was applied based on symmetry-equivalent reflections using the ABSOR program[11] (1014 unique reflections, R_{int} = 0.0436). $H_3GdB_6O_{12}$ crystallizes in space group *R*3*c*. The unit cell parameters, derived by indexing performed from two oscillation images, are *a* = 8.405(1) Å and *c* = 20.771(4) Å. The structure was solved by direct method (SHELXS97) and refined by full-matrix least-squares refinement.[12] Crystallographic data and refined parameters are listed in Table 1. The atomic coordinates and selected bond lengths and angles are listed in Tables 2 and 3, respectively. All other hexaborates $H_3LnB_6O_{12}$ (Ln = Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are isostructural to $H_3GdB_6O_{12}$ as confirmed by powder X-ray diffraction patterns.

Pentaborates LnB_5O_9 were obtained by decomposition of $H_3LnB_6O_{12}$, so it is impossible to obtain crystals suitable for single-crystal structure determination. The crystal structure of GdB_5O_9 was established by an ab initio method using powder X-ray diffraction data. The powder X-ray diffraction pattern of GdB_5O_9 was indexed with a tetragonal cell *a* = 8.23813(6) Å and *c* = 33.6377(4) Å with PowderX.[13] Careful inspection of the reflections revealed that the only possible space group is $I4_1/acd$. Optimal estimates of the individual reflection intensities were extracted by a profile-fitting method using EXTRA.[14] A total of 239 reflections were extracted in the range of $2\theta < 90°$, of which 91 are independent. The initial structure model was established by a direct method (Sirpow92[15]), and at this stage, nine crystallographic positions, that is, one Gd atom, five O atoms, and three B atoms, were located directly from the E-map. Different Fourier analysis was carried out and used to locate the rest of the oxygen positions (GSAS[16]). The final refinement, with isotropic thermal displacement parameters, yielded Rp = 0.0548 and Rwp = 0.0782. Figure 1 shows the profile fit of the diffraction pattern, the crystallographic data are listed in Table 1, and the atomic coordinates and selected bond lengths and angles are listed in Tables 4 and 5. All other pentaborates LnB_5O_{12} (Ln = Sm, Eu, Tb, Dy, Ho, and Er) are isostructural to GdB_5O_9 as confirmed by powder X-ray diffraction patterns.

Results and Discussions

Reaction of rare earth oxides and boric acid in molten boric acid is a simple acid−base reaction but is effective for producing rare earth polyborates. When heated in an open vessel, boric acid dehydrates stepwise and polymerizes to metaboric acid and then to boron oxide.[17−24] The typical polymerization process from boric

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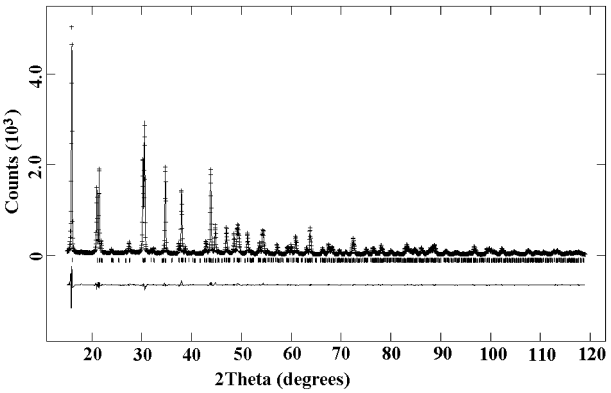

Figure 1. Profile fit to the powder X-ray diffraction pattern of GdB_5O_9. The symbol + represents the observed pattern, solid line represents the calculated pattern; the marks below the diffraction patterns are the calculated reflection positions and the difference curve is shown at the bottom of the figure.

Table 4. Atomic Coordinates and Thermal Displacement Parameters in GdB_5O_9

atom	site	*x*	*y*	*z*	*U*(eq)
Gd1	16d	0	0	0.193806(21)	0.00176(14)
O1	32g	−0.5289(11)	0.2036(17)	0.17275(24)	0.0030(8)
O2	16d	1/2	0	0.12439(19)	0.0030(8)
O3	32g	−0.3001(17)	0.0298(12)	0.17786(24)	0.0030(8)
O4	16f	−0.1229(6)	0.1229(6)	1/4	0.0030(8)
O5	16e	1/4	0.1648(11)	1/8	0.0030(8)
O6	32g	0.1645(8)	0.2392(7)	0.21743(18)	0.0030(8)
B1	16f	−0.2328(16)	0.2328(16)	1/4	0.0061(25)
B2	32g	−0.6287(21)	0.0912(20)	0.1462(4)	0.0061(25)
B3	32g	−0.3916(18)	0.1557(15)	0.1897(5)	0.0061(25)

Table 5. Selected Bond Distances (Å) and Angles (deg) in GdB_5O_9

bond distance (Å)			bond angles (deg)	
Gd1−O1	2	2.553(14)	O4−B1−O6	122.8(7)
Gd1−O2		2.294(6)	O6−B1−O6	114.3(14)
Gd1−O3	2	2.542(13)	O1−B2−O2	102.2(12)
Gd1−O4	2	2.372(4)	O1−B2−O3	100.9(9)
Gd1−O6	2	2.520(6)	O1−B2−O5	115.4(12)
B1−O4		1.280(19)	O2−B2−O3	106.2(10)
B1−O6	2	1.403(11)	O1−B3−O3	125.6(13)
B2−O1		1.527(17)	O1−B3−O6	113.4(12)
B2−O2		1.492(12)	O3−B3−O6	120.4(14)
B2−O3		1.573(17)		
B2−O5		1.369(13)		
B3−O1		1.327(17)		
B3−O3		1.342(17)		
B3−O6		1.354(14)		

acid to B_2O_3 is shown as follows:

$$H_3BO_3 \xrightarrow{175\ ^\circ C} HBO_2 \xrightarrow{230\ ^\circ C} B_2O_3 \qquad (1)$$

This condensation process is reversible in a closed system. In the presence of rare earth oxides, however, hydrated rare earth polyborates are formed with almost quantitative yield. For the rare earth oxides from Sm to Lu, the products are hydrated hexaborates and the reaction can be expressed as

$$12H_3BO_3 + Ln_2O_3 \xrightarrow{240\ ^\circ C} 2H_3LnB_6O_{12} + 15H_2O \qquad (2)$$

A similar reaction is applicable for the early rare earth oxides. In such cases, two new rare earth polyborates, that is, octaborates (La−Nd) and nonaborates (Nd−Sm), were obtained. The characterization of these compounds is underway and will be published elsewhere.

Table 6. Unit Cell Parameters of $H_3LnB_6O_{12}$ and LnB_5O_9

	$H_3LnB_6O_{12}$		LnB_5O_9	
	a (Å)	*c* (Å)	*a* (Å)	*c* (Å)
Sm	8.4336(2)	20.8003(4)	8.2789(4)	33.7320(16)
Eu	8.4191(1)	20.7745(2)	8.2556(2)	33.6625(13)
Gd[a]	8.4081(1)	20.7426(2)	8.2381(6)	33.6377(4)
Tb	8.3952(1)	20.7094(3)	8.2178(2)	33.5759(11)
Dy	8.3895(1)	20.6687(4)	8.2033(2)	33.5165(12)
Ho	8.3825(1)	20.6276(2)	8.1769(2)	33.4525(16)
Er	8.3698(1)	20.5848(6)	8.1546(8)	33.4176(63)
Tm	8.3605(2)	20.5404(7)		
Yb	8.3580(8)	20.5089(33)		
Lu	8.3506(10)	20.4756(46)		

[a] The lattice constants were obtained by powder data, which are not very different from those obtained from single-crystal diffraction.

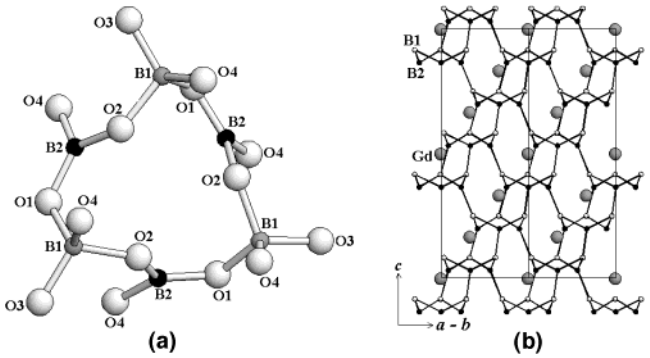

Figure 2. (a) Fundamental structure fragment of B_6O_{15} in $H_3GdB_6O_{12}$; (b) polyborate framework in $H_3GdB_6O_{12}$ showing only the rare earth cations and the connection of the borate groups.

Most of the products are single phases, but a small amount of unknown impurity was present in the samples from Er to Lu. The cell parameters of $H_3LnB_6O_{12}$ exhibit a gradual decrease from Sm to Lu as shown in Table 6 due to the lanthanide contraction. All of the hydrated rare earth hexaborates are isostructural to $H_3GdB_6O_{12}$, consisting of a six-membered ring of B_6O_{15} as the fundamental borate fragment. As shown in Figure 2a, this fragment contains an equal number of BO_3 and BO_4 groups that are linked alternatively, forming a six-membered ring. Nine terminal oxygen atoms are present in the B_6O_{15} unit; three of them are from BO_3 and six from BO_4. All terminal oxygen atoms on BO_3, as well as half on BO_4, are further connected to the neighboring B_6O_{15} rings, so the 3D structure of $H_3GdB_6O_{12}$ is featured in the three vertexes sharing BO_3 and BO_4. The structure refinement was not able to locate the hydrogen atoms, but the bond-valence sums calculation[25] shows a significant deviation from −2 at the O3 position (BVS = −1.2). Furthermore, the valence summation at the Gd position is relatively high (BVS = +3.5), indicating that extra positive charge might be present in this region. In this sense, the borate framework can be expressed as $3\{[BO_{3/2}]^0[BO_{3/2}OH]^-\}$, where the negative charge is localized mostly on the BO_4

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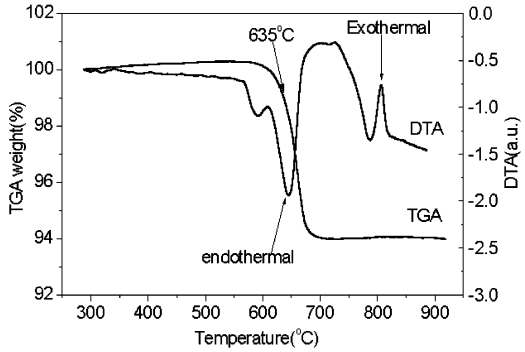

Figure 3. DTA and TGA curves of $H_3GdB_6O_{12}$.

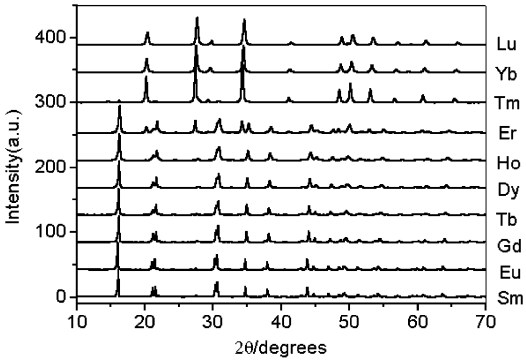

Figure 4. Powder X-ray diffraction patterns of the decomposition products of $H_3LnB_6O_{12}$ with annealing at 650−700 °C. The anhydrous pentaborates LnB_5O_9 were formed for Ln = Sm−Ho, and the orthoborates $LnBO_3$ were observed for Ln = Yb−Lu. The decomposition products of $H_3ErB_6O_{12}$ and $H_3TmB_6O_{12}$ are mixtures of LnB_5O_9 and $LnBO_3$.

groups. To compensate for the negative charge, the hydroxyl groups are further coordinated to the gadolinium atom with a bond distance of 2.392 Å (Gd−O3). Comparatively, in anhydrous polyborates, the negative charges are more delocalized. For example, the borate anion $[B_5O_{10}]^{5-}$ in $LaMgB_5O_{10}$[26] exhibits a layered structure in which BO_4 is four-vertexes connected and BO_3 is only two-vertexes connected, and therefore, the negative charges are equally distributed in all borate groups as $\{[BO_{4/2}]^-\}_3\{[BO_{2/2}O]^-\}_2$.

Figure 2b shows an overview of the framework in $H_3GdB_6O_{12}$. To emphasize the overall connection in the structure, only the boron and gadolinium atoms are illustrated. The overall structure of $H_3GdB_6O_{12}$ could be understood in such a way that the B_6O_{15} units, by thinking them as pseudoatoms, form a close-packed layer (not bonded), which are further stacked as the cubic close-packed array along the *c* axis. The B_6O_{15} units are bonded directly to the six neighbors in the adjacent layers forming a 3D framework. Such a structure arrangement yields additional six- and ten-membered rings as shown in Figure 2b. The polyborate anion $[B_6O_{15}]^{6-}$ itself is an open framework; however, the cavities in the framework are filled by the rare earth atoms that are coordinated by nine oxygen atoms with a tricapped trigonal prismatic polyhedron.

$H_3GdB_6O_{12}$ decomposes at about 635 °C, accompanied by a significant weight loss as shown in Figure 3. At the initial stage of the decomposition, an amorphous phase was formed, which was then crystallized by additional heat treatment. Figure 4 shows the powder X-ray diffraction patterns of the $H_3LnB_6O_{12}$ samples after annealing at 650−700 °C for 5 days. Depending on the ionic radii of the rare earth, two different crystalline products were obtained. LnB_5O_9 is formed for larger rare earths from Sm to Ho. Meanwhile, for the smaller rare earths (Ln = Yb−Lu), $H_3LnB_6O_{12}$ decomposes directly to orthoborate $LnBO_3$. The decomposition products of $H_3ErB_6O_{12}$ and $H_3TmB_6O_{12}$ are mixtures containing both LnB_5O_9 and $LnBO_3$. LnB_5O_9 is dominant for Ln = Er whereas $LnBO_3$ is dominant for Ln = Tm, even if the annealing treatment proceeded as low as 650 °C. The corresponding reactions can be expressed as

$$2H_3LnB_6O_{12} \xrightarrow{650-700\ °C} 2LnB_5O_9 + 3H_2O + B_2O_3 \quad (3)$$

$$2H_3LnB_6O_{12} \xrightarrow{650-700\ °C} 2LnBO_3 + 3H_2O + 5B_2O_3 \quad (4)$$

The weight loss expected from the above equations is 6.473 wt % for $H_3GdB_6O_{12}$, which agrees reasonably well with the observed value in the TGA study (6.04 wt %). B_2O_3 in the product may exist in noncrystalline form, so it does not appear in the diffraction patterns.

All other pentaborates LnB_5O_9 are isostructural to GdB_5O_9 crystallized in a tetragonal structure. The lattice constants decrease continuously from SmB_5O_9 to ErB_5O_9 due to the lanthanide contraction (Table 6). The borate framework in LnB_5O_9 consists of B_4O_9 and BO_3 as the fundamental fragments. The B_4O_9 is a double three-membered ring unit formed by two BO_3 and two BO_4. The B_4O_9 unit is known as a common fundamental fragment in metal polyborates. For example, the Borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) contains an isolated $B_4O_5(OH)_4$ unit[17] in which terminal O atoms bond to hydrogen as the hydroxyl groups. In the structure of GdB_5O_9, the B_4O_9 units are linked via terminal oxygen (on BO_4), forming a one-dimensional chain (Figure 5a). The other two terminal O atoms (on BO_3) are further connected to the additional BO_3 group forming the three-dimensional framework. The 3D framework of $B_5O_9^{3-}$ can, therefore, be expressed as $\{[BO_{3/2}]_2[BO_{4/2}]_2[BO_{2/2}O]\}^{3-}$. Figure 5b shows a projection of the structure of GdB_5O_9. It can be see that the BO_3 and BO_4 groups are connected to form a 3D framework and the Gd atoms occupy the cavities in the framework. The coordination polyhedron of gadolinium is a distorted three-capped trigonal prism.

According to the Lux-Flood acid−base concept, the 3D framework in LnB_5O_9 may not be very stable because of the high valence of rare earth (III); it may decompose to isolated or low-dimensional borate units at high temperature. It was found that the LnB_5O_9 decomposes at high temperature to metaborates or orthoborates. Figure 6 shows a phase diagram for the rare earth borate system. The two critical temperatures, that is, T_{d1} and T_{d2}, are respectively the temperature of weight loss, characteristic for the dehydration of $H_3LnB_6O_{12}$, and the decomposition temperature of LnB_5O_9 to orthoborates or metaborates. T_{d1} is almost constant for all rare earth systems, indicating that the thermal stability is similar for the hydrated hexaborates $H_3LnB_6O_{12}$. T_{d2}, on the other hand, depends on the rare earth cations; it increases slightly from Sm to Tb and then decreases as the ionic radii become smaller. It should be noted that the highest decomposition temperature T_{d2} appeared at the Tb, which coincides with the smallest rare

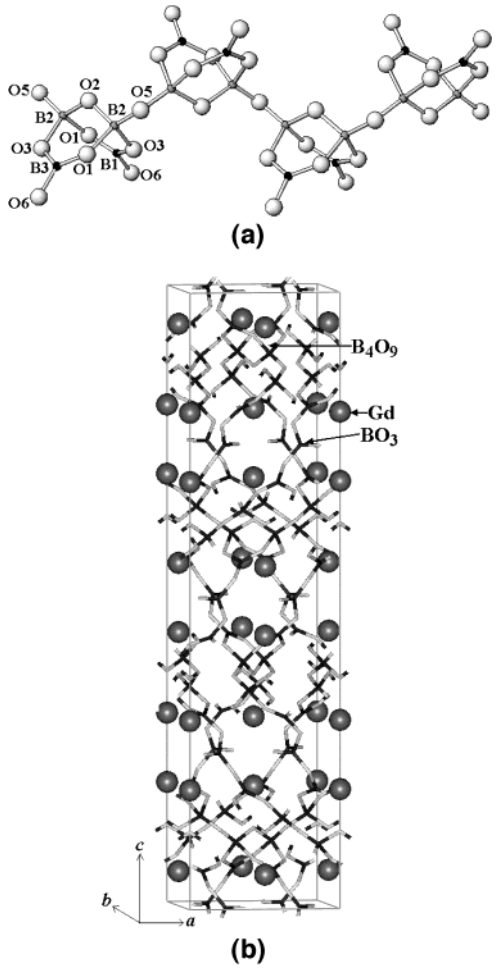

Figure 5. (a) The fundamental borate fragment B_4O_9 in anhydrous pentaborate LnB_5O_9, which forms a one-dimensional chain by sharing the oxygen atoms on the BO_4 group; (b) crystal structure of LnB_5O_9, where the rare earth cations are expressed as balls and the borate network is displayed in line style.

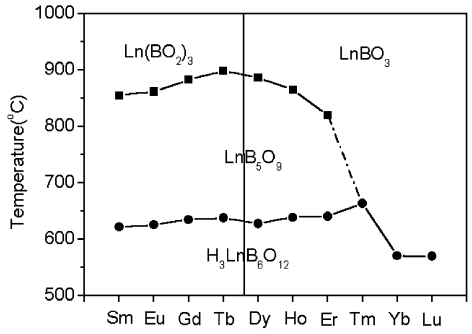

Figure 6. Phase diagram of the rare earth polyborates. T_{d1} represents the dehydration temperature of $H_3LnB_6O_{12}$ and T_{d2} represents the decomposition temperature from LnB_5O_9 to $Ln(BO_2)_3$ or $LnBO_3$ that are separated by a vertical line.

earth for the metaborates. The observed decomposition products of LnB_5O_9 are indeed the metaborates from Sm to Tb and the orthoborates from Dy to Er. The lower dehydration temperature for the two smallest rare earths (Yb and Lu) is presumably related to that the decomposition of $H_3LnB_6O_{12}$ that yields directly to orthoborates. Tm is on the borderline so that only a trace of TmB_5O_9 was observed, even if the decomposition reaction proceeded at 650 °C. The LnB_5O_9 is a well-

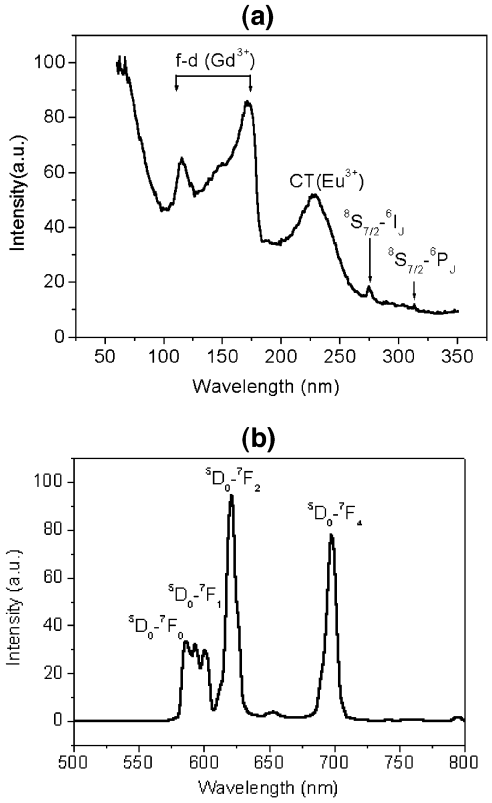

Figure 7. (a) Excitation spectrum (λ_{em} = 615 nm) and (b) emission spectrum (λ_{ex} = 125 nm) of GdB_5O_9:Eu.

defined compound in the $Ln_2O_3-B_2O_3$ system. The absence of this phase in the $Ln_2O_3-B_2O_3$ phase diagram[2] is largely due to the low decomposition temperatures. Furthermore, the borate-rich system has a strong tendency to form a glassy phase at high temperature; thus, the syntheses of polyborates are practically difficult by using the conventional high-temperature techniques.

Europium-doped material GdB_5O_9:Eu^{3+} was prepared by using the same method as described for the pure compound, except a certain amount of Eu_2O_3 was added in the reaction systems. Figure 7 shows the excitation and emission spectra of GdB_5O_9:Eu^{3+}. The excitation spectrum was measured in a vacuum ultraviolet (VUV) range by monitoring the Eu^{3+} emission at 615 nm. The excitation transitions in the spectrum can be categorized into two parts. The strong excitation band at about 120−150 nm and the sharp peaks at 275 and 315 nm originate from the f−d, $^8S_{7/2}-^6I_J$, and $^8S_{7/2}-^6P_J$ transitions of Gd^{3+}, respectively. Another broad excitation band at about 230−260 nm originates from the charge-transfer transition (CT) of $O \rightarrow Eu^{3+}$. The appearance of Gd^{3+} absorption in the excitation spectrum implies an effective energy transfer between Gd^{3+} and Eu^{3+} in this material, which is very important for the luminescent materials used under the excitation of high-energy photons. The emission spectrum (Figure 7b) consists of mainly the $^5D_0-^7F_0$, $^5D_0-^7F_1$, $^5D_0-^7F_2$, and $^5D_0-^7F_4$ transitions. Because the Gd atoms in GdB_5O_9 occupy an ancentrosymmetric site (local symmetry is C_2), the electric dipole−dipole transition of $^5D_0-^7F_2$ is predominant in this material. The concentration quenching of the Eu^{3+} emission is significantly high for this material. As shown in Figure 8, the emission intensity of GdB_5O_9:

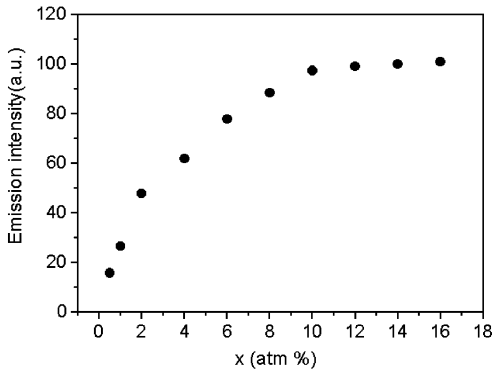

Figure 8. Variation of the emission intensity on the doping concentration in the GdB_5O_9:Eu system. The x value represents the doping concentration in $Gd_{1-x}Eu_xB_5O_9$.

Eu^{3+} increases with the doping concentration up to $x = 0.1$ and then remains almost constant beyond this doping level.

In summary, molten boric acid is an effective reaction medium for syntheses of the hydrated rare earth hexaborates $H_3LnB_6O_{12}$ (Ln = Sm−Lu). Careful annealing of the hexaborates at 650−700 °C results in the formation of anhydrous pentaborates LnB_5O_9 (Ln = Sm−Er). The pentaborates are metastable, so they cannot be synthesized by conventional high-temperature reaction. The preparation strategy for the anhydrous rare earth polyborates proposed here is in fact a precursor method in which the hydrated polyborates are the precursors first prepared in molten boric acid. Then the anhydrous rare earth polyborates are obtained by annealing the precursors at mild conditions. It is believed that this approach will be useful for exploring polyborate chemistry of rare earth and other high valence cations.

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Supporting Information Available: Crystallographic information files for $H_3GdB_6O_{12}$ and GdB_5O_9 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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