CHEMCOMM
Communication
www.rsc.org/chemcomm

A novel synthesis route to rare earth polyborates†

Peichao Lu,[a] Yingxia Wang,[a] Jianhua Lin*[a] and Liping You[b]

[a] *State Key Laboratory for Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China. E-mail: jhlin@chem.pku.edu.cn*

[b] *Laboratory of Electron Microscopy, Department of Physics, Peking University, Beijing 100871, P. R. China*

Received (in Cambridge, UK) 5th March 2001, Accepted 14th May 2001
First published as an Advance Article on the web 30th May 2001

The proposed two-step preparation route for rare earth polyborates, *i.e.* dehydration of boric acid in the presence of rare earth oxide at low temperature followed by careful annealing at 700 °C, led to, for the gadolinium case, a new gadolinium pentaborate (GdB_5O_9) that can not be prepared by conventional high-temperature reaction.

The structural chemistry of borates is characterized by a variety of discrete and condensed BO_3 and BO_4 groups;[1] as a general rule, the tendency to form polyborates is increased by decreasing cation valence.[2] This promotes stability and a wide variety of polyborate structures with 1+ and 2+ valence cations have been produced. The rare earth borates, on the other hand, usually consist of isolated borate anions (BO_3 or BO_4) or low polymerized borate groups; thus, in the Ln_2O_3–B_2O_3 (Ln = rare earth) system[3] only three compounds, oxyborate,[4,5] orthoborate[6] and metaborate,[7] have been identified; the more borate-rich phases remain unknown. Recently, we found that, in the flux of boric acid, hydrated rare earth polyborates are formed by the reaction of boric acid and rare earth oxides at low temperature. Subsequent annealing of the hydrated polyborates yields anhydrous rare earth polyborates. We describe herein our exploratory syntheses in this area.

The synthesis of hydrated gadolinium polyborate was carried out in a sealed Teflon autoclave at 260 °C for 5 days, starting from H_3BO_3 and Gd_2O_3 in a 20 : 1 ratio. The product **1**, isolated by dissolving the excess boric acid in water, consists of colorless well-crystallized polycrystals. Chemical analysis (ICP) reveals that the approximate atomic ratio Gd : B is about 1 : 6.2, and the IR spectrum indicates the presence of both BO_3 and BO_4 groups in this compound. Fig. 1a shows the X-ray diffraction pattern of **1**. Structural analysis using X-ray powder diffraction techniques[8] established that the product **1** is a hydrated gadolinium polyborate with the composition $H_3GdB_6O_{12}$; it crystallizes with a rhombohedral structure in the space group $R3c$ with lattice constants a = 8.4076(2) and c = 20.7427(5) Å. The synthesis reaction is:

$$12H_3BO_3 + Gd_2O_3 \xrightarrow{260\ ^\circ\mathrm{C}} 2H_3GdB_6O_{12} + 15H_2O \quad (1)$$

$H_3GdB_6O_{12}$ is stable at low temperature and decomposes at high temperature. X-Ray powder diffraction studies carried out at high temperatures indicate that the decomposition of $H_3GdB_6O_{12}$ occurs at about 650 °C; it transforms to an amorphous form between 650 °C and 700 °C. During the decomposition, significant weight loss (6.04 wt%) was observed *via* TGA. Therefore, the decomposition reaction is essentially the dehydration of $H_3GdB_6O_{12}$. Careful annealing at 700 °C for 5 days resulted in another new phase (**2**) as shown in Fig. 1b.

The structural study by X-ray powder techniques established that **2** is a rare earth pentaborate GdB_5O_9. It crystallizes in a body centered tetragonal cell (a = 8.2439(4), c = 33.6671(2) Å) in the space group $I4_1/acd$.[9] The basic borate fragments in GdB_5O_9 are B_4O_9 and BO_3 units. The B_4O_9 is a common structure unit in many borates. For example, isolated and 1D chains of B_4O_9 are present in borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) and $Na_2[B_4O_6(OH)_3]$ respectively.[1] In the structure of GdB_5O_9, the B_4O_9 units form 1D chains by sharing the oxygen atoms of the BO_4 groups (Fig. 2); the 3D-polyborate framework is composed of 1D chains linked by additional BO_3 groups. Fig. 3 shows an overview of the structure of GdB_5O_9, where the triangles and tetrahedra represent BO_3 and BO_4 groups respectively. The decomposition reaction of $H_3GdB_6O_{12}$ is then expressed as:

$$2H_3GdB_6O_{12} \xrightarrow{650\text{–}700\ ^\circ\mathrm{C}} 2GdB_5O_9 + 3H_2O + B_2O_3 \quad (2)$$

The expected weight loss from eqn. (2) is 6.473 wt%, which agrees reasonably well with that observed in the TGA study (6.04 wt%). Moreover, GdB_5O_9 is not stable at higher temperatures; further annealing at 900 °C yielded gadolinium metaborate and another unknown phase. Therefore, this compound cannot be synthesized by conventional high temperature solid state reaction.

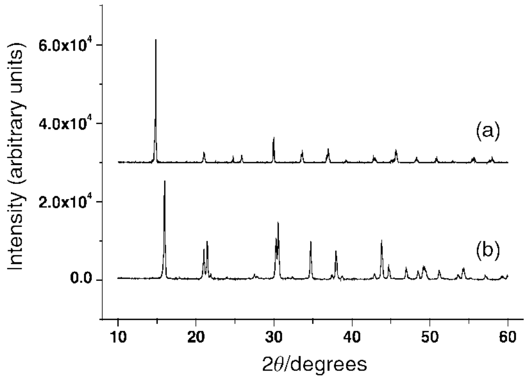

Fig. 1 X-Ray powder diffraction patterns (a) of the hydrated gadolinium polyborate $H_3GdB_6O_{12}$ (**1**) and (b) of the anhydrous gadolinium polyborate GdB_5O_9 (**2**) after annealing at 700 °C for 5 days.

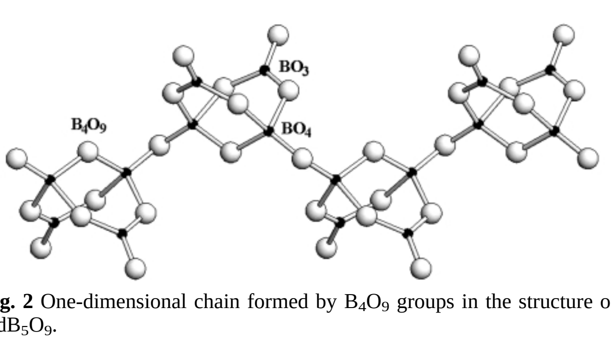

Fig. 2 One-dimensional chain formed by B_4O_9 groups in the structure of GdB_5O_9.

---

† Electronic supplementary information (ESI) available: crystallographic, TGA/DTA, IR and XRD profile fits for $H_3GdB_6O_{12}$ and GdB_5O_9. See http://www.rsc.org/suppdata/cc/b1/b102045p/

DOI: 10.1039/b102045p

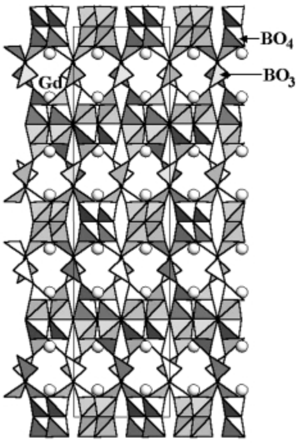

Fig. 3 A projection of the crystal structure of GdB_5O_9 (**2**); triangles and tetrahedra represent BO_3 and BO_4 groups.

In summary, although polyborate is an important resource for functional materials, such as nonlinear optical and luminescent materials, our knowledge of rare earth polyborates was limited due to the instability of these phases at high temperatures. In this communication, we have demonstrated that careful dehydration of a hydrated rare earth polyborate may lead to the anhydrous rare earth polyborate. We believe that the proposed preparative strategy will be very useful in exploiting new polyborate materials for rare earth systems.

We are grateful for the financial support from NSFC (29731010), Rhodia Rare Earth Co. and State Key Basic Research Program of China.

Notes and references

1 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, 5th edn., 1984, p. 1045.

2 N. I. Leonyuk, *J. Cryst. Growth*, 1997, **174**, 301.

3 E. M. Levin, C. R. Robbins and J. L. Warring, *J. Am. Ceram. Soc.*, 1961, **44**, 87.

4 J. H. Lin, M. Z. Su, K. Wurst and E. Schweda, *J. Solid State Chem.*, 1996, **126**, 287.

5 J. H. Lin, S. Zhou, L. W. Yang, G. Q. Yao, M. Z. Su and L. P. You, *J. Solid State Chem.*, 1997, **134**, 158.

6 M. Ren, J. H. Lin, Y. Dong and M. Z. Su, *Chem. Mater.*, 1999, **11**, 1576.

7 G. K. Abdullaev, Kh. S. Mamedov and G. G. Dzhafarov, *Sov. Phys. Crystallogr.*, 1975, **20**, 161.

8 The X-ray powder diffraction pattern was collected for $H_3GdB_6O_{12}$ (**1**) on a Rigaku D/max-2000 diffractometer and indexed by using TEROR90.[10] $H_3GdB_6O_{12}$ crystallizes in a rhombohedral system with lattice constants $a = 8.4076(2)$ and $c = 20.7427(5)$ Å. The systematic absences of reflections indicated that the space group is either $R3c$ or $R\bar{3}$. Optimal estimates of the individual reflection intensities were extracted by a profile-fitting method using the EXTRA program.[11] The gadolinium positions in the structure were obtained by direct methods (Sirpow92[12]). The Rietveld refinement (GSAS)[13] and subsequent difference Fourier analysis identified the oxygen and boron positions. During the structure determination, both space groups $R3c$ and $R\bar{3}$were used, but only $R3c$ led to a chemically reasonable solution. The final refinement using the X-ray diffraction data in the range of 20–120° yielded $R_p = 0.089$ and $R_{wp} = 0.115$. The structure analysis was not able to locate the hydrogen atoms; the hydrogen component in **1** was estimated by charge balance of the compound, as well as the weight loss in TGA analysis.

9 The lattice constants of GdB_5O_9 (**2**) were established by using TREOR90.[10] **2** crystallizes in the tetragonal space group $I4_1/acd$ with lattice constants $a = 8.2380(1)$, $c = 33.6372(6)$ Å. Similar to **1**, the gadolinium positions were located by direct methods (Sirpow92[12]); subsequent Rietveld refinement and different Fourier analysis revealed the oxygen and boron positions. The final refinement yielded $R_p = 0.069$ and $R_{wp} = 0.098$.

10 D. Cheng, *J. Appl. Crystallogr.*, 1999, **32**, 838.

11 A. Altomare, M. C. Burla, G. Cascarana, C. Glacovazzo, A. Guagliardi, A. G. G. Moliterni and G. Polidiori, *J. Appl. Crystallogr.*, 1995, **28**, 842.

12 A. Altomare, G. Cascarana, C. Glacovazzo and A. Guagliardi, *Sirpow User's Manual*, Inst. Di Ric. Per lo Sviluppo di Metodologie Cristllografiche, CNR.

13 A. C. Larson and R. B. von Dreele, *Report LAUR 86-748*, Los Alamos National Laboratory, 1985.