Journal of Solid State Chemistry 183 (2010) 1697–1703

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis of boron suboxide (B_6O) with ball milled boron oxide (B_2O_3) under lower pressure and temperature

Xiaopeng Jiao, Hua Jin, Fuyang Liu, Zhanhui Ding, Bin Yang, Fengguo Lu, Xudong Zhao, Xiaoyang Liu *

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 9 March 2010
Received in revised form
5 May 2010
Accepted 22 May 2010
Available online 1 June 2010

Keywords:
Synthesis
Boron suboxide
Ball milling
High pressure and high temperature
Superhard material

ABSTRACT

Boron reacted with ball milled boron oxide under pressures between 1 and 5 GPa and at temperatures between 1300 and 1700 °C to afford boron suboxide (B_6O). Icosahedral B_6O grains with diameters ranging from 100 nm to 1.3 μm were prepared. The factors that affect the synthesis of B_6O are investigated. The best sample with crystal size up to 1.3 μm is obtained at 2 GPa and 1400 °C for 6 h. The indentation experiment gave an average Vickers hardness of 32.3 GPa for bulk B_6O sample, which is consistent with previous reports. Bulk B_6O sample exhibits oxidation resistance in air up to 1000 °C and mild oxidation in the temperatures of 1000–1200 °C, which is more oxidation resistant than diamond. It is possible that B_6O could be used as a substitute for diamond in industry because of its relatively mild synthesis conditions, high thermal stability and high hardness.

1. Introduction

Superhard materials are widely used in the manufacturing of abrasives, cutting tools and scratch-resistant coatings. Most researchers agree that superhard materials are those with Vickers hardness (H_V) higher than 40 GPa [1]. Currently, only diamond and cubic boron nitride (c-BN) are used in industry as superhard materials. Although diamond, with the highest known hardness ($H_V \sim 70$–100 GPa), has been widely used in the industry, there are limits for its broad use. For example, diamond cannot be used to cut steel or other ferrous metals because the formation of iron carbide is detrimental during high-speed machining. Cubic boron nitride, the second hardest material ($H_V \sim 45$–50 GPa), is more stable than diamond and can be used to cut steel; however, c-BN must be synthesized under high pressure (>5 GPa) and temperature (>1500 °C), making it an expensive alternative [2]. To prepare new superhard materials with better performance properties, such as high hardness and wear resistance like diamond and high thermal stability and chemical inertness like c-BN, is of great importance both in experimental and theoretical researches.

Two boron compounds have been recently synthesized to meet the industrial need for superhard materials. B_6O single crystal has a hardness of 45 GPa, comparable to that of c-BN [3]. Cubic BC_2N, synthesized by Solozhenko et al., [4] has a hardness between c-BN and diamond. The structure of B_6O consists of eight icosahedra at the apexes of the rhombohedral unit cell (space group $R\overline{3}m$). Each icosahedron is composed of twelve boron atoms. Two oxygen atoms are located in the interstices along the [1 1 1] rhombohedral direction [5,6]. Because of its short interatomic bond lengths and strongly covalent character, B_6O displays a range of outstanding physical and chemical properties such as high hardness, low mass density, high thermal conductivity, high chemical inertness and excellent wear resistance [3,7–10].

The two compounds require high pressure to synthesize, exceeding 5 and 18 GPa for B_6O and cubic BC_2N, respectively. While these compounds have the desired hardness for industrial applications, the requirement of high pressure for their synthesis makes them expensive. B_6O can be synthesized by oxidation of boron with boron oxide (B_2O_3), zinc oxide and other oxidants at or near ambient pressure [8–14]. But these boron suboxide materials prepared under these conditions have poor crystallinity and are generally oxygen deficient (B_6O_x, $x < 0.9$). Icosahedrally twined B_6O particles with high crystallinity were first obtained by Hubert et al. [6] under high pressure and high temperature. Well-organized icosahedral B_6O grains ranging from 20 nm to 40 μm in diameter were obtained from amorphous B and B_2O_3 mixtures reacted at 1700–1800 °C between 4 and 5.5 GPa. Icosahedral boron suboxide with the highest O occupancy is $B_6O_{0.96}$. However, the fine-grain fraction ($\ll 1$ μm) in the recovered sample is dominated by well-sorted euhedral to subhedral particles from 20 to 100 nm in diameter, which is comparable to the B_6O single crystals synthesized by He et al., [15] at 5.5 GPa and 2100 °C that have an euhedral morphology with an average size of 60 μm.

---

* Corresponding author. Fax: +86 431 85168316.
E-mail address: Liuxy@jlu.edu.cn (X. Liu).

0022-4596/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2010.05.031

Both of these routes to crystalline B_6O are difficult for industrial production because they require such high pressures and high temperatures similar to diamond synthesis.

A wide range of microhardness (H_V) from 31 to 38 GPa was reported for sintered polycrystalline boron suboxide compacts [8,16–18]. It is known from previous work that the hardness measured from a single crystal is usually higher than that of the corresponding sintered polycrystalline sample [19]. He et al. [3] measured the hardness of B_6O single crystal and reported an average Vickers hardness of 45 GPa, a value close to c-BN.

The aim of this investigation was to synthesize well-crystallized B_6O under milder conditions. The strategy employed was to use milled B_2O_3 instead of B_2O_3 as a starting reagent. The size of milled B_2O_3 was smaller than unmilled B_2O_3 and milled B_2O_3 was expected to have higher activity. We hypothesized that using milled B_2O_3 instead of B_2O_3 as the raw material should lead to milder synthesis conditions for B_6O. Indeed, we found well-crystallized icosahedral B_6O grain that was prepared from milled B_2O_3 and boron at lower pressure and temperature than previously reported.

2. Experimental section

The HP-HT syntheses were performed using a piston-cylinder-type apparatus (Depths of the Earth Co., AZ, USA) with pressures ranging from 1 to 2 GPa. The pressure was calibrated from melting of dry NaCl at 1050 °C [20] and the transformation of quartz to coesite at 500 °C [21]. All the furnace parts were previously burned at 1000 °C in air. The experimental temperature was monitored by inserting a Pt100%–Pt90%Rh10% thermocouple into the high-pressure cell. The starting materials were enclosed in a capsule made of hexagonal boron nitride (h-BN). The reactions were quenched before the pressure was released.

The HP-HT synthesis with pressure at 5 GPa was performed using a Walker-type multianvil apparatus (Rockland Co., PA, USA). The pressure cell, consisting of an 8 mm MgO octahedron and a cylindrical graphite heater, was compressed using WC cubes with 8 mm truncations. The starting materials were contained in an h-BN capsule. Temperature inside the cell was monitored with Pt100%–Pt90%Rh10% thermocouple. Sample was pressurized to high pressure and then heated at 1700 °C. The reaction was quenched before the pressure was released.

The starting materials were powders of boron (98%, Alfa) and B_2O_3 (99.98%, Alfa). B_2O_3 was mechanically milled in a P-7 planetary mill (Fritsch, Germany), in which the silicon nitride balls (10 mm in diameter) were used. The rotational speed of the silicon nitride vials was 600 rpm, and the mass ratio of ball-to-powder (B/P) was 10:1. The total milling time was 10 h. Particularly, the powders were allowed to be cooled for 20 min after every 20 min milling and at the end of every 2 h milling, a small amount of B_2O_3 powder was taken out for X-ray diffraction analysis and scanning electron microscopy analysis.

Boron powder reacted with milled B_2O_3 in different stoichiometric ratios and sample assembly methods (Table 1). Two sample assembly methods were used in these reactions. One was that mixed raw materials were grinded in agate mortar for 30 min and then encapsulated in an h-BN capsule. Another method was that two raw materials were encapsulated in an h-BN capsule layer upon layer, with milled boron oxide at both the bottom and top of the capsule and boron in the middle. The raw materials

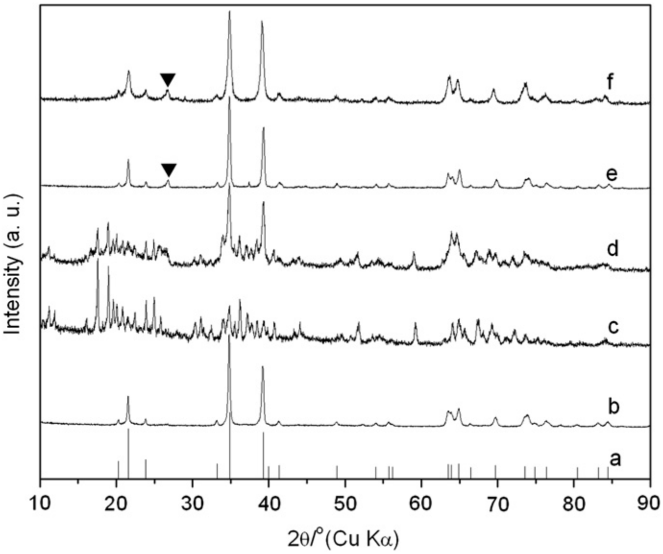

Fig. 1. X-ray diffraction patterns of products from run 056, 098, 055, 054, 100 and B_6O synthesized by Hubert et al.: (a) XRD pattern of B_6O synthesized by Hubert et al. (b) XRD pattern of sample 056, (c) XRD pattern of sample 098, (d) XRD pattern of sample 055, (e) XRD pattern of sample 054 and (f) XRD pattern of sample 100. ▼, h-BN peak (A.U.=arbitrary units).

Table 1
Summary of selected runs prepared between 1 and 5 GPa and from 1300 to 1700 °C.

Run	Initial mixture milled B_2O_3:16B	Press	*P* (GPa)	*T* (°C)	Time (h)	Products	Particle morphology (SEM)	Size of products (nm)
054	1	PCP	1	1400	2	B_6O	euh	
055	1	PCP	1	1300	2	B_6O+B	euh	
056[a]	2.6	PCP	2	1400	6	B_6O	icos > euh	500
098[b]	16B+B_2O_3	PCP	1	1300	2	B		
100[c]	16milled B+B_2O_3	PCP	1	1300	2	B_6O	euh	
104[a]	3.7	PCP	1	1400	2	B_6O	euh	
105	1.2	PCP	1	1400	2	B_6O	euh	
107[a]	3.2	PCP	2	1400	48	B_6O	euh	
109[a]	4.9	PCP	1	1400	6	B_6O	euh	
113[a]	3.2	Walker	5	1700	0.5	B_6O	icos > euh	100
115[a]	3.1	PCP	2	1400	2	B_6O	euh	
117[a]	2.5	PCP	2	1400	24	B_6O	icos≪euh	400
120	1	PCP	2	1400	6	B_6O	euh	
121	1.2	PCP	2	1400	6	B_6O	euh	

[a] The starting materials were encapsulated in the h-BN capsule layer upon layer, with milled B_2O_3 at both the bottom and top of the capsule and boron at the middle.

[b] The starting materials were mixtures of boron and boron oxide with a ratio of 16:1.

[c] The starting materials were mixtures of milled boron and boron oxide with a ratio of 16:1. PCP, piston-cylinder press; Walker, Walker-type multianvil apparatus; euh, euhedral grains and icos, icosahedral grains.

reacted according to the following reaction:

$$16B + B_2O_3 \rightarrow 3B_6O \quad (1)$$

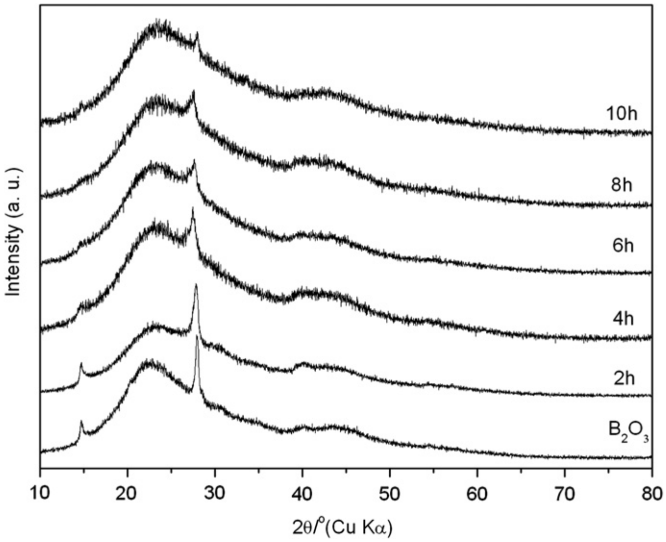

Fig. 2. X-ray diffraction patterns of B_2O_3 and milled B_2O_3 with different milling time (A.U.=arbitrary units).

The composition of the recovered sample was determined by X-ray diffraction (XRD, Cu$K\alpha$ radiation, Rigaku D/max2550VB, Japan). KCl was used as an external standard. The morphology and particle size of the sample were studied by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan). The hardness testing was performed by an indentation experiment using MTS Nanoindenter (MTS, USA) XP with CSM (continuous stiffness measurements) mode. The thermal stability of the recovered sample was studied by thermogravimetry analysis (STA 449 C thermal analyzer, NETZSCH, Germany).

3. Results and discussion

3.1. Run products

Table 1 shows a summary of selected runs prepared between 1 and 5 GPa and from 1300 to 1700 °C. According to these results, the factors that affect the synthesis of B_6O are pressure, temperature, time, reagent ratio and way of sample assembly. Most recovered samples were cylindrical sinters that were very hard and difficult to be triturated. Therefore, the polished plane instead of powder was used for X-ray diffraction analysis. The compositions of most runs were determined by X-ray diffraction and the results are shown in Table 1.

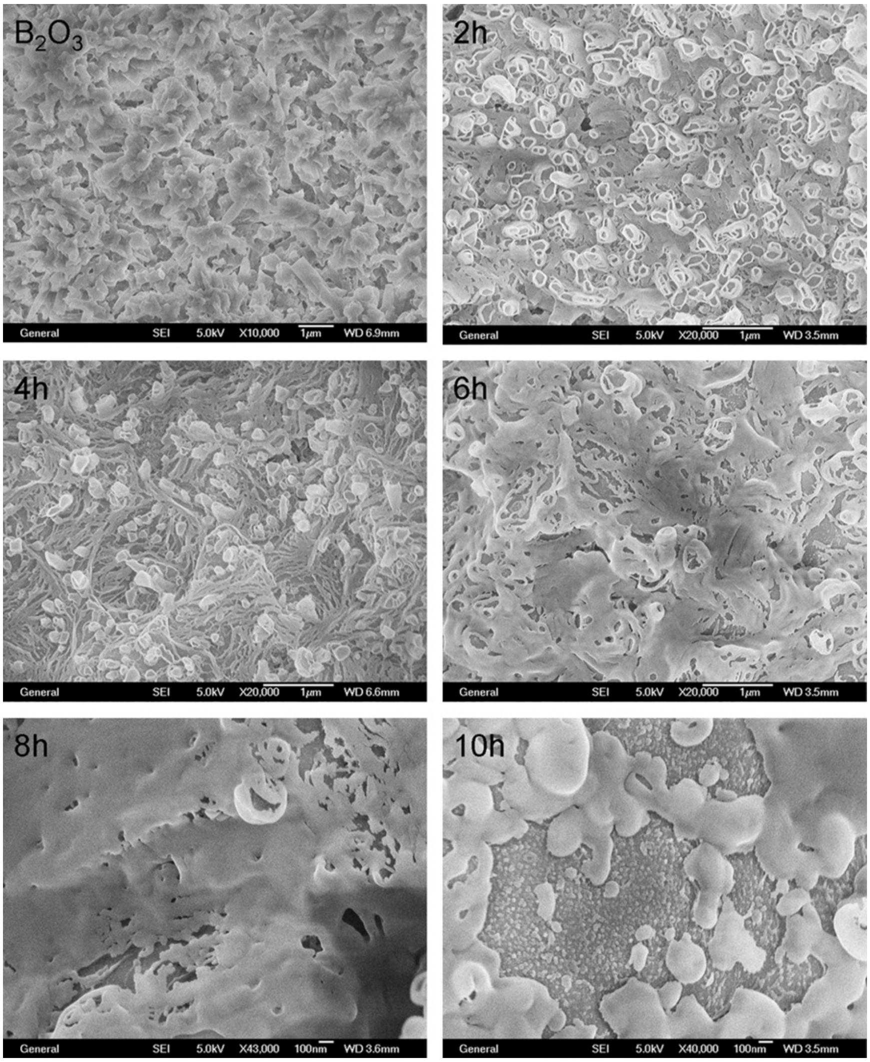

Fig. 3. SEM photographs of B_2O_3 and milled B_2O_3 with different milling time.

Fig. 1 shows the X-ray diffraction patterns of products from run 056, 098, 055, 054, 100 and B_6O synthesized by Hubert et al. [22]. A comparison of the XRD pattern of sample 056 with that of B_6O obtained by Hubert et al. shows that the two patterns agree very well. The products we obtained are confirmed to be B_6O. The XRD patterns of samples 054 and 100 both contain an h-BN peak, which is from residual h-BN capsule.

The product of run 055 contains B_6O and a large amount of unreacted boron, but B_2O_3 was not found in the product. B_2O_3 has a low melting point so it becomes liquid at high temperature; liquid B_2O_3 can be easily extruded from the h-BN capsule at high pressure because h-BN capsule was not sealed. This incomplete reaction suggests that the reaction of boron and milled B_2O_3 at 1 GPa and 1300 °C is not sufficient to prepare B_6O. The product of run 054 performed at 1 GPa and 1400 °C contains pure B_6O; no residual boron indicates complete reaction. Comparing these two reactions, high temperature 1400 °C is favorable for the synthesis of B_6O. Runs like 056, 107 and 115, which were performed at 1400 °C with different pressure and reaction time, have similar XRD patterns like that of sample 054. These runs have the same product B_6O.

The results of XRD patterns of most runs indicate that conditions with pressure above 1 GPa and temperature above 1300 °C are needed to synthesize B_6O, whether the obtained B_6O is crystal or not. The higher temperature of 1400 °C is favorable for the synthesis of B_6O.

In order to confirm that milled B_2O_3 has the expected higher activity than the untreated B_2O_3, run 098 was performed to compare with run 055. The starting material was ground mixture of boron and boron oxide with a stoichiometric ratio of 16:1. Boron and boron oxide were reacted under the same condition as run 055 (1 GPa, 1300 °C, 2 h). The XRD pattern of sample 098 is shown in Fig. 1c and it indicates that the recovered sample did not contain B_6O. This result confirms our hypothesis that using milled B_2O_3 as a starting material can lower the pressure and temperature needed for the synthesis of B_6O.

The reaction of B_2O_3 and milled boron (milled 10 h) was also studied. Run 100 was performed at 1 GPa and 1300 °C for 2 h and the recovered sample was B_6O (Fig. 1f). This result also confirms that the milled starting material can lower the pressure and temperature needed for the synthesis of B_6O.

In order to confirm that the size of milled B_2O_3 is smaller than untreated B_2O_3, milled B_2O_3 samples with different milling time were characterized by X-ray diffraction and scanning electron microscopy. The X-ray diffraction patterns of B_2O_3 and milled B_2O_3 with different milling times are shown in Fig. 2. With long milling time, amorphous B_2O_3 was obtained. The SEM photographs of B_2O_3 and milled B_2O_3 are shown in Fig. 3. With long milling time, the size of B_2O_3 became smaller. The size of B_2O_3 milled for 10 h is about 20 nm. This result confirms our hypothesis that that the size of milled B_2O_3 is smaller than untreated B_2O_3 and milled B_2O_3 is expected to have higher activity. The size of milled B_2O_3 is very small, and thus, the surface area of milled B_2O_3 increased greatly with decreasing particle size. As a result, the contact area between milled B_2O_3 and B also increased, which leads to the solid state reaction between B_2O_3 and B easy to execute.

3.2. Morphology

The crystallinity and the size of recovered sample were used to select the optimal synthesis conditions for B_6O crystals, which can be observed from SEM photographs. Grain morphologies and sizes of selected samples were characterized using SEM and the results are shown in Table 1.

Hubert et al. [6] reported the synthesis of icosahedral B_6O particles with starting mixtures of B_2O_3 and amorphous boron in different ratios. They obtained better B_6O product with starting mixtures containing excess B_2O_3. Because under the same synthesis condition, euhedral grains were the main product with starting mixtures in equivalent ratio but icosahedral grains were

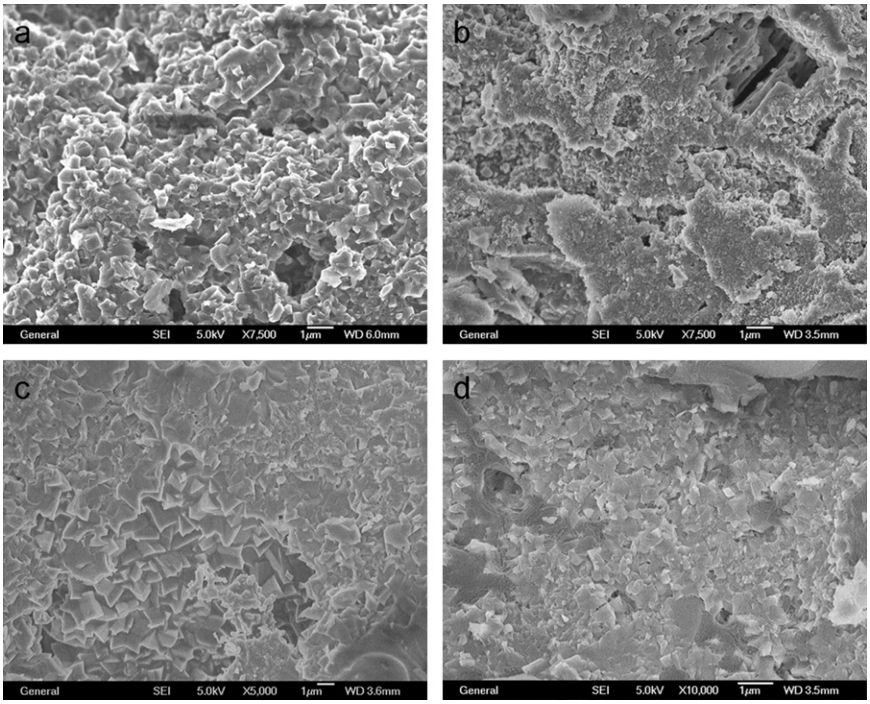

Fig. 4. SEM photographs of samples from run 054, 105, 104 and 109. (a) SEM photograph of sample 054, (b) SEM photograph of sample 105, (c) SEM photograph of sample 104 and (d) SEM photograph of sample 109.

the main products with starting mixtures containing excess B_2O_3. He et al. tested a different sample assembly for B_6O crystal growth at high pressure and temperature, in which a lump of crystalline boron was surrounded by boron oxide powder in an h-BN capsule [15]. They obtained euhedral B_6O single crystals with an average size of 60 μm.

In our experiments, these three types of sample assembly were used for the synthesis of B_6O. For example, the starting materials of run 054, 055 and 120 were mixtures of milled boron oxide and boron in equivalent ratio. The starting materials of run 105 and 121 were mixtures of milled boron oxide and boron with a ratio of 1.2:16. Based on He's sample assembly, we tested a simple sample assembly for B_6O crystal growth. The starting materials were encapsulated in an h-BN capsule layer upon layer, with milled B_2O_3 at both the bottom and top of the capsule, and boron in the middle. Runs 056 and 113, etc. were performed using this sample assembly. Because high temperature of 1400 °C is favored for the synthesis of B_6O, most runs were performed at 1400 °C.

Runs 054, 105 and 104 were performed at 1 GPa and 1400 °C for 2 h under these three reaction conditions. The SEM photographs of the recovered samples are shown in Fig. 4. All the three samples were euhedral B_6O grains. Well-crystallized icosahedral B_6O grains were not found. Run 109 was performed at 1 GPa and 1400 °C for 6 h and the recovered sample was also euhedral B_6O grains (Fig. 4d).

Runs 120, 121 and 056 were performed at 2 GPa and 1400 °C for 6 h under these three reaction conditions. The SEM photographs of the recovered samples are shown in Fig. 5. Samples 120 and 121 were still euhedral B_6O grains, while sample 056 was very different from them. Many icosahedral B_6O grains with sizes ranging from 100 nm to 1.3 μm were found in sample 056. Some euhedral B_6O grains were also found but were less than icosahedral B_6O grains. This result was supported by the photograph Fig. 5f, in which many icosahedral B_6O grains with size around 100 nm were found. The synthesis of icosahedral B_6O particles supports that high pressure applied during the synthesis of B_6O can significantly increase the crystallinity of the products, in line with the results from Hubert's experiments [5,6].

Different reaction conditions resulted in different product morphologies. Better product was obtained with starting materials encapsulated layer upon layer. This result agrees with He's study that sample assembly can affect the reaction outcome [3]. When the starting materials were mixtures of boron and milled boron oxide, B_6O nucleated randomly throughout the sample and the neighboring grains interfered with each other in their growth stage, which prevented the formation of icosahedral B_6O grains.

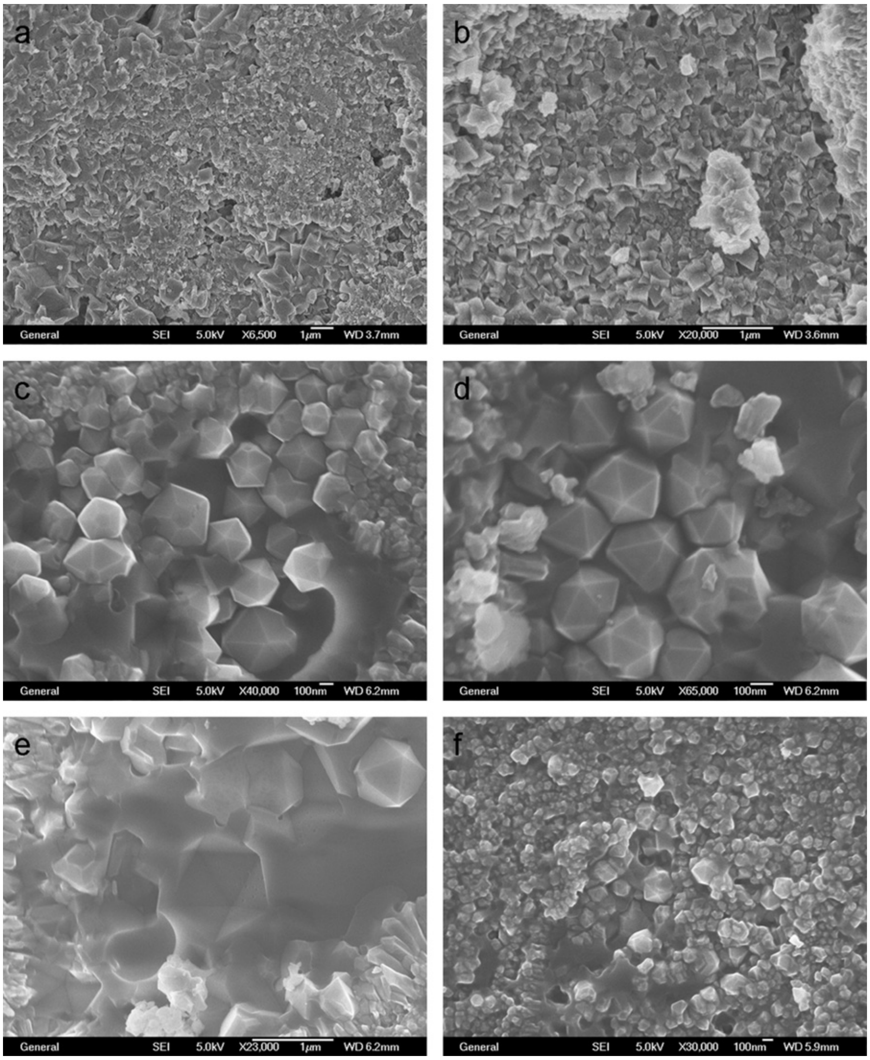

Fig. 5. SEM photographs of samples from run 120, 121 and 056. (a) SEM photograph of sample 120, (b) SEM photograph of sample 121 and (c–f), SEM photographs of sample 056.

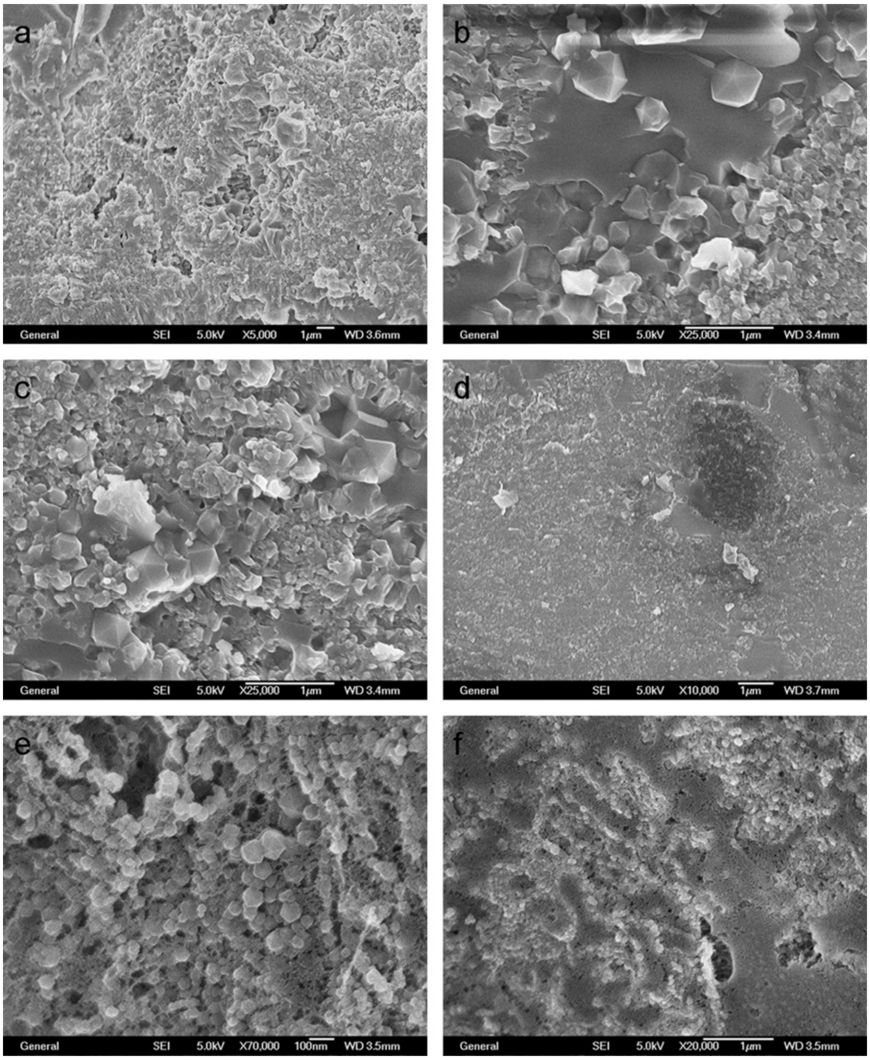

Fig. 6. SEM photographs of samples from run 115, 117, 107 and 113. (a) SEM photograph of sample 115, (b,c) SEM photographs of sample 117, (d) SEM photograph of sample 107 and (e,f) SEM photographs of sample 113.

When the starting materials were encapsulated layer upon layer, a B_6O–B_2O_3 eutectic melt was formed at a suitable pressure–temperature condition while boron in the middle was dissolved into the B_2O_3 flux. When the B_6O–B_2O_3 supersaturated solution was formed, B_6O was deposited at the bottom of the h-BN capsule. When more boron reacted with B_2O_3, more B_6O was deposited, which maintained the growth of B_6O crystals. Eventually, B_6O crystals with size over 1 μm were obtained in sample 056.

The effect of reaction time on the growth of B_6O crystal was studied. Using the same sample assembly in run 056, runs 115, 117 and 107 were performed at 2 GPa and 1400 °C for 2, 24 and 48 h, respectively. The SEM photographs of the recovered samples are shown in Fig. 6. Samples 115 and 107 were composed of euhedral B_6O grains. Icosahedral B_6O grains were found in sample 117. But euhedral B_6O grains were much more than icosahedral B_6O grains, which was different from sample 056. These results indicated that icosahedral B_6O grains with 5-fold symmetry are not stable with long reaction time. The optimal reaction time is 6 h.

Higher pressure was also applied to synthesize B_6O in order to obtain large B_6O crystal, such as the B_6O grain 40 μm in diameter obtained by Hubert et al. [6]. Sample 113 prepared at 5 GPa and 1700 °C for 30 min was a homogeneous B_6O grain with an average size less than 100 nm (Fig. 6e and f). A large B_6O crystal was not obtained.

Based on the results above, the optimal synthesis condition of icosahedral B_6O grain is at 2 GPa and 1400 °C for 6 h, and the favored sample assembly is that the starting materials were encapsulated in an h-BN capsule layer upon layer, with milled B_2O_3 at both the bottom and top of the capsule.

3.3. Hardness

Sample 056 was polished for the Vickers hardness testing. However, most of the B_6O particles are smaller than 1 μm, and thus a precise hardness value of icosahedral B_6O grain cannot be obtained. Because sample 056 is a sinter of small B_6O grains, we can just get a hardness value of B_6O sinter, which is lower than the hardness value of icosahedral B_6O grain. The hardness of B_6O sinter reported previously ranges from 31 to 38 GPa [8,16–18]. An indentation experiment was performed to study the hardness of sample 056. The hardness was evaluated by MTS Nanoindenter XP with CSM (continuous stiffness measurements) mode. Fig. 7 shows the load–displacement curve of sample 056. Based on this curve, an average hardness of 32.3 GPa was obtained, which is consistent with previous reports.

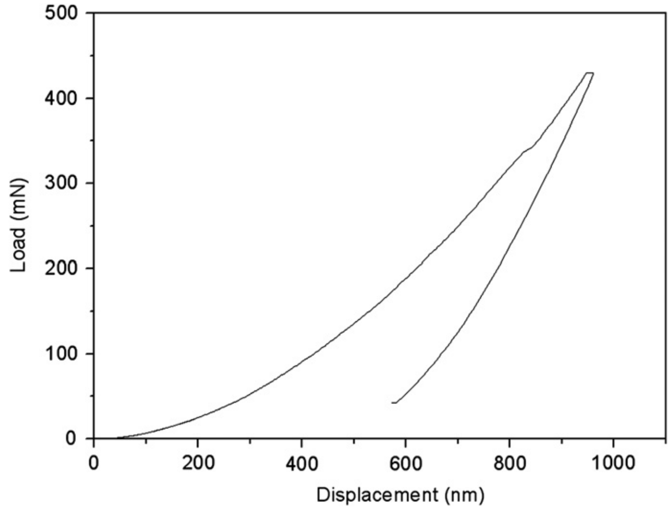

Fig. 7. Load–displacement curves of sample 056.

3.4. Thermal stability

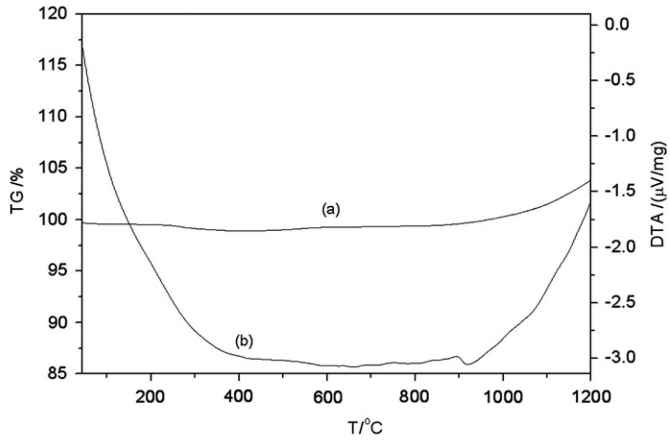

Fig. 8. TG–DTA curves for sample 056. (a) TG curve and (b) DTA curve.

Because the oxygen content of B_6O is lower than that of B_2O_3, B_6O can be oxidized to B_2O_3 at high temperature, with an observable weight increase. Therefore, thermogravimetry analysis was used to study the thermal stability of the recovered sample. Bulk 056 sample was selected for analysis. Fig. 8 shows the thermogravimetry analysis curve of sample 056. Bulk 056 sample exhibited an oxidation resistance in air up to 1000 °C and mild oxidation in the temperature range of 1000–1200 °C, which was higher than the temperatures observed for diamond (about 800 °C) [23]. Itoh et al. [17] reported that sintered B_6O exhibited an oxidation resistance in air up to 600 °C and mild oxidation in the temperature range of 700–1000 °C. Comparing sample 056 with sintered B_6O, the former has higher thermal stability. This result also suggests that B_6O crystal has higher thermal stability than B_6O powder.

A range of outstanding physical and chemical properties of B_6O have been reported, such as high hardness, low mass density, high thermal conductivity, high chemical inertness and excellent wear resistance [3,7–10]. Due to the high pressure and temperature required for the synthesis of B_6O crystal, it is expensive to synthesize B_6O crystal for industrial use. Here we report the synthesis of icosahedral B_6O crystals at 2 GPa and 1400 °C, which is a very mild condition. The high thermal stability of B_6O is also demonstrated. The newly prepared B_6O crystal could be used as a substitute for diamond and c-BN in industry. For instance, B_6O can be used in the manufacturing of abrasives, cutting tools and scratch-resistant coatings.

4. Conclusion

Well-crystallized icosahedral B_6O grains with sizes ranging from 100 nm to 1.3 µm were synthesized using ball milled B_2O_3 under lower pressure and temperature. The milled starting material can lower the pressure and temperature needed for the synthesis of B_6O. Boron and milled B_2O_3 were encapsulated in an h-BN capsule layer upon layer and reacted at 2 GPa and 1400 °C for 6 h. The temperature of 1400 °C is favored for the growth of icosahedral B_6O grains. High pressure applied during the synthesis of B_6O can significantly increase the crystallinity of the products. Long reaction time was found to be detrimental for the growth of well-crystallized icosahedral B_6O grains. The Vickers hardness of our B_6O sample is 32.3 GPa, which is consistent with previous reports. We also showed that the thermal stability of bulk B_6O sample (sample 056) was higher than diamond. B_6O could be a potential substitute for diamond in industry.

Acknowledgments

This work was supported by the National Sciences Foundation of China (nos. 20471022, 40673051 and 20121103) and NCET.

References

[1] C.-M. Sung, M. Sung, Mater. Chem. Phys. 43 (1996) 1–18.
[2] P.F. McMillan, Nat. Mater. 1 (2002) 19–25.
[3] D. He, Y. Zhao, L. Daemen, J. Qian, T.D. Shen, T.W. Zerda, Appl. Phys. Lett. 81 (2002) 643–645.
[4] V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, D.C. Rubie, Appl. Phys. Lett. 78 (2001) 1385–1387.
[5] H. Hubert, B. Devouard, L.A.J. Garvie, M. O'Keeffe, P.R. Buseck, W.T. Petuskey, P.F. McMillan, Nature 391 (1998) 376–378.
[6] H. Hubert, L.A.J. Garvie, B. Devouard, P.R. Buseck, W.T. Petuskey, P.F. McMillan, Chem. Mater. 10 (1998) 1530–1537.
[7] S. Lee, S.W. Kim, D.M. Bylander, L. Kleinman, Phys. Rev. B 44 (1991) 3550–3554.
[8] H.F. Rizzo, W.C. Simmons, H.O. Bielstein, J. Electrochem. Soc. 109 (1962) 1079–1082.
[9] T. Lundström, Y.G. Andreev, Mater. Sci. Eng., A 209 (1996) 16–22.
[10] T. Lundström, J. Solid State Chem. 133 (1997) 88–92.
[11] A.R. Badzian, Appl. Phys. Lett. 53 (1988) 2495–2497.
[12] V. Srikanth, R. Roy, E.K. Graham, D.E. Voigt, J. Am. Ceram. Soc. 74 (1991) 3145–3147.
[13] X. Liu, X. Zhao, W. Hou, W. Su, J. Alloys Compd. 223 (1995) L7–L9.
[14] M. Olofsson, T. Lundström, J. Alloys Compd. 257 (1997) 91–95.
[15] D. He, M. Akaishi, B.L. Scott, Y. Zhao, J. Mater. Res. 17 (2002) 284–290.
[16] R. Sasai, H. Fukatsu, T. Kojima, H. Itoh, J. Mater. Sci. 36 (2001) 5339–5343.
[17] H. Itoh, I. Maekawa, H. Iwahara, J. Soc., Mater. Sci. Jpn. 47 (1998) 1000.
[18] H. Itoh, R. Yamamoto, H. Iwahara, J. Am. Ceram. Soc. 83 (2000) 501–506.
[19] T. Taniguchi, M. Akaishi, S. Yamaoka, J. Mater. Res. 14 (1999) 162–169.
[20] S.R. Bohlen, Neues Jahrb. Mineral. Monatsh. 9 (1984) 404–412.
[21] S.R. Bohlen, A.L. Boettcher, J. Geophys. Res. 87 (1982) 7073–7078.
[22] H. Hubert, L.A.J. Garvie, P.R. Buseck, W.T. Petuskey, P.F. McMillan, J. Solid State Chem. 133 (1997) 356–364.
[23] P. John, N. Polwart, C.E. Troupe, J.I.B. Wilson, Diamond Relat. Mater. 11 (2002) 861–866.