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Synthesis and Crystallization of Hexagonal Boron Nitride in Liquid Sodium Amide

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Hexagonal boron nitride was synthesized from MB_6 (M = Ca and La) in liquid sodium amide at 600 °C. The as-synthesized boron nitride powders were composed of sub-micrometer-sized triangles and hexagons.

In solid-state metal hexaborides, the B_6 clusters are octahedral B_6-cages and form a three-dimensional network with metal atoms. The best-known examples of these metal–polyboron compounds are CaB_6 and LaB_6, in which a corresponding metal atom compensates the binding requirement of a cage by donating two electrons. A lot of studies on structure and aromaticity show that a B_6^{2-} dianion has four π-electrons and has an unusual planar or quasi-planar geometry. B_6-clusters, cages or dianions with this exceptional stable covalent bonding are speculated to have broad implications for both organic and inorganic chemistry, and they may be uniquely suited for certain applications.[1–3]

As a convenient boron source, metal borides have been frequently used for synthesizing various forms of boron nitrides.[4–7] Nanotubes and some interesting structures of boron nitrides were obtained by arc-melting metal–hexaboride powders in nitrogen gas.[8,9] Previously, fullerene-like boron nitride with vessel, hollow sphere, onion, and peanut nanostructures were prepared by a self-propagation reaction of BBr_3 with the solid-state nitriding reagent, $NaNH_2$.[10,11] In this communication, we report a mild isothermic conversion of MB_6 (M = Ca and La) into hexagonal boron–nitride (hBN) powders in liquid $NaNH_2$. The reaction can be described as follows,

$$\begin{aligned}&MB_6\ (M = Ca\ and\ La) + 6NaNH_2\\&\quad\rightarrow 6BN + M + 6Na + 6H_2.\end{aligned}\tag{1}$$

The reaction was carried out in a sealed stainless steel autoclave with a 60 mL capacity. In a typical process, 1.75 g of CaB_6 or 3.4 g of LaB_6 mixed with 4–8 g of $NaNH_2$ in a glove box with flowing dry argon, and the mixture was put in the autoclave. After it was sealed, the autoclave was heated in a furnace at 600 °C for 24 h. Then, absolute ethanol was added into the autoclave to react with residual $NaNH_2$ and metallic sodium after the autoclave cooled to room temperature naturally. There was a high pressure of hydrogen and nitrogen in the sealed autoclave, which was estimated to be about 25–40 MPa, and the crude products in the autoclave were flammable solids, incompatible with water and strong oxidizing agents. After overnight immersion in a beaker, the precipitate was treated with 1 M nitric acid and washed with distilled water. A white powder of hBN was obtained after drying the precipitate at 80 °C for 24 h in vacuum. The yields were more than 97% based on the corresponding metal hexaborides.

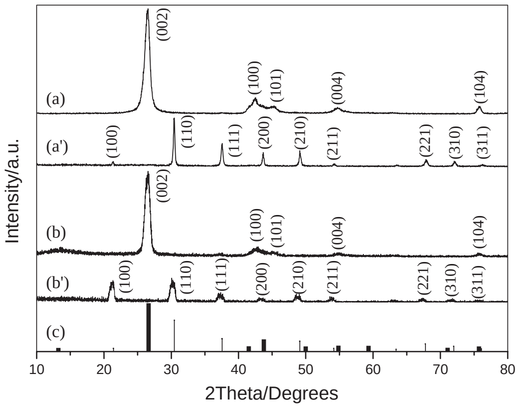

Fig. 1. XRD patterns of the as-synthesized hBN: (a) $CaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; (a′) CaB_6; (b) $LaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; (b′) LaB_6; (c) bold lines: hBN in PCPDF card #85-1068; fine lines: c-CaB_6 in PCPDF card #89-4304.

Before this work, crystallization and growth of hBN have been performed in $NaNH_2$ flux[12] and liquid sodium (700–800 °C).[13,14] According to thermodynamic calculations, the reaction of MB_6 (M = Ca and La) and $NaNH_2$ is exothermic. In our experimental procedure, excessive $NaNH_2$ acts not only as the nitriding agent, but also as crystallization and growth media and a heat sink.

The isothermic conversion of MB_6 (M = Ca and La) into hBN in liquid $NaNH_2$ at 600 °C for 24 h can be seen from the X-ray powder diffractions (XRD) of the final products recorded on an MSAL-XD2 X-ray diffractometer using Cu Kα radiation (wavelength $\lambda = 1.5406$ Å). As shown in Fig. 1a, the five peaks at d-spacings of 3.350, 2.123, 2.004, 1.673, and 1.252 Å can be indexed as the (002), (100), (101), (004), and (110) planes of hBN, respectively. The lattice constants are calculated as $a = 2.484$ and $c = 6.687$ Å, close to the literature values ($a = 2.510$ and $c = 6.690$ Å in PCPDF card #85-1068). A similar result was also found for the product shown in Fig. 1b, and both of the samples have good crystallinity. Figures 1a′ and 1b′ show the XRD spectra of the starting powders CaB_6 and LaB_6, respectively. No residual reactants and other impurities were detected in the final hBN powders.

Further evidence for the complete conversion of the metal hexaborides can be seen from the X-ray photoelectron spectra (XPS) in Fig. 2, which were recorded on an ESCALAB 250 (Thermao Electron Corp.) using Al Kα as the excitation source, and the binding energies were calibrated by using carbon C1s at 285.5 eV as a reference. In the wide-scan spectra of the two samples as shown in Figs. 2a and 2b, both contain boron, reference carbon, nitrogen, and small amount of oxygen. Oxygen may be due to surface adsorption. Ca and La were

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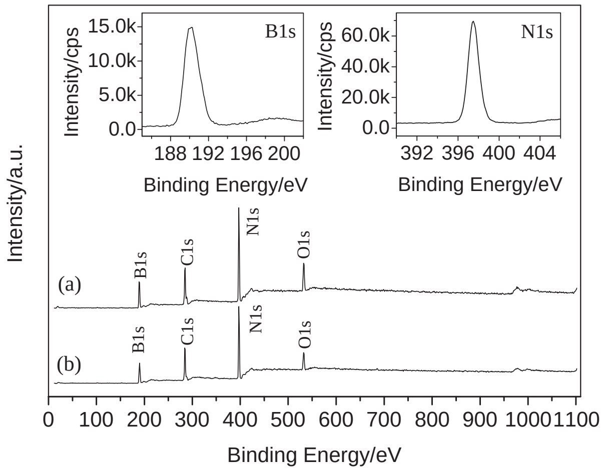

Fig. 2. XPS spectra of the hBN samples: (a) $CaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; (b) $LaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; Inset B1s and N1s spectra of (a).

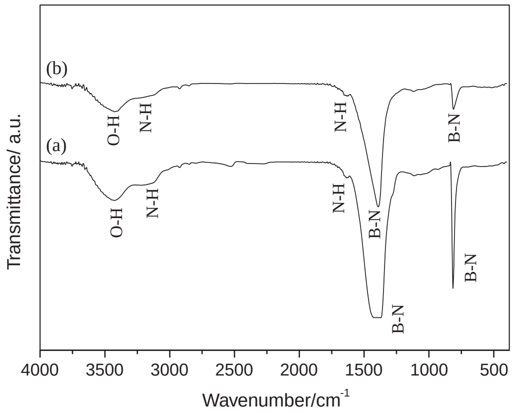

Fig. 3. FT-IR spectra of the hBN samples: (a) $CaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; (b) $LaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h.

not detected. From quantitative analysis, the molar ratios of B:N are 1.021:1 and 1.034:1, respectively, which is close to that of BN. The binding energies of the B1s and N1s peaks (insets) are centered at 190.1 and 379.5 eV, in good agreement with the reported value for hBN.[15]

The Fourier transform infrared (FTIR) spectra of the hBN samples are shown in Fig. 3, which were recorded on a Bruker Equinox 55 Fourier FT-IR spectrometer in transmission mode using a KBr wafer. They show two characteristic absorption peaks that are assigned to hBN. The strongest absorption peak at 1387 cm^{-1} can be ascribed to the in-plane stretching of B–N bonds, and the second at 809.4 cm^{-1} can be attributed to the out-plane bending of the B–N–B bonds.[16] The weak peaks at 3145 and 1635 cm^{-1} are assigned to N–H bonds of surface NH_2 groups, while the broad absorptions around 3438 cm^{-1} for O–H bonds due to the adsorption water.

The as-synthesized hBN is composed of mainly flake-shaped triangles and hexagons, which are nearly equilateral. Figure 4 shows the transmission electron micrographs (TEM) taken on a Philips Tecnai-10 transmission electron microscope and scanning electron micrographs (SEM) taken on an Oxford Quanta 400 FEG/INC/HKL thermal FE scanning electron microscope. Statistically, the triangles have an average side of about 400 nm and thickness of 10–50 nm, while the hexagons have an average side of about 320 nm and thickness of 50–80 nm. Unlike the previous reported nanotubes prepared by an arc-melting method and fullerene-like boron nitrides by rapid synthetic routes,[8–11] the isothermic conversion of MB_6 (M = Ca and La) in liquid $NaNH_2$ led to dominant two-dimensional hBN crystallites. In the sealed autoclave at 600 °C, the excess $NaNH_2$ (melt point 210 °C) and metallic sodium (melt point 97.82 °C) provided a liquid media for crystallization and growth of hBN. The liquid environment may play a significant role in forming the high crystalline triangles and hexagons.

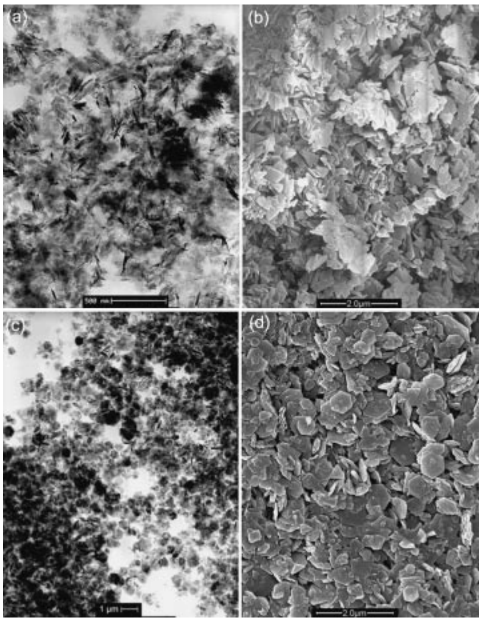

Fig. 4. TEM (left) and SEM (right) micrographs of the hBN samples: (a) and (b), $CaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h; (c) and (d): $LaB_6/nNaNH_2$ ($n = 12$), 600 °C for 24 h. Scale bar: (a) 500 nm, (b) 2 μm, (c) 1 μm, and (d) 2 μm.

In summary, isothermic conversion of MB_6 (M = Ca and La) into hBN in liquid $NaNH_2$ at 600 °C for 24 h in a sealed autoclave was investigated. Hexagonal boron nitride was synthesized with yields of more than 97% based on MB_6. The as-synthesized hBN powders were mainly composed of sub-micrometer-sized flakes of triangles and hexagons.

References

1 J. Aihara, H. Kanno, T. Ishida, *J. Am. Chem. Soc.* **2005**, *127*, 13324.

2 R. N. Grimes, *J. Chem. Educ.* **2004**, *81*, 658.

3 Q. S. Li, Q. J. Jin, *Phys. Chem. A* **2003**, *107*, 7869.

4 B. Bokhonov, M. Korchagin, Y. Borisova, *J. Alloys Compd.* **2004**, *372*, 141.

5 K. P. Loh, M. Lin, M. Yeadon, C. Boothroyd, Z. Hu, *Chem. Phys. Lett.* **2004**, *387*, 40.

6 G. J. Zhang, H. F. Yang, M. Ando, T. Ohji, *J. Am. Ceram. Soc.* **2002**, *85*, 2938.

7 T. E. Warner, D. J. Fray, *J. Mater. Sci.* **2000**, *35*, 5341.

8 A. Nishiwaki, T. Oku, *J. Eur. Ceram. Soc.* **2006**, *26*, 435.

9 I. Narita, T. Oku, *Diamond Relat. Mater.* **2003**, *12*, 1912.

10 L. Y. Chen, Y. L. Gu, L. Shi, Z. H. Yang, J. H. Ma, Y. T. Qian, *Solid State Commun.* **2004**, *130*, 537.

11 F. Xu, Y. Xie, X. Zhang, S. Y. Zhang, X. M. Liu, X. B. Tian, *Inorg. Chem.* **2004**, *43*, 822.

12 A. P. Purdy, *Abstr. Pap. Am. Chem. Soc.* **2004**, *228*, U865.

13 M. Yano, M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori, T. Sasaki, *Diamond Relat. Mater.* **2000**, *9*, 512.

14 M. Yano, Y. K. Yap, M. Okamoto, M. Onda, M. Yoshimura, Y. Mori, T. Sasaki, *Jpn. J. Appl. Phys.* **2000**, *39*, L300.

15 R. Trehan, Y. Lifshitz, J. W. Rabalais, *J. Vac. Sci. Technol., A* **1990**, *8*, 4026.

16 J. M. Caicedo, G. Bejarano, G. Zambrano, E. Baca, O. Moran, P. Prieto, *Phys. Status Solidi B* **2005**, *242*, 1920.