

## Effects of Temperature Raising Speed on the Growth of BN Crystals in Hydrothermal Solutions

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Cubic boron nitride (cBN) and orthorhombic boron nitride (oBN) crystals have been prepared in hydrothermal solutions by reacting  $\text{H}_3\text{BO}_3 + \text{NaN}_3 + \text{P}$  and  $\text{H}_3\text{BO}_3 + \text{NaN}_3 + \text{N}_2\text{H}_4$  respectively. The experimental results indicated that, if the temperature was increased rapidly, both the yield and perfectness of BN crystals became poor. On the contrast, the yield and perfectness of BN crystals can be improved very much by slowly increasing the temperature of the reaction mixture. The results of X-ray powder diffraction (XRD), Fourier transform infrared spectrum (FTIR) and high resolution transmission electron microscopy (HRTEM) proved that the samples were composed of oBN and cBN.

**Keywords** boron nitride, hydrothermal solution, reaction coupling effect

### Introduction

It is well known that boron nitride (BN) has many different phases. Hexagonal BN (hBN) possesses layered structure in which B and N atoms are bonded in  $\text{sp}^2$  form, whereas cubic BN (cBN), wurtzite BN (wBN) and orthorhombic BN (oBN) are formed by closely packed B and N atoms bonded in  $\text{sp}^3$  form.<sup>1</sup> Among them, cubic boron nitride (cBN) has attracted considerable attention for its extraordinary properties, such as extreme hardness, chemical inertness, high melting temperature, wide band gap and low dielectric constant. These merits are very important for the applications in microelectronic devices and protective coatings.<sup>2</sup> Furthermore, unlike diamond, cBN bulk crystals can be easily fabricated into n-type conductor by doping Si and p-type conductor by doping Be or Mg, so it is the ideal material for the fabrication of violet and ultraviolet light emitting diodes and laser diodes.

Since the synthesis of cBN in 1957,<sup>3</sup> a series of methods have been attempted to synthesize cBN micro-crystals. Among them, high temperature & high pressure (HTHP) synthesis method is the most widely used route to obtain cBN.<sup>4</sup> In this paper, we developed a new route to synthesize cBN and oBN micro-crystals in hydrothermal solutions. And for the first time, we noticed from the experimental results that, the raising speed of the temperature of reaction mixture has important effect on the yield and perfectness of BN crystals.

### Experimental

#### Synthesis of BN crystals

The precursors for synthesize BN crystals were boric acid ( $\text{H}_3\text{BO}_3$ , A.R.), sodium azide ( $\text{NaN}_3$ , A.R.), hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , A.R.) and white phosphor (P, A.R.).

At first, 2.50 g of  $\text{H}_3\text{BO}_3$  and 8.00 g of  $\text{NaN}_3$  were dissolved into 80 mL of deionized water. After stirring for 30 min, 2.30 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (or 1.30 g P) was added to the mixed solution. Having been stirred for another 30 min, the mixed solution was transferred into a stainless steel autoclave. After the air was expelled by high purity nitrogen, the autoclave was sealed and heated to 400 °C for 48 h. In order to investigate the effects of temperature raising speed on the formation of BN crystals, three comparative experiments were conducted in which the temperature raising speeds were 0.1, 2.0 and 7.0 °C/min respectively. When the reaction was finished, the resultant products were washed with deionized water and dried in vacuum at 100 °C for 2—3 h.

#### Characterization of the samples

X-ray powder diffraction pattern of BN crystals was obtained on a Rigaku D max- $\gamma$ A X-ray diffractometer with Ni filtered Cu K $\alpha$  radiation ( $E=50$  kV,  $I=100$  mA), the scanning speed was 4 (°)/min. The FTIR measurement was carried out on a Nicolet FTIR760

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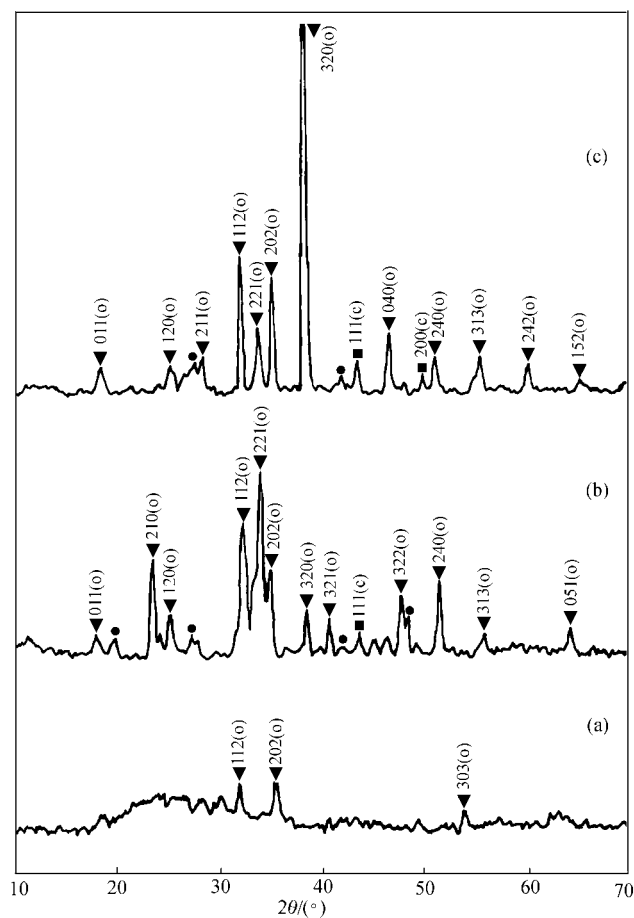
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infrared spectrometer using pressed KBr pellets (BN content was 5%). The morphology of crystalline BN was observed with a Hitachi H-800 transmission electron microscope (TEM) and the high resolution transmission electron microscope (HRTEM) photo graph was taken on a Philips Tecnai 20U-Twin high-resolution transmission electron microscope.

## Results and discussion

It is well known that, in hydrothermal solution,  $B_2O_3$  and  $H_3BO_3$  are much more stable than BN,<sup>5</sup> so it is conventionally believed that BN can not be prepared by hydrothermal synthesis method. On the other hand, if there are enough N atoms and reducing agents in the solution, BN may be more stable than  $B_2O_3$  and  $H_3BO_3$ . This case is just like the growth of diamond film from vapor phase.<sup>6</sup> Here we prepared BN samples from hydrothermal solutions by applying the reaction coupling effect between the reduction of  $H_3BO_3$  and the oxidation of P (or  $N_2H_4$ ), and  $NaN_3$  was used as a source of N atoms.

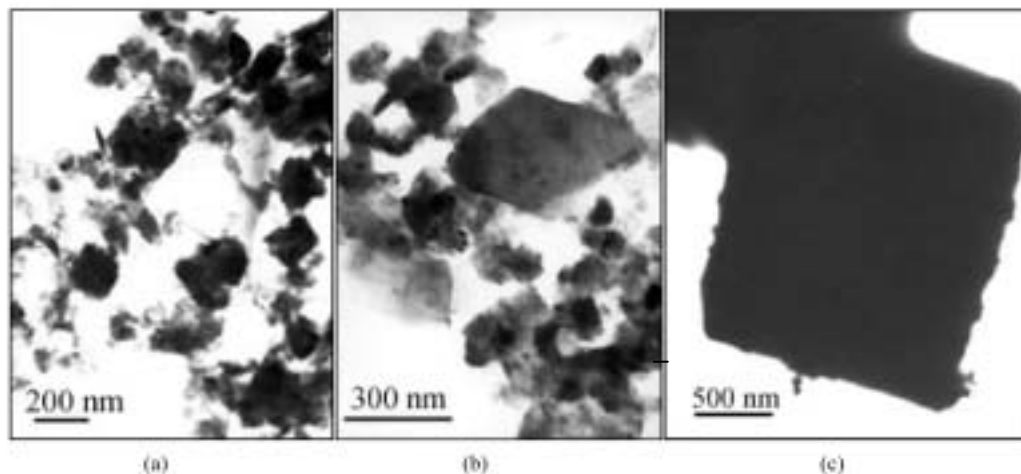
Sample (a) in Figure 1 was prepared by reacting 2.50 g of  $H_3BO_3$  + 8.00 g of  $NaN_3$  + 1.30 g of P at 400 °C for 48 h in water, and the raising speed of temperature was 7.0 °C/min. Samples (b) and (c) were synthesized at the similar condition except that the raising speeds of temperature were 2.0 °C/min and 0.1 °C/min respectively. In Figure 1, the peaks marked with squares belong to cubic BN (cBN), while the others can be indexed to the orthorhombic BN (oBN).<sup>7</sup> From this figure, it can be clearly seen that the crystalline perfectness of sample (a) is rather poor, while that of sample (b) or (c) is much better. Furthermore, both (111) and (200) diffraction peaks of cBN can be clearly seen in Figure 1 (c), whereas only (111) peak of cBN can be seen in Figure 1 (b). This result indicates that, the cBN content of sample (c) is higher than that of samples (b) and (a). From this experimental result, it can be believed that, both the perfectness of BN crystals and the cBN content can be



**Figure 1** XRD patterns of samples prepared with P as reducing agent. The temperature raising speeds are (a) 7.0 °C/min, (b) 2.0 °C/min and (c) 0.1 °C/min.

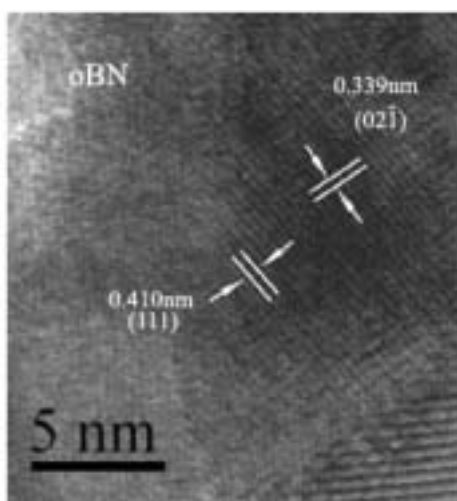
improved by slowing down the temperature raising speed.

Another proof for the above conclusion comes from the TEM photos of samples (a), (b) and (c). Figure 2 (a),



**Figure 2** TEM photos of samples (a), (b) and (c) in Figure 1.

(b) and (c) are the photos of samples (a), (b) and (c) respectively. In sample (a), it is very difficult to find a crystal with large size and perfect shape. On the contrast, the crystal shape in sample (b) is more perfect than that of sample (a). Moreover, crystals with size as large as 1–3  $\mu\text{m}$  and cubical shapes can be easily found in sample (c). Figure 3 is the HRTEM photo of sample (c), the planes with distances of 0.410 nm and 0.339 nm corresponded to (111) and (02 $\bar{1}$ ) planes of oBN respectively. This result shows that oBN crystals can be prepared from hydrothermal solutions.

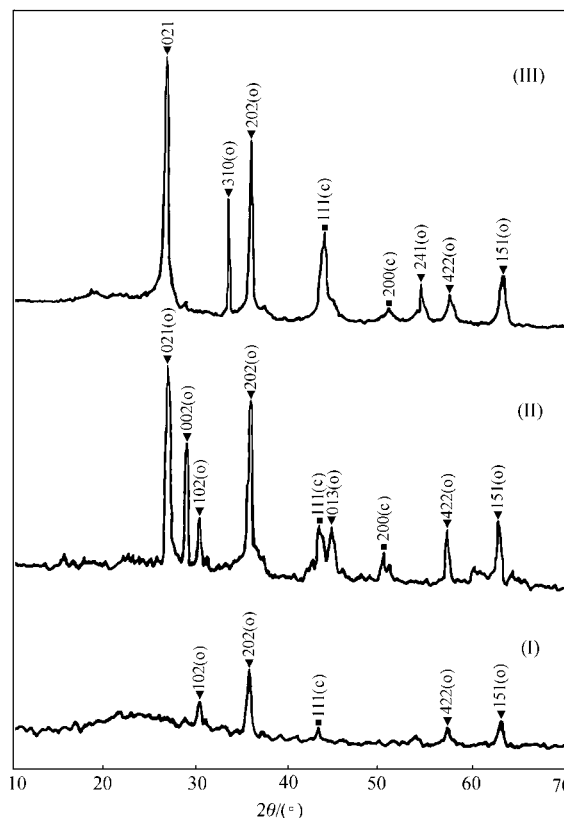


**Figure 3** HRTEM photo of oBN in Figure 1 (c).

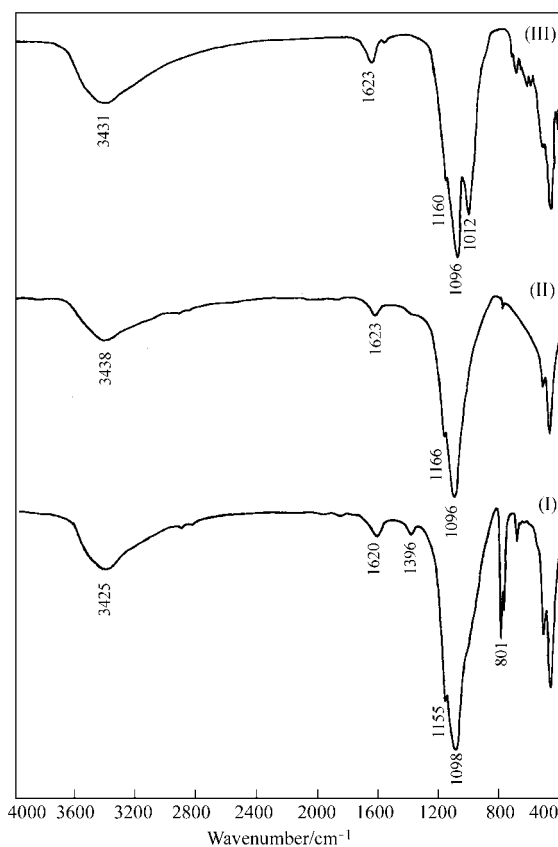
Also in Figure 1, the peaks denoted with “●” can be indexed to  $\text{BPO}_4$ ,<sup>8</sup> and it can be found from the experiments that,  $\text{BPO}_4$  always coexisted with BN when P was used as reducing agent. Aimed to eliminate  $\text{BPO}_4$  from the samples, P was replaced by  $\text{N}_2\text{H}_4$  as reducing agent in the following experiments.

In Figure 4, sample (I) was prepared by reacting 2.50 g of  $\text{H}_3\text{BO}_3$  + 8.00 g of  $\text{NaN}_3$  + 2.30 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  at 400  $^\circ\text{C}$  for 48 h in water, the raising speed of temperature was 7.0  $^\circ\text{C}/\text{min}$ . Samples (II) and (III) were synthesized under the same condition except that the raising speeds of temperature were 2.0  $^\circ\text{C}/\text{min}$  and 0.1  $^\circ\text{C}/\text{min}$  respectively. Again, we found the similar phenomenon with that of Figure 1, namely, slowing down the temperature raising speed is beneficial to both the perfectness of BN crystals and the cBN content in samples.

The IR absorption spectra of the samples provide us another evidence for the above result obtained from the analysis of XRD patterns. In Figure 5 the peaks at 1096–1166  $\text{cm}^{-1}$  can be attributed to the TO modes of cBN and oBN, and the peak at 1012  $\text{cm}^{-1}$  belongs to the reststrahlen spectrum of c-BN, while the peak at 1396  $\text{cm}^{-1}$  is the characteristic one of hBN in-plane B—N bond stretch mode, and 801  $\text{cm}^{-1}$  comes from the absorption of the bending mode of B—N—B bonds



**Figure 4** XRD patterns of samples prepared with  $\text{N}_2\text{H}_4$  as reducing agent. The temperature raising speeds are (I) 7.0  $^\circ\text{C}/\text{min}$ , (II) 2.0  $^\circ\text{C}/\text{min}$  and (III) 0.1  $^\circ\text{C}/\text{min}$ .



**Figure 5** FTIR spectra of samples (I), (II) and (III) in Figure 4.

between the basal planes of hBN.<sup>9</sup> The peaks at 3425—3431  $\text{cm}^{-1}$  and 1620—1623  $\text{cm}^{-1}$  arose from the absorption of  $\text{H}_2\text{O}$  molecules adsorbed on the surface of the BN crystals.<sup>10</sup> It should be noted that, on the spectra of samples (I) and (II), the peaks at 1012, 1096 and 1160  $\text{cm}^{-1}$  are almost undistinguishable from each other. This phenomenon means that the oBN and cBN particles are very small, and there may also be some amorphous phases. On the contrast, the absorption peaks at 1012 and 1096  $\text{cm}^{-1}$  of sample (III) can be clearly distinguished. Furthermore, they become narrower than those of samples (I) and (II), indicating that the perfectness of sample (III) is better than samples (I) and (II). From the TEM photos of these samples in Figure 6, we can find a large amount of amorphous phases in sample (I), and the crystal shape is relatively regular in sample (II), whereas in sample (III), the amount of crystals with cubical shape is obviously increased.

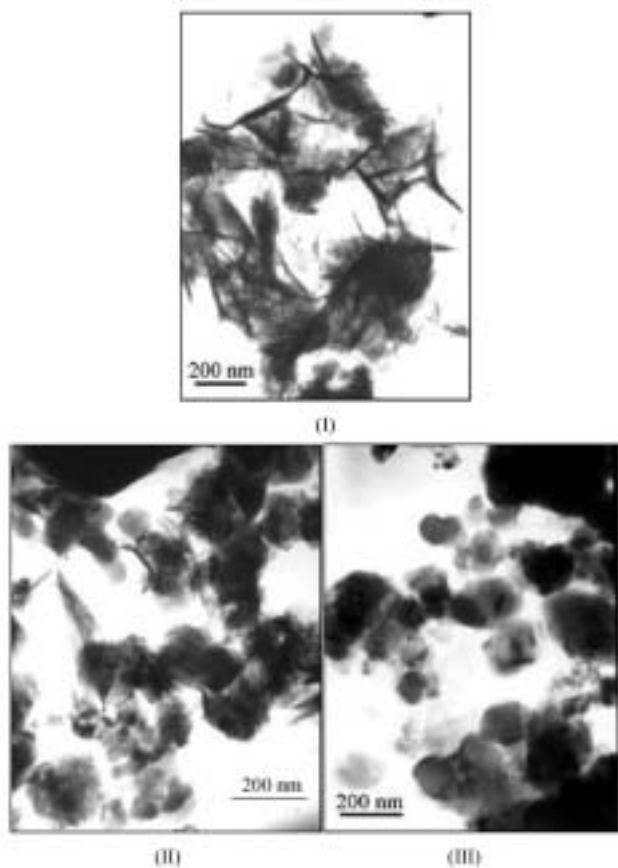
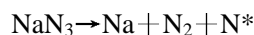


Figure 6 TEM photos of samples (I), (II) and (III) in Figure 4.

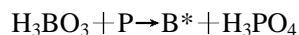
Although much work has to be done to understand the reaction process of synthesizing BN from hydrothermal solutions, a preliminary explanation about the above experimental results may still be proposed. One possible reason for the above results is that, during the process of increasing temperature, the amorphous BN will dissolve into water and re-crystallize later. Thus the crystalline perfectness of BN is improved. Another pos-

sible reason may be as follows:

During the reaction process,  $\text{NaN}_3$  may decompose rapidly in the following way<sup>11</sup>:



On the contrast, the speed of the following reaction may be comparatively slow:



Here  $\text{N}^*$  and  $\text{B}^*$  represent the highly reactive atoms.

If the temperature was increased to high temperature with fast speed, for example 7.0  $^\circ\text{C}/\text{min}$ , there would be too much excess amount of  $\text{N}^*$  in the reaction mixture. At the same time, the concentration of  $\text{B}^*$  is rather low. In this case,  $\text{N}^*$  will be exhausted at the beginning of reaction process. As a result, both the perfectness and the yield of BN crystals become poor.

## Conclusion

Both P and  $\text{N}_2\text{H}_4$  can be used as reducing agents in the synthesis of BN from hydrothermal solutions, but the mismatch in the reaction speed between the reduction of  $\text{H}_3\text{BO}_3$  and the oxidization of P (or  $\text{N}_2\text{H}_4$ ) deteriorated the perfectness and yield of BN. From the results reported in this manuscript, it is known that slowly raising the temperature of the reaction mixture may be an effective way to overcome this difficulty.

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