

# Reaction of Hexagonal Boron Nitride Nano-crystals under Mild Hydrothermal Conditions

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*Dedicated to Professor Gérard Demazeau on the occasion of his 65<sup>th</sup> birthday*

The reaction between hexagonal boron nitride (*h*BN) nano-crystals and water at low temperature and low pressure has been investigated. The results reveal that this reaction can be greatly promoted by increasing the hot-pressing temperature. However, when the temperature is above 280 °C, the reaction is too fast to be controlled by varying the hot-pressing pressure and time. On the other hand, stress and defects are induced in *h*BN nano-crystals by the hydrothermal hot-pressing process, resulting in a shift of the IR absorption bands and a deterioration of crystalline perfection. These results may be useful for synthesizing *c*BN by the hydrothermal method and converting *h*BN nano-crystals into *c*BN under moderate conditions.

**Key words:** Hexagonal Boron Nitride, Hydrothermal Hot-press, Stress, Crystalline Perfection

## Introduction

Analogous to carbon, boron nitride usually exists in two forms: a hard, diamond-like cubic form and a soft, graphite-like hexagonal form [1]. The cubic form, cubic boron nitride (*c*BN), possessing many merits, such as superhardness, high thermal conductivity, high electrical resistivity and a wide band gap (~6.4 eV) *etc.* [2–4], has been widely used [5, 6]. Until now, most of *c*BN is synthesized by converting *h*BN micro-crystals using the high-pressure and high-temperature (HPHT) method [7, 8]. In order to prepare *c*BN at moderate conditions, many kinds of catalysts were investigated [9–12], and the temperature and pressure required for synthesizing *c*BN were greatly reduced. For example, water, urea and boric acid have been used as the catalysts, and the reaction between *h*BN micro-crystals and water has been investigated [13–15].

To the best of our knowledge, no paper about the reaction between *h*BN nano-crystals and water at low temperature and low pressure has been published as yet. It is well known that the stability of a nanocrystal is poorer than that of micro-crystals, just because of its high surface free energy [16, 17]. For example, it has been reported that phase transformations in ZnS nano-crystals can be induced at ambient temperature and

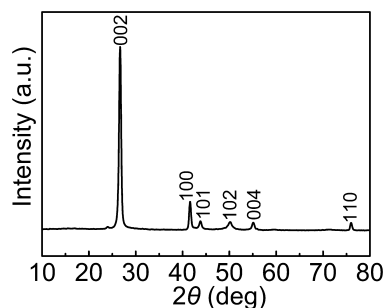


Fig. 1. XRD pattern of the starting material.

pressure by simply modifying its surface [18, 19]. So it can be prospected that *h*BN nano-crystals may possess higher reactivity than *h*BN micro-crystals, and the reaction between *h*BN nano-crystals and water might take place at milder conditions. Besides this, the phase transformation of *h*BN nano-crystals should take place at comparatively lower temperature and pressure. Furthermore, as a product of the reaction between *h*BN nano-crystals and water, the newly formed ammonium borate should be an effective starting reagent for synthesizing *c*BN by the hydrothermal method. On the basis of the above considerations, we have investigated the reaction between *h*BN nano-crystals and water at low temperature and low pressure, and the major results of this study are reported in this paper.

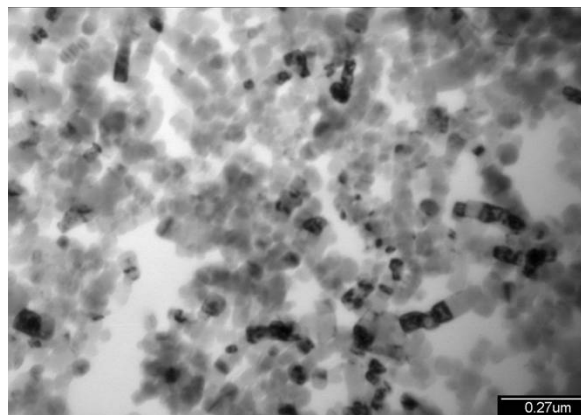


Fig. 2. TEM image of the starting material.

## Results and Discussion

### Characterization of the starting material

The phase of the starting material was identified by an XRD measurement. In Fig. 1, all the diffraction peaks can be indexed (*h*BN, JCPDS 34-0421), which indicates that the starting material should be single-phase *h*BN. Furthermore, the TEM image of the starting material revealed that the average size of the *h*BN particles was ~50 nm, and that it is quite uniform in particles size (Fig. 2).

In order to analyze the composition of the starting material, an XPS measurement was conducted, and the result is shown in Fig. 3. From this figure, it can be found that the bonding energies of B<sub>1s</sub> and N<sub>1s</sub> are 190.72 and 398.46 eV, respectively, which is in good agreement with the reported values [20]. Besides, the ratio of B : N could be estimated to be 1 : 1.04 by comparing the areas of the B<sub>1s</sub> and N<sub>1s</sub> peaks. These results, together with the XRD pattern, proved that the starting material was *h*BN.

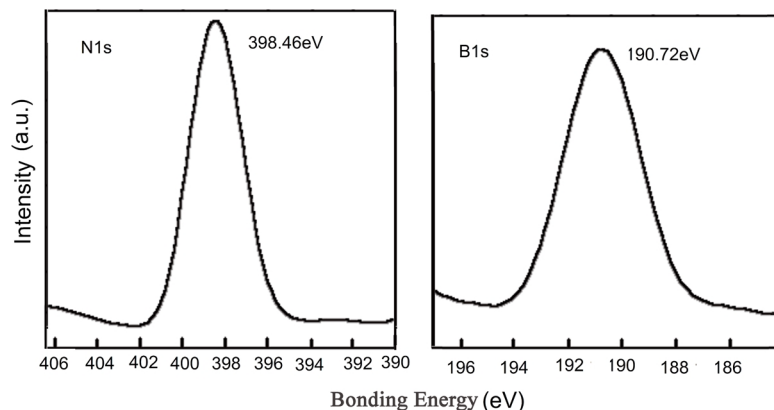


Fig. 3. XPS spectra of the starting material.

### Reaction between *h*BN nano-crystals and water

As a catalyst for synthesizing *c*BN by the HPHT method, the reaction between water and *h*BN micro-crystals under HPHT conditions was already investigated. According to the reported results, water reacts with *h*BN at 1200 °C and 5.6 GPa, yielding ammonium borate [12]. Now we are very interested in understanding this reaction under moderate conditions, because the newly formed ammonium borate may be an ideal starting reagent for synthesizing *c*BN by the hydrothermal method. Our result reveals that the major product is the same as that previously reported. However, the reaction between water and *h*BN nano-crystals starts at very low pressure and temperature, *i. e.* 220 °C and 1.0 MPa. In order to analyze the reaction process, a variable reaction rate ( $R_r$ ) is defined as follows:

$$R_r = \frac{m_f - m_i}{m_i} \times 100\%$$

where  $m_f$  is the residual weight of *h*BN after hydrothermal hot-pressing, and  $m_i$  is the initial weight of *h*BN at the beginning of hydrothermal hot-pressing.

It is clear from Fig. 4 (a) that the hot-pressing temperature plays a critical role in determining the  $R_r$  value of *h*BN nano-crystals, while the pressure plays a comparatively minor role. If the pressure was kept constant, the value of  $R_r$  increased strikingly with increasing temperature, *i. e.* the value of  $R_r$  increased from ~10 to ~95 % with the temperature increasing from 220 to 300 °C. Comparatively, the rate increase of  $R_r$  at a fixed temperature is much slower as the pressure increases. For example,  $R_r$  slowly increases with the pressure increase from 1.0 to 100 MPa at 260 °C, and the effect of pressure further declines when the temperature exceeds 280 °C. On the other hand, the hot-pressing

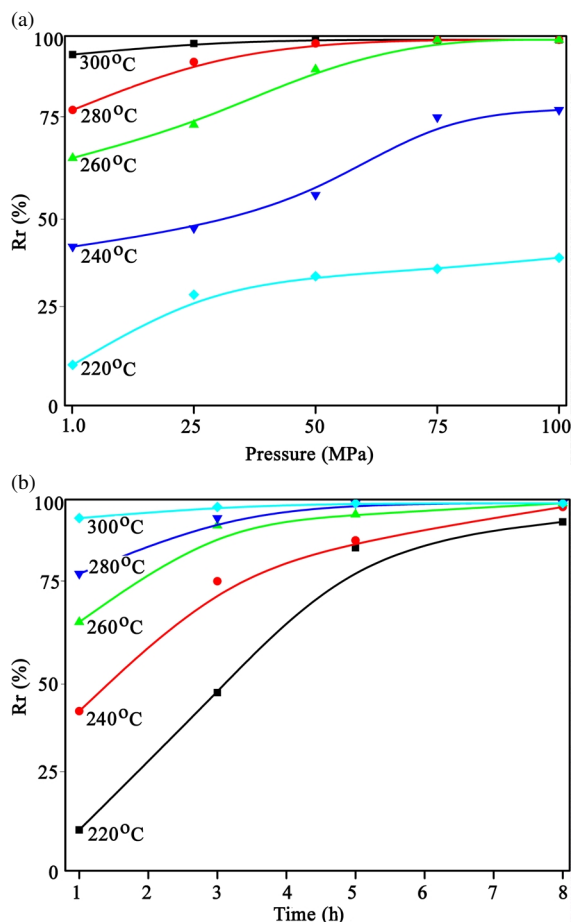


Fig. 4. Dependence of  $R_r$  on temperature, time and pressure. (a)  $R_r$  vs. pressure, the hot-pressing time is 1 h; (b)  $R_r$  vs. time, the pressure is 1.0 MPa.

time also affects the value of  $R_r$ , especially when the temperature is lower than 260 °C. In this instance,  $R_r$  gradually increases with the prolongation of the hot-pressing time. However, the reaction between *h*BN nano-crystals and water proceeds too fast at higher temperature, and is completed in a very short time.

The above results indicate that the rate of the reaction between *h*BN nano-crystals and water can be adjusted by controlling the hot-pressing temperature, pressure and time, and thus the speed of formation of ammonium borate can also be controlled in the same way. Besides, as stated above, the newly formed ammonium borate can be used as the starting reagent for synthesizing *c*BN by the hydrothermal method. This result provides the possibility of controlling the formation and growth process of *c*BN in hydrothermal solutions [21].

Table 1. IR absorption bands ( $\text{cm}^{-1}$ ) of the samples in Fig. 5.

Samples	(a)	(b)	(c)	(d)	(e)
Weak band	801	796	793	792	785
Strongest band	1387	1403	1404	1412	1419

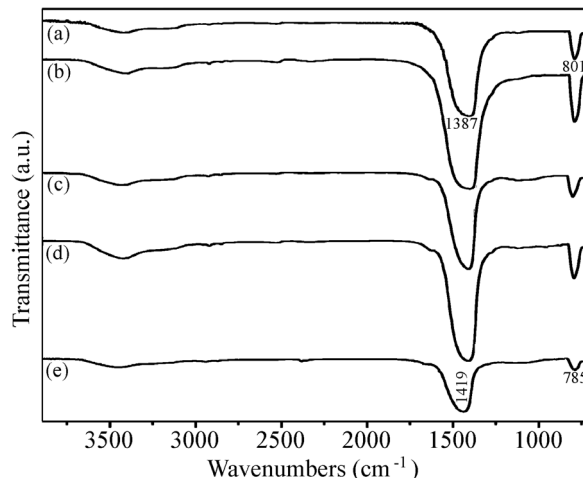


Fig. 5. FTIR spectra of *h*BN samples obtained after hot-pressing at 240 °C. (a) Starting material; (b) 1.0 MPa, 1 h; (c) 25 MPa, 1 h; (d) 50 MPa, 1 h; (e) 75 MPa, 1 h.

#### Stress in *h*BN nano-crystals and the deterioration of its crystalline perfection

Besides enhancing the reaction of *h*BN nano-crystals and water, the hydrothermal hot-pressing process also induces stress in the residual *h*BN nano-crystals and deteriorates their crystalline perfection. As an example, we analyzed the FTIR absorption spectra of the samples obtained by hot-pressing of the *h*BN starting materials at 240 °C, with pressures in the range from 1.0 to 75 MPa. In Fig. 5(a), the strongest band at 1387  $\text{cm}^{-1}$  is the characteristic absorption band of the B–N in-plane stretching vibration of *h*BN [22], while the weak band at 801  $\text{cm}^{-1}$  comes from the absorption of the bending vibration of the B–N–B bond in *h*BN. By comparing spectra (b), (c), (d) and (e) with (a), it can be found that the strongest band of *h*BN is gradually blue-shifted to 1419  $\text{cm}^{-1}$  when the pressure was increased to 75 MPa, while the weak band at 801  $\text{cm}^{-1}$  is red-shifted to 785  $\text{cm}^{-1}$ . The shift of these two bands is mainly caused by the internal stress induced by the hydrothermal hot-pressing process [23,24]. In order to elucidate the variation of the IR absorption bands, their corresponding wavenumbers are listed in Table 1.

At the same time, the intensities of XRD peaks in Fig. 6 decreased, and the FWHM of the (002) diffrac-

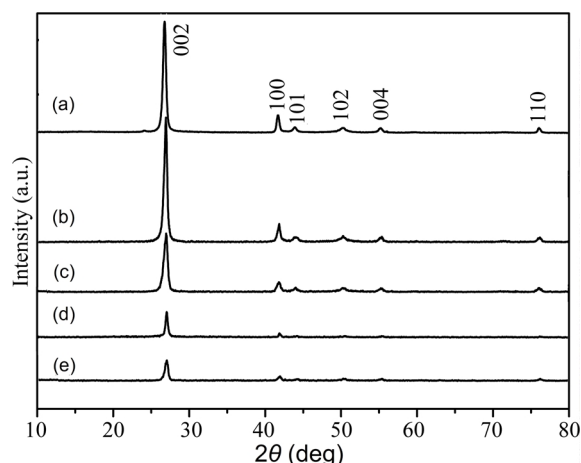


Fig. 6. XRD patterns of *h*BN samples obtained after hot-pressing at 240 °C and different pressures. (a) Starting material; (b) 1.0 MPa, 1 h; (c) 25 MPa, 1 h; (d) 50 MPa, 1 h; (e) 75 MPa, 1 h.

tions increased from  $0.45^\circ$  (sample (a)) to  $0.65^\circ$  (sample (e)), which indicates that the crystalline perfection of *h*BN samples is more and more deteriorated with increase of the hot-pressing pressure.

#### *Prospected application of the above results in the phase transformation of hBN*

Our results demonstrate that both decreasing the particle size and introducing defects/stress into the *h*BN nano-crystals may result in an unstability of their structure, therefore a structural transformation becoming preferred [25–27]. Furthermore, it was found that both the defects and the regions where residual stress exists may act as nucleation centers for *c*BN [28]. In our experiments, a large amount of stress and defects was induced in the *h*BN nano-crystals by the hydrothermal hot-pressing process, thus the temperature and pressure required for the phase transformation decreased significantly. As a result, *c*BN might be obtained by converting *h*BN nano-crystals under much milder conditions. In fact, we have truly observed a compression along the *c* axis in *h*BN nano-crystals hot-pressed at 280 °C and 75 MPa, which may be regarded as the prelude of a phase transformation. However, extensive and intensive investigations are still required in order to clearly explain the phenomena.

#### **Conclusions**

By investigating the reaction between water and *h*BN nano-crystals, it was found that the process can

take place at low temperature and pressure, and that it can be effectively adjusted by controlling the hot-pressing temperature, pressure and time. These results may find applications in the growth of *c*BN crystals from hydrothermal solutions in a controllable way, and provide us helpful clues regarding the conversion of *h*BN into *c*BN under much milder conditions.

#### **Experimental Section**

##### *Preparation of the samples*

0.46 g of *h*BN nano-crystals were mixed with 1 mL of deionized water, and the mixture was ultrasonically treated for 10 min. The resulting mixture was transferred to a hot-press autoclave which has been schematically demonstrated in ref. [25], and a constant pressure was applied on the mixture. The autoclave was heated to the set temperatures and this temperature maintained for 1 ~ 8 h. In order to investigate the effects of pressure and temperature, a series of values were selected within 1.0 ~ 100 MPa and 220 ~ 300 °C. The autoclave was cooled to r.t., and the pressure was released, followed by filtration to recover the sample. Finally, the sample was ultrasonically treated for 30 min and re-filtered using deionized water, until all the byproducts were removed. After heating at 80 °C in vacuum for 8 h, the resulting sample was used for characterization.

##### *Characterization of the samples*

Fourier transformation Infrared (FTIR) absorption spectra of the samples were collected on a Nicolet NEXUS 670 spectrometer, using  $4\text{ cm}^{-1}$  resolution and 32 scans. X-Ray powder diffraction patterns were obtained on a Rigaku D/Max- $\gamma$ A X-ray diffractometer with Ni filtered  $\text{CuK}\alpha$  radiation ( $V = 50\text{ kV}$ ,  $I = 100\text{ mA}$ ), the scanning speed being  $4^\circ\text{ min}^{-1}$ . The morphology of the *h*BN starting material was observed with a Hitachi H-800 transmission electron microscope (TEM), the accelerating voltage being 150 kV. X-Ray photoelectron spectra (XPS) were obtained on a PHI5300 X-ray photoelectron spectrometer, with  $\text{AlK}\alpha$  radiation as the X-ray source.

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