



# Crystallization behavior of cubic boron nitride from an amorphous BN precursor *via* high-pressure, high-temperature treatment with controlled water addition



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## ABSTRACT

Crystallization behavior of cubic boron nitride (c-BN) from amorphous boron nitride (a-BN) by high-pressure, high-temperature (HP-HT) treatment with the intentional addition of a controlled amount of water was studied. The a-BN precursor was prepared by pyrolysis of a boric acid-urea complex with urea/boric acid = 2 at 1000 °C for 3 h under an ammonia atmosphere. Hexagonal BN (h-BN) were initially crystallized from a-BN containing 2 mass% of water after HP-HT treatment at 7.7 GPa and 1200 °C, and the formation of c-BN was observed after 5 min. The crystallization of c-BN from a-BN containing 8 mass% of water after HP-HT treatment at 7.7 GPa and 1200 °C was observed even after 1 min, indicating that the crystallization of c-BN was promoted by increasing the amount of water added. In addition, since neither h-BN nor c-BN was crystallized from a-BN without intentional water addition after the same HP-HT treatment, the addition of water promoted the crystallization of both h-BN and c-BN from a-BN. Since no transformation from h-BN to c-BN was observed during HP-HT treatment at 7.7 GPa and 1200 °C, it was concluded that c-BN was directly crystallized from a-BN. After HP-HT treatment at 7.7 GPa and 1650 °C for 1 min, both h-BN and c-BN were crystallized from a-BN containing 8 mass% of water. These results clearly indicate that the addition of water has a positive effect on crystallization of c-BN from a-BN.

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## 1. Introduction

Ultra-hard materials have been attracting increasing attention, and have been employed in various applications such as cutting and polishing tools [1]. Cubic boron nitride (c-BN), which possesses a diamond-like zinc-blend structure, is the second hardest and the second most thermal conductive material after diamonds, and c-BN is even superior to diamonds in terms of chemical resistance to ferrous alloys and oxidation [2]. c-BN has therefore been employed for making cutting tools for steel materials.

The formation of c-BN from crystalline hexagonal BN (h-BN) *via* phase transition requires a pressure higher than 7.7 GPa and a temperature higher than 2000 °C [3–6]. Thus, the preparation of c-BN

under more moderate conditions has been a challenge for materials science, and there have been enormous efforts to achieve phase transition under less extreme conditions by using additives such as alkali and alkaline earth metals [7], water, urea and ammonium fluoride [8–11]. It was also reported that c-BN was formed from the use of less-ordered starting materials, such as amorphous BN (a-BN) and turbostratic BN (t-BN), under milder conditions of 6 GPa and 1000 °C [12–14]. On the other hand, the formation of c-BN from a-BN prepared by grinding under a dry nitrogen atmosphere was observed after treatment at 7.7 GPa and 2200 °C, and much milder conditions can be applied for the conversion of ground powder exposed to air into c-BN [14]. It is therefore likely that water would be introduced into starting a-BN from atmospheric moisture and that the resulting water seemed to facilitate the formation of c-BN from a-BN or t-BN. Since water was introduced from atmospheric moisture in the previous studies on the conversion of a-BN to c-BN, the amounts of water involved was not known. Thus, to explore the

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effect of water, we should add the controlled amount of water to dry a-BN.

Here, we report crystallization behavior of c-BN from a-BN prepared by pyrolysis of a precursor, a boric acid-urea complex [15]. In the present study, a-BN was prepared by pyrolysis of precursor instead of mechanical grinding, since mechanical grinding could introduce a relatively large number of defects in the structure. For high-pressure, high-temperature treatment, we employed a belt-type apparatus, which permitted relatively large-scale synthesis; we can thus add a precisely controlled amount of water. Two reaction temperatures (1200 °C and 1650 °C) and two water amounts were employed to investigate full conversion and partial conversion processes.

## 2. Experimental

### 2.1. Materials

Starting a-BN was prepared by pyrolysis of a urea-boric acid complex with a molar ratio of urea: boric acid = 2:1 at 220 °C for 3 h under a nitrogen flow and continuing at 1000 °C for 3 h under an ammonia atmosphere [15]. The a-BN powder was annealed at 900 °C under vacuum for 1 h prior to use. Commercially available h-BN (N-1 type, Denka Co. Ltd., Japan) was also used as a starting material.

### 2.2. High-pressure, high-temperature (HP-HT) treatment

Fig. 1 shows the sample cell used in this experiment. The samples were encapsulated in tantalum capsules comprising a sleeve and graphite plug, and treated at 7.7 GPa at 1200 °C or 1650 °C for 1–20 min using a modified belt-type apparatus. To minimize water and oxygen contamination, manipulations for encapsulating the starting materials in tantalum capsules were performed in a glove box under a dry nitrogen atmosphere.

A controlled amount of water (2 or 8 mass%) was mixed with a-BN in the glove box filled with dry nitrogen, and the resulting mixture was encapsulated in a tantalum capsule and treated at 7.7 GPa and 1200 °C or 1650 °C at a heating rate of 80 °C/min for 1–20 min using the same apparatus. As a comparison, h-BN containing 2 mass% of water was treated at 7.7 GPa and 1200 °C for 20 min. The samples were recovered from the tantalum capsules and washed with a mixture of HF and HNO<sub>3</sub>.

### 2.3. Instrumentation

X-ray diffraction (XRD) patterns were obtained with a Rigaku Ultima III diffractometer (Ni-filtered CuK $\alpha$  radiation). Infrared (IR) spectra were recorded on a JASCO FT/IR-460 Plus spectrometer using the KBr disk method. Solid-state <sup>11</sup>B nuclear magnetic resonance (NMR) spectroscopy was performed with a JEOL ECX-400 spectrometer.

## 3. Results and discussion

### 3.1. Characterization of a-BN

The XRD pattern of a-BN showed two broad haloes, indicating amorphous characteristics of a-BN. The IR spectrum of a-BN exhibited absorption bands due to B–N stretching at 1364 cm<sup>-1</sup> and B–N–B out-of-plane bending at 785 cm<sup>-1</sup>. In addition, an N–H stretching band was present at 3414 cm<sup>-1</sup>, indicating the presence of N–H bonds. The solid-state <sup>11</sup>B MAS NMR showed signals at 11 and 23 ppm representing the BN<sub>3</sub> sp<sup>2</sup> environment as expected for a hexagonal BN sheet [16]. These results indicate that the a-BN

employed in the present study possessed boron in the same environment as that of h-BN with N–H bonds. A weak signal at 0 ppm indicated the presence of B–O bonds [14]. Oxygen could be introduced during pyrolysis or NMR measurement, but most of oxygen was expected to be removed by the vacuum annealing before use.

### 3.2. Formation of c-BN from a-BN (7.7 GPa, 1200 °C)

The XRD patterns of the recovered product after HP-HT treatment at 7.7 GPa and 1200 °C are shown in Fig. 2. With no intentional addition of water, the recovered product after HP-HT treatment for 20 min was X-ray amorphous. When 2 mass% of water was added, on the other hand, crystallization of h-BN proceeded even after HP-HT treatment for 1 min, as shown by the presence of broad diffraction lines assignable to h-BN. A trace diffraction line for c-BN was observed for the recovered product after HP-HT treatment for 5 min. With a larger amount of water (8 mass%), crystallization of h-BN proceeded more rapidly after HP-HT treatment for 1 min, as shown by the presence of a larger number of diffraction lines. A diffraction line assignable to c-BN was clearly observed after HP-HT treatment for 1 min. Crystallization of c-BN was observed as the holding time was increased to 5 min. It is worth noting that wrutizite BN (w-BN) formation was not observed in the recovered product using a-BN as a starting material, suggesting that our a-BN's feature prohibits martensitic transformation to w-BN from crystalline nature of h-BN [5].

Using the intensity of the strongest peak of h-BN,  $I_{h\text{-BN}(002)}$ , and that of c-BN,  $I_{c\text{-BN}(111)}$ , the intensity percentage  $\alpha$  is calculated using the following equation:

$$\alpha = \frac{I_{c\text{-BN}(111)}}{I_{c\text{-BN}(111)} + I_{h\text{-BN}(002)}} \times 100 \quad (1)$$

The  $\alpha$  values do not reflect the amount ratios of c-BN and h-BN, but they can be utilized for analyzing their formation behavior, especially their phase transitions. The  $\alpha$  value plots for HP-HT treatment at 7.7 GPa and 1200 °C are shown in Fig. 3. Since no increase in the  $\alpha$  value is observed as holding time is increased, it is concluded that the initially formed h-BN was not converted into c-BN via phase transition; c-BN was formed directly only from a-BN by HP-HT treatment at 7.7 GPa and 1200 °C.

### 3.3. Formation of c-BN from a-BN (7.7 GPa, 1650 °C)

The XRD patterns of the products recovered after HP-HT treatment of a-BN at 7.7 GPa and 1650 °C are shown in Fig. 4. Well-crystallized h-BN was obtained without c-BN formation after HT-HP treatment with no water added for 20 min. From a-BN containing 2 mass% of water, h-BN was crystallized even after 1-min HP-HT treatment. It is clearly demonstrated that well-crystallized h-BN was obtained by HP-HT treatment at 7.7 GPa and 1650 °C. c-BN began to form after HP-HT treatment for 5 min. With the addition of 8 mass% of water, crystallization of h-BN proceeded more rapidly, even after HP-HT treatment for 1 min. A diffraction line for c-BN was clearly observed for the recovered product after HP-HT treatment for 1 min. Crystallization of c-BN was observed as the holding time was increased to 5 min, and no h-BN was observed. It is thus clearly shown that the initially formed h-BN was transformed into c-BN by HP-HT treatment of a-BN at 7.7 GPa and 1650 °C in the presence of 8 mass% of water.

The change in  $\alpha$  values with holding time is shown in Fig. 5. It is clearly demonstrated that the h-BN formed was converted into c-BN. An increase in the  $\alpha$  value with 2 mass% of water indicates h-BN to c-BN phase transformation, and with 8 mass% of water, only c-BN was observed after 5 min.

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