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Phase transformation of boron nitride nanoparticles in aniline under moderate conditions

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In order to synthesize sp^3-bonded phases wurtzitic boron nitride (wBN) and cubic boron nitride (cBN) at moderate conditions, phase transformations of boron nitride (BN) nanoparticles in aniline have been investigated in terms of temperature, pressure and surface modification by solvothermal hot-press method. The results reveal that sp^3-bonded phases wBN and cBN formed at quite low temperature (250~280 °C) and low pressure (15~250 MPa) because the incorporation of bonding interactions between aniline and BN nanoparticles have been induce the formation of sp^3-bonded configurations with minimum energy. A simple model has been proposed to explore the phase transformation mechanism of BN nanoparticles in aniline under hot-press conditions.

Keywords: sp^3-Bonded boron nitride, Nanoparticles, Phase transformation, Aniline, Temperature and pressure

Boron nitride (BN) exists in four crystalline structural modifications, namely, hexagonal BN (hBN), rhombohedral BN (rBN), wurtzitic BN (wBN), and cubic BN (cBN), zinc-blende structures. Among these modifications, wBN (space group = $P6_3mc$) and cBN (Space group = $Fd3m$) have generated tremendous scientific and technological interests because they are hard and dense phases bonded with strong diamond-like sp^3 hybridization (σ bond), whereas hBN (Point group = D_{6h}, Space group = $P6_3/mmc$) and rBN (Space group =$R3m$) are softer phases constructed by B and N atoms in sp^2 hybridization[1–6]. In comparison, explosion BN phase (eBN) is the mixed sp^2 and sp^3 bonded structure (the ratio is 1:1)[7]. Another BN polymorph is amorphous BN, in which B and N atoms are arranged in a nearly random way[8]. Since BN polymorphs, unlike those of carbon, are not naturally available, the synthesis of BN (especially sp^3-bonded BN) is a particularly important task.

With the improvement of BN phase diagram[2,9,10], both the theoretical and experimental results[11–14] have indicated that cBN is the thermodynamically stable phase in 0~1600 K, while hBN is the metastable phase under ambient temperatures and pressures. However, it is difficult to form sp^3-bonded BN at moderate conditions because of the kinetic factors, such as the extremely high energy barrier of 9.4 eV per atom for direct phase transition from ideal hBN to cBN[15]. As is well known that, extreme conditions with high pressures (> 11 GPa) and high temperatures (> 2000 °C) are required for the direct formation of sp^3-bonded wBN and cBN from sp^2-bonded hBN in bulk solids by high pressures and high temperatures (HPHT) method[16]. Even though the incorporation of kinds of catalysts[17–20], such as alkali and alkaline earth metals and their nitrides, alloy solvents, water, urea and boric acid, the synthesis pressure (≥ 2.5 GPa) and temperature(≥ 800 °C) of sp^3-bonded BN were still harsh.

In order to decrease the synthesized temperature and pressure of cBN and wBN, phase transformations in BN under other physical and chemical conditions[1,2,21–23], including ball milling, electron-beam, laser irradiation, carbothermal reduction, vapor deposition, arc-melting, hydrothermal or solvothermal crystallization, have been studied in recent years. Out of these, hydrothermal or solvothermal crystallization consider as a soft chemical method[11–13] which tends to be favorable for the preparation of sp^3-bonded BN at moderate conditions. Considerable effort has been devoted into facilitating the phase transformation between aBN/rBN and cBN nanoparticles by solvothemal hot-press method[14], and our previous work identified that both solvent effect and the initial state of BN nanoparticles were essential to the formation of sp^3-bonded wBN and cBN at mild condition. However, phase transformation of BN nanoparticles in aniline has not been fully investigated yet.

With the aim of exploring the phase transformation mechanism of BN nanoparticles during solvothermal hot-press process, it's necessary to study BN phase transformation behavior induced by different solvent in details. In this study, phase transformation of BN nanoparticles in aniline have been investigated under low pressure (15~250 MPa) and low temperature (250~280 °C) hot-pressed conditions.

Materials and Methods

The BN starting material was synthesized[24] by the reaction of BCl_3 and Li_3N at 250 °C and 3 MPa. The succeeding phase transformation process was carried out as follows:

Firstly, 0.10 g BN nanoparticles were ground for 10 min and dispersed into 7 mL redistilled organic aniline solvent. After being ultrasonically treated for 20 min, the resultant suspension was transferred into a hot-press autoclave, as seen in Fig. 1. In order to eliminate the oxygen and moisture, all the manipulations were carried out in a glove box in which the concentrations of both H_2O and O_2 are less than 1 ppm.

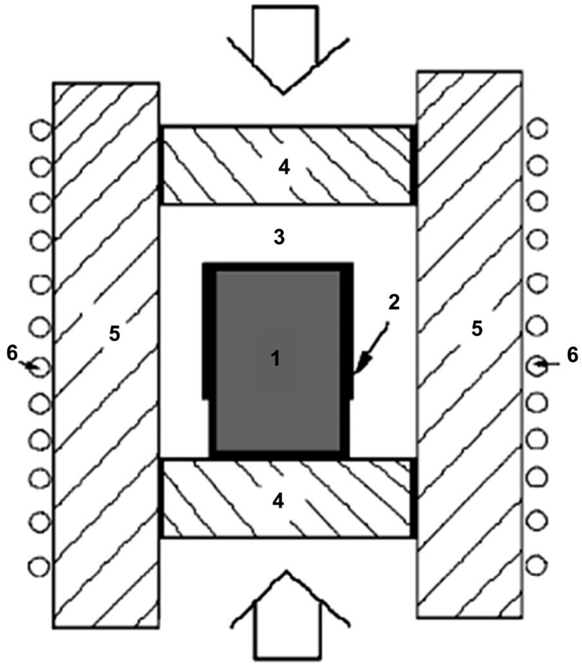

Fig. 1 — Schematic structure of the hot-press autoclave: 1. Resultant suspension, 2. Inside lining, 3. Pressure transmitting medium, 4. Piston, 5. Main autoclave, 6. Heating coil.

After being sealed, the autoclave was applied a pressure of 15~250 MPa and heated to 250~280 °C for 15 h, with a heating rate of 1 °C/min. Thereafter, the autoclave was cooled to room temperature and the pressure was released. Finally, the resultant product was washed with acetone for 4~5 times, and dried at 80 °C in vacuum for 24 h. By varying the temperature and pressure, a series of samples were prepared following the above process.

Characterization of the samples

Fourier transformation infrared (FTIR) absorption spectra of the samples were mostly used for the analysis of phases in the samples. The FTIR spectra were collected on a Nicolet NEXUS 670 infrared spectrometer with the wave number resolution of 4 cm^{-1}. About 3~5% (in weight) BN nanoparticles were mixed with KBr and ground thoroughly, then the mixture was pressed into pellet for characterization. The high resolution transmission electron microscopy (HRTEM) images of the samples were observed on a Phillips Tecnai Twin-20U high resolution transmission electron microscope under accelerating voltage of 200 kV.

Furthermore, the relative content of different BN phases was quantificationally analyzed by a multi-peaks Lorentzian fitting method. Because all the BN phases possess almost the same absorption coefficient to infrared radiation, and a simple linear relationship between the absorption intensity of FTIR peaks versus relative content of BN nanoparticles has ever reported, their relative contents can be calculated according to the following equation[1, 25]:

$$F_X = \frac{A_X}{\sum_i A_i} \times 100\% \qquad \ldots (1)$$

Where F_X is the relative content of a specific phase in the sample, A_X is area of the corresponding peak, and $\sum A_i$ is the total area of the peaks corresponding to all the BN phases in a FTIR spectrum.

Results and Discussion

Analysis of BN phase transformation

Both temperature and pressure are critical factors affecting BN phase transformation, and FTIR spectra of BN samples prepared at 250, 260 and 280 °C under different pressures are presented in

Fig. 2, respectively. As shown in Fig. 2(a), peaks at 1422, 1416 and 1415 cm^{-1} belong to aBN, peaks at 1360 and 1376 cm^{-1} are from rBN, peaks at 1606 and 1024 cm^{-1} come from eBN and the peak at 1158 cm^{-1} should be attributed to wBN[26], while peaks at 1080, 1070 and 1096 cm^{-1} are resulted from cBN[27]. The above results indicate that the aBN in the starting material has been partially converted into sp^3-bonded wBN and cBN with the pressure increased into 150 MPa at 250 °C.

Similar trend can also be found by analyzing Fig. 2(b) and (c), in which the intensity of characteristic peaks belong to wBN and cBN became stronger and stronger with the increase in hot-pressing pressure at 260 and 280 °C, respectively. It can be seen in the figure that the formation of sp^3-bonded wBN and cBN emerged at a very moderate condition (250 °C and 30 MPa) by solvothermal hot-press route, and the increase in pressure promotes the BN phase transformation from sp^2-bonded phases into sp^3-bonded phases.

Moreover, FTIR spectra of BN samples in Fig. 2 were comparatively analyzed by a multi-peak Lorentzian fitting method in order to obtain the exact changes between BN phases, and typically fitting results are shown in Fig. 3. The relative contents of (wBN + cBN) calculated according to equation (1) are 30%, 36% and 28% for the samples obtained under the same 150 MPa at 250, 260 and 280 °C, respectively. In comparison, the relative contents of (eBN + wBN + cBN) for those three samples could be up to 74 %, 82 % and 75 %, indicating that lots of sp^2 and sp^3 hybrid eBN appeared in the BN samples after hot-pressing in aniline for 15 h.

The dependence of the relative content of different BN phases on pressure after hot-pressing for 15 h are shown in Fig. 4. aBN nanoparticles were easily and directly transformed into rBN at quite low temperature (260 °C) and pressure (30 MPa) (shown in Fig. 4a), and the content of cBN and wBN progressively increased as the pressure increased from 30 MPa to 250 MPa, accompanied with continuous decrease of the content of aBN and rBN. In particular, the maximum content of eBN is about 49% for the BN sample hot-pressed under 90 MPa, and then eBN content slightly decreased as the pressure furtherly increased into 250 MPa. The above results indicate that the metastable eBN would transform into sp^3-bonded wBN and cBN with the increase of pressure.

The contents of (wBN + cBN) increased as the pressure increased from 15 MPa to 150 MPa as shown in Fig. 4b and it also demonstrated that the optimal temperature for the formation of sp^3-bonded wBN and

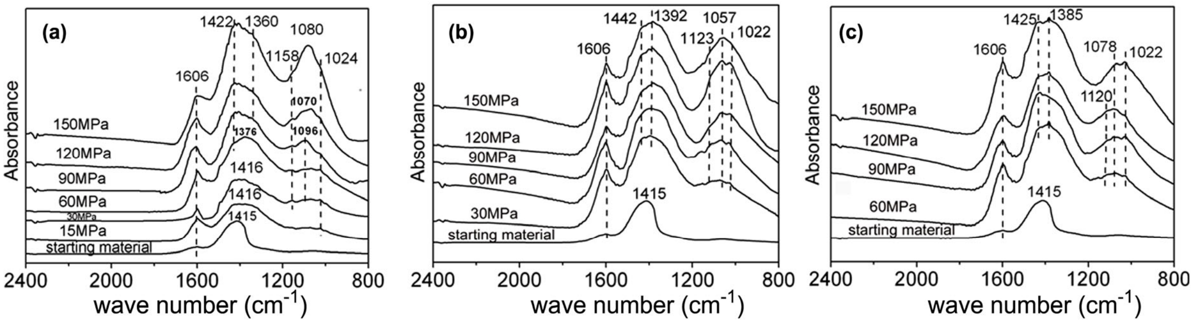

Fig. 2 — FTIR spectra of samples prepared at different temperatures and pressures (a) 250 °C, (b) 260 °C and (c) 280 °C. The hot-pressing duration was 15 h.

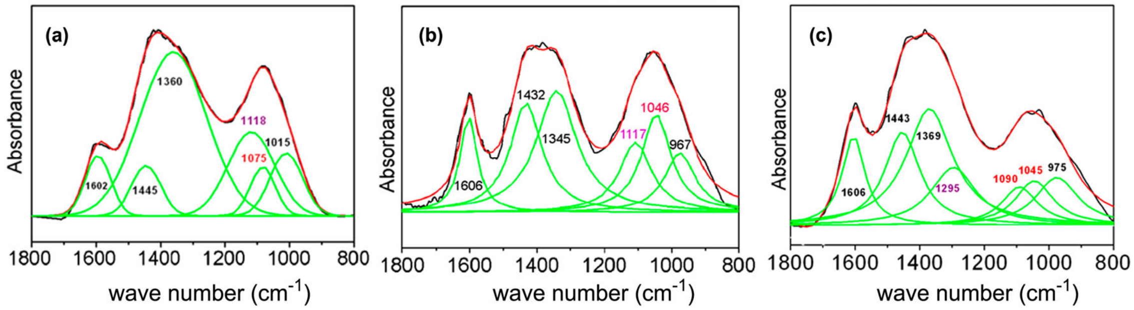

Fig. 3 — Fitting results of the FTIR spectra (shown in Fig. 2) corresponding to BN samples obtained under 150 MPa at (a) 250 °C, (b) 260 °C and (c)280 °C respectively.

cBN is 260 °C. This phenomenon may be mainly due to the interaction between temperature and the effect of surface modification. It has been reported that structural transformations of nanocrystals could be induced by changing their surface energy at mild or even ambient conditions[25, 28–30]. Thereby, the surface modification resulted from bonding interactions between B atoms on the surface of BN nanoparticles and aniline solvent would lead to a decrease of surface energy of BN nanoparticles, and then induce the BN phase transformation from the metastable phase (sp^2-bonded BN) to stable phase (sp^3-bonded BN) with minimum energy state.

However, there's a competition for the surface modification and temperature because excessively high temperature will restrict the formation of chemical bonds between BN nanoparticles and aniline solvent, though the increase of temperature will

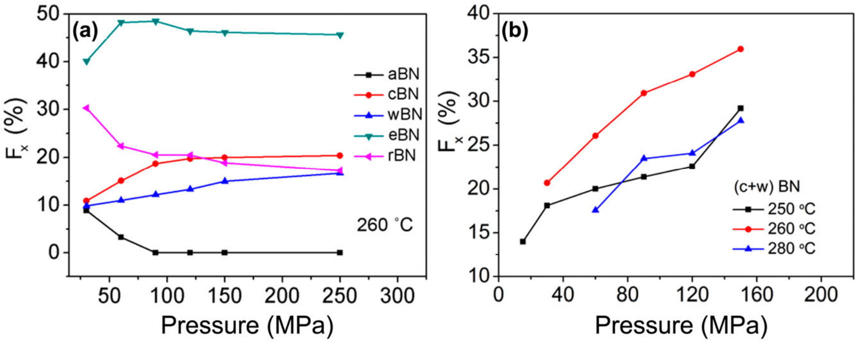

Fig. 4 — Dependence of F_x on pressure under 250 °C, 260 °C and 280 °C.

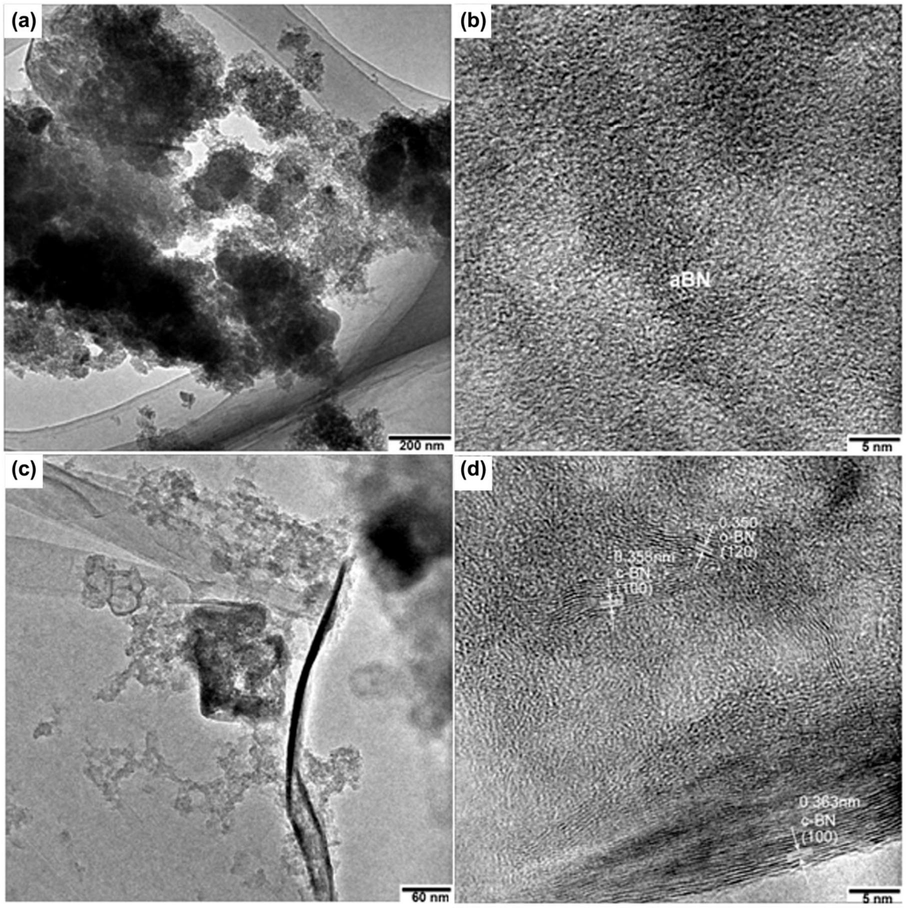

Fig. 5 — HRTEM images of BN samples before and after hot-pressing (a) and (b) starting material; (c) and (d) BN samples obtained at 260 °C under 150 MPa.

favor the phase transformation of sp^3-bonded BN as reported before[9]. At low temperature range (250~260 °C), both the increase of temperature and the formation of chemical bonds accelerated the BN phase transformation; while the further increase of temperature (280 °C) reduced the surface modification effect on BN transformation, which induced the decrease of BN phase transformation.

HRTEM was also employed to verify the amorphous nature of the starting material and the existence of sp^3-bonded BN nucleus. It's clear that the starting materials are composed of poorly crystallized aBN aggregates as shown in Fig. 5a and 5b, while the agglomeration of BN nanoparticles in the sample after hot-pressing in aniline has been partially suppressed (as shown in Fig. 5c) and small domains of cBN and eBN have been observed in Fig. 5d. This observation directly supported the conclusion drawn from the corresponding FTIR spectra results.

The effect of aniline as solvent during the phase transformation

In order to examine the effect of aniline in the above phase transformation, 0.10 g BN starting material was hot-pressed at 260 °C under 150 MPa for 15 h without aniline. FTIR absorption spectrum of the obtained sample and its fitting result by multi-peaks Lorentzian fitting method are shown in Fig. 6. By comparing the spectra (b), (c) and (a), it's obviously that strong peaks of rBN (1385 and 1369 cm^{-1}) emerged in the spectrum of hot-pressed BN sample without aniline, associating with some weak peaks of eBN (1606, 1460 and 1010 cm^{-1}), wBN (1113 cm^{-1}) and cBN (1065 cm^{-1}). The fitting result of spectrum (b) indicate that the relative content of (eBN + wBN + cBN) for sample (b) is 39 %, while the relative content of (wBN + cBN) is only 13 %, far lower than that those of samples with aniline. It's confirmed that phase transformation from sp^2-bonded BN to sp^3-bonded BN has been significantly improved by the introduction of aniline, because the incorporation of aniline induced the surface modification of BN nanoparticles and resulted in a relatively low energy barrier for phase transformation of sp^3-bonded BN.

Mechanism of BN phase transformation under mild condition

It's well known that the fraction of atoms exposed on the surface is high in nanoparticles the surface free energy (G_s) of nanoparticles can be an important determinant of the nanoparticle phase stability[28]. In this present work, dispersed or weakly aggregated BN nanoparticles in suspension (as shown in Fig. 7) have a more distorted internal structure than strongly aggregated nanoparticles through the incorporation of aniline[25]. The above modification of aggregation state would result in higher surface (or interfacial) free energy for the distorted B or N atoms[25,28–30]. Moreover, these distorted B atoms were further modified by the bonding interactions through the incorporation of aniline solvent during hot-press process, making the formation of sp^3 configurations much easier than that in ideal crystals.

In comparison with the energy barrier (E_1) for the for direct phase transition from ideal hBN to cBN, the energy barrier (E_2) for the phase transformation from defective aBN to defective rBN and the energy barrier (E_3) for the phase transformation from

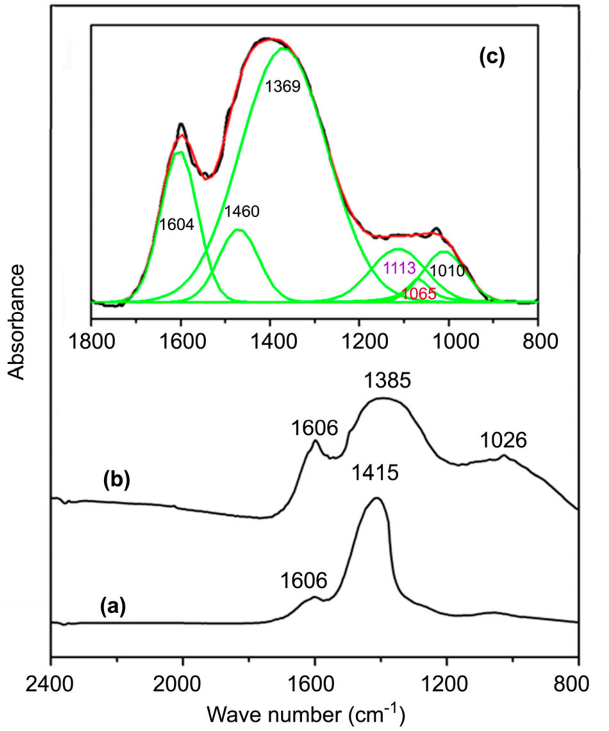

Fig. 6 — FTIR spectra of BN samples (a) Starting material, (b) Hot-pressing at 260 °C under 150 MPa without aniline and (c) The inset is the fitting result of spectrum (b).

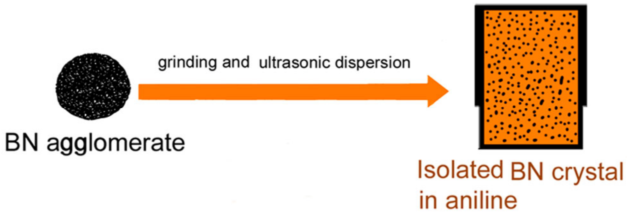

Fig. 7 — Schematic for the existing state of BN nanoparticles.

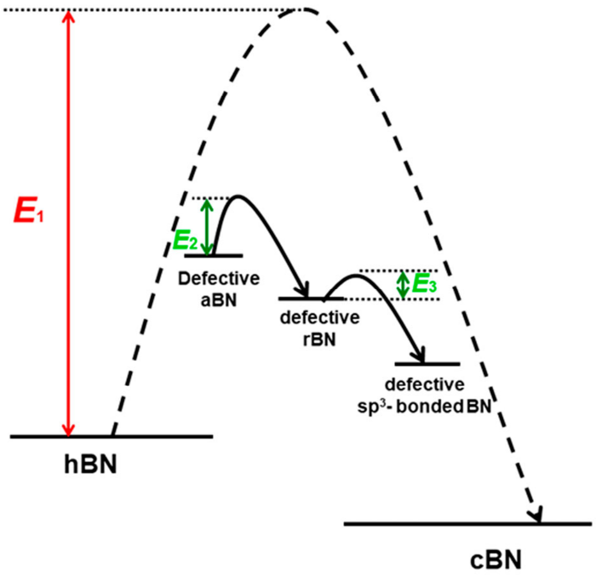

Fig. 8 — Energy barriers of various paths in BN phase transformation process.

defective rBN to defective sp^3-bonded BN have been significantly decreased. As a result, the phase transformation of sp^3-bonded BN under moderate process with the addition of aniline could be achieved by overcoming a relatively low energy barrier (Fig. 8).

Conclusions

This work has experimentally demonstrated that aBN nanoparticles were at first transformed into rBN and then to eBN, wBN and cBN under moderate temperatures and pressures with the introduction of aniline after hot-pressing for 15 h. The relative contents of (eBN + cBN + cBN) are 74%, 82% and 75% for BN samples obtained under the same 150 MPa at 250, 260 and 280 °C, respectively. In particular, the effect of surface modification from bonding interactions between aniline solvent and BN surface atoms facilitated the formation of sp^3-bonded configurations in BN nanoparticles at mild conditions, because the energy barrier for the formation of sp^3-bonded BN from nano-scaled aBN is far lower than that for the direct phase transformation of bulk hBN to cBN.

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