Boron Nitride Revisited

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The phase diagram published by Bundy & Wentorf [2] already shows cBN to be the stable form of boron nitride, in contrast to similar diagrams used today. This picture is supported by theoretical calculations by Maki et al. [5] and Solozhenko [6]. Results of compressibility measurements for cBN and hBN are presented. To clarify the picture of the phase diagram the transformation from hBN to cBN has been studied in a series of time dependent diffraction experiments using synchrotron radiation. The crystallization is found to go through the melt. In a second series of experiments the back-transformation of cBN to hBN was studied. Finally the experimental conditions for high pressure/ high temperature synthesis of cBN could be lowered to 2.5 GPa at 1800°C using amorphous boron nitride as starting material.

Introduction

After the successful synthesis of diamond by high pressure/high temperature experiments speculations arose that boron nitride, commonly known to crystallize in a hexagonal graphite-like form, might also exist in a diamond-like cubic form with zincblende structure. Boron nitride is iso-electronic with carbon and a similar behavior, especially extreme hardness could be expected. The successful synthesis was first reported in a short note in 1957 by Wentorf [1]. This paper already establishes the zinc-blende structure, a cubic unit cell with $a = 3.615(1)$ Å, with boron in 000 and nitrogen in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. In subsequent papers by Wentorf in 1961[1], and Bundy and Wentorf in 1963 [2] details on the experiments are given. Corrigan and Bundy in 1975 [3] reported the direct transformation without a "catalyst". Already in the paper by Bundy and Wentorf in 1963 [2] a phase diagram is shown based on experiments using so-called "catalysts", predominantly alkali and alkaline-earth metals. The region explored was around 45 to 75 kbar and 2000 to 3000 K. Extrapolation to normal conditions showed cBN to be the stable form, in contrast to diamond, where graphite is the stable polymorph at ambient conditions. In nearly all subsequent publications however, without experimental evidence or any other explanation given, the "phase diagram" of boron nitride was adjusted to that of carbon with the cubic form to be metastable.

Present efforts in the study of boron nitride in a number of laboratories concentrate on 3 goals:

1. To establish without ambiguity the phase diagram, and the equilibrium lines.
2. To reduce the transition conditions for the synthesis of cBN.
3. To study the transition process from hBN to cBN, presumably through the melt.

Also in contrast to carbon there are at least four crystalline polymorphic forms of boron nitride: Cubic cBN, graphitic hBN, wurtzitic wBN and a rhombohedral form rhBN. There are speculations about a new ultrahard form of BN with (X-ray)-amorphous, or nano-crystalline atom arrangement [4].

The Phase Diagram of Boron Nitride

The phase diagram of boron nitride published in 1975 by Corrigan & Bundy [3] shows great resemblance to the phase diagram of carbon, where diamond is a metastable form.

Fig. 1. Phase diagram of BN as proposed by Corrigan & Bundy [3] and Bundy & Wentdorf [2]. Shown are also the equilibrium lines calculated by Maki et al. [5] and Solozhenko [6].

Attempts to refine and verify this phase diagram showed considerable disagreement making the validity of this diagram doubtful. Attempts were made to derive an equilibrium diagram from thermodynamic data, especially by Maki et al. [5] and Solozhenko [6]. For these calculations the thermodynamic data must be known reliably, e.g. the pressure/temperature behavior of the polymorphs must be measured and compressibility data must be obtained.

Compressibility Data from In-Situ High Pressure X-ray Diffraction

Compressibilities are determined best by in-situ high pressure/high temperature X-ray diffraction experiments. Because of the high intensity available in synchrotrons they are the most suited radiation sources. Our experiments were done at the HASYLAB/DESY synchrotron in Hamburg/Germany for cBN, hBN and rhBN and the compressibility parameters have been obtained [7,8,9,10].

Fig. 2. Typical diffraction diagram of a hBN sample collected at 7.98 GPa. The NaCl lines served as pressure markers.

The hexagonal graphite-like boron nitride, hBN, has been studied previously at lower pressures by several authors [11,12]. The data are in good agreement at lower pressures, up to 2 GPa. However severe disagreement is found at higher pressures. We have studied [9] a highly ordered hBN sample from Fluka Chemical Company at room temperature up to 12 GPa static pressure. The degree of ordering as described in [13] was calculated to $P_3 = 0.98(2)$. Fig. 2 shows a typical diffraction diagram collected at 7.98 GPa. Fig. 3 shows the results for a/a_0 and c/c_0 (Fig. 3a) and also for V/V_0 (Fig. 3b). The lattice constant a is only insignificantly influenced by pressure, while c is compressed to about 85% of its original value at 12 GPa. This strong anisotropic behavior is in agreement with the crystal structure, e.g. the bonding features in hBN where strongly covalent bonded hexagonal B-N sheets are stacked on top of each other with Van der Waals bonding between the sheets.

Analysis of the data was done by adjusting the data to a first order Murnaghan equation of state [14] of the form

$$V = V_0 [1 + (B'_0/B_0) \cdot p] \exp -1/B'_0.$$

With $V_0 = 10.892 \text{ cm}^3/\text{mol}$ we calculated by a two-parameter least squares fit $B_0 = 36.7(5) \text{ GPa}$ and $B'_0 = 5.6(2)$.

Fig. 3a. Lattice constants a and c of hBN as a function of pressure up to 12 GPa. Open and filled symbols represent data from the first and second run resp.

Fig. 3b. Compression V/V_0 of hBN as a function of pressure up to 12 GPa. Filled circles present work, open symbols data from literature. Solid line is the fit of the data to the Murnaghan equation, the dashed line shows for comparison the compression for rhBN [7].

In a similar series of experiments we have studied the compression of the rhombohedral polymorph, rBN, at room temperature up to 14 GPa [7]. Those experiments were done in a Mao-Bell-type diamond anvil squeezer with 400 μm culets. The data analysis, again by fitting the experimental points to a first order Murnaghan equation, gave $K_0 = 33.4(4)$ GPa and $K'_0 = 5.25(11)$ with $V_0 = 10.899(2)$ cm^3/mol . The pressure behavior of a_0 and c_0 is similar to that of hBN: Insignificant decrease with p of a_0 , and a decrease to about 80% for c_0 .

With these data the equilibrium diagram of boron nitride has been calculated, shown in Fig. 1 (in cooperation with Dr. Solozhenko, Kiev, Ukraine). In order to get experimental information on the transformation of hBN into cBN, and vice versa of cBN to hBN we have made corresponding measurements including the kinetics of the transformation. Such experiments should shed light on the boundary lines in the phase diagram or the equilibrium diagram.

In-Situ High Pressure Xray Diffraction Experiments to Study the Phase Transformations hBN to cBN

The work by Bundy & Wentorf [2] and Corrigan & Bundy [3] demonstrated the direct transformation of hBN to cBN at pressures between 4.5 and 7.5 GPa and temperatures of about 1200 to 2000°C. Use of catalysts decreases significantly temperatures and pressures. This series of experiments was undertaken in order to get first reliable information on the phase diagram, and second to study the mechanism of this transformation, which is still under discussion, despite its significant interest for the understanding of the crystallization of cBN. Synchrotron radiation facilities are available more widely today and recent progress in high pressure / high temperature cells has opened the way to follow the transition directly in-situ. Since the direct transformation is just above the available conditions, we have used a catalyst for our experiments. Li-nitrides, specifically Li_3N proved to be most suitable [16].

Fig. 4. Time-dependent energy-dispersive diffraction pattern of the hBN to cBN transformation in the Li_3N -BN system.

Experiments were done at the HASYLAB, DESY, Hamburg Germany using the *Multi Anvil Xray 80*, MAX80 high pressure apparatus in the energy dispersive diffraction mode. The pressure was calibrated by the shift of the NaCl lines, temperature was measured and controlled with a Pt/Pt10%Rh thermocouple placed in the center of the heater in direct contact with the sample. The error in p was estimated to be 10% at 1200°C, and in T less than 5°C.

Fig. 4 shows the transformation of hBN to cBN at 6.5 GPa and 1100°C by following the (002)-hBN and (111)-cBN diffraction lines in a sequence of 20 seconds. Within 400 seconds the transformation is completed, e.g. the transformation is rather fast. Details of these experiments are given in [16].

To investigate the mechanism of the transformation Fig. 5 gives a series of diffraction patterns, again at 6 GPa, by increasing the temperature from 1050 °C to 1250 °C in steps of 100 °C. (The room temperature diagram is included for comparison). The beginning of the transformation can be recognized clearly around 1050 °C with going through a melt before cBN is crystallized. This is indicated by a distinct broad peak resulting from the melt of the catalyst. hBN is gradually dissolved and cBN crystals are formed. At 1250 °C, when the experiment was terminated, almost all of hBN is transformed into cBN, as can be recognized by the intensities of the corresponding peaks hBN(002) and cBN(111). (Note the change in the intensity scale !!). The transformation was completed in less than 5 minutes. It is interesting to note, that this result is in agreement with the picture proposed already in 1957 by Wentorf in his very first paper [1].

Fig. 5. Transformation of hBN to cBN at 6 GPa through the melt in the System Li_3N -BN.

Reversible Phase Transformation of hBN to cBN and back to hBN

To achieve a clear picture of the formation of cBN and the phase diagram, we have studied in a series of experiments the formation of cBN and the back-transformation to hBN. Fig. 6 gives, for one example, the path which was followed: At 6.5 GPa the temperature was gradually increased (as shown before) to 1200 °C and cBN was formed. The degree of transformation was nearly 100%. Then we lowered pressure and temperature to 2.1 GPa and room temperature, e.g. well below the equilibrium line for cBN. This was then followed by increasing the temperature thus going through the transformation point of cBN to hBN. The resulting transformations can be clearly seen in Fig. 7, where the corresponding diffraction patterns are depicted. This procedure was repeated in two consecutive series., as indicated in Fig. 6.

in situ Investigation of the Phasetransformation
hBN → cBN → hBN in the System Li_3N - BN
- experimental Path -

Fig. 6. Experimental path for the hBN to cBN to hBN transformation in the system Li_3BN . ○ regime of fast cBN formation. ◐ cBN to hBN transformation, fast and complete. ◑ cBN to hBN transformation, slow and incomplete.

Fig. 7. A series of time-dependent x-ray patterns of the experimental path of Fig. 6. Details are given in the text.

Low Pressure Synthesis of cubic Boron Nitride

On the basis of the calculated equilibrium diagrams, by Maki [5] as well as by Solozhenko [6], the equilibrium line hBN to cBN intersects the temperature axis (at ambient pressure) around 1500K. Our own (not yet published) experiments with X-ray diffraction at ambient pressure indicate this transition point around 1200 °C. This implies that synthesis of cBN should be possible at much lower conditions than used today in industrial applications. In a series of experiments we have attempted to lower the conditions which are commonly applied for the synthesis of cBN [17,18]. As starting material we used amorphous BN, prepared chemically by heating a mixture of KBH_4 and NH_4Cl at 1200K in a nitrogen stream. As a catalyst-solvent $\text{Mg}_2\text{B}_2\text{N}_4$ was obtained from the NRD Corporation (Japan). The experiments were carried out in a „belt“-type high pressure apparatus used in our laboratory. The results of a great number of synthesis experiments are shown in Fig. 8 in a p vs. T plot. Filled circles represent the p,T conditions where cBN formation was observed, open circles are experiments without transformation to cBN. The crystals were brownish-black with sizes in the 10-200 μm range. Minimum p,T conditions were 2,5 GPa at 1800°C [17].

These results are in discrepancy to the boundary line suggested by Bundy and Wentorf [2]. They are also much lower than the theoretical values. The calculated equilibrium lines would be in the right hand corner. The experimental points however do fall within the thermodynamic stability region of cBN [5,6].

Fig.8. cBN crystallization in the system aBN-Mg₃B₂N₄. Filled circles indicate the presence of cBN, open circles absence of cBN. BW is the boundary line suggested by Bundy and Wentorf [2].

The analysis of these results also indicates the decisive role of kinetic factors, which depend strongly on the starting material (here amorphous boron nitride), the catalyst, the stoichiometry and the experimental conditions like pressure and temperature gradients, cooling rate etc.

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