

On Nucleation of Cubic Boron Nitride in the BN–MgB₂ System

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X-ray powder diffraction with synchrotron radiation was used to study the formation of cubic boron nitride (cBN) in the MgB₂–BN system at pressures to 6.8 GPa and temperatures to 2000 K. For the formation of cBN, when it crystallizes from a BN solution in the melt of the system under study, the threshold pressure (4.5 ± 0.1 GPa) and low-temperature boundary (T (K) = $1633 - 9.2p$ (GPa)) have been established. We have calculated pressure and temperature dependences of the rate of cBN nucleation and have found that the position of the high-temperature boundary of the p,T region of the cBN crystallization is specified by the nucleation of the cubic phase. The existence of the threshold pressure of cBN crystallization is dictated by the strong pressure dependence of the nucleation rate. It is just this dependence that is responsible for the fact that the region of the cBN spontaneous crystallization is well off the hBN \rightleftharpoons cBN equilibrium line by several hundred degrees.

Introduction

Diamond and cubic boron nitride, the world's two hardest materials, are isoelectronic compounds and have similar structures, similar chemical bonds, and close physical properties. Both these phases are usually synthesized at high pressures and temperatures from the corresponding layered polymorphs of carbon (graphite) and boron nitride (graphite-like BN). Therefore, the attempts of many researchers to extend the existing similarity of properties to the phase diagrams of carbon and boron nitride and regularities of formation of their dense phases are not unreasonable.

In 1988 Solozhenko suggested the equilibrium phase diagram of boron nitride,¹ which differs drastically from the phase diagram of carbon. According to this diagram, the diamond-like phase of BN (cBN) is thermodynamically stable at ambient pressure, and not the graphite-like form (hBN), as was previously thought.

Another fact, which cannot be adequately explained in terms of the similarity between diamond and cBN, is the existence of the threshold pressure for cBN crystallization from melts of systems traditionally used for its commercial synthesis (hBN–Mg₃N₂, hBN–Li₃N, etc.)^{2–4} that is not defined by the hBN \rightleftharpoons cBN equilibrium line.

Regularities of diamond crystallization from carbon solutions in melts of transition metals were established by Bundy.⁵ For all studied systems, the region of diamond spontaneous crystallization in the p vs T coordinates is limited at the right by the graphite \rightleftharpoons diamond equilibrium line and at the left by the melting curve of the eutectic in the graphite–metal system. In this case, the lowest pressure of diamond crystallization is defined by the parameters of the point of intersection of these two lines.

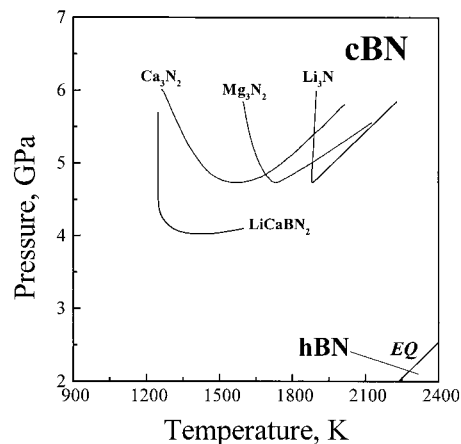


Figure 1. Regions of cBN spontaneous crystallization in various systems.^{2–4} cBN forms in the region above each curve. EQ is the hBN \rightleftharpoons cBN equilibrium line.⁶

However, the regularities found by Bundy cannot be extended to the crystallization of cubic boron nitride. p,T regions of cBN crystallization from melts of a number of systems^{2–4} and the hBN \rightleftharpoons cBN equilibrium line⁶ are presented in Figure 1. By analogy with diamond, the low-temperature boundary of the region of cBN crystallization was expected to be defined by the melting curve of the eutectic (or peritectic) with boron nitride and the high-temperature boundary by the hBN \rightleftharpoons cBN equilibrium line. In fact, however, the high-temperature boundary of the region of cBN formation offsets by several hundred degrees from the equilibrium line and, despite the presence of a liquid phase, below some threshold pressure the spontaneous crystallization of cBN in the region of its thermodynamic stability is not observed.

In the present work by the example of the BN–MgB₂ system, we show that the existence of the threshold pressure of spontaneous crystallization of cubic boron nitride from BN

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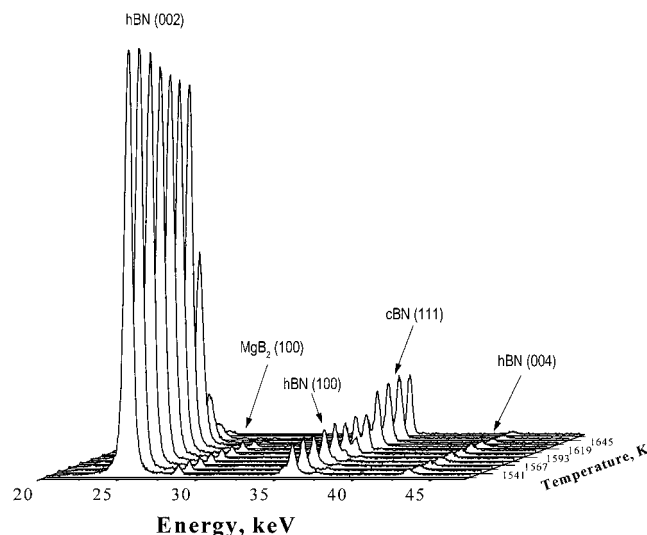


Figure 2. Diffraction patterns of the BN–MgB₂ mixture taken during heating at 6.3 GPa.

solutions in melts is defined by the kinetics of nucleation of the cubic phase, which is the rate-limiting step of cBN formation at high temperatures.

Experimental Section

Highly ordered hBN (three-dimensional ordering degree P_3 was found to be 0.98 ± 0.02) was received from Fluka AG. To remove impurities, the powder was annealed at 2100 K for 5 h in nitrogen containing less than 0.003 vol % oxygen. MgB₂ (99%) was used as received from Alpha Products. Samples were prepared by mixing MgB₂ and hBN powders in the weight ratio 1:4.

The experiments were carried out using the multianvil type X-ray system MAX80 with anvils of tungsten carbide. The diffraction measurements were performed in an energy-dispersive mode at the beam line F2.1 of HASYLAB-DESY (Hamburg).

The experimental setup has been described earlier.⁷ The primary polychromatic synchrotron beam was collimated to 60 μm (height) by 100 μm (width) and was perpendicular to the vertical axis of the sample chamber. The diffracted beam was collected in the vertical plane using an intrinsic Ge solid-state detector and a Canberra multichannel analyzer.

A radioactive ²⁴¹Am-source provided X-ray fluorescence K α and K β lines from Rb, Mo, Ag, Ba, and Tb targets for energy calibration of the detector. The diffraction angle $\theta = 4.709 \pm 0.002^\circ$ was calculated from the X-ray diffraction pattern of NaCl taken at ambient conditions.

The temperature of the high-pressure cell was controlled by a Eurotherm PID regulator within ± 2 K. The sample temperature was measured by a Pt 10% Rh–Pt thermocouple with its junction 300 μm below the sample region under study. The correction for the pressure effect on a thermocouple electromotive force was made using the data of Getting and Kennedy⁸ extrapolated to 7 GPa. Pressures at different temperatures were determined from the d_{002} value of hBN using its thermoelastic equation of state.⁹

Results and Discussion

Figure 2 shows a typical sequence of diffraction patterns of the BN–MgB₂ mixture taken at heating from 1528 to 1658 K at 6.3 GPa.

In a set of experiments in the 3.2–6.8 GPa pressure range with a step heating (steps were 100 and 25 K below and above 1300 K, respectively), pressure dependence of the lowest temperature of the cBN formation in the BN–MgB₂ system has been determined to be T (K) = $1633 - 9.2p$ (GPa). Below 4.4 GPa the formation of cubic boron nitride has not been observed up to about 2000 K. This fact indicates that there exists a threshold pressure of the cBN spontaneous crystallization, which is estimated at 4.5 ± 0.1 GPa.

The appearance of cBN lines in the diffraction patterns is accompanied by a decrease in the intensity of the lines of the initial MgB₂ (in a number of cases to the point of disappearance), which together with a considerable increase of the background is evidence for the formation of a liquid in the system. In the experiment at 4.4 GPa in the course of a linear heating at a rate of 25 K/min, at 1538 K the 012, 102, and 110 lines of Mg₃BN₃ were recorded up to their disappearance at 1550 K. This bornitride (Mg₃BN₃) forms due to the reaction between MgB₂ and hBN and then dissolves in the liquid phase as the temperature increases. No formation of Mg₃BN₃ was observed in experiments with a step heating due to the narrow temperature range (~ 20 K) of the existence of this phase under conditions of these particular experiments.

Diffraction patterns of the reaction mixture cooled to 1093 K at a constant pressure exhibit MgB₄ and Mg₃BN₃ lines in addition to the boron nitride lines. Reheating of the reaction mixture up to 1493 K (3.7 GPa) results in disappearance of the lines from magnesium boride and bornitride, which suggests the possibility of the existence of the $L \rightleftharpoons \text{MgB}_4 + \text{Mg}_3\text{BN}_3 + \text{BN}$ ternary eutectic. (The lines of boron nitride do not disappear since BN is present in large excess.) Thus, the formation of cubic boron nitride in the system under study is a result of crystallization from the BN solution in a melt of the Mg–B–N ternary system. In the present work we use the term “the MgB₂–BN system” to indicate the composition of the initial reaction mixture despite the fact that the MgB₂–BN quasibinary section of the Mg–B–N ternary system does not exist.

With the aim of studying the possibility of cBN growth on nuclei of cubic boron nitride at pressures lower than the threshold pressure of spontaneous crystallization, the following experiments were carried out at 4.2, 4.0, 3.8, and 3.6 GPa. To obtain cBN nuclei, the reaction volume was heated to 1600 K at 5.9 GPa. After 10 s holding time the temperature was dropped to 1300 K; then the pressure was decreased to the preset value and the temperature was increased back to 1600 K. At all stages of the experiment, we controlled the relative intensity (I/I_0) of the 111 line of cBN. The I/I_0 values were calculated with respect to the 002 and 100 lines of hBN. It has been found that the cBN growth on nuclei terminates at a pressure of about 3.9 GPa (Figure 3). Thus, the threshold pressure of cBN spontaneous crystallization is the pressure below which the nucleation of cubic boron nitride is impossible but cBN growth on existing nuclei is possible.

The rate of nucleation of a new phase (the number of nuclei formed in a unit volume in a unit of time) is described by¹⁰

$$J = J_0 \exp\left(-\frac{\partial \Phi_n}{RT}\right) \quad (1)$$

where, for the case of heterogeneous nucleation, the energy of formation of a spherical nucleus of a critical size is

$$\partial \Phi_n = \frac{16\pi\Omega^2 a^3}{3(\Delta\mu)^2} \frac{(1 - \cos \Theta)^2 (2 + \cos \Theta)}{4} \quad (2)$$

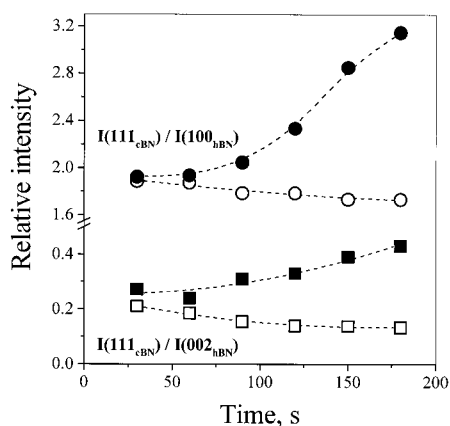


Figure 3. Isothermal kinetics of growth of cubic boron nitride on cBN nuclei in the MgB_2 -BN system at 1600 K and 3.6 GPa (open symbols) and 4.2 GPa (solid symbols).

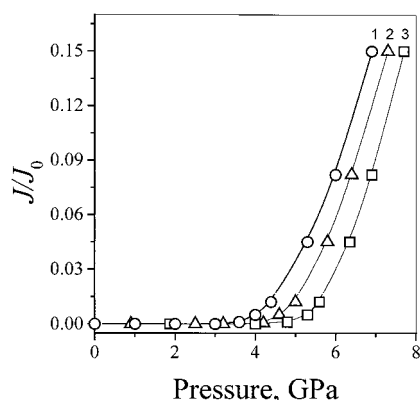


Figure 4. Pressure dependence of the relative rate of the cBN nucleation at 1600 K (1), 1900 K (2), and 2200 K (3).

where Ω is an average volume per an atom of the nucleus, α is the specific free surface energy of the crystal-melt interface, Θ is a contact angle, $\Delta\mu$ is the difference in chemical potential between the substance in the melt and in the solid phase under p, T conditions of crystallization. As in the course of dissolution of hBN in the melt of the Mg-B-N system, this melt becomes saturated and the liquid phase proves to be in equilibrium with undissolved hBN, then the equations $\mu_{\text{hBN}} = \mu_{\text{BN}_1}$ and $\Delta\mu = \mu_{\text{cBN}} - \mu_{\text{hBN}}$ are valid.

In our further calculations, we used the $\Delta\mu(p, T)$ and $\Omega(p, T)$ dependences found from the data on thermodynamic properties of boron nitride.⁶ Taking into account the data reported in ref 11, α was assumed to be 1.6 J/m² and the contact angle $\Theta = 30^\circ$. The pressure dependence of the relative rates of cBN nucleation (J/J_0) at 1600, 1900, and 2200 K are shown in Figure 4. It is seen that at pressures below 4 GPa the nucleation rate is close to zero, while a considerable growth of J/J_0 is observed only at pressures exceeding the experimentally found threshold pressure of cBN spontaneous crystallization.

The curve of the constant nucleation rate $J/J_0 = 1.2 \times 10^{-2}$ corresponding to a pressure of 4.5 GPa (the threshold pressure of the cBN spontaneous crystallization) (line AB) is given in Figure 5. This figure shows also the low-temperature boundary of the cBN crystallization in the MgB_2 -BN system found in the present work (line AC) as well as the data on cBN crystallization in this system previously obtained by Petrusha¹² using quenching from high pressures and temperatures. As in the case of diamond crystallization, the low-temperature boundary fits the parameters of the appearance of the liquid phase in the system, while the high-temperature boundary of the cBN

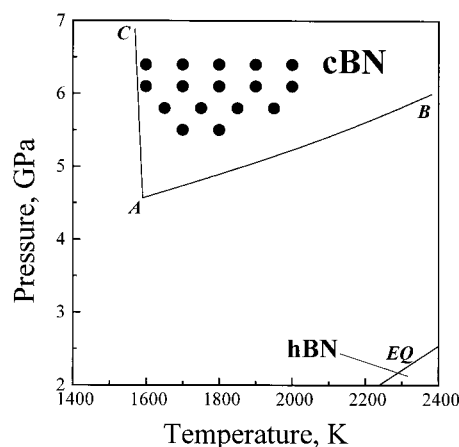


Figure 5. p, T region of the cBN spontaneous crystallization in the MgB_2 -BN system. The AC line is the low-temperature boundary of the region of cBN formation according to the in situ experiments; the AB line is the calculated high-temperature boundary of this region; dark circles are the results of quenching experiments.¹² EQ is the hBN \rightleftharpoons cBN equilibrium line.⁶

formation is defined not by the position of the hBN \rightleftharpoons cBN equilibrium line but by the curve of the constant rate of nucleation ($J/J_0 \approx 1\%$), i.e., the rate that ensures cBN formation in quantities that can be registered in the real experiment. Thus, the nucleation is a rate-limiting step of the cBN crystallization at high temperatures. The observed difference between the results obtained in the present work and the data of Petrusha¹² is due to the error of the pressure assessment in quenching experiments. In ref 12 the experimental cell was calibrated against pressure at room temperature.

The preexponential factor J_0 in the equation for the nucleation rate in solutions depends on the rates of diffusion and cluster incorporation into the growing nucleus and is proportional to the square of the density (n) of the dissolved substance and to the stream of clusters toward the surface of the nucleus:¹⁰

$$J_0 = 2\pi R_c^2 (1 - \cos \Theta) n^2 \nu a \exp\left(\frac{E}{kT}\right) \quad (3)$$

where ν is the mean frequency of thermal vibrations of atoms of a BN crystal, a is the interatomic spacing in the nucleus, E is the activation energy of incorporation of clusters into the nucleus, and R_c is the radius of the nucleus. For simplicity, the frequencies of thermal vibrations of atoms in the crystal and in the melt are assumed to be equal.

A comparison between crystallization processes of diamond and cubic boron nitride leads to the following conclusions. The coefficients of BN diffusion in melts are 2 orders of magnitude lower than those for carbon.¹³ The incorporation of BN clusters that approach the surface of a growing cBN crystal is hampered by the necessity to form only the B-N bonds (in this case, the formation of B-B and N-N bonds is inadmissible), which should result in an increase in the E value. Besides, diamond is much better wetted with melts of growth systems than cBN.¹¹ The foregoing is responsible for the fact that the preexponential factor in eq 1 for cBN turns out to be 2 (or even 3) orders of magnitude lower than that for diamond, while the energy of formation of a critical nucleus is higher. All this requires much higher supersaturation $\Delta\mu^2$ in the case of cBN crystallization. To a first approximation $\Delta\mu^2 \sim \Delta T_p^2$, where ΔT_p is the difference between the temperature of the hBN \rightleftharpoons cBN equilibrium and the experimental temperature at constant pressure. Therefore, the high-temperature boundary of cBN

crystallization is offset by several hundred degrees from the line of equilibrium between the cubic and graphite-like phases, while for diamond, ΔT_p does not exceed tens of degrees.

Conclusion

Our findings show that due to the high energy of formation of a cBN nucleus of a critical size and the high activation energy of incorporation of BN clusters into a nucleus of the new phase as well as due to the low coefficients of BN diffusion in melts of the systems conventionally used for cBN synthesis, rates of cBN nucleation and crystal growth are several orders of magnitude lower than those values for diamond. These factors require much higher supersaturation in the case of cBN crystallization. Because of this the cBN crystallization region in the p,T diagram of boron nitride is far off the $\text{hBN} \rightleftharpoons \text{cBN}$ equilibrium line by several hundred degrees.

The low-temperature boundary of the region of cBN crystallization is defined by p,T parameters of the appearance of the liquid phase in the system, while the high-temperature boundary is defined by the frequency of cBN nucleation that ensures its formation in quantities, which can be recorded in the real experiment. The threshold pressure of the cBN formation is specified by the intersection of these high- and low-temperature

boundaries. For the BN-MgB_2 system, the threshold pressure is 4.5 GPa.

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References and Notes

- (1) Solozhenko, V. L. *Dokl. Phys. Chem.* **1988**, 301, 592.
- (2) DeVries, R. C.; Fleischer, J. F. *J. Cryst. Growth* **1972**, 13/14, 88.
- (3) Nakano, S.; Fukunaga, O. *Diamond Relat. Mater.* **1993**, 2, 1409.
- (4) Bocquillon, G.; Loriers-Susse, C.; Loriers, J. *J. Mater. Sci.* **1993**, 28, 3547.
- (5) Bundy, F. P.; Bovenkerk, H. P.; Strong, H. M.; Wentorf, R. H. *J. Chem. Phys.* **1961**, 35, 383.
- (6) Solozhenko, V. L. *Properties of Group III Nitrides*; INSPEC: London, 1994; p 43.
- (7) Solozhenko, V. L.; Turkevich, V. Z. *Mater. Lett.* **1997**, 32, 179.
- (8) Getting, I. C.; Kennedy, G. C. *J. Appl. Phys.* **1970**, 41, 4552.
- (9) Solozhenko, V. L.; Peun, T. *J. Phys. Chem. Solids* **1997**, 58, 1321.
- (10) Chernov, A. A.; Givargizov, E. I.; Bagdasarov, Kh. S.; et al. *Formation of Crystals*; Nauka: Moscow, 1980 (in Russian).
- (11) Naidich, Yu. V., Ed. *Surface Properties of Melts and Solids and their Use in Materials Science*; Kiev: Naukova Dumka, 1991 (in Russian).
- (12) Petrusha, I. A. private communication.
- (13) Solozhenko, V. L.; Turkevich, V. Z. *Diamond Relat. Mater.* **1998**, 7, 43.