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New Experimental Results on the Phase Diagram of Boron Nitride

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In order to clarify the discrepancy of the phase diagram on boron nitride as it is found in the literature we have made numerous *in situ* diffraction experiments using synchrotron radiation. The conditions were temperatures in the range of 1600°C and pressures up to 6.5 GPa. For the experiments diamond anvil squeezers and the MAX80 high-pressure/high-temperature device installed at the DESY synchrotron facility in Hamburg/Germany were used. We studied the transformation from hBN to cBN at 6.5 GPa/1200°C and the backtransformation from cBN to hBN around 0.9 to 2 GPa. The experiments included kinetics measurements. The experiments verified the theoretical results by V. L. Solozhenko (1991, *High Pressure Res.* 7, 201) and J. Maki *et al.* (1991, "Proceedings II: International Conference on New Diamonds Research and Technology"). Further on the calculations for the equilibrium boundary between cBN and hBN were repeated including uncertainties of the thermodynamic data. The cubic phase, cBN, is definitely the stable phase, in contrast to metastable diamond. © 2000 Academic Press.

1. INTRODUCTION

Boron nitride crystallizes in several polymorphic forms with hexagonal hBN and cubic cBN the most important ones. cBN crystallizes in the zincblende structure, similar to the structure of diamond, with boron in 000 and nitrogen in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ in a fcc lattice. After the successful synthesis of diamond it was immediately speculated that cBN should be of extreme hardness, similar to diamond, because of the similarity in the bonding features: tetrahedrally covalent bonded atoms (1). cBN does not exist in nature. The first successful synthesis by high pressure and high temperatures, similar to the synthesis of diamond, but using Li_3N as a catalyst, was reported in a short note by Wentdorf in 1957 (2), followed by a second more detailed paper in 1961 (3). This paper reported already the important details. Several papers followed by Wentorf, Corrigan, and Bundy (4, 5).

A phase diagram of boron nitride was reported for the first time by Bundy and Wentorf in 1963 (4), with cBN being the stable phase at ambient conditions. This was changed, however, in an ensuing publication by Corrigan and Bundy in 1975 (5), who took a phase transition line parallel to that of graphite/diamond, thereby intersecting at room temperature at 1.3 GPa and thus implying now cBN at low pressures a meta stable phase. This picture was adopted for many years, until calculations by Maki and Fukunaga (6) and Solozhenko (7, 8) demonstrated cBN as the stable phase. The phase transition lines are compiled in Fig. 1. We have tried to solve this discrepancy in numerous experiments. Results are reported here.

Our efforts must concentrate on several goals:

to establish without ambiguity the phase diagram with respect to the phase transition line;

to study the transition process from hBN to cBN;

to study the backtransition from cBN to hBN;

to determine whether the phase line depends on the catalysts used for synthesis;

to determine whether it is a solid–solid phase transformation.

2. THE PHASE DIAGRAM OF BORON NITRIDE

Figure 1 shows the phase diagram as we consider it correct today. It is based on our *in situ* high-pressure/high-temperature experiments. Included are the original phase lines given by Bundy and Wentorf (4), the later line by Corrigan and Bundy (5), and the recent (theoretical) equilibrium line calculated by Solozhenko (7, 8). A previously published theoretical phase line by Maki and Funkunaga (6) is also shown. It differs only a little from the Solozhenko calculation. Despite the shift between the new experimental and the calculated lines we must accept today that the commonly used phase diagram of BN with cBN being a metastable polymorph is not correct. Clarity on the phase diagram can be obtained with kinetics measurements and especially by studying the path from hBN to cBN and back to hBN. Recent developments in Synchrotron radiation facilities and progress in high-pressure/high-temperature cells has opened the way to following the transitions *in situ.*

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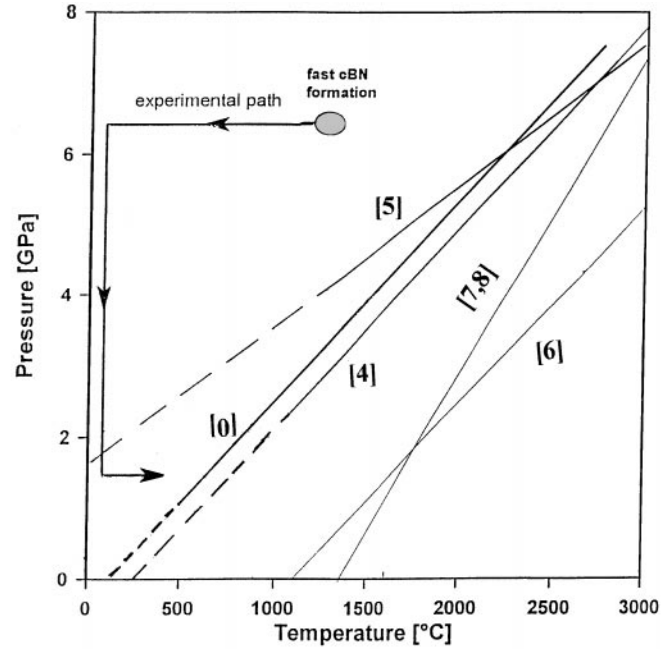

FIG. 1. Phase diagram of boron nitride. Shown are the published transition lines by Bundy and Wentorf (4) and Corrigan and Bundy (5) and the equilibrium lines calculated by Solozhenko (7, 8) and Maki *et al.* (6). Included is also the "kinetic" phase boundary derived from our own experiments (0) and the area used for the *in situ* synthesis of cBN as well as the experimental path for studying the phase transformation.

3. *IN SITU* DIFFRACTION EXPERIMENTS

All diffraction experiments were done by *in situ* high-pressure/high-temperature measurements using synchrotron radiation at the HASYLAB, DESY, Hamburg, Germany by energy dispersive diffraction techniques with the multianvil MAX80 apparatus. For the determination of compressibility data, necessary for calculating the equilibrium line, a diamond anvil squeezer was used allowing much higher pressures than the MAX80.

4. COMPRESSIBILITY DATA FROM *IN-SITU* HIGH-PRESSURE X-RAY DIFFRACTION

Calculations of equilibrium diagrams are to a great extent dependent on the thermodynamic data, mainly the formation enthalpies, but especially on compressibility data. Because of the high intensity available in synchrotrons they are the most suited radiation sources for our experiments. The hexagonal graphite-like boron nitride, hBN, has been studied previously at lower pressures by several authors (9, 10). The data are in good agreement with data from dynamic compression (9), but in severe disagreement above 2 GPa with the data by Lynch and Drickamer (10) from static compression. We have studied a highly ordered hBN sample from Fluka at room temperature up to 12 GPa static pressure (11). The degree of ordering was calculated to $P_3 = 0.98(2)$. Figure 2 shows a typical diffraction diagram collected at 7.98 GPa. Figure 3 shows the results for a/a_0 and c/c_0. 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 strong covalent bonds between B and N stacked on top of each other at a sequence AA′AA′, … , with weak Van der Waals bonding between the layers.

Analysis of the data was done by adjusting the data to a first-order Murnaghan equation of state (12) of the form

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

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

In a similar series of experiments we have studied the compression the rhombohedral polymorph, rBN, at room temperature up to 14 GPa (13, 14). 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 $B_0 = 33.4(4)$ GPa and $B'_0 = 5.25(11)$ with $V_0 = 10.899(2)\ \text{cm}^3/\text{mol}$. The pressure behavior of a_0 and c_0 is similar to that of hBN: insignificant decrease of a_0 with p and a decrease to about 80% for c_0.

Similarly we also investigated the wurtzitic phase including the thermal expansion (15). The results for the compressibility parameters at 300 K are $B_0 = 25.0(5)$ GPa and $B'_0 = 4.1(4)$ with $V_0 = 7.167\ \text{cm}^3/\text{mol}$. In case of wBN we

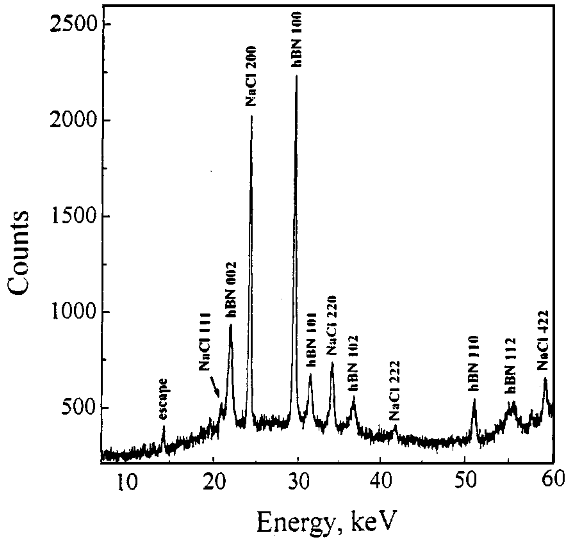

FIG. 2. Typical diffraction diagram of a hBN sample collected at 7.98 GPa in a diamond anvil squeezer. The NaCl lines served as pressure markers.

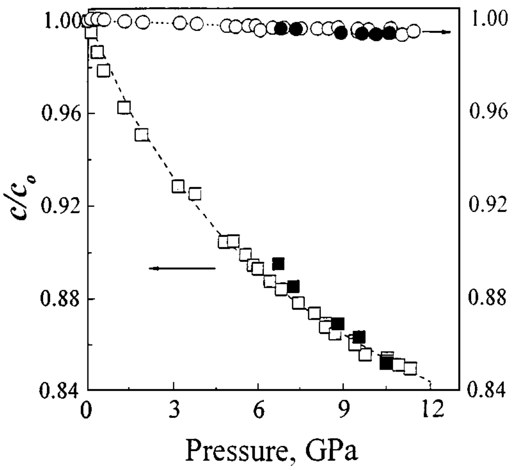

FIG. 3. Compression of hBN as a function of pressure up to 12 GPa derived from diagram as shown in Fig. 2. Open and filled symbols represent data from two different runs.

have also determined the thermal expansion up $T = 1440$ K at 3.4 and 6.0 GPa with $\alpha = 9.3(4) \times 10^{-6}\ \mathrm{K}^{-1}$ at 3.4 GPa and $11.4(5) \times 10^{-6}\ \mathrm{K}^{-1}$ at 6.0 Gpa.

5. *IN-SITU* DIFFRACTION EXPERIMENTS TO STUDY PHASE TRANSFORMATIONS BETWEEN hBN AND cBN

In order to get unquestionable information on the transformation it is necessary to follow in a unique path all the phase transformations (16). Thereby we first synthesize cBN from hBN at conditions around 6.5 GPa, 1250°C, which is depicted in Fig. 4. The beginning of the transformation can be recognized very clearly around 1150°C with melting occurring before around 1050°C.

Figure 5 shows the kinetics of the phase transformation at 6.5 GPa and 1100°C in a time sequence of 20 s interval. The transformation is completed within 400 s; i.e., the transformation is very fast, an observation well known in industrial synthesis of cBN.

In the same experimental setup we continue and first release temperature and pressure as low as possible, ca. 0.9 to 2 GPa. The experiments were then continued to increase the temperature again so we could observe the backtransformation to hBN. It is worth noting that the whole experimental cycle used the same setup and the same sample. Figure 6 depicts a complete sequence of diffraction diagrams, from the synthesis of cBN to releasing pressure and temperature and heating up the setup again to show the transformation back to hBN.

6. INFLUENCE OF CATALYSTS

Conditions for a direct transformation cannot be obtained today at synchrotron sources. A direct transformation was reported by Bundy and Wentorf (4) at extreme high temperatures above 2000 K and pressures exceeding 11 GPa. The first synthesis experiments by Wentorf (2) used catalysts, which decreases significantly temperatures and pressures. Due to our experimental abilities we also used

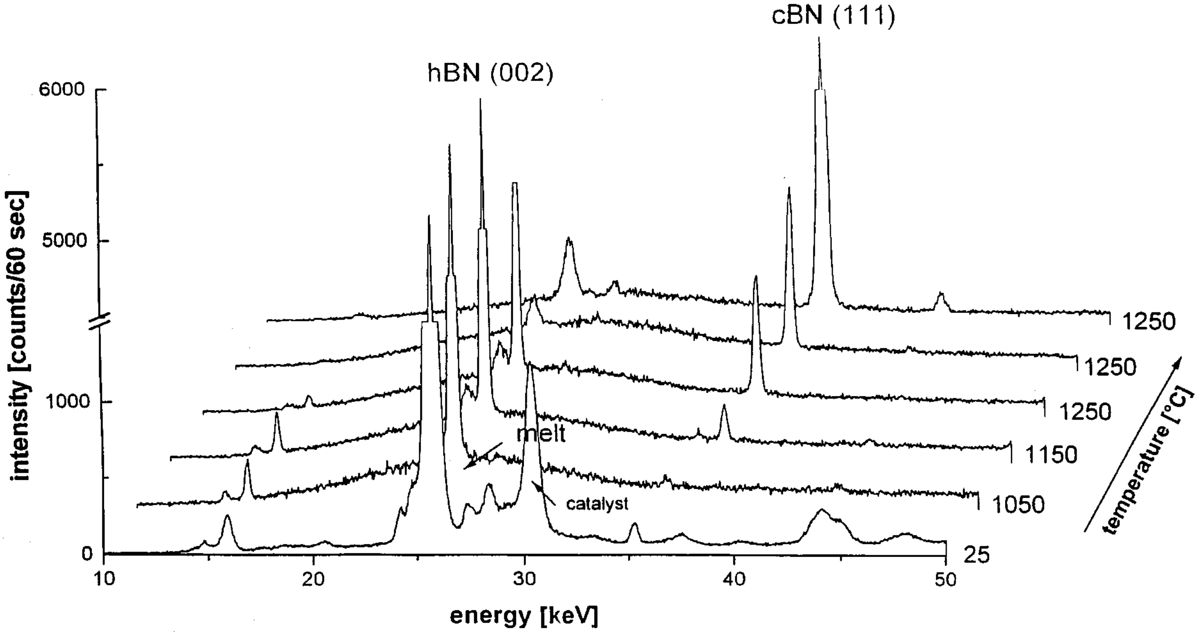

FIG. 4. Transformation of hBN to cBN in the system Li_3N–hBN at 6 GPa. The transformation goes through the melt around 1050°C, and cBN begins to appear around 1150°C.

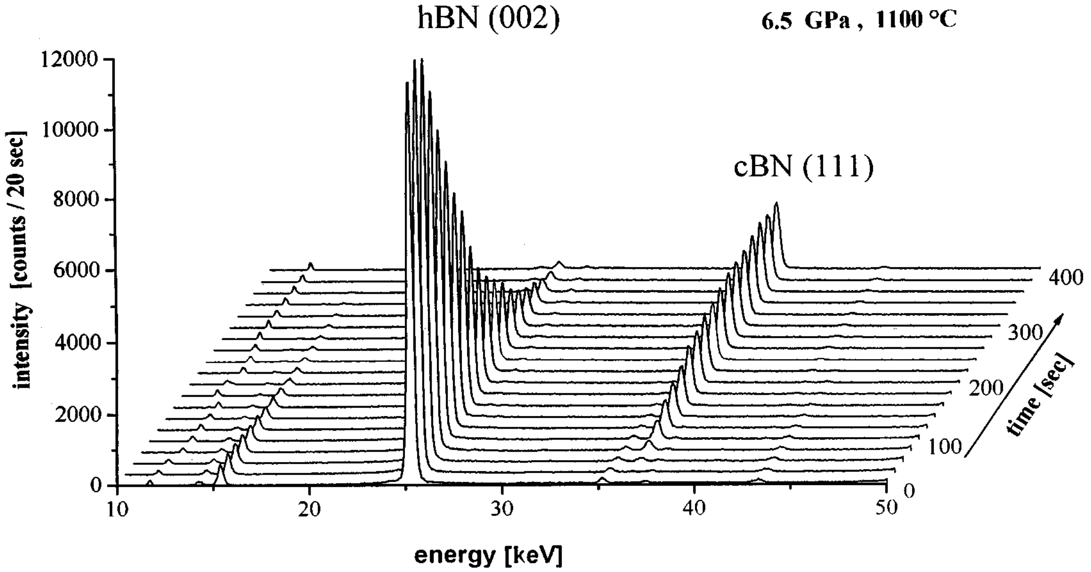

FIG. 5. Kinetics of the transformation of hBN into cBN at 6.5 GPa and 1100°C by following the hBN (002) cBN (111) diffraction lines. Within 400 s the transformation is completed.

catalysts. In discussions about the observed transition data the question of catalysts was brought forward. We normally work with Li-nitrades, specifically Li_3N, which proved to be most suitable. In order to approach this question of catalysts we have repeated our experiments described above with a number of different catalysts. About 20 such experiments were performed under different conditions. Eleven of them are depicted in Fig. 7. There is no difference and consequently the use of catalysts is insignificant to the phase transformation.

7. KINETICS MEASUREMENTS

Most of our measurements were done including kinetics. The synthesis transformation of hBN to cBN at 65 GPa from RT up to 1250°C was done in steps of 100°C in 60-s intervals and is shown in one example in Fig. 5. The transformation to cBN was completed in less than 5 min. It is very fast, as is well known in industry. The transformation back to hBN is more difficult to investigate. The speed of this transformation is widely determined how close the

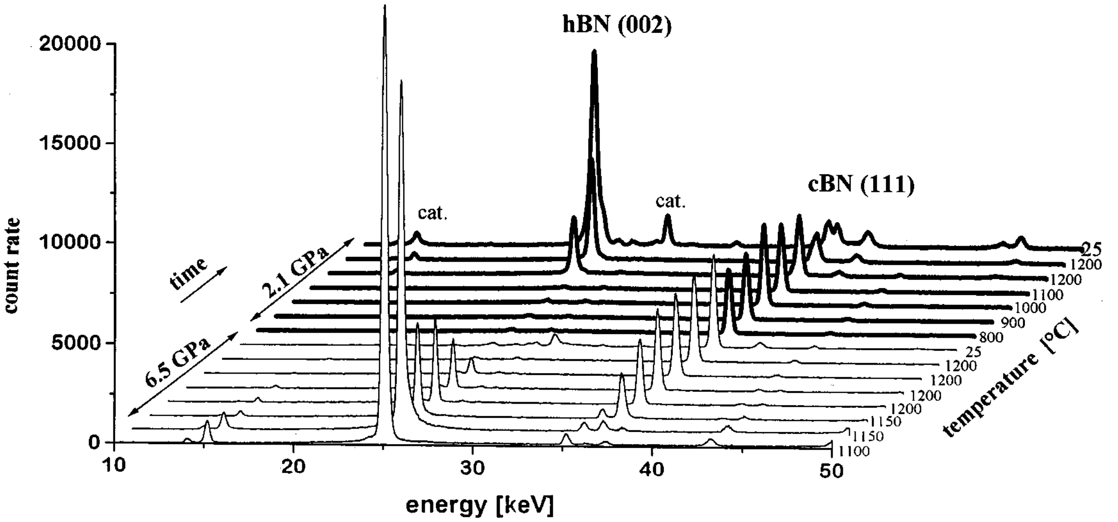

FIG. 6. Series of diffraction diagrams going through the complete path of transformations: hBN to cBN at 6.5 GPa, releasing the pressure to 2.1 GPa and then raising the temperature and appearance of hBN around 1200°C.

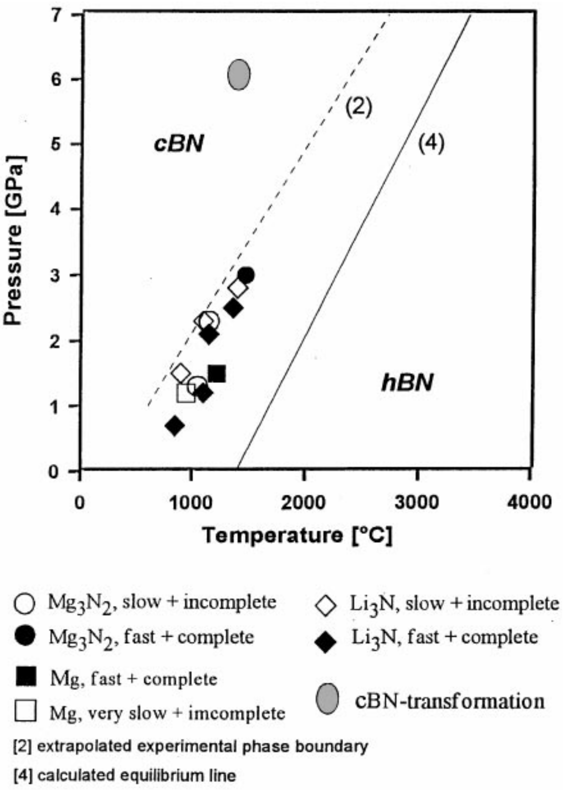

FIG. 7. Experimental results of the cBN to hBN backtransformation in several systems using different catalysts for the formation of cBN (at 6.5 GPa, 1100°C).

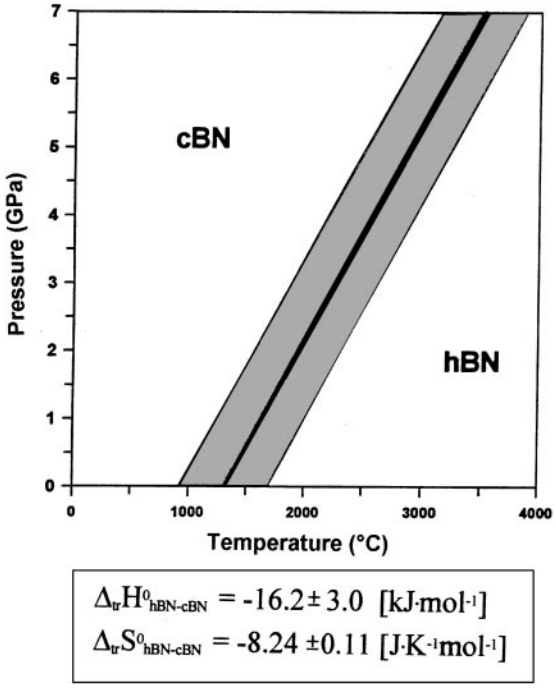

FIG. 8. Calculated transition between hBN to cBN based on the thermodynamic parameters given by Solozhenko and now including uncertainties in the entropy and enthalpy values. The result is a band rather than an equilibrium line.

data points are to the transition line. This can be realized from the data depicted in Fig. 7. When we follow the kinetics of the backtransformation from cBN to hBN there is at first an immediate onset of transition, for example at 1100°C, which we could follow by the appearance of hBN (002), and disappearance of cBN (111). The transformation, however, was never completed in the time, partly because the time available at the synchrotron source was too short, in other cases because we were too close to the phase boundary. In order to arrive at reliable values we started to analyze the experimental by using the Avrami equation (17):

$$X(t) = 1 - \exp(-k \cdot t^n). \qquad [2]$$

This equation contains in the exponent the speed of transformation, while n describes the growth mode (18), $n = 1$ means growth on a seed plane. Our analysis of one first diagram yielded $n = 0.79$ (0.03). We have begun to analyze all our experimental kinetical data this way, which is still in progress.

8. EQUILIBRIUM LINE

The equilibrium lines shown by Solozhenko and also by Maki *et al.*, do not consider experimental uncertainties. These errors are especially high for the thermodynamic enthalpy and entropy values and they will influence significantly the transformation line. K. D. Grevel, Ruhr University Bochum (pers. commun.), has kindly repeated the calculation using the same data as Solozhenko, however, including the uncertainties. The result is shown in Fig. 8. Instead of an equilibrium line we now obtain an equilibrium band. As a final result we arrive at ambient pressure at a transformation temperature from cBN to hBN at 1320°C ± 380°C. Uncertainties of the compressibility

TABLE 1
Compressibility Data for Several Polymorphs of Boron Nitride Derived from High-Pressure *in Situ* Diffraction Experiments Using a Diamond Anvil Squeezer

Compound	Volume (cm^3/mol)	Isothermic bulk modulus, B_0 (GPa)	First derivative B'_0
Cubic BN[a]		36.9(1.4)	4.0(2)
Hexagonal BN	10.892	36.7(5)	5.6(2)
Rhomohedral BN	10.899	33.4(4)	5.25(11)
Wurtzitic BN	7.167	25.0(5)	4.1(4)

[a] Taken from E. Knittle, R. M. Wentzcivitch, R. Jeanloz, and M. L. Cohen, *Nature* **337,** 349 (1989).

TABLE 2
Results from DTA Measurements of the Transformation of cBN into hBN at Elevated Temperatures

Sample	MicronABN 300 containing 5% boron oxide	ABN 300	ABN 600
Grain size (μm)	0.75–1.5	40–80	600–1000
Onset temperature (°C)	900	1300	1500

Note. The uncertainties in the temperature are 25°C. The transformation temperature is highly dependant on the quality of the starting phase cBN.

values, which are smaller than the thermodynamic data, are not yet included and may yield another small, so certainly not significant, widening of the 1-bar transformation temperature.

9. DISCUSSION AND CONCLUSION

Our experiments demonstrate without doubt that the phase diagram of boron nitride is not comparable to that of carbon, as it has been assumed in the past. The cubic phase, cBN, is definitely the stable phase at low pressures. It also demonstrated that the kinetics is a decisive factor. As a consequence, the transformation temperature from cBN to hBN is obviously not well defined. The transformation depends strongly on parameters like grain size, defect concentration, and purity of the starting material. This has been shown, for example, by a series of experiments by Sachdev, whose results are with the kind permission of Dr. Sachdev shown in Table 2. He demonstrated a transformation from the cubic to the hexagonal polymorph at temperatures around 1000°C, with significant dependence on the material used. Also, our own high-temperature X-ray diffraction experiments without pressure show significant differences in the temperature when hBN is observed.

The transformation into the cubic phase is considered a solid–solid transformation by several authors. The set of diffraction diagrams in Fig. 4 following the transformation indicates, however, a melting process before the formation of the cubic phase, therefore indicating a transformation through the melt. It is worth noticing that, in the very early papers by Wentorf in 1957 (2), also a formation process through the melt is suggested. Also, H. Lorenz (pers. commun.), in a study using Mg_3N_2 as a catalyst, observed the precipitation of cBN from a melt.

The remaining open questions are, why is it necessary to synthesize cBN at high pressures and high temperatures? There are more and more indications and experiments to reduce the formation of cBN at lower and lower conditions. For example, we could crystallize cBN crystals as low as 2.5 GPa at 1800°C by using amorphous boron nitride as a starting material (19). Second, why is it so difficult (at least at the moment) to grow thin films of cBN, while the deposition of diamond seems to be possible without severe difficulties? The reports of cBN films so far always have a hexagonal layer on the substrate before cBN begins to grow.

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REFERENCES

1. G. Will, A. Kirfel, and B. Josten, *J. Less-Common Metals* **117,** 61 (1986).
2. R. H. Wentorf, *J. Chem. Phys.* **26,** 956 (1957).
3. R. H. Wentorf, *J. Chem. Phys.* **34,** 809 (1961).
4. F. P. Bundy and R. H. Wentorf, Jr., *J. Chem. Phys.* **38,** 1144 (1963).
5. F. R. Corrigan and F. P. Bundy, *J. Chem. Phys.* **63,** 3812 (1975).
6. J. Maki *et al.*, "Proceedings II: Int. Conf. on New Diamonds Science and Technology, Washington, DC, 1990." Materials Research Society, Pittsburgh, PA, 1991.
7. V. L. Solozhenko, *High Pressure Res.* **7,** 201 (1991).
8. V. L. Solozhenko, *High Pressure Res.* **13,** 199 (1995).
9. R. W. Lynch and H. G. Drickamer, *J. Chem. Phys.* **44,** 181 (1966).
10. N. L. Coleburn and J. W. Forbes, *J. Chem. Phys.* **48,** 555 (1968).
11. V. L. Solozhenko, G. Will, and F. Elf, *Solid State Commun.* **96,** 1 (1995).
12. F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA.* **30,** 244 (1944).
13. V. L. Solozhenko, G. Will, H. Hüpen, and F. Elf, *Solid State Commun.* **90,** 65 (1994).
14. V. L. Solozhenko and G. Will, *High Pressure Mater. Sci. Geosci.* **57,** (1994).
15. G. Will and V. L. Solozhenko, "HASYLAB." Jahresbericht, 1995.
16. J. von der Gönna, H. J. Meurer, G. Nover, T. Peun, D. Schönbohm, and G. Will, *Solid Mater. Lett.* **33,** 321 (1998).
17. J. W. Cahn, *Acta Metall.* **4,** 449 (1956).
18. G. Will and J. Lauterjung, "High-Pressure Research in Mineral Physics." American Geophysical Union Washington, DC, 1987.
19. B. P. Singh, G. Nover, and G. Will, *J. Crystal Growth* **125,** 143 (1995).