Refined Phase Diagram of Boron Nitride

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The equilibrium phase diagram of boron nitride thermodynamically calculated by Solozhenko in 1988 has been now refined on the basis of new experimental data on BN melting and extrapolation of heat capacities of BN polymorphs into high-temperature region using the adapted pseudo-Debye model. As compared with the above diagram, the hBN ⇆ cBN equilibrium line is displaced by 60 K toward higher temperatures. The hBN−cBN−L triple point has been calculated to be at 3480 ± 10 K and 5.9 ± 0.1 GPa, while the hBN−L−V triple point is at $T = 3400 \pm 20$ K and $p = 400 \pm 20$ Pa, which indicates that the region of thermodynamic stability of vapor in the BN phase diagram is extremely small. It has been found that the slope of the cBN melting curve is positive whereas the slope of hBN melting curve varies from positive between ambient pressure and 3.4 GPa to negative at higher pressures.

Introduction

Wentorf's synthesis of cubic boron nitride (cBN) in 1957[1] initiated immediate attempts to construct the phase *p*,*T*-diagram for boron nitride. A first version of such a diagram[2] was proposed by Bundy and Wentorf in 1963 based on Wentorf's experimental data on conversion of graphite-like hexagonal BN (hBN) into the cubic form[1,3,4] and data on hBN melting under high pressures.[5] By analogy with the carbon diagram,[6] Corrigan and Bundy[7] improved the diagram of 1963 by extrapolating the hBN ⇆ cBN boundary line to the low-temperature region and estimating the melting curve for cBN. This version of the BN phase diagram was generally accepted up to the late 80s.

Subsequent attempts to refine the BN phase diagram dealt only with the hBN−cBN boundary line. The analysis of numerous publications[8−13] on hBN → cBN and cBN → hBN conversions, both direct and "catalytic", showed a considerable disagreement between experimental data for different systems. This disagreement cast doubt upon the validity of identification of the hBN−cBN experimental boundaries with the hBN ⇆ cBN equilibrium line because of the crucial importance of kinetic factors in the BN phase formation at high pressures and temperatures. Therefore, it was concluded[14] that the correct positions of equilibrium lines in the BN phase diagram could be obtained only in the framework of a thermodynamic approach. For this reason Solozhenko et al. have studied heat capacities and enthalpies,[15−23] formation enthalpies,[24−27] equations of state,[28−30] and thermal expansion[31] of all the BN crystalline polymorphs. On the basis of these data, a new equilibrium phase diagram was suggested[14] and then improved in the succeeding years.[32−39] This diagram differs drastically from the earlier BN diagrams,[2,7] since at ambient pressure cBN rather then hBN was found to be thermodynamically stable.[14] (The up-to-date version of this diagram is published in ref 39.) The previously assumed parallels between phase diagrams of carbon and boron nitride were thereby rejected.

It should be, however, noted that all equilibrium lines in this new phase diagram are located above 1600 K, while the experimental data on heat capacities and enthalpies were measured only up to 1650 K. Therefore, it is clear that these data had to be extrapolated into the high-temperature region. For this purpose the empirical equation for heat capacity suggested by Reshetnikov[40] was used.[36−39]

More recently, an adapted pseudo-Debye model (APD) was proposed[41,42] that allows more reasonable extrapolations. Besides, new experimental data on BN melting in the 0.05−10 GPa range were published[43−45] that provided a possibility of refining the equilibrium phase diagram of BN as illustrated in the present paper.

Results and Discussion

All the experimental data on thermodynamic properties of hBN and cBN are represented here in the framework of an adaptive pseudo-Debye model[41,42] in the form

$$C_p(T) = 3R\tau^3 \frac{4C_0 + 3C_1\tau + 2C_2\tau^2 + C_3\tau^3}{(C_0 + C_1\tau + C_2\tau^2 + C_3\tau^3)^2}\left[1 + A\frac{\tau^4}{(a+\tau)^3}\right] \tag{1}$$

which allows significant deviations from a simple Debye model by the use of four additional free parameters C_0, C_1, C_2, and A. Here, R is the gas constant, $\tau = T/\theta$ denotes the reduced temperature, θ corresponds to the high-temperature value of the usual Debye temperature, and $C_3 = 1$ is then prefixed. The parameter a in the anharmonic correction term is most reasonably fixed to the value of $^1/_8$, which represents the best high-temperature limit of the simple Debye model. As input data for the fits, experimental values of low- and high-temperature heat capacities (for hBN in the 15−305 K range,[21] for cBN in the

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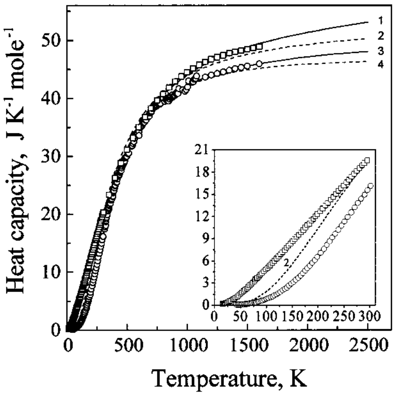

Figure 1. Heat capacities of BN polymorphs vs temperature: (1, 3) extrapolation by APD model for hBN and cBN, respectively; (2, 4) extrapolation by Reshetnikov's equation for hBN and cBN, respectively. Circles and squares present experimental data on hBN[21,23] and cBN.[15,16,19]

TABLE 1: Free Parameters of the APD Model Describing the Temperature Dependencies of the Heat Capacities for cBN and hBN

	A	C_0	C_1	C_2
hBN	0.0399	0	0.1291	0.4257
cBN	0.0064	0.0274	0.0264	0.4548

4–302 K range[16] and in the 300–1100 K range[19]) and high-temperature enthalpies (for hBN in the 435–1652 K range,[23] for cBN in the 386–1702 K range[15,18]) were used. To obtain high-temperature heat capacity values, the high-temperature enthalpies of hBN and cBN were processed according to the procedure suggested by Shomate[46] followed by a differentiation of the resulting Shomate functions. The APD coefficients given in Table 1 are then obtained by least-squares refinements.[41]

Figure 1 shows the Reshetnikov and APD representations of the experimental data and their extrapolations into the high-temperature region. It is clear from the figure that the APD model fits the experimental data better than the Reshetnikov form, both in the low-temperature and high-temperature regions.

The hBN ⇆ cBN equilibrium line was then calculated using the heat capacity data obtained by APD extrapolation together with the formation enthalpies, isothermal bulk moduli, and thermal expansion coefficients of cBN and hBN taken from ref 36. On the basis of the hBN melting entropy of 25 J/(mol K)[47] and melting temperature of 3400 K at 50 MPa,[43] the melting enthalpy of hBN was estimated at 85 kJ/mol. From the value of the initial slope of the hBN melting curve (70 K/GPa[5]), the molar volume of the liquid boron nitride under standard conditions was found to be 12.42×10^{-6} m^3/mol. To describe the compressibility of liquid boron nitride, Murnaghan's equation of state was used with the bulk modulus $K_0 = 13.3$ GPa and its pressure derivative $K_0' = 2$, by analogy with Gustafson's approach to describing the molar volume of liquid carbon.[48] The thermal expansion of liquid boron nitride was assumed to be equal to the thermal expansion of hBN.

To calculate the equilibria with contribution of vapor, thermodynamic data for gaseous boron nitride given in ref 47 were used. Dissociation and formation of gaseous species that differ from monomeric BN molecules have been neglected. The calculations of curves of hBN ⇆ liquid, hBN ⇆ vapor, and liquid ⇆ vapor equilibria have shown that the hBN–L–V triple point has the following coordinates: $T = 3400 \pm 20$ K and $p = 400 \pm 20$ Pa. Hence, the region of vapor thermodynamic stability in the BN phase diagram is extremely small (for comparison, the coordinates of the graphite–L–V triple point are 4766 K and 10.3 MPa[48]).

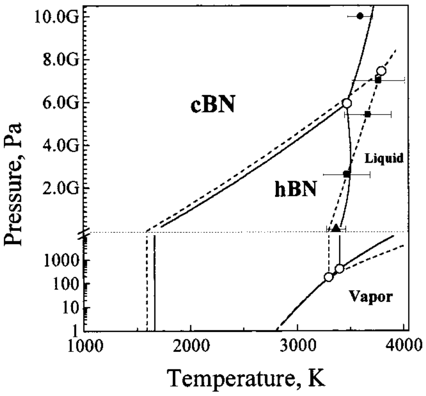

Figure 2. Phase p,T-diagram of boron nitride (solid lines, refined diagram from present paper; dashed lines, Solozhenko's diagram[39]). Solid squares show Wentorf's data on hBN melting.[5] Solid circle is the melting point of cBN at 10 GPa,[45] [45] and solid triangle is hBN melting point at 50 MPa.[43]

The refined equilibrium phase diagram of boron nitride is given in Figure 2. Compared with the latest version of Solozhenko's diagram,[39] the hBN ⇆ cBN equilibrium line is displaced by 60 K toward higher temperatures. The higher compressibility of the liquid phase with respect to graphite-like hexagonal boron nitride first causes the slope of the hBN melting curve to increase with pressure up to 3.4 GPa, and then the slope becomes negative. The intersection of the calculated hBN melting curve with the hBN ⇆ cBN equilibrium line defines the hBN–cBN–liquid triple point at 3480 ± 10 K and 5.9 ± 0.1 GPa.

A comparison of the experimental data on hBN melting[5] with the hBN melting curve calculated in the present work shows that the calculation agrees with the experimental data within the experimental errors. Obviously, Wentorf's experimental point at 6.7 GPa corresponds not to hBN but to cBN melting. The calculated curve of cBN melting meets within experimental error with the cBN melting point at 10 GPa measured by Zerr et al.[45] This fact supports the validity of Gustafson's approach[48] also for liquid boron nitride.

Very recently, Eremets et al.[44] have reported 8.6 GPa as the lowest limit for the hBN–cBN–liquid triple point. These authors based their conclusion on the observation that above this pressure liquid BN crystallizes into the cubic phase only while a crystallization of an hBN–cBN mixture occurs at 7.3 GPa. However, a positive slope of the cBN melting curve corresponds to a lower molar volume of the cubic phase compared to the liquid BN. Hence, cBN crystallization should result in a local decrease in the pressure down to the values that match the thermodynamic stability region of hBN. A similar effect was reported by Bundy,[49] who observed without any exception a crystallization of liquid carbon to graphite–diamond mixtures even in the stability region of diamond.

Conclusions

The APD model has been successfully used to describe all the existing experimental data on heat capacity of cubic and graphite-like hexagonal BN polymorphs with reasonable extrapolations to the high-temperature region.

On the basis of these data and the assumption of a higher compressibility of liquid boron nitride with respect to the crystalline BN phases, the equilibrium p,T-diagram of boron nitride has been refined. The results agree well with the latest experimental data on cBN melting.

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