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Thermodynamics of dense boron nitride modifications and a new phase P,T diagram for BN

V. L. Solozhenko

Institute for Superhard Materials of the Ukrainian Academy of Sciences, Kiev 254153, USSR

ABSTRACT

On the basis of experimental measurements of thermodynamic properties of BN dense phases, the equilibria between various boron nitride phases over a wide range of pressures and temperatures were calculated and a new BN phase p,T-diagram was proposed. This new phase diagram drastically differs from the generally accepted one.

KEYWORDS: boron nitride, thermodynamic properties, p,T phase diagram

INTRODUCTION

The current knowledge on the BN phase diagram is based on experimental data on catalytic synthesis of cubic boron nitride (cBN) at high pressures and temperatures under nonequilibrium conditions (Wentorf, 1961). Also, until recently, information on the enthalpies of formation for the wurtzite (wBN) and cubic forms of dense boron nitride were not available and the published data on their thermodynamic properties should be considered to be estimations. Because of this lack of data, correct calculation of the equilibrium curves for different BN phases was not possible.

Given on the above, it may be said that present knowledge on the thermodynamic aspects of BN polymorphism is based on the adopted analogy of the phase p,T-diagrams for carbon and boron nitride (Corrigan and Bundy, 1975). In the frame of this theory, the equilibrium line of graphite-like boron nitride (gBN) and cubic modifications is parallel to the equilibrium line graphite = diamond and intersects the pressure axis at the point $p = 1.3$ GPa. This indicates that cBN is metastable at low pressures over the entire temperature range.

In the present work, on the basis of measured experimental data on thermodynamic properties of dense modifications of BN, an attempt was made to calculate the equilibrium phase diagram for boron nitride over a wide p,T-range.

EXPERIMENTAL

Thermodynamic properties of boron nitride were measured over the range 4-1700 K using inverse drop-calorimetry, adiabatic calorimetry and thermoanalytical (DSC,DTA) methods. The samples studied included single crystals of cubic boron nitride obtained in conventional growth systems (Rapoport, 1985) and under pressure of supercritical fluids (Solozhenko et al,1989b). cBN polycrystalline samples were produced both using high pressure-high temperature sintering of cBN powders and as a result of direct phase transformation of pyrolytic gBN under similar conditions. Finally, measurements were made on wBN samples which were produced by shock compression (Soma *et al.*,1975), and thermostabilization (Solozhenko, 1989c).

RESULTS AND DISCUSSION

Low temperature adiabatic calorimetry was used for measuring the heat capacity of cubic boron nitride single crystals (Solozhenko *et al.*,1987b) and polycrystals (Solozhenko *et al.*, 1989a) in the 4-300 K interval. The data obtained enabled one to calculate standard values of cBN thermodynamic functions. The results of these calculations are given in Table 1.

Experimental enthalpies $H^0(T)-H^0(298.15\ K)$ of cubic BN single crystals obtained by the inverse drop-calorimetry method using aluminum capsules in the 386- 697 K temperature range (Solozhenko *et al.*, 1987a) and in the 804-1103 K range using tantalum capsules (Solozhenko and Holodov,1990). Enthalpies for polycrystals obtained by cBN powder sintering (Solozhenko *et al.*, 1989c) were made in the 420-1598 K temperature range. The enthalpies associated with the direct transformation of gBN to cBN were made in the 923-1702 K temperature range and are shown in Figure 1.

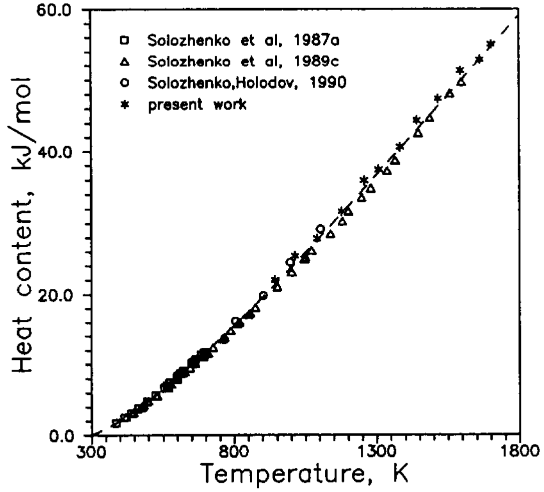

Figure 1. Heat content of cubic boron

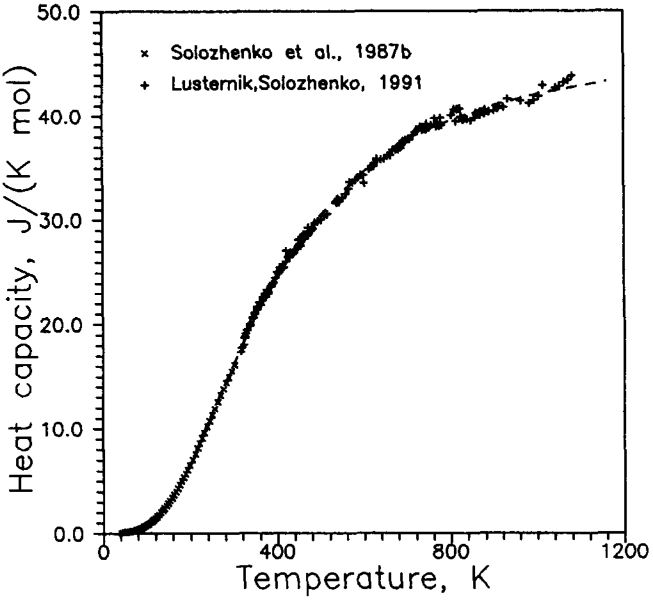

Figure 2. Heat content of cubic boron nitride.

The heat capacity of cBN single crystals over the range 300-1100 K was measured using scanning adiabatic calorimetry (Lusternik and Solozhenko, 1991). Experimental values are shown in Figure 2. The figure also shows heat capacity of cBN single crystals (Solozhenko *et al.*, 1987b) over the range 4-300 K.

All the experimental data on heat capacity in the 4-1100 K range were approximated using Reshetnikov's (1966) equation which is very suitable for extrapolation of Cp(T) dependence both to high- and low-temperature ranges. The dependence is expressed by the equation

$$C_p^0(T) = 46.290\left(\frac{T^2}{T^2 - 18.727T + 67447.464}\right)^2 \quad (1)$$

which is shown as a dashed curve in Figure 2. Since agreement between the experimental and calculated enthaplies of cBN over the range 300-1700 K was observed (Figure 1), the equation was used for calculation of cBN thermodynamic functions values in that temperature range.

The heat content of wurtzite boron nitride in the 300-1300 K range was measured using inverse drop-calorimetry. Figure 3 shows experimental enthalpy values for thermostabilized wBN (Solozhenko and Holodov, 1990) and corresponding values for wBN obtained by shock-wave synthesis (Solozhenko, 1991). The mathematical treatment of experimental data was carried out by Shomate's (1944) method, considering the C_p^0(298.15 K) value for wBN determined earlier (V. E. Gorbunov *et al.*,1988). If $F(T) = A + B\,T + C\,T^2$, Shomate's function, which provides

Table 1. Standard values of the cubic boron nitride thermodynamic functions

Substance	$H^0(298)$-$H^0(0)$	$S^0(298)$	$Cp^0(298)$
Monocrystalline cBN	1436±2	6.59±0.01	15.79±0.03
Polycrystalline cBN	1442±3	6.64±0.02	15.77±0.04

optimal approximation of points is used, the temperature dependence of wBN heat content over the range 300-1300 K is given by equation

$$H^0(T)-H^0(298.15K)=-164.666-17.763T+6.935\cdot10^{-2}T^2-2.666\cdot10^{-5}T^3+1491.357\cdot T^{-1} \qquad (2)$$

with deviations between experimental and calculated values less than 1.2% (a dashed curve in Figure 3). Using equation (2) and standard values of wBN thermodynamic functions (V.E.Gorbunov *et al.*, 1988) the values of heat capacity, entropy and Gibbs energy for wurtzite boron nitride were tabulated in the 300-1300 K temperature range.

The thermochemistry of cBN and wBN interaction with fluorine was studied using fluorine calorimetry, and standard values of formation enthalpies for cubic (V. Ya. Leonidov *et al.*, 1987) and wurtzite (V.Ya. Leonidov *et al.*, 1988) BN modifications were determined which allowed us to calculate standard enthalpy values for boron nitride polymorphic transformations. These results are given in Table 2. The calculations were made using $\Delta_f H^0$(gBN, 298) = -250.3 kJ/mole (Wise, *et al.*, 1966) and the standard enropy values of Gorbunov, et al. (1988) for wBN and gBN.

Using a high temperature heat flux calorimeter, the cBN - gBN transition was studied over the range 1500-2000 K and the enthalpy of transition was estimated to be ΔH^0(1800 K) = 22 kJ/mole with the uncertainty range being between (11 and 27 kJ/mole) which sufficiently agrees with 19±3 kJ/mole calculated using the standard value of the cBN - gBN transformation enthalpy and high temperature heat content data for cBN (present work) and gBN (McDonald and Stull, 1961) as well.

On the basis of the results obtained for cBN in the 0-1700 K range and corresponding data for gBN, the temperature dependence of Gibbs energy variation for gBN - cBN transformation at p = 0.1 MPa was calculated (a solid line in Figure 4). Analysis of the temperature dependence allows us to conclude that at atmospheric pressure cBN is thermodynamically stable form of boron nitride in the 0-1640 K temperature range and therefore the equilibrium curve gBN = cBN intersects not the pressure axis as it was previously thought (Corrigan and Bundy,1975), but rather the temperature axis at T = 1640 K which drastically changes the established notion of thermodynamic stability regions for cBN and gBN.

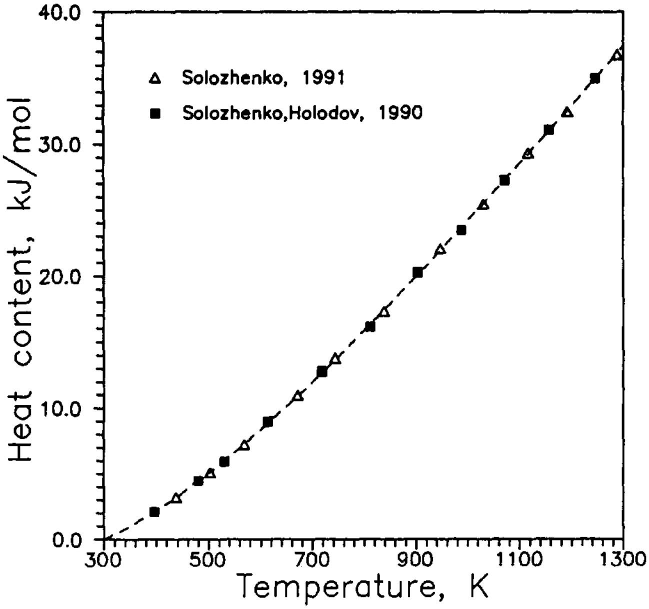

Figure 3. Heat Content of wurtzite boron nitride

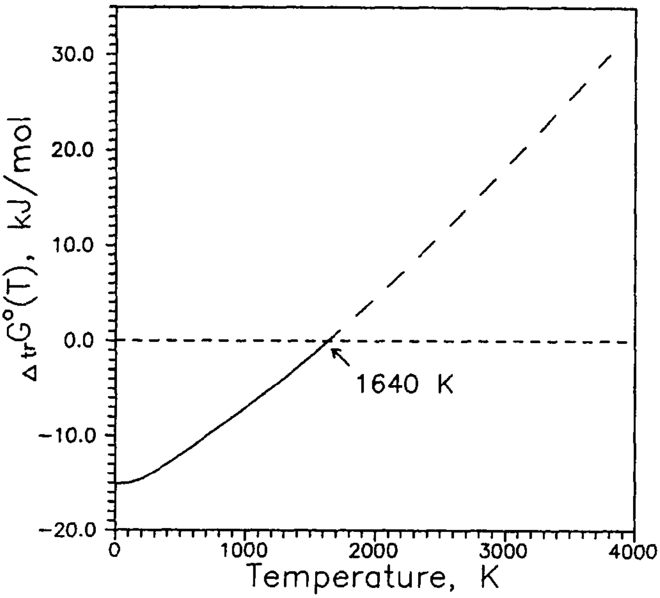

Figure 4. Temperature dependence of Gibbs energy variation for gBN → cBN transformation

Table 2. Standard values of the thermodynamic functions for boron nitride polymorphic transformations.

Transformation	$\Delta_{tr}H^0(298)$ kJ/mole	$\Delta_{tr}S^0(298)$ J/mol·K	$\Delta_{tr}G^0(298)$ kJ/mol
gBN → cBN	-16.5	-8.56	-13.9
gBN → wBN	-12.9	-7.91	-10.5
wBN → cBN	-3.6	-0.65	-3.9

Using our (unpublished) data on the thermal expansion of cBN and Pease's (1952) results for gBN, as well as data on the compressibility of cBN (Knittle *et al.*, 1989) and gBN (Lynch and Drickamer,1966) the volumetric effect values for cBN - gBN transition were calculated over a wide p,T-region. The $\Delta_{tr}G^0(T)$ temperature dependence of gBN → cBN transformation was extrapolated to the high temperatures (dashed line in Figure 4) using Leipunsky's (1939) equation with an error not exceeding 10%.

The above data allowed us to calculate the equilibrium line cBN = gBN over a wide range of pressures and temperatures. Similar calculations of equilibrium curves wBN = gBN and wBN = cBN showed that in the temperature range of 0 to 4000 K, the wurtzite boron nitride is not thermodynamically stable, at least to pressures up to 10 GPa. Based on the results obtained as well as on Wentorf's (1959) data on high pressure melting of boron nitride a new phase diagram for boron nitride is proposed which differs from the generally accepted one (Figure 5). The proposed diagram allows us to explain our (Solozhenko *et al.*, 1989b) recently obtained experimental data for cBN crystallization at low (down to atmospheric) pressures , which was impossible in the frame of Corrigan and Bundy's (1975) diagram.

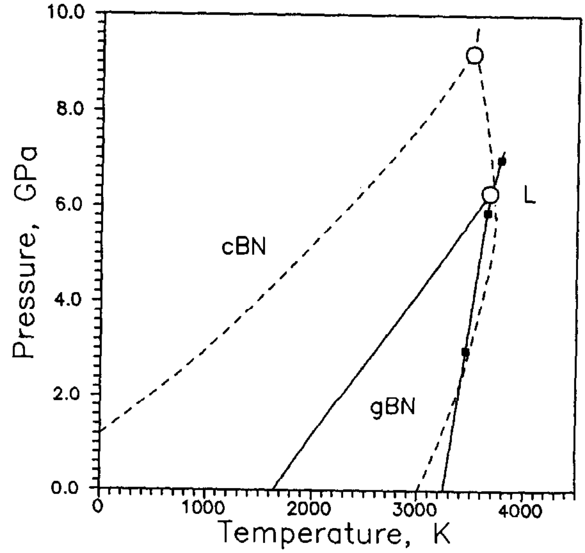

Figure 5. Phase p,T diagram of boron nitride (the dashed curve is for Corrigan and Bundy's diagram). Solid squares represent Wentorf's (1959) data for BN melting.

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