Thermochimica Acta, 217 (1993) 77–89
Elsevier Science Publishers B.V., Amsterdam

Low-temperature heat capacity and thermodynamic properties of four boron nitride modifications

K.S. Gavrichev[a], V.L. Solozhenko[b], V.E. Gorbunov[a], L.N. Golushina[a], G.A. Totrova[a] and V.B. Lazarev[a,*]

[a] *The Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907 (Russian Federation)*
[b] *Bakul Institute for Superhard Materials, Ukrainian Academy of Sciences, Kiev 254153 (Ukraine)*

(Received 26 June 1992)

Abstract

A short review of the low-temperature heat capacity studies of four boron nitride (BN) modifications is presented. C_p versus (T) dependences of high-ordered hexagonal and disordered (turbostratic) modifications were studied by adiabatic calorimetry. The influence of disordering on the heat capacity of boron nitride is shown. The values of thermodynamic properties (heat capacity, entropy, enthalpy, and formation enthalpy) of four BN modifications is reported.

INTRODUCTION

Boron nitride, first synthesized 150 years ago by W.H. Balmain, is now successfully used in many fields of science and technology. Electronics and nuclear engineering materials, superhard construction materials, lubricants, and refractory materials are only a few of the applications of different boron nitride modifications.

THE STRUCTURE OF THE BORON NITRIDE POLYMORPHOUS MODIFICATION

Under normal conditions, boron nitride exists in four polymorphous modifications: two graphite-like forms, hexagonal (hBN) (Fig. 1) and uncommon rhombohedral (rBN) (Fig. 2), and two dense forms, wurtzitic

---

[*] Corresponding author.

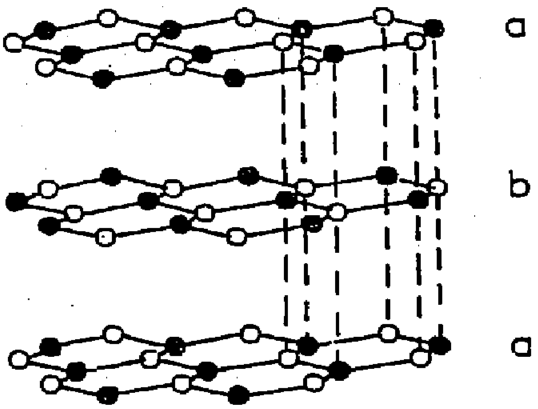

Fig. 1. Crystal structure of graphite-like BN modification (a and b are types of layers).

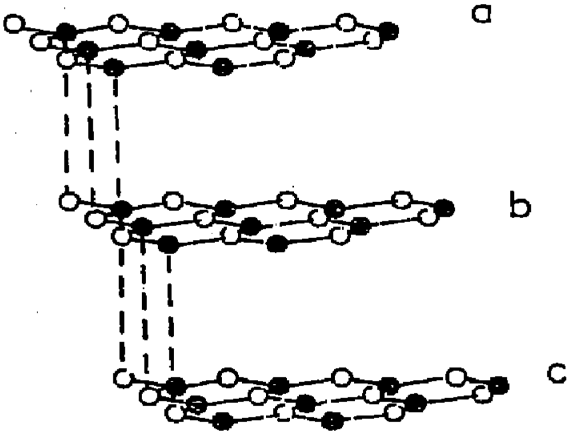

Fig. 2. Crystal structure of rhombohedral BN modification (a, b and c are types of layers)

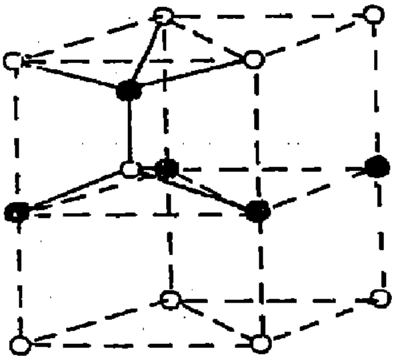

Fig. 3. Crystal structure of wurtzitic BN modification.

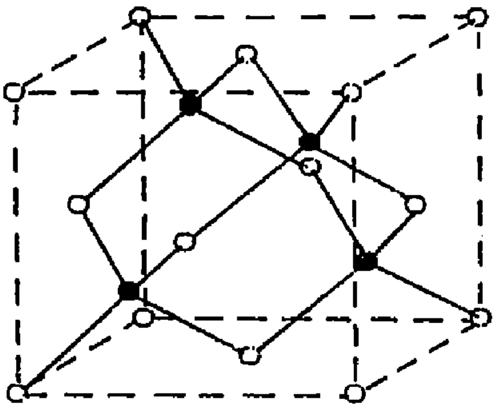

Fig. 4. Crystal structure of cubic BN modification.

(wBN) (Fig. 3) and cubic (cBN) (Fig. 4). The characteristics of these boron nitride modifications are given in Table 1.

LOW-TEMPERATURE HEAT CAPACITY

Graphite-like hexagonal BN

The low-temperature heat capacity studies of hBN were reported in refs. 5–7. Dworkin et al. [5] determined the C_p versus (T) dependence in the 20–300 K range using adiabatic calorimetry. The studied sample of hBN

TABLE 1

Crystallochemical characteristics of BN polymorphous modifications

Space group	hBN $P6_3/mmc$	rBN $R3m$	cBN $F\bar{4}3m$	wBN $P6_3mc$
Lattice period (Å)				
a	2.504 [1]	2.504(5) [2]	3.6160(3) [3]	2.551(0) [4]
c	6.6612 [1]	10.000(2) [2]	–	4.214(8) [4]
Density [a] (from X-ray data) (g cm^{-3})	2.279	2.276	3.486	3.470
Shortest interatomic distance B–N (Å) [a]	1.446	1.450	1.565	1.568

[a] Calculated from the indicated lattice parameters.

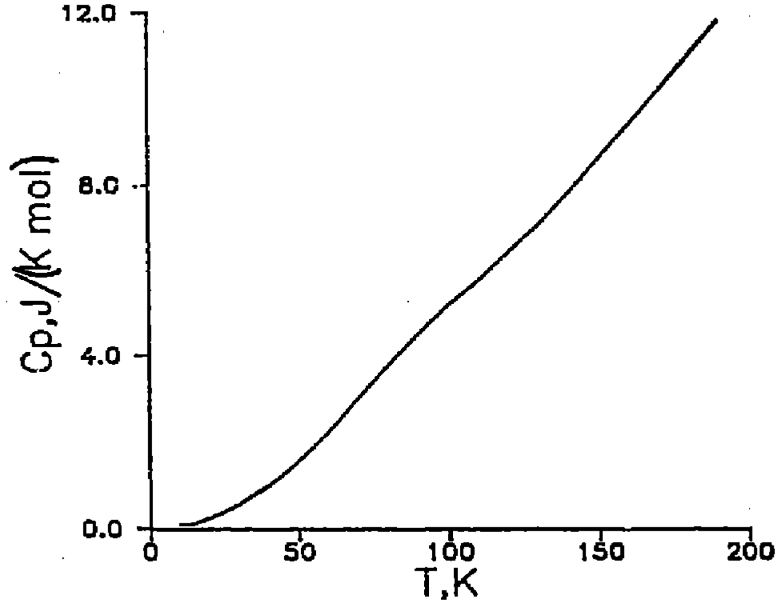

Fig. 5. C_p versus (T) curve for graphite-like BN [7] in the region of a slightly convex anomaly.

contained 0.15% of iron and boron oxides impurities. Later, Sirota et al. [6] investigated the heat capacity of this modification, but their sample contained larger amounts of impurities (≈2.8%) and their C_p versus (T) data had a large deviation of experimental points (3–10%). In ref. 7, the C_p versus (T) dependence of hBN was determined in the 10–300 K range in an adiabatic calorimeter. The content of impurities in the sample was less than 0.15%; here [7], the authors took into account the influence of impurities on the C_p versus (T) data.

A comparison of these results [5–7] show that they differ slightly (in the order of percents). A slightly convex anomaly is a common feature for all the experimental curves [5–7] in the range of 60–140 K (Fig. 5). It is interesting that the C_p versus (T) dependence for graphite has no anomaly in this region [8].

Cubic BN

The low-temperature heat capacity studies of cubic boron nitride are reported in refs. 9–12. The cBN sample studied by Sirota and Kofman [9] contained up to 4% of impurities, whereas samples studied in refs. 10–12 contained 99.8–99.9% of the main material. Moreover, the methods of heat capacity measurement used in ref. 9 did not provide accurate C_p versus (T) data. The results of refs. 10–12 are in good agreement with one another (deviations of about 1%), unlike those of ref. 9 which are sufficiently lower (dozens of percent). Therefore, only the more reliable results of refs. 10–12 were used for the estimation of cBN thermodynamic properties.

Wurtzitic BN

The low-temperature heat capacity studies of boron nitride wurtzitic modification are reported in refs. 7 and 13. The sample studied in ref. 13 contained only about 92% wBN. The results of this research had a considerable deviation of experimental points (up to 5%). Gorbunov et al. [7] studied the heat capacity of wBN in the 6–300 K range using adiabatic calorimetry. The sample contained ≈99.7% of the main material. A small anomaly with a maximum at 21 K was found on the C_p versus (T) curve of wBN. The nature of this anomaly was not explained by the authors. A comparison of the above results has shown that the C_p versus (T) curve in ref. 13 lies considerably higher than the curve in ref. 7 (up to 25%) and even higher than the curve for hBN. This demonstrates the low reliability of data in ref. 13.

Rhombohedral BN

The rhombohedral modification of BN usually occurs as an admixture in the graphite-like hexagonal modification; its properties have been insufficiently studied. Recently, Solozhenko et al. [14] proposed a method of rBN synthesis involving the interaction of boron and ammonia at high pressure and high temperature.

The low-temperature heat capacity of the synthesized material has been measured by adiabatic calorimetry [15]. The studied sample contained 2% of hBN and 0.8% of boron oxide, and carbide and magnesium nitride impurities. The degree of three-dimensional ordering was 0.93. The authors took into consideration the influence of impurities while calculating the thermodynamic properties. No anomaly of the heat capacity was observed, unlike hBN.

THE INFLUENCE OF DISORDERING ON THE HEAT CAPACITY OF BORON NITRIDE

A small convex anomaly of graphite-like hexagonal boron nitride, reported in ref. 7, attracted our attention. We have analysed the possible factors which may result in the appearance of an anomaly on the C_p versus (T) curve of hBN. This anomaly can probably be explained as the consequence of (1) the influence of impurities; (2) the high dispersion of the sample; (3) the increased distance between layers in the crystal structure.

The literature contains conflicting information on the influence of impurities on the heat capacity. An impurity may either penetrate into the crystal lattice of the studied material (as, for example, on doping ammonium chloride with heavy metals [16]), or intercalate in the layered structures (as described for PbI_2 [17]). Both cases featured a slightly convex anomaly of heat capacity in the region below 40 K, caused by the interaction of atoms or molecules of intercalants. But for the hBN reported in ref. 7 (content of impurities ≈0.15%), the interaction of admixtural atoms is improbable, and we assume that this does not occur.

Because the graphite-like hexagonal boron nitride studied in ref. 7 was a very dispersed powder with a particle size of ≥ 1 μm, an anomaly of hBN heat capacity may be attributed to the influence of the size-factor on the C_p values, because it is known that the surplus heat capacity of ultra-dispersed samples yields a curve with the maximum at 100 K [18, 19].

However, we believe that the most probable reason for the appearance of a slightly convex anomaly of the C_p of hBN [5–7] was the occurrence of a low-frequency mode in the vibrational spectrum of this modification because of the increased distance between layers caused by the disordering of the layers alternating along the *c*-axis. The disordering of graphite-like hexagonal boron nitride due to the displacement of layers in arbitrary positions by translation or turning in the basal plane, has been investigated earlier [20] and was named turbostratic defects of packing.

For the experimental examination of our hypothesis, we studied two samples of graphite-like boron nitride: high-ordered hBN and fully disordered (turbostratic) BN. The particles sizes were nearly equal to minimize the size-factor influence on the heat capacity.

For the heat capacity investigation, a sample of turbostratic BN (tBN) synthesized according to ref. 21, and a sample of Fluka AG fine-fraction hBN were studied. The starting powders were subjected to thermal treatment: tBN at 1400 K in a vacuum of 0.1 Pa for 3 h; hBN at 2100 K in nitrogen atmosphere (oxygen content less than 0.003%) for 5 h. All subsequent operations with the samples were carried out in an atmosphere of dry inert gas.

According to granulometric and electron microscopic analyses, the size of the tBN particles varied within the limits 0.1–0.2 μm; the specific surface of the studied sample, calculated by the BET method from the isotherms of nitrogen absorption at 77 K, was 210 ± 20 m^2 g^{-1}. However, the value of the specific surface area may be slightly high due to the possible sorption of nitrogen in the sample volume. The degree of three-dimensional ordering of the tBN crystal lattice measured by the method in ref. 22 using the X-ray data, was equal to 0; the distance between layers d_{002} was 3.56 Å and the closest B–N interatomic distance was 1.45 Å, i.e. the same as for high-ordered hBN.

The mean value of hBN particle size according to granulometric

TABLE 2

Impurity contents of BN samples (mass%)

	C	O	Si	Ca	Al	Mg	Fe	Cl
tBN	0.1	0.1	0.01	0.0002	0.0004	0.0001	0.0003	0.01
hBN	0.4	0.1	0.03	0.02	0.015	0.0006	0.0025	–

measurements was 0.4 μm and the specific surface area was 60 ± 10 m^2 g^{-1}. The degree of three-dimensional ordering of the crystal lattice was 0.98 ± 0.2, and the distance between layers d_{002} was 3.330(4) Å.

The contents of impurities in the studied samples determined by mass spectrometric investigation and X-ray microanalysis, are given in Table 2.

TABLE 3

Experimental heat capacity of high-ordered hBN

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
15.04	0.1654	82.71	3.698	182.79	11.01
16.04	0.1798	85.42	3.847	186.75	11.46
17.28	0.1983	88.14	4.099	190.67	11.63
18.80	0.2259	91.34	4.327	194.34	12.02
20.54	0.2777	94.99	4.571	198.19	12.30
22.47	0.2996	98.62	4.819	203.23	12.68
24.50	0.3534	102.42	5.066	208.37	13.05
26.80	0.4224	105.29	5.261	213.54	13.44
29.19	0.5458	107.69	5.459	218.53	13.83
31.85	0.6129	111.36	5.722	223.96	14.26
34.78	0.7394	115.16	5.987	229.04	14.65
37.53	0.8604	119.23	6.275	234.01	15.03
40.46	0.9911	123.28	6.594	238.99	15.46
43.72	1.160	127.13	6.866	243.97	15.79
46.59	1.322	131.05	7.133	248.96	16.18
49.68	1.525	135.11	7.431	254.21	16.61
52.68	1.706	139.00	7.737	259.40	16.96
55.92	1.899	142.68	8.033	264.38	17.36
58.91	2.069	146.56	8.308	269.43	17.76
61.88	2.228	150.51	8.617	274.48	18.14
64.74	2.432	154.41	8.911	279.54	18.51
67.59	2.660	158.16	9.216	284.57	18.87
70.36	2.840	161.93	9.480	289.55	19.23
73.09	3.040	167.03	9.854	294.65	19.59
75.85	3.244	171.07	10.16	299.82	19.95
78.57	3.444	174.96	10.47	304.81	20.30
81.27	3.640	178.84	10.83		

TABLE 4

Experimental heat capacity of turbostratic BN

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
11.59	0.1635	76.38	4.210	178.80	12.04
12.87	0.1713	79.32	4.449	183.71	12.43
14.01	0.2645	82.29	4.672	188.65	12.82
15.02	0.3472	85.15	4.886	193.47	13.21
15.99	0.3709	87.95	5.069	198.44	13.62
17.11	0.4429	91.24	5.329	203.47	14.02
18.59	0.5261	95.19	5.571	209.01	14.47
20.42	0.6173	99.05	5.868	213.91	14.87
22.42	0.7323	102.76	6.110	218.88	15.30
24.49	0.8495	106.51	6.363	223.85	15.68
26.58	0.9678	110.24	6.614	229.11	16.10
28.44	1.076	113.94	6.889	234.38	16.50
30.82	1.187	117.71	7.190	238.30	16.83
33.76	1.338	121.51	7.456	242.82	17.23
36.86	1.501	125.20	7.725	246.91	17.57
40.26	1.663	130.36	8.093	250.99	17.95
43.84	1.852	135.11	8.478	255.04	18.22
47.32	2.128	139.92	8.849	259.58	18.60
50.63	2.341	144.55	9.230	264.59	18.96
54.33	2.604	149.05	9.599	269.59	19.39
56.26	2.629	149.25	9.603	274.64	19.79
59.22	2.949	151.89	9.847	280.07	20.22
62.22	3.129	154.80	10.10	285.37	20.59
65.07	3.344	158.76	10.38	290.25	21.03
67.90	3.568	163.57	10.80	295.23	21.41
70.74	3.785	168.43	11.20	300.06	21.66
73.55	4.004	173.66	11.62	[illegible]	22.06

The heat capacities of hBN and tBN were determined by adiabatic calorimetry in the temperature range of 1[illegible] [illegible]. The experimental C_p versus (T) data are given in Tables 3 and 4. The [illegible] of the C_p versus (T) curves was performed by LSM [illegible] polynomial. Values of the thermodynamic functions [illegible] Tables 5 and 6, respectively.

It is obvious from the C_p ver[illegible] high-ordered hBN has no anomaly and [illegible] than given in ref. 7, with the exception of th[illegible] 6). The investigation of the low-temperature [illegible]ed graphite-like boron nitride shows that its [illegible] considerably higher than the corresponding hBN [illegible] the C_p versus (T) curve for tBN, a convex anomaly is clearly featured. [illegible]is demonstrates that the size

TABLE 5

Thermodynamic properties of high-ordered hBN

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$H^\ominus(T) - H^\ominus(0)$ (J mol^{-1})	$-[G^\ominus(T) - H^\ominus(0)]/T$ (J K^{-1} mol^{-1})
16	0.1603	0.0530	0.641	0.0129
20	0.2501	0.0981	1.462	0.0249
25	0.3914	0.1685	3.066	0.0458
30	0.5632	0.2545	5.452	0.0728
35	0.7635	0.3560	8.769	0.1055
40	0.9906	0.4724	13.15	0.1436
45	1.242	0.6033	18.74	0.1870
50	1.517	0.7482	25.63	0.2355
60	2.129	1.077	43.86	0.3463
70	2.813	1.456	68.57	0.4761
80	3.556	1.879	100.4	0.6236
90	4.221	2.336	139.3	0.7878
100	4.900	2.815	184.9	0.9660
110	5.602	3.315	237.4	1.156
120	6.323	3.833	297.0	1.357
130	7.060	4.368	363.9	1.568
140	7.809	4.918	438.3	1.788
150	8.567	5.483	520.2	2.015
160	9.332	6.060	609.7	2.249
170	10.10	6.649	706.8	2.491
180	10.88	7.248	811.7	2.738
190	11.65	7.857	924.4	2.992
200	12.43	8.474	1045	3.250
210	13.20	9.099	1172	3.514
220	13.97	9.731	1308	3.782
230	14.74	10.37	1452	4.054
240	15.50	11.01	1603	4.331
250	16.26	11.66	1762	4.611
260	17.02	12.32	1929	4.894
270	17.77	12.97	2103	5.181
273.15	18.02	13.18	2159	5.272
280	18.51	13.63	2284	5.471
290	19.25	14.29	2473	5.764
298.15	19.85	14.84	2632	6.012
300	19.99	14.96	2669	6.063

of the particles is not the reason for the appearance of the convex anomaly of hBN heat capacity. Differences in the heat capacities of turbostratic and high-ordered hBN (1), and hBN [7] and high-ordered hBN (2) in the range of 15–300 K are given in Fig. 7. We believe that the similarity of these curves testifies to the partial disordering of the sample studied in ref. 7.

TABLE 6

Thermodynamic properties of turbostratic BN

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$H^\ominus(T) - H^\ominus(0)$ (J mol^{-1})	$-[G^\ominus(T) - H^\ominus(0)]/T$ (J K^{-1} mol^{-1})
12	0.211	0.0703	0.632	0.0176
15	0.340	0.1306	1.458	0.0334
20	0.597	0.2619	3.799	0.0719
25	0.877	0.4242	7.484	0.1248
30	1.152	0.6079	12.56	0.1893
35	1.405	0.8042	18.95	0.2683
40	1.648	1.008	26.58	0.3431
45	1.962	1.220	35.61	0.4283
50	2.308	1.444	46.28	0.5184
60	3.022	1.927	72.93	0.7111
70	3.751	2.446	106.0	0.9207
80	4.481	2.994	148.0	1.145
90	5.203	3.564	196.4	1.382
100	5.918	4.148	252.0	1.629
110	6.628	4.746	314.7	1.885
120	7.344	5.353	384.6	2.148
130	8.080	5.970	461.7	2.418
140	8.853	6.597	546.4	2.694
150	9.684	7.236	639.0	2.975
160	10.49	7.886	739.9	3.262
170	11.30	8.546	848.9	3.553
180	12.11	9.215	965.9	3.849
190	12.93	9.892	1091	4.149
200	13.75	10.58	1224	4.453
210	14.57	11.27	1366	4.761
220	15.38	11.96	1515	5.073
230	16.20	12.66	1674	5.387
240	17.01	13.37	1839	5.705
250	17.81	14.08	2013	6.026
260	18.61	14.80	2196	6.349
270	19.40	15.51	2386	6.676
273.15	19.66	15.74	2447	6.779
280	20.19	16.24	2584	7.004
290	20.96	16.95	2789	7.335
298.15	21.58	17.54	2963	7.606
300	21.72	17.68	3003	7.667

THERMODYNAMIC PROPERTIES OF BORON NITRIDE POLYMORPHOUS MODIFICATIONS

Based on the expert evaluation of the low-temperature heat capacities of cubic, wurtzitic and rhombohedral BN modifications, indicated in this paper, as well as on the heat capacity values of the ordered-graphite-like

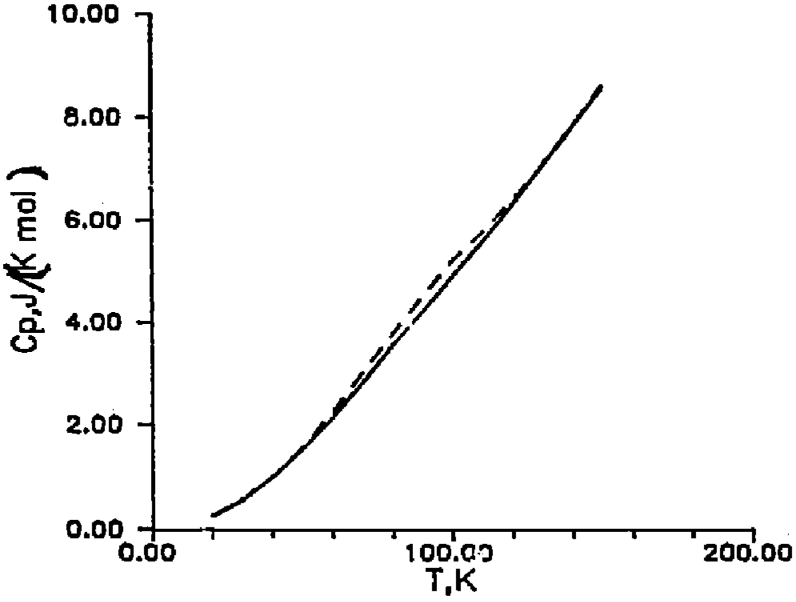

Fig. 6. C_p versus (T) curves for hBN: ——, present work; – – –, ref. 7.

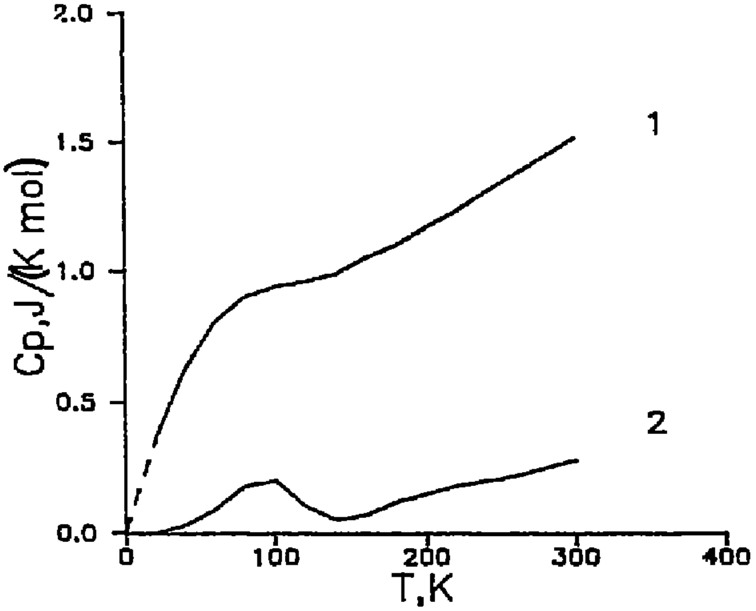

Fig. 7. Differences in the heat capacities of (curve 1) turbostratic and high-ordered hBN; (curve 2) hBN [7] and high-ordered hBN.

TABLE 7

Thermodynamic properties of boron nitride polymorphous modifications

	hBN [a]	rBN [15]	cBN [10–12]	wBN [7]
$C_p^\ominus$(298.15 K) (J K^{-1} mol^{-1})	19.85 ±0.06	20.63 ±0.06	15.95 ±0.10	16.45 ±0.05
$S^\ominus$(298.15 K) (J K^{-1} mol^{-1})	14.90 ±0.10	15.83 ±0.10	6.710 ±0.06	7.340 ±0.05
$H^\ominus$(298.15 K) – $H^\ominus$(0) (J mol^{-1})	2632 ±25	2805 ±25	1457 ±15	1541 ±15

[a] This work.

TABLE 8

Formation enthalpies for hBN, cBN and wBN

	hBN [23]	cBN [24]	wBN [25]
$\Delta H^{\ominus}$(298.15 K)	-250.6 ± 2.1	-266.8 ± 2.2	-263.6 ± 2.3

hexagonal modification, we propose the following data as reference thermodynamic values for the four boron nitride modifications, see Table 7.

The standard formation enthalpies of three boron nitride modifications are given in Table 8. The corresponding data for the rhombohedral modification of boron nitride will be published in the near future. And thus the determination of the key standard thermodynamic values for boron nitride will be complete.

REFERENCES

1 R.S. Pease, Acta Crystallogr., 5 (1952) 356.
2 V.L. Solozhenko, personal communication.
3 V.L. Solozhenko, V.V. Chernyshev, G.V. Fetisov, V.B. Rybakov and I.A. Petrusha, J. Phys. Chem. Solids, 51 (1990) 1011.
4 V.B. Zelyavskii, A.V. Kurdyumov and V.L. Solozhenko, Sov. Phys. Dokl., 35 (1990) 911.
5 A.S. Dworkin, D.J. Sasmor and J. Van Artsdalen, J. Chem. Phys., 22 (1954) 837.
6 N.N. Sirota, N.A. Kofman and J.K. Petrova, Izv. Akad. Nauk. BSSR, 6 (1975) 75.
7 V.E. Gorbunov, K.S. Gavrichev, G.A. Totrova, A.V. Bochko and V.B. Lazarev, Russ. J. Phys. Chem., 62 (1988) 9.
8 W. DeSorbo and W.W. Tyler, J. Chem. Phys., 21 (1953) 1660.
9 N.N. Sirota and N.A. Kofman, Sov. Phys. Dokl., 20 (1975) 861.
10 V.L. Solozhenko, V.E. Yachmenev, V.A. Vil'kovskii, A.N. Sokolov and A.A. Shul'zhenko, Russ. J. Phys. Chem., 61 (1987) 1480.
11 V.E. Gorbunov, K.S. Gavrichev, G.A. Totrova, A.V. Bochko and V.B. Lazarev, Russ. J. Phys. Chem., 61 (1987) 1768.
12 V.L. Solozhenko, V.E. Yachmenev, V.A. Vil'kovskii and I.A. Petrusha, Inorg. Mater., 25 (1989) 134.
13 N.N. Sirota and N.A. Kofman, Sov. Phys. Dokl., 21 (1976) 516.
14 V.L. Solozhenko, V.A. Mukhanov and N.V. Novikov, Dokl. Chem., 312 (1990) 125.
15 K.S. Gavrichev, V.E. Gorbunov, V.L. Solozhenko, L.N. Golushina and G.A. Totrova, Russ. J. Phys. Chem., 66 (1992) 2824.
16 K.S. Gavrichev, V.E. Gorbunov, N.Kh. Makhmetov, T.A. Kuketaev and V.M. Jurov, Proc. 12th All-Union Conf. Chem. Thermodyn., vol 1, GSU, Gorky, 1988, p. 10.
17 A.M. Gurevich, B.Ya. Sukharevsky and A.V. Alapina, Proc. 9th All-Union Conf. Chem. Thermodyn., Mezniereba, Tbilisi, 1982, p. 234.
18 T.S. Chen, F.W. De Wett, L. Kleinmann and D.C. Dempsey, Phys. Rev. B, 17 (1978) 835.
19 T.H. Barron, W.T. Berg and J.A. Morrison, Proc. R. Soc. London Ser. A, 250 (1959) 70.
20 J. Tomas, N.E. Weston and T.E. O'Connor, J. Am. Chem. Soc., 84 (1963) 4619.

21 Pat. 1193485DER. Verfahren und Anlage zur Herstellung von Nitriden der Elemente Aluminium, Bor, Silizium order Zirkonium (G. Heimer, H. Harnisch, 06.10.66).
22 A.V. Kurdyumov, Russ. J. Crystallogr., 20 (1975) 969.
23 V.Ya. Leonidov, I.V. Timofeyev and V.L. Solozhenko, in I.B. Rabinovich (Ed.), Thermodynamics of Chemical Substances, GSU, Gor'ky, 1988, p. 16.
24 V.Ya. Leonidov, I.V. Timofeyev, V.L. Solozhenko and I.V. Rodionov, Russ. J. Phys. Chem., 61 (1987) 1503.
25 V.Ya. Leonidov, I.V. Timofeyev, V.B. Lazarev and A.V. Bochko, Russ. J. Inorg. Chem., 33 (1988) 906.