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The Enthalpy of Formation of Hexagonal Boron Nitride

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The energies of combustion in fluorine of three specimens of hexagonal boron nitride with different degree of ideal crystalline structure have been measured in a two-compartment calorimetric bomb at 298.15 K according to reaction: $BN(cr) + 3/2F_2(g) = BF_3(g) + 1/2N_2(g)$, and new standard molar enthalpies of formation $\Delta_f H_m^0$ have been calculated and used to rank the samples in order of stability: $\Delta_f H_m^0 = -(245.8\pm1.1)$ kJ/mol for turbostratic sample, that deviates most from the crystalline structure; $\Delta_f H_m^0 = -(248.5\pm0.9)$ kJ/mol for the sample with an interlayer spacing that is only about 0.5% larger than the ideal crystalline h-BN; and $\Delta_f H_m^0 = -(250.8\pm1.2)$ kJ/mol for crystalline h-BN.

Key words: standard molar enthalpy of formation, hexagonal boron nitride, turbostratic boron nitride, pyrolytic boron nitride

All polymorphic forms of boron nitride are in recent years important in material science. The keen analysis of the vast literature on boron nitride covering the period to 1988 has been performed by Anton Meller in two supplementing volumes of Gmelin Handbook [1]. Three phases of this compound are of interest: hexagonal (α-BN), cubic (β-BN), and wurzite form (γ-BN). System of crystalline phases of boron nitride is analogous to that of carbon: α-BN has a graphite structure, cubic β-BN has a cubic diamond structure and wurzite type γ-BN has a hexagonal diamond structure. Between the reviews concerning transformation of other boron nitride phases into cubic β-BN the most comprehensive study was compiled by Eliezer Rapoport [2] in 1985. Reading this literature, one can notice that there is considerable conflict between phase diagram and thermodynamic information on the boron nitrides. The thermodynamic behavior of boron nitride is still not well understood and it is most simply illustrated by the current chaotic state of its phase diagram. There is a controversy as to whether a cubic form is more stable than the hexagonal. In order to give the reliable answer to the posed above questions, the phase diagram and thermodynamic properties have to be verified. From the thermodynamic side it requires careful determinations of the enthalpies of formation, entropies and high temperature heat capacities of three forms of boron nitride.

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Objective of this study was to determine the standard molar enthalpy of formation $\Delta_f H_m^0$ of hexagonal boron nitride by combustion calorimetry in fluorine. The research was carried out in Physical and Chemical Properties Division at National Institute of Standards and Technology, using unique and very precise fluorine combustion bomb system. All previous experience of boron nitrides combustion in excess of fluorine showed that the only products are gaseous nitride and boron trifluoride according to:

$$BN(c) + 3/2\ F_2(g) = BF_3(g) + 1/2\ N_2(g) \tag{1}$$

irrespective of the phase of the boron nitride. The enthalpy of reaction (1) may be combined with the standard molar enthalpy of formation of boron trifluoride, that was already well established to obtain the standard enthalpy of formation of $\Delta_f H_m^0$ (BN). Because the material, on which calorimetric measurements are to be performed should always be of the highest purity, it was very crucial to obtain a proper product. Since hexagonal boron nitride is very reactive toward air, this substance is nearly always contaminated with oxygen. Searching for best materials several samples, some of them also synthesized in Warsaw Technical University were preliminary analyzed, but their content of oxygen was too high – the best result was 1.31 mass %. Finally, three different specimens of boron nitride characterized by different degree of crystalline hexagonal structure were investigated.

EXPERIMENTAL

Materials: Boron nitride powder sample of crystalline hexagonal structure was furnished by Aldrich Co.. Anal. Calcd. for BN: B, 43.6; N, 56.4. Found: B, 43.3; N, 56.0. Chemical analysis showed the following impurities (in %): O, 0.516; C, total carbon 0.0852, free carbon 0.07265, H, 0.0314 and trace metals; 0.0427 (Al, 0.015; Ca, 0.0197; Cr, 0.0062; Cu, 0.0007; Si, 0.0008; Ti, 0.0011; V, 0.0018; Mg, 0.0032; Na, < 0.0005; Ni, < 0.0005; Zn, < 0.0005). Two samples of pyrolytic boron nitride were provided by Dr. A.W. Moore (Advanced Ceramics Corporation, Cleveland, Ohio). Samples were prepared at temperatures in the range 1710÷2000°C and pressures of 0.66÷1.06 kPa using BCl_3 and NH_3 reactant gases by a hot-wall CVD (chemical vapor deposition) method [3,4].

Sample PBN-8601 (density of 1.94 g/cm^3 and an average interlayer spacing 2÷4% larger than that of ideal boron nitride – 3.33 Å) was turbostratic, *i.e.*, it had a high percentage of layer stacking disorder. Anal. Calcd. for PBN-8601: B, 43.6; N, 56.4. Found: B, 43.59; N, 56.39. Impurities were determined to be (in %): O; 0.0101; C; 0.0084; H; 0.00216. Sample (PBN-8614) was more crystalline (had a density of 2.22 g/cm^3 and an interlayer spacing only about 0.5% larger than ideal hexagonal boron nitride). Anal. Calcd. for PBN-8614: B, 43.6; N, 56.4. Found: B, 43.59; N, 56.39. Impurities were determined to be (in %): O; 0.01261; C; 0.0111; H, 0.00299.

The impurities O, C, H and trace metals of BN samples were analyzed by the following methods. Oxygen was determined by inert gas fusion with IR detection; hydrogen by inert gas fusion and thermal conductivity; total amount of carbon by high-temperature combustion with IR detection (LECO Corporation, St. Joseph, Michigan) and trace metals by a direct-current-plasma, optical-emission spectroscopic technique (Luvac Inc, Boylston, MA). Because carbon impurity can exist as free carbon or carbon combined as B_4C, it has significant influence on the measured value of enthalpy of combustion in fluorine. That is why the amount of free carbon in boron nitride sample from Aldrich was additionally analyzed on LECO

RC412 “multiphase” carbon determinator, that incorporated sophisticated resistance heated combustion system (possibility of ramp heating from 25 to 1100°C) coupled to IR detection system, designed to measure carbon as CO_2. The basic theory of this procedure is that free carbon will oxidize and will be released at a lower temperature than combined carbon. The results of analysis (presented by Dr. D. Lawrenz from LECO) showed that free carbon was oxidized between 50÷600°C.

The other products used in calorimetric experiments were: fluorine of 98% purity purchased from Air Products, prepared by distillation and before use passed through a column filled with NaF to remove any traces of HF; high-purity hexagonal selenium (batch no. S75045), purchased from Johnson Matthey, studied previously in the same NIST laboratory [5] and used in this work as ignition aid. The only impurity of Se was 0.001 mass % of oxygen determined by neutron-activation analysis.

Fluorine calorimetric system: Laboratory with calorimetric system equipped with related accessories: manifold placed in ventilated hood for transferring F_2 and gaseous products, and glovebox with purification unit, has been set up at NIST in 1990 by P. O’Hare [6,7] . The calorimetric system contained an isoperibol calorimeter, constructed for rotation bomb (Argonne National Laboratory designation, ANL-R2) [8] and two-compartment (bomb + tank) calorimetric vessel, designed for compounds spontaneously reacting with fluorine [9]. Calorimetric experiment started after the calorimetric vessel arranged for reaction was immersed in a can, which was filled with an accurately weighed amount of water and placed in a calorimeter thermostat. The temperatures of the can and the calorimeter thermostat were monitored by probes of the quartz-crystal thermometer (Hewlett-Packard, model 2804-A) and registered on PC computer. The inner part of the vessel was a nickel combustion bomb of volume 0.306 dm^3 while the outer part, where fluorine was stored, was a stainless steel tank of volume 0.2356 dm^3 connected to the bomb by stainless steel tube and an isolation valve. Gaskets in the vessel were made from gold or Teflon and all O-rings made from Teflon. They were cleaned by acetone before exposure to F_2 in order to eliminate possibility of ignition. The calorimetric system was calibrated by combustion in oxygen of standard reference material NIST SRM 39i benzoic acid, which has a certified specific energy of combustion of –(26434±3) J/g under prescribed conditions. During the calibration, the fluorine tank was evacuated, the valve was kept close, and oxygen at 3.0396 MPa pressure was contained only in the proper bomb. The determined mean value for ε(calor) – the energy equivalent of the calorimetric system was (13926.6±0.7) J/K. After calibration procedure and before experiments with fluorine, the bomb was preconditioned by initial exposure to F_2 when a thin, strongly adhering film of NiF_2 was formed, that protected the bomb from further fluorine attack. A manifold for handling fluorine at maximum pressure 2÷3 MPa was, for security reason, constructed from 316 stainless steel lines and valves (Autoclave Engineers, Inc.) with fittings designed with substantial margin of safety and was kept under vacuum (pressure < 1 Pa) with Fomblin fluid rotary pumps. The fluorine was stored in a Monel cylinder connected to the manifold. The outer part (storage tank) separated from the calorimetric vessel and connected to the manifold was filled with fluorine before experiment. Before and after experiment, the calorimetric vessel fixed up was attached to the manifold and all present gases were evacuated from the combustion bomb. Gaseous products of combustion and waste fluorine removed from vessel were passed through a copper column with activated alumina. Because of the extreme reactivity of F_2 all interior surfaces of the reaction vessel had to be kept dry in order to eliminate possibility of adsorption of H_2O. Thus all operations with open bomb, such as preparing, loading the samples and connecting the tank filled with fluorine were carried out in the glovebox filled with recirculating dry nitrogen purified of O_2 and H_2O by continuos passage over finely divided copper and molecular sieves. Inside the glovebox an analytical balance (Sartorius R1605) was installed, used to weigh the samples with precision $\pm 3\cdot10^{-5}$ g.

Calorimetric procedure: Trial experiments with Aldrich h-BN sample showed that it ignited spontaneously with F_2 at ambient temperature. However, both pyrolytic samples did not react spontaneously and they required a small quantity of Se, used as a fuse material. Reacting with fluorine, Se initiated combustion of pyrolytic samples and converted to SeF_6(g). All operations that exposed the interior of the bomb or BN samples were performed in a glovebox. Sample was weighed directly into 7.6 g prefluorinated nickel crucible, and on the top of the sample a selenium shot was later placed and weighed. Then the crucible was rested on the lid of the reaction bomb. Meanwhile the tank connected to a manifold was filled with fluorine of 1.0 MPa and at 293 K. Next the tank and bomb were assembled together in a glovebox, the reaction vessel was again connected to the manifold and the nitrogen (present in a glovebox) was removed to a vacuum system from the reaction bomb. When pressure inside a bomb decreased to 1 Pa, valve was closed and the reaction vessel was placed in the calorimeter. When the monitored temperature has reached the steady state, the valve of fluorine tank was opened, combustion of BN started and temperature was rising swiftly. Experiment was finished when temperature again became steady (close to 298 K). Afterwards, the reaction vessel was connected to the manifold, the gaseous products of fluorination were isolated in the gas trap immersed in a liquid nitrogen and later identified by FTIR spectrometer. Only peaks attributable to BF_3(g) and (in case of combustion of the PBN samples) also SeF_6(g) were observed The reaction vessel was returned to the glovebox for further examination of solid residues and checking the mass of crucible. In few experiments small residues (mass less than 1 mg) of unreacted BN were found, and corrections for these residues were made. The increase of crucible mass was not observed, thus, the formation of NiF_2 was excluded in this case. Between sequential BN combustion experiments was also performed a series of blank experiments. When fluorine expands from the tank to the bomb, it also reacts with some traces of impurities adsorbed on the walls. Because the expansion and the reaction occur during combustion experiment, the correction for their thermal effect must be applied. Blank experiments were carried out in a usual way by expanding fluorine into an empty bomb without a sample.

RESULTS AND DISCUSSION

The results of three series of the combustion experiments on samples h-BN, PBN8614 and PBN8601 are given in Tables 1, 2 and 3. The symbols in the tables are defined as follows: m denotes the mass of sample or fuse (Se), converted from the apparent mass measured in nitrogen; $\Delta\theta_c$, the corrected temperature increase calculated by the method of Hubbard *et al.* [10]; ΔU(blank), an empirical correction calculated by method described by O'Hare [11]; ΔU(gas), correction for expansion and compression of F_2 and the combustion gases; ΔU(cont), change of substrates and products energy content; ΔU(Se), contribution of the energy of reaction of selenium fuse with fluorine to the total energy measured; ε(calor), the energy equivalent of the calorimetric system was described previously; $\Delta_c u$, the massic energy of combustion of the specimen.

Massic energy of combustion (T = 298.15 K) of Se(cr) in F_2 according to the reaction:

$$Se(cr) + 3\ F_2(g) = SeF_6(g) \qquad (2)$$

determined by O'Hare [5] was taken to be –(14097±6) J/g, and from this ΔU(Se) was obtained.

Computation of ΔU(gas) and ΔU(cont) was described by Hubbard [12]. For the calculation of ΔU(gas), the second virial coefficient B of the gaseous mixture and its temperature derivative T (δB/δT) were estimated [13] from intermolecular force constant data for F_2 [14], BF_3 [15] and N_2 [16]. Auxiliary quantities used to calculate ΔU(cont) included: (0.809 [20] and 0.317 [5]) $J{\cdot}K^{-1}{\cdot}g^{-1}$ for c_p^0 of BN and Se and (22.99 [17], 20.81 [17], 42.13 [16] and 99.8 [5]) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $C_{v,m}$ of F_2, N_2, BF_3 and SeF_6. For the conversion of apparent mass to mass m, densities of: 2.20 Mg /m^3, 2.22 Mg /m^3, 1.94 Mg/m^3 and 4.81 Mg /m^3 were used for h-BN, PBN8614, PBN8601 and Se. Individual values of $\Delta_c u$ of the samples were calculated by summing the energy quantities in each column of Tables 1÷3 and dividing by the corresponding mass of sample m(BN).

The mean values of energy of combustion were then calculated from individual values with uncertainty determined as standard deviation of the mean: (h-BN) $<\Delta_c u>$ $= -(35652\pm15)$ J·g^{-1}; (PBN8614) $<\Delta_c u>$ $= -(35790\pm6)$ J·g^{-1}; (PBN8601) $<\Delta_c u>$ $= -(35898\pm11)$ J·g^{-1}. To convert the obtained results to real values for the reaction (1) required calculation of corrections for the impurities in the samples.

Table 1. Massic energy of combustion of h-BN in fluorine (Aldrich sample); T = 298.15 K, p^0 = 101.325 kPa, ε(calor) = (13926.6±0.7) J/g.

	1	2	3	4	5	6	7
m(BN)/g	0.30072	0.52029	0.38248	0.33188	0.34477	0.32175	0.36843
$\Delta\theta_c$/K	0.76979	1.33221	0.97943	0.84976	0.88218	0.82337	0.94228
ΔU(blank)/J	0.7	0.7	0.7	0.7	0.7	0.7	0.7
ΔU(gas)/J	2.0	3.3	2.5	2.2	2.3	2.2	2.4
ΔU(cont)/J	–4.2	–7.5	–5.5	–4.7	–5.0	–4.7	–5.3
$\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)$/J	–10720.6	–18553.2	–13640.1	–11834.3	–12285.8	–11466.8	–13122.8
$\Delta_c u$/(J/g)	–35654.5	–35666.2	–35668.35	–35663.7	–35640.6	–35644.4	–35624.1

$<\Delta_c u> = -(35652\pm15)$ J/g[a]
Impurity correction = –(42.4±8.5) J/g[b]
$\Delta_c u^0 = -(35694\pm34)$ J/g[c]

[a] Uncertainty is the standard deviation of the mean of individual values $\Delta_c u$/(J/g). [b] Uncertainty corresponds to twice standard deviation of the mean. [c] The final uncertainty $2s = 2(\Sigma s_i^2)^{1/2}$ comprises the accumulated individual uncertainties expressed as standard deviations s_i: ±15 J/g for $<\Delta_c u>$; ±1.5 J/g from ΔU(blank)/m, ±0.5 J/g from ΔU(gas)/m, ±1.7 J/g for $\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)/m$, where m = 0.366 is the average mass of calorimetric sample, and the uncertainty of impurity correction is ±8.5 J/g.

Table 2. Massic energy of combustion of pyrolytic crystalline h-(PBN8614) sample in fluorine; T = 298.15 K, p^0 = 101.325 kPa, ε(calor) = (13926.6±0.7) J/g.

	1	2	3	4	5
m(BN)/g	0.27192	0.25490	0.29088	0.28902	0.24439
m(Se)/g	0.05068	0.04739	0.05586	0.05549	0.05054
$\Delta\theta_c$/K	0.74960	0.70275	0.80396	0.79903	0.67942
ΔU(blank)/J	0.6	0.6	0.6	0.6	0.6
ΔU(gas)/J	1.9	1.8	2.0	2.0	1.8
ΔU(cont)/J	–4.2	–3.9	–4.6	–4.5	–3.8
ΔU(Se)/J	714.4	668.1	787.5	782.2	712.5
$\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)$/J	–10439.4	–9786.9	–11196.4	–11127.8	–9462.0
$\Delta_c u$/(J/g)	–35770	–35780	–35791	–35802	–35807

$<\Delta_c u> = -(35790\pm6)$ J/g
Impurity correction = 6.3 J/g
$\Delta_c u^0 = -(35784\pm13)$ J/g[a]

[a] The final uncertainty $2s = 2(\Sigma s_i^2)^{1/2}$ comprises the accumulated individual uncertainties expressed as standard deviations s_i: ±6 J/g for $<\Delta_c u>$; ±2.1 J/g from ΔU(blank)/m, ±1.1 J/g from ΔU(Se)/m; ±0.7 J/g from ΔU(gas) /m, ±2.0 J/g for $\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)/m$, where m = 0.270 is the average mass of calorimetric sample.

Table 3. Massic energy of combustion of turbostratic h-(PBN8601) sample in fluorine; T = 298.15 K, p^0 = 101.325 kPa, ε(calor) = (13926.6±0.7) J/g.

	1	2	3	4	5	6
m(BN)/g	0.24496	0.26457	0.23009	0.26007	0.23537	0.25506
m(Se)/g	0.05014	0.04729	0.05153	0.04385	0.05595	0.04223
$\Delta\theta_c$/K	0.68201	0.72939	0.64492	0.71665	0.66314	0.69971
ΔU(blank)/J	1.4	1.4	1.4	1.4	1.4	1.4
ΔU(gas)/J	1.8	1.9	1.7	1.8	1.7	1.8
ΔU(cont)/J	–3.8	–4.1	–3.6	–4.0	3.7	–3.9
ΔU(Se)/J	706.8	664.6	726.4	618.1	788.7	595.3
$\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)$/J	–9498.1	–10157.9	–8981.5	–9980.5	–9235.3	–9744.6
$\Delta_c u$/(J/g)	–35903	–35888	–35892	–35916	–35901	–35885

$\langle\Delta_c u\rangle = -(35898\pm11)$ J/g
Impurity correction = 4.5 J/g
$\Delta_c u^0 = -(35894\pm23)$ J/g[a]

[a] The final uncertainty $2s = 2(\Sigma s_i^2)^{1/2}$ comprises the accumulated individual uncertainties expressed as standard deviations s_i: ±11 J/g for $<\Delta_c u>$; ±2.2 J/g from $\Delta U(\text{blank})/m$, ±1.2 J/g from $\Delta U(\text{Se})/m$; ±0.8 J/g from $\Delta U(\text{gas})/m$, ±1.9 J/g for $\varepsilon\Delta(\text{calor})\cdot(-\Delta\theta_c)/m$, where $m = 0.248$ is the average mass of calorimetric sample.

Impurity corrections: Corrections for the combustion of the impurity phases are based upon their amount and differences between their massic energies of combustion in F_2 and energy of boron nitride combustion. For the sample of hexagonal BN (Aldrich) the H, O impurities were assumed to be present as B_2O_3, H_2O and metals traces as borides or nitrides. The carbon impurities are in the form of free carbon and B_4C. Reactions of the impurity phases with fluorine are assumed to be the following:

$$B_4C(s) + 8F_2(g) = 4BF_3(g) + CF_4(g) \quad (3) \qquad C(s) + 2F_2(g) = CF_4(g) \quad (4)$$

$$B_2O_3(s) + 3F_2(g) = 2BF_3(g) + 3/2O_2(g) \quad (5) \qquad H_2O(1) + F_2(g) = 2HF(g) + O_2(g) \quad (6)$$

The corrections calculated for each assumed impurity phase on the basis of obtained analytical results and detailed auxiliary thermodynamic data [18,19] are collected in Table 4 and 5. The content of impurities in both pyrolytic BN samples was very small. The ratio of H amount compared to amount of O impurity was larger when it could be expected, assuming that hydrogen impurity is present as H_2O. However, in case of pyrolytic samples, NH_3 contamination was of concern because NH_3 was used in the synthesis of the specimens and probably could be adsorbed inside the structure.

$$NH_3(g) + 3/2F_2(g) = 3HF(g) + 1/2N_2(g) \qquad (7)$$

Calculated impurity corrections for crystalline pyrolytic (PBN8614) and turbostratic (PBN8601) samples are presented in Tables 6 and 7. The amount of carbon was very small in both samples and the distribution between B_4C and C was not analytically ratified, so in correction it was assumed that the ratio of two carbon forms was the same as in case of h-BN Aldrich sample.

Table 4. Impurity corrections for h-BN (Aldrich) sample.

Element	$w \cdot 10^2$ Impurity mass fraction	Impurity phase	$W \cdot 10^2$ Impurity phase mass fraction	$\Delta_f H_m^0$(imp) (kJ/mol)	$\Delta_c u^0$(imp) (kJ/g)	$\Delta(\Delta_c u)^a$ (kJ/g)	Correction $W \cdot \Delta(\Delta_c u)$ (J/g)
C	0.07265	C	0.07265	0	–10.50	41.9	30.4
C	0.01255	B_4C	0.05778	–72±11	–97.62	61.98	35.8
O	0.24416	B_2O_3	0.3544	–1273.5±1.4	–14.38	–21.27	–75.4
O	0.27184						
H	0.03398	H_2O	0.30582	–285.83±0.04	–26.01	–9.65	–29.5
Trace elements	0.0427	borides nitrides					–3.7
Total impurity correction: –42.4 J/g							

[a] $\Delta(\Delta_c u) = \Delta_c u(\mathrm{BN}) - \Delta_c u(\mathrm{imp})$; correction calculated on the basis of determined value of $\Delta_c u(\mathrm{BN}) = -(35652 \pm 15)$ J/g and $\Delta_c u$(imp) values calculated for reactions 3÷6 using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [18] and Barin [19].

Table 5. Corrections for trace elements in h-BN (Aldrich) sample.

Element	$w \cdot 10^6$ Impurity mass fraction	Assumed impurity phase	$W \cdot 10^6$ (impurity phase mass fraction)	$\Delta_f H_m^0$(imp) (kJ/mol)	$\Delta_c u$(imp) (kJ/g)	$\Delta(\Delta_c u)^a$ (kJ/g)	$W \cdot \Delta(\Delta_c u)$ (J/g)
Al	15	AlN	23	–317.98	–29.0	–6.6	–0.15
Ca	197	Ca_3N_2	242.9	–430.99	–21.87	–13.8	–3.35
Cr	62	CrN	75	–75.31	–17.44	18.27	–1.37
Cu	7	Cu_3N	22	–74.47	–3.73	–31.92	–0.25
Fe	62	FeB	74	–71.13	–30.8	–4.85	–0.36
Ni	< 5	Ni_3N_2	91	–311.71	–21.39	–14.26	–0.08
Si	8	SiN	40	–828.9	–28.62	–7.03	–0.09
Ti	11	TiB_2	16	–279.5	–51.68	16.03	0.26
V	18	VN	22	–138.5	–39.35	3.69	0.08
Zn	< 5	Zn_3N_2	17	–22.6	–9.59	–26.07	–0.15
Mg	32	Mg_3N_2	60	–92.0	–71.88	36.23	1.70
Impurity correction: –3.7 J/g							

[a] $\Delta(\Delta_c u) = \Delta_c u(\mathrm{BN}) - \Delta_c u(\mathrm{imp})$; correction calculated on the basis of determined value of $\Delta_c u(\mathrm{BN}) = -(35652 \pm 15)$ J/g and $\Delta_c u$(imp) values calculated using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [18] and Barin [19].

Table 6. Impurity corrections for pyrolytic turbostratic sample (PBN8601).

Element	w·10^2 (impurity mass fraction)	Assumed impurity phase	W·10^2 (impurity phase mass fraction)	$\Delta_f H_m^0$(imp) (kJ/mol)	$\Delta_c u^0$(imp) (kJ/g)	$\Delta(\Delta_c u)^a$ (kJ/g)	W·$\Delta(\Delta_c u)$ (J/g)
C	0.0084	B_4C	0.0057	–72±11	–97.62	61.98	3.5
		C	0.0075		–10.50	41.9	3.1
O	0.0101	B_2O_3	0.0147	–1273.5±1.4	–14.38	–21.52	–3.2
H	0.00216	NH_3	0.0122	–45.98±0.4	–45.206	9.31	1.1

Impurity correction: 4.5 J/g

[a] $\Delta(\Delta_c u) = \Delta_c u(BN) - \Delta_c u(imp)$; correction calculated on the basis of determined value of $\Delta_c u$(BN) = –(35898 ± 11) J/g and $\Delta_c u$(imp) values obtained for reactions 3÷5 and 7 using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [18] and Barin [19].

Table 7. Impurities correction for crystalline pyrolytic sample (PBN8614).

Element	w·10^2 (impurity mass fraction)	Assumed impurity phase	W·10^2 (impurity phase mass fraction)	$\Delta_f H_m^0$(imp) (kJ/mol)	$\Delta_c u^0$(imp) (kJ/g)	$\Delta(\Delta_c u)^a$ (kJ/g)	W·$\Delta(\Delta_c u)$ (J/g)
C	0.0111	B_4C	0.0075	–72±11	–97.62	61.98	4.6
		C	0.0095	0	–10.50	41.9	4.0
O	0.0126	B_2O_3	0.01828	–1273.5±1.4	–14.38	–21.41	–3.9
H	0.00299	NH_3	0.0169	–45.98±0.4	–45.206	9.31	1.6

Impurity correction: 6.3 J/g

[a] $\Delta(\Delta_c u) = \Delta_c u(BN) - \Delta_c u(imp)$; calculated on the basis of determined value of massic energy of combustion $\Delta_c u(BN) = -(35790 \pm 6)$ J/g and $\Delta_c u$(imp) values obtained for reactions 3÷5 and 7 using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [18] and Barin [19].

Standard molar enthalpies of formation: As a consequence of the application of impurity corrections, the standard massic energies of combustion listed in the bottom of Tables 1, 2 and 3 were deduced to be: for h-BN $\Delta_c u^0 = -(35694 \pm 34)\ \mathrm{J \cdot g^{-1}}$; for PBN8614 $\Delta_c u^0 = -(35784 \pm 13)\ \mathrm{J \cdot g^{-1}}$; and for turbostratic sample PBN8601 $\Delta_c u^0 = -(35894 \pm 23)\ \mathrm{J \cdot g^{-1}}$. In addition to the experimental results of massic energies of combustion and impurity corrections, in the calculated values of the $\Delta_c u^0$ final uncertainty $2s = 2(\Sigma s_i^2)^{1/2}$ comprises the accumulated individual uncertainties expressed as standard deviations s_i. In Table 8, the thermodynamic properties of the boron nitrides determined by fluorine bomb calorimetry are summarized. With the use of molar mass M(BN) = 24.8167 g/mol the standard molar energies of combustions (and enthalpies) $\Delta_c U_m^0 = \Delta_c H_m^0$ were calculated. In calculations of the BN enthalpies of formation $\Delta_f H_m^0$ from the enthalpies of combustion $\Delta_c H_m^0$ the value of boron trifluoride enthalpy of formation $\Delta_f H_m^0(BF_3$, gas, 298.15 K) = –(1136.6± 0.9) kJ/mol [17] was used. The reaction, to which $\Delta_f H_m^0$ refers, is ($T = 298.15$ K, $p^0 = 101.325$ kPa): $B(cr) + 1/2N_2(g) = BN(cr,hex)$.

Table 8. Summary of standard thermochemical results for the hexagonal boron nitrides.

	$\Delta_c u_m^0$ (J/g)	$\Delta_c U_m^0 = \Delta_c H_m^0$ (kJ/mol)	$\Delta_f H_m^0$ (kJ/mol)
turbostratic PBN8601	–35894±23	–890.8±0.6	–245.8±1.1
crystalline PBN8614	–35784±13	–888.1±0.3	–248.5±0.9
crystalline h-BN	–35694±34	–885.8±0.8	–250.8±1.2

Determined values of standard molar enthalpies of formation: $\Delta_f H_m^0 = -(245.8\pm1.1)$ kJ/mol for turbostratic sample, that deviates most from the crystalline structure; $\Delta_f H_m^0 = -(248.5\pm0.9)$ kJ/mol for the sample that differs in interlayer spacing by about 0.5% from crystalline h-BN; and $\Delta_f H_m^0 = -(250.8\pm1.2)$ kJ/mol for crystalline h-BN correlate well with the stabilities expected solely on the basis of the interlayer separations. The value from this work derived for the enthalpy of formation of crystalline h-BN is in good agreement with the most accurate measurements of well described samples that were performed by Wise *et al.* [20] ($\Delta_f H_m^0 = -(250.3\pm1.5)$ kJ/mol), Gross *et al.* [21] ($\Delta_f H_m^0 = -(253.2\pm2.1)$ kJ/mol) and Leonidov *et al.* [22] ($\Delta_f H_m^0 = -(250.6\pm2.1)$ kJ/mol).

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REFERENCES

1. Meller A., The System Boron-Nitrogen, Gmelin Handbook B 4th Suppl. Vol. 3a, (1992).
2. Rapoport E., Cubic Boron Nitride – A Review, *Ann. Chim.*, **10**, 607 (1985).
3. Moore A.W. and Strong S.L., *Ceram. Eng. Sci. Proc.*, **10**, 846 (1989).
4. Moore A.W., *Nature*, Vol. 221, **5186**, 1136 (1969).
5. O'Hare P.A.G., *J. Chem. Thermodyn.,* **25***,* 391 (1993).
6. O'Hare P.A.G., *J. Chem. Thermodyn.*, **24***,* 639 (1992).
7. O'Hare P.A.G., The Nuts and Bolts and Results of Fluorine Bomb Calorimetry, Energetics of Stable Molecules and Reactive Intermediates, Ed. Minas de la Piedade M.E., Kluver Academic Publishers (1999).
8. Hubbard W.N., Katz C. and Waddington G.J., *J. Phys. Chem.*, **58**, 142 (1954).
9. Nuttall R.L., Wise S. and Hubbard W.N., *Rev. Sci. Instrum.*, **32**, 1402 (1961).
10. Hubbard W.N., Scott D.W. and Waddington G.J., Experimental Thermochemistry, Ed. Rossini F.D., NY (1956), chap. 5.
11. O'Hare P.A.G., *J. Chem. Thermodyn.*, **17***,* 349 (1985).
12. Hubbard W.N., Experimental Thermodynamic, Vol. II, Ed. Skinner H.A., Interscience: NY (1962), chap. 6.
13. Hirschfelder J.O., Curtiss C.F. and Bird R.B., Molecular Theory of Gases and Liquids, Wiley: NY (1954).
14. White D., Hu J.-H. and Johnston H.L., *J. Chem. Phys.*, **21**, 1149 (1953).
15. Brooks G.L. and Raw C.J.G., *Trans. Farad. Soc.*, **54**, 972 (1958).
16. Heintz A. and Lichtenthaler R.N., *Ber. Bunsenges. Phys. Chem.*, **80**, 962 (1976).
17. Johnson G.K., Feder H.M. and Hubbard W.N., *J. Chem. Phys.*, **70**, 1 (1966).
18. Gurvich L.V., Veyts I.V. and Alcock C.B., Thermodynamic Properties of Individual Substances, Vol. 2, Hemisphere: NY (1991).
19. Barin I., Thermochemical Data of Pure Substances, Vol. I and II, VCh Verlagsgesellschaft, Germany (1995).
20. Wise S.S., Margrave J.L., Feder H.M. and Hubbard W.N., *J. Chem. Phys.*, **70**, 7 (1966).
21. Gross P., Hayman C. and Stuart M.C., *Proc. Brit. Ceram. Soc.*, **8**, 39 (1967).
22. Leonidov V.Ya. and Timofeev I.V., *Russ. J. Phys. Chem.*, **61**, 1503 (1987).