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The Enthalpy of Formation of Cubic Boron Nitride

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The massic energies of combustion in fluorine of two specimens of cubic boron nitride have been measured in a bomb calorimeter, the standard molar enthalpy of formation $\Delta_f H^0_m$ (c-BN, cr, 298.15 K) = –254.6±1.5 and the enthalpy of polymorphic transition $\Delta_{trs} H^0_m$ (298.15 K) = –3.5±1.5 of the process: h-BN (cr) $\rightarrow$ c-BN (cr) have been determined. Those quantities are compared with the values determined previously.

Key words: enthalpy of formation**,** cubic boron nitride, fluorine combustion calorimetry

Cubic boron nitride, the second hardest material after diamond, has been synthesized in 1957 starting from hexagonal BN [1,2] by use of high pressure – high temperature techniques [3–5]. Now, in major scale the catalyst methods are used for production [6–8]. Due to the chemical stability – cubic BN is superior to diamond in high temperature oxidation resistance and inertness to many metal melts. It is an important engineering material as an abrasive and component of cutting tools. Also semiconductor properties of thin c-BN layers are applied. For technologists is important to know: if c-BN is the stable phase of boron nitride under standard conditions, what is the precise stability under those conditions, moreover is it possible to synthesize cubic BN at low temperature.

The objective of this work, performed in Physical and Chemical Properties Division at National Institute of Standards and Technology, was to determine the standard molar enthalpy of formation $\Delta_f H^0_m$ (cr, c-BN, 298.15 K) by fluorine combustion calorimetry.

EXPERIMENTAL

Materials: Two specimens of cubic boron nitride manufactured by Sumitomo Electric Company (Japan) were designated as grade A and grade B. Sample grade B, grains of size 4÷8 μm in gray color, contained the following impurities (in mass %): O, 0.147; C, 0.145±0.002; H, 0.01673. This sample was additionally analyzed for trace metals: 0.0658 (Al, 0019; Ca; 0.0201; Cr, 0.0056; Cu; 0.0015; Si, 0.0014; Ti; 0.0096; V, 0.0020; Mg, 0.0033; Fe, 0.0093; Ni, 0.0033; Zn, 0.0064). Sample designated as grade A, grains of size 0.5÷2 μm in dark gray color, contained following impurities: O, 0.487; C, 0.383±0.002; free

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C, 0.313±0.003; H, 0.08562. The performed analysis of BN impurities were: O – determined by inert gas fusion with IR detection; H – by inert gas fusion and thermal conductivity; total C – by high-temperature combustion with IR detection, free C – by LECO RC412 "multiphase" carbon determinator with IR detection (LECO Corporation, St. Joseph, Michigan), and trace metals by a direct-current-plasma, optical-emission spectroscopic technique (Luvac Inc, Boylston, MA). Other products used in combustion experiments were: fluorine of 98% purity from Air Products, prepared by distillation and before use passed through a column filled with NaF to remove traces of HF; high-purity hexagonal selenium (batch no. S75045) from Johnson Matthey used here as an ignition aid (impurity of Se was only 0.001 mass % of oxygen determined by neutron-activation analysis); tungsten foil of 99.99 mass % purity was formed into saucers of diameter ≈ 4 cm, and used as an auxiliary combustant (Schwarzkopf Technologies Corp., Holliston, MA).

Calorimetric procedure: A two-chamber reaction vessel and the calorimetric system described previously [9–11] were employed. All experiments were designed to have a final temperature close to T = 298.15 K. The outer chamber was charged with F_2 at a pressure of 1 MPa at T ≈ 293 K and it was separated from the c-BN sample in evacuated inner chamber by a valve, that could be opened from outside. When the valve was open after the temperature of the calorimeter had reached a steady state, F_2 entered the inner chamber and expanded to about 0.6 MPa at T ≈ 298 K. Preliminary experiments showed that, c-BN did not ignite spontaneously when exposed to fluorine, and required the use of small quantity of Se ($Se + 3F_2 = SeF_6$) to initiate the reaction. Even so the reaction did not go to completion and, therefore a tungsten foil was employed as an auxiliary combustant. To burn cubic boron nitride a special arrangement was made: c-BN sample was placed in a tungsten saucer that sat on top of a nickel crucible, that, in turn, was placed on the lid of the inner chamber. Similar procedure was used in the past [12]. Upon ignition of selenium fuse (forming SeF_6) the vigorous reaction of fluorine with tungsten was initiated (to form WF_6) leading to completion of the boron nitride reaction with fluorine:

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

However, the combustion of cubic boron nitride in some experiments was not complete, and minor amounts of unburned BN remained in the crucible. Residues were brushed from the crucible, and calculated by difference of weights. After removal of the residue, the mass of the crucible was found to have increased (less than 1 mg) in several experiments. It was caused by formation of NiF_2, a common event in fluorine combustion calorimetry, although in the present work the crucible has been pretreated with F_2. Corrections for all these residues were made later in calculations.

In few selected cases, when the combustion experiment was finished, the gaseous products of reaction were transferred to a liquid-nitrogen cooled trap, the excess of F_2 was removed by pumping, and the remaining products were analyzed by FTIR spectrometer. Only the presence of BF_3 was evident, apart from WF_6 and SeF_6 (products of fluorination of auxiliary materials). Gaseous products (from the C, B_4C or H_2O impurities combustion), such as CF_4 or HF were not detected.

RESULTS AND DISCUSSION

Detailed calorimetric information for the combustion in fluorine of two samples (B and A) of cubic boron nitride is contained in Tables 1 and 2. Many of the symbols used in those tables have been defined by Hubbard [13]. Thus, by m are denoted masses of material placed in the bomb, they were converted from apparent masses by the densities given in Table 3; $\Delta\theta_c$ is the corrected temperature increase; ε(calor) is the energy equivalent of the system, determined as a mean value from a series of calibration experiments, based on the combustion of benzoic acid in oxygen; ΔU(cont), allows for the net energy equivalent of the contents (crucible, samples, gases) of the bomb, calculated using massic heat capacities and standard molar heat capacities shown in Table 3; ΔU(gas) is a standard-state correction, that was calculated by use of the intermolecular-force constants from the literature for F_2 [14], WF_6 [15], N_2 [16] and BF_3 [17]; the small quantities of SeF_6 have been neglected. The quantity ΔU(blank) measured in separate experiments by expansion of F_2 into an evacuated bomb was calculated as it was discussed in [18]. The quantities ΔU(W) and ΔU(Se) give the contributions of fluorination of the tungsten saucer and the selenium fuse to the total energy measured in the experiment. Corrections for the fluorination of the selenium fuse to SeF_6 and of the tungsten auxiliary to WF_6 according to the reactions:

$$W(cr) + 3F_2(g) = WF_6(g) \qquad (2) \qquad\qquad Se(cr) + 3F_2(g) = SeF_6(g) \qquad (3)$$

were derived from massic energies of combustion in F_2 of Se $-(14097\pm6)\ J\cdot g^{-1}$ [19] and W $-(9374.4\pm3.1)\ J\cdot g^{-1}$ [12]. Finally, $\Delta U(NiF_2)$ is the correction for fluorination of the nickel crucible based on $\Delta_f H_m^0$ (NiF_2, 298.15 K) = $-(657.7\pm1.7)\ kJ\cdot mol^{-1}$ [20]. For calibration of the calorimetric system were used the NIST-RSM-39j samples of benzoic acid, whose certified massic energy of combustion in oxygen is $-(26434\pm3)\ J\cdot g^{-1}$. The massic energy of combustion $\Delta_c u$ of the sample was calculated as the sum of the energy contributions in each column divided by the corresponding mass of sample m(BN). The mean values of energy of combustion were then derived from individual values with uncertainty determined as standard deviation of the mean: (sample A c-BN) $<\Delta_c u> = -(35885.0\pm20.6)\ J\cdot g^{-1}$; (sample B c-BN) $<\Delta_c u> = -(35802.9\pm11.1)\ J\cdot g^{-1}$.

Impurity corrections: Calculation is based upon difference of the energies of combustion in F_2 between considered impurity phase and c-BN. Results of the analyses of two c-BN samples were already presented in the materials description. Sample B was more pure (0.3745 mass % of total impurity elements) than sample A (0.9556 mass %). It was considered previously [11,21] that carbon impurity could be present as B_4C, free carbon or as a mixture of both. However, content of free carbon in sample B could not be defined, because an access to the analysis on LECO RC412 “multiphase” carbon determinator has been gained when the specimen was entirely used up in calorimetric experiments. For this reason correction of the carbon impurity of B sample (see Table 4) has been combined as a main value of two corrections, assuming the presence of total C as B_4C or free carbon. That is why the calculated uncertainty of the impurity correction for sample B is so large. The O, and H impurities in sample B were assumed to be present as B_2O_3 and H_2O. The values of oxygen mass fraction in B_2O_3 and H_2O were deduced assuming that total amount of oxygen can be expressed by $0.147\cdot10^{-2} = x + y$ and in H_2O it can be $y = 0.01673\cdot(M_O/2M_H)$. The sample B was additionally analyzed for presence of trace metals, that were assumed to be present as stable borides or nitrides. The corrections calculated for each assumed impurity phase on the basis of obtained results of chemical analysis and detailed auxiliary thermodynamic data are collected in Tab. 5. These calculations show that they have a negligible impact on the final thermochemical values derived from the calorimetric measurements.

Table 1. Massic energy of combustion of c-BN (sample B) in fluorine; T = 298.15 K, p^0 = 101.325 kPa; ε(calor) = (13926.6±0.9) J/K.

	1	2	3	4	5	6	7	8
m(BN)/g	0.14601	0.11510	0.16969	0.10748	0.09711	0.24877	0.13858	0.12151
m(W)/g	0.0	0.89083	0.90067	0.60087	0.85838	0.95296	0.88302	0.93867
m(Se)/g	0.04639	0.05891	0.05667	0.05257	0.05541	0.04814	0.05221	0.04606
$\Delta\theta_c$/K	0.42256	0.95553	1.09935	0.73422	0.88372	1.32890	1.00328	0.99047
ΔU(blank)/J	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85
ΔU(gas)/J	1.1	0.9	1.3	1.0	1.0	1.8	1.2	1.1
ΔU(cont)/J	–2.4	–5.8	–6.9	–4.5	–5.5	–8.4	–6.3	–6.3
ΔU(Se)/J	654.0	830.45	798.9	741.1	781.2	678.6	736.0	649.3
ΔU(W)/J	0.0	8349.9	8442.2	5632.1	8045.8	8932.3	8276.7	8798.3
$\Delta U(\mathrm{NiF_2})$/J	–	–	–	–	4.48	3.28	–	–
ε(calor) $(-\Delta\theta_c)$/J	–5884.8	–13307.3	–15310.2	–10225.2	–12307.2	–18507.1	–13972.3	–13793.9
$\Delta_c u/(\mathrm{J \cdot g^{-1}})$	–35859.6	–35864.2	–35776.9	–35836.3	–35800.3	–35760.6	–35798.1	–35779.6

$\langle\Delta_c u\rangle = -(35802.9 \pm 11.1)\ \mathrm{J \cdot g^{-1}}$
Impurity correction = +(214 ± 176) $\mathrm{J \cdot g^{-1}}$
$\Delta_c u^0 = -(35589 \pm 206)\ \mathrm{J \cdot g^{-1}}$

The uncertainty expressed as comprises the individual uncertainties expressed as the standard deviations s_i: ±7.6 $\mathrm{J \cdot g^{-1}}$ < for $\Delta_c u^0$ >, ± 3 $\mathrm{J \cdot g^{-1}}$ for $\Delta U(\mathrm{blank})/\langle m \rangle$, ± 1 $\mathrm{J \cdot g^{-1}}$ for weighing, ±5 $\mathrm{J \cdot g^{-1}}$ for $\langle\varepsilon(\mathrm{calor})\rangle \cdot \Delta\theta_c/\langle m \rangle$, ±1 $\mathrm{J \cdot g^{-1}}$ for $\Delta U(\mathrm{gas})/\langle m \rangle$, ±2.7 $\mathrm{J \cdot g^{-1}}$ for $\Delta U(\mathrm{W})/\langle m \rangle$, ±1 $\mathrm{J \cdot g^{-1}}$ for $\Delta U(\mathrm{NiF_2})/\langle m \rangle$, where $\langle m \rangle$ = 0.1430 g is the average mass of a calorimetric sample. The final uncertainty value is here a sum of impurity correction ±176 $\mathrm{J \cdot g^{-1}}$ added to $2s = 2 \cdot (\Sigma s_i^2)^{1/2}$.

Table 2. Massic energy of combustion of c-BN (sample A) in fluorine T = 298.15 K, p^0 = 101.325 kPa; ε(calor) = (13926.6 ±0.9) J/K.

	1	2	3	4	5
m(BN)/g	0.23987	0.08872	0.10593	0.08813	0.09255
m(Se)/g	0.06741	0.04374	0.06339	0.05740	0.04492
m(W)/g	0.89218	0.78948	0.76402	0.80039	0.79149
$\Delta\theta_c$/K	1.28836	0.80473	0.85130	0.82375	0.81677
ΔU(blank)/J	3.4	3.4	3.4	3.4	3.4
ΔU(gas)/J	1.68	0.97	1.0	0.94	1.0
ΔU(cont)/J	–8.1	–5.0	–5.3	–5.1	–5.1
ΔU(W)/J	8362.6	7399.9	7159.6	7502.2	7416.9
ΔU(Se)/J	950.4	616.0	893.6	809.0	633.1
$\Delta U(NiF_2)$/J	8.62	4.83	7.41	–	4.31
$<\varepsilon(\text{calor})>\cdot(-\Delta\theta_c)$/J	–17942.5	–11207.1	–11855.7	–11472.0	–11374.8
$\Delta_c u/(J\cdot g^{-1})$	–35953.6	–35915.5	–35819.0	–35872.82	–35864.0

$(\Delta_c u) = -(35885.0 \pm 20.6)\ J\cdot g^{-1}$
Impurity correction = +(330 ± 10.5) $J\cdot g^{-1}$
$\Delta_c u^0 = -(35555 \pm 48)\ J\cdot g^{-1}$

The final uncertainty, expressed as $2s = 2\cdot(\Sigma s_i^2)^{1/2}$, comprises the individual uncertainties expressed as the standard deviations s_i: ±14 $J\cdot g^{-1}$ <for $\Delta_c u^0$>, ± 3 $J\cdot g^{-1}$ for ΔU(blank)/<m>, ± 1 $J\cdot g^{-1}$ for weighing, ±6 $J\cdot g^{-1}$ for $<\varepsilon(\text{calor})>\cdot\Delta\theta_c/<m>$, ±1 $J\cdot g^{-1}$ for ΔU(gas)/<m>, ±3 $J\cdot g^{-1}$ for ΔU(W)/<m>, ±1 $J\cdot g^{-1}$ for $\Delta U(NiF_2)$/<m>, where <m> = 0.123 g is the average mass of a calorimetric sample and the uncertainty of impurity correction ±10.5 $J\cdot g^{-1}$.

Table 3. Auxiliary quantities used in calculations of the massic energy of combustion of c-BN.

	c-BN	Se[c]	W[d]	Ni[d]
ρ ($Mg\cdot m^{-3}$)	3.4879[a]	4.81	19.42	8.91
c_p^0 ($J\cdot K^{-1}\cdot g^{-1}$)	0.649[b]	0.317	0.707	0.444

	BF_3[c]	N_2[e]	SeF_6[c]	WF_6[d]	F_2[d]
$C_{p,m}^0$ ($J\cdot K^{-1}\cdot mol^{-1}$)	42.13	20.81	99.8	119.03	22.99

[a] Ref. [31], [b] Ref. [30], [c] Ref. [19], [d] Ref. [20], [e] Ref. [21].

Table 4. Impurity corrections for c-BN (Sumitomo Electric, sample grade B).

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	0.145		free C B_4C	0.145 or 0 0 or 0.6694	0 –72±11	–77.76 –97.62	41.9 61.81	60.8±0.8 or 0 0 or 412.6±5.6
O	0.147	0.0141	B_2O_3	0.0204	–1273.5±1.4	–14.38	–21.49	–4.4±0.3
		0.1329	H_2O	0.1496	–285.83±0.04	–26.01	–9.8	–14.7±0.2
H	0.01673							
Trace elements	0.0658		borides nitrides					–4.1±0.1
								37.6±0.8 or 389.4±5.6
Total impurity correction: 214±176 J/g								

[a] $\Delta(\Delta_c u) = \Delta_c u(BN) - \Delta_c u(imp)$; correction calculated on the basis of determined value of $\Delta_c u(BN) = -(35803 \pm 11)$ J/g and $\Delta_c u$(imp) values calculated for impurity phases reactions with F_2 using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [33] , Barin [40] and Domalski [41].

Table 5. Corrections for trace elements in sample c-BN (Sumitomo Electric grade B).

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)	$\Delta_c u^0$ (imp) (kJ/g)	$\Delta(\Delta_c u)^a$ (kJ/g)	$W \cdot \Delta(\Delta_c u)$ (J/g)
Al	19	AlN	29	–318.0	–29.0	–6.6	–0.19
Ca	201	Ca_3N_2	248	–431.0	–21.9	–13.8	–3.41
Cr	56	CrB	68	–75.3	–17.4	–18.3	–1.23
Cu	15	Cu_3N	16	–74.5	–3.73	–31.9	–0.51
Fe	93	FeB	111	–71.1	–30.8	–4.8	–0.54
Ni	33	Ni_4B_3	50	–311.7	–21.4	–14.3	–0.71
Si	14	Si_3N_4	23	–828.9	–28.6	–7.0	–0.16
Ti	96	TiB_2	139	–279.5	–51.7	16.0	2.23
V	20	VB	24	–138.5	–39.3	3.7	0.09
Zn	64	Zn_3N_2	74	–22.6	–9.6	–26.1	–1.94
Mg	33	MgB_2	63	–92.0	–71.9	36.2	2.29
Impurity correction: –4.08 J/g							

[a] $\Delta(\Delta_c u) = \Delta_c u(BN) - \Delta_c u(imp)$; correction calculated on the basis of determined value of $\Delta_c u$(c-BN) = –(35891±10) J/g and $\Delta_c u$(imp) values calculated using auxiliary data $\Delta_f H_m^0$(imp) taken from Gurvich [33] and Barin [40].

For sample A the complete analyses of contents of free and total carbon impurities have been made, thus, calculation of C impurity correction (see Tab. 6) is accurate. The ratio of H to O contents in sample A was too large, comparing to sample B, so combination of the impurity phase presence only as B_2O_3 and H_2O in sample B was not sufficient. The oxygen content was then combined in B_2O_3 and H_2O, using the same O:H ratio as for sample B, and the remaining part of H had to be interpreted in a different way. It seems that this part of H impurity phase could depend on the sample production method. In Sumitomo Electric Industries large scale production of c-BN is performed by catalyst-aided procedures [22–25] or hard c-BN coatings are prepared by microwave plasma from the boron source gas B_2H_6 or BCl_3 and the nitrogen source N_2 or NH_3 mixed with H_2 [26,6]. We had no exact information how the samples studied by us were produced. So, to interpret the hydrogen impurity correction one can assume, that part of H_2 (g) has been absorbed in BN crystal structure. This interpretation can be confirmed by a statement, found recently in [27], that exfoliated laminar crystal structure of graphite or boron nitride could be used for storage of fuel gases such as hydrogen or methane.

Standard molar enthalpy of formation: Thus corrected values of the massic energies of combustion (given in the bottom of Tab. 1 and 2) are following:

Sample B – $\Delta_c u^0$(BN-c) = –(35589±206) J/g and sample A – $\Delta_c u^0$(BN-c) = –(35555±48) J/g

Converting it to molar quantities with the use of M (BN) = 24.8167 g/mol and taking into account that for reaction (1), $\Delta_v^g \cdot RT = 0$ kJ/mol, we obtain $\Delta_c U_m^0 = \Delta_c H_m^0$ values presented below in Table 7. In calculations of $\Delta_f H_m^0$(BN-c, cr, 298.15 K) from $\Delta_c H_m^0$ the value of $\Delta_f H_m^0$ (BiF_3, g, 298.15 K) = –(1136.6±0.9) kJ/mol [28] was used, and here uncertaintes were combined in quadrature. The reaction, to which $\Delta_f H_m^0$ relates is:

$$B(s) + 1/2N_2 = BN\ (cr, c) \qquad (4)$$

The data of standard molar enthalpy of formation obtained for two cubic BN samples presented in Tab. 7 are compatible. The more reliable result (because of the uncertainty limits) $\Delta_f H_m^0$(cr, c-BN) = –254.3±1.5 kJ·mol^{-1}, combined with $\Delta_f H_m^0$ (cr, h-BN) = –250.8±1.2 kJ·mol^{-1}, that was determined previously [11], leads to the enthalpy of the polymorphic transition $\Delta_{trs} H_m^0$ (298.15 K) = –3.5±1.5 kJ·mol^{-1} for the process: h-BN (cr) → c-BN (cr). Using data of standard molar entropies S_m^0 (298.15 K): 15.15±0.03; 6.767±0.01 J·mol^{-1}·K^{-1} for h-BN [29] and c-BN [30] the entropy for the transition $\Delta_{trs} S_m^0$ (298.15 K) = –8.38±0.03 J·mol^{-1}·K^{-1} is calculated. From these data $\Delta_{trs} G_m^0$ (298.15 K) = –1.10 kJ·mol^{-1} is obtained. Few different values for $\Delta_f H_m^0$ (cr, c-BN) have already been reported in the literature. Makedon and Feldgun [32] calculated the enthalpy of polymorphic transition $\Delta_{trs} H_m^0$ (298.15 K) = –4.6 kJ·mol^{-1} for h-BN (cr) = c-BN (cr) by the Clapeyron-Clausius equation extrapolating experimentally determined equilibrium curve (within pressure range 4÷7 GPa, and temperature

Table 6. Impurity corrections for c-BN (Sumitomo Electric, sample grade A).

Element	$w \cdot 10^2$ Impurity element 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	0.383	0.313	free C	0.313	0	–77.76	41.88	131.1±0.8
		0.07	B_4C	0.3222	–72±11	–97.62	61.74	198.9±10.4
O	0.487	0.0517	B_2O_3	0.0750	–1273.5±1.4	–14.38	–21.5	–16.1±0.1
		0.4283	H_2O	0.2412	–285.83±0.04	–26.01	–9.87	–23.8±0.2
H	0.08562	0.0268	H_2O					
		0.0588	H_2	0.0588	0	–27.11	–8.65	–5.1±0.1
Total impurity correction: 330.0 ± 10.5 J/g								

[a] $\Delta(\Delta_c u) = \Delta_c u(BN) - \Delta_c u(imp)$; correction calculated on the basis of determined value of $\Delta_c u(BN) = -(35885 \pm 20)$ J/g and $\Delta_c u(imp)$ values calculated for impurity phases reactions with F_2 using auxiliary data $\Delta_f H_m^0(imp)$ taken from Gurvich [33] , Barin [40] and Domalski [41].

600÷1550 K) to standard temperature and pressure. Combining reported result with data recommended by Gurvich [33] $\Delta_f H^0_m$ (cr, h-BN) = –250.5±1.5 kJ·mol^{-1} value $\Delta_f H^0_m$ (cr, c-BN) = –255 kJ·mol^{-1} was obtained. However, in [34] appeared the new value of $\Delta_{trs} H^0_m$ (298.15 K) = 3.5 kJ·mol^{-1}, that would lead to $\Delta_f H^0_m$ (cr, c-BN) = –247 kJ·mol^{-1}. This result obtained also ($\Delta_{trs} H^0_m$ (298.15 K) = 3.5 kJ·mol^{-1}) in [35] has been, however, discredited in [36], where the energies of combustion of cubic, wurzite and hexagonal BN in F_2 were measured using fluorine bomb calorimetry [37–39]. For cubic BN the standard enthalpy of formation was determined $\Delta_f H^0_m$ (cr, c-BN) = –266.8±2.2 kJ·mol^{-1} and for hexagonal form of BN $\Delta_f H^0_m$ (cr, h-BN) = –250.6±2.1 kJ·mol^{-1}. The last value is in a good agreement with results obtained recently [11] and determined in Argonne laboratory [21]. Samples used by Leonidov *et al.* [37] were purified from carbon impurities by a successive combustion in oxygen and subsequently of B_2O_3 by heating at 1573 K in vacuum. Their result $\Delta_f H^0_m$ obtained for c-BN is more negative than reported in this work, however, both indicate that cubic form of boron nitride is more stable than hexagonal in standard conditions.

Table 7. Summary of standard thermochemical results for cubic BN.

Sample	$\Delta_c u^0_m$ J·g^{-1}	$\Delta_c U^0_m = \Delta_c H^0_m$ kJ·mol^{-1}	$\Delta_f H^0_m$ kJ·mol^{-1}
Crystalline c-BN (grade A from Sumitomo Electric)	–35555 ± 48	–882.3 ± 1.2	–254.3 ± 1.5
Crystalline c-BN (grade B from Sumitomo Electric)	–35589 ± 206	–883.2 ± 5.1	–253.4 ± 5.2

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