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The evaluation of thermochemical properties of group-III nitrides: BN and GaN

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Abstract

Studies by fluorine bomb calorimetry that lead to the evaluation of thermodynamic properties of group-III nitrides are described. Results of the studies of the standard molar enthalpy of formation $\Delta_f H^0_m$ of two BN polymorphic forms and initial experiments on the combustion of GaN are presented.

Keywords: Fluorine bomb calorimetry; BN; GaN

1. Introduction

The III group nitride semiconductors are important in material science. The thermodynamic modelling in order to develop high technology is used for prediction the stability and behaviour of these substances. Effectiveness of the calculations depends on the reliability of the thermodynamic databases, part of which unfortunately needs to be corrected. The research studies that provided evaluated thermodynamic data were realized by use of fluorine calorimetry at Chemical and Physical Properties Division at NIST (Gaithersburg, MD. USA). Similar investigations are continuing now in calorimetric laboratory at Institute of Physical Chemistry Polish Academy of Sciences. Grace to cooperation with Dr. P.A.G. O'Hare we have received from NIST isoperibol calorimeter and two-chamber combustion bomb, which were important part of apparatus planned to form fluorine combustion calorimetric system (in the Project No. 7 T09A 131 21 financed by the State Committee for Scientific Research KBN). Studies in our laboratory are intended to provide reliable data of thermodynamic quantities for group-III nitrides (GaN, InN and AlN) that are experiencing exiting development in modern optoelectronics and high-power, high-temperature electronic devices. The most useful for the examination of high-temperature equilibria and materials stability is $\Delta_f G^0_m(T)$ – the Gibbs free energy of formation in function of temperature. The precise information about $\Delta_f G^0_m(T)$ comes from data of enthalpy of formation $\Delta_f H^0_m(T)$ and entropy of formation $\Delta_f S^0_m(T)$

$$\Delta_f G^0_m(T) = \Delta_f H^0_m(T) - T\,\Delta_f S^0_m(T) \quad (1)$$

The quantity $\Delta_f H^0_m(T)$ can be calculated by combining enthalpy increments of compound and its elements $[H^0(T) - H^0(298.15\,\mathrm{K})]$ obtained from the database of heat capacities $C^0_p(T)$, with $\Delta_f H^0_m(298.15\,\mathrm{K})$ determined from combustion calorimetry. Entropy of formation $\Delta_f S^0_m(T)$ is also derived from the $C^0_p(T)$ database. The present paper shows in brief results of measurements $\Delta_f H^0_m$ (298.15 K) for two polymorphic forms of boron nitride, h-BN and c-BN, compared with all previous investigations. These study performed during recent work at NIST was planned to assess relative stabilities of BN crystalline forms. This paper will also describe some information about our fluorine calorimetry system and preliminary results of gallium nitride studies.

1.1. *Procedure of fluorine bomb calorimetry and nitrides*

Technique of the combustion calorimetry in fluorine has been used to investigate inorganic substances that cannot readily or completely react with oxygen. The construction and operation of the high-precision fluorine combustion bomb system at NIST, containing isoperibol calorimeter, two-compartment reaction vessel, quartz-crystal thermometer monitoring temperature increase of the calorimeter, and

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other components of the laboratory has been described in details by P.A.G. O'Hare [1,2]. Calorimetric system in our laboratory Institute of Physical Chemistry is made similarly, the manifold for handling F_2 and gaseous fluorides is constructed from the Autoclave Engineers fittings and placed in ventilated hood. Some differences in construction of manifold appeared only because according to safety rules in our Institute, gas cylinders have to be placed outside the laboratory. The experimental procedure is also the same as performed before at NIST [1,2].The tank of bomb is charged with pure fluorine in the manifold to a pressure of 1 MPa. All investigated materials are handled in a glovebox (UNI-LAB for M. Braun Com.) equipped with analytical balance and filled with a purified recirculating atmosphere of dry nitrogen. Usually samples are weighed into a nickel crucible, but sometimes they are weighed on a tungsten saucer that was then positioned on a top of nickel crucible. Crucible is rested on the lid of the inverted bomb, and then storage tank is connected to it. Connected (bomb + tank) reaction vessel is then placed in the calorimeter and after end of experiment, attached again to the manifold to remove unreacted fluorine and gaseous fluorides, which are pumped into a column filled with activated Al_2O_3. Afterwards, evacuated reaction vessel is returned to the glovebox, and the interior of the bomb is inspected (Fig. 1).

The reaction of fluorine with nitrides gives simple products, because nitrogen forms only as N_2 (g)

$$\mathrm{BN(cr)} + \tfrac{3}{2}\mathrm{F_2(g)} = \mathrm{BF_3(g)} + \tfrac{1}{2}\mathrm{N_2(g)} \qquad (2)$$

To derive $\Delta_f H^0_m$ (BN, cr) one must measure enthalpy of reaction $\Delta_r H^0_m(2)$ and have correct value enthalpy of formation for $\Delta_f H^0_m(\mathrm{BF_3, g})$

$$\Delta_f H^0_m(\mathrm{BN, cr}) = \Delta_f H^0_m(\mathrm{BF_3, g}) - \Delta_r H^0_m(2) \qquad (3)$$

1.2. Results for BN

There are three crystalline forms of boron nitride: hexagonal, cubic and wurtzite, but attainable for our study were only two polymorphic forms: h-BN and c-BN. In the literature there was a controversy as to whether a cubic form was more stable than the hexagonal [3]. We investigated three specimens of hexagonal BN, characterized by different degree of crystalline structure and two specimens of cubic BN manufactured by Sumitomo Electric Company [4,5].

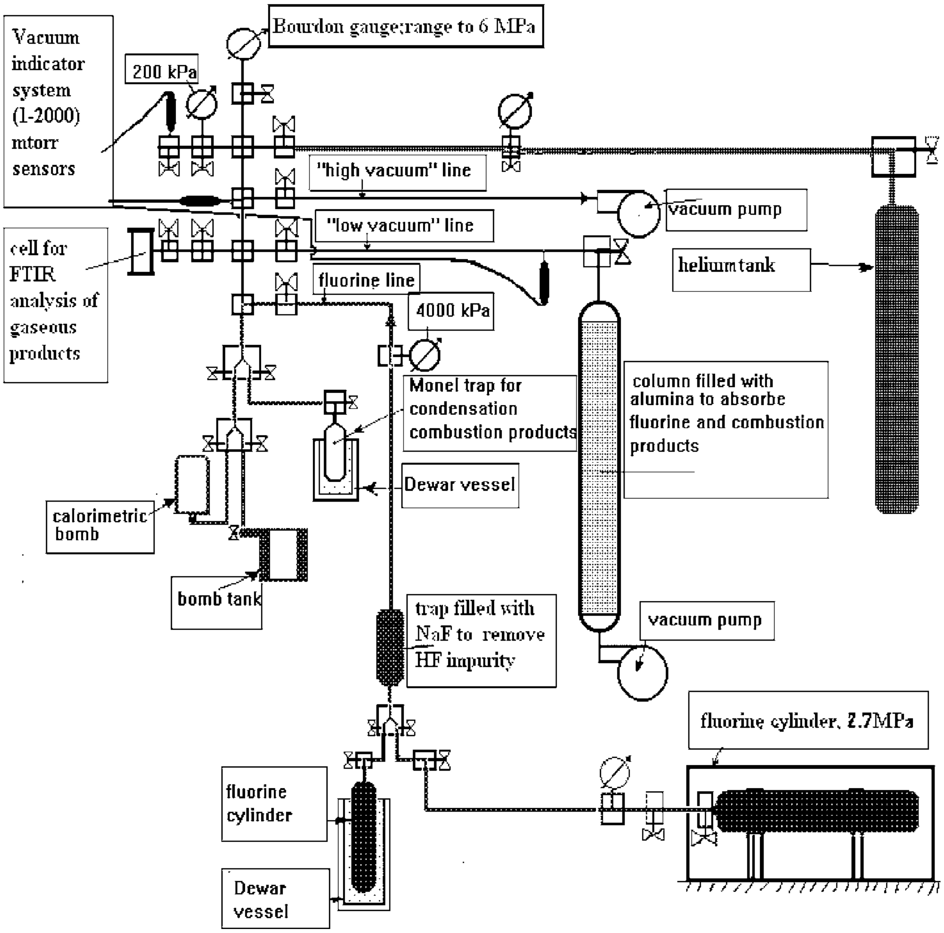

Fig. 1. Manifold for handling fluorine and gaseous fluorides developed at Institute of Physical Chemistry.

Table 1
Summary of standard thermochemical results for polymorphic forms of BN

Sample	$\Delta_c u_m^0$ (J g^{-1})	$\Delta_c U_m^0 = \Delta_c H_m^0$ (kJ mol^{-1})	$\Delta_f H_m^0$ (kJ mol^{-1})	$\Delta_f H_m^0$ (references)
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 ± 23	−885.8 ± 0.8	−250.8 ± 1.2	250.3 ± 1.5 [8]
				−253.2 ± 2.1 [9]
				−250.6 ± 2.1 [10]
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	

Hexagonal BN materials were: powder crystalline sample from Aldrich Co. (impurities in %: O, 0.516; C, total carbon 0.0852, free carbon 0.07265; H, 0.0314 and trace metals; 0.0427) and two pure samples of pyrolytic boron nitride provided by Dr. A.W. Moore (Advanced Ceramics Corporation, Cleveland, Ohio) prepared by chemical vapor deposition method [6]. Sample PBN-8601 was turbostratic (it was an average interlayer spacing 2–4% larger than ideal boron nitride, −3.33 Å) with impurities (in %: O, 0.0101; C, 0.0084; H, 0.00216). Sample (PBN-8614) was more crystalline with an interlayer spacing only about 0.5% larger than ideal h-BN (impurities in %: O, 0.01261; C, 0.0111; H, 0.00299). Two c-BN samples were designated as Grade A (grain size 0.5–2 μm) with impurities (in % : O, 0.487; total C, 0.383; free C, 0.313; H, 0.08562) and Grade B (grain size 4–8 μm) with following impurities (in %: O, 0.147; C, 0.145; H, 0.01673 and trace metals: 0.0658).

Only crystalline h-BN sample reacted spontaneously with F_2, for two pyrolytic samples few mg of fuse (Se) was used and for c-BN samples not only fuse, but also tungsten saucer was used. Determined massic energies of reaction including corrections for impurities present in each sample are shown below in Table 1. The corresponding molar enthalpies of combustion $\Delta_c H_m^0$ combined with $\Delta_f H_m^0$ (BF_3, g) = −(1136.6 ± 0.9) kJ mol^{-1} [7] yielded the desired standard molar enthalpies of formation $\Delta_f H_m^0$ for all polymorphic forms.

$$B(s) + \frac{1}{2}N_2(g) = BN(cr) \qquad (4)$$

The results of $\Delta_f H_m^0$ for both pyrolytic and hexagonal BN samples correlate well with the stabilities expected from the interlayer separation. Value for $\Delta_f H_m^0$ (cr, h-BN) is in a good agreement with previous experimental data [8–10]. The results of $\Delta_f H_m^0$ for two cubic BN samples are also compatible. The enthalpy of the polymorphic transition calculated from the more reliable result $\Delta_f H_m^0$ (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}, is: $\Delta_{trs} H_m^0$ (298.15 K) = −3.5 ± 1.5 kJ mol^{-1} for the process:

$$h - BN(cr) \rightarrow c - BN(cr) \qquad (5)$$

Using data of standard molar entropies S_m^0 (298.15 K) = 15.15 ± 0.03 J mol^{-1} K^{-1} for h-BN [. . .] and 6.767 ± 0.01 J mol^{-1} K^{-1} for c-BN [30] have been calculated the entropy for the transition $\Delta_{trs} S_m^0$ (298.15 K) = −8.38 ± 0.03 J mol^{-1} K^{-1} and Gibbs energy $\Delta_{trs} G_m^0$ (298.15 K) = −1.10 kJ mol^{-1}. Few different values for $\Delta_f H_m^0$ (cr, c-BN) have been reported in the literature. Makedon and Feldgun [11] calculated $\Delta_{trs} H_m^0$ (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 600 ± 1550 K) to standard temperature and pressure. This result combined with data from Gurvich et al. [12] $\Delta_f H_m^0$ (cr, h-BN) = −250.5 ± 1.5 kJ mol^{-1} gives value of $\Delta_f H_m^0$ (cr, c-BN)= −255 kJ mol^{-1}. Later [13,14] appeared two times the new value of $\Delta_{trs} H_m^0$ (298.15 K) = 3.5 kJ mol^{-1}, that leads to $\Delta_f H_m^0$ (cr, c-BN)= −247 kJ mol^{-1}. These results have been later discredited by Leonidov and Timofeev [10], who determined $\Delta_f H_m^0$ (cr, c-BN)= −266.8 ± 2.2 kJ mol^{-1} and $\Delta_f H_m^0$ (cr, h-BN)= −250.6 ± 2.1 kJ mol^{-1} using fluorine bomb calorimetry. Their result $\Delta_f H_m^0$ obtained for c-BN is more negative than reported by us, however, both indicate that cubic form of boron nitride is more stable than hexagonal in standard conditions.

1.3. Investigation of gallium nitride

Presented in literature values of $\Delta_f H_m^0$ (GaN, 298.15 K) change from −111.2 kJ mol^{-1} [15] up to −263.6 kJ mol^{-1} [16]. Because of such large range of the results fluorine combustion bomb is used to evaluate these data. The reaction of fluorine with GaN is similar to reaction with BN, but its product GaF_3 is formed in the solid phase.

$$GaN(cr) + \frac{3}{2}F_2(g) = GaF_3(cr) + \frac{1}{2}N_2(g) \qquad (6)$$

To derive $\Delta_f H_m^0$ (GaN, cr) one must measure enthalpy of combustion $\Delta_c H_m^0$ (6) and also determine value enthalpy of formation for $\Delta_f H_m^0$(GaF_3, s), because these data found in the literature are also different

$$\Delta_f H_m^0(GaN, cr) = \Delta_f H_m^0(GaF_3, g) - \Delta_r H_m^0(2) \qquad (7)$$

Two specimens of GaN have been preliminary studied: hexagonal powder GaN from Sigma Aldrich (trace metal impurities 0.01%) and crystalline wurzite sample provided from High Pressure Research Center Polish Academy of Sciences (Warszawa, Poland) by Dr. I. Grzegory. Part of powder hexagonal GaN sample reacted with F_2 (g) spontaneously, but because only part of sample was burned, it was better to place the sample on a tungsten saucer and also use small amount of fuse (S or Se).

Preliminary result of combustion (without impurity corrections) are $\Delta_c H_m^0 = -(912.3 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$. Crystalline wurzite samples does not react with fluorine and must be burned with tungsten saucer and fuse. Preliminary combustion result are $\Delta_c H_m^0 = -(1011.3 \pm 6.5)\,\mathrm{kJ\,mol^{-1}}$.

It appear that wurzite GaN has much better stablity. To calculated $\Delta_c H_m^0$ (GaN) impurities correction and the value of $\Delta_f H_m^0(\mathrm{GaF_3}, \mathrm{cr})$ must be also determined.

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