

Enthalpy of Formation of Gallium Nitride

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Received: October 21, 1999; In Final Form: February 14, 2000

A major discrepancy in the literature concerning the enthalpy of formation of GaN has been resolved using oxidative oxide melt solution calorimetry. Four samples of differing nitrogen contents were measured by dropping them into molten $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ in a calorimeter at 975 K with oxygen gas bubbling through the solvent. The samples were characterized by X-ray diffraction, chemical analysis, transmission electron microscopy, particle size analysis, and BET measurements. The enthalpy of drop solution (kJ/g) varied approximately linearly with nitrogen content. Extrapolated to stoichiometric GaN, the data yield a value of -156.8 ± 16.0 kJ/mol for the standard enthalpy of formation from the elements at 298 K. The relatively large error reflects the deviation of individual points from the straight line rather than uncertainties in each set of data for a given sample. This new directly measured enthalpy of formation is in excellent agreement with that obtained from the temperature dependence of the equilibrium pressure of nitrogen over GaN, -157.7 kJ/mol, measured by Madar et al. (Madar, R.; Jacob, G.; Hallais, J.; Fruchart, R. *J. Crystal Growth* **1975**, *31*, 197.) and Karpinski and Porowski (Karpinski, J.; Porowski, S. *J. Cryst. Growth* **1984**, *66*, 11). This value of -156.8 kJ/mol should replace the commonly tabulated value of -110 kJ/mol determined by Hahn and Juza (Hahn, H.; Juza, R. *Z. Anorg. Chem.* **1940**, *244*, 111) using combustion calorimetry on an uncharacterized sample over 50 years ago.

Introduction

Gallium nitride (GaN) is an important electronic and optical material with exciting new applications in semiconductor devices such as quantum wells, lasers, and display devices.^{1–8} Processing of GaN thin films, nanoparticles, and single crystals is at the forefront of current electronic materials research, but the underlying thermochemical data, essential for understanding growth and phase stability issues, are still poorly defined. Several tabulations report thermodynamic data for solid GaN. The tabulated values of the standard heat of formation (ΔH_f^0 (298 K) = -109.621 ,^{9,10} -110.5 ,¹¹ and -109.620 kJ/mol^{12,13}) are derived from the over 50 year old combustion calorimetric measurements of Hahn and Juza.¹⁴ The small scatter in various compilations is probably due to the differences in the heat of formation of Ga_2O_3 used in the thermochemical cycle to calculate the heat of formation of GaN. In their work, Hahn and Juza observed that a part of the GaN used in calorimetry formed a sublimate while the rest formed a melt. Although they attempted to burn the product a second time to complete the combustion, there is some question as to the reliability of these calorimetric measurements.¹⁵ Furthermore, the GaN sample used was not well characterized by modern standards.

Thermodynamic data for GaN have also been obtained by several equilibrium pressure studies.^{16–18} Madar et al.¹⁷ noted that the heat of formation of GaN, ΔH_f^0 (298 K) = -157.7 kJ/mol, derived from their high-pressure experiments, was much more exothermic than the tabulated value. Karpinski and

Porowski also obtained the same value, -157.7 kJ/mol, during the study of equilibrium pressure of N_2 over solid GaN.¹⁸ Most of the previous studies use the calorimetric value.^{3,19–21} Gordienko and Fenchka^{22,23} proposed a value of -200.8 kJ/mol. Leitner et al.²¹ presented an optimized heat of formation of -150.0 kJ/mol, while the data edited by Edgar²⁴ list -157.7 kJ/mol as determined by Madar et al.¹⁷ and Karpinski and Porowski.¹⁸ The discrepancy between values of ΔH_f^0 obtained from calorimetry and from gas equilibration studies is about 50 kJ/mol, or about 50% of the calorimetric value. This magnitude of discrepancy will seriously affect the vapor pressure calculations and decomposition temperature of GaN. It is therefore highly desirable to measure the enthalpy of formation of GaN by state of the art calorimetric techniques on well-characterized samples.

In the present work we have measured the heat of formation of four different GaN samples by oxidative drop solution calorimetry using a molten sodium molybdate solvent, a methodology developed recently in our laboratory and applied successfully to Si_3N_4 ,²⁵ AlN ,²⁶ and other nitrides and oxynitrides.^{27–31} Parallel with the calorimetric measurement, samples were characterized for phase purity, oxygen content, particle size, and surface area by a number of analytical techniques.

Experimental Section

Materials and Sample Details. A number of GaN samples have been used for this study. GaN from Atomergic Chemetals Corp. (99.9%) is a gray powder (GSHR). A GaN sample from R. F. Davis (North Carolina State University) is dark gray (NCSU). The synthesis and the characterization of the NCSU sample are provided elsewhere.⁵ FT1 and FT2 samples are light

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TABLE 1: Thermochemical Data and Chemical Analyses from LECO Corporation for GaN Samples

sample	source	lattice parameters ^a		wt % N	wt % O	ΔH_{ds} (kJ/g) ^b
		<i>a</i> (Å)	<i>c</i> (Å)			
GSHR	Atomergic Chemetals Corp. Item no. 0230–5653 Lot no. L5031	3.1888(5)	5.1837(12)	15.8	0.12	−4.60 ± 0.04(7)
NCSU	Balkas et al., ⁵ NCSU	3.1894(1)	5.1851(1)	16.6	0.5	−4.20 ± 0.02(7)
FT1	F. Tessier, Cornell University	3.1894(2)	5.1854(3)	16.7	0.18	−4.02 ± 0.01(10)
FT2	F. Tessier, Cornell University	3.1874(3)	5.1822(6)	15.6	0.08	−4.31 ± 0.03(8)

^a Lattice parameters from the literature are (JCPDS card no. 2-1078) $a = 3.1844$ Å and $c = 5.1717$ Å and (JCPDS card no. 50-0792 to be published in Sept. 2000) $a = 3.1891$ Å and $c = 5.1855$ Å. ^b Value is the mean of number of experiments indicated in parentheses. Error is two standards deviations of the mean.

gray in color. They were synthesized by a nitridation reaction by treating gallium metal in an alumina boat under flowing commercial ammonia gas (NH₃ flow rate 30–40 L/h, heating rate 5 K/min to reach 1273 K, which was then maintained for 2 days). The furnace was then switched off, allowing the powder to cool to room temperature under a nitrogen atmosphere. For FT1, two nitridations were performed at 1273 K with an intermediate grinding. For FT2, two nitridations were performed, a first at 1273 K followed by a second at 873 K, with an intermediate grinding. Because of the moisture sensitive nature of GaN, all samples were handled in a glovebox filled with argon gas (oxygen <15 ppm and moisture <1 ppm). Ga₂O₃ used in this study (Alfa Aesar, 99.999% metals basis, Batch # 10508, and Lot # RD920518) was a mixture of α - and β -Ga₂O₃ polymorphs, which, after heating at 973 K for 24 h, converted to β -Ga₂O₃. This heat-treated Ga₂O₃ sample was used for calorimetry.

Characterization. The samples were characterized using X-ray diffraction (XRD) with a step size of 0.02 and collection time of 3 s/step (no internal standard), transmission electron microscopy (TEM), specific surface area measurement using the Brunauer–Emmett–Teller (BET) technique, particle size analysis using laser scattering, microprobe analysis, chemical analysis, weight gain experiments, and thermogravimetric analysis (TGA) and differential thermal analysis (DTA). XRD data were collected using a Scintag XDS-2000 (Cu K α , 45 kV, and 40 mA). TEM data were obtained from a Philips EM-400 electron microscope operated at 100 kV. Samples were prepared by suspension in methanol, followed by dispersion onto a holey carbon-coated 400 mesh copper grid. BET analysis was performed with a Micromeritics Gemini 2360 instrument. Particle size analyses were performed using a laser scattering apparatus (Horiba Instruments, model 910). Nitrogen and oxygen analyses were obtained from LECO Corporation, using a thermal conductivity cell and infrared cell respectively, from the inert gas fusion technique (Table 1). The weight gain experiment involved heating a known mass of GaN at 973 K in a silica glass crucible for approximately 24 h in a box furnace in air. The GaN oxidized to Ga₂O₃. The difference between the observed weight gain and the anticipated weight gain was used to calculate the amount of Ga₂O₃ initially present in the GaN. TGA-DTA was performed using Netzsch STA 409 instrument.

Calorimetry. Nitride calorimetry involves an oxidative dissolution to convert the nitride into a dissolved oxide plus evolved nitrogen gas at high temperature in a Tian–Calvet twin microcalorimeter.^{32,33} GaN samples of ~10 mg were dropped from room temperature into liquid 3Na₂O·4MoO₃ solvent at 975 K in the calorimeter. Oxygen gas was flushed through the calorimeter at ~90 mL/min and bubbled through the solvent at

~5 mL/min. The calorimetry utilizes a rapid redox reaction between MoO₃ in the melt and N^{3−}, which supplies a pathway for elimination of N^{3−} as N₂ gas. Subsequent oxidation of any reduced molybdenum species returns the solvent to its initial oxidation state. Calibration was performed using ~4 mg benzoic acid pellets (ACROS Organics, Fischer Scientific catalog no. 22180–2500). Upon reaching the hot zone of the calorimeter, the benzoic acid burned and produced exothermic heat effects of nearly equal magnitude to the nitride reactions. A calibration constant was then calculated on the basis of known enthalpy of combustion of benzoic acid and the heat contents of O₂, CO₂, and H₂O. The applicability of the benzoic acid calibration has been discussed previously.³⁴ For the smaller endothermic reaction in the thermochemical cycle, i.e., drop solution calorimetry of Ga₂O₃ a laboratory standard platinum drop calibration was used.

Results and Discussion

XRD patterns for all samples (GSHR, NCSU, FT1, and FT2) show sharp peaks. The lattice parameters (see Table 1) calculated using UnitCell program (method of Holland and Redfern)³⁵ are close to the literature values. We did not pursue Rietveld refinement for the samples. TEM analysis of a representative sample (FT2) yielded a selected area electron diffraction pattern (Figure 1) with rings corresponding to lattice spacings of 2.78, 2.62, 2.43, 1.92, 1.60, and 1.46 Å; closely matching the 100 (2.76 Å), 002 (2.59 Å), 101 (2.43 Å), 102 (1.89 Å), 110 (1.59 Å), and 103 (1.46 Å) lattice spacings of hexagonal GaN. No phase other than GaN was observed in the XRD or TEM for any of the samples. The specific surface area for all samples (BET measurement) is <0.4 m²/g, that suggests an average particle size ≥ 1.2 μ m for all samples. The particle size analyses with laser scattering also indicate average particle size of ≥ 1 μ m for all samples. The results of the weight gain experiments and TGA-DTA experiments suggest the presence of oxygen impurity since the observed weight gain was less than the anticipated weight gain from transforming GaN to Ga₂O₃ for all the samples. The chemical analyses (Table 1) show that all the samples have nitrogen contents lower than stoichiometric (16.73 wt %) and they contain some oxygen impurity. Microprobe analyses indicate that all the samples are homogeneous and there is no separate second phase detected in any of the sample. The quantitative microprobe results of nitrogen and oxygen contents show similar trends as the LECO chemical analyses for all the samples. The LECO technique is more accurate than the microprobe analysis for quantitation of nitrogen content.

Stoichiometric GaN has 16.73 wt % nitrogen. All the samples used in this study show lower nitrogen contents. Similar

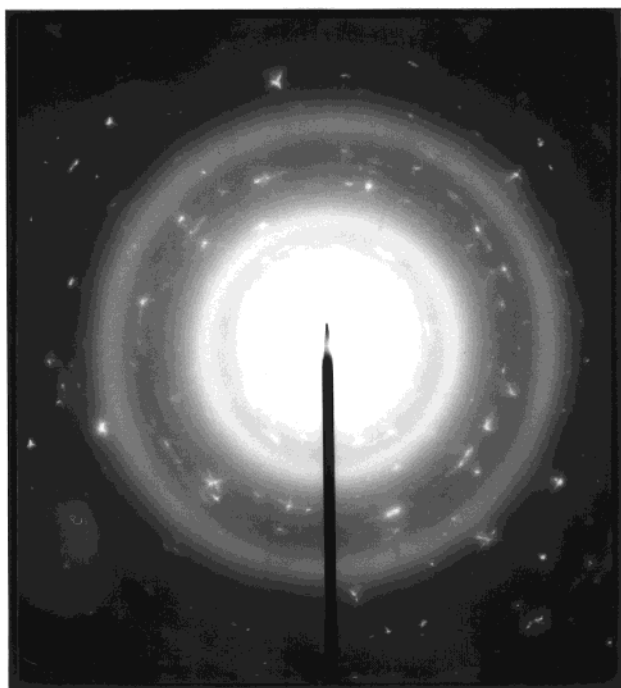


Figure 1. Representative selected area electron diffraction pattern from sample FT2. Rings correspond to the hexagonal phase of GaN.

deviations are reported in the literature.^{14,36–37} The deviation may be due to oxygen present either in solid solution in the GaN structure or in a separate phase. None of the samples shows X-ray diffraction peaks indicative of a separate Ga₂O₃ phase. However, the detection limit of X-ray diffraction is 3–5% of a crystalline second phase. An amorphous or poorly crystalline oxide or oxynitride coating on the grains could miss detection even if present in larger amounts. On the basis of the energy-dispersive X-ray spectroscopy (EDS) results, Kang and Ogawa suggest that oxygen is present at the nitrogen site in GaN.³⁸ Mattila and Nieminen also support this view on the basis of ab initio calculations,³⁹ and they conclude that oxygen at the nitrogen site is more favorable than oxygen at the interstitial site or at the Ga site.

Because of the presence of oxygen and the decrease of nitrogen will significantly affect the enthalpy observed and the stoichiometric coefficients in the thermodynamic cycles used, these effects must be included in the thermodynamic analysis. Without linking the interpretation of calorimetric data to any assumptions about the structural state of the oxygen impurities, we have chosen the following approach. First we plot the observed enthalpy of oxidative drop solution (kJ/g) versus the analyzed nitrogen content (wt % N). The commercial chemical analysis may involve steps where samples were exposed to the atmospheric oxygen significantly. This might influence the detected oxygen contents but such an exposure will not affect the detected nitrogen contents. The points (see Figure 2) define (with some scatter) a straight line from which the enthalpy of oxidative drop solution of stoichiometric GaN (16.73 wt % N) can be obtained. This value (in kJ/mol) is used in the calculation of heat of formation by the thermochemical cycle given in Table 2. This analysis produces fairly large uncertainties arising not so much for the uncertainties in the individual data for each sample but from the scatter in fitting a line to the points. However, different samples may have different modes of impurity and defect incorporation, even at similar nitrogen contents (compare NCSU and FT1 or FT2 and GSHR in Table 1). The impurity distribution might be seen from the variation

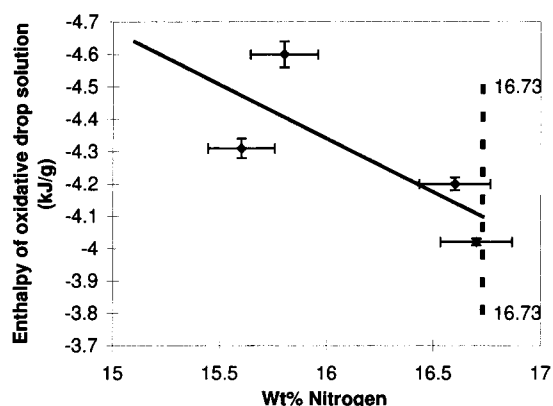


Figure 2. Variation of enthalpy of oxidative drop solution (kJ/g) versus wt % nitrogen.

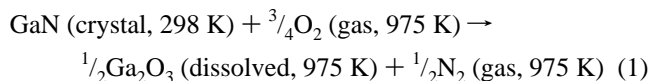
TABLE 2: Thermochemical Cycle to Calculate the Heat of Formation of GaN

	reaction	ΔH (kJ/mol)	ref
(1)	2GaN (crystal, 298 K) + $\frac{3}{2}$ O ₂ (gas, 975 K) → Ga ₂ O ₃ (dissolved, 975 K) + N ₂ (gas, 975 K)	-343.2 ± 15.9	a,b
(2)	Ga ₂ O ₃ (crystal, 298 K) → Ga ₂ O ₃ (dissolved, 975 K)	$104.3 \pm 0.6(8)^c$	a
(3)	N ₂ (gas, 298 K) → N ₂ (gas, 975 K)	20.65	c
(4)	O ₂ (gas, 298 K) → O ₂ (gas, 975 K)	21.84	c
(5)	2Ga (crystal, 298 K) + $\frac{3}{2}$ O ₂ (gas, 298 K) → Ga ₂ O ₃ (crystal, 298 K)	-1092.2 ± 1.5	d
	Ga (crystal, 298 K) + $\frac{1}{2}$ N ₂ (gas, 298 K) → GaN (crystal, 298 K)	-156.8 ± 16.0	
	$\Delta H_f^0 = \frac{1}{2}(-2\Delta H_1 + \Delta H_2 + \Delta H_3 - \frac{1}{2}\Delta H_4 + \Delta H_5)$		

^a This work, value for GaN extrapolated to stoichiometric nitrogen content. ^b The heat of drop solution for ideal GaN composition (wt % N = 16.73%) is obtained using a linear fit of the values listed in Table 1, see text. ^c Robie et al.⁴⁰ ^d Mah.⁴¹ ^e Value is the mean of number of experiments indicated in the parentheses. Error is the two standard deviations of the mean.

in the lattice parameters (see FT2 and GSHR in Table 1); however, at this point we do not have sufficient information to predict the effect of the impurity distribution on the thermochemical properties. This thermodynamic treatment includes no assumptions about what impurities and defects are present.

The large exothermic enthalpy of oxidation of the nitride when it reacts with the solvent



is the dominant term in determining the energetics of formation. The results are shown in Table 1 and in Figure 2. The heat of drop solution for stoichiometric GaN (wt % N = 16.73) is -4.1 ± 0.2 kJ/g, or -343.2 ± 15.9 kJ/mol. Using this value in the thermochemical cycle (Table 2), we get the heat of formation of GaN as ΔH_f^0 (GaN, 298 K) = -156.8 ± 16.0 kJ/mol. To further reduce the uncertainty would require a GaN sample with even lower impurity content. Despite this relatively large standard deviation, the obtained value, -156.8 kJ/mol, is very close to that determined by gas equilibration techniques, -157.7

kJ/mol,^{17,18} and is very different for that, -110 kJ/mol, reported by combustion calorimetry.¹⁴ We suspect that the latter experiments, in addition to having problems in attaining a reproducible final state in calorimetry, may also have used a GaN sample containing significant oxygen impurity. The present data conclusively show that the enthalpy of formation of GaN, -156.8 kJ/mol, is in agreement with gas equilibration studies. Even though many nitrides inherently contain some oxygen impurities, it is possible to get useful thermochemical data, when these impurities are properly taken into account in terms of a stoichiometric chemical reaction. A similar approach was used successfully recently for the α -Si₃N₄ phase.²⁵

The methodology used here can be extended to the study of nanocrystalline GaN and to III–V alloys such as Al_{1-x}Ga_xN and In_{1-x}Ga_xN. The control and analysis of chemical composition will be critical. The sensitivity of oxidative drop solution calorimetry to chemical and structural variability in the sample makes it a practical tool, when combined with rigorous analytical methods, for studying the defect chemistry and nonstoichiometry of technically significant materials.

Acknowledgment. The work was supported by the U.S. Department of Energy (Grant DOE DE-FG03-97ER45654). We thank Z. A. Munir for the use of a laser scattering apparatus and W. H. Casey for the use of a BET apparatus.

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