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Thermochemical studies of nitrides and oxynitrides by oxidative oxide melt calorimetry

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Abstract

High temperature oxidative solution calorimetry is a versatile technique for obtaining enthalpies of formation of nitrides and oxynitrides. In this method, the solid phase is dissolved in a molten oxide solvent (sodium molybdate or an alkali borate) while oxygen gas is bubbled through the melt. The nitrogen is evolved as N_2 and the final state is a dilute solution of dissolved oxides in the solvent. A thermochemical cycle may then be written to obtain the enthalpy of formation. The energetics of silicon nitride and of binary and ternary nitrides are discussed to illustrate the methodology.

Keywords: Thermochemistry; Oxynitrides; Calorimetry

1. Introduction

Nitrides and oxynitrides represent a group of modern ceramic materials of increasing technological importance. Their hardness and durability leads to applications in cutting tools, turbine blades, and other highly abrasive environments. Chemical durability of oxynitride glasses suggests their use as corrosion resistant fibers in both construction (reinforced concrete) and electronic applications. Their high refractive index also suggests novel optical applications.

Broadly speaking, nitrides and oxynitrides can be grouped into five classes. The first is ionic nitrides such as Li_3N, generally stoichiometric, often light colored, and generally highly chemically reactive compounds with few materials applications. The second is transition metallic nitrides, e.g. nitrides of Fe, V, Ti, etc. analogous to borides, carbides, and silicides. They are usually refractory and often metallic. These are used as bulk materials and thin film coatings on metals. The thermodynamic properties of binary nitrides are frequently complicated by nonstoichiometry, but, in general, measurements or estimates of their thermodynamic properties are available. Novel synthetic techniques, including sol–gel, combustion synthesis, vapor deposition, containerless synthesis, and ion implantation form a frontier of research in these materials, and some novel structures, including amorphous films, have been made. The energetics, kinetics, and mechanisms of these processes are not fully understood.

A third class of materials is ternary nitrides formed from binary nitrides of the first two groups. A rich variety of ternary nitrides can be formed, and that, although the stability of binary nitrides is limited by the strength of the N–N bond in N_2, this limitation is far less important for the formation of ternary nitrides from binary nitrides. Because these phases are fairly new, potential applications have not been worked out in detail. From a fundamental crystal chemical point of view, the richness of structures and oxidation states in ternary nitrides has opened a new field of chemistry [1,2]. Many of their structures are different from those of oxides, and stoichiometries implying lower formal oxidation states are common.

The fourth group represents nitrides and oxynitrides with largely covalent structures, often analogous to those of silicates [2,3]. These include Si_3N_4, the sialons, compounds related to Si_3N_4 by the substitution $Si^{4+}+N^{3-}=Al^{3+}+O^{2-}$, and compounds containing Si, Al, N, O and cations such as Mg, Ca, Y, La, whose oxides are thermodynamically stable in coexistence with Si_3N_4 (do not react with it to form metals plus nitrogen gas). Silicon nitride

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and the sialons are complicated by extensive polymorphism, and the multicomponent phases may show order–disorder. Applications as refractories, protective coatings, and structural ceramics are beginning to be made. The thermodynamics of these multicomponent complex oxides is poorly known.

The fifth group contains oxynitride (and in a few cases, pure nitride) glasses of compositions similar to the fourth group [2]. Ceramic, fiber, and coating applications are possible. Though for aluminosilicate glasses, there is a reasonable level of understanding in relating structure, thermodynamics, and the extent and ease of glass formation [4,5], such understanding is far more rudimentary for nitrogen-containing glasses.

Despite the importance and fascination of this wide-ranging group of materials, thermochemical data are few and far between. This review, in celebration of Professor Ole Kleppa's career and in acknowledgment of his influence on mine, summarizes our recent calorimetric work on various classes of nitrides. Several examples illustrate both the methodology and the systematics obtained.

2. Calorimetric methodology

We use high temperature oxide melt calorimetry in a Calvet calorimeter [6,7]. The lead borate solvent commonly used for solution calorimetry of oxides is not suitable for nitrides because the reduction of lead and its possible alloying with the platinum crucible would lead to an ill-defined final state. Because our interest include oxynitrides, we have not pursued metallic solvents. Rather, we have focused on the path of oxidative drop solution calorimetry pioneered by Elder et al. [8] for nitrides containing alkali ions, molybdenum, and tungsten. That early work in our laboratory oxidized reactants and products to a molten mixture of alkali molybdates (and tungstates) with the same cation ratios as the starting materials.

In this method, nitride pellets were dropped into a calorimeter at ~700°C under flowing O_2. The heat effect from the ensuing reaction of the nitride with O_2 to form liquid oxides and nitrogen gas (a stable final state) was used to determine enthalpies of formation through appropriate thermodynamic cycles. However, experiments have shown that the nitrides in several other systems do not completely react with O_2 after 2 h at 700°C. This was quite surprising as most of these compounds decompose in seconds to minutes upon exposure to moist air at room temperature. The products of this room temperature decomposition are metal hydroxides (or hydrous oxides) and NH_3, which indicates that the reaction with H_2O has a significantly lower activation energy than the reaction with O_2. In fact, based on our preliminary studies with over ten ternary and binary metal nitrides, it appears that the complete and rapid reaction with O_2 at 700°C is an exception rather than the rule.

Other solvents have been used for high temperature solution calorimetry on oxide systems for which $2PbO \cdot B_2O_3$ has proved unsuitable. A sodium molybdate melt of composition $3Na_2O \cdot 4MoO_3$ has been shown to be very effective for dissolution of titanium- and zirconium-bearing phases at ~700°C [9,10]. We have found that solvent well suited for nitride calorimetry, due partly to a reduction process similar to that which has proved problematic with $2PbO \cdot B_2O_3$. The MoO_3 in the melt is reduced upon introduction of a nitride at ~700°C. However, the reduction does not proceed to the metal, but only produces lower molybdenum oxides (see below), which do not attack Pt. Reoxidizing the solvent provides a reproducible final state. The ready reduction of Mo^{6+} at 700°C provides a rapid pathway for elimination of N^{3-} as N_2 gas [11,12].

We chose the Ca–Zn–N system as the starting point for our thermochemical studies of ternary metal nitrides in $3Na_2O \cdot 4MoO_3$ [11–13]. At first, furnace experiments at 700°C were performed on the nitride samples to see if they would dissolve in the solvent in a time suitable for calorimetry (~1 h). Upon addition of a nitride, the solvent, which was initially a clear amber melt, turned black and opaque. It returned to its original appearance with no evidence of undissolved material in less than 1 h at 700°C for all nitrides studied in the Ca–Zn–N system. To check if the MoO_3 was being reduced to the metal, which would potentially alloy with the Pt crucible and cause problems, a 2 g sample of the solvent was quenched from 700°C to room temperature 1 min after addition of 100 mg of Zn_3N_2 (which is two orders of magnitude higher in concentration than the actual calorimetric experiment) and studied by powder X-ray diffraction (XRD) and electron microprobe. The XRD pattern of this quenched solvent showed no evidence of metallic Mo. However, MoO_2 was detected in addition to the expected phases Na_2MoO_4 and $Na_2Mo_4O_{13}$. Electron microprobe analysis revealed three phases distinguished by levels of brightness in back-scattered electron images. Energy-dispersive spectrometry revealed that the two darker phases contained Na and Mo, and the third, brightest population of crystallites (in the back-scattered electron images) contained little to no Na. Wavelength dispersive spectrometry revealed that these bright crystallites contained significant amounts of oxygen, and could not be metallic molybdenum, but were probably MoO_2.

We suspected that the reduction of MoO_3 in the solvent to MoO_2 upon addition of a nitride was accompanied by rapid oxidation of N^{3-} to N_2 gas. To verify this assumption, a 10 mg pellet of Zn_3N_2 was dropped into 10 g of sodium molybdate at 700°C in a vertical tube furnace. Oxygen was flushed through the system at 90 ml min^{-1}, and the exit gas was sampled by a Balzers Thermocube mass spectrometer. A rapid release of N_2 was observed immediately after addition of Zn_3N_2 to the solvent. This supports the conclusion that upon addition of a nitride sample, a reaction with the stoichiometry in Eq. (1) occurs, where M represents a metal in the 2+ oxidation state.

$$\begin{aligned} M_3N_2(\mathrm{s}, 25°\mathrm{C}) + 3MoO_3(1, 700°\mathrm{C}) &\rightarrow 3MO(\mathrm{s}, 700°\mathrm{C}) \\ &+ 3MoO_2(\mathrm{s}, 700°\mathrm{C}) + N_2(\mathrm{g}, 700°\mathrm{C}) \qquad (1) \end{aligned}$$

As written, this reaction does not represent a stable final state that can be used in a thermochemical cycle. The MO must dissolve in the sodium molybdate and the MoO_2 must be oxidized to MoO_3 and returned to the solvent, as in reaction (2).

$$\begin{aligned} 3MO(\mathrm{s}, 700°\mathrm{C}) + 3MoO_2(\mathrm{s}, 700°\mathrm{C}) + {}^3/_2O_2(\mathrm{g}, 700°\mathrm{C}) \\ \rightarrow 3MO(\mathrm{soln}, 700°\mathrm{C}) + 3MoO_3(\mathrm{soln}, 700°\mathrm{C}) \qquad (2) \end{aligned}$$

This is relatively slow compared to reaction (1). The calorimeter glassware was therefore adapted to allow for a 2 mm inner diameter Pt tube to be inserted into the crucible; through this, O_2 could be bubbled through the solvent (~5 ml min^{-1}) in addition to the O_2 already flowing through the calorimeter above the melt (see Fig. 1). This served to speed up reaction (2) by supplying oxygen directly to the solvent. It also provided a means of stirring the solvent which accelerated the dissolution of any solid material. Combination of Eqs. (1) and (2) yields Eq. (3), which corresponds to the enthalpy change measured.

$$\begin{aligned} M_3N_2(\mathrm{s}, 25°\mathrm{C}) + {}^3/_2O_2(\mathrm{g}, 700°\mathrm{C}) &\rightarrow 3MO(\mathrm{soln}, 700°\mathrm{C}) \\ &+ N_2(\mathrm{g}, 700°\mathrm{C}) \qquad (3) \end{aligned}$$

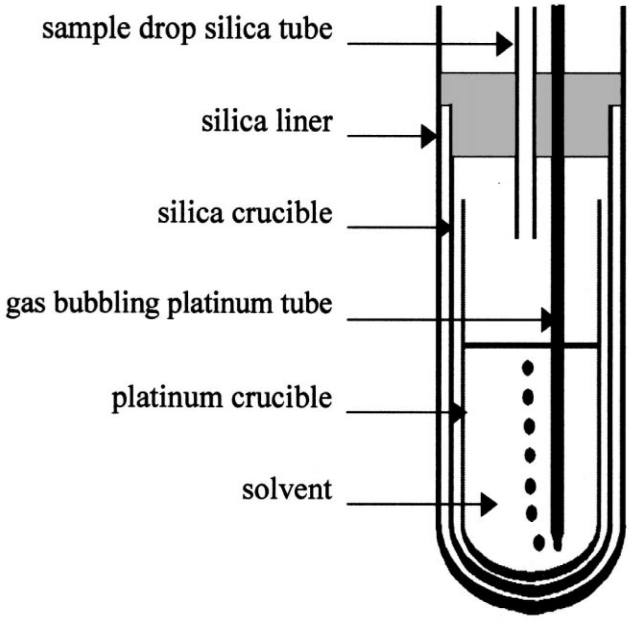

Fig. 1. Assembly for oxidative drop solution calorimetry using gas bubbling through the solvent as well as gas flow through the atmosphere in the calorimeter above the solvent.

This gas bubbling through the melt has proven to be a major advance in calorimetric methodology. For samples which require oxidation (nitrides, oxynitrides, oxides in lower valence states) it provides rapid and reproducible reactions. For oxide samples which tend to dissolve slowly and/or locally saturate the solvent, the effective stirring disperses the dissolving solid and greatly enhances its dissolution rate. The gas bubbling does not disturb the calorimeter and eliminates the need for mechanical stirring and its associated correction terms.

$3Na_2O \cdot 4MoO_3$ has proven an excellent solvent for a variety of nitrides, including those in the Ca–Zn–N system [12], Li–Zn–Ca–N system [11], Ca–Ta–N system [11], (Li,Ca)–(B,Al)–N system [13], the P–O–N system [14], VN, Ca_3CrN_3, $Ca_3Mg_3N_4$ [11–13], and the Zr–X–O–N (X = Ca, Mg, Y) [15].

However, for the molybdate to be a suitable solvent, it must readily dissolve the oxides of all cations which are components of the nitride. In accord with earlier experience, neither quartz nor other silica polymorphs dissolve significantly in the sodium molybdate melt. Thus for silicon nitride and sialons, this is not a good solvent.

In work on oxides and silicates, an alkali borate solvent (52 wt.% $LiBO_2$–48 wt.% $NaBO_2$) has been used when one needs to avoid the easy reducibility of lead [7,16]. It effectively dissolves silica and alumina. A typical thermochemical cycle for oxynitrides using this solvent is shown in Table 1.

3. Silicon nitride

Silicon nitride as a ceramic material presents great technological interest. Its chemical durability, low density, great hardness, and high mechanical strength at high temperature make it uniquely applicable to extreme conditions. The two polymorphs of silicon nitride, α and β, also represent the fundamental structure types of a group of modern ceramic materials, the silicon aluminum oxynitrides (sialons) and metal silicon aluminum oxynitrides (sialons) and metal silicon aluminum oxynitrides (Me-sialons) [3]. Determining energetics of formation of silicon nitride is the first step toward understanding phase stability and materials compatibility, and why phases form, with regard to this entire class of oxynitride materials. There is also a practical purpose in studying the energetics of the two polymorphs. The α- to β-phase transition of silicon nitride has been utilized in tailoring the microstructure of silicon nitride ceramics. Such controlled microstructures are essential for the application of the materials as structural ceramics, for example in automobile and aircraft engines. Crystal structure considerations suggest that the β-polymorph, formed at high temperature (1500–1800°C), is energetically more favorable than the α-polymorph [18], and therefore, the α→β transition is irreversible. There was, however, also speculation [19] that the α-polymorph

Table 1
Thermochemical data and cycles used in calculations of enthalpy of formation of $Y_{10}(SiO_4)_6N_2$ from elements[a]

	Reaction	ΔH (kJ/mol) [17]
(1)	$Y_{10}(SiO_4)_6N_{2\ (crystal,\ 25°C)} + 3/2\ O_{2\ (gas,\ 800°C)} \rightarrow 6SiO_{2\ (dissolved,\ 800°C)} + 5Y_2O_{3\ (dissolved,\ 800°C)} + N_{2\ (gas,\ 800°C)}$	-92.60 ± 2.35 (15)
(2)	$Y_2O_{3\ (crystal,\ 25°C)} \rightarrow Y_2O_{3\ (dissolved,\ 800°C)}$	107.47 ± 2.19 (8)
(3)	$2Y_{\ (solid,\ 25°C)} + 3/2O_{2\ (gas,\ 25°C)} \rightarrow$ $Y_2O_{3\ (crystal,\ 25°C)}$	-1905.31
(4)	$Si_{\ (solid,\ 25°C)} + O_{2\ (gas,\ 25°C)} \rightarrow$ $SiO_{2\ (crystal,\ 25°C)}$	-910.70
(5)	$SiO_{2\ (crystal,\ 25°C)} \rightarrow SiO_{2\ (dissolved,\ 800°C)}$	38.26 ± 0.72 (11)
(6)	$O_{2\ (gas,\ 25°C)} \rightarrow O_{2\ (gas,\ 800°C)}$	25.25
(7)	$N_{2\ (gas,\ 25°C)} \rightarrow N_{2\ (gas,\ 800°C)}$	23.87
	$10Y_{(solid,\ 25°C)} + 6Si_{(solid,\ 25°C)} + N_{2\ (gas,\ 25°C)} + 12O_{2(gas,\ 25°C)} \rightarrow Y_{10}(SiO_4)_6N_{2\ (crystal,\ 25°C)}$	
	$\Delta H_f^o = -\Delta H_1 + 5\ \Delta H_2 + 5\ \Delta H_3 + 6\ \Delta H_4 + 6\ \Delta H_5 - 3/2\ \Delta H_6 + \Delta H_7$	$-14\ 154.5 \pm 16.48$

[a] Value is mean of a number of experiments indicated in parentheses. Error is 2 standard deviations of the mean [17].

is stable below 1500°C. Another speculation [20,21] was that α silicon nitride is not pure Si_3N_4 but an oxynitride solid solution, which may be stable under relatively high oxygen partial pressure, whereas the β-phase is pure Si_3N_4. The dissolution limit was represented by the formula $Si_{11.9}O_{0.5}N_{15.5}$ which corresponds to 1.43 wt.% oxygen.

A recent calorimetric study of the Si_3N_4 polymorphs gave enthalpies of formation of -828.9 ± 3.4 and -827.8 ± 2.5 kJ/mol for the α- and β-polymorphs, respectively based on fluorine bomb calorimetry [22]. The results suggest that there is basically no distinction in energetics between the two Si_3N_4 polymorphs. That study attempted to correct for impurities present in the two materials (one of α, one of β) used.

We measured the enthalpy of oxidative drop solution of silicon nitride in molten alkali borate solvent [23]. We selected for our calorimetric study, in an attempt to answer the question of "what drives the α→β transition?", a number of α-Si_3N_4 samples, ranging in quality from α-Si_3N_4 single crystal with very low oxygen content to industrial raw material that contains considerable amount of O- and C-impurities. We confirmed that there is no energetic difference between the two polymorphs. Furthermore, we found that the α-Si_3N_4 polymorph is destabilized by O- and C-impurities (see Fig. 2).

Using the impurity corrected values of the enthalpy of drop solution, the standard enthalpy of formation can be calculated. For the reaction

$$3Si_{(solid,\ 25°C)} + 2N_{2\ (gas,\ 25°C)} \rightarrow Si_3N_{4(crystal,\ 25°C)} \qquad (4)$$

the molar enthalpies of formation (from the elements at 25°C) determined by using the alkali borate solvent are -852.2 ± 11.3 and -852.0 ± 8.7 kJ/mol for sample β1 and β2, respectively. Measurement by using a potassium vanadate solvent on β2 gave -850.2 ± 2.7 kJ/mol, thus confirming the determination using the alkali borate solvent. Taking into account the estimated errors, the two β samples give essentially identical results. This implies that the thermochemical characteristics of β-Si_3N_4 are not affected by varying thermal history or by varying impurity contents of individual samples. This suggests that the impurity correction, based on the sample being a mechanical mixture of β-Si_3N_4, SiO_2 (glass), and SiC, is correct.

The same thermochemical cycle as for the β-Si_3N_4 samples was used for the calculation of the standard molar enthalpy of formation for the α-Si_3N_4 samples. In contrast to the β samples, the α samples give a range of standard enthalpy of formation from -776 to -854 kJ/mol, under the assumption that the impurities occur as separate phases. These results argue that at least some of the impurities are dissolved in the α-phase.

As the microscopic nature of the impurities is not known, one has to examine the influence of the level of impurity on the relative stability (enthalpy of formation) of

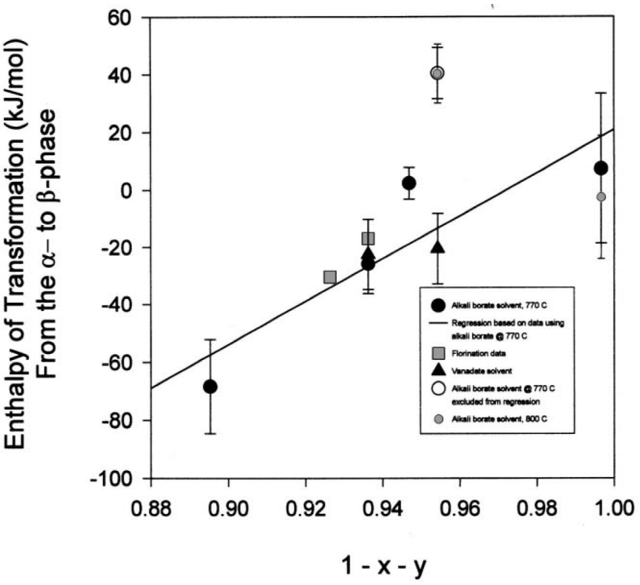

Fig. 2. Enthalpy of the reaction $(1-x/3-y/3)$ α-$Si_3N_4 \cong x SiO_2 \cong y SiC \rightarrow (1-x/3-y/3)$ β-$Si_3N_4 + x SiO_2 + y SiC$, as a function of O- and C-impurity contents expressed as $1-x-y$ [23].

the α-Si_3N_4 samples without making assumptions on the speciation of the impurities. We can write a general formula for the impure α samples as

$$(1 - x/3 - y/3)\ \alpha\text{-}Si_3N_4 \cong xSiO_2 \cong ySiC \qquad (5)$$

where x and y are numbers of moles. The notation of SiO_2 and SiC bears no speciation information and just represents the stoichiometrically balanced presence of O and C impurities in the sample. The stability of the α-phases can then be considered based on the enthalpy of the following reaction which represents an isocompositional decomposition of impure α to pure β plus exsolved impurities:

$$\begin{aligned}&(1 - x/3 - y/3)\ \alpha\text{-}Si_3N_4 \cong xSiO_2 \cong ySiC\\ &\quad \rightarrow (1 - x/3 - y/3)\ \beta\text{-}Si_3N_4 + xSiO_2 + ySiC \qquad (6)\end{aligned}$$

This enthalpy can be calculated using a thermochemical cycle. The enthalpy of reaction, ΔH, is plotted against the impurity level expressed as $1 - x - y$ (Fig. 2), ΔH approaches 0 as the α sample becomes pure (the term $1 - x - y$ approaches 1). This formally establishes, as pointed out earlier, that there is no difference in the molar enthalpy of formation between pure α- and β-Si_3N_4.

We can now understand the energetic driving force behind the process of α- to β-Si_3N_4 conversion widely used in industry in shaping the microstructure of Si_3N_4 ceramic parts. Most commercial α-Si_3N_4 contains considerable amounts of impurities. These samples give off considerable heat, e.g. 66 kJ/mol in the case of sample α1 during the transformation from α to β, with the transfer of impurities from possible solid solution in α to separate SiO_2 and SiC phases coexisting with β. This will clearly drive the conversion energetically. Once converted, the product will not revert back to α-Si_3N_4 with decreasing temperature, as the transformation is exothermic, implying that the α-phase (with impurities) is metastable under all conditions.

4. Binary and ternary nitrides

The energetics of ternary (and higher) oxide formation is reasonably well established, and tends to be dominated by the difference in acid–base character of the cations [24]. Many new and structurally diverse ternary metal nitrides have been discovered in recent years, but little is known of the thermodynamics that controls their formation. It is known that binary nitrides have small enthalpies of formation due mainly to the stability of dinitrogen. However, the energetics of formation of ternary nitrides from binaries is quite substantial. The multitude of ternary nitride phases being discovered certainly suggests considerable stabilization for ternaries. By measuring the enthalpy change of a reaction between $LiMoN_2$ and O_2 gas at 700°C, Elder et al. [8] determined the enthalpy of formation of $LiMoN_2$ from Li_3N, Mo_2N and N_2 to be -224.0 kJ mol^{-1}, which is a large fraction of the enthalpy of formation from the elements, -386.0 ± 6.4 kJ mol^{-1}. However, the formation of $LiMoN_2$ as calculated involves an increase in the formal oxidation state of molybdenum, which surely contributes to the large exothermic enthalpy of formation from the binary nitrides. To explore the energetics of ternary nitride formation unaccompanied by oxidation or reduction we have included in our study ternaries in the Li–Ca–Zn–N system [11]. These three metals form well defined binary nitrides, Li_3N, Ca_3N_2, and Zn_3N_2, and three ternaries in which the metal ions are in the same formal oxidation state, Ca_2ZnN_2, LiCaN, and LiZnN. In addition, $CaTaN_2$ and Ta_3N_5 were studied, which together with literature data for H_f° (TaN) provide a means of estimating the contribution of Ta reduction in the energetics of $CaTaN_2$ formation from Ca_3N_2 and Ta_3N_5. The calorimetric results for these and other nitrides are shown in Table 2.

The standard enthalpies of formation obtained for the binary nitrides are relatively small in magnitude, sometimes an order of magnitude smaller than those of the oxide of the same metal. However, the enthalpy of formation of ternary nitrides from binaries can be quite substantial in both magnitude and as a fraction of the

Table 2
Enthalpies of formation of nitrides from the elements at 25°C

Nitride	$\Delta H^\circ_{\pm,\ 298}$ (kJ/mol)	Refs.
AlN	-311.1 ± 4.3	[12]
	-316.0 ± 1.8	[25,26]
	-313.6 ± 4.6	[25,26]
β-Si_3N_4	-852.0 ± 11.3	[23]
	-850.2 ± 2.7	[23]
α-Si_3N_4	-850.9 ± 22.4	[23]
sialons	various	[25,26]
Li_3N	-166.1 ± 4.8	[11]
Ca_3N_2	-439.7 ± 6.6	[11]
Zn_3N_2	-43.5 ± 4.1	[11]
Ca_2ZnN_2	-378.9 ± 8.6	[11]
Sr_2ZnN_2	-385.6 ± 14.3	[11]
LiCaN	-216.8 ± 10.8	[11]
LiZnN	-137.5 ± 6.8	[11]
$CaTaN_2$	-643.8 ± 9.6	[11]
VN	-218.3 ± 2.1	[12]
Ca_3VN_3	-784.9 ± 13.4	[12]
Ca_3CrN_3	-715.0 ± 9.8	[12]
Li_3BN_2	-534.5 ± 16.7	[12]
Li_3AlN_2	-567.8 ± 12.4	[12]
$Ca_3B_2N_4$	-1062.1 ± 15.4	[12]
$Ca_2Al_2N_4$	-1149.1 ± 10.3	[12]
$Ca_3Mg_3N_4$	-889.5 ± 8.6	[12]
GaN	-156.8 ± 16.0	[27]
Fe_4N	-12.2 ± 20.3	[28]
Fe_3N	-40.0 ± 9.9	[28]
Fe_3N_{1-10}	-23.8 ± 11.5	[28]
Fe_3N_{1-22}	-45.1 ± 8.0	[28]
Fe_3N_{1-30}	-35.3 ± 10.0	[28]
Fe_3N_{1-33}	-43.3 ± 6.5	[28]
Fe_2N	-34.3 ± 7.8	[28]
$FeN_{0.91}$	-47.1 ± 3.5	[28]

enthalpy of formation from the elements (see Fig. 3A). The enthalpy of formation of LiZnN from binary nitrides in the same oxidation state is nearly 50% of the enthalpy of formation from the elements. This indicates significant energetic stability for this ternary. Sr_2ZnN_2 and Ca_2ZnN_2 also have fairly large enthalpies of formation from the binaries. LiCaN, on the other hand, has a small ΔH_f (from binary nitrides). No lithium calcium oxides are known with which to compare this value. There are no ternary phases in the CaO–ZnO system, but a $SrZnO_2$ phase is known as are several stable phases in the Li_2O–ZnO system. We have measured the enthalpy of formation of $SrZnO_2$ from the oxides as -5.70 ± 4.12 kJ mol^{-1}. The lack of ternary oxides in the CaO–ZnO and Li_2O–CaO systems, and the small (near zero) value of $H_f(O)$ for $SrZnO_2$ are testaments to the similar basicities of these oxides: There is little or no energetic advantage in forming a ternary.

Numerous attempts have been made to quantify the acidity or basicity of a cation. It is generally agreed that acidity scales as some function of the size and charge of the cation (i.e. Z/r, Z^2/r, Z/r^2, etc.). The simplest of these empirical expressions is the ionic potential, ϕ, the ratio of charge to ionic radius, Z/r. The dominance of acid–base reactions in the energetics of ternary nitride formation becomes evident upon consideration of Fig. 3, where the $\Delta H_f(N)$ values in kJ mol^{-1} N^{3-} for ternary nitrides are plotted as a function of the ratio of ϕ for the two metal ions (i.e. ϕ of the more acidic cation, ϕ_A, divided by ϕ of the more basic cation, ϕ_B). Placing thermochemical data for ternary oxides on the plot in Fig. 3B reveals that the stabilization of ternary nitrides obtained via combination of an acidic cation with a more basic cation is much greater than that achieved in oxides. The slope obtained from data on over 80 ternary oxides (including aluminates, titanates, zirconates, chromates, tungstates, zirconates, chromates, tungstates, molybdates, silicates, and carbonates) is an order of magnitude smaller in magnitude than that obtained from these nitrides. This is likely to be related to the greater polarizability of the N^{3-} anion, and the high energy of formation of N^{3-} from atomic N ($+2300$ kJ mol^{-1}) compared to the energy of formation of O^{2-} from atomic O ($+700$ kJ mol^{-1}). These factors lead to a higher degree of covalency in the bonding in ternary nitrides which reveals itself through relatively exothermic values of $\Delta H_f(N)$ (Table 2).

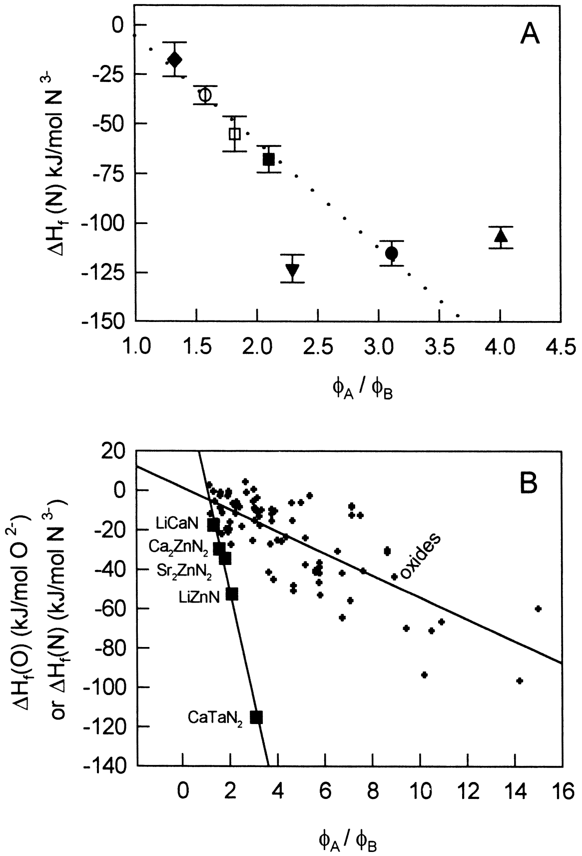

Fig. 3. (A) The enthalpies of formation of ternary nitrides from binary nitrides as a function of the ratio of ϕ of the acidic cation over ϕ of the basic cation. Enthalpies are given per mole of N^{3-}. Symbols represent ♦, LiCaN; ○, Ca_2ZnN_2; □, Sr_2ZnN_2; □, LiZnN; □, $CaTaN_2$ from TaN, Ca_3N_2 and N_2; □, $CaTaN_2$ from Ta_3N_5 and Ca_3N_2; and □, CaTaN from Ca_3N_2, TaN and Ta_3N_5. (B) The $\Delta H_f(N)$ data from (A) with data for ternary oxides of similar stoichiometry on a kJ/mol O^{2-} basis (+) [12].

These systematics provide a framework for further study. The goal is linking nitride thermochemistry to structural, crystal chemical, and bonding parameters.

5. Other oxynitride systems

Initial work on β-sialon phases has been published [25,26]. The PON system is under investigation [14] as are glasses in the Li–P–O–N system [14]. Sialon glasses and α-sialon solid solutions are being prepared for calorimetric study.

6. Conclusions

Oxidative drop solution calorimetry is a versatile tool for studying materials and oxynitrides. It has already more than doubled the number of compounds for which heats of formation are known. From the viewpoints of fundamental solid state chemistry and technological applications, the data provide new insight. This still largely unexplored field of nitride thermochemistry offers many new opportunities and challenges.

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References

[1] R. Niewa, F.J. DiSalvo, Chem. Mat. 10 (1998) 2733.

[2] R. Marchand, Y. Laurent, Eur. J. Solid State Inorg. Chem. 28 (1991) 57.

[3] K.H. Jack, J. Mat. Sci. 11 (1976) 1135.

[4] A. Navrotsky, in: C.M. Scarfe (Ed.), Mineral Association of Canada Short Course in Silicate Melts, Vol. 12, Mineral Association, Canada, 1986, p. 130.

[5] A. Navrotsky, K.L. Geisinger, P.F. McMillan, G.V. Gibbs, Phys. Chem. Min. 11 (1985) 284.

[6] O.J. Kleppa, Colloq. Int. CNRS No. 201: Thermochimie (1972) 119.

[7] A. Navrotsky, Phys. Chem. Min. 14 (1997) 222.

[8] S.H. Elder, F.J. DiSalvo, L. Topor, A. Navrotsky, J. Solid State Chem. 106 (1993) 349.

[9] A. Navrotsky, O.J. Kleppa, Inorg. Chem. 30 (1968) 479.

[10] A. Navrotsky, O.J. Kleppa, Inorg. Chem. 8 (1969) 796.

[11] J.M. McHale, A. Navrotsky, G.R. Kowach, V.E. Balbarin, F.J. DiSalvo, Chem. Mater. 9 (1997) 1538.

[12] J.M. McHale, A. Navrotsky, F.J. DiSalvo, Chem. Mater. 11 (1999) 1148.

[13] J.M. McHale, G.R. Kowach, A. Navrotsky, F.J. DiSalvo, Chem. Eur. J. 2 (1996) 1514.

[14] F. Tessier, A. Navrotsky, A. LeSauze, R. Marchand, Chem. Mater. 12 (2000) 148.

[15] I. Molodetsky, A. Navrotsky, F.J. DiSalvo, M. Lerch, J. Mat. Res. 15 (2000) 2558–2570.

[16] C. Chatillon-Colinet, R.C. Newton, D.L. Perkins III, O.J. Kleppa, Geochim. Cosmochim. Acta 47 (1983) 439.

[17] J.-J. Liang, A. Navrotsky, T. Ludwig, H.J. Seifert, F. Aldinger, J. Mater. Res. 14 (1999) 1181.

[18] C.M. Wang, X. Pan, M. Ruhle, F.L. Riley, M. Mitomo, J. Mat. Sci. 31 (1996) 5281.

[19] D.J. Messier, W.J. Croft, Prep. Prop. Solid State Mat. 7 (1982) 132.

[20] S. Hampshire, H.K. Park, D.B. Thompson, K.H. Jack, Nature 274 (1978) 880.

[21] K.H. Jack, in: F.L. Riley (Ed.), Progress in Nitrogen Ceramics, Martinus Niihoff Publishers, 1983, pp. 45–60.

[22] P.A.G. O'Hare, I. Tomaskiewicz, C.M. Bekk II, H.J. Seifert, J. Mat. Res. 12 (1997) 3203.

[23] J.-J. Liang, L. Topor, A. Navrotsky, M. Mitomo, J. Mat. Res. 14 (1999) 1959.

[24] A. Navrotsky, Am. Min. 79 (1994) 589.

[25] A. Navrotsky, S.H. Risbud, J.-J. Liang, V.J. Leppert, J. Phys. Chem. B101 (1997) 9433.

[26] J.-J. Liang, A. Navrotsky, V.J. Leppert, M.J. Paskowitz, S.H. Risbud, T. Ludwig, H.J. Seifert, F. Aldinger, M. Mitomo, J. Mater. Res. 14 (1999) 4630.

[27] M.R. Ranade, F. Tessier, A. Navrotsky, V.J. Leppert, S.H. Risbud, F.J. DiSalvo, C.M. Balkas, J. Phys. Chem. B 104 (2000) 4060–4063.

[28] F. Tessier, A. Navrotsky, R. Niewa, A. Leineweber, H. Jacobs, S. Kikkawa, M. Takahashi, T. Kanamaru, F.J. DiSalvo, Solid State Sci. 2 (2000) 457–462.