1538 *Chem. Mater.* **1997,** *9,* 1538−1546

Energetics of Ternary Nitrides: Li−Ca−Zn−N and Ca−Ta−N Systems

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Received November 5, 1996. Revised Manuscript Received April 11, 1997[⊗]

High-temperature oxide melt drop solution calorimetry was used to study the energetics of ternary nitride formation. The standard enthalpies of formation of several binary and ternary nitrides were determined. These values in kJ mol^{-1} are $\Delta H_f°(Li_3N) = -166.1 \pm 4.8$, $\Delta H_f°(Ca_3N_2) = -439.7 \pm 6.6$, $\Delta H_f°(Zn_3N_2) = -43.5 \pm 4.1$, $\Delta H_f°(Ta_3N_5) = -849.7 \pm 11.7$, $\Delta H_f°(Ca_2ZnN_2) = -378.9 \pm 8.6$, $\Delta H_f°(Sr_2ZnN_2) = -385.6 \pm 14.3$, $\Delta H_f°(LiCaN) = -216.8 \pm 10.8$, $\Delta H_f°(LiZnN) = -137.5 \pm 6.8$, and $\Delta H_f°(CaTaN_2) = -643.8 \pm 9.6$. These enthalpies of formation are small in magnitude compared to analogous values for oxides. However, the enthalpies of formation of the ternaries from binary nitrides can be quite substantial, confirming significant energetic stabilization of ternary nitrides. The energetics of ternary nitride formation appears to be dominated by the acid/base character of the cations. A linear relationship was found between the enthalpies of formation of the ternaries from binary nitrides and the ionic potential ratio of the two cations.

Introduction

The energetics of ternary (and higher) oxide formation is reasonably well established and tends to be dominated by the difference in acidity (or basicity) of the cations.[1] Many new and structurally diverse ternary metal nitrides[2−5] have been discovered in recent years (see Table 1), 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.[6] However, the energetics of formation of ternary nitrides from binaries might be 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 ~973 K, Elder et al.[7] determined the enthalpy of formation of $LiMoN_2$ from Li_3N, Mo_2N, and N_2 to be −224.0 kJ mol^{-1}, which was very large in magnitude relative to the enthalpy of formation from the elements, −386.0 ± 6.4 kJ mol^{-1}. However, the formation of $LiMoN_2$ as calculated involves oxidation of "$Mo^{1.5+}$" to Mo^{5+}, 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. 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,[8] LiCaN,[9] and LiZnN.[10] In addition, $CaTaN_2$ and Ta_3N_5 were studied,[11,12] which together with literature data for $\Delta H_f°(TaN)$ 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.

Many of these ternary nitrides were surprisingly resistant to reaction with O_2 gas at ~973 K. In addition, Li_2O formed via reaction of a Li-containing nitride with O_2 is very reactive with almost every possible container material at high temperature. These factors prevented utilization of the technique developed by Elder et al.[7] High-temperature solution calorimetry has been instrumental in the study of ternary oxides, and we have recently reported new methodology making this technique applicable to study of nitrides.[13] The solvent we have found useful for nitride calorimetry is $3Na_2O\cdot 4MoO_3$ at ~973 K. The calorimetry utilizes a redox reaction between the MoO_3 component of the melt and "N^{3-}" which supplies a rapid pathway for elimination of "N^{3-}" as N_2 gas:

$$M_3N_2(s, 298) + 3MoO_3(\text{in melt}, 979\ K) \rightarrow 3MO(\text{soln}, 979\ K) + 3MoO_2(s, 979\ K) + N_2(g, 979\ K) \quad (1)$$

where M is a metal in the +2 oxidation state. Any

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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S0897-4756(97)00244-5 CCC: $14.00

Table 1. Examples of Recently Discovered Ternary Nitrides Displaying Interesting Structures and Properties

structural type or structural features	compound	properties of interest	ref
anti-$CaTiO_3$	Ca_3MN (M = P, As, Sb, Bi, Ge, Sn, Pb)	distortional phase transitions, ferroelectric properties, unusual oxidation states (M^{3-}), metallic behavior	*a*
sheets of trigonal planar $(MN_3)^{6-}$ units (analogous to $CO_3{}^{2-}$)	Ca_3CrN_3, Ca_3VN_3, Ba_3FeN_3, Sr_3FeN_3, Li_3FeN_3	unusual trigonal planar environment for N, multiple metal−nitrogen bonding, low spin Cr^{3+}	*b*, *c*, *d*
Ni−N chains	$Li_2Sr_2Ni_4N_4$, BaNiN, $Ba_8Ni_6N_7$, CaNiN	short bonds, low oxidation states (Ni+)	*e*, *f*, *g*
infinite corner linked square planar $[CrN_3]^{8-}$ chains	Ce_2CrN_3	infinite polyanionic network	*h*
ordered rock salt	$CaTaN_2$	superconducting, $T_c \approx 9$ K	*i*
Na_2HgO_2 type	A_2ZnN_2 (*A* = Ca, Sr, Ba)	linear $[N{=}Zn{=}N]^{4-}$ anions	*j*, *k*
layered structure	$LiMoN_2$, $Li_{1-x}MoN_2$ ($0 < x < 0.64$)	Li deintercalation, variable oxidation state, possible low-dimensional electronic properties	*l*

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molybdenum dioxide formed in a transient way is subsequently oxidized to MoO_3 by bubbling O_2 through the solvent during calorimetry:

$$3MoO_2(\text{s, 979 K}) + {}^3/_2O_2(\text{g, 979 K}) \rightarrow 3MoO_3\ (\text{in melt, 979 K}) \quad (2)$$

Combination of reactions 1 and 2 yields

$$M_3N_2(\text{s, 298}) + {}^3/_2O_2(\text{g, 979 K}) \rightarrow 3MO(\text{soln, 979 K}) + N_2(\text{g, 979 K}) \quad (3)$$

This reaction represents the heat effect measured through drop solution calorimetry. Herein we apply this methodology to determine the enthalpies of formation of Li_3N, Ca_3N_2, Zn_3N_2, Ta_3N_5, Ca_2ZnN_2, Sr_2ZnN_2, LiCaN, LiZnN, and $CaTaN_2$ and show that the energetics of ternary nitride formation are dominated by the differences in basicities of the cations.

Experimental Section

A. Synthesis and Sample Characterization. All manipulations were carried out in an Ar- or He-filled glovebox. Phase identification was accomplished with powder XRD using a Scintag XD S2000 diffractometer and Cu Kα radiation. Thermogravimetric analysis (TGA) was performed in a Perkin-Elmer TA7 or Netszch STA 409. Nitrogen analysis was performed by hydrolyzing a known amount of nitride in molten KOH (~673 K) under a wet Ar flow and collecting the resulting NH_3 in aqueous boric acid (Kjehldahl method). This solution was then back-titrated to the original acidity with a standardized HCl solution. The synthesis of Ca_2ZnN_2 is discussed in ref 13.

Ca_3N_2 was prepared from the elements. Pieces of Ca metal (Aldrich, 99.999%) were loaded into an alumina boat which was heated in a tube furnace at 1273 K for 24 h under 1 atm of N_2. Ta foil was wrapped around the inside of the fused silica reaction tube to prevent attack of the SiO_2 by Ca vapors. A second batch was prepared from a 72 h soak at 1273 K and otherwise identical conditions. The brown powder thus obtained was identified by powder XRD for both batches as single-phase α-Ca_3N_2. TGA of the first batch (24 h at 1273 K) revealed a weight gain of 13.6% upon complete oxidation to CaO (theoretical value for $Ca_3N_2 \rightarrow 3CaO$ is 13.5%). The weight percentage of N was determined to be 18.89 ± 0.14%, with the theoretical weight percentage of N in Ca_3N_2 at 18.90%. The N content of the second batch was determined to be 18.79 ± 0.11 wt %.

Zn_3N_2 was synthesized from Zn metal powder (Alfa 99.9%, 100 mesh) which was placed into an alumina boat and heated in a quartz flow tube under a constant flow of NH_3. The temperature was slowly raised to 773 K over 20 h, maintained at 773 K for 17 h, raised to 823 K over 1 h, maintained at 823 K for 8 h, raised to 873 K over 1 h, and maintained at 873 K for 24 h. During this thermal treatment, about half of the Zn metal vaporized and deposited on the cooler ends of the flow tube while the remaining Zn was converted to Zn_3N_2. The black product obtained was identified as nearly single-phase Zn_3N_2 by powder XRD. Nitrogen analysis gave 12.39 ± 0.05 wt % (theoretical value = 12.496%), which is consistent with a 0.54% ZnO impurity. Pellets pressed from Zn_3N_2 powder were very fragile and nearly impossible to keep intact during sample handling prior to calorimetry. For this reason, the material was mixed with ZnO in an agate mortar and pestle (in an Ar-filled glovebox) in 1:1, 5:4, and 3:2 mass ratios. These mixtures formed sturdy, easily handled pellets which were used for calorimetry. The heat effect due to ZnO was subtracted from the total measured value.

Li_3N was prepared from the elements. Lithium metal pieces were placed into a molybdenum boat and fully nitrided under a back-pressure of N_2. The reaction tube was heated to 1023 K over 20 h and soaked at 1023 K for an additional 20 h. The inside of the tube was lined with titanium foil to prevent attack of the quartz by Li vapors. The material was identified as single-phase Li_3N via powder X-ray diffraction (XRD). The N content of the sample was determined to be 40.16 ± 0.07 wt % with 40.22 wt % theoretical for Li_3N.

Sr_2ZnN_2 was synthesized from a Na flux as previously described by Yamane and DiSalvo.[14] After extracting the Sr_2ZnN_2 crystals from the flux with liquid ammonia, the product was pressed into a pellet, placed into an alumina boat, and sintered (ramp over 7 h to 973 K and soak for 2 h) under a back-pressure of N_2. SrO was detected at approximately 2% by powder XRD.

LiCaN was synthesized from a mechanical mixture of Li_3N and Ca_3N_2. A 1:1 molar ratio of the binaries was ground in an agate mortar and pestle and pressed into a pellet. The pellet was sealed in a Ta tube which was subsequently sealed in an evacuated quartz tube and heated at 873 K for 48 h. The orange powder obtained was identified as LiCaN via powder XRD. Some CaO impurity peaks were also detected at about a 1.5% level.

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LiZnN was synthesized from a mechanical mixture of Li_3N and Zn_3N_2 following the procedure of Juza and Hund.[10] A 1:1 molar ratio of the two binaries was ground in an agate mortar and pestle and pressed into a pellet. The pellet was placed in a Ta boat and heated at 673 K for 48 h under flowing NH_3. The black product obtained was verified as single-phase LiZnN by XRD.

Ta_3N_5 was synthesized following the procedure outlined by Rauch and DiSalvo.[12] Under flowing NH_3 gas, $TaCl_5$ was heated at 1.5 K/min to 973 K and soaked at 973 K for 1 h. The brick red product was identified as single-phase Ta_3N_5 by powder XRD.

$CaTaN_2$ was synthesized by heating $Ca(NH_2)_2$ and Ta_3N_5 at ~1473 K for 8 min in a RF furnace under a N_2 atmosphere using an open Mo container as the susceptor. A small amount of Ca_3N_2 was then added to keep the Ca content in excess, and the sample was annealed in a sealed Mo susceptor for 30 min at 1473 K.[11] The black product obtained was identified as $CaTaN_2$ with ~5% TaN via powder XRD.

$SrZnO_2$ was synthesized via an acetate-based sol−gel method.[15] Both 5.000×10^{-3} mol of $SrCO_3$ and 5.000×10^{-3} mol of ZnO were placed in a Pt crucible and dissolved in 20 mL of glacial acetic acid and 5 mL of H_2O. The mixture was heated to boiling and concentrated to a clear highly viscous liquid which rapidly crystallized upon further heating. This precursor was then calcined at 1373 K for 12 h and quenched to room temperature by quick removal from the furnace. The product thus obtained was identified as single-phase $SrZnO_2$ by powder XRD.

To complete thermochemical cycles, drop solution calorimetry was also performed on thin Ta wire (obtained from Fansteel, 99.9%, 0.2 mm diameter) and $CaCO_3$, $SrCO_3$, ZnO, and Li_2CO_3 (obtained from Johnson Matthey Co., ≥99.9%).

B. Calorimetry. High-temperature oxide melt drop solution calorimetry was performed in a Tian-Calvet twin microcalorimeter described in detail by Navrotsky.[16] Nitride samples of approximately 5−10 mg were dropped from room temperature into liquid $3Na_2O{\cdot}4MoO_3$ at 979 K in the calorimeter. Oxygen gas was flushed through the calorimeter at ~90 mL min^{-1} and bubbled through the solvent at ~5 mL min^{-1}. Further details of the experimental procedure are provided elsewhere.[13] Many of these reactions were rapid and highly exothermic and very different from the endothermic Pt drop experiment used as the standard calibration in our laboratory. For this reason, calibration was performed by dropping ~5 mg pellets of benzoic acid (NIST, SRM 39i) which produced exothermic heat effects of nearly equal magnitude to the nitride reactions. A calibration constant was then calculated based on the known enthalpy of combustion of benzoic acid and the heat contents of CO_2 and H_2O. This calibration was verified by dropping ~5 mg pieces of thin Mo and Al wire (0.2 mm diameter, Johnson Matthey, ≥99.99%), Mg turnings (Johnson Matthey, 99.999%), and Zn (freshly prepared lathe turnings from a Baker ACS grade Zn rod) into $3Na_2O{\cdot}4MoO_3$ in the calorimeter. The metals oxidized, and the resulting metal oxides dissolved in the solvent. After completing a thermochemical cycle incorporating the enthalpies of drop solution of the metal oxides and the heat content of O_2 gas, the enthalpies of formation of MoO_3, $\alpha\text{-}Al_2O_3$, MgO, and ZnO could be calculated. The values thus determined with a benzoic acid calibration (in kJ mol^{-1}) were $\Delta H_f°(MoO_3) = -747.7 \pm 1.8$, $\Delta H_f°(\alpha\text{-}Al_2O_3) = -1664.4 \pm 4.3$, $\Delta H_f°(MgO) = -599.1 \pm 4.2$, and $\Delta H_f°(ZnO) = -349.1 \pm 4.1$, with the values listed for these oxides in the JANAF tables[39] being -745.2 ± 0.4, -1675.7 ± 0.8, -601.24 ± 0.63, and -350.46 ± 0.27, respectively. With a Pt or $\alpha\text{-}Al_2O_3$ drop calibration, the heat effects appeared to be 4−5% more exothermic. The $\Delta H_f°$ of the above oxides obtained with a benzoic acid calibration tended to be slightly less exothermic than the literature values, which is consistent with the expected presence of a thin oxide coating on the surface of the metals. For other reactions in the thermochemical cycles which were endothermic or not highly exothermic (i.e., drop solution calorimetry of oxides and carbonates), the standard Pt drop calibration was used. We note that the ready oxidative dissolution of these metals suggests that our technique may be a useful alternative to combustion calorimetry for determining heats of formation of oxides from the elements.

Some of the nitrides could not be synthesized as single phases, and it was necessary to correct the calorimetric data for the presence of impurities. When nitrogen content data was not available, the percentage of impurity was estimated from the powder diffraction data by the direct comparison method.[17] Multiplicities of reflections were taken into account. The uncertainty in the percentage of impurity was taken to be half of the estimated impurity level or a minimum of ±1.0 wt %. Throughout this work, errors were propagated as the square root of the sum of the squares of the individual uncertainties. Thermogravimetric analysis (TGA) was also used to estimate the impurity content by measuring the weight gain upon reaction of a nitride with wet O_2 to form an oxide. However, TGA sometimes provided higher impurity contents than seemed logical based on XRD data. This was most likely due to vaporization of some of the metal oxide product (especially Li_2O and ZnO) during the long experimental time needed for complete reaction (~12 h).

Results

Ca_3N_2. The results of drop solution calorimetry appear in Table 2. The calorimetric signal generally returned to the stable base line within 1 h of introducing

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Table 2. Data Used in Thermodynamic Cycles To Determine Nitride Enthalpies of Formation from Drop Solution Calorimetry (All Values in kJ mol^{-1})

	ΔH_{ds}[a] or ΔH_{cds}[b]	$H_{979} - H_{298}$[c]	$\Delta H_f°$ [d]
Li_3N	−873.2 ± 2.9 (7)[b]		
Ca_3N_2	−1748.2 ± 5.6 (18)		
Zn_3N_2	−968.1 ± 3.9 (12)		
Ta_3N_5	−2071.9 ± 8.5 (8)		
LiCaN	−858.9 ± 10.3 (7)[b]		
LiZnN	−546.1 ± 6.4 (8)		
Ca_2ZnN_2	−1416.8 ± 8.1 (7)		
Sr_2ZnN_2	−1417.7 ± 13.4 (8)[b]		
$CaTaN_2$	−1062.9 ± 8.0 (8)[b]		
$SrZnO_2$	−114.30 ± 1.57 (6)		
Li_2CO_3	+166.8 ± 1.3 (7)		−1216.0 ± 0.2
Li_2O[e]	−90.3 ± 2.5		−598.7 ± 2.1
$CaCO_3$	+121.6 ± 0.7 (6)		−1207.4 ± 1.3
CaO[e]	−90.3 ± 1.8		−635.09 ± 0.88
$SrCO_3$	+130.7 ± 1.3 (6)		−1218.7 ± 1.5
SrO[e]	−137.2 ± 3.8		−592.0 ± 3.3
ZnO	+17.2 ± 0.3 (6)		−350.46 ± 0.27
Ta	−991.6 ± 5.0 (10)[b]		
O_2		+21.98	
N_2		+21.31	
CO_2		+33.32	−393.52 ± 0.05

[a] Enthalpy of drop solution calorimetry, ΔH_{ds}. Values from this work. Reported uncertainty is two standard deviations of the mean. Number in parentheses is the number of experiments performed. [b] Corrected enthalpy of drop solution calorimetry, ΔH_{cds}. [c] From ref 38. [d] From ref 39. [e] From drop solution calorimetry on the carbonate.

Table 3. Summary of Enthalpies of Formation Obtained in This Work and the Literature Data Available for These Compounds

	$\Delta H_f°$ (kJ mol^{-1})		ΔH_f(N) (kJ mol^{-1})
	this work	lit.	this work
Li_3N	−166.1 ± 4.8	−164.9 ± 1.1	
Ca_3N_2	−439.7 ± 6.6	−439.3	
Zn_3N_2	−43.5 ± 4.1	−22.6	
Ta_3N_5	−849.7 ± 11.7		
LiCaN	−216.8 ± 10.8		−17.6 ± 8.6
LiZnN	−137.5 ± 6.8		−67.7 ± 6.6
Ca_2ZnN_2	−378.9 ± 8.6		−71.4 ± 9.1
Sr_2ZnN_2	−385.6 ± 14.3		−110.3 ± 17.6
$CaTaN_2$	−643.8 ± 9.6		−229.9 ± 12.5[a]

[a] From $^1/_3Ca_3N_2 + {}^1/_2TaN + {}^1/_6Ta_3N_5$.

a nitride sample, which is indicative of trouble-free calorimetry. No adverse effects were observed due to the bubbling of O_2 through the solvent. Calorimetric results and enthalpies of formation of Ca_3N_2, Zn_3N_2, and Ca_2ZnN_2 were reported in a previous publication,[13] but these data were calculated using an α-Al_2O_3 drop calibration which we now realize to be inappropriate for highly exothermic reactions. The adjusted values for Ca_2ZnN_2 appear in Tables 2 and 3. The $\Delta H_f°$ of Ca_3N_2 was determined again in this work from two separately prepared batches of better characterized, essentially single-phase Ca_3N_2. The measured enthalpy of drop solution, ΔH_{ds}, from the first batch of Ca_3N_2 was −11 779.0 ± 51.6 J g^{-1}, and that of the second batch was −11 773.2 ± 60.4 J g^{-1}. Based on N analysis, the second batch contained a 0.35 wt % CaO impurity. The corrected enthalpy of drop solution, ΔH_{cds}, for this sample is then

$$\Delta H_{ds}(Ca_3N_2) = 0.9965\Delta H_{cds}(Ca_3N_2) + 0.0035\Delta H_{ds}(CaO) \tag{4}$$

Due to the affinity of CaO for reaction with atmospheric H_2O and CO_2, the ΔH_{ds} value for CaO (eq 11) was determined from drop solution calorimetry on $CaCO_3$ through the following thermodynamic cycle:

$$CaCO_3(s, 298\ K) \rightarrow CaO(soln, 979\ K) + CO_2(g, 979\ K) \tag{5}$$

$$CO_2(g, 298\ K) \rightarrow CO_2(g, 979\ K) \tag{6}$$

$$CaO(s, 298\ K) + CO_2(g, 298\ K) \rightarrow CaCO_3(s, 298\ K) \tag{7}$$

$$\text{net:}\ \ CaO(s, 298\ K) \rightarrow CaO(soln, 979\ K) \tag{8}$$

$$\Delta H_9 = \Delta H_5 - \Delta H_6 + \Delta H_7 \tag{9}$$

The value of ΔH_{cds} for the second batch of Ca_3N_2 is then −11 808.9 ± 67.4 J g^{-1}, which yields an overall average for the two batches of −11 792.3 ± 37.8 J g^{-1} or −1748.2 ± 5.6 kJ mol^{-1}. The enthalpy of formation of Ca_3N_2 can then be determined from the thermochemical cycle:

$$Ca_3N_2(s, 298\ K) + {}^3/_2O_2(g, 979\ K) \rightarrow 3CaO(soln, 979\ K) + N_2(g, 979\ K) \tag{10}$$

$$CaO(s, 298\ K) \rightarrow CaO(soln, 979\ K) \tag{11}$$

$$N_2(g, 298\ K) \rightarrow N_2(g, 979\ K) \tag{12}$$

$$O_2(g, 298\ K) \rightarrow O_2(g, 979\ K) \tag{13}$$

$$Ca(s, 298\ K) + {}^1/_2O_2(g, 298\ K) \rightarrow CaO(s, 298\ K) \tag{14}$$

$$\text{net:}\ \ 3Ca(s, 298\ K) + N_2(g, 298\ K) \rightarrow Ca_3N_2(s, 298\ K) \tag{15}$$

$$\Delta H_f°(Ca_3N_2) = \Delta H_{15} = -\Delta H_{10} + 3\Delta H_{11} + \Delta H_{12} - {}^3/_2\Delta H_{13} + 3\Delta H_{14} \tag{16}$$

Using the data in Table 2, the value thus obtained was $\Delta H_f°(Ca_3N_2)$ = −439.7 ± 6.6 kJ mol^{-1}. This is slightly more exothermic than that obtained via combustion calorimetry by Franck and Bodea[18] of −429.3 ± 4.2 kJ mol^{-1} but agrees within the experimental errors. Our determination is in very good agreement with that recommended by Kubaschewski and Alcock, −439.3 kJ mol^{-1}.[19] This latter value is probably an average of Franck and Bodea's[18] calorimetric data and the value calculated from equilibrium data in the literature by Satoh,[20] −452.7 kJ mol^{-1}.[21]

Zn_3N_2. We have previously reported calorimetric results for Zn_3N_2 which were calibrated with α-Al_2O_3 drop experiments.[13] As we now realize this calibration to be inaccurate for highly exothermic reactions, we performed drop solution calorimetry on a new batch of Zn_3N_2. The measured $\Delta H_{ds}(Zn_3N_2)$ was −4293.7 ± 12.7 J g^{-1}. Based on XRD and nitrogen analyses, this sample contained 0.54 ± 0.25 wt % ZnO. The ΔH_{ds} value was then corrected for this impurity as with Ca_3N_2 above yielding $\Delta H_{cds}(Zn_3N_2)$ = −4318.2 ± 17.2 J g^{-1} or −968.1 ± 3.8 kJ mol^{-1}. Through a cycle analogous to that shown for Ca_3N_2 above, we obtain $\Delta H_f°(Zn_3N_2)$ = −43.5 ± 4.1 kJ mol^{-1}. This value does not agree with the −22.2 ± 4.2 kJ mol^{-1} that Juza et al.[22] determined via aqueous solution calorimetry. The reason for the discrepancy is unclear.

Sr_2ZnN_2. In continuation of our study on alkaline earth zinc nitrides, drop solution calorimetry was performed on Sr_2ZnN_2, which is isostructural with Ca_2ZnN_2.[14] We measured $\Delta H_{ds} = -5190.3 \pm 25.3$ J g^{-1} for this compound. The material contained a SrO impurity estimated at 2.2 ± 1.1 wt % via powder XRD. The corrected enthalpy of drop solution calorimetry, ΔH_{cds}, was then obtained from the equation

$$\Delta H_{ds}(Sr_2ZnN_2) = 0.978\Delta H_{cds}(Sr_2ZnN_2) + 0.022\Delta H_{ds}(SrO) \quad (17)$$

which yields $\Delta H_{cds}(Sr_2ZnN_2) = -5277.3 \pm 49.7$ J g^{-1} or -1417.7 ± 13.4 kJ mol^{-1}. Due to the affinity of SrO for atmospheric H_2O and CO_2, we performed drop solution calorimetry on $SrCO_3$ and determined ΔH_{ds} for SrO as with CaO above (eqs 5−9). The data used in calculating ΔH_{ds} values for oxides from the respective carbonates appear in Table 2, along with the resulting value for ΔH_{ds} on the oxide. The enthalpy of formation of Sr_2ZnN_2 was then determined from $\Delta H_{cds}(Sr_2ZnN_2)$ and the following thermodynamic cycle:

$$Sr_2ZnN_2(s, 298\ K) + {}^3/_2O_2(g, 979\ K) \rightarrow 2SrO(soln, 979\ K) + ZnO(soln, 979\ K) + N_2(g, 979\ K) \quad (18)$$

$$SrO(s, 298\ K) \rightarrow SrO(soln, 979\ K) \quad (19)$$

$$ZnO(s, 298\ K) \rightarrow ZnO(soln, 979\ K) \quad (20)$$

$$N_2(g, 298\ K) \rightarrow N_2(g, 979\ K) \quad (21)$$

$$O_2(g, 298\ K) \rightarrow O_2(g, 979\ K) \quad (22)$$

$$Sr(s, 298\ K) + {}^1/_2O_2(g, 298\ K) \rightarrow SrO(s, 298\ K) \quad (23)$$

$$Zn(s, 298\ K) + {}^1/_2O_2(g, 298\ K) \rightarrow ZnO(s, 298\ K) \quad (24)$$

$$\text{net:}\ 2Sr(s, 298\ K) + Zn(s, 298\ K) + N_2(g, 298\ K) \rightarrow Sr_2ZnN_2(s, 298\ K) \quad (25)$$

$$\Delta H_f°(Sr_2ZnN_2) = \Delta H_{25} = -\Delta H_{18} + 2\Delta H_{19} + \Delta H_{20} + \Delta H_{21} - {}^3/_2\Delta H_{22} + 2\Delta H_{23} + \Delta H_{24} \quad (26)$$

which yields $\Delta H_f°(Sr_2ZnN_2) = -385.6 \pm 14.3$ kJ mol^{-1}.

Unlike calcium, strontium and barium do not form A_3N_2 phases (A = alkali earth metal). Reaction of these metals with nitrogen yields a mixture of AN and A_2N materials.[23] However, a value for the enthalpy of formation of "Sr_3N_2" of −391.2 kJ mol^{-1} can be found in the literature.[24] If we assume that this value was actually obtained from a one to one molar mixture of Sr_2N and SrN, the enthalpy of formation of Sr_2ZnN_2 from binary nitrides, $\Delta H_f(N)$

$$ {}^1/_3Zn_3N_2(s, 298\ K) + {}^2/_3[Sr_2N(s, 298\ K) + SrN(s, 298\ K)] \rightarrow Sr_2ZnN_2(s, 298\ K) \quad (27)$$

can be calculated as -110.3 ± 17.6 kJ mol^{-1}.

For comparison of the $\Delta H_f(N)$ value for Sr_2ZnN_2 with similar values for ternary oxides in the SrO−ZnO system, drop solution calorimetry was performed on $SrZnO_2$, yielding $\Delta H_{ds}(SrZnO_2) = -114.92 \pm 1.66$ kJ mol^{-1}. The enthalpy of formation of $SrZnO_2$ from the binary oxides, $\Delta H_f(O)$ ($SrZnO_2$), was then determined from the thermochemical cycle:

$$SrZnO_2(s, 298\ K) \rightarrow SrO(soln, 979\ K) + ZnO(soln, 979\ K) \quad (28)$$

$$SrO(s, 298\ K) \rightarrow SrO(soln, 979\ K) \quad (29)$$

$$ZnO(s, 298\ K) \rightarrow ZnO(soln, 979\ K) \quad (30)$$

$$\text{net:}\ SrO(s, 298\ K) + ZnO(s, 298\ K) \rightarrow SrZnO_2(s, 298\ K) \quad (31)$$

$$\Delta H_{31} = -\Delta H_{28} + \Delta H_{29} + \Delta H_{30} \quad (32)$$

The value thus obtained was $\Delta H_f(O)$ ($SrZnO_2$) = -5.70 ± 4.12 kJ mol^{-1}. Upon adding this number to the standard enthalpies of formation of ZnO and SrO (see Table 2), we obtain $\Delta H_f°(SrZnO_2) = -948.16 \pm 5.27$ kJ mol^{-1}.

Li_3N. Lithium forms a well-defined binary nitride with a unique structure.[25] A careful determination of $\Delta H_f°$ of Li_3N was made by O'Hare and Johnson,[26] who found $\Delta H_f°(Li_3N) = -164.9 \pm 1.1$ kJ mol^{-1} by aqueous solution calorimetry. To determine $\Delta H_f°$ for Li_3N from high-temperature oxide melt drop solution calorimetry, we measured $\Delta H_{ds}(Li_3N) = -25\,046.5 \pm 78.1$ J g^{-1}. This sample of Li_3N contained 40.16% N, which corresponds to a 0.09 wt % LiOH impurity. The value of $\Delta H_{cds}(Li_3N)$ is then

$$\Delta H_{ds}(Li_3N) = 0.9991\Delta H_{cds}(Li_3N) + 0.0009\Delta H_{ds}(LiOH) \quad (33)$$

which yields $\Delta H_{cds}(Li_3N) = -25\,070.1 \pm 85.1$ J g^{-1} or -873.2 ± 2.9 kJ mol^{-1}. The ΔH_{ds} values for Li_2O and LiOH were obtained from drop solution calorimetry on Li_2CO_3 and a thermodynamic cycle analogous to that shown for CaO above. The $\Delta H_f°(Li_3N)$ was then calculated from these values (see Table 2) through the following thermodynamic cycle:

$$Li_3N(s, 298\ K) + {}^3/_4O_2(g, 979\ K) \rightarrow {}^3/_2Li_2O(soln, 979\ K) + {}^1/_2N_2(g, 979\ K) \quad (34)$$

$$Li_2O(s, 298\ K) \rightarrow Li_2O(soln, 979\ K) \quad (35)$$

$$N_2(g, 298\ K) \rightarrow N_2(g, 979\ K) \quad (36)$$

$$O_2(g, 298\ K) \rightarrow O_2(g, 979\ K) \quad (37)$$

$$2Li(s, 298\ K) + {}^1/_2O_2(g, 298\ K) \rightarrow Li_2O(s, 298\ K) \quad (38)$$

$$\text{net:}\ 3Li(s, 298\ K) + {}^1/_2N_2(g, 298\ K) \rightarrow Li_3N(s, 298\ K) \quad (39)$$

$$\Delta H_f°(Li_3N) = \Delta H_{39} = -\Delta H_{34} + {}^3/_2\Delta H_{35} + {}^1/_2\Delta H_{36} - {}^3/_4\Delta H_{37} + {}^3/_2\Delta H_{38} \quad (40)$$

Using the data in Table 2 and eq 40, the enthalpy of formation of Li_3N is $\Delta H_f°(Li_3N) = -166.1 \pm 4.8$ kJ mol^{-1}, which is in very good agreement with the work of O'Hare and Johnson.[26]

LiZnN. Drop solution calorimetry was performed on LiZnN and we obtained $\Delta H_{ds} = -546.1 \pm 6.4$ kJ mol^{-1}. The material was judged single phase by XRD, and no correction of the data was necessary. The enthalpy of formation of LiZnN was then determined from the following thermodynamic cycle:

$$\mathrm{LiZnN(s, 298\ K)} + {}^{3}/_{4}\mathrm{O_2(g, 979\ K)} \rightarrow {}^{1}/_{2}\mathrm{Li_2O(soln, 979\ K)} + \mathrm{ZnO(soln, 979\ K)} + {}^{1}/_{2}\mathrm{N_2(g, 979\ K)} \tag{41}$$

$$\mathrm{Li_2O(s, 298\ K)} \rightarrow \mathrm{Li_2O(soln, 979\ K)} \tag{42}$$

$$\mathrm{ZnO(s, 298\ K)} \rightarrow \mathrm{ZnO(soln, 979\ K)} \tag{43}$$

$$\mathrm{N_2(g, 298\ K)} \rightarrow \mathrm{N_2(g, 979\ K)} \tag{44}$$

$$\mathrm{O_2(g, 298\ K)} \rightarrow \mathrm{O_2(g, 979\ K)} \tag{45}$$

$$\mathrm{2Li(s, 298\ K)} + {}^{1}/_{2}\mathrm{O_2(g, 298\ K)} \rightarrow \mathrm{Li_2O(s, 298\ K)} \tag{46}$$

$$\mathrm{Zn(s, 298\ K)} + {}^{1}/_{2}\mathrm{O_2(g, 298\ K)} \rightarrow \mathrm{ZnO(s, 298\ K)} \tag{47}$$

$$\text{net: } \mathrm{Li(s, 298\ K)} + \mathrm{Zn(s, 298\ K)} + \mathrm{N_2(g, 298\ K)} \rightarrow \mathrm{LiZnN(s, 298\ K)} \tag{48}$$

$$\Delta H_f°(\mathrm{LiZnN}) = \Delta H_{48} = -\Delta H_{41} + {}^{1}/_{2}\Delta H_{42} + \Delta H_{43} + {}^{1}/_{2}\Delta H_{44} - {}^{3}/_{4}\Delta H_{45} + {}^{1}/_{2}\Delta H_{46} + \Delta H_{47} \tag{49}$$

Using the data in Table 2, we obtain $\Delta H_f°(LiZnN) = -137.5 \pm 6.8$ kJ mol^{-1}.

The enthalpies of formation of Li_3N and Zn_3N_2 have been determined in this work as −166.1 ± 4.8 and −43.5 ± 4.1 kJ mol^{-1}, respectively, which allows us to calculate the enthalpy of formation of LiZnN from the binary nitrides:

$$ {}^{1}/_{3}\mathrm{Li_3N(s, 298\ K)} + {}^{1}/_{3}\mathrm{Zn_3N_2(s, 298\ K)} \rightarrow \mathrm{LiZnN(s, 298\ K)} \tag{50}$$

We thus obtain $\Delta H_f(N)$ (LiZnN) = −67.6 ± 7.1 kJ mol^{-1}, which is quite substantial compared to the −137.5 ± 6.8 kJ mol^{-1} we determined as the enthalpy of formation of this compound from the elements. As drop solution calorimetry was performed on Li_3N, Zn_3N_2, and LiZnN, the shortest thermochemical cycle which can be used to determine the value of $\Delta H_f(N)$ for LiZnN is a direct combination of the ΔH_{ds} values:

$$\mathrm{Li_3N(s, 298\ K)} + {}^{3}/_{4}\mathrm{O_2(g, 979\ K)} \rightarrow {}^{3}/_{2}\mathrm{Li_2O(soln, 979\ K)} + {}^{1}/_{2}\mathrm{N_2(g, 979\ K)} \tag{51}$$

$$\mathrm{Zn_3N_2(s, 298\ K)} + {}^{3}/_{2}\mathrm{O_2(g, 979\ K)} \rightarrow \mathrm{3ZnO(soln, 979\ K)} + \mathrm{N_2(g, 979\ K)} \tag{52}$$

$$\mathrm{LiZnN(s, 298\ K)} + {}^{3}/_{2}\mathrm{O_2(g, 979\ K)} \rightarrow {}^{1}/_{2}\mathrm{Li_2O(soln, 979\ K)} + \mathrm{ZnO(soln, 979\ K)} + {}^{1}/_{2}\mathrm{N_2(g, 979\ K)} \tag{53}$$

$$\text{net: } {}^{1}/_{3}\mathrm{Li_3N(s, 298\ K)} + {}^{1}/_{3}\mathrm{Zn_3N_2(s, 298\ K)} \rightarrow \mathrm{LiZnN(s, 298\ K)} \tag{54}$$

$$\Delta H_f(\mathrm{N})(\mathrm{LiZnN}) = \Delta H_{54} = {}^{1}/_{3}\Delta H_{51} + {}^{1}/_{3}\Delta H_{52} - \Delta H_{53} \tag{55}$$

This cycle eliminates any uncertainty in the values of ΔH_{ds} and $\Delta H_f°$ for the carbonates and oxides included in eqs 34−50 and yields −67.7 ± 6.6 kJ mol^{-1} for ΔH_f(N)(LiZnN).

LiCaN. LiCaN readily dissolved in sodium molybdate at 979 K, and we obtained $\Delta H_{ds} = -13\,744.9 \pm 41.0$ J g^{-1}. The sample contained a 2.1 ± 1.1% CaO impurity as estimated from powder XRD data. The corrected enthalpy of drop solution for LiCaN is then

$$\Delta H_{ds}(\mathrm{LiCaN}) = 0.979\Delta H_{cds}(\mathrm{LiCaN}) + 0.021\Delta H_{ds}(\mathrm{CaO}) \tag{56}$$

which yields $\Delta H_{cds}(LiCaN) = -14\,074.3 \pm 169.7$ J g^{-1} or −858.9 ± 10.3 kJ mol^{-1}. From a thermodynamic cycle analogous to that shown for LiZnN above, we obtained $\Delta H_f°(LiCaN) = -216.8 \pm 10.8$ kJ mol^{-1}.

The enthalpies of formation of Li_3N and Ca_3N_2 have been determined in this work as −166.1 ± 4.8 and −439.7 ± 6.6 kJ mol^{-1}, respectively, which allows us to calculate the enthalpy of formation of LiCaN from the binary nitrides:

$$ {}^{1}/_{3}\mathrm{Li_3N(s, 298\ K)} + {}^{1}/_{3}\mathrm{Ca_3N_2(s, 298\ K)} \rightarrow \mathrm{LiCaN(s, 298\ K)} \tag{57}$$

as $\Delta H_f(N)(LiCaN) = -14.9 \pm 11.1$ kJ mol^{-1}. Again, a shorter thermochemical cycle for determining this value is possible through direct combination of the ΔH_{ds} values as in eqs 51−55, which yields −14.9 ± 10.5 kJ mol^{-1}.

Ta_3N_5. The fully nitrided Ta_3N_5 has the pseudobrookite structure.[27] No previous determination of the enthalpy of formation of Ta_3N_5 has been made. The enthalpy of formation of TaN, however, has been determined as −251.4 kJ mol^{-1}.[24,28] As the Ta in Ta_3N_5 is fully oxidized, it can be expected that $\Delta H_f°(Ta_3N_5)$

will be more exothermic than $3\Delta H_f°(\text{TaN})$. Ta_3N_5 dissolved slowly but completely in the sodium molybdate solvent and we measured $\Delta H_f°(Ta_3N_5) = -2071.9 \pm 8.5$ kJ mol^{-1}. The sample was judged single phase by powder XRD, and no impurity correction was applied. Ta_2O_5 would not dissolve in the solvent in a time period suitable for calorimetry (<2 h). Metallic Ta, however, would oxidize and dissolve, and drop solution calorimetry was performed on thin Ta wire (Fansteel, 99.9%, 0.2 mm diameter). TGA of this Ta wire yielded a +22.00% weight gain upon oxidation to Ta_2O_5, with the theoretical weight gain of this reaction being +22.10%. This indicated that the material contained a 0.45% oxide impurity, which is consistent with a ~450 nm oxide film on the surface of the wire. The measured $\Delta H_{ds}(\text{Ta})$, -5455.0 ± 25.4 J g^{-1}, was then corrected for this oxide impurity as in eqs 32 and 62, which yielded $\Delta H_{cds}(\text{Ta}) = -5480.1 \pm 27.8 \pm$ J g^{-1} or -991.6 ± 5.0 kJ mol^{-1}. The enthalpy of formation of Ta_3N_5 can then be obtained from the relatively simple thermochemical cycle

$$Ta_3N_5(\text{s, 298 K}) + {}^{15}/_4O_2(\text{g, 979 K}) \rightarrow {}^{3}/_2Ta_2O_5(\text{soln, 979 K}) + {}^{5}/_2N_2(\text{g, 979 K}) \quad (58)$$

$$\text{Ta(s, 298 K)} + {}^{5}/_4O_2(\text{g, 979 K}) \rightarrow {}^{1}/_2Ta_2O_5(\text{soln, 979 K}) \quad (59)$$

$$N_2(\text{g, 298 K}) \rightarrow N_2(\text{g, 979 K}) \quad (60)$$

$$\text{net: } 3\text{Ta(s, 298 K)} + {}^{5}/_2N_2(\text{g, 298 K}) \rightarrow Ta_3N_5(\text{s, 298 K}) \quad (61)$$

$$\Delta H_f°(Ta_3N_5) = \Delta H_{61} = -\Delta H_{58} + 3\Delta H_{59} + {}^{5}/_2\Delta H_{60} \quad (62)$$

which yields $\Delta H_f°(Ta_3N_5) = -849.7 \pm 11.7$ kJ mol^{-1}. As expected, this value is more exothermic than $3\Delta H_f°(\text{TaN})$.

$CaTaN_2$. The $CaTaN_2$ studied in this work had a significant impurity of TaN estimated as $5.2 \pm 2.6\%$ from powder XRD data. We measured $\Delta H_{ds}(CaTaN_2) = -4239.5 \pm 28.5$ J g^{-1} for this material. The ΔH_{cds} value for $CaTaN_2$ is then

$$\Delta H_{ds}(CaTaN_2) = 0.948\Delta H_{cds}(CaTaN_2) + 0.052\Delta H_{ds}(\text{TaN}) \quad (63)$$

A value of -3717.2 J g^{-1} (-724.7 kJ mol^{-1}) for $\Delta H_{ds}(\text{TaN})$ was estimated by subtracting the enthalpy of formation of TaN and adding the heat content of ${}^1/_2N_2$ gas between 298 and 979 K to $\Delta H_{ds}(\text{Ta})$. Equation 62 then yields $\Delta H_{cds}(CaTaN_2) = -4268.1 \pm 32.1$ J g^{-1} or -1062.9 ± 8.0 kJ mol^{-1}. The enthalpy of formation of $CaTaN_2$ was then determined from the thermochemical cycle:

$$CaTaN_2(\text{s, 298 K}) + {}^{7}/_4O_2(\text{g, 979 K}) \rightarrow \text{CaO(soln, 979 K)} + {}^{1}/_2Ta_2O_5(\text{soln, 979 K}) + N_2(\text{g, 979 K}) \quad (64)$$

$$\text{CaO(s, 298 K)} \rightarrow \text{CaO(soln, 979 K)} \quad (65)$$

$$\text{Ta(s, 298 K)} + {}^{5}/_4O_2(\text{g, 979 K}) \rightarrow {}^{1}/_2Ta_2O_5(\text{soln, 979 K}) \quad (66)$$

$$N_2(\text{g, 298 K}) \rightarrow N_2(\text{g, 979 K}) \quad (67)$$

$$O_2(\text{g, 298 K}) \rightarrow O_2(\text{g, 979 K}) \quad (68)$$

$$\text{Ca(s, 298 K)} + {}^{1}/_2O_2(\text{g, 298 K}) \rightarrow \text{CaO(s, 298 K)} \quad (69)$$

$$\text{net: Ca(s, 298 K)} + \text{Ta(s, 298 K)} + {}^{1}/_2N_2(\text{g, 298 K}) \rightarrow CaTaN_2(\text{s, 298 K}) \quad (70)$$

$$\Delta H_f°(CaTaN_2) = \Delta H_{70} = -\Delta H_{64} + \Delta H_{65} + \Delta H_{66} + \Delta H_{67} - {}^{1}/_2\Delta H_{68} + \Delta H_{69} \quad (71)$$

which yields $\Delta H_f°(CaTaN_2) = -643.8 \pm 9.6$ kJ mol^{-1}. The enthalpy of formation of $CaTaN_2$ from the binary nitrides

$$ {}^{1}/_3Ca_3N_2(\text{s, 298 K}) + {}^{1}/_3Ta_3N_5(\text{s, 298 K}) \rightarrow CaTaN_2(\text{s, 298 K}) + {}^{1}/_6N_2(\text{g, 298 K}) \quad (72)$$

can then be calculated as -214.0 ± 10.8 kJ mol^{-1}. As calculated, this value of $\Delta H_f(\text{N})$ ($CaTaN_2$) includes reduction of Ta^{5+} to Ta^{4+}. Using the literature value of $\Delta H_f°(\text{TaN}) = -251.4$ kJ mol^{-1},[24,28] $\Delta H_f(\text{N})$ ($CaTaN_2$) can be calculated from a different reaction incorporating oxidation of Ta

$$ {}^{1}/_3Ca_3N_2(\text{s, 298 K}) + \text{TaN(s, 298 K)} + {}^{1}/_6N_2(\text{g, 298 K}) \rightarrow CaTaN_2(\text{s, 298 K}) \quad (73)$$

which yields $\Delta H_f(\text{N})$ ($CaTaN_2$) $= -245.8 \pm 14.2$ kJ mol^{-1}.[29] The difference in these two values provides a means of estimating the contribution of Ta oxidation (or reduction) to the energetics.

Discussion

The standard enthalpies of formation obtained for the nitrides are indeed 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 both in magnitude and as a fraction of the enthalpy of formation from the elements. This was noted by Elder et al.,[7] who determined $\Delta H_f(\text{N})$ of $LiMoN_2$ to be

~58% of the value of $\Delta H_f°$. The significance of this value was somewhat clouded by the fact that the reaction it accompanies entails oxidation of "$Mo^{1.5+}$" to Mo^{5+}. We have demonstrated that the enthalpy of formation of LiZnN from binary nitrides in the same oxidation state is likewise 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 $\Delta H_f(N)$. No lithium calcium oxides are known with which to compare this value. There are no known 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}. This small magnitude can be explained in terms of the Lux−Flood[30] acidities of the binary oxides. It is known that large enthalpies of formation of ternary oxides occur when a binary oxide of acidic character combines with one of basic character.[31] The lack of ternary oxides in the CaO−ZnO and Li_2O−CaO systems and the small (near zero) value of $\Delta H_f(O)$ for $SrZnO_2$ are testaments to the similar basicities of these oxides: there is little or no energetic advantage in forming a ternary.

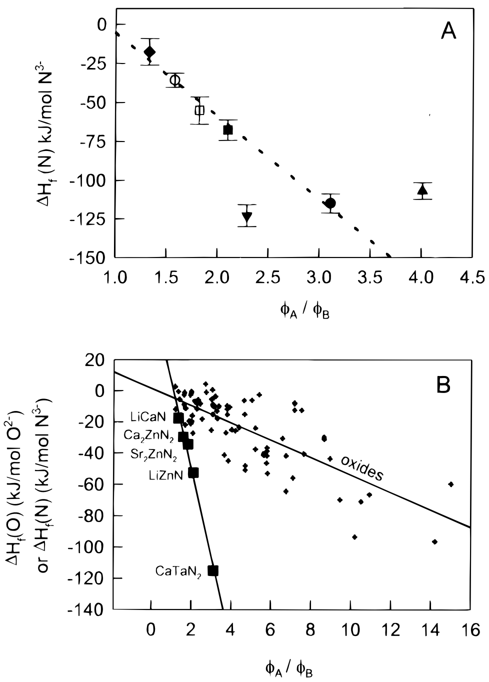

Figure 1. (A) Enthalpies of formation of ternary nitrides from binary nitrides as a function of the ratio of ϕ of the acidic cation over ϕ of the basic cation. Enthalpies are given per mole of N^{3-}. Symbols: ◆, LiCaN; ○, Ca_2ZnN_2; □, Sr_2ZnN_2; ■, LiZnN; ▼, $CaTaN_2$ from TaN, Ca_3N_2, and N_2; ▲, $CaTaN_2$ from Ta_3N_5 and Ca_3N_2; ●, CaTaN from Ca_3N_2, TaN, and Ta_3N_5. (B) The $\Delta H_f(N)$ data from part A (■) with data for ternary oxides of similar stoichiometry on a kJ/mol O^{2-} basis (+).

Table 4. Ionic Radii and Ionic Potentials (ϕ) for Cations in Binary Nitrides. Radii Calculated by Subtracting Radius of N^{3-} (1.46 Å)[34] from Average M−N Bond Distance

cation	M−N distance in binary nitride (Å)	ionic radius in binary nitride (Å)	ϕ (arb units)
Li^+	2.13[a]	0.67	1.49
Sr^{2+}	na[b]	1.16	1.72
Ca^{2+}	2.47[c]	1.01	1.98
Zn^{2+}	2.1[d]	0.64	3.13
Ta^{3+}	2.12[e]	0.66	4.54
Ta^{5+}	2.09[f]	0.63	7.95

[a] Rabenau, A.; Schultz, H. *J. Less-Common Met.* **1976**, *50*, 155. [b] Sr_3N_2 does not exist. Shannon-Prewitt[28] value for Sr^{2+} in octahedral coordination is given. [c] Laurent, Y.; Lang, J.; LeBihan, M. T. *Acta Crystallogr.* **1968**, *B24*, 494. [d] Juza, R.; Neuber, A.; Hahn, H. *Z. Anorg. Allg. Chem.* **1938**, *239*, 273. [e] Christensen, A. N.; Lebech, B. *Acta Crystallogr.* **1978**, *B34*, 261. [f] Brese, N. E.; O'Keeffe, M.; Rauch, P.; DiSalvo, F. J. *Acta Crystallogr.* **1991**, *C47*, 2291.

Numerous attempts have been made to quantify the acidity or basicity of a cation.[32] 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.[33] The dominance of acid−base reactions in the energetics of ternary nitride formation becomes evident upon consideration of Figure 1, wherein 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). The radii of the metal ions used in calculating ϕ was taken from the average M−N bond distances in Li_3N, Ca_3N_2, Zn_3N_2, Ta_3N_5, and TaN, with the radius of N^{3-} as 1.46 Å.[34,35] These radii and the resulting values of ϕ are given in Table 4. The radius for Sr^{2+} is the Shannon−Prewitt[34] value for octahedral coordination.[36] For the phases in the Li−A−Zn−N system, the points obtained fall on a straight line.[37] This line crosses zero at a ratio near unity, which logically indicates that binaries of very similar basicity would have a $\Delta H_f(N)$ value near zero. Placing thermochemical data for ternary oxides on the plot in Figure 1B 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, molybdates, silicates, and carbonates)[38,39] was an order of magnitude smaller 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 $\Delta H_f(N)$. A similar increase in the enthalpies of mixing (ΔH_{mix}) of molten alkali halides occurs as the anion is changed, with ΔH_{mix} increasing as fluorides < chlorides < bromides < iodides (i.e., upon increasing the polarizability of the anion).[40]

The $\Delta H_f(N)$ of $CaTaN_2$ was calculated from two reactions, one involving oxidation of Ta^{3+} and one involving reduction of Ta^{5+}. These data appear as the triangular points which do not fall on the line in Figure 1. The value obtained through the reaction involving oxidation of Ta (eq 73) falls below the line, indicating an additional exothermic contribution in the formation of the ternary. Analogously, the value obtained through

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(40) (a) Kleppa, O. J.; Meschel, S. V. *J. Phys. Chem.* **1968**, *67*, 668. (b) Holm, J. L.; Kleppa, O. J. *J. Chem. Phys.* **1968**, *49*, 2425. (c) Melnichak, M. E.; Kleppa, O. J. *J. Chem. Phys.* **1970**, *52*, 1790.

the reaction involving reduction of Ta (eq 72) falls above the line, indicating an additional endothermic contribution to the reaction. The average of the values obtained as $\Delta H_f(N)$ ($CaTaN_2$) from eqs 72 and 73, -229.9 ± 12.5 kJ mol^{-1}, can be viewed as that accompanying the reaction

$$^{1}/_{3}Ca_3N_2(s, 298\ K) + {}^{1}/_{6}Ta_3N_5(s, 298\ K) + {}^{1}/_{2}TaN(s, 298\ K) \rightarrow CaTaN_2(s, 298\ K) \quad (74)$$

The average oxidation state of Ta in the above reaction is +4, as in $CaTaN_2$. The radii of Ta^{3+} in TaN and Ta^{5+} in Ta_3N_5 are very similar, 0.66 and 0.63 Å, respectively (see Table 4). It is then reasonable to assume that a hypothetical Ta_3N_4 phase would have a Ta^{4+} radius of ~0.65 Å. This treatment of the data places the value of $\Delta H_f(N)$ $CaTaN_2$ obtained from eq 74 in very good agreement with the trend observed in the Li−A−Zn−N nitrides (see Figure 1). Therefore, it appears that the energetics of formation of $CaTaN_2$ is likewise dominated by acid−base contributions, but reduction (or oxidation) of Ta shifts $\Delta H_f(N)$ to a less exothermic (or more exothermic) value.

The energetics of the Li−A−Zn−N system and $CaTaN_2$ are well represented by a simple ionic model which considers only the differences in basicity of the cations. This may be somewhat surprising as the bonding in nitrides is expected to be more covalent than that in oxides. For example, using simple approximations made by Pauling,[41] the Li−O bond is ~80% ionic whereas the Li−N bond is ~60% ionic, and the Ta−O bond is ~60% ionic whereas the Ta−N bond is only ~40% ionic. Furthermore, the covalency of a particular bond can increase due to inductive effects when an electropositive species is included in the compound.[42] Indeed, the success of an ionic model in predicting the energetics of a system is not a sufficient criterion for the dominance of ionic bonding. For example, BF_3, SiF_4, and SF_6 clearly consist of discrete molecules, yet accurate enthalpies of formation can be calculated through the Born−Haber cycle if one assumes these materials consist of B^{3+}, Si^{4+}, S^{6+}, and F^- ions.[43] Although our ionic interpretation of nitride energetics may enable prediction of which metal systems will form energetically stable ternary nitrides, it does not necessarily imply substantial ionic character in all of the bonds.

Acknowledgment. We thank Dr. R. C. Haushalter for allowing occasional use of his glovebox. This work was supported by the U.S. Department of Energy, Grant DE-FG02-89ER-45394, and the National Science Foundation, Grant NSF DMR-95-08522.

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[41] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; pp 97−102.

[42] Etourneau, J.; Portier, J.; Menil, F. *J. Alloys Compd.* **1992**, *188*, 1.

[43] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Permagon: New York, 1984.