Thermochemistry of Metal Nitrides in the Ca/Zn/N System

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Abstract: The energetics of ternary oxide formation is reasonably well understood, but little is known of the energetics of ternary nitride formation. We have developed new procedures for high-temperature oxide melt solution calorimetry on metal nitrides and employed them to study compounds in the Ca/Zn/N system. The calorimetry utilized the easy reduction of MoO_3 in the solvent to supply a pathway for rapid oxidation of "N^{3-}" to N_2 gas. These experiments represent the first high-temperature solution calorimetry of ternary metal nitrides. The results indicate that Ca_3N_2 acts as a basic nitride analogous to CaO in oxide systems, while Zn_3N_2 acts as an acidic nitride ("N^{3-}" acceptor) in this ternary nitride system.

Keywords
calcium compounds · calorimetry · nitrides · ternary metal nitrides · zinc compounds

Introduction

Many new and structurally diverse ternary metal nitrides have been discovered in recent years,[1] but little is known of the thermodynamics that controls their formation. High-temperature solution calorimetry has been very useful in elucidating the energetics of ternary (and higher) oxide formation,[2] and the technique has been extended to many classes of oxide materials, including metastable phases,[3] hydrated phases,[4] variable oxidation state materials,[5] and microporous materials.[6] The major obstacle preventing the utilization of high-temperature solution calorimetry for study of nitride materials has been the lack of a suitable solvent. The nitride ion, "N^{3-}", is a very unstable species compared with dinitrogen, N_2, which makes N^{3-} a strong reducing agent. The solvent of choice for oxide calorimetry, $2PbO \cdot B_2O_3$, is unsuitable, as PbO in the melt is easily reduced to Pb^0 at around 973 K. Solution calorimetry relies on the formation of a well-defined final state after dissolution, to which heat effects can be linked and for which enthalpies of formation calculated by appropriate thermodynamic cycles. As enthalpy is a state function, the production of Pb^0 is not a problem in itself, as long as it is reoxidized to PbO during the calorimetric experiment. However, this lead metal attacks Pt, and as some of the lead will remain in (or on) the Pt crucibles that contain the solvent, the reaction does not provide a reproducible final state.

Some success has been achieved in nitride calorimetry by Elder et al.,[7] who used oxidative reaction calorimetry to determine enthalpies of formation of $LiMoN_2$, Na_3WN_3, and Na_3WO_3N. In this method, nitride pellets were dropped into a calorimeter at ≈973 K 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, our initial experiments have shown that all of the nitrides in the Ca/Zn/N system do not completely react with O_2 after 2 h at 973 K. This was quite surprising as most of these compounds will decompose in a matter of minutes upon exposure to 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 more than ten ternary and binary metal nitrides, it appears that the complete and rapid reaction with O_2 at 973 K utilized by Elder et al.[7] 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 973 K that dissolve only slowly in $2PbO \cdot B_2O_3$.[8, 9] We have found that this solvent is perfectly suited for nitride calorimetry, mainly as a result of 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 ≈973 K). 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 979 K provides a rapid pathway for elimination of N^{3-} as N_2 gas. Herein we describe the first high-temperature solution calorimetry of metal nitrides.

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Results and Discussion

We have chosen the Ca/Zn/N system[10, 11] as the starting point for our thermochemical studies of ternary metal nitrides. At first, furnace experiments at 979 K were performed on the nitride samples to see if they would dissolve in the solvent in a time period suitable for calorimetry (≈ 1 h). Upon addition of a nitride, the solvent, which is 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 979 K 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 erroneous results, a 2 g sample of the solvent was quenched from 973 K 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 and electron-beam 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. However, wavelength dispersive spectrometry revealed that these bright crystallites contained significant amounts of oxygen and could not be metallic molybdenum, but were probably MoO_2. As we were mainly concerned with ruling out the possible formation of metallic Mo, we did not attempt to determine quantitatively the Mo:Na:O ratios in the phases. The results from the electron-beam microprobe were in good agreement with XRD, which showed the presence of two sodium molybdate phases and 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 979 K 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 Equation (i) occurs, where M represents a metal in the 2+ oxidation state.

$$\begin{aligned}&M_3N_2\ (s,\ 295\ K) + 3\,MoO_3\ (l,\ 979\ K) \longrightarrow \\ &\qquad 3\,MO\ (s,\ 979\ K) + 3\,MoO_2\ (s,\ 979\ K) + N_2\ (g,\ 979\ K)\end{aligned} \tag{i}$$

As written, this reaction does not represent a stable final state that can be used in a thermochemical cycle. The $MO_{(s,\,979\ K)}$ must dissolve in the sodium molybdate and the MoO_2 must be oxidized to MoO_3 and returned to the solvent, as in reaction (ii),

$$\begin{aligned}&3\,MO\ (s,\ 979\ K) + 3\,MoO_2\ (s,\ 979\ K) + {}^3/_2\,O_2\ (g,\ 979\ K) \longrightarrow \\ &\qquad 3\,MO\ (soln,\ 979\ K) + 3\,MoO_3\ (soln,\ 979\ K)\end{aligned} \tag{ii}$$

which is relatively slow compared with reaction (i). The calorimeter glassware was therefore adapted to allow 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. This served to speed up reaction (ii) 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 Equations (i) and (ii) yields equation (iii), which corresponds to the enthalpy change measured by drop solution calorimetry, ΔH_{ds}.

$$\begin{aligned}&M_3N_2\ (s,\ 295\ K) + {}^3/_2\,O_2\ (g,\ 979\ K) \longrightarrow \\ &\qquad 3\,MO\ (soln,\ 979\ K) + N_2\ (g,\ 979\ K)\end{aligned} \tag{iii}$$

Elder et al.[7] observed that the first $LiMoN_2$ or Na_3WN_3 sample dropped into the calorimeter reacted only slowly with O_2 at ≈ 973 K, as evidenced by heat being evolved for >90 min. Subsequent samples reacted more rapidly. They attributed the enhancement to the presence of the liquid Li_2O:MoO_3 or Na_2O:WO_3 mixture in the calorimeter. It is now clear that the reaction was probably accelerated by the redox process discussed above. As the resulting liquid levels in the calorimetry crucibles were much lower than in the present study, the MoO_2 or WO_2 formed through the oxidation of "N^{3-}" could be oxidized by the flowing O_2 without a bubbling tube.

The results of drop solution calorimetry, which was performed in a twin microcalorimeter (Tian–Calvet type) operating at 979 K described in detail by Navrotsky,[2] appear in Table 1. The calorimetric signal generally returned to the stable baseline within 1 h of introducing a nitride sample, which is indicative of trouble-free calorimetry. No adverse effects due to the bubbling of O_2 through the solvent at a flow rate of ≈ 5 mL min^{-1} were observed, despite the significant mechanical disturbance this must cause. With the ΔH_{ds} values determined, enthalpies of formation for the nitrides were obtained from appropriate thermodynamic cycles. For Zn_3N_2, the thermodynamic cycle is shown in Equations (iv)–(x).

Table 1. Data used in thermodynamic cycles to determine nitride enthalpies of formation from drop solution calorimetry (all values are in kJ mol^{-1}).

	ΔH_{ds} [a]	$H_{979} - H_{298}$ [b]	ΔH_f° [c]
Zn_3N_2	-980.0 ± 3.2 (8)	-	-
Ca_3N_2	-1759.9 ± 6.7 (7)	-	-
Ca_2ZnN_2	-1464.8 ± 6.5 (6)	-	-
CaO [d]	-90.3 ± 1.8 (6)	-	-635.09 ± 0.88
ZnO	$+17.2 \pm 0.3$ (6)	-	-350.46 ± 0.27
O_2	-	+21.98	-
N_2	-	+21.31	-

[a] This work. Reported uncertainty is two standard deviations of the mean. Number in parentheses is the number of experiments performed. [b] Ref. [22]. [c] Ref. [23]. [d] From drop solution calorimetry on $CaCO_3$.

$$\begin{aligned}&Zn_3N_2\ (s,\ 295\ K) + {}^3/_2\,O_2\ (g,\ 979\ K) \longrightarrow \\ &\qquad 3\,ZnO\ (soln,\ 979\ K) + N_2\ (g,\ 979\ K)\end{aligned} \tag{iv}$$

$$ZnO\ (s,\ 295\ K) \longrightarrow ZnO\ (soln,\ 979\ K) \tag{v}$$

$$N_2\ (g,\ 295\ K) \longrightarrow N_2\ (g,\ 979\ K) \tag{vi}$$

$$O_2\ (g,\ 295\ K) \longrightarrow O_2\ (g,\ 979\ K) \tag{vii}$$

$$Zn\ (s,\ 295\ K) + {}^1/_2\,O_2\ (g,\ 295\ K) \longrightarrow ZnO\ (s,\ 295\ K) \tag{viii}$$

$$3\,Zn\ (s,\ 295\ K) + N_2\ (g,\ 295\ K) \longrightarrow Zn_3N_2\ (s,\ 295\ K) \tag{ix}$$

$$\Delta H_f^\circ(Zn_3N_2) = \Delta H_{ix} = -\Delta H_{iv} + 3\,\Delta H_v + \Delta H_{vi} - {}^3/_2\,\Delta H_{vii} + 3\,\Delta H_{viii} \tag{x}$$

The ΔH_{ds} values for Zn_3N_2 and ZnO in combination with literature values for the heat content of O_2 and N_2 and

ΔH_f° of ZnO (see Table 1) yield $\Delta H_f = -24.1 \pm 3.3\ \mathrm{kJ\,mol^{-1}}$ for Zn_3N_2. This value is in good agreement with the $-22.6\ \mathrm{kJ\,mol^{-1}}$ reported in ref. [12] and the $-22.2\ \mathrm{kJ\,mol^{-1}}$ reported in the early work of Hahn and Juza.[13]

The measured ΔH_{ds} for Ca_3N_2 was $-1759.9 \pm 6.7\ \mathrm{kJ\,mol^{-1}}$. With this information, the enthalpy of formation of Ca_3N_2 was calculated from a thermodynamic cycle analogous to that given for Zn_3N_2 above. To complete the cycle, it was necessary to determine ΔH_{ds} for CaO. Because of the hygroscopic nature of CaO, we performed drop solution calorimetry on $CaCO_3$ and determined ΔH_{ds} for CaO through an appropriate thermodynamic cycle, as in ref. [14]. The resulting value for ΔH_{ds} of CaO was $-90.30 \pm 1.82\ \mathrm{kJ\,mol^{-1}}$, which is $\approx 4.6\ \mathrm{kJ\,mol^{-1}}$ more exothermic than the result we obtained directly from drop solution calorimetry with CaO, the difference presumably being due to adsorbed H_2O on the latter. The value then obtained for ΔH_f of Ca_3N_2 was $-427.9 \pm 7.5\ \mathrm{kJ\,mol^{-1}}$. This is in good agreement with the $-430.9\ \mathrm{kJ\,mol^{-1}}$ reported in ref. [12] and the value obtained from combustion calorimetry by Frank et al.[15] of $-429.3\ \mathrm{kJ\,mol^{-1}}$.

For the ternary phase Ca_2ZnN_2, we measured $\Delta H_{ds} = -1464.8 \pm 6.5\ \mathrm{kJ\,mol^{-1}}$. The enthalpy of formation of Ca_2ZnN_2 was then obtained from the thermodynamic cycle of Equations (xi)–(xix). From the values in Table 1,

$$\begin{aligned}&Ca_2ZnN_2\ (s,\ 295\ K) + {}^3/_2 O_2\ (g,\ 979\ K) \longrightarrow \\ &\qquad 2\,CaO\ (soln,\ 979\ K) + ZnO\ (soln,\ 979\ K) + N_2\ (g,\ 979\ K)\end{aligned} \tag{xi}$$

$$CaO\ (s,\ 295\ K) \longrightarrow CaO\ (soln,\ 979\ K) \tag{xii}$$

$$ZnO\ (s,\ 295\ K) \longrightarrow ZnO\ (soln,\ 979\ K) \tag{xiii}$$

$$N_2\ (g,\ 295\ K) \longrightarrow N_2\ (g,\ 979\ K) \tag{xiv}$$

$$O_2\ (g,\ 295\ K) \longrightarrow O_2\ (g,\ 979\ K) \tag{xv}$$

$$Ca\ (s,\ 295\ K) + {}^1/_2 O_2\ (g,\ 295\ K) \longrightarrow CaO\ (s,\ 295\ K) \tag{xvi}$$

$$Zn\ (s,\ 295\ K) + {}^1/_2 O_2\ (g,\ 295\ K) \longrightarrow ZnO\ (s,\ 295\ K) \tag{xvii}$$

$$\begin{aligned}&2\,Ca\ (s,\ 295\ K) + Zn\ (s,\ 295\ K) + N_2\ (g,\ 295\ K) \longrightarrow \\ &\qquad\qquad Ca_2ZnN_2\ (s,\ 295\ K)\end{aligned} \tag{xviii}$$

$$\begin{aligned}\Delta H_f^\circ(Ca_2ZnN_2) = \Delta H_{xviii} = &-\Delta H_{xi} + 2\Delta H_{xii} + \Delta H_{xiii} \\ &+ \Delta H_{xiv} - {}^3/_2\Delta H_{xv} + 2\Delta H_{xvi} + \Delta H_{xvii}\end{aligned} \tag{xix}$$

$\Delta H_f^\circ = -328.5 \pm 6.5\ \mathrm{kJ\,mol^{-1}}$ for Ca_2ZnN_2. With this value for the enthalpy of formation of the ternary nitride, along with the enthalpies of formation for the binary nitrides determined above, the enthalpy of formation of Ca_2ZnN_2 from the binary nitrides, $\Delta H_f(N)$ [Eq. (xx)], was determined to be $-35.2 \pm 8.7\ \mathrm{kJ\,mol^{-1}}$. Although this would generally be considered a

$$\begin{aligned}&{}^2/_3 Ca_3N_2\ (s,\ 298\ K) + {}^1/_3 Zn_3N_2\ (s,\ 298\ K) \longrightarrow \\ &\qquad\qquad Ca_2ZnN_2\ (s,\ 298\ K)\end{aligned} \tag{xx}$$

rather small enthalpy of formation for a ternary phase, it is quite significant compared with the enthalpy of formation of Ca_2ZnN_2 from the elements. No ternary calcium zinc oxides are known with which to compare the enthalpy of formation from 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.[16, 17] The optical basicities[18] of CaO and ZnO are very similar (1.00 and 0.95, respectively). If any ternary oxide did form between CaO and ZnO, it would have a near-zero ($\approx 0 \pm 20\ \mathrm{kJ\,mol^{-1}}$) enthalpy of formation. The only data on ternary nitride formation with which this value can be compared is again the work of Elder et al.[7] They found the enthalpy of formation of $LiMoN_2$ from Li_3N, Mo_2N, and N_2 to be $-224.0\ \mathrm{kJ\,mol^{-1}}$, which was likewise very large compared with the enthalpy of formation from the elements, $-386.0 \pm 6.4\ \mathrm{kJ\,mol^{-1}}$. Table 2 shows a comparison of the enthalpies of formation of Ca_2ZnN_2 and $LiMoN_2$ from the elements, ΔH_f°, and from binary nitrides, $\Delta H_f(N)$, with analogous values for oxides in the same metal systems. The enthalpy of formation for the hypothetical "Ca_2ZnO_3" phase was estimated from $2\Delta H_f^\circ(CaO) + \Delta H_f^\circ(ZnO)$. In both cases, $\Delta H_f(N)/\Delta H_f^\circ$ are more than an order of magnitude greater than expected based on the values for oxides in the same metal system. Although the formation of $LiMoN_2$ as calculated involves oxidation of "$Mo^{1.5+}$" to Mo^{5+}, which surely contributes to the large value of $\Delta H_f(N)/\Delta H_f^\circ$, the observed trend may be significant, and is probably indicative of different acid/base properties for nitrides.

Table 2. A comparison of the enthalpies of formation of Ca_2ZnN_2 and $LiMoN_2$ from the elements (ΔH_f°) and from binary nitrides ($\Delta H_f(N)$), with analogous values for oxides in the same metal systems. The enthalpies of formation for the hypothetical "Ca_2ZnO_3" phase were estimated from $2\Delta H_f^\circ(CaO) + \Delta H_f^\circ(ZnO)$ (all enthalpies are in $\mathrm{kJ\,mol^{-1}}$).

	Ca_2ZnN_2	"Ca_2ZnO_3"	$LiMoN_2$	Li_2MoO_4
ΔH_f°	-328.5 ± 6.5	-1621 ± 20	-386.0 ± 6.4	-1520.30
$\Delta H_f(O)$	-	0 ± 20	-	-180.0
$\Delta H_f(N)$	-35.2 ± 8.7	-	-224.0	-
$\Delta H_f/\Delta H_f^\circ$	0.1072	0.0123	0.6095	0.0291

Some insight into the apparent energetic stability of Ca_2ZnN_2 with respect to the binaries can be obtained by comparison of the structures of these phases. Ca_3N_2 and Zn_3N_2 crystallize in the anti-Mn_2O_3 structure, which is a supercell of anti-fluorite (anti-CaF_2). Six metal atoms and two vacancies occupy the fluorine sites and four nitrogen atoms occupy the calcium sites. The N is coordinated by six metal atoms in a distorted octahedron and the metal atoms are tetrahedrally coordinated by four nitrogen atoms.[19] In Ca_2ZnN_2, which crystallizes in a Na_2HgO_2 type structure (space group $I4/mmm$), the nitrogen atoms are likewise coordinated by six metal atoms (five Ca and one Zn) and the calcium atoms have five nearest neighbors. The Zn is linearly coordinated by two nitrogens, forming discrete $[N{=}Zn{=}N]^{4-}$ anions; this is the most striking structural dissimilarity between the binaries and the ternary.[10] Similar $[N{=}Fe{=}N]^{4-}$ groups occur in Li_4FeN_2,[20] and trigonal planar carbonate-like $[MN_3]^{6-}$ groups occur in Ca_3CrN_3.[21] Such groups are formed in ternary oxides when highly acidic oxides, such as CO_2, combine with more basic oxides, such as CaO. The relatively large enthalpies of formation that accompany such reactions have been discussed in terms of acid/base concepts above. The existence of discrete $[N{=}Zn{=}N]^{4-}$ anions and the relatively large $\Delta H_f(N)$ of Ca_2ZnN_2 indicates that Ca_3N_2 acts as a basic nitride in exact analogy to CaO in oxide systems, while Zn_3N_2 acts as an acidic nitride ("N^{3-}" acceptor) in this ternary nitride system. Further study of ternary nitride systems should enable classification of binary nitrides into those of acidic or basic character, and possibly lead to the design and synthesis of new materials.

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Experimental Procedure

Sample preparation: All manipulations were carried out in an argon- or helium-filled glovebox. Ca_3N_2 was synthesized from Ca metal (Aldrich 99%) heated in an Al_2O_3 boat within a quartz flow tube under a backpressure of N_2. The quartz tube was protected from direct attack of Ca vapor by a piece of Ti foil. The metal was fully nitrided by heating at 1273 K for 72 h. A brown-black product was obtained, which, when ground into a fine powder, took on a reddish hue. It was identified as α-Ca_3N_2 by powder XRD by means of a Scintag XDS2000 diffractometer. TGA oxidation of the Ca_3N_2 yielded a weight percent of 113.14%, suggesting a 0.3% by weight impurity of CaO present in the nitride (pure nitride would have a final weight percent of 113.48%). Zn_3N_2 was synthesized from Zn metal powder (Alfa 99.9%, 100 mesh) which was placed in 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. This product was identified by powder XRD; a few small ZnO peaks were observed at around 1% impurity. Ca_2ZnN_2 was synthesized by reaction of a mixture of Ca_3N_2 and Zn metal powder. This powder was pressed into a pellet and placed in an alumina crucible. The initial ratio of Ca:Zn was 3:2. Excess Zn is necessary to produce single-phase Ca_2ZnN_2 owing to Zn vaporization during the reaction. The pellet and boat were placed in a flow tube apparatus similar to that used in the Ca_3N_2 preparation. Under a N_2 backpressure the reaction was heated to 923 K over 10 h and held there for an additional 62 h. The pellet had a brown color and was easily powdered. This powder was subsequently heated to 773 K for 8 h to remove any remaining elemental Zn. Ca_2ZnN_2 begins to decompose to Ca_3N_2 and Zn around 973 K. Samples annealed at 950 K always contained significant amounts of Ca_3N_2. Calorimetry was performed on two Ca_2ZnN_2 samples with levels of Ca_3N_2 impurity of $\approx 3\%$ and $\approx 10\%$. The intensity ratio of the most intense XRD peak of Ca_2ZnN_2 and Ca_3N_2 was plotted against the corresponding ΔH_{ds} value. A linear extrapolation to an intensity ratio of zero indicated that a pure Ca_2ZnN_2 sample should have $\Delta H_{ds} = -1464.0\ \mathrm{kJ\,mol^{-1}}$, which is well within the error of our measurement on the sample with $\approx 3\%$ Ca_3N_2. Therefore, the results reported here are from this sample without any adjustment for the $\approx 3\%$ Ca_3N_2 impurity.

Calorimetry: The Tian–Calvet microcalorimeter was calibrated by dropping small (≈ 100 mg) pieces of α-Al_2O_3 of accurately known mass into the calorimeter. As the heat content of α-Al_2O_3 in the temperature range of interest is well known, a calibration constant in $\mathrm{J\,\mu V^{-1}\,min^{-1}}$ was calculated. The sodium molybdate solvent, $3Na_2O \cdot 4MoO_3$, was prepared from $Na_2MoO_4 \cdot 2H_2O$ and MoO_3 (obtained from Johnson Matthey, ACS grade and 99.95% purity, respectively), dehydrated and liquefied at 973 K, and quenched to room temperature by pouring into a graphite dish. The melt does not quench to a glass, so the entire batch was ground to a powder to homogenize it before it was loaded into the calorimetry crucibles. As the composition is at a buffer region in the Na_2O/MoO_3 system, small variations in stoichiometry do not greatly affect the resulting enthalpies of solution [8,9]. With the exception of Zn_3N_2, the nitride samples studied in this work are very air-sensitive (Zn_3N_2 is mildly air-sensitive), and special precautions were necessary to prevent decomposition before calorimetry. In a He-filled glovebox, nitride samples were pressed into pellets of ≈ 10 mg, weighed to within ± 0.01 mg, and sealed in small screw-top glass vials. Oxygen gas was flushed through the calorimeter above the solvent at $90\ \mathrm{mL\,min^{-1}}$ and bubbled through the solvent at $\approx 5\ \mathrm{mL\,min^{-1}}$. When a stable baseline signal was achieved, a sample vial was quickly opened and the nitride was poured from the vial into the calorimeter. Exposure time to the atmosphere was ≈ 1 s.

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