Energetics of Ternary Nitride Formation in the (Li,Ca)−(B,Al)−N System

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High-temperature oxide melt drop solution calorimetry was used to study the energetics of nitride formation. The standard enthalpies of formation of several binary and ternary nitrides were determined. These values (in kJ mol^{-1}) are as follows: $\Delta H_f°$ (AlN) = −311.1 ± 4.3, $\Delta H_f°$ (Li_3BN_2) = −534.5 ± 16.7, $\Delta H_f°$ (Li_3AlN_2) = −567.8 ± 12.4, and $\Delta H_f°$ ($Ca_3B_2N_4$) = −1062.1 ± 15.4. From these values and others available in the literature, the enthalpies of formation of the ternary nitrides from the binary nitrides were calculated. The energetics of ternary nitride formation appear to be dominated by differences in the acid/base character of the cations.

Introduction

Many new and structurally diverse ternary metal nitrides[1−4] 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.[5] This, however, does not necessitate that the enthalpies of formation of ternary nitrides *from binary nitrides*, ΔH_f(N), also be small in magnitude. We have been exploring the energetics of ternary nitride formation via high-temperature solution calorimetry in $3Na_2O\cdot4MoO_3$ at 979 K, and have found that ΔH_f(N) can substantially exothermic.[6,7] For example, the enthalpy of formation of LiZnN from $^1/_3Li_3N$ and $^1/_3Zn_3N_2$ is −67.7 ± 6.6 kJ mol^{-1}, which is nearly 50% of its enthalpy of formation from the elements, −137.5 ± 6.8 kJ mol^{-1}. Using the ionic potential, ϕ (defined as the ratio of the charge to ionic radius, Z/r),[8] as a semiquantitative measure of the Lux−Flood acidity[9] of a cation, we also demonstrated, at least for a small number of compositions, that the energetics of ternary nitride formation appears to be dominated by the difference in acidity of the two cations in the ternary. The magnitude of ΔH_f(N) for ternaries in the Li−Ca−Zn−N and Ca−Ta−N systems was found to increase nearly linearly with an increasing ionic potential ratio for the two cations (i.e., $\phi_{acidic}/\phi_{basic}$). Furthermore, the increase in stability with increasing value of $\phi_{acidic}/\phi_{basic}$ was much greater than that generally observed in ternary oxides. We attributed this phenomenon to the greater polarizability of N^{3-} (5.55 Å^3 in Li_3N)[10] as compared to O^{2-} (2.07 Å^3 in Li_2O),[11] and the higher energy of formation of N^{3-} from atomic N (+2300 kJ mol^{-1})[3] compared to the energy of formation of O^{2-} from atomic O (+700 kJ mol^{-1}).[3] These factors should lead to a higher degree of covalency in the bonding in ternary nitrides which reveals itself through more exothermic values of ΔH_f(N).

In this contribution, we discuss the continuation of our study to the binary nitride AlN, and ternary nitrides in the (Li,Ca)−(Al,B)−N system: Li_3AlN_2, Li_3BN_2, and $Ca_3B_2N_4$. As in our previous work, we have chosen systems of metals which form well-defined binary nitrides and ternary nitrides in which the metals are in the same formal oxidation state as the binary. This allows determination of ΔH_f(N) values which are not

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dominated by oxidation or reduction. We made several attempts at the synthesis of a $Ca_3Al_2N_4$ phase under conditions given by Jager,[12] but could not obtain a sample of purity sufficient for thermochemical measurements.

Experimental Methods

A. Synthesis and Sample Characterization. All manipulations were carried out in an Ar- or He-filled glovebox. All NH_3 used in syntheses was dried as the liquid over sodium metal, and N_2 was purified by being passed through a Ti getter at 1173 K. Phase identification was accomplished with powder XRD using a Scintag XD S2000 diffractometer and Cu Kα radiation. 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 AlN studied was supplied by the Dow Chemical Company and said to contain 0.73 wt % O. Our N analysis of this sample gave 33.68 ± 0.05 wt % N, which is in good agreement with that stated by Dow (theoretical = 34.17 wt % N). The syntheses of Ca_3N_2 and Li_3N were discussed in ref 7. Ternary nitrides were synthesized from stoichiometric mechanical mixtures of the binary nitrides. The binary nitrides were ground in an agate mortar and pestle and pressed into a pellet. The pellet was then sealed under Ar in a Ta or Nb tube (by arc welding) which was subsequently sealed in an evacuated quartz tube and heated as specified below.

Li_3BN_2 was synthesized from a mechanical mixture of Li_3N and BN (Aldrich, 99.9%) following the procedure of Goubeau and Anselment.[13] The mixture of binaries was heated at 1073 K for 24 h. The gray product was identified as nearly single phase α-Li_3BN_2 via comparison of its powder XRD pattern to that reported by Yamane et al.[14] Nitrogen analysis of the product yielded 45.96 ± 0.46% N (theoretical = 46.96%), which corresponds to a 2.1 ± 1.0 wt % LiOH impurity.

Li_3AlN_2 was synthesized from a mechanical mixture of Li_3N and AlN (Dow) following the procedure of Juza and Hund.[15] The mixture of binaries was heated at 1073 K for 24 h. The black product was identified as nearly single phase Li_3AlN_2 via powder XRD. Nitrogen analysis of the product yielded 36.10 ± 0.29% N (theoretical = 36.95%), which corresponds to a 2.3 ± 0.8 wt % LiOH impurity.

$Ca_3B_2N_4$ was synthesized from a mechanical mixture of Ca_3N_2 and BN (Aldrich, 99.9%) following the procedure of Goubeau and Anselment.[13] The mixture of binaries was heated at 1273 K for 24 h. The bright yellow product thus obtained was identified as nearly single phase α-$Ca_3B_2N_4$ via powder XRD.[16] Nitrogen analysis of the product yielded 27.08 ± 0.18% N (theoretical = 28.31%), which corresponds to 4.3 ± 0.6 wt % of an impurity phase. As no other phases were detected via XRD, the impurity is probably oxygen as solid solution in $Ca_3B_2N_4$. Calorimetric data were corrected by approximating the heat effect due to this impurity as that obtained from a mixture of 3CaO and B_2O_3.

Table 1. Data Used in Thermodynamic Cycles To Determine Nitride Enthalpies of Formation from Drop Solution Calorimetry

	ΔH_{ds}[a] or ΔH_{cds},[b] kJ mol^{-1}	H_{979} - H_{298},[c] kJ mol^{-1}	$\Delta H_f°$,[d] kJ mol^{-1}
Li_3N	−873.2 ± 2.9 (7)[b,e]	–	–
Ca_3N_2	−1748.2 ± 5.6 (18)[b,e]	–	–
AlN	−507.6 ± 2.6 (7)[b]	–	–
Li_3BN_2	−1082.6 ± 16.2 (8)[b]	–	–
Li_3AlN_2	−1262.6 ± 11.7 (8)[b]	–	–
$Ca_3B_2N_4$	−2281.3 ± 14.4 (6)[b]	–	–
Li_2O	−90.3 ± 2.5[e]	–	−598.7 ± 2.1
CaO	−90.3 ± 1.8[e]	–	−635.09 ± 0.88
$LiBO_2$	+102.8 ± 1.9 (6)	–	−1019.2 ± 0.8
B_2O_3	+129.6 ± 4.6		−1273.5 ± 1.4
Al_2O_3	+105.2 ± 2.7 (7)[f]	–	−1675.7 ± 1.3
O_2	–	+21.98	–
N_2	–	+21.31	–

[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 28. [d] From ref 23. [e] From ref 7. [f] From ref 29.

B. Calorimetry. High-temperature oxide melt drop solution calorimetry was performed in a Tian-Calvet twin microcalorimeter described in detail by Navrotsky.[17] Nitride samples of 5 to 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}. The calorimetry utilizes a rapid redox reaction between MoO_3 in the melt and N^{3-}, which supplies a pathway for elimination of N^{3-} as N_2 gas.[6] Subsequent oxidation of any reduced molybdenum species returns the system to the initial state. The net measured heat effect is that accompanying the general reaction:

$$(M^{y+})_xN_{y\cdot x/3}\ (s,\ 298) + {}^{x\cdot y}/4O_2\ (g,\ 979\ K) \rightarrow xMO_{y/2}\ (soln,\ 979\ K) + {}^{x\cdot y/6}N_2\ (g,\ 979\ K) \quad (1)$$

where M is a metal in the $y+$ oxidation state. Further details of the experimental procedure are provided elsewhere.[6,7] Calibration was performed by dropping ~5-mg pellets of benzoic acid (NIST, SRM 39i) into molten $3Na_2O{\cdot}4MoO_3$ at 979 K in the calorimeter. Upon reaching the hot zone of the calorimeter, the ensuing combustion produced exothermic heat effects of nearly equal magnitude to the nitride reactions. A calibration constant was then calculated on the basis of the known enthalpy of combustion of benzoic acid and the heat contents of O_2, CO_2, and H_2O. The validity of this calibration has been verified.[7] For reactions in the thermochemical cycles which were endothermic or not highly exothermic (i.e., drop solution calorimetry of oxides) the standard Pt drop calibration was used. Due to the affinity of ionic nitrides for reaction with atmospheric H_2O and CO_2, pellets for calorimetry were pressed, weighed, and sealed in small screw-top glass vials in an Ar-filled glovebox. When a stable calorimetric baseline signal was achieved, a vial was removed from the glovebox, opened near the calorimeter, and the pellet immediately dropped into the calorimeter. Exposure time to the atmosphere was ~1 s.

To complete thermochemical cycles, drop solution calorimetry was also performed on $LiBO_2$, and α-Al_2O_3 (obtained from Johnson Matthey Co. ≥ 99.9%). Calorimetry data for Ca_3N_2, CaO, Li_3N, and Li_2O were taken from our previous study.[7]

Results

The enthalpies of drop solution 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 were observed due to the bubbling of O_2 through the solvent.

AlN. AlN crystallizes in the wurtzite structure.[18] Aluminum ions are tetrahedrally coordinated by four

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N^{3-} ions, which are in turn tetrahedrally coordinated by four Al^{3+}. Drop solution calorimetry was performed on a high-quality sample of AlN obtained from The Dow Chemical Company yielding ΔH_{ds} (AlN) = −11 512.9 ± 19.0 J g^{-1}. On the basis of Dow's elemental analysis, which was in agreement with our N analysis, the sample contained 1.55 ± 0.05 wt % Al_2O_3. The corrected enthalpy of drop solution, ΔH_{cds} for this sample is then:

$$\Delta H_{ds}\ (\mathrm{AlN}) = 0.9845\Delta H_{cds}\ (\mathrm{AlN}) + 0.0155\Delta H_{ds}\ (\mathrm{Al_2O_3}) \quad (2)$$

which yields ΔH_{cds} (AlN) = −11 710.4 ± 99.0 J g^{-1} or −480.0 ± 4.1 kJ mol^{-1}. The enthalpy of formation of AlN was then determined via the following thermochemical cycle:

$$\mathrm{AlN\ (s,\ 298\ K)} + {}^{3}/_{4}\mathrm{O_2\ (g,\ 979\ K)} \rightarrow {}^{1}/_{2}\mathrm{Al_2O_3\ (soln,\ 979\ K)} + {}^{1}/_{2}\mathrm{N_2\ (g,\ 979\ K)} \quad (3)$$

$$\alpha\text{-}\mathrm{Al_2O_3\ (s,\ 298\ K)} \rightarrow \mathrm{Al_2O_3\ (soln,\ 979\ K)} \quad (4)$$

$$\mathrm{N_2\ (g,\ 298\ K)} \rightarrow \mathrm{N_2\ (g,\ 979\ K)} \quad (5)$$

$$\mathrm{O_2\ (g,\ 298\ K)} \rightarrow \mathrm{O_2\ (g,\ 979\ K)} \quad (6)$$

$$2\mathrm{Al\ (s,\ 298\ K)} + {}^{3}/_{2}\mathrm{O_2\ (g,\ 298\ K)} \rightarrow \alpha\text{-}\mathrm{Al_2O_3\ (s,\ 298\ K)} \quad (7)$$

$$\mathrm{Al\ (s,\ 298\ K)} + {}^{1}/_{2}\mathrm{N_2\ (g,\ 298\ K)} \rightarrow \mathrm{AlN\ (s,\ 298\ K)} \quad (8)$$

$$\Delta H_f^\circ\ (\mathrm{AlN}) = \Delta H_8 = -\Delta H_3 + {}^{1}/_{2}\Delta H_4 + {}^{1}/_{2}\Delta H_5 - {}^{3}/_{4}\Delta H_6 + {}^{1}/_{2}\Delta H_7 \quad (9)$$

With the use of the data in Table 1, the value thus obtained was ΔH_f° (AlN) = −311.1 ± 4.3 kJ mol^{-1}. This is slightly less exothermic than the −316.3 ± 1.7 kJ mol^{-1} which Mah et al.[19] determined via oxidation combustion calorimetry, and the −319.9 ± 0.8 kJ mol^{-1} which Neugebauer and Margrave[20] determined via direct nitridation. Our value is in better agreement with the −312.5 and −313.0 ± 4.8 kJ mol^{-1} calculated from equilibrium data by Satoh[21] and Hildenbrand and Hall,[22] respectively. We note that small differences in impurity content, especially when the impurity like Al_2O_3 cannot be oxidized or nitrided, could account for these differences.

Li_3BN_2. α-Li_3BN_2 crystallizes in a tetragonal lattice, space group $P4_22_12$. The structure contains nearly linear $[N-B-N]^{3-}$ anions,[14] which was first suggested by Gobeau and Anselment[13] on the basis of the IR spectrum of the material. Drop solution calorimetry was performed on Li_3BN_2, yielding ΔH_{ds} (Li_3BN_2) = −17 739.1 ± 189.4 J g^{-1}. On the basis of N analysis and XRD, the sample contained 2.1 ± 1.0 wt % LiOH. The ΔH_{ds} value for LiOH was taken from ref 7, and the data were corrected for this impurity as above, yielding ΔH_{cds} = −18 150.0 ± 272.3 J g^{-1} or −1082.6 ± 16.2 kJ mol^{-1}. After the ΔH_{ds} of $LiBO_2$ was measured and with the use of the ΔH_{ds} of Li_2O from ref 7, the enthalpy of formation of Li_3BN_2 was determined via the following thermochemical cycle:

$$\mathrm{Li_3BN_2\ (s,\ 298\ K)} + {}^{3}/_{2}\mathrm{O_2\ (g,\ 979\ K)} \rightarrow {}^{3}/_{2}\mathrm{Li_2O\ (soln,\ 979\ K)} + {}^{1}/_{2}\mathrm{B_2O_3\ (soln,\ 979\ K)} + \mathrm{N_2\ (g,\ 979\ K)} \quad (10)$$

$$\mathrm{Li_2O\ (s,\ 298\ K)} \rightarrow \mathrm{Li_2O\ (soln,\ 979\ K)} \quad (11)$$

$$\mathrm{LiBO_2\ (s,\ 298\ K)} \rightarrow {}^{1}/_{2}\mathrm{Li_2O\ (soln,\ 979\ K)} + {}^{1}/_{2}\mathrm{B_2O_3\ (soln,\ 979\ K)} \quad (12)$$

$$\mathrm{N_2\ (g,\ 298\ K)} \rightarrow \mathrm{N_2\ (g,\ 979\ K)} \quad (13)$$

$$\mathrm{O_2\ (g,\ 298\ K)} \rightarrow \mathrm{O_2\ (g,\ 979\ K)} \quad (14)$$

$$2\mathrm{Li\ (s,\ 298\ K)} + {}^{1}/_{2}\mathrm{O_2\ (g,\ 298\ K)} \rightarrow \mathrm{Li_2O\ (s,\ 298\ K)} \quad (15)$$

$$\mathrm{Li\ (s,\ 298\ K)} + \mathrm{B\ (s,\ 298\ K)} + \mathrm{O_2\ (g,\ 298\ K)} \rightarrow \mathrm{LiBO_2\ (s,\ 298\ K)} \quad (16)$$

$$3\mathrm{Li\ (s,\ 298\ K)} + \mathrm{B\ (s,\ 298\ K)} + \mathrm{N_2\ (g,\ 298\ K)} \rightarrow \mathrm{Li_3BN_2\ (s,\ 298\ K)} \quad (17)$$

$$\Delta H_f^\circ\ (\mathrm{Li_3BN_2}) = \Delta H_{17} = -\Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} - {}^{3}/_{2}\Delta H_{14} + \Delta H_{15} + \Delta \mathrm{H}_{16} \quad (18)$$

With the use of the data in Table 1 and eqs 10−18, ΔH_f° (Li_3BN_2) = −534.5 ± 16.7 kJ mol^{-1}. For this material and all ternary nitrides to follow, no previous determination of ΔH_f° (Li_3BN_2) has been made with which to compare the present value.

We have previously determined the enthalpy of formation of Li_3N as −166.1 ± 4.8 kJ mol^{-1}.[7] We attempted to determine the enthalpy of formation of hexagonal BN (h-BN) in this work, but the material proved extremely resistant to attack by the sodium molybdate solvent. By using the enthalpy of formation of h-BN listed in JANAF tables, −250.91 ± 1.55 kJ mol^{-1}, we can calculate the enthalpy of formation of Li_3BN_2 from the binary nitrides:

$$\mathrm{Li_3N\ (s,\ 298\ K)} + \mathrm{BN\ (s,\ 298\ K)} \rightarrow \mathrm{Li_3BN_2\ (s,\ 298\ K)} \quad (19)$$

as ΔH_f(N) (Li_3BN_2) = −117.5 ± 17.5 kJ mol^{-1}. The significance of this and other ΔH_f(N) values will be discussed below.

Li_3AlN_2. Li_3AlN_2 crystallizes in an anti-fluorite structure,[15] similar to several other ternary lithium nitrides (e.g., LiZnN).[2] The Al ions are displaced from their ideal tetrahedral positions such that the Al−N distances are ∼12% shorter than the distances from the N^{3-} to the other tetrahedral sites. This is probably indicative of substantial covalency in these Al−N bonds. Drop solution calorimetry was performed on Li_3AlN_2, yielding ΔH_{ds} (Li_3AlN_2) = −16 241.1 ± 58.0 J g^{-1}. On the basis of N analysis and XRD, the sample contained 2.3 ± 0.8 wt % LiOH. Again, the ΔH_{ds} value for LiOH was taken from ref 7, and the data were corrected for this impurity as above, yielding ΔH_{cds}(Li_3AlN_2) = −16 652.4 ± 154.4

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J g^{-1} or -1262.6 ± 11.7 kJ mol^{-1}. The enthalpy of formation of Li_3AlN_2 was then determined via the following thermochemical cycle:

$$Li_3AlN_2\text{ (s, 298 K)} + {}^3/_2O_2\text{ (g, 979 K)} \rightarrow {}^3/_2Li_2O\text{ (soln, 979 K)} + {}^1/_2Al_2O_3\text{ (soln, 979 K)} + N_2\text{ (g, 979 K)} \tag{20}$$

$$Li_2O\text{ (s, 298 K)} \rightarrow Li_2O\text{ (soln, 979 K)} \tag{21}$$

$$\alpha\text{-}Al_2O_3\text{ (s, 298 K)} \rightarrow Al_2O_3\text{ (soln, 979 K)} \tag{22}$$

$$N_2\text{ (g, 298 K)} \rightarrow N_2\text{ (g, 979 K)} \tag{23}$$

$$O_2\text{ (g, 298 K)} \rightarrow O_2\text{ (g, 979 K)} \tag{24}$$

$$2Li\text{ (s, 298 K)} + {}^1/_2O_2\text{ (g, 298 K)} \rightarrow Li_2O\text{ (s, 298 K)} \tag{25}$$

$$2Al\text{ (s, 298 K)} + {}^3/_2O_2\text{ (g, 298 K)} \rightarrow \alpha\text{-}Al_2O_3\text{ (s, 298 K)} \tag{26}$$

$$3Li\text{ (s, 298 K)} + Al\text{ (s, 298 K)} + N_2\text{ (g, 298 K)} \rightarrow Li_3AlN_2\text{ (s, 298 K)} \tag{27}$$

$$\Delta H_f^\circ\ (Li_3AlN_2) = \Delta H_{27} = -\Delta H_{20} + {}^3/_2\Delta H_{21} + {}^1/_2\Delta H_{22} + \Delta H_{23} - {}^3/_2\Delta H_{24} + {}^3/_2\Delta H_{25} + {}^1/_2\Delta H_{26} \tag{28}$$

With the use of the data in Table 1 and eqs 20−28, ΔH_f° (Li_3AlN_2) = -567.8 ± 12.4 kJ mol^{-1}.

After the enthalpies of formation of Li_3N[7] and AlN were determined to be -166.1 ± 4.8 kJ mol^{-1} and -311.3 ± 4.3 kJ mol^{-1}, respectively, the enthalpy of formation of Li_3AlN_2 from the binary nitrides

$$Li_3N\text{ (s, 298 K)} + AlN\text{ (s, 298 K)} \rightarrow Li_3AlN_2\text{ (s, 298 K)} \tag{29}$$

can be calculated as ΔH_f (N) (Li_3AlN_2) = -90.6 ± 14.0 kJ mol^{-1}. As drop solution calorimetry was performed on Li_3N, AlN, and Li_3AlN_2, the shortest thermochemical cycle which can be used to determine the value of ΔH_f(N) for Li_3AlN_2 is a direct combination of the ΔH_{ds} values:

$$Li_3N\text{ (s, 298 K)} + {}^3/_4O_2\text{ (g, 979 K)} \rightarrow {}^3/_2\ Li_2O\text{ (soln, 979 K)} + {}^1/_2N_2\text{ (g, 979 K)} \tag{30}$$

$$AlN\text{ (s, 298 K)} + {}^3/_4O_2\text{ (g, 979 K)} \rightarrow {}^1/_2\ Al_2O_3\text{ (soln, 979 K)} + {}^1/_2N_2\text{ (g, 979 K)} \tag{31}$$

$$Li_3AlN_2\text{ (s, 298 K)} + {}^3/_2O_2\text{ (g, 979 K)} \rightarrow {}^3/_2Li_2O\text{ (soln, 979 K)} + {}^1/_2\ Al_2O_3\text{ (soln, 979 K)} + N_2\text{ (g, 979 K)} \tag{32}$$

$$Li_3N\text{ (s, 298 K)} + AlN\text{ (s, 298 K)} \rightarrow Li_3AlN_2\text{ (s, 298 K)} \tag{33}$$

$$\Delta H_f(N)\ (Li_3AlN_2) = \Delta H_{33} = \Delta H_{30} + \Delta H_{31} - \Delta H_{32} \tag{34}$$

This cycle eliminates any uncertainty in the values of ΔH_{ds} and ΔH_f° for the oxides included in eqs 20−29 and yields -90.6 ± 12.7 kJ mol^{-1} for ΔH_f(N) (Li_3AlN_2).

$Ca_3B_2N_4$. α-$Ca_3B_2N_4$ crystallizes in a cubic structure (space group $Im\bar{3}m$) and contains linear $[BN_2]^{3-}$ anions.[16] Drop solution calorimetry was performed on $Ca_3B_2N_4$, yielding ΔH_{ds} ($Ca_3B_2N_4$) = $-11\,058.5 \pm 30.6$ J g^{-1}. Nitrogen analysis of this sample found only 95.6% of the theoretical N content, indicating 4.3 ± 0.6 wt % of an impurity phase. As no impurities were detected by XRD, we suspect the impurity to be oxygen as solid solution in $Ca_3B_2N_4$. We therefore corrected the calorimetric data by approximating the solid solution as a mechanical mixture of 95.6 wt % $Ca_3B_2N_4$ and 4.3 wt % ($3CaO + B_2O_3$). The data were corrected for this impurity as above, yielding $\Delta H_{cds}(Ca_3B_2N_4) = -11\,528.6 \pm 72.6$ J g^{-1} or -2281.3 ± 14.4 kJ mol^{-1}. The enthalpy of formation of $Ca_3B_2N_4$ was then determined via the following thermochemical cycle:

$$Ca_3B_2N_4\text{ (s, 298 K)} + 3O_2\text{ (g, 979 K)} \rightarrow 3CaO\text{ (soln, 979 K)} + B_2O_3\text{ (soln, 979 K)} + 2N_2\text{ (g, 979 K)} \tag{35}$$

$$CaO\text{ (s, 298 K)} \rightarrow CaO\text{ (soln, 979 K)} \tag{36}$$

$$B_2O_3\text{ (s, 298 K)} \rightarrow B_2O_3\text{ (soln, 979 K)} \tag{37}$$

$$N_2\text{ (g, 298 K)} \rightarrow N_2\text{ (g, 979 K)} \tag{38}$$

$$O_2\text{ (g, 298 K)} \rightarrow O_2\text{ (g, 979 K)} \tag{39}$$

$$Ca\text{ (s, 298 K)} + {}^1/_2O_2\text{ (g, 298 K)} \rightarrow CaO\text{ (s, 298 K)} \tag{40}$$

$$2B\text{ (s, 298 K)} + {}^3/_2O_2\text{ (g, 298 K)} \rightarrow B_2O_3\text{ (s, 298 K)} \tag{41}$$

$$3Ca\text{ (s, 298 K)} + 2B\text{ (s, 298 K)} + 2N_2\text{ (g, 298 K)} \rightarrow Ca_3B_2N_4\text{ (s, 298 K)} \tag{42}$$

$$\Delta H_f^\circ\ (Ca_3B_2N_4) = \Delta H_{42} = -\Delta H_{35} + 3\Delta H_{36} + \Delta H_{37} + 2\Delta H_{38} - 3\Delta H_{39} + 3\Delta H_{40} + \Delta H_{41} \tag{43}$$

The ΔH_{ds} value for B_2O_3 (see Table 1) was calculated from the ΔH_{ds} values of $LiBO_2$ and Li_2O. With the use of the data in Table 1 and eqs 35−43, ΔH_f° ($Ca_3B_2N_4$) = -1062.1 ± 15.4 kJ mol^{-1}.

After the the enthalpy of formation of Ca_3N_2 in ref 7 was determined to be -439.7 ± 6.6 kJ mol^{-1}, and with the use of ΔH_f°(BN) = -250.91 ± 1.55 kJ mol^{-1},[23] the enthalpy of formation of $Ca_3B_2N_4$ from the binary nitrides

$$Ca_3N_2\text{ (s, 298 K)} + 2BN\text{ (s, 298 K)} \rightarrow Ca_3B_2N_4\text{ (s, 298 K)} \tag{44}$$

kJ mol can be calculated as ΔH_f (N) ($Ca_3B_2N_4$) = -120.6 ± 15.6 kJ mol^{-1}.

Discussion

The standard enthalpies of formation obtained for the nitrides are indeed small in magnitude, sometimes

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(23) Chase, M.; et al. *JANAF Thermochemical Tables*; 3rd ed.; American Chemical Society and American Institute of Physics: New York, 1985; Vol. 14.

Table 2. Enthalpies of Formation of Nitrides from the Elements ($\Delta H_f°$), from Binary Nitrides ($\Delta H_f(N)$), and the Percentage of $\Delta H_f(N)$ in $\Delta H_f°$

	$\Delta H_f°$, kJ mol^{-1}	$\Delta H_f(N)$, kJ mol^{-1}	$\Delta H_f(N)$, kJ (mol atoms)$^{-1}$	%[c]
AlN[a]	-311.1 ± 4.3	–	–	
Li_3BN_2[a]	-534.5 ± 16.7	-117.5 ± 17.5	-19.6 ± 2.9	22
Li_3AlN_2[a]	-567.8 ± 12.4	-90.6 ± 12.1	-15.1 ± 2.0	16
$Ca_3B_2N_4$[a]	-1062.1 ± 15.4	-120.6 ± 15.6	-13.4 ± 1.7	11
LiCaN[b]	-216.8 ± 10.8	-17.6 ± 8.6	-5.9 ± 2.9	8
LiZnN[b]	-137.5 ± 6.8	-67.7 ± 6.6	-22.6 ± 2.2	49
Ca_2ZnN_2[b]	-378.9 ± 8.6	-71.4 ± 9.1	-14.3 ± 3.0	19
Sr_2ZnN_2[b]	-385.6 ± 14.3	-110.3 ± 17.6	-22.1 ± 5.9	29
$CaTaN_2$[b]	-643.8 ± 9.6	-229.9 ± 12.5	-57.5 ± 4.2	36

[a] Data from this work. [b] From ref 7. [c] $\Delta H_f(N)/\Delta H_f°$.

nearly an order of magnitude smaller than those of the oxide of the same metal(s). However, the enthalpy of formation of ternary nitrides from binaries can be quite substantial in both magnitude and as a fraction of the enthalpy of formation from the elements (see Table 2). This was previously noted by Elder et al.,[24] who studied the Li–Mo–N and Na–W–N systems. We also found rather large $\Delta H_f(N)$ values in our recent thermochemical study of the Li–Ca–Zn–N and Ca–Ta–N systems (included in Table 2).[7] The energetics of ternary (and higher) oxide formation tends to be dominated by the difference in Lux–Flood[9] acidity of the cations,[25] and this also appears to be the case in ternary nitride formation.[6,7]

Table 3. Average M–N Bond Lengths (d) in Binary Nitrides and Calculated Values of *Z*/*d* for Each Cation

cation	M–N distance in binary nitride, Å	*Z*/*d* in nitride, arbitrary units
Li^+	2.13[a]	0.469
Ca^{2+}	2.47[b]	0.810
Al^{3+}	1.86[c]	1.61
B^{3+}	1.45[d]	2.07

[a] Rabenau, A.; Schultz, H. *J. Less Common Metals* **1976**, *50*, 155. [b] Laurent, Y.; Lang, J.; LeBihan, M. T. *Acta Crystallogr.* **1968**, *B24*, 494. [c] Baur, W. H. *Crystallogr. Rev.* **1987**, *1*, 59. [d] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Permagon: New York, 1984; p 235.

Numerous attempts have been made to quantify the acidity or basicity of a cation.[26] It is generally agreed that acidity scales as some function of the size and charge of the cation. In ref 7, we reported an empirical correlation of $\Delta H_f(N)$ values with the ratio of the ionic potential (ϕ, the ratio of charge to ionic radius, Z/r)[27] of the acidic cation to that of the basic cation. As a test of this correlation, we have chosen for the present study ternary nitrides of the highly acidic cations B^{3+} and Al^{3+}, which should give large exothermic values of $\Delta H_f(N)$ when combined with basic cations such as Li^+ and Ca^{2+}. As B^{3+} is often given an illogical negative or near zero ionic radius, we have chosen to use Z/d, the ratio of the cation charge to metal–nitrogen (M–N) bond length, as our semiquantitative measure of acidity. The average M–N bond length in the binary nitrides considered here and the resulting values of Z/d for the cations appear in Table 3. Large values of $\Delta H_f(N)$ are expected when there is a large difference between the Z/d values of the cations in the ternary. Thus, Li–B–N nitrides should have the most exothermic $\Delta H_f(N)$ and Ca–Al–N nitrides the least exothermic $\Delta H_f(N)$ on the basis of simply on ionic considerations. Ternaries in the Li–Al–N and Ca–B–N systems should fall somewhere between these two extremes. In Table 2, the $\Delta H_f(N)$ values of the ternaries studied are given (in kJ/mol and kJ (mol atom)$^{-1}$). When expressed in kJ (mol atom)$^{-1}$, the measured values are in good agreement with the above expectations. The percentage of $\Delta H_f(N)$ in $\Delta H_f°$ also follows this expected trend. This suggests that the energetics of ternary nitride formation in the (Li,Ca)–(Al,B)–N system are dominated by acid–base contributions, as we have likewise demonstrated for the Li–Ca–Zn–N system.[7]

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(28) Robie, R. A.; Hemmingway, B. S.; Fisher, J. R. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures*; Geological Survey Bull. 1452; Government Printing Office: Washington, DC, 1979.

(29) McHale, J. M.; Navrotsky, A.; Perrotta, A. J. *J. Phys. Chem.* **1997**, *101*, 603.