Lithium Calcium Imide [Li$_2$Ca(NH)$_2$] for Hydrogen Storage: Structural and Thermodynamic Properties

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In an attempt to tailor the dehydrogenation temperature of lithium imides, we have investigated the ternary imide Li$_2$Ca(NH)$_2$, which crystallizes in a structure (space group $P\bar{3}m1$) different from that of Li$_2$Mg(NH)$_2$ (space group $Iba2$). First-principles density functional calculations yield the stable ground-state structure along with the correct hydrogen positions. Compared with the structural and thermodynamic data of the pure lithium imides, those Ca or Mg partially substituted ternary imides show decreased reaction enthalpies as well as dehydrogenation temperatures.

Introduction

Complex binary hydrides involving light metals such as Li and Mg have been extensively investigated because of their high gravimetric storage capacity. In particular, lithium nitride and imides/amides have been found to exhibit strong affinity for H$_2$ because of the reversible reactions[1,2]

$$\text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH} \quad (1)$$

The enthalpies of formation of each of the constituents, as well as the heats of reaction (exothermic) have been estimated from first-principles density functional calculations.[3,4] Li atoms are ionized as Li$^+$ cations, while [NH$_2$]$^-$ forms a complex anion, and it is the strength of the interaction between Li$^+$ and [NH$_2$]$^-$ that dictates the enthalpy of reactions and hence the desorption kinetics of H$_2$.[5] In order to lower the desorption temperature to the permissible range, one has to tailor the above-mentioned bonding between Li$^+$ and [NH$_2$]$^-$. One way to do this is to alloy the binary hydride with some divalent alkaline earth metal such as Ca or Mg, and these ternary complex hydrides have been synthesized in recent years.[6,7]

First-principles density functional calculations can reliably predict the reaction enthalpies and hence can serve as a guide to tailor the dehydrogenation temperature, ensuring that it lies in a realistic range.[8,9] In this paper we present the results of our systematic first principles investigations of the binary as well as ternary imides/amides whose structural parameters have been measured.[6,10–12] Powder X-ray diffraction data yield lattice parameters as well as positions of Li, N, and Ca for Li$_2$Ca(NH)$_2$; however, the H positions have not been conclusively established. There are several possible high-symmetry positions (Wyckoff positions 2d, 6i) that can be occupied by H. We use total energy criterion to identify the ground-state structure and configuration for Li$_2$Ca(NH)$_2$. A closely related compound Li$_2$Mg(NH)$_2$ has orthorhombic structure space group $Iba2$ (no. 45),[6] in contrast to that of Li$_2$Ca(NH)$_2$, which has a trigonal structure space group $P\bar{3}m1$ (no. 164).[7] Detailed investigation of Li$_2$Mg(NH)$_2$ has been reported by two groups,[13,14] while there has been no such studies on Li$_2$Ca(NH)$_2$ for hydrogen storage. It is to be noted that,

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TABLE 1: Optimized H-Atom Coordinates in Li$_2$Ca(NH)$_2$ (Space Group $P\bar{3}m1$) with N, Ca, and Li Atom Positions Obtained from X-ray Diffraction Data[7]

H1 (near atom N1)	H2 (near atom N2)	Wyckoff positions
(0.3333, 0.6667, 0.4307)	(0.6667, 0.3333, 0.5693)	2d
(0.3333, 0.6667, 0.0909)	(0.6667, 0.3333, 0.9091)	2d
(0.1838, 0.8162, 0.1723)	(0.8162, 0.1838, 0.8277)	6i (set 1)
(0.6324, 0.8162, 0.1723)	(0.3676, 0.1838, 0.8277)	
(0.1838, 0.3676, 0.1723)	(0.8162, 0.6324, 0.8277)	
(0.4278, 0.5722, 0.1179)	(0.5722, 0.4278, 0.8821)	6i (set 2)
(0.1444, 0.5722, 0.1179)	(0.8556, 0.4278, 0.8821)	
(0.4278, 0.8556, 0.1179)	(0.5722, 0.1444, 0.8821)	
(0.4875, 0.5125, 0.3243)	(0.5125, 0.4875, 0.6757)	6i (set 3)
(0.0250, 0.5125, 0.3243)	(0.9750, 0.4875, 0.6757)	
(0.4875, 0.9750, 0.3243)	(0.5125, 0.0250, 0.6757)	

compared to Li, Mg is more electronegative, while K is a more electropositive element.[15] However, the electronegativity of Ca has more or less the same value as that of Li. Because of the similarity between these two compounds from the H-storage point of view, we have carried out a comparative study of the ground-state cohesive and thermodynamic properties of Li$_2$Mg(NH)$_2$ and Li$_2$Ca(NH)$_2$ along with the parent compounds, using the same computational scheme and under identical conditions.

Computational Details

Electronic structure and total energies were calculated with the Vienna *ab initio* simulation package (VASP),[16,17] based on density functional theory (DFT).[18,19] Projector-augmented wave (PAW) potentials[20] were employed for the elemental constituents, viz., H, Li, N and Ca, Mg potentials, which contained one, three, five, two, and two valence electrons, respectively. The GGA calculation was performed with the Perdew–Wang[21,22] exchange-correlation potential. The *k*-points mesh was generated by the Monkhorst–Pack method,[23] and all results were tested for convergence with respect to the mesh size. In all calculations, self-consistency was achieved with a 0.1 meV convergence total energy. For high-precision calculation, we used a cutoff energy of 600 eV for plane wave basis. For obtaining the optimized ground-state
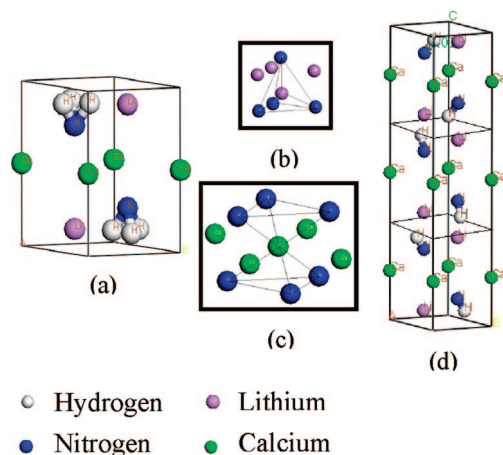
Figure 1. (a) Li$_2$Ca(NH)$_2$ structure in 6i (set 2) configuration (see text for details); Hydrogen occupies any of the one out of three equivalent positions above and below the respective nitrogen atoms. (b) The Tetrahedral hole created by the N-lattice that is occupied by the Li → 2d site (1/2, 2/3, 0.8841). d(Li−N) = 2.223 Å × 3, d(Li−Li) = 2.479 Å. (c) The octahedral hole created by the N-lattice that is occupied by the Ca →1b site (0, 0, 1/2). d(Ca−N) = 2.518 Å × 6, d(Ca−Ca) = 3.566 Å. (d) Supercell constructed by repeating the unit cell along the *c*-axis with different possible N−H bond orientations.

geometry,[24,25] atomic forces were converged to less than 0.001 eV/Å. We first carried out the fully relaxed self-consistent electronic structure calculations of the parent compound (i.e., without H-insertion) Li$_2$CaN$_2$.

Since no neutron diffraction data are available and X-ray diffraction is insensitive to hydrogen atoms, first-principles calculations were performed to identify the positions of the hydrogen atoms in the Li$_2$Ca(NH)$_2$ lattice. The lattice parameters as well as the positions of Li, N, and Ca in Li$_2$Ca(NH)$_2$ yielded by powder X-ray diffraction analyses were fixed.[7] Only the H atom coordinates are relaxed. The initial sites of each H were randomly selected around each N. After relaxation, H atoms were located at 2d and 6i sites of space group $P\bar{3}m1$, as shown in Table 1. H atoms can not fully occupy equivalent positions of the 6i sites. It is likely that each H in Li$_2$Ca(NH)$_2$ is delocalized over the 6i equivalent positions around each N to satisfy the crystallographic symmetry. Next we have constructed several model structures for Li$_2$Ca(NH)$_2$ with H occupying different possible 2d or 6i positions (Table 1) and fully relax. The estimated total energies are lowered by ~600 meV for the 6i configuration, which is therefore energetically more favorable, and this structure is shown in Figure 1a with the three possible orientations of the N−H bond in Li$_2$Ca(NH)$_2$. The Li atoms in the 2d site occupy the tetrahedral hole created by the N-lattice (Figure 1b), while Ca atoms in the 1b site occupy the trigonal prismatic hole created by the N-lattice (Figure 1c). Li−Ca separation (~3.077 Å) is ~25% elongated as compared to the Li−Li bond length, which is very similar to the asymmetric Li−Li bond lengths in Li$_3$N.[26] Most crucial, however, is the N−H bond where hydrogen can partially or randomly occupy

the three possible positions with 1/3 probability of occupancy at any instant of time. In order to mimic this quantum delocalization effect,[27] we have constructed a supercell by repeating the unit cell three times along the C axis and considered all these three possible H-positions built in the first, second, and third one-third of the super cell (Figure 1d). We have estimated the total energy for all the three different configurations designated as 6i (set 1), 6i (set 2), and 6i (set 3) and found that configuration 6i (set 2) is energetically most favorable.

Results and Discussion

Electronic Structure. We first calculate the self-consistent electronic structure of pure Li-imide Li$_2$NH without any ternary addition. There have been calculations reported in the literature for Li$_2$NH with different symmetries. Song and Guo[28] found cubic $F\bar{4}3m$ structure to be more stable than $Fm\bar{3}m$. However, our results indicate orthorhombic $Ima2$ structure[12] to have lower ground-state energy (by ~0.6 eV) than the cubic structure. Our resulting total as well as partial densities of states (DOS; Figure 2) clearly show a semiconducting behavior with a GGA band gap of ~2.3 eV and a two-humped structure of the occupied part of DOS that agrees with the published results.[3] N-2p bands predominantly contribute to the occupied DOS as expected, while H-s character prevails in the lowest occupied band. Li behaves like a cation transferring its electron to [NH]$^{2-}$.

The parent compound Li$_2$CaN$_2$ of the ternary hydride Li$_2$Ca(NH)$_2$ turns out to be metallic with the Fermi level lying near the anti-bonding peak. However, on introduction of hydrogen in this anti-La$_2$O$_3$ structure, this peak is pushed down below Fermi level, thereby opening a band gap of ~2.3 eV, which is very similar to that of the pure imide. The Ca-4s band has a dominant contribution to the DOS and also affects the bonding between the Li$^+$ cation and the [NH]$^{2-}$ anion. The lower bonding peak arises because of strong hybridization between the H-s and N-p orbitals. The upper bonding peaks arise out of Li−N interactions.

For the sake of comparison, we have also carried out first-principles electronic structure calculation of Li$_2$Mg(NH)$_2$, which crystallizes in orthorhombic structure with a space group of $Iba2$.[6] The supercell contains 112 atoms. The optimized structure has a band gap of ~2.35 eV, which agrees with the other published results[8] available on Li$_2$Mg(NH)$_2$.

Cohesive and Thermodynamic Properties. We have estimated the average N−H bond lengths, hydrogen removal energies, and the enthalpy of formation of Li$_2$Ca(NH)$_2$ and Li$_2$Mg(NH)$_2$ and compared the results with the same quantities estimated for the pure Li imides and amides.

The enthalpy of formation is the most fundamental and important quantity for hydrogen storage materials, which can be estimated from the difference between the energies before and after hydriding reaction. The enthalpy change in a reaction at 0 K was calculated using

TABLE 2: Enthalpies of Formation, H-Removal Energies, and the N−H Bond Lengths for Pure Li Amide/Imide and That with Ternary Substitution

system	structure space group (formula unit)	chemical reaction	reaction enthalpy kJ/mol-H$_2$	ΔE_H eV	average N−H bond length Å
LiNH$_2$	tetragonal $I\bar{4}$ (4f.u)[10,11]	LiNH$_2$ + LiH ↔ Li$_2$NH + H$_2$	68.9 [73.6][3]	2.78	1.03
Li$_2$NH	orthorhombic $Ima2$ (8f.u)[12]	Li$_2$NH + LiH ↔ Li$_3$N + H$_2$	108.8 [118][14]	1.99	1.04
Li$_2$Ca(NH)$_2$	trigonal $P\bar{3}m1$ (3f.u)[7]	3Li$_2$Ca(NH)$_2$ + 2LiH ↔ 4Li$_2$NH + Ca$_3$N$_2$ + 2H$_2$	102.6	1.88	1.05
Li$_2$Mg(NH)$_2$	orthorhombic $Iba2$ (16f.u)[6]	3Li$_2$Mg(NH)$_2$ + 2LiH ↔ 4Li$_2$NH + Mg$_3$N$_2$ + 2H$_2$	82.8 [84][14]	1.89	1.05

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$$\Delta H = \sum E_{products} - \sum E_{reactants} \quad (2)$$

where E is the total energy of one of the bulk structures of interest as calculated by DFT. We investigate the thermodynamics of hydrogen release from the mixture of Li₂Ca(NH)₂ and LiH, which allows us to draw comparisons with the thermodynamics of hydrogen release from the other Li−N based compounds, viz., parent imides and amides along with Li₂Mg(NH)₂ and LiH. Table 2 summarizes our results for the specific exothermic chemical reactions that take place for H₂

desorption in different binary and ternary hydrides. We observe that ΔH decreases from 108.8 kJ/mol-H₂ in Li-imide to 102.6 kJ/mol-H₂ and to 82.8 kJ/mol-H₂ for Ca and Mg ternary imides, respectively.[29] The corresponding ΔH value estimated by Araujo et al.[14] is 118 kJ/mol-H₂ for Li₂NH, assuming *Pnma* space group, and for Li₂Mg(NH)₂ is 84 kJ/mol-H₂. It is interesting to note that the N−H bond lengths increase on ternary addition, indicating the weakening of the N−H bonds. Hydrogen removal energy ΔE_H for Li₂Ca(NH)₂ has been calculated using the relation[14]
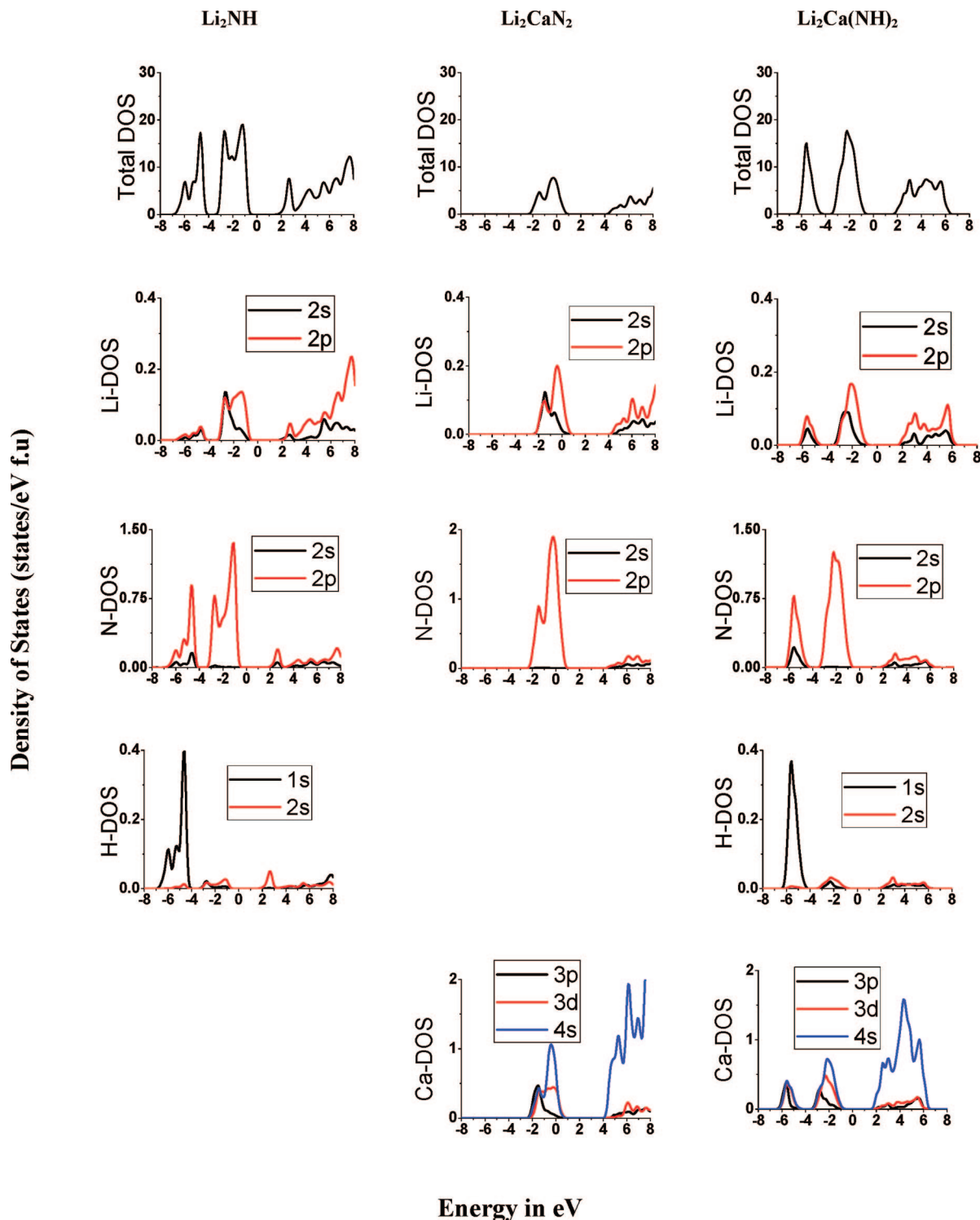

Figure 2. Total and partial electronic DOS calculated for Li₂NH, Li₂CaN₂, and Li₂Ca(NH)₂.

$$\Delta E_{\mathrm{H}}[\mathrm{Li_2Ca(NH)_2}] = E_{\mathrm{T}}[\mathrm{Li_6Ca_3N_6H_5}] + (1/2)E_{\mathrm{T}}[\mathrm{H_2}] -$$
$$E_{\mathrm{T}}[\mathrm{Li_6Ca_3N_6H_6}] \quad (3)$$

where $E_{\mathrm{T}}[\mathrm{Li_6Ca_3N_6H_5}]$, $E_{\mathrm{T}}[\mathrm{Li_6Ca_3N_6H_6}]$, and $E_{\mathrm{T}}[\mathrm{H_2}]$ are the ground-state total energies of $\mathrm{Li_6Ca_3N_6H_5}$, the $\mathrm{Li_6Ca_3N_6H_6}$ cell, and the $\mathrm{H_2}$ molecule in the gas phase, respectively. For $\mathrm{Li_2Ca(NH)_2}$, we have used the optimized structure shown in Figure 1, and those for the others are optimized structures as shown in Table 2. It is interesting to note that ΔE_{H} reduces by $\sim$5.5% for the ternary Ca-imide and $\sim$5.0% for ternary Mg-imide.

Conclusion

The ternary imide $\mathrm{Li_2Ca(NH)_2}$ synthesized via thermal dehydrogenation of a mixture of $\mathrm{LiNH_2}$ and $\mathrm{CaH_2}$ has been investigated experimentally and using density functional calculations. While the positions of lithium, calcium, and nitrogen have been successfully determined from careful structure analysis, a first-principles approach has been used to determine the hydrogen positions. The enthalpy of reaction $\Delta H = T\Delta S$ for pure lithium imide decreases on ternary addition. Assuming the entropy change ΔS to remain more or less constant during the reactions, the dehydrogenation temperature T is expected to come down to a desirable range. The H removal energy correspondingly decreases by about 5.5% with a concomitant increase in the N—H bond length by about 0.01 Å for the ternary Ca imide system. These numbers are comparable to those for a closely related ternary compound, viz., $\mathrm{Li_2Mg(NH)_2}$.

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(29) We have neglected the small corrections arising out of the zero point energy (ZPE) difference between the reactants (Table 2), which are estimated to be in the range $\sim$80−130 meV (*vide* ref. 13, Table 1).