3

Ternary Imides For Hydrogen Storage

3.1 Introduction

Complex binary hydrides involving light metals such as Li and Mg have been extensively investigated due to 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:

\begin{equation}
\ce{Li_3N + 2H2 <-> Li2NH + LiH + H2 <-> LiNH2 + 2LiH} \tag{3.1}
\end{equation}

The enthalpies of formation of each of the constituent, as well as the heats of reactions (exoergic) have been estimated from first principle density functional calculations.\(^3,4\) Li atoms are ionized as $\text{Li}^+$ cations, while $[\text{NH}_2]^{-}$ forms a complex anion and it is the strength of the interaction between $\text{Li}^+$ and $[\text{NH}_2]^{-}$ 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 $\text{Li}^+$ and $[\text{NH}_2]^{-}$. 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 chapter we present the results of our systematic first principles investigations of the binary as well as ternary imides/amides whose structural
Powder X-ray diffraction data yield lattice parameters as well as positions of Li, N, and Ca for $Li_2Ca(NH)_2$, 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 $Li_2Ca(NH)_2$. A closely related compound $Li_2Mg(NH)_2$ has orthorhombic structure space group $Iba2$ (no: 45), in contrast to that of $Li_2Ca(NH)_2$ which has a trigonal structure space group $P-3m1$ (no: 164). Detailed investigation of $Li_2Mg(NH)_2$ has been reported by two groups while there has been no such studies on $Li_2Ca(NH)_2$ for hydrogen storage. It is to be noted that compared to Li, Mg is more electronegative while K is more electropositive element. However 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 $Li_2Mg(NH)_2$ and $Li_2Ca(NH)_2$ along with the parent compounds using the same computational scheme and under identical conditions.

### 3.2 Computational Details

Electronic structure and total energies were calculated with the Vienna ab initio simulation package (VASP), based on DFT. Projector-augmented wave (PAW) potentials 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 exchange-correlation potential. The k-points mesh was generated by the Monkhorst-Pack method 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 geometry, 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) $Li_2CaN_2$. Since no neutron diffraction data are available and X-ray diffraction is insensitive to hydrogen atom, first principles calculation was applied to identify the position of hydrogen.
atom in the $Li_2Ca(NH)_2$ lattice. The lattice parameters as well as the positions of Li, N, and Ca in $Li_2Ca(NH)_2$ yielded by powder X-ray diffraction analyses were fixed. Only the H atom coordinates are relaxed. The initial sites of each H are randomly selected around each N. After relaxation, H atoms are located at 2d and 6i sites of space group P-3m1, as shown in the Table 3.1. H atoms can not fully occupy equivalent positions of the 6i sites. It is likely that each H in $Li_2Ca(NH)_2$ is delocalized over the 6i equivalent positions around each N to satisfy the crystallographic symmetry. Next we have constructed several model structures for $Li_2Ca(NH)_2$ with H occupying different possible 2d or 6i positions (Table 3.1) and fully relaxed. The estimated total energies are lowered by $\approx 600$ meV for the 6i configuration which is therefore energetically more favorable and this structure is shown in Figure 3.1(a) with the three possible orientations of the N-H bond in $Li_2Ca(NH)_2$. The Li atoms in 2d-site occupies the tetrahedral hole created by the N-lattice [Figure 3.1(b)], while Ca atoms in 1b site occupy the trigonal prismatic hole created by the N-lattice [Figure 3.1(c)]. Li-Ca separation ($\approx 3.077$ Å) is $\approx 25\%$ elongated as compared to the Li-Li bond length which is very similar to the asymmetric Li-Li bond lengths in $Li_3N$. 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 we have constructed a supercell by repeating the unit cell three times along the C axis and considered all these 3 possible H-positions built in the first, second and third 1/3rd of the super cell [Figure 3.1(d)]. 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.

3.3 Results And Discussion

3.3.1 Electronic Structure

We first calculate the self consistent electronic structure of pure Li-imide $Li_2NH$ without any ternary addition. There have been calculations reported in the literature for $Li_2NH$ with different symmetries. Song and Guo found cubic $F43m$ structure to be more
Figure 3.1: (a) $Li_2Ca(NH)_2$ 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 Li $\rightarrow$ 2d site (1/3, 2/3, 0.8841). $d(\text{Li-N}) = 2.223 \text{ Å}$, $d(\text{Li-Li}) = 2.479 \text{ Å}$. (c) The Octahedral hole created by the N-lattice that is occupied by Ca $\rightarrow$ 1b site (0, 0, 1/2). $d(\text{Ca-N}) = 2.518 \text{ Å}$, $d(\text{Ca-Ca}) = 3.566 \text{ Å}$. (d) Supercell constructed by repeating the unit cell along the c-axis with different possible N-H bond orientations.
Table 3.1: 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 XRD data

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Wyckoff positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 (Near atom N1)</td>
<td>H2 (Near atom N2)</td>
<td></td>
</tr>
<tr>
<td>(0.3333, 0.6667, 0.4307)</td>
<td>(0.6667, 0.3333, 0.5693)</td>
<td>2d</td>
</tr>
<tr>
<td>(0.3333, 0.6667, 0.0909)</td>
<td>(0.6667, 0.3333, 0.9091)</td>
<td>2d</td>
</tr>
<tr>
<td>(0.1838, 0.8162, 0.1723)</td>
<td>(0.8162, 0.1838, 0.8277)</td>
<td>6i (set 1)</td>
</tr>
<tr>
<td>(0.6324, 0.8162, 0.1723)</td>
<td>(0.3676, 0.1838, 0.8277)</td>
<td>6i (set 1)</td>
</tr>
<tr>
<td>(0.1838, 0.3676, 0.1723)</td>
<td>(0.8162, 0.6324, 0.8277)</td>
<td>6i (set 1)</td>
</tr>
<tr>
<td>(0.4278, 0.5722, 0.1179)</td>
<td>(0.5722, 0.4278, 0.8821)</td>
<td>6i (set 2)</td>
</tr>
<tr>
<td>(0.1444, 0.5722, 0.1179)</td>
<td>(0.8556, 0.4278, 0.8821)</td>
<td>6i (set 2)</td>
</tr>
<tr>
<td>(0.4278, 0.8556, 0.1179)</td>
<td>(0.5722, 0.1444, 0.8821)</td>
<td>6i (set 2)</td>
</tr>
<tr>
<td>(0.4875, 0.5125, 0.3243)</td>
<td>(0.5125, 0.4875, 0.6757)</td>
<td>6i (set 3)</td>
</tr>
<tr>
<td>(0.0250, 0.5125, 0.3243)</td>
<td>(0.9750, 0.4875, 0.6757)</td>
<td>6i (set 3)</td>
</tr>
<tr>
<td>(0.4875, 0.9750, 0.3243)</td>
<td>(0.5125, 0.0250, 0.6757)</td>
<td>6i (set 3)</td>
</tr>
</tbody>
</table>

stable than $Fm\bar{3}m$. However, our results indicate orthorhombic $Ima2$ structure to have lower ground state energy (by $\approx 0.6$ eV) than the cubic structure. Our resulting total as well as partial densities of states [Figure 3.2] clearly shows an semi conducting behavior with a GGA band gap of $\approx 2.3$ eV and a two humped structure of the occupied part of DOS that agrees with the published results 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 $[NH]^2\text{--}$. 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 $\approx 2.3$ eV which is very similar to that of the pure imide. Ca-4s band has a dominant contribution to the DOS and also affects the bonding between the Li$^+$ cation and the $[NH]^2\text{--}$ anion. The lower bonding peak arises because of strong hybridization between H-s and N-p orbital. The upper bonding peaks arise out of Li-N interactions. For the sake of comparison we have also carried out first principle electronic structure calculation of Li$_2$Mg(NH)$_2$ which crystallizes in Orthorhombic structure with a space group $Iba2$.
The supercell contains 112 atoms. The optimized structure has a band gap of \( \approx 2.35 \text{ eV} \) which agrees the other published results\(^8\) available on \( \text{Li}_2\text{Mg}(NH)_2 \).

### 3.3.2 Cohesive And Thermodynamic Properties

We have estimated the average N-H bond lengths, hydrogen removal energies and the enthalpy of formation of \( \text{Li}_2\text{Ca}(NH)_2 \) and \( \text{Li}_2\text{Mg}(NH)_2 \) and compared the results with the same quantities estimated for the pure Li imides and amides.

Table 3.2: Enthalpies of Formation, H-Removal Energies, and the N-H Bond Lengths for Pure Li Amide/Imide and That with Ternary Substitution

<table>
<thead>
<tr>
<th>system</th>
<th>structure space group (formula unit)</th>
<th>chemical reaction</th>
<th>reaction enthalpy ((\text{KJ/mol-H}_2))</th>
<th>(\Delta E_H) ((\text{eV}))</th>
<th>average N-H bond length ((\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LiNH}_2)</td>
<td>tetragonal (I4) ((4\text{f.u})^{10,11})</td>
<td>(\text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2)</td>
<td>68.9 ((73.6)^3)</td>
<td>2.78</td>
<td>1.03</td>
</tr>
<tr>
<td>(\text{Li}_2\text{NH})</td>
<td>orthorhombic (Ima2) ((8\text{f.u})^{12})</td>
<td>(\text{Li}_2\text{NH} + \text{LiH} \leftrightarrow \text{Li}_3\text{N} + \text{H}_2)</td>
<td>108.8 ((118)^{14})</td>
<td>1.99</td>
<td>1.04</td>
</tr>
<tr>
<td>(\text{Li}_2\text{Ca}(NH)_2)</td>
<td>trigonal (P3\text{m1}) ((3\text{f.u})^{7})</td>
<td>(3\text{Li}_2\text{Ca}(NH)_2 + 2\text{LiH} \leftrightarrow 4\text{Li}_2\text{NH} + \text{Ca}_3\text{N}_2 + 2\text{H}_2)</td>
<td>102.6</td>
<td>1.88</td>
<td>1.05</td>
</tr>
<tr>
<td>(\text{Li}_2\text{Mg}(NH)_2)</td>
<td>orthorhombic (Iba2) ((16\text{f.u})^6)</td>
<td>(3\text{Li}_2\text{Mg}(NH)_2 + 2\text{LiH} \leftrightarrow 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 2\text{H}_2)</td>
<td>82.8 ((84)^{14})</td>
<td>1.89</td>
<td>1.05</td>
</tr>
</tbody>
</table>

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

\[
\Delta H = \Sigma E_{products} - \Sigma E_{reactants} \tag{3.2}
\]

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
Figure 3.2: Total and partial Electronic Density of States calculated for Li₂NH, Li₂CaN₂, Li₂Ca(NH)₂


\[ \Delta E_H[Li_2Ca(NH)\_2] = E_T[Li_6Ca_3N_6H_5] + \frac{1}{2}E_T[H_2] - E_T[Li_6Ca_3N_6H_6] \] (3.3)

Where \( E_T[Li_6Ca_3N_6H_5] \), \( E_T[Li_6Ca_3N_6H_6] \), and \( E_T[H_2] \) are the ground state total energies of \( Li_6Ca_3N_6H_5 \), \( Li_6Ca_3N_6H_6 \) cell and \( H_2 \) molecule in the gas phase, respectively. For \( Li_2Ca(NH)_2 \) we have used the optimized structure shown in Figure 3.1 and that of for the others are optimized structure of as shown in Table 3.2. It is interesting to note that \( \Delta E_H \) reduces by \( \approx 5.5\% \) for the ternary Ca-imide and \( \approx 5.0\% \) for ternary Mg-imide.

### 3.4 Conclusion

The ternary imide \( Li_2Ca(NH)_2 \) synthesized via thermal dehydrogenation of a mixture of \( LiNH_2 \) and \( CaH_2 \) 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, first principle 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 \( \Delta S \) 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

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1We have neglected the small corrections arising out of the Zero Point Energy (ZPE) difference between the reactants (Table 3.2) which are estimated to be in the range 80 -130 meV (vide Reference, Table 3.1)
ternary Ca imide system. These numbers are comparable to those for a closely related ternary compound viz; $Li_2Mg(NH)_2$. 
Bibliography


