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First-Principles Study of the Li-Na-Ca-N-H System: Compound Structures and Hydrogen-Storage Properties

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First-Principles Study of the Li-Na-Ca-N-H System: Compound Structures and Hydrogen-Storage Properties

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in Materials Science and Engineering

by

Pattanasak Teeratchanan

2012
ABSTRACT OF THE THESIS

First-Principles Study of the Li-Na-Ca-N-H System: Compound Structures and Hydrogen-Storage Properties

by

Pattanasak Teeratchanan

Master of Science in Materials Science and Engineering
University of California, Los Angeles, 2012
Professor Vidvuds Ozolins, Chair

With the goal of finding new materials as a resource for alternative energy, various classes of hydrogen storage materials have been developed. One of the possible candidates is solid-state metal amide/imide. These chemically bounded solid-state materials will release hydrogen when heated and rehydrogenate upon an increase in pressure. Therefore, this practical requirement limits the operating temperature to between -40 to 80 °C and the pressure to between 1 to a few hundred bars. The main goal is to find new metal amide/imide materials within these specified thermodynamics ranges. Note that normally not only the thermodynamics but kinetics properties are also crucial. While a kinetics study would tell how fast hydrogen can be released and absorbed, this research focuses on the thermodynamics part only.
First-principle calculations are useful tools for predicting new materials structures and exploring hydrogen-released reactions. Since density functional theory (DFT) can provide the accuracy as small as quantum-mechanical level, it is used to calculate properties of these amide/imide materials. Other tools used in this research include: prediction of ground-state structures of some amide/imide materials has been explored by electrostatics-based calculation (PEGS), Grand Canonical Linear Programming Method (GCLP) is used to calculate allowed hydrogen-released reactions under the specified thermodynamics range, and zero-point vibrational energy is calculated by phonons calculations.

Here, all known and predicted crystal structures of materials in the Li-Na-Ca-N-H system are investigated in order to find the allowed hydrogen-released reactions.
The thesis of Pattanasak Teeratchanan is approved.

Dwight C. Streit

Bruce S. Dunn

Vidvuds Ozolins, Committee Chair

University of California, Los Angeles

2012
To my family
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CHAPTER 1

Introduction

1.1 Hydrogen Storage

1.1.1 General Background

The fuel cell is a device used to convert chemical energy to electrical energy. Since hydrogen is the most common fuel for the fuel cell, hydrogen storage materials provide a gaseous hydrogen supply as the input to the fuel cell. The particular type of fuel cell that uses hydrogen as the input is the proton exchange membrane (PEM) fuel cell. As shown schematically in Fig 1.1, \( \text{H}_2 \) molecules are dissociated at the anode side into electrons and protons. The electrons pass through an external circuit, while the protons can pass through the proton-conducting membranes to recombine with electrons and oxygen, resulting in \( \text{H}_2\text{O} \) as the product at the cathode side.

![Figure 1.1: PEM fuel cell](image)

Figure 1.1: PEM fuel cell [1]
Solid-state hydrogen storage is desirable due to the fact that it has superior volume density when compared to liquid and gaseous forms. Moreover, the chemical or physical bonds of solid-state hydrogen storage reduce the cooling cost of compressed hydrogen. For solid-state hydrogen storage, not only is the volumetric density important but also a higher gravimetric density is significant for mobile applications.

The goal of this work is to study the thermodynamics properties of both the dehydrogenation and rehydrogenation reactions. In practice, dehydrogenation only occurs at ambient pressure (1 bar) and a maximum temperature of 80 °C. As a result of these conditions, the corresponding dehydrogenation entropy is 0.135 kJ/K.mol H₂ and the reaction enthalpy is 47 kJ/mol H₂. In contrast, for the rehydrogenation, the temperature should be at ambient temperature and the pressure should not be higher than a few-hundred bar. The rehydrogenation entropy corresponding to a temperature of 300K and a pressure of 200 bar is 0.087 kJ/K.mol H₂, leading to a reaction enthalpy of 26 kJ/mol H₂. Thus, the thermodynamics limits the enthalpy of reaction of the candidate solid-state hydrogen storage materials to range of 25 to 45 kJ/mol H₂ [2].

While the thermodynamics sets a limitation of the enthalpy of reaction and determines the theoretical amount of hydrogen released, calculation of the kinetics of the reaction will provide insight into how practical this reaction can be overall. A study of the kinetics can tell us how fast hydrogen absorption and desorption occurs, what the limiting process is, and how to improve the reaction.
1.1.2 Free Energy of Hydrogen

From the equipartition theorem, the enthalpy of H$_2$ per molecule is:

$$H_{H_2} = \frac{7}{2} k_B T$$  \hspace{1cm} \text{Eq 1}

This is due to the three translational degrees of freedom, two rotational modes, and the pV term. The vibrational mode is neglected when studying hydrogen storage reactions.

From the Gibbs free energy, given by \( dG = Vdp - SdT \), we can determine the entropy due to constant-pressure and constant-temperature, respectively, by:

$$S(T) = \frac{7}{2} k_B \ln(T) + A_0$$  \hspace{1cm} \text{Eq 2}

and

$$S(p) = -k_B \ln(p) + B_0$$  \hspace{1cm} \text{Eq 3}

Fitting Eq 2 and Eq 3 with experimental data where

$$S_{H_2}(T = 300 K, p = 1 \text{ bar}) = 130.6 \text{ J/K mol}(H_2)$$  \hspace{1cm} \text{Eq 4}

, and the entropy of gaseous H$_2$ equals:

$$S_{H_2}(T, p) = k_B \left( \frac{7}{2} \ln(T) - \ln(p) - 4.22 \right)$$  \hspace{1cm} \text{Eq 5}

From Eq 1, Eq 5, and \( G = H + TS \),

$$G_{H_2}(T, p) = k_B T \left[ \frac{7}{2} (1 - \ln(T)) + \ln(p) + 4.22 \right] + H_{ZPE} + H_{\text{stat}}$$  \hspace{1cm} \text{Eq 6}

, where \( H_{ZPE} \) is the zero-point vibrational energy of an H$_2$ molecule and \( H_{\text{stat}} \) is the electronic energy from DFT calculations [2].
CHAPTER 2

General Methods

2.1 Density Functional Theory (DFT)

In order to understand the properties of matter at the atomic level, one must devise a method for simulating the interactions between atoms. The impossibility of solving Schrödinger equation of complex systems prohibits us from getting exact analytical solution. The recent proliferation of computational methods has resulted in a slew of techniques for numerically solving wavefunctions and energies. Still, these computational techniques are inhibited by unknown parameters, i.e. interaction energies in complicated system calculations. The need for simpler computational methods within the limit of acceptable accuracy and computation time is clear. One of the most widely used methods is density functional theory.

2.1.1 Fundamental Theory

From the Schrödinger equation,

\[ \hat{H} \psi = E \psi \quad \text{Eq 7} \]

where \( \hat{H} \) is the Hamiltonian operator, \( E \) is the energy eigenstate, and \( \psi \) is the wavefunction. The analytic solution of this equation is possible only for a one electron element, notably hydrogen atom. In case of atoms with many electrons, the complication arises from the higher degrees of freedom of the system from both electrons and nuclei. For simplicity, the effect of the nuclei on surrounding electrons can be broken into a separate calculation. This is called Born Oppenheimer approximation. The reason behind this is that nuclei have mass 1800 times the
mass of electrons, so, the changes of nuclei are much slower than that of electrons. We can treat nuclei as having fixed positions and solve for a given set of electrons moving in the field of a set of nuclei to find the lowest energy state of electrons. The Schrodinger equation corresponding to this is

$$\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \psi = E\psi$$  \hspace{1cm} \text{Eq 8}$$

where, m is the electron mass. The three terms in the brackets are the kinetic energy of each electron, the interaction energy between each electron and the sum of atomic nuclei, and the interaction between different electrons, respectively. This equation applies to each electronic wavefunction of the N electrons’ positions, $\psi = \psi(r_1, \ldots, r_N)$. Although the wavefunction can be treated as a non-interacting electrons wavefunction or $\psi = \psi_1(r)\psi_2(r)\ldots\psi_N(r)$, it is still computationally expensive because it involves three degrees of freedoms for each electron.

The computationally feasible approach is to calculate the electron density, instead of the individual electron wavefunctions. The density of electrons at position r can be written as

$$n(r) = 2 \sum_i \psi_i^*(r)\psi_i(r).$$  \hspace{1cm} \text{Eq 9}$$

The factor 2 comes from the spin contributions (up and down spins). This density calculation reduces the dimension of the problem to only three degrees of freedoms.

Hohenberg and Kohn proposed two theorems: The first theorem states that the ground state energy is a unique functional of the electron density. The second theorem states that the density that minimizes the energy of overall functional is the true ground state density. Unfortunately, there is still an unknown density functional. The messages from two theorems above only imply that there exists the functional and the one that gives the lowest energy is the ground state density functional [3, 4, 5, 6, 7, 8].
2.1.2 Kohn-Sham DFT

The Kohn-Sham equations have the form

$$
\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \tag{Eq 10}
$$

The four terms in the blanket are the kinetic energy of electron, the potential energy of an electron and a collection of atomic nuclei, the Hartree potential that describes the Coulomb interaction between an electron and the total electron density, and the exchange-correlation energy, respectively. It is worth noting that the Hartree potential actually overcounts the interaction because the electron density includes all electrons including the one in calculation. This error, however, is accounted for in the exchange-correlation term.

The Hartree potential can be expressed by

$$
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r'. \tag{Eq 11}
$$

The exchange potential is the derivative of the exchange energy with respect to electron density:

$$
V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)}. \tag{Eq 12}
$$

2.1.3 Exchange-Correlation Functional

As mention above, this exchange-correlation functional is not known. This functional includes all the corrections to the Kohn-Sham equation. In general, there are two common ways to approximate this functional.

2.1.3.1 Local Density Approximation

In the non-interacting uniform electron gas, the density is constant at all points in space, i.e. $n(r) = \text{constant}$. Then, the exchange-correlation potential can be written as

$$
V_{XC}(r) = V_{XC}^{\text{electron gas}}[n(r)] \tag{Eq 13}
$$
This approximation uses only the local density to define the exchange-correlation functional [3, 4, 5].

2.1.3.2 Generalized Gradient Approximation

Another way to approximate the exchange-correlation is called the generalized gradient approximation, GGA, method. This method includes the gradient of electron density term. The exchange-correlation potential is now given as

\[ V_{xc}^{GGA}(r) = V_{xc}[n(r), \nabla n(r)]. \]  \hfill (Eq 14)

Although, the GGA includes one more term than its LDA counterpart, it does not necessarily provide more accuracy in the results. The exchange-correlation also depends on the system considered [3, 4, 5].

2.1.4 Cut-off Energies

From the Bloch theorem, the solution of the Schrodinger equation in a periodic solid has the form

\[ \phi_k(r) = \exp(i k \cdot r) u_k(r) \]  \hfill (Eq 15)

where \( u_k(r) \) is the periodic function in the supercell, and \( \exp(i k \cdot r) \) is the plane wave in which \( k \) is the wave vector. The \( u_k(r) \) term can also be expanded in term of plane waves as

\[ u_k(r) = \sum_G c_G \exp[i G \cdot r] \]  \hfill (Eq 16)

where \( G \) is the vector in reciprocal space of any real lattice vector \( a_i \).

From this, the Bloch equation can be given as

\[ \phi_k(r) = \sum_G c_{k+G} \exp[i (k + G) \cdot r] \]  \hfill (Eq 17)

The kinetic energy of a plane wave with wavevector \( k+G \) is

\[ E = \frac{\hbar^2}{2m} |k + G|^2 \]  \hfill (Eq 18)
The solutions of lower energies are important than the higher ones. This limits the solutions, in which we are interested, to those with energies less than some values [2, 5]. By setting some maximum energies $E_{\text{cut}}$, Eq 18 can be written as,

$$\frac{\hbar^2}{2m} |k + G|^2 < E_{\text{cut}}$$

Eq 19

or in terms of the corresponding wavevector $G_{\text{cut}}$ as,

$$|k + G| < G_{\text{cut}}$$

Eq 20.

2.1.5 Pseudopotential Method

In general, the outer shell electrons are the most important due to the fact that a majority of interactions involve these electrons. The core electrons, however, cannot be neglected. Since these core electrons are contained within a small radius in real-space, a large cut-off energy is needed in reciprocal-space, which leads to increased computational complexity. The addition of pseudopotentials is then important in helping to reduce the number of planewaves needed to represent these core electrons and subsequently reduces the overall computational cost. One such commonly used pseudopotential method is known as projector augmented wave, or PAW [5].
CHAPTER 3
First-Principles Study of the Li-Na-Ca-N-H System: Compound Structures
and Hydrogen-Storage Properties

3.1 Introduction
The reaction of lithium amide with lithium hydride to form lithium imide and hydrogen reported by Chen et al [9] is shown in as the following equations:

\[
\text{LiNH}_2 + \text{LiH} \leftrightharpoons \text{Li}_2\text{NH} + \text{H}_2 \quad \text{Eq 21}
\]
\[
2\text{LiH} + \text{Li}_2\text{NH} \leftrightharpoons \text{Li}_4\text{NH} + \text{H}_2 \quad \text{Eq 22}
\]
These multiple-step reactions determine the total capacity of hydrogen output to be 11.3 wt.% H\(_2\) (6.8 and 4.5 wt.% H\(_2\), respectively). However, its operating temperature is too high (T = 283 °C and T = 569 °C, respectively) at p = 1 bar. Many attempts have been made to improve the thermodynamics of these reactions by mixing in other materials. Examples of systems that have already been calculated include: Li-Mg-N-H [10], Li-Ca-N-H [11], Na-Mg-N-H [12], and Mg-Ca-N-H [13].

In this work, the Li-Na-Ca-N-H compound system is chosen for study in the hope of finding a reaction with better thermodynamics properties.
3.2 Procedures and methods

3.2.1 Grand Canonical Linear Programming Method (GCLP)

To predict the allowed reactions in the Li-Na-Ca-N-H system, Akbarzadeh et al [14] developed the Grand Canonical Linear Programming Method (GCLP). Its formula is

\[ G(T, p) = \sum_{i=1}^{N_{\text{Compd}}} x_i F_i(T) - \frac{\mu_{H_2}(T, p)}{2} \sum_{i=1}^{N_{\text{Compd}}} x_i n_i^H \]  

**Eq 23**

Here, \( F_i(T) \) is the free energy of compound \( i \) with the total of \( N_{\text{Compd}} \) compounds in the system, \( x_i \) is the normalized molar fraction of compound \( i \), \( \mu_{H_2}(T, p) \) is the chemical potential of \( H_2 \), and \( n_i^H \) is the number of hydrogen atoms in compound \( i \). The Gibbs free energy is minimized with respect to \( x \) subject to the following constraint

\[ \sum_{i=1}^{N_{\text{Compd}}} x_i n_i^s = \text{const} \]  

**Eq 24**

where \( n_i^s \) is the number of atoms of type \( s \) in compound \( i \). In other words, the constraint is applied to all atoms except hydrogen. Therefore, we can predict those reactions, which are functions of temperature, resulting from a change in molar fraction \( x_i \).

3.2.2 Prototype electrostatic ground state search (PEGS)

The crystal structure of each compound has to be known in order to calculate its free energy. Unfortunately, some experimental data cannot always provide the exact positions of hydrogen atoms. Or some may give partially occupied atomic sites, which are the probability of that atom can be found in that certain position. In 2008, E. H. Majzoub and V. Ozolins [15] introduced a procedure for crystal structure generation and prediction for ionic compounds. This method uses
Metropolis Monte Carlo (MMC) simulated annealing to find the minimization energy. Its Hamiltonian can be presented as

\[ H = \sum_{i>j} \frac{Q_i Q_j}{R_{ij}} + \sum_{i>j} \frac{\mathcal{E}_{ss}}{R_{ij}^{12}}. \]  

Eq 25

The first term is electrostatic Coulomb energy, where \( Q_i \) denotes the ionic charges and the second term is the soft-sphere repulsive potential energy, which acts only when the atoms start to overlap. From this method, the ground state crystal structure of some otherwise incomplete structures can be predicted.

3.2.3 Vienna Ab-initio Simulation Package (VASP) Settings

The energy of each compound was calculated by VASP with a projector augmented wave (PAW) potential and the generalized gradient approximation (GGA) for the electronic exchange-correlation calculation. For static-energy calculations, the plane wave cutoff energy was set to 875 eV and a k-point mesh was set so that its calculated energy is converged to better than 1 meV/atom. For vibrational-energy calculation, the calculated force for the relaxed structure was forced to converge below 0.02 eV/\( \AA \) and stresses were below 0.05 GPa.

3.2.4 Vibrational Energy Calculation

The total free energy can be written in the form

\[ F = E_{\text{config}} - T S_{\text{config}} + E_{\text{vib}} - T S_{\text{vib}} \]  

Eq 26

where \( E_{\text{config}} \) is the energy of frozen atoms at their average position at a given temperature. \( E_{\text{vib}} \) can be determined by the equipartition theorem in the limit of high temperature, \( S_{\text{vib}} \) is related to the stiffness of an alloy, or in the sense of harmonic oscillation, the stiffer the alloy (small \( S_{\text{vib}} \)), the smaller the oscillation amplitude [16, 17, 18, 19, 20].
In order to calculate the lattice vibrational energy, the harmonic approximation is implemented.

The energy of the system can be written as

\[ H = \frac{1}{2} \sum_i M_i |\ddot{u}(i)|^2 + \frac{1}{2} \sum_{i,j} u^T(i)\Phi(i,j)u(j) \]  \hspace{1cm} \text{(Eq 27)}

and

\[ \Phi_{\alpha\beta}(i,j) = \frac{\partial^2 E}{\partial u_\alpha(i) \partial u_\beta(j)} \bigg|_{u(i)=0 \forall i} \]  \hspace{1cm} \text{(Eq 28)}

where \( M_i \) is the mass of atom \( i \), and \( u(i) \) is its displacement away from its equilibrium position.

The \( 3 \times 3 \) matrices \( \Phi(i,j) \) is the force constant tensors.

By using

\[ e(i) = \sqrt{M_i}u(i) \]  \hspace{1cm} \text{(Eq 29)}

the Hamiltonian can be written as

\[ H = \frac{1}{2} \left( \sum_i \ddot{e}^2(i) + \sum_{i,j} e^T(i) \Phi(i,j) \frac{\sqrt{M_i M_j}}{e(j)} e(j) \right) \]  \hspace{1cm} \text{(Eq 30)}

The corresponding \( 3N \) eigenvalues \( \lambda_m \) of the matrix

\[ D = \begin{pmatrix}
\Phi(1,1) & \cdots & \Phi(1,N) \\
\sqrt{M_1 M_1} & \cdots & \sqrt{M_1 M_N} \\
\vdots & \ddots & \vdots \\
\Phi(N,1) & \cdots & \Phi(N,N) \\
\sqrt{M_N M_1} & \cdots & \sqrt{M_N M_N}
\end{pmatrix} \]  \hspace{1cm} \text{(Eq 31)}

provide the frequencies \( \nu_m = (1/2\pi)\sqrt{\lambda_m} \) of each normal mode of the oscillations.

Here, the supercell method is implemented to determine the unknown force constants

\[ F(i) = \Phi(i,j)u(j) \]  \hspace{1cm} \text{(Eq 32)}
This equation relates the displacement of atom j under the force $F$ exerted on atom i [20].

The calculated frequencies of each normal mode can be used to find the partition function of a quantum mechanical harmonic oscillator as the following

$$Z = \prod_{i=1}^{3N_{\text{atom}}-3} \frac{1}{2 \sinh(\beta \hbar \nu_i / 2)}$$

Eq 33

The enthalpy, entropy, and Gibbs free energy are given by

$$H = -\frac{\partial \ln Z}{\partial \beta}$$

Eq 34

$$S = k_B \frac{\partial (T \ln Z)}{\partial T}$$

Eq 35

$$G = H - TS$$

Eq 36.

3.3 Results

3.3.1 PEGS Prediction

3.3.1.1 NaCa(NH$_2$)$_3$, Structure

![Experimental crystal structure of NaCa(NH$_2$)$_3$](image)

Figure 3.1: Experimental crystal structure of NaCa(NH$_2$)$_3$
The structure of NaCa(NH$_2$)$_3$, which belongs to the F d d d space group, was first discovered by H. Jacobs et al. in 1982 [21]. Its structure obtained by XRD, is devoid of hydrogen positions, and some positions of Ca and Na are given in terms of partially occupied sites. In this work, PEGS is used to find the missing information. The procedures are as follows:

1) create the amide groups which have H-N-H bond angles fixed at 104.6°
2) allow the hydrogen atoms of these amide groups to orientate freely under the electrostatic forces of the cations (Na and Ca)
3) allow the partial occupancy sites of Na and Ca to swap their own sites
4) find the lowest energy that yields the most stable structure of NaCa(NH$_2$)$_3$

Then, the result from PEGS, which is the electrostatic-based crystal structure prediction, is used as an input for the VASP calculation for higher accuracy.

The result from VASP relaxation is

![Predicted crystal structure of NaCa(NH$_2$)$_3$ by PEGS and VASP relaxation](image)

Figure 3.2: Predicted crystal structure of NaCa(NH$_2$)$_3$ by PEGS and VASP relaxation
This can be explained by electrostatic forces alone. Hydrogen atoms in the amide groups try to avoid the effect of cations nearby so they arrange themselves to locate in the directions that experience the least effect from the cations.

3.3.1.2 Li$_2$Ca(NH)$_2$ structure

The result for Li$_2$Ca(NH)$_2$ from inorganic crystal structures database (ICSD) (P-3m1 space group) obtained by neutron powder diffraction method [22] does not give the exact position of hydrogens. These locations are given in term of partial occupancies as shown.

![Experimental structure of Li$_2$Ca(NH)$_2$](image)

Figure 3.3: Experimental structure of Li$_2$Ca(NH)$_2$

The hydrogen positions of the Li$_2$Ca(NH)$_2$ can be predicted by using PEGS to allow the hydrogens in imide groups to orientate freely and then do VASP relaxation. The lowest energy obtained by VASP is the most stable structure.
Figure 3.4: Predicted crystal structure of Li$_2$Ca(NH)$_2$ by PEGS and VASP relaxation

3.3.1.3 Ca(NH$_2$)$_2$ structure

The structure of Ca(NH$_2$)$_2$ was first predicted by P. Bouclier et al. [23] in 1969. The proposed structures obtained by XRD are tetragonal (I4$_1$/amd) for the high-temperature phase and cubic (Fm$ar{3}$m) for the low-temperature phase. The proposed structures are the following:

Figure 3.5: Proposed structures of Ca(NH$_2$)$_2$ (HT-left, LT-right)

Notice that, in the high-temperature phase, the hydrogen atoms in the amide groups point toward the nitrogen atoms.
In 1999, J. Senker et al. [24] extensively studied the Ca(NH$_2$)$_2$ system via neutron powder diffraction and NMR spectroscopy. Their results show that Ca(NH$_2$)$_2$ consists of two phases: a high-temperature and a low-temperature phases, with a transition temperature at around 90K. A difference from Bouclier’s results [23] is that, for the high-temperature phase, the orientation of hydrogen atoms in the amide groups point toward, instead of away from, each other, even though they both have tetragonal (I4$_1$/amd) crystal structure. Additionally, for the low-temperature phase, the suggested structure is monoclinic (P2$_1$/c), rather than cubic.

![Figure 3.6: Proposed structures of Ca(NH$_2$)$_2$ (HT-left, LT-right)](image)

In this work, the structures of Ca(NH$_2$)$_2$ in both phases are calculated via PEGS by allowing the amide groups to orientate themselves to find the structures, then by using those that structures as inputs for VASP relaxation calculation. The lowest energy one is the most stable structure. The results obtained by VASP are in agreement with the newer papers [24] as shown here.
Figure 3.7: Proposed HT structure of Ca(NH$_2$)$_2$ (top), compared to the predicted one by PEGS and VASP (bottom)
Figure 3.8: Proposed LT structure of Ca(NH$_2$)$_2$ (top), compared to the predicted one by PEGS and VASP (bottom)
For the high-temperature phase, the hydrogen atoms in the amide face toward each other, which can be explained by electrostatic forces wherein hydrogen atoms try to avoid the repulsive forces from Ca ions and as a result align themselves to minimize these repulsive forces.

3.3.2 Allowed reactions

Thermodynamically allowed reactions predicted by GCLP are listed in Table 3.2.

**Reaction (i):** At \( T = 178 \, ^\circ\text{C} \), \( \text{CaH}_2 \) and \( \text{Ca(NH}_2\text{)}_2 \) react to form \( \text{CaNH} \) and 3.53 wt. \% \( \text{H}_2 \). The calculated enthalpy at 500K is 61.1 kJ/mol \( \text{H}_2 \). Compared to the experimental result of 57 kJ/mol \( \text{H}_2 \), this calculation is very close and the critical temperature is in the range of experimental data (60-300 \(^\circ\text{C}\)).

**Reaction (ii):** At \( T = 221 \, ^\circ\text{C} \), \( \text{NH}_4\text{N}_3 \) and \( \text{LiNH}_2 \) are predicted to form \( \text{LiN}_3 \) and release 7.61 wt. \% \( \text{H}_2 \).

**Reaction (iii):** At \( T = 221 \, ^\circ\text{C} \), a mixture of \( \text{NH}_4\text{N}_3 \), \( \text{LiNH}_2 \) and \( \text{LiNa}_2(\text{NH}_2)_3 \) is predicted to form \( \text{LiN}_3 \) and \( \text{NaNH}_2 \). This reaction yields 5.56 wt. \% \( \text{H}_2 \).

**Reaction (iv):** At \( T = 222 \, ^\circ\text{C} \), \( \text{NH}_4\text{N}_3 \) and \( \text{LiNa}_2(\text{NH}_2)_3 \) are predicted to react and form \( \text{LiN}_3 \) and \( \text{NaNH}_2 \) while releasing 3.08 wt. \% \( \text{H}_2 \).

**Reaction (v):** At \( T = 286 \, ^\circ\text{C} \), \( \text{NH}_4\text{N}_3 \) and \( \text{Ca(NH}_2\text{)}_2 \) react and form \( \text{CaN}_6 \). This reaction releases 6.1 wt. \% \( \text{H}_2 \).

**Reaction (vi):** At \( T = 298 \, ^\circ\text{C} \), \( \text{LiH} \) and \( \text{LiNH}_2 \) are predicted to form \( \text{Li}_2\text{NH} \), releasing 6.52 wt. \% \( \text{H}_2 \). This is the most-studied reaction. The predicted enthalpy at 500K is 67.7 kJ/mol \( \text{H}_2 \), compared to the experimental result of 66.6 kJ/mol \( \text{H}_2 \). The experimental critical temperature is 283 \(^\circ\text{C}\).
**Reaction (vii):** At $T = 346 \, ^\circ C$, NaH decomposes to Na and releases 4.2 wt. % $H_2$. The calculated enthalpy at 500 K is 95.2 kJ/mol $H_2$, compared to the experimental 102 kJ/mol $H_2$. The experimental critical temperature is 327 $^\circ C$.

**Reaction (viii):** At $T = 361 \, ^\circ C$, a mixture of $NH_4N_3$ and $Li_2Ca(NH)_2$ is predicted to form $LiN_3$ and $CaN_6$, while releasing 5.57 wt. % $H_2$.

**Reaction (ix):** At $T = 364 \, ^\circ C$, Na and $Ca(NH)_2$ are predicted to react and form $NaNH_2$ and $CaNH$. This reaction yields 1.06 wt. % $H_2$.

**Reaction (x):** At $T = 426 \, ^\circ C$, $CaH_2$ and $CaNH$ react and form $Ca_2NH$. This reaction provides 2.07 wt. % $H_2$. The calculated enthalpy at 500 K is 73.3 kJ/mol $H_2$, while the experimental result is 88.7 kJ/mol $H_2$. The predicted critical temperature is in the range of the experimental data, which is around 350-500 $^\circ C$.

**Reaction (xi):** At $T = 543 \, ^\circ C$, Na and $LiNH_2$ are predicted to form $Li_2NH$ and $LiNa_2(NH_2)_3$, releasing 1.25 wt. % $H_2$.

**Reaction (xii):** At $T = 661 \, ^\circ C$, $Li_4NH$ is produced from $LiH$ and $Li_2NH$. The predicted amount of hydrogen released is 4.5 wt. % $H_2$. The predicted enthalpy at 500K is 116.9 kJ/mol $H_2$, compared to the experimental results of 114.3 kJ/mol $H_2$. And the experimental critical temperature is 569$^\circ C$.

**Reaction (xiii):** At $T = 688 \, ^\circ C$, $Li_2NH$ and $Li_4NH$ react and form $Li_3N$, yielding 2.81 wt. % $H_2$.

**Reaction (xiv):** At $T = 694 \, ^\circ C$, $Ca(NH)_2$ decomposes to $CaN_6$ and $CaNH$, releasing 4.47 wt. % $H_2$.

**Reaction (xv):** At $T = 976 \, ^\circ C$, $LiNH_2$ decomposes to $LiN_3$ and $Li_2NH$. This provides 7.02 wt. % $H_2$. 

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Notice that some predicted reactions involve NH$_4$N$_3$ and release a moderate amount of hydrogen. However, this NH$_4$N$_3$ is a highly explosive material so it is not suited for most practical hydrogen storage applications.
Table 3.1: List of all compounds included in GCLP reaction predictions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNH₂</td>
<td>PdCl₂</td>
<td>m</td>
</tr>
<tr>
<td>LiCaH</td>
<td>PdCl₂</td>
<td>m</td>
</tr>
<tr>
<td>Na₂</td>
<td>P4/m mm</td>
<td>m</td>
</tr>
<tr>
<td>NaN₂</td>
<td>P6/m mm</td>
<td>m</td>
</tr>
<tr>
<td>Li₂</td>
<td>P3 m</td>
<td>m</td>
</tr>
<tr>
<td>NaH</td>
<td>Fd 3 c</td>
<td>m</td>
</tr>
<tr>
<td>CaN₃</td>
<td>P42/m nm</td>
<td>m</td>
</tr>
<tr>
<td>CaH₂</td>
<td>Pnma</td>
<td>m</td>
</tr>
<tr>
<td>LiN₂</td>
<td>I m</td>
<td>m</td>
</tr>
<tr>
<td>NaH</td>
<td>F 3 d</td>
<td>m</td>
</tr>
</tbody>
</table>

Note: The table includes various compounds with their respective space groups and symmetries.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Formula</th>
<th>DFT Energy (kJ/mol)</th>
<th>Static Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂NH</td>
<td>2-3 m 3</td>
<td>235.9</td>
<td>234.71</td>
</tr>
<tr>
<td>Li₄NH</td>
<td>4/a z</td>
<td>46.6</td>
<td>49.2</td>
</tr>
<tr>
<td>Ca₂NH</td>
<td>2-3 m z</td>
<td>311.52</td>
<td>324.27</td>
</tr>
<tr>
<td>Ca(NH₂)₂</td>
<td>41/amd</td>
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<td>324.27</td>
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<td>NaCaH₃P</td>
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<td>Li₃Na(NH₂)₄</td>
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<td>324.27</td>
<td>324.27</td>
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<tr>
<td>Li₂Ca(NH)₂P</td>
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<td>416.92</td>
<td>324.27</td>
</tr>
</tbody>
</table>

*Only static, DFT energies at 0 K.*
Table 3.2: List of all thermodynamically reversible reactions predicted in the Li-Na-Ca-N-H system.

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>wt% H</th>
<th>wt% K</th>
<th>S500K</th>
<th>G500K</th>
<th>Tcrit</th>
<th>Tcrit (Other)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(i)</td>
<td></td>
<td></td>
<td>3.53</td>
<td>70.3</td>
<td>53.8</td>
<td>61.1</td>
</tr>
<tr>
<td>2</td>
<td>(ii)</td>
<td></td>
<td></td>
<td>7.61</td>
<td>85.3</td>
<td>53.6</td>
<td>62.3</td>
</tr>
<tr>
<td>3</td>
<td>(iii)</td>
<td></td>
<td></td>
<td>5.56</td>
<td>53.2</td>
<td>61.8</td>
<td>125</td>
</tr>
<tr>
<td>4</td>
<td>(iv)</td>
<td></td>
<td></td>
<td>3.08</td>
<td>52.1</td>
<td>60.2</td>
<td>121.7</td>
</tr>
<tr>
<td>5</td>
<td>(v)</td>
<td></td>
<td></td>
<td>6.1</td>
<td>88.5</td>
<td>58.3</td>
<td>65.9</td>
</tr>
<tr>
<td>6</td>
<td>(vi)</td>
<td></td>
<td></td>
<td>6.52</td>
<td>83.1</td>
<td>62.9</td>
<td>74.4</td>
</tr>
<tr>
<td>7</td>
<td>(vii)</td>
<td></td>
<td></td>
<td>4.2</td>
<td>88.5</td>
<td>62.9</td>
<td>86.8</td>
</tr>
<tr>
<td>8</td>
<td>(viii)</td>
<td></td>
<td></td>
<td>5.57</td>
<td>103</td>
<td>70.1</td>
<td>79.4</td>
</tr>
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<td>(ix)</td>
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<td></td>
<td>1.06</td>
<td>96.8</td>
<td>69.3</td>
<td>74.4</td>
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<td>(x)</td>
<td></td>
<td></td>
<td>2.07</td>
<td>86.7</td>
<td>64</td>
<td>73.3</td>
</tr>
<tr>
<td>11</td>
<td>(xi)</td>
<td></td>
<td></td>
<td>1.25</td>
<td>72.5</td>
<td>78.7</td>
<td>88.7</td>
</tr>
<tr>
<td>12</td>
<td>(xii)</td>
<td></td>
<td></td>
<td>2.81</td>
<td>128.4</td>
<td>113.4</td>
<td>121.7</td>
</tr>
<tr>
<td>13</td>
<td>(xiii)</td>
<td></td>
<td></td>
<td>4.5</td>
<td>125.1</td>
<td>108.8</td>
<td>116.9</td>
</tr>
<tr>
<td>14</td>
<td>(xiv)</td>
<td></td>
<td></td>
<td>2.81</td>
<td>128.4</td>
<td>113.4</td>
<td>121.7</td>
</tr>
<tr>
<td>15</td>
<td>(xv)</td>
<td></td>
<td></td>
<td>7.02</td>
<td>136.5</td>
<td>107.6</td>
<td>114.1</td>
</tr>
</tbody>
</table>

Notes:
- **a**: Only static DFT energies
- **b**: Static DFT plus ZPE energies
- **c**: Only static DFT energies
- **d**: Static DFT plus ZPE energies
- **e**: Only static DFT energies
- **f**: Only static DFT energies

*Table 3.2: List of all thermodynamically reversible reactions predicted in the Li-Na-Ca-N-H system.*
3.3.3 Van’t Hoff Plot

The van’t Hoff plot is the plot between pressure and temperature of the allowed predicted reactions obtained from GCLP. The van’t Hoff equation is described by

$$\ln p = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where $p$ is the pressure, $R$ is the ideal gas constant, $H$ is the enthalpy, and $S$ is the entropy.

Figure 3.9: The van’t Hoff plot of the allowed predicted reactions from GCLP in the Li-Na-Ca-N-H system.

From figure 3.9, the graph is plotted between P(bar) and T(K). The lines correspond to each of the equations. The slope is the enthalpy and the x-intersection is $\frac{\Delta S}{R}$. The rectangle is the ideal temperature (-40 to 80 °C) and pressure (1 to 400 bars). Practical reaction should pass through
this rectangle to ensure that hydrogen atoms are absorbed and desorbed within the practical operating temperatures and pressures.

3.3.4 Phase Diagrams

The phase diagram obtained by the predicted reactions from GCLP in the Li-Na-Ca-N-H system is shown in Fig 3.10.

![Phase diagram of the Li-Na-Ca-N-H system](image)

**Figure 3.10: Phase diagram of the Li-Na-Ca-N-H system**

Considering only the Li-Ca-N-H system, which has high wt. % H\textsubscript{2} released, the phase diagram up to T = 426 °C is shown in Fig 3.11. Vertices in the phase diagram are the most stable metal phases. Points on the phase diagram are the relative fraction of metal species while colors show percentage amount of hydrogen released.
Each figure in the phase diagram corresponds to a change in the phase diagram obtained from reactions in the table. When increasing temperature, the free energy of hydrogen is lower due to higher entropy. This results in a higher amount of hydrogen released. The effect of entropy also gives more stable phases.

3.3.5 Discussion

PEGS is a useful tool to predict ionic crystal structures. In this work, both phases (high-temperature and low temperature phases) of Ca(NH$_2$)$_2$ are in good agreement with the experimental results. Some missing information of hydrogen atoms, due to limited experimental techniques, includes hydrogen positions and some partial occupancies of crystal structures which can also be predicted by using PEGS, for example, NaCa(NH)$_2$, and Li$_2$Ca(NH)$_2$. The results from PEGS fill in the missing information for some compounds in the Li-Na-Ca-N-H system and...
provide a higher degree of accuracy when predicting the reactions of all possible compounds in that system.

From the van’t Hoff plot, it is obvious that no predicted reaction in the Li-Na-Ca-N-H is suitable for practical applications in fuel cell vehicles. However, this helps screen the compounds in this system and reduces the experimental cost and time to investigate the reactions of these compounds.

3.4 Results if excluding NH$_4$N$_3$ in GCLP reaction prediction

From the previous session, most of the allowed predicted reactions from GCLP involved NH$_4$N$_3$, which is an explosive material. As such, we repeated the GCLP calculation without NH$_4$N$_3$ compound.

3.4.1 Allowed reactions

The thermodynamically allowed reactions predicted by GCLP are listed in Table 3.3.

**Reaction (i):** At T = -76 °C, N$_2$H$_5$N$_3$ reacts with LiNH$_2$ to form LiN$_3$ and release 7.61 wt. % H$_2$.

**Reaction (ii):** At T = -27 °C, a mixture of N$_2$H$_5$N$_3$ and Ca(NH$_2$)$_2$ reacts to form CaN6. This reaction yields 6.1 wt. % H$_2$.

**Reaction (iii):** At T = 66 °C, LiNH$_2$ and Ca(NH$_2$)$_2$ are predicted to form LiN$_3$ and Li$_2$Ca(NH)$_2$, while releasing 5.95 wt. % H$_2$.

**Reaction (iv):** At T = 160 °C, LiN$_3$ and Ca(NH$_2$)$_2$ react and form CaN$_6$ and Li$_2$Ca(NH)$_2$. This reaction releases 3.06 wt.% H$_2$. 

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**Reaction (v):** At $T = 178$ °C, a mixture of CaH$_2$ and Ca(NH$_2$)$_2$ reacts and form CaNH, releasing 3.53 wt. % H$_2$. This is a known reaction as mentioned in the previous section. The calculated enthalpy at 500K is 61.1 kJ/mol H$_2$, compared to the experimental data of 57 kJ/mol H$_2$.

**Reaction (vi):** At $T = 298$ °C, LiH and LiNH$_2$ are predicted to form Li$_2$NH, while yielding 6.52 wt. % H$_2$. This is a well-known reaction as mentioned in the previous section. The predicted enthalpy at 500K is 67.7 kJ/mol H$_2$, compared to the experimental result of 66.6 kJ/mol H$_2$.

**Reaction (vii):** At $T = 346$ °C, NaH decomposes to Na and releases 4.2 wt. % H$_2$. The calculated enthalpy at 500K is 95.2 kJ/mol H$_2$, compared to the experimental result 102 kJ/mol H$_2$.

**Reaction (viii):** At $T = 400$ °C, Na and Ca(NH$_2$)$_2$ react to form NaNH$_2$ and CaNH. This reaction yields 1.06 wt. % H$_2$.

**Reaction (ix):** At $T = 426$ °C, a mixture of CaH$_2$ and CaNH are predicted to form Ca$_2$NH, releasing 2.07 wt. % H$_2$. This is also a known reaction. The predicted enthalpy at 500K is 72.8 kJ/mol H$_2$, compared to the experimental data of 88.7 kJ/mol H$_2$.

**Reaction (x):** At $T = 543$ °C, Na reacts with LiNH$_2$ to form Li$_2$NH and LiNa$_2$(NH$_2$)$_3$. This reaction releases 1.25 wt. % H$_2$.

**Reaction (xi):** At $T = 661$ °C, LiH and Li$_2$NH are predicted to react and form Li$_3$NH, while releasing 4.5 wt. % H$_2$. The calculated enthalpy at 500K is 116.9 kJ/mol H$_2$, compared to 114 kJ/mol H$_2$ from other calculations [2].

**Reaction (xii):** At $T = 688$ °C, Li$_2$NH and Li$_3$NH react and form Li$_4$N. This reaction gives 2.81 wt. % H$_2$. 
**Reaction (xiii):** At $T = 694 \degree C$, Ca(NH$_2$)$_2$ decomposes to CaN$_6$ and CaNH, while releasing 4.47 wt. % H$_2$.

**Reaction (xiv):** At $T = 703 \degree C$, LiNH$_2$ decomposes to LiN$_3$ and Li$_2$NH. This reaction gives 7.02 wt. % H$_2$. 
### Table 3.3: List of all thermodynamically reversible reactions predicted in the Li-Na-Ca-N-H system, excluding NH₃

<table>
<thead>
<tr>
<th>no.</th>
<th>Reaction</th>
<th>$\Delta H^o$ (kJ/mol H₂)</th>
<th>$\Delta S^o$ (J/K mol H₂)</th>
<th>$\Delta G^o$ (kJ/mol H₂)</th>
<th>$T_{crit}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>$2\text{LiH} + \text{LiNH}_2$ $\rightarrow$ $\text{Li}_2\text{NH} + \text{H}_2$</td>
<td>7.62</td>
<td>56.7</td>
<td>17.5</td>
<td>26.6</td>
</tr>
<tr>
<td>(ii)</td>
<td>$4\text{Li}\text{H} + \text{LiNH}_2 + 2\text{Ca}(\text{NH}_2)_2$ $\rightarrow$ $\text{Ca}_2\text{NH} + 4\text{LiNH}_2 + 2\text{H}_2$</td>
<td>6.1</td>
<td>59.9</td>
<td>22.2</td>
<td>30.3</td>
</tr>
<tr>
<td>(iii)</td>
<td>$3\text{LiNH}_2 + 2\text{Ca}(\text{NH}_2)_2$ $\rightarrow$ $\text{Li}_2\text{NH} + \text{Li}_2\text{NH}_3 + 2\text{Ca}(\text{NH})_2 + 9\text{H}_2$</td>
<td>5.95</td>
<td>62.7</td>
<td>33.9</td>
<td>40.9</td>
</tr>
<tr>
<td>(iv)</td>
<td>$5\text{Li}\text{H} + \text{Li}_2\text{NH}_3 + 11\text{Ca}(\text{NH}_2)_2$ $\rightarrow$ $7\text{CaN}_6 + 4\text{Li}_2\text{NH} + 2\text{Ca}(\text{NH})_2 + 18\text{H}_2$</td>
<td>3.06</td>
<td>67.6</td>
<td>41.1</td>
<td>46.6</td>
</tr>
<tr>
<td>(v)</td>
<td>$\text{CaH}_2 + \text{Ca}(\text{NH}_2)_2$ $\rightarrow$ $2\text{CaNH} + 2\text{H}_2$</td>
<td>3.53</td>
<td>70.3</td>
<td>53.8</td>
<td>61.1</td>
</tr>
<tr>
<td>(vi)</td>
<td>$\text{LiH} + \text{LiNH}_2$ $\rightarrow$ $\text{Li}_2\text{NH} + \text{H}_2$</td>
<td>6.52</td>
<td>80.8</td>
<td>60.6</td>
<td>67.7</td>
</tr>
<tr>
<td>(vii)</td>
<td>$\text{NaH}$ $\rightarrow$ $2\text{Na} + \text{H}_2$</td>
<td>4.2</td>
<td>88.5</td>
<td>86.5</td>
<td>95.2</td>
</tr>
<tr>
<td>(viii)</td>
<td>$2\text{Na} + 2\text{Ca}(\text{NH}_2)_2$ $\rightarrow$ $2\text{NaNH}_2 + 2\text{CaNH} + \text{H}_2$</td>
<td>1.06</td>
<td>96.8</td>
<td>69.3</td>
<td>74</td>
</tr>
<tr>
<td>(ix)</td>
<td>$\text{CaH}_2 + \text{CaNH}$ $\rightarrow$ $\text{Ca}_2\text{NH} + \text{H}_2$</td>
<td>2.07</td>
<td>86.7</td>
<td>64</td>
<td>72.5</td>
</tr>
<tr>
<td>(x)</td>
<td>$\text{NaH} + \text{Na}_2\text{NH}$ $\rightarrow$ $2\text{NaNH}_2 + \text{H}_2$</td>
<td>4.5</td>
<td>88.7</td>
<td>72.5</td>
<td>78.7</td>
</tr>
<tr>
<td>(xi)</td>
<td>$\text{LiH} + \text{Li}_2\text{NH}_3$ $\rightarrow$ $\text{Li}_2\text{NH} + \text{LiNa}(\text{NH}_2)_3 + \text{H}_2$</td>
<td>1.25</td>
<td>112.1</td>
<td>87.3</td>
<td>101.6</td>
</tr>
<tr>
<td>(xii)</td>
<td>$\text{Li}_2\text{NH} + \text{Li}_2\text{NH}_3$ $\rightarrow$ $2\text{Li}_3\text{N} + \text{H}_2$</td>
<td>2.81</td>
<td>113.4</td>
<td>118.4</td>
<td>121.7</td>
</tr>
<tr>
<td>(xiii)</td>
<td>$\text{CaH}_2 + \text{Ca}(\text{NH})_2$ $\rightarrow$ $\text{Ca}_2\text{NH} + \text{H}_2$</td>
<td>2.07</td>
<td>86.7</td>
<td>64</td>
<td>72.5</td>
</tr>
</tbody>
</table>

**Notes:**
- **$\Delta H^o$** refers to the enthalpy change.
- **$\Delta S^o$** refers to the entropy change.
- **$\Delta G^o$** refers to the free energy change.
- **$T_{crit}$** refers to the critical temperature.

*Only static DFT energies.*

*Static DFT plus ZPE energies.*

---

Table 3.3 lists all thermodynamically reversible reactions predicted in the Li-Na-Ca-N-H system, excluding NH₃.
3.4.2 Van’t Hoff Plot

The van’t Hoff plot of the allowed reversible reaction predicted by GCLP is shown in Figure 3.12. From this plot, some of the reactions (reaction (i), (ii), and (iii)) pass through the ideal temperature and pressure rectangle. That means those reactions are thermodynamically viable on hydrogen storage.

Notice that the reaction (i) and (ii) are involved with N$_2$H$_4$N$_3$. This N$_2$H$_4$N$_3$ compound is also an explosive material.

Figure 3.12: Van’t Hoff plot of the predicted reaction in Li-Na-Ca-N-H system excluding NH$_4$N$_3$ compound.
3.4.3 Discussion

After excluding NH$_4$N$_3$ in the reactions prediction by GCLP, some reactions are thermodynamically applicable for practical usage. Reaction (i), (ii), and (iii) can release 7.61, 6.1 and 5.95 wt. % H$_2$, respectively. However, reactions (i) and (ii) involve N$_2$H$_5$N$_3$ which is also a highly explosive material.

Compared to the previous session, the reactions involving NH$_4$N$_3$ are more thermodynamically favorable. However, those reactions may be prohibited by low kinetics. The reactions in this section are alternative choices if NH$_4$N$_3$ is found to have poor kinetics.
REFERENCES

[1] Adapted from http://solarcellcentral.com


