Density Functional Theory Studies on a Reversible Hydrogen Storage "Li-Mg-B-N-H" System

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Many experimental and theoretical studies have been carried out to find hydrogen storage materials with reversible properties, low desorption temperatures[1], accelerated kinetics[1] and optimum storage capacity (at 298 K, the US DOE target for gravimetric hydrogen storage capacity is 6.0 wt %)[2]. Experiments suggest that complex hydrides of *Li*, *Na*, *Mg*, *B*, *Al* and *N* have such properties[1]. In this study, a density functional theory study with the generalized gradient approximation (GGA) and projected augmented wave method (PAW) is performed to find the hydrogen storage properties for different molar ratios *X* of MgH_2 in the complex storage material $(LiNH_2)_2$ - $LiBH_4$ - $(MgH_2)_X$. Using *ab-initio* methods, stabilities of the structures are established and thermodynamic properties such as heat of reaction and Gibbs energy are found for each reactant and product in the reaction step for proposed reactions. These are compared with literature values to validate the proposed reactions. The reversibility and storage capacity of these materials will be verified from the desorption behavior observed at different temperatures. These theoretically obtained data can be used to validate the suggested mechanism from experimental observations for the reaction. These efforts are expected to contribute towards identification of suitable hydrogen storage materials.

Motivation

Recent research has gained pace to find a reversible material with efficient hydrogen storage properties. Metal hydrides as hydrogen storage materials have gained importance in the past few years. Storage properties of metal hydrides were found to improve in their combinations. Undesired properties of these hydrides such as ammonia liberation, poor kinetics and irreversibility were overcome by their binary systems[1]. $LiBH_4$-MgH_2 system was found to have 8-10 wt% reversible hydrogen storage at about 350 °C[3]. $LiNH_2$-MgH_2 system operates at 200 °C with 4.5 wt% reversible hydrogen storage[4]. Experiments on the ternary systems of these hydrides also showed promising results and further improved their storage properties. The combined $LiNH_2$-MgH_2-$LiBH_4$ system was found to have lowered desorption temperatures, increased hydrogen purity, accelerated kinetics and partial reversibility[1]. The stoichiometry of this mixture was also a major factor controlling the storage properties.

DFT studies on hydrogen storage materials using projected augmented wave (PAW) potentials pertaining to generalized gradient approximation (GGA) are considered to be the most appropriate for energy calculations due to their better accuracy than Local Density Approximation (LDA)[5]. The thermodynamic properties calculated using plane

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wave DFT and those found experimentally are in good agreement for a number of reversible hydrogen storage systems[6].

Computational details

In this work, we tested the hydrogen storage properties of the $(LiNH_2)_2$ - $LiBH_4$ - $(MgH_2)_X$ reactant mixtures using DFT studies. The reactants and products of the proposed reaction mechanism were checked for stability and then the thermodynamic properties of the compounds were calculated and compared with literature. We used VASP (Vienna Ab Initio Simulation package) to perform the DFT calculations and the PHONON[8] code to perform lattice dynamics for finite temperature crystal stability and thermodynamics.

The most favored structure of each compound was found from literature and its equilibrium volume was calculated by a quadratic fit of energy. These calculations were performed using Monkhorst Pack meshes containing 4 x 4 x 4 *k*- points. The energy cutoff for all the compounds was set to 600 eV. For the volume relaxations the cutoff energy was increased to about 800 eV. The external pressures acting on each of these compounds were reduced by relaxing the volume and ionic positions of the structure. PAW potentials were used for these relaxations. The relaxations were continued till the forces on the atoms were reduced to about 0.1 meV $A^{\circ -1}$. Hellmann–Feynman (HF) forces were calculated using a super cell of the relaxed structure to avoid the interaction between the atoms and then by displacing its atomic positions.

The calculated HF forces were then used to find the phonon density of states (DOS) for the structure at finite temperatures, which would be positive for a stable structure. Entropy and internal energy of the structure can be obtained from the phonon DOS, which can be used to calculate the Gibbs energy of the reactions. The reversibility and hydrogen storage capacity of the reaction for different mole ratios can then be calculated. The experimentally observed XRD pattern will be compared with the theoretically observed ones to validate the structure of the newly identified phase ($LiMgBN_2$). To specify the atomic positions of the compounds with fractional occupancies such as $Li_2Mg(NH)_2$ and $LiMgBN_2$,we used the super cell approach.

Results/Discussion

In this study, we calculated the equilibrium volumes for all the compounds, namely, $LiNH_2$, $LiBH_4$, MgH_2, $Mg(NH_2)_2$, LiH, H_2, Li_3BN_2,Mg_3N_2, $LiMgBN_2$, $Li_2Mg(NH)_2$ and $Li_4(NH_2)_3(BH_4)$ involved in the reaction mechanism. We reduced the pressure acting on the compounds to less than -0.1 kB. The stability of about 8 compounds was tested by using DFT to calculate the HF forces, which were then used in lattice dynamics calculations to derive the phonon spectra, which allowed us to establish stability of these structures at finite temperature

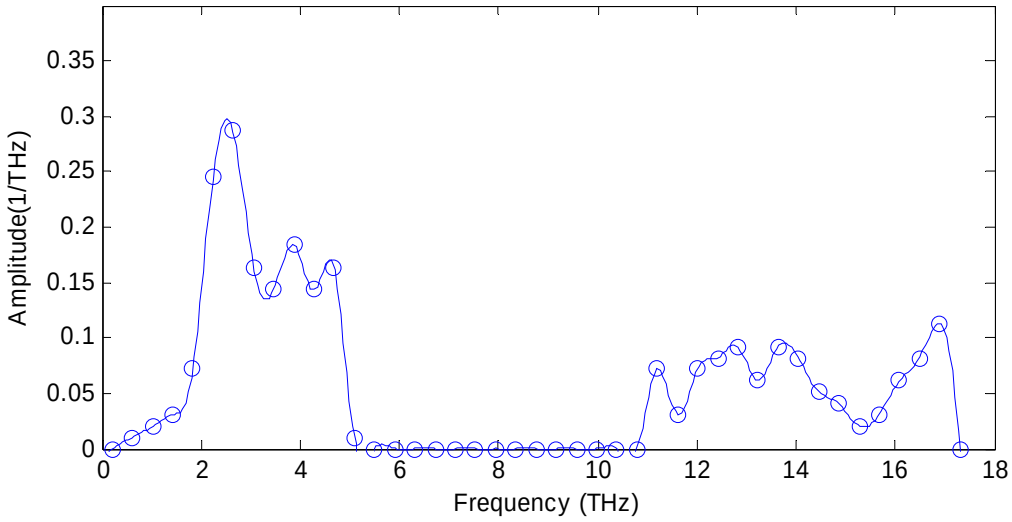

Figure 1: Phonon DOS for Mg_3N_2

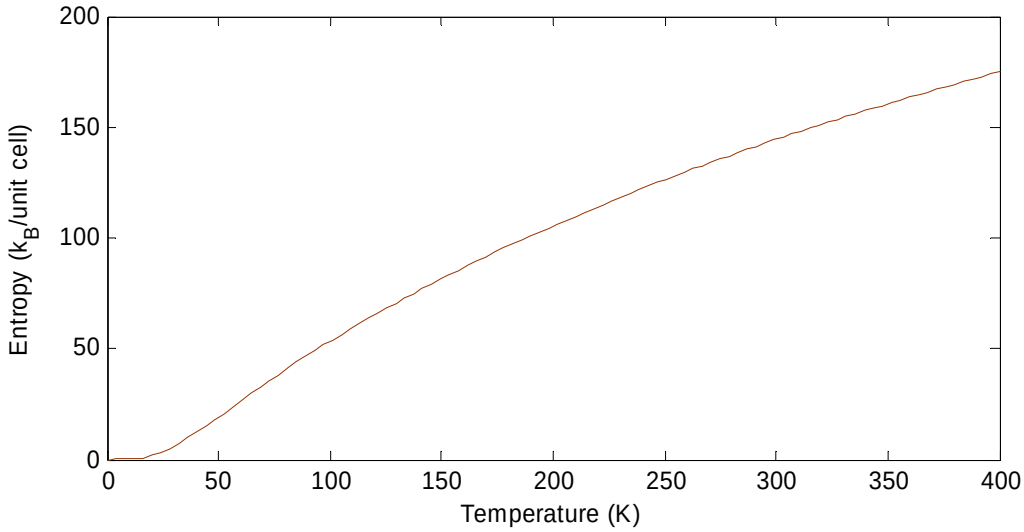

Figure 2: Entropy as a function of temperature for Mg_3N_2

These stable structures will be used to calculate the thermodynamic properties of the reactions. Experimentally proposed multistep hydrogen release reactions for the intermediate quaternary phase $Li_4(NH_2)_3(BH_4)$[1] that is formed will be examined, and the impact of MgH_2 in the storage material for X = 0, 0.25, 0.5, 0.75 and 1.0 will be calculated. The amount of hydrogen desorbed for different mole ratios will also be calculated.

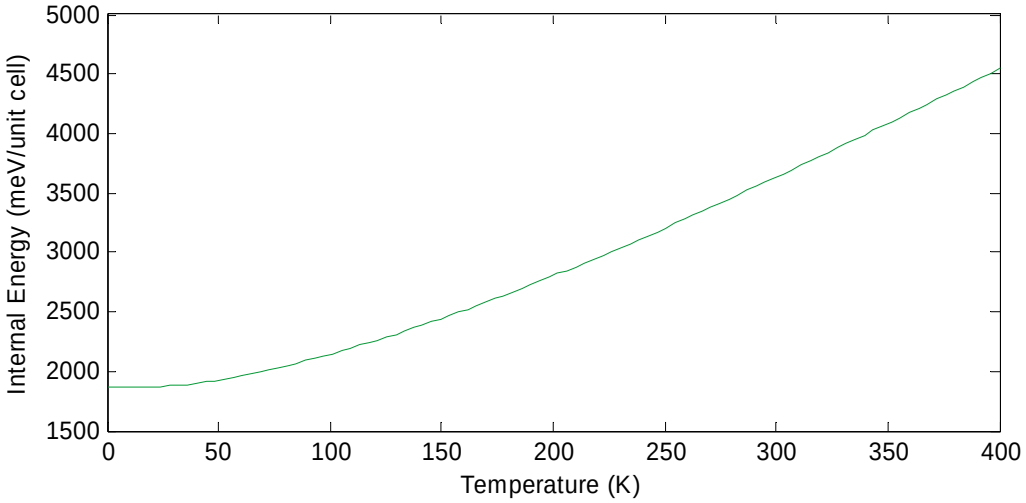

Figure 3: Internal Energy as a function of temperature for Mg_3N_2

Conclusion

The stability of the structures involved in a hydrogen desorption reaction set was evaluated. The thermodynamic properties of these compounds will be calculated and the feasibility of the mechanism will be validated. This DFT study could supplement experiments in testing the metal hydrides for hydrogen storage properties.

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