Ab-initio study of electronic and elastic properties of Mg(BH$_4$)(NH$_2$) complex hydride

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ABSTRACT

Structural and electronic properties of complex hydride Mg(BH$_4$)(NH$_2$), applicable in hydrogen storage, were studied in framework of pseudopotential-density functional theory. This compound shows an indirect band gap of 4.95 eV which is categorized in insulator materials. The calculated total and partial density of states of this compound show that the hydrogen bonding in BH$_4$ anion is mainly covalent and the hydrogen-hydrogen repulsion is more in anion BH$_4$ than in anion NH$_2$. The calculated bulk modulus from Birch-Murnaghan equation of state is in close agreement with that obtained from the elastic constants. The obtained bulk modulus (19.27 GPa) shows this compound is more ductile than binary and ternary hydrides and it does not have a brittle structure. Therefore, it is a good candidate for hydrogenation and dehydrogenation cycles. The stability of the structure in ambient pressure is also declared by calculating the elastic coefficients. However, the existence of elastic anisotropy in the compound demonstrates the less compressibility of it along the *c* axis than *a* and *b* axes. The small amount of Poisson ratio indicates that it is more stable against shear compared to common borohydrides. This point is important for hydride stability in hydrogenation and dehydrogenation cycles.

Introduction

By increasing the energy demand in the world especially in the developing countries, more attention has been directed to the alternative available energy sources [1]. Hydrogen, one of the most abundant elements in the universe, may be a good candida as an ideal clean energy [2]. However, to turn this idea into the reality, it is required to consider four key technologies including preparation, storage, transport and application [3]. In this regard, hydrogen storage technology is one of the most important issues considered by the researchers. Many

materials have been proposed as a potential hydrogen storage media. Mostly; hydrogen storage alloys [3,4], carbon based materials [5,6], metal organic frameworks (MOFs) [7,8], and complex hydrides [9–12] have been studied both theoretically and experimentally as the new hydrogen storage systems. The complex hydrides are generally formed from alkali or alkaline earth metals and [AlH$_4$]$^-$, [NH$_2$]$^-$, and [BH$_4$]$^-$ anionic hydrides. Recently, the complex hydrides composed of light elements have attracted great deal of attention for reversible hydrogen storage which is due to their high gravimetric and volumetric hydrogen densities [12]. Therefore, significant attentions have paid to them. However, difficulty in reducing

their dehydrogenation temperature is their major drawback. Moreover, their reversibility has to be noticed carefully for practical usage such as fuel cell vehicles [13].

Early novel complex hydride was found by the mixture of $LiBH_4$ and $LiNH_2$, with the dehydrogenation temperature much lower than $LiBH_4$ hydride [14–18]. Following this finding, many mixture systems of borohydrides and amide compounds in the form of $A^{n+}(BH_4)_n + B^{m+}(NH_2)_m$ (A = Li, Na, Mg, Ca; B = Li, Na, Mg) have been studied [19–22]. For example, $Li_2(BH_4)(NH_2)$ and $Li_4(BH_4)(NH_2)_3$ complex hydrides are crystallized by ball-milling or heat treatment of the mixture $LiBH_4 + nLiNH_2$ (n = 1–3) [23–25]. The same procedure has been used for further development on the system of $Mg(BH_4)_2 + Mg(NH_2)_2$ mixture. The $Mg(BH_4)_2$ is thermodynamically less stable than the $Li(BH_4)$ [26–28]. So, the produced complex hydride may have a lower dehydrogenation temperature. The novel $Mg(BH_4)(NH_2)$ complex hydride was created from the mentioned mixture at temperature 453 K in ambient pressure. Its crystal structure was found by in situ synchrotron X-ray diffraction [29], which was tetragonal. Due to its outstanding properties, we have focused on electronic and elastic properties of this compound by the first principles calculations. Ab-initio density functional theory calculations are one of the most available and popular methods leading to the reliable results [30–34] that are used at the current work. The computational details are summarized in the next section. The third section covers the obtained results and discusses about them. Finally, at the last part, the conclusions are drawn.

Computational details

The unit cell of $Mg(BH_4)(NH_2)$ crystal was shown in Fig. 1. Its space group has been experimentally determined to be I4$_1$ (No. 80) with lattice parameters a = b = 5.8141 Å, and c = 20.4504 Å [29]. Each conventional unit cell contains 8 primitive unit cells. This compound contains cation Mg^{2+} and anions $(BH_4)^{-1}$ and $(NH_2)^{-1}$. It can be seen that each B atom is surrounded by four nearest neighboring H atoms to form a BH_4 tetrahedron (Fig. 1).

Density functional theory calculations [35] were performed using Quantum ESPRESSO package that is a first principles quantum mechanical code based on plane-wave basis sets and pseudopotentials [36]. The Perdew and Wang (PW91) [37] generalized gradient approximation (GGA) was used for the exchange and correlation potential. The core electrons were replaced by ultrasoft pseudopotentials [38,39] in reciprocal space. The 2p, 3s, and 3p orbitals of Mg, 2s and 2p orbitals of B and N atoms, and 1s orbital of H atom were included in ultrasoft pseudopotentials. We have tested the dependence of the total energy on the energy cutoff values and number of k-points, the same as what have already been done for the other cases by the authors [40]. For all calculations, a plane-wave expansion cutoff of 75 Ry was used. The Brillouin zone (BZ) integration was calculated using a 10 × 10 × 2 Monkhorst-Pack scheme [41] resulting in 80 k-points in the irreducible first BZ. The structure was fully relaxed until the tension on the unit cell and forces on the ions were less than 0.003 GP and 0.0001 eV/Å, respectively. In addition, the convergence
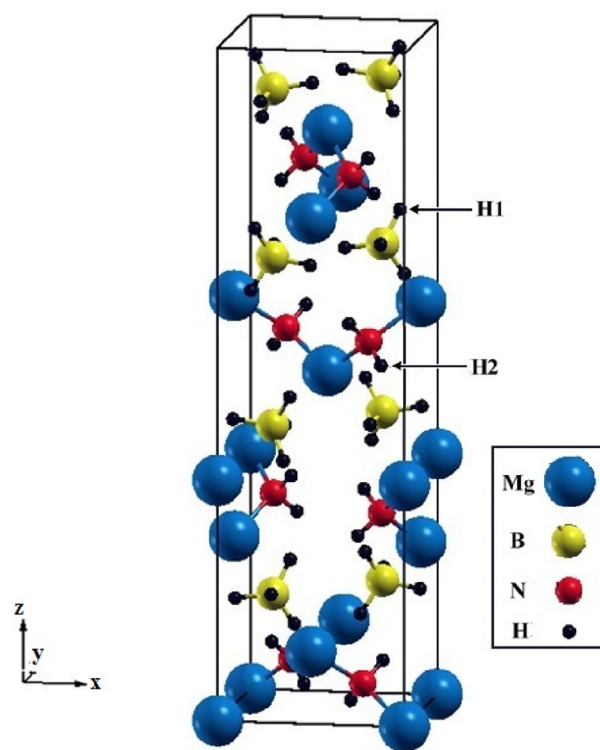

Fig. 1 – Conventional unit cell of $Mg(BH_4)(NH_2)$ structure. H1 (H2) denoted on the picture is H bonded to B (N).

threshold on energy was set to 10^{-7} eV during self-consistent calculations.

Results and discussion

The calculated lattice parameters and all atomic positions of $Mg(BH_4)(NH_2)$ compound were reported in Table 1.

According to obtained data, the calculated volume is slightly larger than the experimental one [42] by less than 1% that shows the reliability of the present calculations. However, it should be mentioned that our calculated data are

Table 1 – Calculated lattice parameters and the relative atomic positions of $Mg(BH_4)(NH_2)$ compound and the experimental values for comparison.

Lattice constants (Å)	a = 5.778, c = 20.853 [This work]		
	a = 5.792 (1), c = 20.632 (4) [42]		
Relaxed atomic positions	x	y	z
Mg1	0.000	0.000	0.000
Mg2	0.000	0.000	0.352
N1	0.748	0.165	0.052
B1	0.245	0.267	0.173
H1	0.328	0.356	0.130
H2	0.327	0.082	0.171
H3	0.057	0.252	0.164
H4	0.284	0.359	0.225
H5	0.673	0.274	0.019
H6	0.817	0.279	0.086