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Density-functional theory study of high hydrogen content complex hydrides Mg(BH₄)₂ at low temperature



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ABSTRACT

We present a systematic study of the low temperature and hexagonal structure of magnesium borohydride, a crystalline material designed for hydrogen storage purpose. We investigated, using *ab-initio* calculations, the structural, electronic and optical properties. Our calculated results for structural parameters nicely agree to the experimental measurements. The predicted elastic constants and related mechanical properties demonstrate its profound mechanical stability as well. The analysis of electronic structure reveals an insulator nature with a direct band gap about 6.55 eV in the Γ - Γ direction. This distinguish feature of Mg(BH₄)₂, like many other hydrides, depicts it as suitable substitute for large band gap material. The bonding behavior was also investigated in detail from the charge densities and effective charge populations. The hydrogen (H₂) storage capacity is found to be 14.94 wt.% within a reasonable reaction enthalpy of -44.35 kJ mol⁻¹. This might be easily affordable to consider Mg(BH₄)₂ as potential material for practical H₂ storage devices.

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1. Introduction

Hydrides in the future economy are considered to be imperative players of the energy sector [1–4]. Mainly hydrides caught attention of the researchers because of showing potential as hydrogen storage materials [4] and smart windows [5]. For these applications, the knowledge of hydrogen bonding with the atoms of host lattice and the kinetics of adsorption and desorption is crucial [6]. Though lot investigations have been conducted, a comprehensive solution is still away from the reality. Recently investigations on some hydride materials have uncovered their potential for novel photovoltaic and optoelectronics applications [7] besides showing application for the semiconductor electronics as well [8,9]. However such applications require comprehensive understanding of their electronic band structure/band gap and optical properties. Moreover these applications also need "conducting hydrides" with open fundamental band-gap structure [7]. Although some previous investigations on semiconducting hydrides have given sharp clue that the band-gap of the hydrides can be tuned from 0.6 to 7.0 eV [3,10–12], deep and thorough studies of such hydride materials are important.

Magnesium borohydride Mg(BH₄)₂ (hydrogen rich hydride containing ~15% of hydrogen by weight) is one of the important hydride material that fulfill requirements of standard hydrogen storage material. Though $Mg(BH_4)_2$ is reported for a long time [13], in fact, first time was synthesized via the reaction of MgH₂ with diborane by Plešek and Hermánek in 1966 [14]. Later on 1971, synthesis of Mg(BH₄)₂ was reported by Konoplev and Bakulina using exchange reaction of MgCl₂ with NaBH₄. In the same study they also provided the XRD pattern of its two crystal phases [15]. Recently, two other experimental studies on Mg(BH₄)₂ structures were conducted: one by a combination of the synchrotron and the neutron powder diffraction technique on the hexagonal α -phase [16]. The second one was performed, using the synchrotron X-ray powder diffraction technique, on the α -phase as well as on the high-temperature orthorhombic β -phase of the Mg(BH₄)₂ [17]. Theoretically, some studies based on density functional theory (DFT), were also conducted on the experimentally observed phases



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[18,19], where using experimental crystal data as a starting point, optimized results of the crystal structure parameters of the tetrahydroborates were reported. Then, Ozolins et al. [20] performed DFT calculations and concluded that both, α and β , phases of $Mg(BH_4)_2$ have nearly same energy as that of *I*-4m2 phase. These results later on were confirmed by Zhou et al. [21], where they modeled the structure of Mg(BH₄)₂ by taking start with a prototype structure $A(BH_4)_4$ rather than a comprehensive model of $A(BC_4)_2$. From this model structure they predicted two new and stable phases (F222 as well as I4122) of Mg(BH₄)₂ beside giving an explanation about the stability of I-4m2. Although some other investigations related to ground state and high pressure phases were found in literature [22]. For a long time, disagreement among the experimental and theoretical results has affected the identification of the ground state phase. Hence, exploring new structures/phases has attracted a growing attention among researchers until the publication of Filinchuk et al. work [23], which dispelled all confusions. Therefore, to highlight its potential for different applications, further studies at both experimental as well as theoretical level were crucial since many physical properties of Mg(BH₄)₂ have attracted attention from experimentalists and theorists especially in the hexagonal phase.

In this work, due to the anticipating role of $Mg(BH_4)_2$ in the energy sector, we present our investigation on low-temperature hexagonal $P6_122$ phase of $Mg(BH_4)_2$ [23] to unveil its potential as a hydrogen storage and material for visible and UV parts of the electromagnetic in optical devices as well. To perform our calculations we employed projector augmented wave (PAW) [24,25] method framed within the DFT at the level of generalized gradient approximation. Optimized geometrical parameters, and related reaction enthalpy and H₂ storage capacity, electronic structures, bonding nature and optical properties are determined. Our main purpose of this study is to endow with an overview about its structural, bonding and optical properties that are obligatory for improving and tailoring the electronic features for practical applications in various applications such as energy sector and H₂ storage.

2. Theoretical approaches and computational details

Our first principles DFT calculations have been performed by employing PAW approach [21] as implemented in "Vienna Ab-initio Simulation Package" (VASP) [25,26]. Perdew, Ernzerhof and Burke (PBE) [27] variant of the GGA is used for the exchange-correlation functional. This scheme of calculation grants an opportunity to generate wave functions similar to all electron schemes for the atoms of a material. In our calculations 500 eV value of plane wave cut off kinetic energy was used. To observe the effect of cut off energy, the value is varied over a range from 500 to 550 eV. No appreciable effect was noted of this variation on the main parameters, and the value of 500 eV was found to be suitable for all properties. To ensure convergence criterion of total energy difference between two consecutive iterations to less than 10^{-5} eV/atom, a mesh of $12 \times 12 \times 12$, using Monkhorst and Pack [28] approach of k-point sampling, was used to perform integration within irreducible wedge of the Brillouin zone. The bonding analysis was performed using the full potential method as implemented in WIEN2k code [29] for the charge density contours plots. We also employed the CASTEP code for computing Hirshfeld and Mulliken populations [30].

3. Results and discussion

We have initiated our DFT calculations by considering the hexagonal structure of $Mg(BH_4)_2$, which has been reported to be crystallize in the P6₁22 space group no. 169 below 453 K, with lattice constants a = 10.341 Å and c = 37.086 Å [23]. It can be seen. from the Fig. 1 that the low temperature (LT) Mg(BH₄)₂ crystal structure is a novel three dimensional complex network of Mg²⁺ ions and [BH₄] units, where each Mg²⁺ is surrounded with four [BH₄] tetrahedrons, and each [BH₄] is almost linearly connected with two Mg²⁺, resulting into an atypical eightfold asymmetrical hydrogen coordination environment. Its unit cell contains 330 atoms including "five symmetry independent Mg²⁺ cations and ten [BH₄] anions" [23]. This complexity of Mg(BH₄)₂ crystal structure might be due to the big differences in the sizes of cations and anions [23]. Another intriguing feature of this network is; Mg ions at local level look like amorphous [15]. Our optimized structural parameters and related structural features obtained after stress and force minimizations are listed, as in Table 1, together with experimental data obtained from X-ray diffraction [31]. Results obtained are nicely agree with the available experimentally measurements [23,31], as we have done a full (volume, shape of the cell, main distances and angles) structure relaxation. Our calculated results of lattice parameters are slightly underestimated ~0.5% to the experiment. This slight difference is mainly due to a relaxation of the atomic distances. However, the bond lengths and bond angles are within 2% of the measured values, with the slight deviation being the B-H distance. The reaction enthalpy of Mg(BH₄)₂ estimated at -44.35 kJ/mol is found by taking a difference between the sum of isolated atomic energies of its constituents and the total energy of $Mg(BH_4)_2$ for the reaction $Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$. Moreover, the negative value of reaction enthalpy indicates that the investigated phase of $Mg(BH_4)_2$ is thermodynamically stable. Most importantly, this reaction enthalpy is found closer to the experimental value (-39 kJ/mol) reported in Ref. [32] and corresponding to the following reaction pathway: $MgH_2 + B_2H_6 \rightarrow Mg(BH_4)_2$ [32].

After obtaining the detailed information about the structural parameters, we are able to analyze the mechanical properties. Using strain-stress technique, zero-pressure elastic constants 'C_{ii}' were calculated. The obtained values of elastic constants C_{11} , C_{12} , C₁₃, C₃₃, C₄₄ and C₆₆ are 42.0, 3.0, 2.1, 46.9, 9.0 and 19.7 GPa, respectively. The Born-Huang criterion [33] of elastic stability was verified over the whole set of elastic constants. The calculated anisotropic factor $A = \frac{4C_{44}}{C_{11}+C_{33}-2C_{13}}$ is found to be equal to 0.4. This indicates that the LT phase of Mg(BH₄)₂ is mechanically anisotropic owing to the fact that a value of A = 1 characterizes it completely isotropic, whereas the value > 1 or < 1 measures level of its elastic anisotropy. Using the calculated elastic constants, the bulk modulus was thus determined by using the Voigt-Reuss-Hill approximation [34]. Our calculated value for the bulk modulus, 15.9 GPa, is lower than the value of MgH₂ [34], 44 GPa [35]. In addition, this value is larger than those reported for the other phases of $Mg(BH_4)_2$ [36]. In fact, we could not find any 150 experimental data for the sake of comparison. However, the experimental bulk modulus for the alpha-phase, as long as for a few other $Mg(BH_4)2$ polymorphs were reported in Ref. [37]. Therefore comparison might be made with intermetallic hydride structures [35]. Low value of bulk modulus of $Mg(BH_4)_2$ shows that it is a soft and easily compressible solid. At room temperature, the capacity of H_2 -storage $Mg(BH_4)_2$ is estimated at 14.94 wt.% with reaction enthalpy -44.35 kJ mol⁻¹. This value is very competitive compared to characteristics of other potential H₂-storage materials such as MgH₂ and Mg₂FeH₆, with respectively reaction enthalpies of 82 and -78 kJ mol⁻¹, and H₂storage capacity 7.65 wt.% and 5.4 wt.%, respectively [12,38].

In the above calculations, temperature has no role, as the computation of the elastic constants was referred to zero temperature. In the other hand, it is well known that for a harmonic lattice the mean lattice parameters and elastic constants are independent of temperature. The observed temperature dependence of these quantities devolves from anharmonic behavior of the energy. This Download English Version:

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