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First principle study of hydrogen storage in doubly substituted Mg based hydrides Mg_5MH_{12} (M = B, Li) and Mg_4BLiH_{12}

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ABSTRACT

The effect of single and double substitution with lightweight elements Boron (B) and Lithium (Li) on the thermodynamic properties of MgH_2 are investigated by using first principles calculations. Our results show an improvement of hydrogen storage properties of double substituted MgH_2, in contrast to the case of single substitution, along with a remarkable increase of its gravimetric and volumetric capacities which exceed those of pure MgH_2. Given that Mg_4LiBH_{12} exposes a heat of formation around −32.03 kj/mol as well as a gravimetric and volumetric capacity of 9.45 wt% and 123.08 gH_2/l respectively, it may be considered as a potential candidate for hydrogen storage transportation applications. A detailed analysis of the density of states and charge transfer, of the studied systems, is presented to understand the underlying mechanisms behind MgH_2 thermodynamics improvements.

Introduction

Nowadays, Hydrogen is one of the most promising renewable energies that has emerged as a solution to overcome the rarity of fossil fuels and to protect the environment. It is the most abundant element on earth and its energy density is three times that of diesel. Moreover the outcome of its combustion is water. These qualities make hydrogen the ideal energy of tomorrow.

Hydrogen storage method should involve high volumetric, gravimetric capacity, a fast sorption rate at relatively low temperatures, and a recycling high tolerance. Alternative methods have been proposed including high pressure gas cylinders, liquid hydrogen, physisorption of hydrogen on materials with a high specific surface area, and hydrogen storage through hydrides. Among the different methods for hydrogen storage, the solid storage proves to be the best.

The magnesium based hydride (MgH_2) is one of the most promising materials for hydrogen storage applications due to its high gravimetric and volumetric capacities (7.65 wt% and 110 gH_2/l, respectively) [1]. However, the rather slow hydrogen sorption proprieties, as well as the high desorption

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temperature (573–673 K) hinder its commercial applications [2]. That is why various attempts have been made in order improve MgH_2 hydrogen absorbing and desorbing characteristics.

Experimentally, Nobuko Hanada et al. (2003) clarified the correlation between hydrogen storage and crystallographic properties in nanostructural magnesium hydride MgH_2 prepared by mechanical milling under hydrogen gaseous atmosphere. At the early stage of milling process, the rapid decrease in powder size leads to lowering the hydrogen desorption temperature (by 70 K), while the reduction of crystallite size of MgH_2 during milling dominates and controls the decrease in hydrogen storage capacity from 7.3 to 6.1 wt% [3].

Recently, it has been reported that adding additives or catalysts is considered as one of the most effective strategy to decrease the metal-hydrogen bonds energy and reduce the stability and desorption temperature of MgH_2 [4–19] by facilitating the Mg–H dissociation. Especially, the transition metals additive including their oxides.

Various theoretical calculations have been performed to understand the relevant mechanism dealing with the thermodynamic properties on magnesium hydride [20–22]. Combining the density functional theory (DFT) and Kinetic Monte Carlo simulation we have shown, in a previous work, that the pure MgH_2 presents a high stability and a high decomposition temperature [23,24]. At high temperature and pressure, the results of simulations indicate that the hydride involves slow kinetics [24].

On the other hand alloying MgH_2 with small amounts of transition metals mixture TM (TM = Ti, V and Fe, Sc, Zn) [23,25–27] or alkaline metal AM (AM = Ca, Sr and Ba) [28] or Al [25] improve the stability and the desorption temperature of hydrogen in Mg with decrease in the storage capacity from 7.65 wt% for the pure MgH_2 to 6.97 wt% for $Mg_{15}ZnH_2$ [26]. Also we have proposed a double substitution, with Al and Li as a second element due to their small weight, firstly to decrease the heat of formation and also the desorption temperature, and secondly to preserve the gravimetric storage capacity of MgH_2 [26].

The aim of this paper is to improve the thermodynamic properties of MgH_2 while increasing its storage capacities by studying the effect of substitution by lightweight metals like Li and B. This approach was proposed to overcome the drop of the gravimetric and volumetric capacities, which occurs in the large case cited above.

In the first part of the calculations we initiate a single substitution, where the system is doped by either Li or B (Mg_5LiH_{12}, Mg_5BH_{12}). The results show a decrease of MgH_2 stability and desorption temperature, however the results were not sufficient to reach the optimum values of heat of formation [29] and desorption temperature for a PEMFC (Proton Exchange Membrane Fuel Cells or Polymer Electrolyte Membrane Fuel Cells) [30]. In the second part we study the effect of double substitution with Li and B (Mg_4LiBH_{12}) as an approach to improve the results already obtained. Indeed, such approach leads to an important improvement of the thermodynamic properties accompanied by an increase of the gravimetric and volumetric capacities from 7.65 to 9.45 wt% and from 110 to 123.08 g H_2/l respectively.

Computational details

In this paper, we used ab initio calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34 [31,32]. This has been performed to solve the Kohn–Sham equations using the scalar-relativistic scheme. The parameterization of the exchange-correlation energy has been done within the generalized gradient approximations [33]. To ensure a high accuracy in our performed computations, we used both self-consistent criterions of the energy and the density together with a precision of 10^{-8} Ha and 10^{-6} Ha^{-1} $Å^{-3}$ respectively. For an accurate Brillouin zone integration, we considered a 12 × 12 × 4 K-point mesh.

MgH_2 has a tetragonal symmetry ($P4_2/mnm$, Group No.136). Mg and H atoms occupy the Wyckoff positions (0, 0, 0) and (0.304, 0.304, 0) respectively. MgH_2 lattice parameters are a = b = 4.501 Å and c = 3.010 Å [34]. A supercell of 1 × 1 × 3 of MgH_2 unit cell has been used for this study. For the case of single substitution 1 Mg atom was substituted by either B or Li (Mg_5LiH_{12}, Mg_5BH_{12}), whereas for double substitution two Mg atoms were substituted by B and Li respectively (Mg_4BLiH_{12}). The different systems are presented in Fig. 1.

Results and discussion

First of all, we relax the lattice parameters using the relaxation method, then we calculate the total energies and deduce the heat of formation and desorption temperature for each system. Finally, based on the charge exchange values and the density of states, we discuss the effect of doping on the stability of the systems.

Equilibrium structure and storage capacities

The systems relaxed lattice parameters are listed in Table 1, our calculated values are in fair agreement with other works results [23,35].

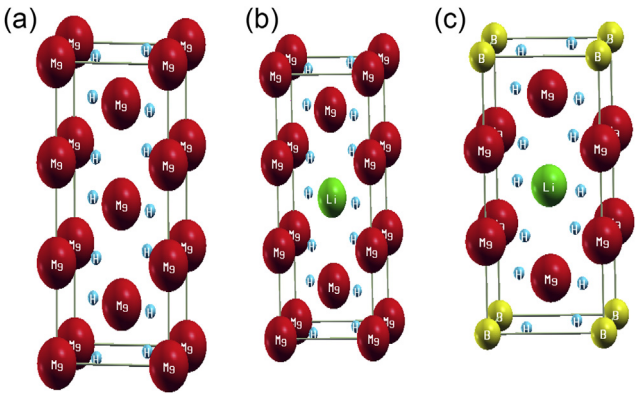

Fig. 1 – Crystal structures of (a) pure, (b) M-doped MgH_2 where M = B or Li; (c) Co-doped MgH_2. Red, blue, green and yellow balls represent respectively Mg, H, Li and B atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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