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Energetics and electronic properties of Mg_7TMH_{16} (TM = Sc, Ti, V, Y, Zr, Nb): An ab initio study

Xiao-Bing Xiao [a], Wei-Bing Zhang [a], Wei-Yang Yu [a], Na Wang [a], Bi-Yu Tang [a,b,*]

[a] Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Department of Physics, Xiangtan University, Hunan Province 411105, China
[b] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

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ABSTRACT

First-principles calculations have been performed on the face-centered cubic (FCC) magnesium–transition metal (TM) hydrides Mg_7TMH_{16} (TM = Sc, Ti, V, Y, Zr, Nb). The cohesive energies are calculated to analyze the stability, and the obtained enthalpies of formation for hydrides Mg_7TMH_{16} have been used to investigate the possible pathways of formation reaction. The calculated enthalpy changes show that the decomposition temperatures of Mg_7TMH_{16} are lower than that of MgH_2. The electronic densities of states reveal that all the hydrides studied here exhibit metallic characteristics. The bonding nature of Mg_7TMH_{16} is investigated, showing stronger covalent bonding between TM and H than between Mg and H.

1. Introduction

The use of fossil fuels has increasingly produced unwanted side effects: environmental pollution that threatens human health, carbon dioxide emissions that accelerate global warming, and the nonuniform distribution of fossil resources that leads to geopolitical tensions throughout the world. Great efforts are being made to develop sustainable and clean energy sources to replace the use of fossil fuels. Hydrogen has been viewed as a highly appealing energy carrier for renewable energy because of its abundance and environmental friendliness [1–3]. Achieving the object of hydrogen as an efficient, sustainable, and environmental friendly fuel requires widespread innovation and development of the means for its production, storage, and use [4]. Foremost among these is the issue of hydrogen storage. Existing technologies for hydrogen storage are limited to compressed gas and liquefaction, both of which are used now in demonstration vehicles. The most promising hydrogen storage routes are solid-state materials that chemically bind or physically adsorb hydrogen at volume densities greater than that of liquid hydrogen. An ideal solid hydrogen storage material for an on-board storage system should meet the requirements of high performance (high H-capacity, fast kinetics, and favorable thermodynamics), safety, and cost effectiveness simultaneously [5–7]. The US Department of Energy (DOE) has set the target for hydrogen storage at 6.0 wt% in the temperature range 253–353 K in 2010 [8].

The light metal hydrides have received a lot of attention, since hydrogen can be stored in these materials with high volumetric and reasonable gravimetric densities at a relatively low cost. Magnesium hydride (MgH_2) is a particularly interesting material, as it has an excellent theoretical hydrogen storage capacity of 7.6 wt%. This hydrogen capacity is enough for mobile applications, if all the hydrogen could be available. However, the enthalpy of hydrogenation is $\Delta H = -76$ kJ/mol H_2, which means that a temperature as high as 570 K is required to desorb hydrogen at atmospheric pressure. The high stability and slow absorption and desorption kinetics make this material unsuitable for potential application. Therefore, an important challenge enabling MgH_2 for practical applications is to find a way to destabilize it to lower its dehydrogenation temperature. A number of attempts are being made to modify this material to improve its properties, including doping it with small amounts of transition metals (TMs) [9–16].

* Corresponding author at: Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Department of Physics, Xiangtan University, Hunan Province 411105, China. Tel.: +86 732 8292195; fax: +86 732 8292468.
E-mail address: tangbiyu@xtu.edu.cn (B.-Y. Tang).

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Alloying magnesium with transition metals can improve effectively the hydrogenation/dehydrogenation kinetics, and also reduce the decomposition temperature of the hydride [12]. Besides the transition metals, some transition metal oxides, fluorides and halides also show positive catalytic effects on the dehydrogenation of MgH_2 [17–21].

Recently, it has been reported that novel ternary hydrides based on magnesium can be obtained using ultra-high pressure techniques, which possess unique hydrogen storage properties. Kyoi et al. [22] have synthesized a serious of new ternary magnesium–titanium hydrides, Mg_7TiH_x, in a high-pressure anvil cell by blending MgH_2 and $TiH_{1.9}$ at 8 GPa and 873 K, which shows a better dehydrogenation property than binary magnesium or titanium hydrides. Mg_7TiH_x has a face-centered cubic (FCC) structure with space group $Fm\bar{3}m$ (no. 225) and its hydrogen desorption temperature is lower by 130 K than that of MgH_2. Detailed crystal structure analysis for Mg_7TiH_x using high energy X-ray synchrotron radiation data has shown that hydrogen atoms occupy full tetrahedral sites (32f) [23], providing an estimated unit formula Mg_7TiH_{16} (6.9 wt% hydrogen). The FCC phase Mg_7NbH_x has also been obtained and investigated [24], which exhibits large amount of hydrogen desorption (4.5 wt%) and its hydrogen desorption temperature is lower by 140 K than that of MgH_2.

Density functional theory (DFT) has become a valuable tool in the effort to explore possible hydrogen storage materials [25]. It has greatly expanded our understanding of the properties of known hydrides, including electronic structure, hydrogen bonding characteristic, enthalpy of formation, elastic behavior, and vibrational energetics. Despite a considerable amount of experimental work, a fundamental and comprehensive understanding of the thermodynamic and electronic properties of magnesium–transition metal hydrides is still lacking. In the present paper, we have systematically calculated the enthalpy of formation, cohesive energy, and electronic structure for magnesium–transition metal hydrides using a face-centered cubic structure to model the hydrides Mg_7TMH_{16} (TM = Sc, Ti, V, Y, Zr, Nb). The transition metals Sc, Ti and V belong to early 3d elements and Y, Zr and Nb belong to early 4d elements, which are lighter than other 3d and 4d transition metals, respectively.

2. Computational method

The present calculations were carried out using Vienna ab initio simulation package (VASP) [26–29] based on the density functional theory [30]. The electron–ion interaction was described by the projector augmented wave (PAW) method [31,32]. A plane-wave basis set was used with a cutoff energy of 375 eV. It is well known that the generalized-gradient approximation (GGA) [33,34] generally gives better equilibrium structural parameters and energetics of different phases. Hence, the exchange and correlation energies were calculated using the GGA as proposed by Perdew and Wang (PW91) [35]. For Mg_7TMH_{16} hydrides (TM = Sc, Ti, V, Y, Zr, Nb), we used an $8\times8\times8$ Monkhorst–Pack [36] k-point mesh for sampling Brillouin zone. For TMH_2 which had been calculated using the fluorite structure, k-point sampling was performed on a $12\times12\times12$ grid. For rutile structure MgH_2, a $12\times12\times16$ Monkhorst–Pack k-point mesh was used. A Gamma centered $18\times18\times12$ mesh was used for hexagonal close-packed metals Mg, Sc, Ti, Y and Zr, and an $18\times18\times18$ Monkhorst–Pack k-point mesh was used for body-centered cubic metal V and Nb. The valence electronic configurations were taken to be $2p^63s^2$ for Mg, $3s^23p^63d^14s^2$ for Sc, $3p^63d^24s^2$ for Ti, $3p^63d^34s^2$ for V, $4s^24p^64d^15s^2$ for Y, $4s^24p^64d^25s^2$ for Zr, $4p^64d^45s^1$ for Nb, and $1s^1$ for H. In order to get the precise crystal structures and total energies, all structural degrees of freedom including unit-cell volume and shape as well as atomic positions were relaxed simultaneously. The relaxations of cell geometry and atomic positions were carried out using a conjugate gradient algorithm until the Hellman–Feynman force on each of the unconstrained atoms was less than 0.01 eV/Å. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 10^{-6} eV at consecutive steps. When the optimized crystal structures were obtained, the total energies were calculated using the tetrahedron method with Blöchl corrections which could give very accurate total energies in bulk materials.

3. Results and discussion

3.1. Crystal structure

Understanding the structural properties of hydrides is the primary step toward their experimental characterization, and also a prerequisite for finding or designing materials with specific storage thermodynamics [37]. The series of Mg_7TMH_{16} (TM = Sc, Ti, V, Y, Zr, Nb) compounds have a face-centered cubic unit cell with Ca_7Ge space group containing 96 atoms. The primitive cell of Mg_7TMH_{16} consists of 24 atoms with magnesium atoms in 4b (1/2,1/2,1/2) and 24d (0,1/4,1/4) sites, transition metal atoms in 4a (0,0,0) site and hydrogen atoms locating in tetrahedral sites (32f) between the close packed layers of magnesium and transition metal. The conventional unit cell and primitive cell of Mg_7TMH_{16} are shown in Fig. 1, and each conventional unit cell has four primitive cells. In order to save computational cost, we have used the primitive cell of hydrides Mg_7TMH_{16} for our calculations. The theoretical equilibrium lattice constants and bulk moduli (B) of the hydrides Mg_7TMH_{16} are determined by fitting the total energies as a function of volumes to Murnaghan equation of states (EOS) [38]. Murnaghan equation of states can be written as

$$E_{Murn}(V)-E(V_0)=\frac{B_0V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0'-1}+1\right]-\frac{B_0V_0}{B_0'-1} \quad (1)$$

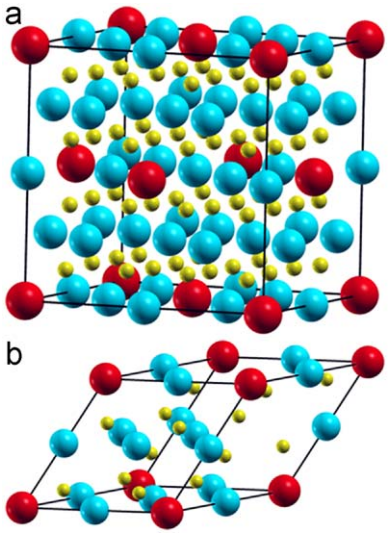

Fig. 1. Crystal structure of Mg_7TMH_{16} (TM = Sc, Ti, V, Y, Zr, Nb): (a) conventional unit cell and (b) primitive cell. Green (middle), red (large), and yellow (small) spheres represent magnesium, transition metal, and hydrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web vesion of this article.)