

Energetic, structure stability, electronic structure, and optical properties of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ crystal from first principles calculations

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We report a first-principles study of energetic, structural and electronic properties of TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. While the optical properties was studied for only $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. Our calculated structural parameters are found in good agreement with the experiment and other theoretical results. The formation enthalpies are calculated to analyze the stability of the two hydrides. The calculated enthalpy changes show that the stability of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is lower than that of TiH_2 . The electronic density of states reveals that the two hydrides studied here exhibit metallic characteristics. And the origin of the change of density of states for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ caused by adding magnesium to TiH_2 is studied. We also study electronic charge density distribution contours in the (110) crystallographic plane and Mulliken charge populations, which indicates that the bonding nature of the two hydrides is covalent bond between Ti and H and bonds between Ti and H in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ are weakened by the addition of magnesium. Furthermore, the optical features such as dielectric function, refractive index, extinction coefficient, reflectivity, absorption coefficient, photoconductivity and electron energy-loss function of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ were calculated for photon energy up to 16 eV. The calculated results show that $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ has a considerable absorption, high photoelectric conversion efficiency for sunlight with the longer wavelengths. These results provide a theoretical basis for preparing Mg-Ti-H photoelectric materials as switchable coatings for solar collector applications.

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1. Introduction

Recently, metastable $\text{Mg}_x\text{Ti}_{1-x}\text{H}_2$ hydrides ($x \geq 0.5$) have been shown to exhibit remarkable optical properties which could be especially useful for smart solar cell coatings [1] and hydrogen sensor applications [2], due to the hydrogen-induced optical transition from a shiny metallic state to a black light-absorbing state. In the dehydrogenated state the Mg-Ti-H are highly reflective. Upon hydrogenation they become black, i.e., they have a low reflection and high absorption in the energy range of the solar spectrum. The origin of the “black state” is not understood. Its explanation is, of course, intimately related to electronic structure of the hydrides. Borsa and co-workers [3-5] reported that $\text{Mg}_x\text{Ti}_{1-x}\text{H}_2$ ($x \geq 0.7$) thin films have remarkable optical properties. For example, highly reflective in the metallic state, the films become strongly absorbing upon hydrogen absorption. The switching between the two optical states is fast, robust, and reversible. The combination of these properties highlights the applicability of Mg-Ti-H thin films as switchable smart coatings for solar collector applications.

However, for Mg-Ti-H hydrides with high Ti content,

such as $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$, the electronic and optical properties have been not investigated so far. In an effort to advance the understanding of those properties for the hydrides, in this study, the first-principles calculations were performed to determine the stabilization, the electronic and optical properties of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 by using the pseudopotential plane-wave method based on density functional theory. The present study will provide a theoretical basis for preparing Mg-Ti-H photoelectric materials with excellent absorption and photoelectric conversion efficiency over the entire visible range.

2. Computational methods

All calculations were performed using Density Functional Theory (DFT) as implemented in the Quantum-ESPRESSO [6]. The Kohn-Sham equations were solved using a basis of Projector Augmented Wave-functions with a plane-wave energy cut-off 310 eV, and using pseudopotentials [7] to describe the core electrons. The Perdew-Wang 1991 generalized gradient

approximation (GGA) was used for the electron-exchange correlation potential [8]. For $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydrides, we used an $8 \times 8 \times 8$ Monkhorst-Pack [9] k -point mesh for sampling Brillouin zone. For TiH_2 which had been calculated using the fluorite structure, k -point sampling was performed on a $12 \times 12 \times 12$ grid. A Gamma centered $18 \times 18 \times 12$ mesh was used for hexagonal close-packed metals Mg and Ti. Convergence with respect to the k -point sampling for the Brillouin zone (BZ) integration is tested independently on the two compounds using regular meshes of increasing density. Tests indicate that the total energy converges to 1 meV/atom. The valence electronic configurations were taken to be $2p^63s^2$ for Mg, $3s^23p^63d^24s^2$ for Ti, and $1s^1$ for H. For all structures the lattice parameters, the volume and the atom positions were allowed to relax 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 $0.01 \text{ eV/\text{Å}}$. 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. After the structures are optimized, the total energies are recalculated self-consistently with the tetrahedron method [10]. The latter technique is also used to calculate the electronic density of states (DOS).

To model the optical response of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydride due to an external electromagnetic field with a small wave vector, The frequency dependent dielectric function (dispersion of dielectric function) $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is used. The equation of the frequency dependent imaginary part of a dielectric function $\varepsilon_2(\omega)$ for cubic crystal as given in ref.[11] is

$$\varepsilon_2 = \frac{4\pi^2}{m^2\omega^2} \sum_{c,v} \int_{BZ} \frac{2}{(2\pi)^3} \cdot |eM_{cv}(K)|^2 \delta[E_c(K) - E_v(K) - \hbar\omega] d^3k \quad (1)$$

where c and v denotes conduction band and valence band respectively, e is electron charge, m is electron mass, $\hbar\omega$ is the energy of the incident photon, BZ is the first Brillouin zone, K is reciprocal lattice vector, $|eM_{cv}(K)|^2$ is transition momentum matrix, $E_c(K)$ and $E_v(K)$ is intrinsic energy level of the conduction band and valence band respectively. The real part of the dielectric function $\varepsilon_1(\omega)$ can be obtained from $\varepsilon_2(\omega)$ by Kramers-Kronig relation as given

$$\varepsilon_1 = 1 + \frac{8\pi^2 e^2}{m^2} \sum_{c,v} \int_{BZ} \frac{2}{(2\pi)^3} \cdot \frac{|eM_{cv}(K)|^2}{E_c(K) - E_v(K)} \cdot \frac{\hbar^3}{[E_c(K) - E_v(K)]^2 - \hbar^2\omega^2} d^3k \quad (2)$$

The other optical constants like refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, photoconductivity $\sigma(\omega)$ and electron energy-loss function $L(\omega)$ now immediately are calculated in terms of the components of the complex dielectric

function as follows:

$$\varepsilon_1(\omega) = n^2(\omega) - \kappa^2(\omega) \quad (3)$$

$$\varepsilon_2(\omega) = 2n(\omega) \cdot \kappa(\omega) \quad (4)$$

$$\alpha(\omega) = \frac{\omega}{nc} \varepsilon_2 \quad (5)$$

$$R(\omega) = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (6)$$

$$\sigma(\omega) = \sigma_1 + i\sigma_2 = -i \frac{\omega}{4\pi} [\varepsilon(\omega) - 1] \quad (7)$$

$$L(\omega) = \text{Im}\left(-\frac{1}{\varepsilon(\omega)}\right) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \quad (8)$$

3. Results and discussion

3.1. Crystal structure

The $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydride has a face-centered cubic unit cell with Ca_7Ge space group ($Fm\bar{3}m$) containing 96 atoms. The primitive cell of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ consists of 24 atoms with magnesium atoms in 4a (0,0,0) sites, titanium atoms in 4b (1/2,1/2,1/2) and 24d (0,1/4,1/4) site and hydrogen atoms locating in tetrahedral sites (32f) between the close packed layers of magnesium and titanium. The conventional unit cell of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is shown in Fig. 1(a). The TiH_2 crystal has the fluorite structure, space group $Fm\bar{3}m$, see Fig.1(b), where the Ti atoms occupy 4a (0, 0, 0) sites and hydrogen atoms reside at 8c (0.25, 0.25, 0.25) sites [12].

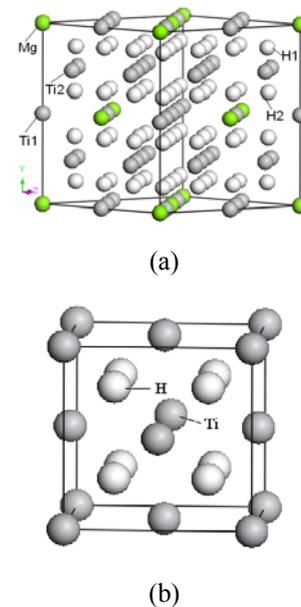


Fig.1 Model of (a) $\text{Mg}_{0.125}\text{Ti}_{0.875}\text{H}_2$ conventional unit and (b) TiH_2 crystal cell.

First, we calculate the cell unit parameters and the total energy of pure metal Mg and Ti, H₂ molecule, Ti_{0.875}Mg_{0.125}H₂ and TiH₂. Table 1 gives the calculated values of the equilibrium lattice constants, cell unit volume and the total energy for above structures and the experimental results. The calculated cell unit parameters of elemental crystal Mg and Ti, H₂ molecule and TiH₂ are in good agreement with experimental results. For Ti_{0.875}Mg_{0.125}H₂ compound, it has been not experimentally synthesized so far. Süleyman et al. [15] reported 0.8889 nm of the lattice parameters obtained from DFT calculation for the face-centered cubic Ti_{0.875}Mg_{0.125}H₂. The calculated value in this study is in good agreement with the result reported by Süleyman et al. Moreover, Table 2 gives the Wyckoff positions and the hydrogen-metal coordination of the calculated structure of Ti_{0.875}Mg_{0.125}H₂ and TiH₂ hydrides. As seen in Table 2, the hydrogen atoms in Ti_{0.875}Mg_{0.125}H₂ occupy two kinds of tetrahedral interstice positions. The tetrahedral environment of an H1 atom consists of an Mg atom at a

distance of 0.1994 nm and three Ti2 atoms at 0.1917 nm. The tetrahedral environment of an H2 atom consists of a Ti1 atom at a distance of 0.1927 nm and three Ti2 atoms at 0.1938 nm. For TiH₂ hydride, the hydrogen atoms reside at the ideal tetrahedral interstice positions. The calculated value of the Ti-H distance is 0.1914 nm, and the experimental distance is 0.1916 nm [12]. Asano et al. [16] analyzed the crystal structures of Mg-Ti-H compounds (fcc structure) synthesized by the high energy ball-milled method, and concluded the hydrogen atoms in Mg-Ti-H and TiH₂ structures both reside the tetrahedral interstice positions. Thus it can be seen that our calculation results are in good agreement with experimental data. Furthermore, we find that the distances of Ti2-H1, Ti1-H2 and Ti2-H2 in Ti_{0.875}Mg_{0.125}H₂ structure are larger than that of Ti-H distance in TiH₂ structure. It is shown that the addition of a certain amount of Mg to TiH₂ structure should reduce the stabilization of TiH₂. The change trend of the stabilization for the two hydrides will be also discussed in latter sections.

Table 1 Results for Mg, Ti, H₂ molecule, Ti_{0.875}Mg_{0.125}H₂ and TiH₂ including equilibrium lattice constants, total energy E_{tot} (eV/formula unit) and formation enthalpy ΔH (kJ/(mol H₂)).

Compound	Lattice parameter (nm)		Space group	Volume (nm ³ /f.u.)	Total energy E_{tot} (eV/f.u.)	Formation enthalpy ΔH (kJ/(mol H ₂))
	<i>a</i>	<i>c</i>				
Mg	0.3156 (0.321) ^[13]	0.5428	<i>P6₃/mm</i>	—	-1957.0216	—
Ti	(0.521) ^[13]	—	<i>c</i>	—	-3212.5050	—
Ti _{0.875} Mg _{0.125}	0.2941 (0.295) ^[13]	0.4684	<i>P6₃/mm</i>	0.7143	-49977.424	-78.583
H ₂	(0.468) ^[13]	—	<i>c</i>	0.08793	-6557.3392	-146.312
TiH ₂	0.8939	—	<i>Fm3m</i>	—	-31.5652	—
H ₂	0.4420	(0.4454) ^[12]	<i>Fm3m</i>	—	—	—
	—		Gas			
	d = 0.0745 (0.0756) ^[14]					

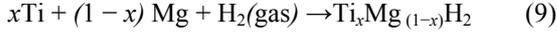
Note: experimental data is given in parentheses.

Table 2 Optimized atomic positions of Ti_{0.875}Mg_{0.125}H₂ and TiH₂

	Atom	Wyckoff site	Position		
			<i>x</i>	<i>y</i>	<i>z</i>
Ti _{0.875} Mg _{0.125} H ₂	Ti1	4b	0.5	0.5	0.5
	Ti2	24d	0	0.25	0.25
	Mg	4a	0	0	0
	H1	32f	0.1288	0.1288	0.1288
	H2	32f	0.3755	0.3755	0.3755
TiH ₂	Ti	4a	0	0	0
	H	8c	0.25	0.25	0.25
Exp.[12]	Ti	4a	0	0	0
	H	8c	0.25	0.25	0.25

3.2. Formation enthalpy

To estimate the stability of Mg-Ti-H structures we look at the reaction



where x is the mole fraction of Ti in hydrides ($x=1$ and 0.875).

In principle one should consider the change in Gibbs free energy $G(T, P) = U + PV - TS$ of equation (9). As the thermodynamic properties of hydrogen gas are well documented [17], one can focus upon the solid phases involved in the reaction. In addition, the temperature dependence of G of such solids tends to be relatively small over the temperature range of interest [18, 19]. A

$$\Delta H(\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2) = \frac{1}{32} [E_{\text{tot}}(\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2) - 28E_{\text{tot}}(\text{Ti})_{\text{solid}} - 4E_{\text{tot}}(\text{Mg})_{\text{solid}} - 32E_{\text{tot}}(\text{H}_2)] \quad (11)$$

where $E_{\text{tot}}(\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2)$ and $E_{\text{tot}}(\text{TiH}_2)$ are the total energy of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 cell unit respectively, $E_{\text{tot}}(\text{Mg})_{\text{solid}}$ and $E_{\text{tot}}(\text{Ti})_{\text{solid}}$ are the total energy of per atom of pure solid states Mg and Ti respectively, $E_{\text{tot}}(\text{H}_2)$ is the total energy of hydrogen molecule, which was calculated as 31.5652 eV using the von Barth-Hedin exchange correlation potential [20]. Results of the formation enthalpy of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 systems were also listed in Table 1. The present formation enthalpy of TiH_2 is close to the values $-1.30 \sim -1.50$ eV ($-125.37 \sim -144.66$ kJ/mol $\cdot\text{H}_2$) measured experimentally [21]. Comparing the formation enthalpy of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 in Table 1, it was shown that replacing titanium by magnesium reduces the stabilization of the compound $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$, and hence, is favor of enhancing the dehydrating kinetics of the compound.

3.3. Electronic structure

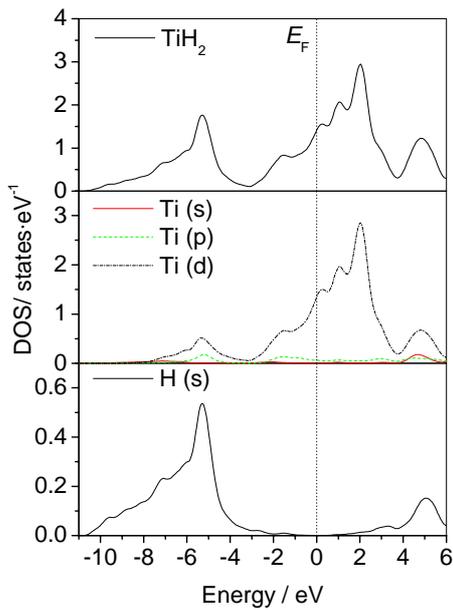
To understand the effect of Mg on electronic bonding properties and the stability of Ti-Mg-H systems, the density of states (DOS), the charge density distribution and Mulliken charge populations are analyzed for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 . Fig. 2 shows the total densities of states (TDOS) and partial densities of states (PDOS) for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ and TiH_2 . The most remarkable feature of the total densities of states for the two hydrides is that both the hydrides exhibit metallic characteristic. Fig (2a) shows the DOSs of TiH_2 without magnesium. There are three bonding peaks in the energy range between 5.0 eV and

calculation of the change in enthalpy $H = U + PV$ at $T = 0$ K should therefore be adequate to assess the relative stability of metal hydrides. Since moreover the PV contribution of solids can be neglected, it suffices to focus upon the change in energy U .

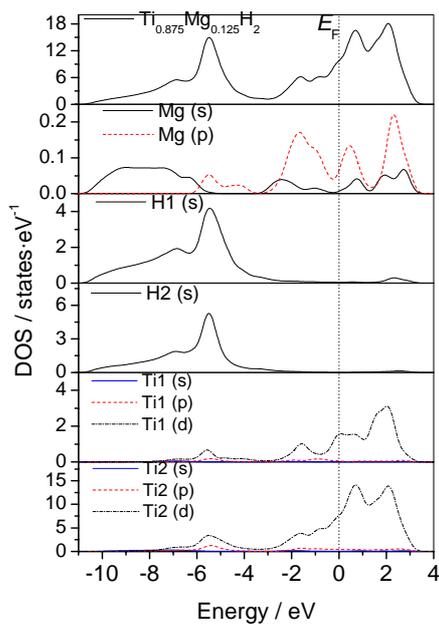
In the present work we employ the formation enthalpy to study the stabilization of titanium hydrides with and without magnesium. The lower the formation enthalpy is, the more stable the crystal structure is. The formation enthalpy (ΔH) of per mole hydrogen in solution and in the TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydrides were calculated, respectively:

$$\Delta H(\text{TiH}_2) = \frac{1}{4} [E_{\text{tot}}(\text{TiH}_2) - 4E_{\text{tot}}(\text{Ti})_{\text{solid}} - 4E_{\text{tot}}(\text{H}_2)] \quad (10)$$

-6.0 eV. The main peak (about 2.0 eV) is mainly from contribution of Ti 3d electrons. The second peak (about -5.3 eV) is mainly caused by the hybridization between H 1s and Ti 3d, 3p orbital electrons. The third peak (about 5.0 eV) is duo to the hybridization between H 1s and Ti 3d, 4s orbital electrons. Moreover, the valence band is mainly attributed to H 1s electrons and the conduction band is mainly dominated by the contribution of Ti 3d band. However, the DOSs of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ are distinctly different from those of TiH_2 , as shown in Fig. 2(b). Comparing the DOSs of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ with TiH_2 , it is found that $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ has the following characteristics: (i) the bonding peaks near Fermi level (about 0.71 eV and 2eV) are dominated by the stronger Ti-H, H-H and the weaker Mg-H interaction. (ii) the structure of DOS of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ below the Fermi level is dominated by the Ti1-H1, Ti1-H2, Ti2-H1, Ti2-H2, H1-H2 interaction. (iii) The bonding electron numbers at the Fermi level, $N(E_F)$ are higher for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ than that for TiH_2 . This is mainly attributed to the addition of Mg atoms to change the local electronic environment of Ti atoms. In general, $N(E_F)$ on DOS plot can be used to characterize the activity of valance electrons of the atoms in crystal. Namely, the smaller $N(E_F)$, the less is change probability of the electronic structures of the crystal when external conditions change, thus the crystal has the higher stability [22]. It is shown that the stability of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is lower than that of TiH_2 . The conclusion consists with the forementioned result from energetic analysis.



(a)

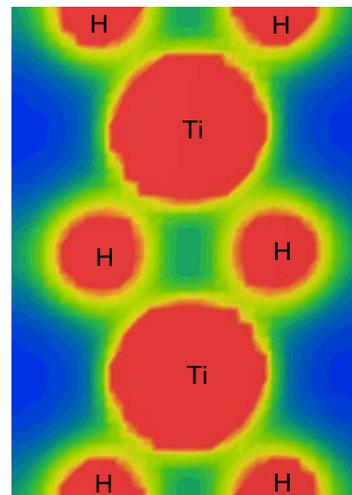


(b)

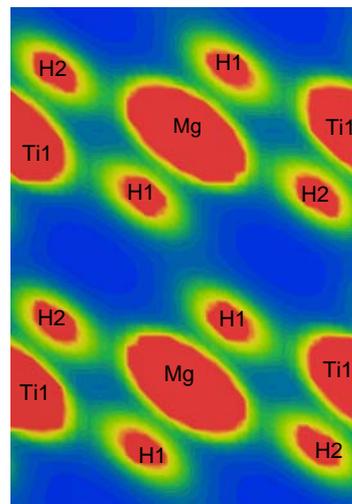
Fig. 2 Total and partial density of states of TiH_2 (a) and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ (b).

In order to understand the bonding nature of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ in more details, the charge density distribution and Mulliken charge population analysis have been investigated. The charge density distributions on the (110) plane of TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ systems are shown in Fig. 3. It is clearly shown that the charge density distribution between Ti and H in TiH_2 is much stronger than that between Ti and H, Mg and H in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$.

This shows that the bonds between Ti and H in is weakened because the charge density between these atoms is reduced by the addition of magnesium. Table 3 shows the charge populations and average charge populations per unit bond length between two atoms in TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. It is found that there are the valence bonds between H1 and Ti2, H2 and Ti1, H2 and Ti2, and not between H and Mg in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. The reason is that the chemical affinity between Mg and H atoms is less than that between Ti and H atoms. The stronger is the chemical affinity between Ti and H atoms, the stronger is the capability of bonding between Ti and H atoms. Moreover, the charge populations and average charge populations per unit bond length of Ti-H (H1-Ti2, H2-Ti1, H2-Ti2,) in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is smaller than that in TiH_2 . It is indicated that the bonding interaction between Ti and H in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is weakened. It is favorable to decrease dehydrogenation temperature of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$.



(a)



(b)

Fig. 3 Total charge density distribution on the (1 1 0) plane of TiH_2 (a) and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ (b).

Table 3 Charge population between two atoms in TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$.

Compounds	Bond	Charge population	Bond Length/ nm	Average charge population per unit bond length/ nm
$\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$	H1-Ti2	0.27	0.191653	1.409
	H2-Ti1	0.16	0.192693	0.8303
	H2-Ti2	0.18	0.193820	0.9287
	H1-Mg	-0.28	0.199432	-1.404
TiH_2	H-Ti	0.34	0.191448	1.776

3.4. Optical properties

The linear optical properties of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydride has been investigated by calculating the optical parameters, dielectric function $\epsilon(\omega)$, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, photoconductivity $\sigma(\omega)$ and electron energy-loss function $L(\omega)$. The dispersion of the real and imaginary parts of the dielectric function, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ are shown in Fig. 4. It is clear from Fig. 4 that $\epsilon_2(\omega)$ shows an energy spectral peak at low energy (about 1.0 eV), followed by a relative flat tail in the range of 2-12 eV. The peak in the dielectric function at low energy arises from Ti d-d electrons transitions. From the analysis of the above DOS of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ (Fig. 2 (b)), the structure around the Fermi level mainly results from titanium-d states. This shows a high effective mass of the titanium-d electron or a possible localization of these electrons. Thus, it is expected that low energy optical excitation results from a contribution of transitions between titanium-d states. van Setten et al. [23] also obtained the same results as this work from the optical properties of Mg-Ti-H systems by first-principle calculation.

The main features of the dispersive part $\epsilon_1(\omega)$ of the dielectric function are: a maximum peak in the curve at around 0.46 eV and a minimum peak at around 1.62 eV; there is a rather steep decrease from 0.46 to 1.62 eV; after the minimum peak (1.62 eV), $\epsilon_1(\omega)$ rises slowly up to 5.9 eV, and then $\epsilon_1(\omega)$ has a little unobvious decrease from 5.9 eV to 7.17 eV followed by a slow increase toward the value of 1.0 at high energies. For $\epsilon_1(\omega)$, the most important quantity is the zero frequency limit $\epsilon_1(0)$, which gives the static dielectric constant of 68.9.

Fig. 5 depicts the absorption coefficient of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. It is shown from Fig. 5 that $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ has a significant absorption in the energy range 0-12.09 eV. Especially for the whole visible range (1.62-3.11 eV), $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ presents a black appearance. It is very significant for the applicability of Mg-Ti-H thin films as switchable coatings for solar collector applications [3].

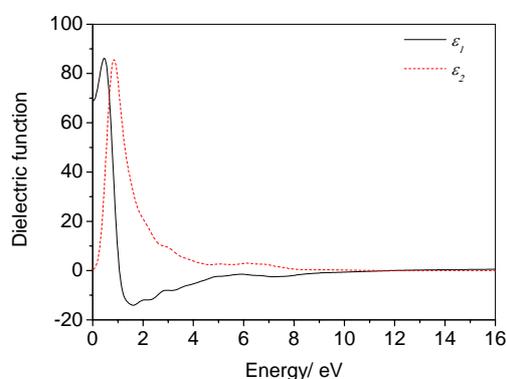


Fig. 4 Imaginary part of dielectric function of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

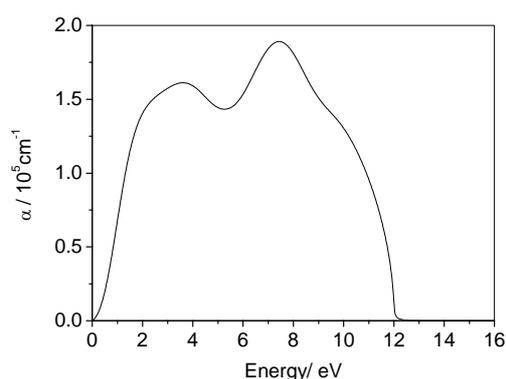


Fig. 5 Adsorption coefficient of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ are shown in Fig. 6 for $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. The refractive index $n(\omega)$ above 2 eV becomes close to the smaller constant. It consists with the results reported by Süleyman et al. [15] that the refractive index of $\text{Mg}_x\text{Ti}_{1-x}\text{H}_2$ ($x=0.5, 0.75$ and 0.875) above 1 eV becomes close to constant. The calculated static refractive index $n(0)$ is

equal to 8.30 while $n(\omega)$ and $k(\omega)$ have the maximum values at 0.523 eV and 1.04 eV, respectively. The local maxima of $k(\omega)$ corresponds to the zero of $\varepsilon_1(\omega)$ ($E = 1.04$ eV). The large $k(\omega)$ (below 2 eV) is typical for the electron plasma response of metals, which matches the DOS shown in Fig. 2(b). The extinction coefficient of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is zero at the photon energy larger than 12.09 eV. It corresponds to the edge of absorption spectra. Namely, the frequency of the incidence light is not less than the natural oscillation frequency at the photon energy greater than 12.09 eV. The amount of optical absorption used for the characterizing solid are close to zero, the refractive index change into the normal dispersion with frequency. $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ convert into transparent again. Moreover, we note that the obtained refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ is similar to the imaginary part $\varepsilon_2(\omega)$ of the dielectric function and the dispersive part $\varepsilon_1(\omega)$ of the dielectric function, respectively.

Fig. 7 shows the reflectance spectra of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ at normal incidence. The reflectivity of the hydride is in the range of 0.64-0.66 over infrared and the entire visible region. However, the reflection over the ultraviolet region is irregular, and the maximum of reflectivity (0.9 or 90%) is at 12.09 eV, which is in the ultraviolet region. Therefore $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ can be considered as shielding from ultraviolet radiation.

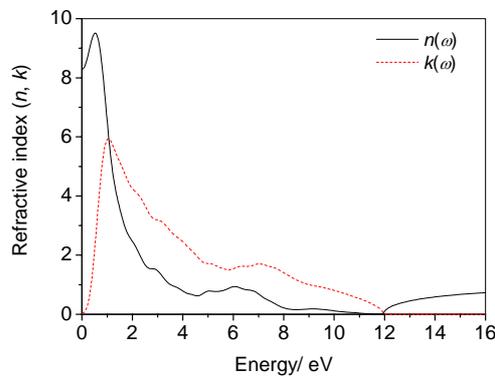


Fig. 6 Index of refraction (n, k) of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

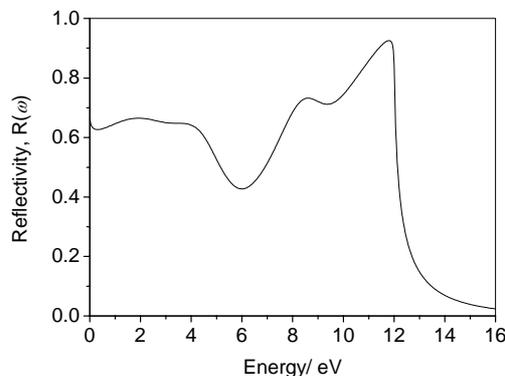


Fig. 7 Reflectance of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

The electron energy loss function, $L(\omega)$, is an important factor appraising the energy loss of a fast electron passing through a material. The $L(\omega)$ shows a peak at 12.09 eV in Fig. 8. The peak represents the feature that is associated with plasma resonance, and the corresponding frequency is called plasma frequency, ω_p [24]. The peak also corresponds to the edge in the reflectivity spectrum in which an abrupt reduction occurs at this peak value. It is related with the zero crossing of $\varepsilon_1(0)$.

The photoconductivity is mainly used to measure the variation of conductivity of semiconductor caused by the light radiation. It is intimately associated with solar photovoltaic energy conversion. Fig. 9 shows the variation of the real part, σ_1 and imaginary part, σ_2 of photoconductivity with photon energy. There are two peaks on the plot of the σ_1 in the studied energy range. The maximum of the photoconductivity is about 1.37 eV ($\lambda=905.6$ nm) which is in near infrared region. Moreover, the photoconductivity in entire visible region (about 1.62-3.11 eV) is relatively large. Therefore, we shall predict that $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ have a considerable absorption, high photoelectric conversion efficiency for sunlight with the longer wavelengths. These properties highlight the applicability of Mg-Ti-H as switchable coatings for solar collector applications.

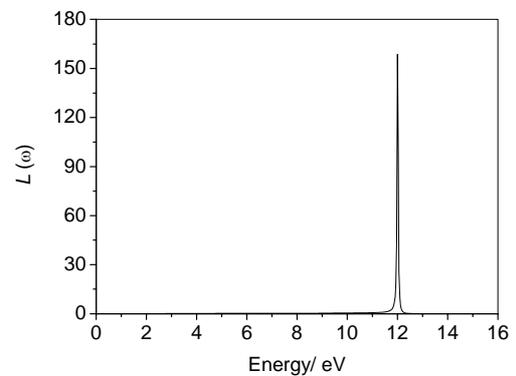


Fig. 8 Electron energy-loss function of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

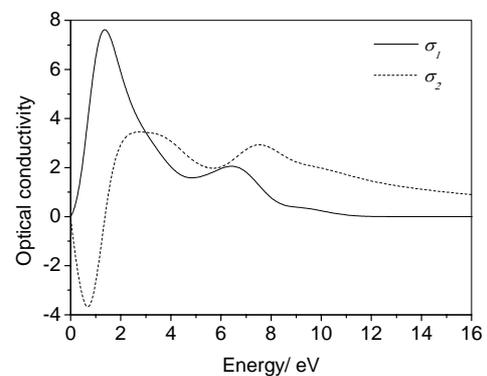


Fig. 9 Photoconductivity of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$

To the best of our knowledge, we first investigated the structural stability, electronic structure and the optical properties of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ hydride. These results may give insight related to its performance in applied fields and becomes motivation for the researchers to do more experiments in this field.

4. Conclusions

In the present study, we have performed the first-principles calculation of energetic, structural and electronic properties of TiH_2 and $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ using a basis of a plane-wave pseudo-potential method within a framework of the density function theory. The optical properties was studied for only $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$. The structural parameters have been calculated and found to be in good agreement with the existing experimental and theoretical data. The calculated enthalpies of formation reveal that the stabilization of the hydride $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ is lower than that of TiH_2 by adding Mg atom to TiH_2 hydride. The analysis of the density of states, charge density and Mulliken charge population indicates that the bonding nature of the two hydrides is covalent bond between Ti and H and bonds between Ti and H in $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ are weakened by the addition of magnesium. The calculated results from the optical properties of $\text{Ti}_{0.875}\text{Mg}_{0.125}\text{H}_2$ show that the hydride has a considerable absorption, high photoelectric conversion efficiency for sunlight with the longer wavelengths. These results provide a theoretical basis for preparing Mg-Ti-H photoelectric materials as switchable coatings for solar collector applications.

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