Zinc substituted MgH₂ - a potential material for hydrogen storage applications

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Abstract
The search for efficient materials for onboard hydrogen storage applications is an emerging research field. Using density functional calculations, we demonstrate Zn substituted MgH₂ as a potential material for hydrogen storage. We predicted the ground state crystal structure of ZnH₂ which is found to be Pna2₁ (orthorhombic) structure with meta-stable behavior. The structural phase stability and phase transition of Mg₁ₓZnₓH₂ systems have been analyzed. The H site energy of Mg₁ₓZnₓH₂ systems is calculated to understand the hydrogen desorption process. Our calculations suggest that Zn substitution reduces the stability of MgH₂, thereby it may reduce the decomposition temperature of MgH₂. The band structure and density of states calculations reveal that the Mg₁ₓZnₓH₂ systems are insulators. The chemical bonding behavior of Mg₁ₓZnₓH₂ systems is established as ionic-covalent in nature. Moreover, Zn substitution in MgH₂ induces disproportionate Mg–H bonds which could also contribute the reduction in the decomposition temperature as well as H sorption kinetics.

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Introduction
The worldwide energy demand coupled with shrinking fossil fuel resources and environmental pollution are continuously rising every year which have lead us to an increasing curiosity to find alternative energy resources. Hydrogen is an ideal chemical energy carrier that exhibits a high calorific value per unit mass and is environmentally friendly [1–7]. However, the main challenge is to store hydrogen safely and efficiently for mobile and stationary applications. Based on this, many researchers considered light weight magnesium hydride (MgH₂) for onboard hydrogen storage applications owing to its high hydrogen storage capacity, low cost, and abundance. But the practical use of MgH₂ for hydrogen storage is hampered by its high decomposition temperature and quite slow hydrogen sorption kinetics [8–29]. The high decomposition temperature in MgH₂ is associated with strong ionic bonding. One of the key solutions for this issue is by adding catalysts or substituting other elements to make Mg–H bond weaker. It is demonstrated that by increasing the covalency in the hydrides, one can reduce their decomposition temperature [30]. Recently, it was reported that additive catalysts added MgH₂ improve the hydrogen sorption kinetics and reduce the...
absorption temperature of MgH$_2$ [31–38]. Based on these, we have currently explored how solid solutions involving meta-stable hydrides such as zinc hydride (ZnH$_2$) with MgH$_2$ can reduce the bond strength and enthalpy of formation and hence, the decomposition temperature of MgH$_2$.

Zinc hydride has been known for many years as a meta-stable compound with a white color that will decompose easily. So, its crystal structure is not yet identified experimentally. Zinc hydride was first synthesized by Schlesinger et al. in 1947 [39] via the reaction between dimethyl zinc and lithium aluminium hydride. In 1951, Barbaras et al. [40] synthesized zinc hydride using metal alkyls and lithium aluminium hydride in ethyl ether solutions. Watkins and Ashby [41] prepared ZnH$_2$ using zinc halides and alkali metal aluminium hydride in ethyl ether solutions. Watkins and Ashby [41] prepared ZnH$_2$ using zinc halides and alkali metal hydrides. Few theoretical studies have also been made on electronic structure, equilibrium geometry, and harmonic vibrational frequencies of molecular ZnH$_2$ [42–45]. A linear Zn–H molecular structure has been predicted and the equilibrium Zn–H bond distances (range of 1.492–1.662 Å) are also estimated by the above theoretical studies. From density functional calculations, Koning et al. [46] reported that, as like beryllium hydride and magnesium hydride, molecular ZnH$_2$ is also possess highly associated hydrogen-bridged coordination polymer behavior.

Later, Breckenridge et al. [47–49] studied the reaction of ZnH$_2$ by laser ablation of Zn under hydrogen atmosphere. The infrared spectra of ZnH$_2$ trapped in low-temperature matrices have been studied by Greene et al. [50] and later by Wang et al. [51] Shayesteh et al. [52–54] synthesized gaseous ZnH$_2$ molecule by electrical discharge inside a high temperature furnace. Huang et al. [55] studied the potential energy surface and vibrational energy levels of molecular ZnH$_2$ using ab-initio calculations. A few years back, Panagopoulos et al. [56] investigated the effect of cathodic hydrogen charging on the structural and mechanical characteristics of zinc. Using X-ray diffraction, the formation of metastable ZnH$_2$ was detected on the surface layers of zinc after cathodic hydrogen charging. They have also observed that due to dislocation pinning mechanisms, the ductility of zinc decreases with the increase of cathodic hydrogen charging.

MgH$_2$ is strongly ionic with high thermal stability, whereas, ZnH$_2$ has noticeable covalency with poor stability and hence there are practical problems with their use in hydrogen storage applications. The possible ways to destabilize MgH$_2$ is substituting various elements at the cation or at the anion sites [57,58]. In our recent studies [59], we attempted to destabilize MgH$_2$ by substituting fluorine at the anion site. However, though one can substitute fluorine at H sites in MgH$_2$, the system behaves highly stable and its decomposition temperature increased. So in the present study, we attempted to substitute Zn at the Mg site to destabilize MgH$_2$. The reason is that ZnH$_2$ is meta-stable in nature and hence Zn substitution at Mg site in MgH$_2$ is expected to improve the hydrogen sorption properties and induce changes in the formation enthalpy, H site energy, chemical bonding, and electronic structure of MgH$_2$. From theoretical and experimental studies, it is reported that Zn substitution in MgH$_2$ improve kinetics and thermodynamic properties of MgH$_2$ as follows. Chen et al. [60] reported that stability of MgH$_2$ cluster can be reduced by substituting transition metals such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn at a central atom in MgH$_2$ cluster. So, they concluded that the substitution of the above said transition metals in MgH$_2$ may improve the hydrogen sorption kinetics. From experimental studies, Liang et al. [61] noted that substituting Mg with Zn, Al, Ag, Ga, In or Cd reduces the stability of MgH$_2$.

Vegge et al. [62] calculated hydride formation energies of magnesium-3d transition metal alloys and reported that there is a gradual increase in the stability of the hydrides (from MgSc to MgFe), which is followed by a rapid decrease in the stability (from MgCo to MgZn). Zhou et al. [63] reported that the heat of formation decreases when MgH$_2$ is chemically modified with 3d transition metals. They found that the reduction of formation enthalpy increases in an order of Fe, Ti, Co, Zn, Ni, V, Mn, Cu, and Cr. Tsuda et al. [64] presented the catalytic activities of 3d transition metals M on Mg–H dissociation by attaching M on the top of Mg in a MgH$_2$ cluster. They reported that the catalytic activity of transition metal is considerably low (except Sc and Ni) due to fully occupied orbitals of Zn which does not receive any electrons from MgH$_2$. Milanese et al. [65] studied the hydrogen sorption kinetics and storage efficiencies of mechanically activated binary mixtures of Mg (MgH$_2$) with nine different metals (Al, Cu, Fe, Mn, Mo, Sn, Ti, Zn, and Zr). They concluded that Mg–Zn mixture has good reversibility with cyclic effect for hydrogen and also has high storage efficiency with poor sorption kinetics.

Polanski et al. [66] described the influence of nano-sized metal oxides such as Cr$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, Fe$_3$O$_4$, In$_2$O$_3$, and ZnO on MgH$_2$ powder and found that these metal oxides (except In$_2$O$_3$) improve the dehydrogenation properties. The effect of partial substitution of Mg with 3d transition metals on the formation enthalpy and electronic structure of MgH$_2$ have been studied by Zeng et al. [67] Their results show that Zn substitution lowers the formation enthalpy. Further, they showed that the bonding nature of MgH$_2$-3d systems are governed by ionic as well as covalent bonding. Bhihi et al. [68] reported that 6.25% of Zn substitution in MgH$_2$ (Mg$_{100-z}$Zn$_{2z}$) reduce the gravimetric density of hydrogen (6.97 wt%) and on the other hand, it decreases the formation enthalpy (~35.04 kJ/molH$_2$) which is the advantageous properties for hydrogen storage applications. They also reported that increasing the % of Zn substitution affects the gravimetric density and this can be overcome through a double substitution (transition metal and either Li or Al) on MgH$_2$. It is interesting to note that the crystal structure of ZnH$_2$ is not yet explored in any of the theoretical and experimental studies so far.

Our main objective in the present study is to destabilize MgH$_2$ by reducing the strong ionic interaction between Mg and H so that it can be used for practical hydrogen storage applications. So, we focus on predicting the ground state crystal structure of ZnH$_2$ and analyzed the chemical bonding by substituting Mg with Zn in MgH$_2$. The important properties like enthalpy of formation, enthalpy of mixing, and hydrogen site energy of Mg$_{1-x}$Zn$_x$H$_2$ systems were calculated. The band structure and density of states (DOS) of Mg$_{1-x}$Zn$_x$H$_2$ systems were analyzed to understand the electronic ground state by Zn substitution. The chemical bonding analyses of these systems have been done through partial DOS, charge density, electron localization function, Bader effective charge, Born
We have considered thirty seven potential AB2 types of MgH2 at the B site. The involved structure types for our structural variants and substituted with Zn at the A site and H at the B site. The involved structure types for our structural phase study are SnF2 (C12/c1) [74], BaF2 (Fm3m) [75], BeH2 (Ibam) [76], MgH2 (P42/mmm) [77], BeF2 (P33m) [78], SrH2 (P63/mmc) [79], BeF2 (P3121) [80], BeF2 (P6322) [81], SrH2 (Pnma) [82], BaH2 (Pnma) [83], CaH2 (Pnma) [84], BeF2 (R3m) [78], ZnCl2 (P42/mmc) [85], ZnCl2 (P12/n1) [86], ZnF2 (Pbcm) [87], ZnCl2 (Pna21) [88], MgF2 (Pnmm) [89], TiH2 (I4/mmm) [90], ZnBr2 (I4/acd) [91], ZnI2 (I4/acd) [92], ZnCl2 (P2 zd) [86], MgH2 (Pnma) (93), MgH2 (Pbcn) [94], MgH2 (R3m) [89], Cdl2 (P63/mmc) [94], HgBr2 (Cmc21) [95], HgBr2 (P3) [96], MgCl2 (P3m1) [97], ZnBr2 (I4/a) [91], ZnCl2 (P42/mn) [85], TiO2-nanocrystals (I4/amd) [9], MgB2 (P6mm) [98], TeAg2 (P21/c) [9], r-MgH2 (P23) [99], r-SnF2 (P42/21) [100], r-SnF2 (P221) [100], and r-MgH2 (Pn3m) [9].

The structure type specifications found above refer to the symmetry of the initial guess structures. From the chosen structural starting points, full geometry optimization have been carried out using force as well as stress minimization. The calculated total energy per formula unit (f.u) and the corresponding equilibrium volume per f.u of all the 37 different structures considered are tabulated in supporting information Table S1. Analyzing the total energy values for the above 37 different structural types, we have found that the minimum energy structure for the compound ZnH2 is Pna21 (orthorhombic). It may be noted that ZnCl2 also possess the same crystal structure as that of ZnH2 in the ground state. In order to have a wide view of the competitive lower energy structures, we have displayed the optimized energy/f.u versus volume/f.u curve for 10 structural variants with the lowest energy in Fig. 1. The calculated total energy as a function of volume has been fitted to so-called the universal equation of state (UEOS) to calculate the bulk modulus (B') and its pressure derivative (B''). The equilibrium volume for the ground state structure of ZnH2 (Pna21) was obtained as 38.84 Å³. From the UEOS fitting, the calculated bulk modulus and its pressure derivative for ZnH2 are 7.408 GPa and 5.681, respectively. The lower bulk modulus of ZnH2 indicates that it is comparatively soft material.

The calculated total energy versus volume relation in Fig. 1 shows that pressure-induced structural transitions occur in ZnH2 upon increasing pressures as well as expanded volumes. So, if ZnH2 in Pna21 phase is exposed to external pressures, it transforms to P42/mnm phase at 0.75 GPa. It may be noted that MgH2 also posses this tetragonal structure at high pressure. It is interesting to note from Fig. 1(b) that when we expand the ZnH2 lattice, it transforms to an orthorhombic structure with space group P212121. In general, when one applies pressure, the systems usually transform from lower symmetry structure to a high symmetry structure and the present observation of orthorhombic-to-tetragonal pressure induced structural transition in ZnH2 is consistent with the above viewpoint.

The calculated equilibrium volume, bulk modulus, and pressure derivative of bulk modulus for ZnH2 in high pressure tetragonal P42/mnm phase are 36.90 Å³, 7.057 GPa, and 6.726, respectively. The bulk modulus and its pressure derivative for the orthorhombic P212121 phase which is stable in the extended volume are 7.891 GPa and 5.782, respectively. In order to identify the transition pressure with an associated volume jumps, we show a pressure-volume curve for ZnH2 in Fig. 2. From Fig. 2, we found that the pressure induced phase transition occurs at 0.75 GPa and the associated volume change is 3.14%. So, this phase transition can be considered as a first order phase transition. The transition pressure for the...
The Pna2₁ to P2₁2₁2₁ phase transition occurred at ~0.22 GPa with an associated volume jump of 2.41%.

The optimized equilibrium structural parameters for MgH₂ in its ground state and that for ZnH₂ in its ground state structure along with high pressure tetragonal as well as expanded volume orthorhombic phase for ZnH₂ were listed in Table 1. The calculated equilibrium structural parameters for MgH₂ are found to be in good agreement with corresponding experimental data and that from previous DFT calculations. The predicted ground state crystal structure of ZnH₂ is visualized in Fig. 3(a) along with stable phases at high pressure and the expanded volume in Fig. 3(b) and 3(c), respectively. In the ground state structure of ZnH₂, each unit cell contains four Zn atoms and eight H atoms where each Zn atom is tetrahedrally coordinated with H atoms and each H atom is coordinated with two Zn atoms as shown in Fig. 3(a). At the equilibrium volume, the calculated average Zn–H bond length is 1.674 Å and the shortest H–H separation in ZnH₂ is 2.687 Å. In the high pressure phase as well as the orthorhombic phase that stabilize at an expanded volume of ZnH₂ also has similar coordinations for both H and Zn atoms (see Fig. 3(b) and 3(c)). The calculated average Zn–H bond length is 1.671 Å and the shortest H–H bond length is 2.632 Å for the high pressure phase at the phase transition point i.e at 0.75 GPa. The calculated average Zn–H bond length is 1.675 Å and the shortest H–H bond length is 2.696 Å for the orthorhombic phase in the phase transition point.

The ground state crystal structure of MgH₂ along with 12.5% (Mg₀.875Zn₀.125H₂) and 62.5% (Mg₀.375Zn₀.625H₂) Zn substituted MgH₂ are plotted in supporting information Figs. S1(a), S1(b), and S1(c), respectively. Fig. S1(a) represents the ground state crystal structure of α-MgH₂ in P4₂/mnm (tetragonal) phase and each unit cell contains two Mg and four H atoms. Each Mg atom is octahedrally coordinated to six H atoms, whereas each H atom is coordinated to three Mg atoms as shown in Fig. S1(a). At the equilibrium volume, the calculated average bond length between Mg and H is 1.942 Å and minimum H–H bond length is 2.487 Å. In 12.5% Zn substituted MgH₂, the Pna2₁ phase transition occurred at ~0.22 GPa with an associated volume jump of 2.41%.

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Fig. 1 – (Color online) (a) Normal and (b) Enlarged view of the calculated unit cell volume versus total energy curves for ZnH₂ in its ground state and other closer energy structures. The inset shows the energy versus volume range where pressure-induced structural phase transitions happening.

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Fig. 2 – (Color online) The calculated pressure versus volume curve for ZnH₂.
MgH₂, each cation is octahedrally surrounded by 6 H atoms (see Fig. S1(b)) and for 62.5% Zn substituted MgH₂, each cation is surrounded by 4 H atoms as depicted in Fig. S1(c).

### Phase stability, phase transition, and phase mixing by Zn substitution in MgH₂

In order to understand the structural phase stability of Mg<sub>1</sub><sup>x</sup>Zn<sub>x</sub>H<sub>2</sub> systems, we have calculated the enthalpy of formation (ΔH<sub>f</sub>) of these systems using the following equation,

\[
\Delta H_f = E(Mg_{1-x}Zn_xH_2) - (1-x)E(Mg) - xE(Zn) - E(H_2)
\]

where \(E(Mg_{1-x}Zn_xH_2), E(Mg), E(Zn), \) and \(E(H_2)\) are the total energy obtained for the optimized geometry of Mg<sub>1-x</sub>Zn<sub>x</sub>H<sub>2</sub>, hexagonal Mg, hexagonal Zn, and molecular H<sub>2</sub>, respectively. The calculated ΔH<sub>f</sub> for all these systems in their ground state structure are listed in Table 2. Fig. 4 represents the calculated ΔH<sub>f</sub> for Mg<sub>1-x</sub>Zn<sub>x</sub>H<sub>2</sub> systems in both P4<sub>2</sub>/mmn and Pna2₁ phases as a function of Zn concentration. This figure illustrates that one can reduce the stability of MgH₂ by substituting Zn at Mg site since the calculated absolute value of ΔH<sub>f</sub> decrease with increase of Zn concentration in MgH₂.

Hence the Zn substituted MgH₂ systems are less stable compared with pure MgH₂.

The decreasing trend in stability with Zn substitution in MgH₂ can be understood as follows. In pure MgH₂, the presence of strong ionic bonding between Mg and H make it highly stable. On the other hand, our bonding analyses discussed...
later (subsection Analysis of chemical bonding in MgH₂ by Zn substitution) show that Zn substitution reduces the ionicity by introducing covalency into the system and hence the enthalpy of formation decrease with the increase of Zn concentration. From the decreasing trend in structural stability with Zn substitution in MgH₂, one may expect that the dehydrogenation enthalpy of Mg₁ₓZnₓH₂ also decreases with increasing Zn concentration. As a result, one can reduce the decomposition temperature which is one of the desirable properties for MgH₂ to use in hydrogen storage applications. The linear variation between the enthalpy of formation and Zn concentration implies that these systems obey Vegard’s law. We have calculated the difference between the enthalpy of formation and Zn concentration implies that these systems obey Vegard’s law. We have calculated the difference between the enthalpy of formation of P4₂/mmm and Pna₂₁ structures of Mg₁ₓZnₓH₂ as a function of Zn concentration to understand the phase stability and phase transition point and found that the structural phase transition from P4₂/mmm to Pna₂₁ occurs at 40% Zn substitution in MgH₂ (see Fig. 5).

The enthalpy of mixing (ΔHₘ) of Mg₁ₓZnₓH₂ has been estimated using the following equation,

\[
\Delta H_m(Mg_{1-x}Zn_xH_2) = E(Mg_{1-x}Zn_xH_2) - (1-x)E(MgH_2) + xE(ZnH_2)
\]

where E(Mg₁ₓZnₓH₂), E(MgH₂), and E(ZnH₂) are the total energies for Mg₁ₓZnₓH₂, MgH₂, and ZnH₂ in their optimized ground state geometry. The ΔHₘ of Mg₁ₓZnₓH₂ systems as a function of Zn concentration are shown in Fig 6. The calculated ΔHₘ of end materials (MgH₂ and ZnH₂) is zero since these are ideal compounds. For the intermediate systems in P4₂/mmm phase, the estimated ΔHₘ values are positive and low, which gives hint that single phase of Mg₁ₓZnₓH₂ may form at a reasonable temperature and other thermodynamic conditions. On the other hand, for the intermediate systems in Pna₂₁ phase, the calculated ΔHₘ are negative. This implies that these systems are stable and it is experimentally possible to synthesize them. In our previous study [59], we have reported that the enthalpy of mixing of fluorinated MgH₂ is less positive (below 4 kJ/mol) and hence the single phase of Mg₂H₂·F₂ may be synthesized experimentally [101]. The present calculations are valid only at 0 K. In order to account for
temperature effects to analyze phase mixing one should go beyond first principle calculations as done by Pinatel et al. [102].

The binary phase diagram of Mg–Zn system show that no binary intermetallic compounds will form up to 50 atomic percentage of Zn in Mg for the temperature up to 340 °C [103]. Our calculated enthalpy of formation as a function of Zn substitution show that the optimum Mg–Zn composition useful for H storage application with desirable H desorption temperature lye within the composition range (i.e. Mg_0.5Zn_0.5H_2) and hence, one may expect a robust reversible H storage system from Zn substituted MgH2 with desirable other hydrogen storage properties.

**Hydrogen site energy in Zn substituted MgH2**

In order to interpret the influences of Zn substitution on the stability of MgH2, we have calculated the H site energy (H desorption enthalpy) [104–106]. The H site energy is the energy needed to remove an H atom from its host lattice and is calculated [107] by the following relation,

\[ E_d(H) = E(A_nH_{2n-1}) + \left( \frac{1}{2} \right) E(H_2) - E(A_nH_{2n}) \]  

(3)

The calculated H site energy versus composition for Mg_{1-x}Zn_xH_2 in their corresponding ground state structure is plotted in Fig. 7 where H desorption enthalpy is reduced from 115.69 kJ/mol (1.20 eV) to 87.29 kJ/mol (0.91 eV) when we completely replace Mg with Zn in MgH_2. The calculated H site energy of MgH2 is relatively high which point out that the H atoms are strongly bound to the Mg. This is the reason for high H desorption temperature since the desorption temperature mainly involves the breaking of Mg–H bonds. Besides, one can expect poor reaction kinetics because the diffusion of hydrogen atom through this highly stable hydride is expected to be slow. Our calculated [59] H site energy for MgH2 is in good agreement with corresponding value reported by Vajeeston et al. [108]. The calculated H site energy as a function of Zn substitution in MgH2 varies in zig-zag manner as shown in Fig. 7. The overall observation is that the H site energy decreases with respect to that of MgH2 by Zn substitution except for the compositions Mg_{0.375}Zn_{0.625}H_2 and Mg_{0.125}Zn_{0.875}H_2.

Hence, one can expect that the Zn substitution reduces the hydrogen desorption temperature of MgH2, thereby hydrogen sorption reaction could be improved for Zn substituted MgH2. For pristine ZnH2, the H site energy is very low (87.29 kJ/mol or 0.91 eV) as compared to that of MgH2 due to the meta-stable nature of ZnH2 and hence, one could expect lower decomposition temperature in ZnH2 over MgH2.

**Electronic structure of Mg_{1-x}Zn_xH_2**

The computed band structures for MgH2, 50% Zn substituted MgH2, and ZnH2 are shown in Fig. 8(a)–8(c), respectively. The band structure shows that MgH2 is an indirect bandgap material since the valence band maxima (VBM) and the conduction band minima (CBM) do not meet at the same k-point in the Brillouin zone. The calculated bandgap of MgH2 is 3.69 eV and this is consistent with previous studies [59,109]. However, this value is deviated from experimental optical measurements [110] for MgH2 (5.6 ± 0.1 eV) since the bandgap calculated from GGA/LDA is usually underestimate. To predict the accurate bandgap one should use either hybrid functional or GW calculations but this is out of the scope of the present study.

For 50% Zn substituted MgH2 (see Fig. 8(b)), the calculated bandgap value is 4.06 eV. In this system, the VBM and CBM are located at the same k-point and hence, it is a direct bandgap material. Moreover, Zn substitution brings additional states to the valence band (VBM) and CBM located at different k-point. Our calculations suggest that the Mg_{1-x}Zn_xH_2 systems can be classified as an insulator. Moreover, Zn substitution in MgH2 brings indirect to direct transition and hence this may improve the optical absorption coefficient of MgH2 by Zn substitution.

The total DOS for Mg_{1-x}Zn_xH_2 systems in their ground state crystal structures are shown in Fig. 9. The calculated bandgap values of Mg_{1-x}Zn_xH_2 listed in Table 2. The non-linear variation of the bandgap of MgH2 as a function of Zn concentration in P4_3/mnm phase is mainly due to the change in unit cell volume as well as competition between ionicity and covalency by Zn substitution in MgH2. It is evident from Fig. 9 that the bandgap of pure ZnH2 is smaller compared with that of pure MgH2. The smaller bandgap value of ZnH2 is associated with weaker bond strength (as evident from H site energy calculations). Moreover, there is a gradual decrease in the band gap value as a function of Zn concentration until 37.5% Zn substitution. Consistent with our results, previous theoretical studies reported that 6% Zn substituted MgH2 (Mg_{0.94}Zn_{0.06}H_2) [67,111] and 20% Zn substituted MgH2 (Mg_{0.8}Zn_{0.2}H_2) [63] have the band gap value of around 3.1 eV and 2.5 eV, respectively.

**Analysis of chemical bonding in MgH2 by Zn substitution**

Partial density of states, charge density, and electron localization function analyses

To characterize the bonding interaction between the constituents of Mg_{1-x}Zn_xH_2 systems, we have plotted partial DOS, charge density, and electron localization function (ELF) [112–114]. In the partial DOS of MgH2 (refer Fig. 10(a)), it is to be noted that the VB is mainly originated from H-s state with a

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**Fig. 7** – The calculated H site energy as a function of Zn concentration in MgH2.
small contribution from Mg-$s$ and Mg-$p$ states since there is a charge transfer from the Mg sites to H sites. The small Mg-$s,p$ electronic states present in the valence band are energetically degenerate with the H-$s$ states in the entire valence band indicating that there is noticeable covalent interaction present in-between Mg and H. Hence, one can conclude that MgH$_2$ has a strong ionic bonding with small covalent character.

For Mg$_{0.5}$Zn$_{0.5}$H$_2$ system, the partial DOS is plotted in Fig. 10(b). From the VB, one can notice that the Mg-$s$ states are smaller than that of neutral Mg and at the same time H-$s$ states at the VB have higher value indicating that Mg donated its valence electrons to H. On the other hand, the Zn-$s$ states in the VB is higher than Mg-$s$ states indicating that Mg donated most of its $s$ electrons to H. From the partial DOS of Mg$_{0.5}$Zn$_{0.5}$H$_2$ and ZnH$_2$ shown in Fig. 10(b) and 10(c), respectively, one can notice that the Zn($s$)--H($s$) bonding hybrids are formed around $-3.5$ and $-4.5$ eV and also Zn-$s$ and H-$s$ states are energetically degenerate in the entire valence band reflecting the presence of substantial covalent type of interaction between Zn and H. The charge transfer from Mg/Zn-$s$ to H states along with charge sharing between Zn-$s$ states and H are the dominant bonding interaction in Zn substituted MgH$_2$.

![Fig. 8](Color online) The calculated band structures of (a) MgH$_2$, (b) Mg$_{0.5}$Zn$_{0.5}$H$_2$, and (c) ZnH$_2$. The Fermi level is set to zero.

![Fig. 9](Color online) The calculated total DOS of MgH$_2$ as a function of Zn substitution. The Fermi level is set to zero.
The contribution increases with the increase of Zn concentration. The charge density and ELF of MgH2 are plotted in Fig. 11(a) and 11(d), respectively. Due to charge transfer from Mg to H site in MgH2, the highest charge density resides in the immediate vicinity of the nuclei at the H site. Almost spherical charge distribution at the H site reconfirms that the interaction between Mg and H is dominantly ionic. However, the finite non-spherical charges present in-between Mg and H as well as in-between H atoms indicate the presence of noticeable covalent bonding between the constituents. It is known that the region with an ELF value of 1.00, 0.50, and 0.00 represents fully localized electrons, fully delocalized electrons, and very low charge density, respectively. The calculated ELF plot for MgH2 (see Fig. 11(d)) shows that the electrons have a paired character with predominant maximum ELF of about 0.9 at the H sites and non-spherical ELF distribution between H atoms indicate that there is finite covalent bonding between the H atoms. Moreover, there is a non-spherical ELF distributed between Mg and H indicating partial covalency. The overall conclusions from charge density and ELF analyses for MgH2 is that there is predominantly ionic bonding present between Mg and H with small directional character present between Mg and H as well as between H atoms.

In order to understand the role of Zn substitution on variation in the bonding behavior of MgH2, we have plotted charge density and ELF plot for Mg0.5Zn0.5H2 in Fig. 11(b) and 11(e), respectively. The nature of charge distribution seen in Fig. 11(b) appears to be typical for compounds with ionic-covalent bonding. The charge density analysis shows that the H closer to Mg has more spherically distributed charge than that closer to Zn. Further, there is negligible charge density present between Mg and H and in contrast, there is substantial charge accumulated in between Zn and H. The important observation is that the Zn substitution introduces covalency which weakens the strong ionic bonding present between Mg and H in the undoped MgH2. ELF of Mg0.5Zn0.5H2 system is shown in Fig. 11(e) also clearly indicate that there is negligable amount of paired electron present in-between Mg and H and there is a large amount of paired electrons present in-between Zn and H. Further, the non-spherical distribution of ELF in-between H atoms and in-between H and Zn along with higher non-spherical character of ELF than that in MgH2 substantiate that Zn substitution enhances the covalency. From the partial DOS, charge density, and ELF plot of Mg0.5Zn0.5H2 system, it was indeed confirmed that the Zn substitution reduced the ionic bonding interaction between Mg and H and enhance the covalency in the system.

In contrast to MgH2, in the case of ZnH2, the calculated charge density and ELF showed in Fig. 11(c) and 11(f) clearly indicate that Zn is bonded with H in a directional manner. The non-spherical distribution of charge density and ELF along with the large value of charge and ELF value in-between Zn and H as well as in-between H indicates that there is a strong covalent interaction between these atoms. So, when we compared the bonding interaction of MgH2 with that of ZnH2, we conclude that ZnH2 has more covalency.

**Bader topological analysis**

To quantify the amount of electrons present at the constituents of the compounds, we have made Bader topological analysis. In the Bader charge analysis, each atom in a compound is surrounded by a surface (called Bader regions) that run through minima of the charge density and the total charge of an atom is determined by integration within the Bader region [115–117]. The calculated Bader effective charge (BC) for the constituents in Mg1−xZnH2 are listed in Table 3. The positive value of BC represents electron depletion while the negative value represents electron accumulation. The estimated BC of the constituents in MgH2 shows that Mg donates around 1.59 electrons to the H sites which reflects ionic character. But the smaller value of the BC at the H sites (−0.79) over the pure ionic value (−1) clearly indicates that MgH2 do not reach a purely ion bond with H in −1 state. Our calculated BC values for the constituents in MgH2 is in good agreement with the corresponding value calculated by Vajeeston et al. [118].

In the case of Mg0.5Zn0.5H2, Mg and Zn donate 1.56 and 0.69 electrons to the H sites respectively which is much smaller than the value obtained from the pure ionic picture. Moreover, H atom neighboring to Mg and Zn receives 0.54 electrons whereas that neighboring to Mg atoms alone receives 0.78 electrons (see Table 3). This is mainly due to disproportionate bond induced by Zn substitution in MgH2. Our analyses show that for 50% Zn substituted MgH2, the H atoms receives an average of around 0.23 electrons less than that in pure MgH2. These results reflect that the Zn substitution weakens the ionic bond between the Mg and H.

In contrast to the MgH2 system, the calculated BC for Zn and H systems. The overall observation is that Mg1−xZnH2 systems are governed by mixed ionic-covalent bond and the covalent contribution increases with the increase of Zn concentration.
atoms in ZnH₂ indicate that the ionicity is drastically reduced in ZnH₂ over MgH₂. The conclusions arrived from the BC analysis are consistent with the charge density, ELF, and partial DOS analyses.

Born effective charge analysis

Born effective charge (BEC) analysis is another tool to quantify charges in each atomic sites to evaluate the bonding characteristics and were calculated using the Berry-phase approach based on the modern theory of polarization which is implemented in the VASP code. We have used the King-Smith and Vanderbilt [119,120] method to calculate the polarizations of perturbed cells. The Born effective charge tensors Z* of the ions of Mg₁₋ₓZnxH₂ systems have been calculated and listed in Table 4. The diagonal components of the BEC tensors will carry information about how much charge is transferred from one site to other sites. For an ionic compound, the off-diagonal components of the BEC tensor will be zero or very small. For both atoms, most of the off-diagonal components are turn out to be zero except Zyx components indicating strong ionic bonding. The overall conclusion is that the Mg–H bond has a large ionic character with a small woof of covalency.

For Mg₀.₅Zn₀.₅H₂, the diagonal components of the effective charges at the Zn, Mg, and H sites are not equal (Zₓₓ ≠ Zᵧᵧ ≠ Zzz) and the off-diagonal components have finite values. This clearly reflects that the Zn atom brings covalency when it is substituted in the MgH₂ system. Further, the H neighbored by Mg has the BEC value of 0.82 and that neighboring to Mg and Zn has a value of −0.57 clearly showing that the introduction of Zn brings a disproportionate bond. As like Mg₀.₅Zn₀.₅H₂, the pure ZnH₂ has a covalent bond since the diagonal components of the effective charges at Zn and H sites are not equal and the off-diagonal components have noticeably large values. Moreover, the diagonal components of BC at H site is more than nominal ionic value due to the fact that the dynamic charges arising from covalency also added to the static charge. These results are consistent with the other chemical bonding analysis done above.

Crystal orbital Hamiltonian population analysis

In order to get more insight into the chemical bonding, we have also calculated the crystal orbital Hamiltonian population (COHP). COHP [121–123] is the DOS weighted by the corresponding Hamiltonian matrix elements and this identifies the location of bonding, antibonding, and nonbonding states of the bonding pair and also measures the strength of bonding (magnitude of bonding) interaction between the constituents. The negative COHP designates the bonding character whereas the positive COHP denote the antibonding character. The

<table>
<thead>
<tr>
<th>Table 3 – Calculated Bader effective charges (BC) for the constituents of Mg₁₋ₓZnxH₂ systems.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>MgH₂</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Mg₀.₅Zn₀.₅H₂</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>ZnH₂</td>
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</tbody>
</table>
calculated bond strength of the bonding pairs obtained from integrated COHP (iCOHP) up to Fermi level for Mg1–xZnH2 systems are listed in Table 5. Fig. 12(a) shows the calculated COHP of bonding pairs in MgH2. If we analyze the COHP of Mg–H bonding pair, all the bonding states are filled and the antibonding states are empty (see Fig. 12(a)) so one could expect high stability. Apart from our enthalpy of formation analysis, the high stability of MgH2 was already found through experimental [21] as well as other theoretical studies [26]. Due to the filling of maximum bonding states in Mg–H pair, one can expect strong bond between Mg and H. Consistent with this viewpoint, the calculated iCOHP value for Mg–H bonding pair is relatively high. So if one wants to reduce the decomposition temperature of MgH2, one should weaken the Mg–H bond. Moreover, the bonding interaction between H atoms are considerably weak since both of the bonding and antibonding states are present within the VB region of COHP and hence the iCOHP value is very small.

From the analyses of the calculated COHP for Mg1–xZn0.5H2 (see Fig. 12(b)), we found that the Mg–H bonding pair has bonding states located in the whole valence band range and the calculated average iCOHP value for Mg–H pair is −0.63 eV. As the substitution of Zn introduces disproportionate bonds, the detailed analysis of bond strength for Mg–H bonds from the calculated iCOHP values in Table 5 vary between −0.49 to −0.71 eV. Because of this disproportionate bond formation, the H site energy calculated for H neighboring to Mg atoms alone has a value of 108.85 kJ/mol and that neighboring to Zn and Mg has a value varying from 91.14 to 98.07 kJ/mol. The hydrogen closer to Zn is weakly bonded with neighboring Mg and that neighboring to Mg atoms alone is strongly bonded to Mg as evident from calculated iCOHP values. So, the present study suggests that the Zn substitution weaken some of the Mg–H bonds in Mg0.5Zn0.5H2 and hence one can expect that H will be removed in relatively lower temperature than that in

Table 4 – The calculated diagonal and off-diagonal components of Born-effective-charge-tensor elements (Z) for the constituents of Mg1–xZn0.5H2 systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>atom</th>
<th>Zxx</th>
<th>Zyy</th>
<th>Zzz</th>
<th>Zyz</th>
<th>Zzx</th>
<th>Zzy</th>
<th>Zzy</th>
<th>Zzz</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH2</td>
<td>Mg</td>
<td>1.851</td>
<td>1.851</td>
<td>1.942</td>
<td>0.120</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.120</td>
</tr>
<tr>
<td>H</td>
<td>−0.902</td>
<td>−0.902</td>
<td>−0.948</td>
<td>−0.201</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>−0.201</td>
</tr>
<tr>
<td>Zn1.50Zn0.5H2</td>
<td>Zn</td>
<td>1.052</td>
<td>1.462</td>
<td>1.138</td>
<td>−0.216</td>
<td>0.106</td>
<td>−0.130</td>
<td>0.083</td>
<td>−0.050</td>
</tr>
<tr>
<td>Mg</td>
<td>1.705</td>
<td>1.692</td>
<td>1.835</td>
<td>0.112</td>
<td>0.066</td>
<td>0.138</td>
<td>−0.177</td>
<td>0.033</td>
<td>−0.069</td>
</tr>
<tr>
<td>H1</td>
<td>−0.577</td>
<td>−1.018</td>
<td>−0.415</td>
<td>−0.229</td>
<td>−0.114</td>
<td>−0.075</td>
<td>−0.122</td>
<td>−0.098</td>
<td>−0.239</td>
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<tr>
<td>H3</td>
<td>−0.854</td>
<td>−1.045</td>
<td>−0.658</td>
<td>−0.134</td>
<td>0.032</td>
<td>−0.005</td>
<td>0.107</td>
<td>0.027</td>
<td>−0.125</td>
</tr>
<tr>
<td>H5</td>
<td>−0.787</td>
<td>−0.556</td>
<td>−0.839</td>
<td>0.059</td>
<td>−0.039</td>
<td>0.251</td>
<td>0.302</td>
<td>0.004</td>
<td>0.025</td>
</tr>
<tr>
<td>H8</td>
<td>−0.563</td>
<td>−0.521</td>
<td>−1.061</td>
<td>−0.036</td>
<td>−0.040</td>
<td>−0.188</td>
<td>−0.189</td>
<td>−0.019</td>
<td>0.005</td>
</tr>
<tr>
<td>ZnH2</td>
<td>Zn</td>
<td>1.503</td>
<td>1.335</td>
<td>1.483</td>
<td>−0.281</td>
<td>0.304</td>
<td>−0.130</td>
<td>0.010</td>
<td>−0.263</td>
</tr>
<tr>
<td>H1</td>
<td>−0.466</td>
<td>−0.679</td>
<td>−1.009</td>
<td>−0.030</td>
<td>−0.302</td>
<td>−0.090</td>
<td>−0.077</td>
<td>−0.270</td>
<td>−0.149</td>
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<tr>
<td>H2</td>
<td>−1.042</td>
<td>−0.649</td>
<td>−0.479</td>
<td>−0.301</td>
<td>−0.002</td>
<td>−0.013</td>
<td>−0.016</td>
<td>−0.000</td>
<td>−0.325</td>
</tr>
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</table>

Table 5 – The calculated bond strength between the bonding pairs in Mg1–xZn0.5H2 systems from integrated crystal orbital Hamiltonian population.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Interaction</th>
<th>Bond strength (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH2</td>
<td>Mg–H</td>
<td>−0.63</td>
</tr>
<tr>
<td></td>
<td>H–H</td>
<td>−0.07</td>
</tr>
<tr>
<td>Mg0.5Zn0.5H2</td>
<td>Mg–H</td>
<td>−0.63 (average)</td>
</tr>
<tr>
<td></td>
<td>Mg–H4</td>
<td>−0.69</td>
</tr>
<tr>
<td></td>
<td>Mg–H5</td>
<td>−0.49</td>
</tr>
<tr>
<td></td>
<td>Mg–H8</td>
<td>−0.71</td>
</tr>
<tr>
<td></td>
<td>Zn–H</td>
<td>−0.52 (average)</td>
</tr>
<tr>
<td></td>
<td>Zn–H2</td>
<td>−0.36</td>
</tr>
<tr>
<td></td>
<td>Zn–H5</td>
<td>−0.66</td>
</tr>
<tr>
<td></td>
<td>Zn–H8</td>
<td>−0.56</td>
</tr>
<tr>
<td></td>
<td>H–H</td>
<td>−0.09</td>
</tr>
<tr>
<td>ZnH2</td>
<td>Zn–H</td>
<td>−0.40</td>
</tr>
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<td></td>
<td>H–H</td>
<td>−0.02</td>
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</table>

Fig. 12 – (Color online) The calculated COHP between constituents in (a) MgH2, (b) Mg0.5Zn0.5H2, and (c) ZnH2.
pure MgH$_2$ system. If we analyze the COHP of Zn–H pair in Mg$_{0.5}$Zn$_{0.5}$H$_2$, we found that both bonding and antibonding states are present within the valence band and hence the calculated average iCOHP value for Zn–H pair is only $-0.56$ eV. It is well known that the filling of antibonding states lowers the stability of the system. The observation of filling of antibonding states in Zn–H pair could explain why the enthalpy of formation for Mg$_{0.5}$Zn$_{0.5}$H$_2$ is lower than that of MgH$_2$.

In the case of ZnH$_2$, the COHP for the Zn–H pair is shown in Fig. 12(c). It may be noted that for the Zn–H bonding pairs, the antibonding states are dominated in the top of the valence band. The band filling of the bonding analysis shows that in order to achieve the maximum stability, all the bonding states should be filled and the antibonding states should be empty. However, the filling of antibonding states in the COHP of Zn–H pair could explain why ZnH$_2$ is meta-stable in nature.

Conclusions

Though ZnH$_2$ is synthesized experimentally long back, due to the meta-stable nature of this compound its ground state crystal structure is unknown till date. Using the state-of-the-art density functional calculations we have predicted the ground state structure and the unit cell parameters of ZnH$_2$ by considering 37 potential trial structures. Also, in order to reduce the strong ionic bonding between Mg and H, we have substituted Zn at the Mg sites in MgH$_2$ and executed a systematic study of the phase stability, phase transition, phase mixing, electronic structure, and chemical bonding of Mg$_{1-x}$Zn$_x$H$_2$ systems and made the following conclusions.

- Using the total energy minimization, we have predicted that the ground state crystal structures of ZnH$_2$ is orthorhombic with space group Pna2$_1$ and the calculated equilibrium structural parameters are listed. The calculated enthalpy of formation for ZnH$_2$ is a small positive value and this could explain why this material is meta-stable.
- The calculated enthalpy of formation and H site energy of Mg$_{1-x}$Zn$_x$H$_2$ systems affirm that MgH$_2$ is highly stable, and Zn substituted MgH$_2$ systems are less stable than MgH$_2$.
- From the calculated total energy as a function of Zn substitution in MgH$_2$, we have predicted a composition induced structural phase transition from tetragonal P4$_2$/mm to orthorhombic Pna2$_1$ structure occurred at 40% Zn substitution in MgH$_2$.
- From the calculated enthalpy of mixing, we concluded that Mg$_{1-x}$Zn$_x$H$_2$ systems can form single phase and they can be experimentally synthesized using appropriate thermodynamical conditions.
- The calculated H site energy of Mg$_{1-x}$Zn$_x$H$_2$ systems indicates that the H neighboring to Zn can be removed more easily than that neighboring to Mg atoms alone.
- The electronic structure studies reveal that Mg$_{1-x}$Zn$_x$H$_2$ systems are insulators. The non-linear variation in the bandgap values as a function of Zn substitution is mainly due to the competition between ionic and covalent bond in these systems.
- The chemical bonding analyses from partial DOS, charge density, ELF, BEC, and COHP concludes that Mg$_{1-x}$Zn$_x$H$_2$ systems have ionic-covalent interaction between the constituents.
- From the detailed chemical bonding analysis, we have found that Zn substitution induced disproportionate bonds and this could reduce the decomposition temperature.

Overall, the present results suggest that one can reduce the stability of MgH$_2$ by Zn substitution. From the calculated H site energy and the identification of the formation of disproportionate bonds by Zn substitution in MgH$_2$, we have indicated that H can be removed easily in Zn substituted MgH$_2$. Hence, the Mg$_{1-x}$Zn$_x$H$_2$ systems can be considered as a promising H storage materials.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2019.04.016.

R E F E R E N C E S


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