Structural Phase Stability in Fluorinated Calcium Hydride

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Abstract. In order to improve the hydrogen storage properties of calcium hydride (CaH2), we have tuned its thermodynamical properties through fluorination. Using ab-initio total energy calculations based on density functional theory, the structural stability, electronic structure and chemical bonding of CaH2, F Ca systems are investigated. The phase transition of fluorinated systems from orthorhombic to cubic structure has been observed at 18% fluorine doped CaH2. The phase stability analysis shows that CaH2, F Ca systems are highly stable and the stability is directly correlating with their ionicity. Density of states (DOS) plot reveals that CaH2, F Ca systems are insulators. Partial DOS and charge density analyses conclude that these systems are governed by ionic bonding. Our results show that H closer to F can be removed more easily than that far away from F and this is due to disproportionation induced in the bonding interaction by fluorination.

Keywords: Ab-initio calculations, Hydrogen storage, Phase transitions
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INTRODUCTION

Calcium hydride (CaH2) is considered as a saline hydride which has been used as hydrogen storage material due to its high hydrogen-to-metal ratio and also used for hydrogen production techniques. Experimentally observed that CaH2 has high enthalpy of formation (-181.5 kJ/mol) and hence the dehydrogenation temperature is also high (>600 °C). The advantages of using CaH2 as hydrogen storage materials due to relative abundance, cheap and high gravimetric density. Reducing the decomposition temperature of CaH2 is the challenging task for onboard applications. Doping hydrogen with other isovalent element can improve the hydrogen storage properties of hydrides. Utke et al. [1] reported that metal-fluorine-catalyzed Ca(BH4)2 improves the kinetics of Ca(BH4)2 and also hydrogen storage capacity. In this paper we are reporting the structural phase stability and transition, electronic structure, chemical bonding, and H site energy for fluorinated CaH2.

STRUCTURAL ASPECTS AND COMPUTATIONAL DETAILS

The ground state crystal structure of CaH2 and calcium fluoride (CaF2) are shown in Fig. 1. At ambient condition, CaH2 crystallize in the orthorhombic structure (Pnma) while CaF2 crystallize in face centered cubic (Fm-3m). The unit cell of CaH2 contains four calcium atoms and eight hydrogen atoms, where each Ca is surrounded by nine H atoms. Contrarily each hydrogen of type1 (H1) and type2 (H2) is surrounded by four and three Ca atoms, respectively. Similarly CaF2 contains four calcium and eight fluorine atoms in its unit cell and each F is tetrahedrally coordinated with Ca.

FIGURE 1. Crystal structure of (a) CaH2 (Pnma) and (b) CaF2 (Fm-3m).

The total energy calculations were done using the projector augmented plane wave method (PAW) implemented in Vienna abinitio simulation package (VASP). [2] The generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (GGA-PBE) was used for structural optimizations (force as well as stress are minimized). Fluorination was achieved by using supercell approach. We used an energy cut off of
300 eV for all the compositions considered here. The k-points were generated using the Monkhorst Pack method for structural optimization while the Gamma centered grid for electronic structure calculations.

RESULTS AND DISCUSSION

The optimized and experimentally observed structural parameters of CaH$_2$ and CaF$_2$ are listed in Table 1 and the calculated equilibrium lattice parameters and volumes are in good agreement with the corresponding experimental data. The calculated enthalpy of formation ($\Delta H_f$) of CaH$_2$ and CaF$_2$ are found to be in good agreement with available experimental results in Table 2. From the $\Delta H_f$ values, it is to be concluded that CaH$_2$ prefer to be in orthorhombic (Pnma) while CaF$_2$ in cubic (Fm-3m) structure in consistent with experimental observations. The $\Delta H_f$ of CaH$_2$ is as a function of fluorine concentration is shown in Fig. 2(a). It is to be noted that all the fluorinated systems are relatively more stable compared with pure CaH$_2$. The difference in the enthalpy of formation between cubic and orthorhombic structure of CaH$_2$F$_x$ systems are also calculated and displayed in Fig. 2(b). From that we found the phase changing is occurring from Pnma to Fm-3m around 18% fluorine substitution in CaH$_2$.

The chemical bonding between the constituents has been studied using partial density of states (DOS). The obtained bandgap of CaH$_2$ is 3.02 eV and it is very close to value 2.97 eV calculated by Yinwei et al. [6] In Fig. 3(a), it is observed that the valence band of CaH$_2$ mainly originating from H states indicating the presence of ionic bonding between the constituents. For CaHF, the calculated bandgap is 2.71 eV. The F-$p$ states are well localized (-6 eV to -4 eV) and H-$s$ states are dominating the valence band (see Fig 3(b)).

Due to high electronegativity, F outermost states are completely filled resulting this well localized electronic states. As F draws more charges towards itself, it weakens the Ca-H bond as evident from our charge density analysis. This results reflects that phase stability of the system is governed mainly by ionic bonding. While seeing the pure fluoride system, the bandgap increased to 7.26 eV and in agreement with previous calculations. DOS analysis of CaF$_2$ shows (see Fig. 3(c)) that there is a strong ionic bonding is present between Ca and F.

The variation in bandgap as a function of fluorine substitution is shown in Fig. 4(a). The increase trend in bandgap with fluorine substitution is due to increase in ionicity. The calculated H site energy versus composition (see Fig. 4(b)) concludes that the energy required to remove H closer to F is low compared to H.

TABLE 1. Theoretically calculated and experimentally observed (enclosed in bracket) structural parameters.

| Structure type | Lattice parameter (Å) | Volume (Å$^3$) |
|----------------|----------------------|----------------|
| CaH$_2$ (Pnma) | a = 5.8806            | 141.47         |
|               | b = 3.5619            |
|               | c = 6.7537            |
| CaF$_2$ (Fm-3m)| a = 5.4585            | 162.64         |
|               | b = 5.4585            |
|               | c = 5.4585            |

The enthalpy of mixing ($\Delta H_m$) of CaH$_2$F$_x$ systems in their ground state structure are calculated and plot between $\Delta H_m$ and composition is shown in Fig. 2(c). Interestingly the calculated $\Delta H_m$ of CaH$_2$F$_x$ systems are positive (except in case of 25% fluorination where the value is -15.6 J/mol) and very low implies that these compounds may expected to form at reasonable thermodynamic conditions. In support our finding, Pinatel et al. [5] discussed phase diagram of fluorinated CaH$_2$ by both experimentally and theoretically in their paper.

TABLE 2. Calculated enthalpy of formation per f.u.

| Structure type | Calculated $\Delta H_f$ (kJ/mol) | Experimentally observed $\Delta H_f$ (kJ/mol) |
|----------------|---------------------------------|---------------------------------------------|
| CaH$_2$ (Pnma) | -161.31                         | -181.50                                     |
| CaH$_2$ (Fm-3m)| -154.19                         |                                             |
| CaF$_2$ (Pnma) | -1111.53                        |                                             |
| CaF$_2$ (Fm-3m)| -1128.81                        | -1219.60                                    |
far from F. So this indicating that F draws more charge towards itself due to its high electronegativity and hence it weakens the Ca-H bond closer to it.

Charge density plot of CaH$_2$ (see figure 5(a)) shows that there is an isotropic charge distribution is present in the constituents of CaH$_2$ indicating ionic nature of the compound. Fig. 5(b), shows that the charge density between Ca and H is reduced in CaHF compared with CaH$_2$ and also the charge density between Ca and F is large indicating that fluorination brings disproportionate bonding. Even though there is an isotropic charge distribution is seen in CaHF, still there is anisotropic charge distribution present at the H site indicating small amount of covalency is present in this system. For fluoride case (see Fig. 5(c)), it is clearly seen that CaF$_2$ has perfect ionic bonding due to an isotropic distribution of charges at both Ca and F sites.

FIGURE 4. (a) Bandgap versus composition plot and (b) H site energy versus composition plot.

CONCLUSIONS

The total energy calculations for fluorinated CaH$_2$ were done using VASP. The calculated enthalpy of formation reveals that the CaH$_2$-F$_x$ systems are highly stable. The structural phase transition occurred at 18% fluorinated CaH$_2$. The phase mixing analysis shows that these systems can be formed at reasonable thermodynamical conditions. Partial DOS and charge density plots concludes that these systems are governed mainly by ionic bonding. From the calculated H site energy, we observed that one can easily remove hydrogen closer to fluorine compared to hydrogen far away from fluorine due to the formation of disproportionate bond. Also these systems are insulators and the bandgap increased from hydride to fluoride systems due to increase in ionicity.

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