

First-Principles Investigation of NaMgH₃ Hydrogenating Properties Affected by Catalyst

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Abstract—We reported density functional studies of the structure and thermodynamics of NaMgH₃ in the cubic perovskite structure as well as corresponding fluorides. Analyses of the calculation results in terms of formation enthalpies, substitution enthalpies, reaction enthalpies showed that partial H were replaced with halogen in catalyst which improved thermodynamic properties, facilitate dehydrogenation of hydrides. The obtained calculation results suggested that halide-doped in NaMgH₃ may result in a favorable thermodynamics modification, and accordingly result in a favorable modification for onboard hydrogen storage application.

Keywords—component; first-principles; hydrogen absorption; F-doped

I. INTRODUCTION

Hydrogen would be ideal as the most promising alternative energy carrier because of its lightweight, highly abundant and nonpolluting nature during combustion, but storage remains a critical problem. Hydrides are found to be an important class of materials due to their potential use for energy economy^[1-2]. The basic attention to study hydrides has so far been focused on the acceleration of kinetics for the hydrogenation/dehydrogenation processes and on the increase of weight percentage of hydrogen^[3]. Complex hydrides are expected to have potential as viable modes for storing hydrogen at moderate temperatures and pressures^[4]. Recent experimental finding have shown that the decomposition temperature for complex hydrides can be modified by introduction of additives^[5-6]. It has opened up for research activity on identification of appropriate admixtures for unexplored complex hydrides.

II. DETAILS OF THE COMPUTATION

A new material Mg-based perovskite-type hydrides which composed of the 1A group elements such as Li, Na, K and the 2A group elements such as Be, Mg, Ca in the periodic table attracted our attention^[7], because they had lower weight and manufacturing costs. In particular, in the NaMgH₃ phase one can be store up to 6 wt% of hydrogen. However, Many studies^[5-6, 8-9] had shown that titanium (Ti) was the additive that most efficiently increased the hydrogenation and dehydrogenation rates. But no attention had yet been paid to the question as to NaMgH₃ hydrogenation properties affected by halide anion catalyst.

The aim of this study was to investigate the catalysis action for Na₄Mg₄H₁₂ by first-principles, to substitute H by F or Cl respectively. We attempted to assess the reliability of such methods for predicting energies for reactions involving

complex hydrides, and for enthalpies of formation and PDOS for alkali magnesates in particular. The results showed that partial H was replaced with F in catalyst, which directly reduced the hydride formation enthalpy and the reaction enthalpy, improved thermodynamic properties, facilitates dehydrogenation of hydrides. Practice was proved the functional effect of halide anions in hydrogen absorption and desorption properties within the scope of density-functional theory^[10].

The present calculations were performed using the plane-wave pseudopotential method^[10] based on density functional theory^[11]. First-principles calculations were performed the generalized gradient approximation (GGA) to density functional theory (DFT). We used a Vanderbilt^[12] type ultrasoft potential with Perdew Burke Ernzhof^[13] exchange correlation. Atomic structures were fully optimized for Na₄Mg₄H_{12-x}F_x using the pulay^[14] scheme for a more rapid convergence. A finite basis set correction was applied to the total energy and stress tensor when a geometric optimization of variable cell parameters was made. In all calculations, the plane-wave energy cutoff was set to 370 eV while the self-consistent field convergence limit was 10⁻⁶ eV. For all structures the total energy were converged to 10⁻⁵ eV/atom, and the force components on each atom were relaxed to less than 10⁻² eV/Å. The maximum displacement with changing lattice constant was limited at 0.01nm.

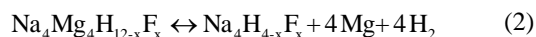
III. RESULTS AND DISCUSSION

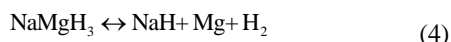
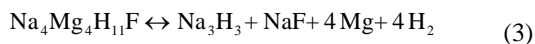
The formation enthalpy was calculated using Equation^[15] (1).

$$\Delta H_{\text{form}}(\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x) = \frac{E(\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x) - [4E(\text{Na}) + 4E(\text{Mg}) + \frac{12-x}{x}E(\text{H}_2) + \frac{x}{2}E(\text{F}_2)]}{N_{\text{atom}}}$$

$x=0, 1, 2 \text{ and } 3$ (1)

Where E was the total energy of reactants and products. The enthalpies change in the dehydrogenation reaction ΔH_{reac} were also estimated by the total energy calculations, assuming two reaction paths for dehydrogenation. The possible reaction equations were written as follows:





The total energy of Mg, NaH, $\text{Na}_4\text{H}_{4-x}\text{F}_x$, Na_3H_3 , NaF and H_2 have been computed for the ground-state structures. E_{Na} and E_{Mg} were the energies of single Na, Mg which had been calculated using a cubic supercell with large lattice parameter to guarantee a small intermolecular interaction.

NaMgH_3 has an orthorhombic GdFeO_3 type perovskite structure with space group $Pnma$, and its unit cell consists of 20 atoms. Lattice parameter is $a=5.4634 \text{ \AA}$, $b=7.703 \text{ \AA}$, $c=5.4108 \text{ \AA}$. Na atoms occupy $4c (x, 0.5, z)$ site, Mg atoms occupy $4b (0, 0, 0.5)$ site while the two type of H atoms are located respectively at $4c (x, 0.5, z)$ and $8d (x, y, z)$ sites^[16], where $4c$, $4b$ and $8d$ are the Wyckoff symbols. 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 optimized simultaneously. The optimized results were given in table 1, which were in good with other calculations.

TABLE I. TABLE TYPE STYLES OPTIMIZED CRYSTAL STRUCTURE OF NaMgH_3 , COMPARED TO OTHER CALCULATED RESULTS.

	Na(x)	Na(z)	H1(x)	H1(z)	H2(x)	H2(y)	H2(z)
X-ray [18]	0.021	0.006	0.503	0.093	0.304	0.065	0.761
NPD [19]	0.015	-0.018	0.483	0.064	0.292	0.040	0.708
LDA [20]	0.036	0.993	0.466	0.090	0.295	0.048	0.702
This work	0.035	-0.004	0.475	0.081	0.292	0.043	0.707

This $\text{Na}_4\text{Mg}_4\text{H}_{12}$ unit cell was used to model the substitution of halogen at H site in NaMgH_3 bulk. As shown in Fig. 1, we have considered substitution ratio F: H=1: 11, 2: 10, 3: 9, respectively. For these compounds, there are hundreds of possible substitutions. In the present work, we have chosen higher symmetry structure, which has been investigated. First, the crystal structure almost had no change with increasing the F substitution at H sites in NaMgH_3 , but only the lattice constant changed a little that may originate from similar characters.

Formation enthalpy is the best aid to establish whether theoretically predicted phase is likely to be stable. In this paper, the related $\text{Na}_4\text{Mg}_4\text{H}_{12}$ and $\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}_1$ (two unequivalent sites H1, H2) formation enthalpies were evaluated. The formation enthalpies (ΔH_{form}) have been calculated to be -72.99 kJ/mol H_2 according to the equation (1). Here, the substitution enthalpies (ΔH_{subst}) of $\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}_1$ were given to be -23.84(H1), -23.83(H2) kJ/mol H_2 , respectively, following equation (5)^[15].

$$\Delta H_{\text{subst}}(\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}) = \frac{E(\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}) - E(\text{Na}_4\text{Mg}_4\text{H}_{12}) + 0.5E(\text{H}_2) - 0.5E(\text{F}_2)}{N_{\text{atom}}} \quad (5)$$

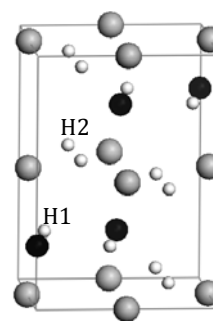


FIGURE 1. CRYSTAL STRUCTURE OF NaMgH_3 . NA BLACK, MG GREY AND H WHITE.

It should be noted that incorporation of F anion into the NaMgH_3 lattice was an exothermic process. The negative (exothermic) ΔH_{subst} was indicative of a thermodynamically favorable substitution reaction. From point of view of thermodynamics, it is feasible to F substitute for H. The stability of substituted hydride was examined by experiment^[16,17].

For the hydrogenation/dehydrogenation reactions, the reaction enthalpies are the most important thermodynamic parameters used to identify and classify hydrogen storage materials since they determine the heat of the overall hydriding reaction, which, in turn, affects the temperatures of the reversible hydrogenation/dehydrogenation processes^[19]. Two possible reaction pathways (eqs2-3) were used to estimate the associated reaction enthalpies. For pure $\text{Na}_4\text{Mg}_4\text{H}_{12}$, the computed reaction enthalpy was 76.18 kJ/mol H_2 , which agreed well with the other results, $\pm 94 \pm 15$ kJ/mol H_2 ^[20]. While for $\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}_1$, the reaction enthalpies following equations (2) and (3) were calculated to be 73.98 and 73.12 kJ/mol H_2 , respectively, with a slight difference of 0.86 kJ/mol H_2 . The difference on the reaction enthalpy made it easy to judge the practical preference reaction 2. On the other hand, F substitution of partial H into NaH lattice has been experimentally attested by XRD examination. Based on experimental and theoretical results, it showed that F could effectively tuned the thermodynamics of dehydrogenation reaction for $\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x$ system, which was helpful for our understanding of the detail mechanism of F substitution in NaMgH_3 .

The effect of F partial substitution was further examined by varying substitution ratio from 1: 11 to 3: 9 in the $\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x$ supercell as listed in Fig. 2. To ensure the reliability of the function of F-doped, we recalculated the reaction enthalpies by taking into account the zero-point energy (ZPE) corrections. After considering the ZPE correction, the reaction enthalpies were 65.42, 64.19, 63.91 and 59.23 kJ/mol H_2 for pure $\text{Na}_4\text{Mg}_4\text{H}_{12}$, $\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}_1$, $\text{Na}_4\text{Mg}_4\text{H}_{10}\text{F}_2$ and $\text{Na}_4\text{Mg}_4\text{H}_9\text{F}_3$, respectively. The thermodynamics of the reaction of NaMgH_3 became increasingly favorable with increasing the F-doped level. Moreover, reaction enthalpies of F-doped NaMgH_3 with and without ZPE correction exhibited similar dependence on the F-doped level.

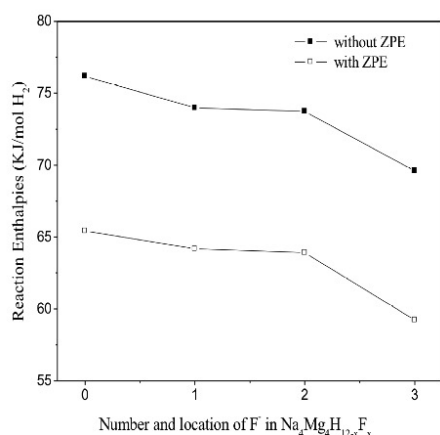


FIGURE II. CALCULATED REACTION ENTHALPIES WITH AND WITHOUT ZERO-POINT ENERGIES OF F-DOPED NAMGH3 AT VARIOUS DOPING LEVELS.

This work further investigated the electronic densities of states and projection electronic densities of states for NaMgH_3 , $\text{Na}_4\text{Mg}_4\text{H}_{11}\text{F}$, $\text{Na}_4\text{Mg}_4\text{H}_{10}\text{F}_2$ and $\text{Na}_4\text{Mg}_4\text{H}_9\text{F}_3$. As shown in Fig. 3, the calculations showed that the hydrides $\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x$ ($x = 0, 1, 2$ and 3) were wide-band gap insulators. It can be seen that the partial density of states (PDOS) of the Na and Mg s and p states were mainly contribution to the conduction bands, and the F-p states and H-s states of all compounds were essential in the valence bands. The contribution of H-s states to the total densities of states became larger and that of Na s and p states became less with increasing the F substitution Level from $x=1$ to $x=3$. More information can be obtained in Fig. 3(d) that the contribution of F-p states became smaller compared to Fig. 3(b) and 3(c). For these TDOS, all band shift towards the high energy states gradually with increasing the F substitution level from $x=0$ to $x=3$. It indicated that the hydride $\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x$ became more instable with increasing x , in accordance with the formation enthalpies. These calculation results have well confirmed F substitute for H in a favorable thermodynamic modification.

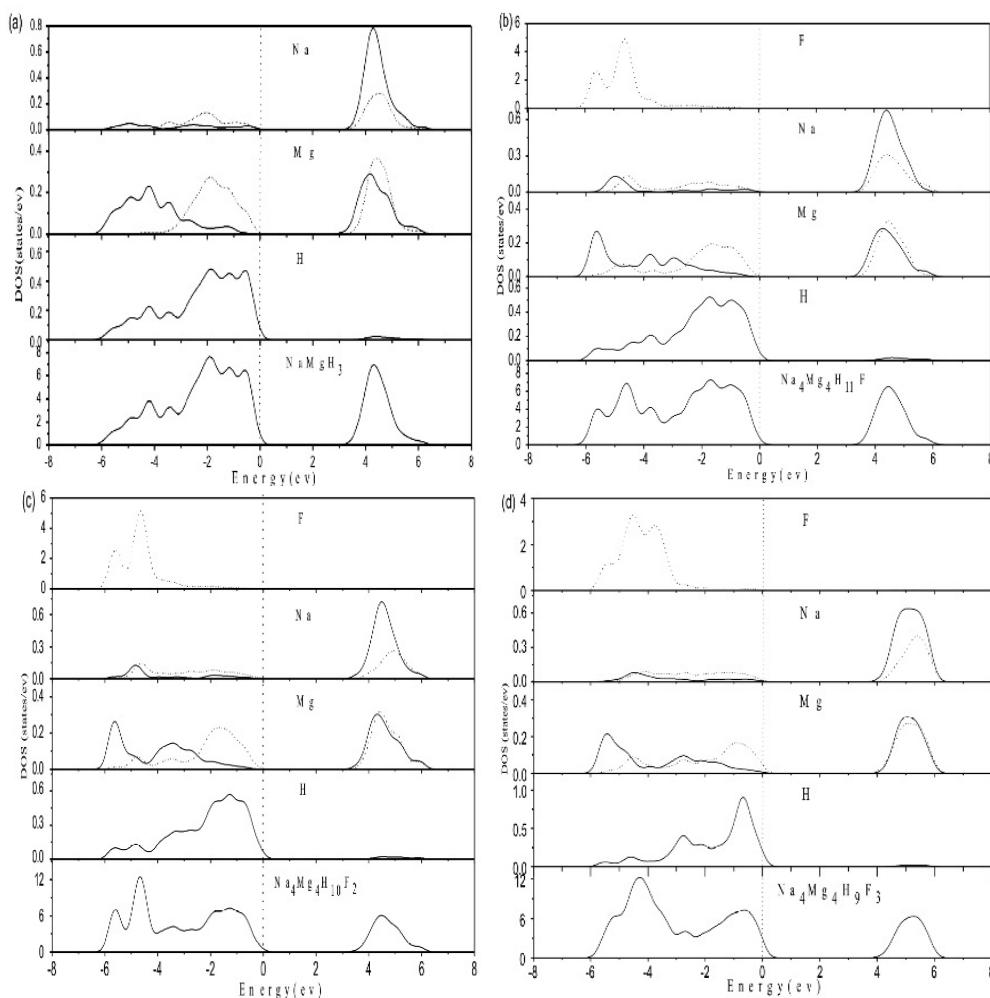


FIGURE III. CALCULATED TOTAL AND PARTIAL DENSITY OF STATES FOR THE $\text{Na}_4\text{Mg}_4\text{H}_{12-x}\text{F}_x$, S STATES ARE REAL LINE AND P STATES ARE DASHED LINE. E_F IS SET TO ZERO ENERGY AND MARKED BY THE VERTICAL DASHED LINE. (A) $x=0$, (B) $x=1$, (C) $x=2$ AND (D) $x=3$.

In order to compare with variation of halide anions, we analyzed function of Cl anion in my study. Table 2 presented calculated reaction enthalpies, which allowed us to judge the preference of reaction. Reaction enthalpies were 73.98 and 73.12 kJ/mol H_2 for $Na_4Mg_4H_{11}F$ following equations (2) and (3), which for $Na_4Mg_4H_{11}Cl$, the reaction enthalpies were calculated to be 63.14 and 50.52 kJ/mol H_2 , respectively. The results can be seen from the role of chlorine more significantly than fluorine. So it is easy to determine the practical preference reaction 2.

TABLE II. CALCULATED REACTION ENTHALPIES (KJ/MOL-1 H_2) OF $NaMgH_3$ AND $Na_4Mg_4H_{11}F(Cl)$.

Reaction enthalpy	Eq. (6)	Eq. (3)	Eq. (4)
$NaMgH_3$ (kJ/mol)	76.18		
$Na_4Mg_4H_{11}F-1$ (kJ/mol)		73.98	73.12
$Na_4Mg_4H_{11}Cl-1$ (kJ/mol)		63.14	50.52

IV. SUMMARY

The crystal structure and stability of $Na_4Mg_4H_{12-x}F_x$ ($x=0, 1, 2$ and 3) and $Na_4Mg_4H_{11}Cl$ have been systematically investigated by first-principles calculations. The stability of system is much more sensitive to vary the number of x and study on it show that F additive induces phase stability of hydrides with more negative formation enthalpies, in agreement with the experimental data. According to the calculation results, the formation enthalpy reducing with F substitution H facilitates dehydrogenating process of $NaMgH_3$, as well as the favorable thermodynamic modification. It requires convective experimental evidences to clarify the state of F in the reversible dehydrogenation of $NaMgH_3$, Which may open up new directions to modify and design new complex hydrides with desirable storage properties.

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