

---

**Yuanyuan Li**

Chatchai Rodwihok, Sung Gu Kang, Jin Suk Chung\*

School of Chemical Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 44610, Republic of Korea

jschung@mail.ulsan.ac.kr

---

# Hydrogen Release from $\text{KMgH}_3$ Hydride with Alkali Metal Dopants : A First-Principles Study

## Abstract

Hydrogen has been considered as a promising alternative energy carrier. However, there are still problems about the hydrogen storage [1]. Several perovskite-type hydride materials become the focus of attention and research to explore their suitability and stability for hydrogen storage recently. Among them,  $\text{AMgH}_3$  (A-alkali elements) has attracted a lot of interest [2, 3]. In particular,  $\text{KMgH}_3$  shows more advantages as one of the new promising candidates for hydrogen storage due to its light weight and relatively low cost [4]. A number of experimental and theoretical works have been performed on the structural and thermodynamic properties of  $\text{KMgH}_3$  [5-7]. However, there is still a general disadvantage of Mg-based hydrides which is the low hydrogen release [8]. Modifying the hydrides by doping other elements is beneficial to improve the properties of hydrogen storage [9]. In addition, pressure can induce the decomposition of hydrides [10]. Hence, it is an important factor for hydrides to release hydrogen. Therefore, in order to facilitate the hydrogen release in  $\text{KMgH}_3$ , we primarily focus on the effects of different alkali metal dopants M (M = Li, Na, Rb or Cs) and pressure (0-2GPa) on  $\text{KMgH}_3$  hydride using first-principles density functional theory (DFT) calculations. Obtaining the structures of phase stability, the most possible reaction pathway to release hydrogen, the potentially promising dopants for hydrogen release and the influence of applied pressure are the main objectives. All of our density-functional theory (DFT) calculations were performed using a plane-wave basis set with the projector augmented plane wave (PAW) [11] method as implemented in the Vienna ab initio simulation package (VASP) [12]. The possible crystal models with three different space groups ( $Pm3m$ ,  $Pnma$ ,  $R3c$ ) of  $\text{KMgH}_3$  have been taken into consideration. The zero-point energy ZPE is ignored due to the small effect on the dehydrogenation reaction. To explore the influence of partial replacement of K by alkali elements on the structural and dehydrogenation properties of  $\text{KMgH}_3$ , the reaction enthalpies of hydrides  $\text{K}_{1-x}\text{M}_x\text{MgH}_3$  ( $x=0, 0.0833, 0.1667$ ) are calculated. By comparing the simulation results, we can observe that dehydrogenation reaction of  $\text{K}_{1-x}\text{M}_x\text{MgH}_3$  to the metal hydride  $x\text{MH}$ ,  $(1-x)\text{KH}$ , Mg and  $\text{H}_2$  was the most favorable among all reaction pathways tested. In addition, Li was the most promising dopant to release hydrogen due to the lower reaction enthalpy of  $\text{K}_{1-x}\text{Li}_x\text{MgH}_3$  as shown in Fig. 1. The Fig. 2 displayed the stable modified structures on the basis of Li dopant. Moreover, the pressure effects on the reaction enthalpies were systematically examined on the basis of the modified structure. It is clear that all of the reaction enthalpies became linear decrease as the applied pressures increased. The reaction enthalpies of modified structures were lower integrally than the results of  $\text{KMgH}_3$ . To make a further investigation, the partial density of states (PDOS) of  $\text{K}_{1-x}\text{Li}_x\text{MgH}_3$  were also calculated after the pressure applied with 0GPa and 2GPa. We can draw the conclusion that the hybridization between Li-s with K- and Mg-s and p may decrease the stability. It may be the reason that reaction enthalpies was reduced. In summary, the dopant and pressure were valuable to release hydrogen for  $\text{KMgH}_3$  due to the reduced reaction enthalpies. It will be useful to efficiently design the new promising perovskite-type hydrides for hydrogen storage based on these studies.

## References

- [1] Schlappbach L, Züttel A. Nature, 414 (2001), 353-358.
- [2] Reshak AH. International Journal of Hydrogen Energy, 40 (2015), 16383-16390.

- [3] Pottmaier D, Pinatel ER, Vitillo JG, et al. Chemistry of Materials, 23 (2011), 2317-2326.  
 [4] Bouhadda Y, Kheloufi N, Bentabet A, et al. Journal of Alloys and Compounds, 509 (2011), 8994-8998.  
 [5] Komiya K, Morisaku N, Rong R, et al. Journal of Alloys and Compounds, 453 (2008), 157-160.  
 [6] Reshak A H, Shalaginov M Y, Saeed Y, et al. The Journal of Physical Chemistry B, 115 (2011), 2836-2841.  
 [7] Ghebouli M A, Ghebouli B, Bouhemadou A, et al. Solid State Sciences, 13 (2011), 647-652.  
 [8] Zhao D L, Zhang Y H. Rare Metals, 33 (2014), 499-510.  
 [9] Li Y, Ding X, Wu F, et al. The Journal of Physical Chemistry C, 120 (2016), 1415-1420.  
 [10] Shamp A, Terpstra T, Bi T, et al. Journal of the American Chemical Society, 138 (2016), 1884-1892.  
 [11] Blöchl P E, Physical review B, 50 (1994), 17953.  
 [12] Kresse G, Furthmüller J, Computational Materials Science, 6 (1996), 15-50.

## Figures

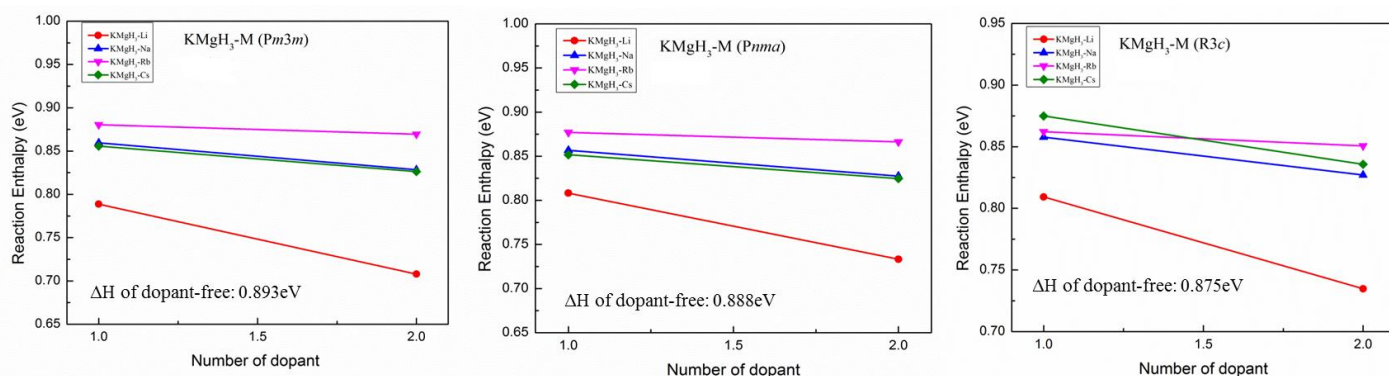


Figure 1. The reaction enthalpies of  $K_{1-x}M_xMgH_3$  with dopants Li, Na, Rb and Cs.

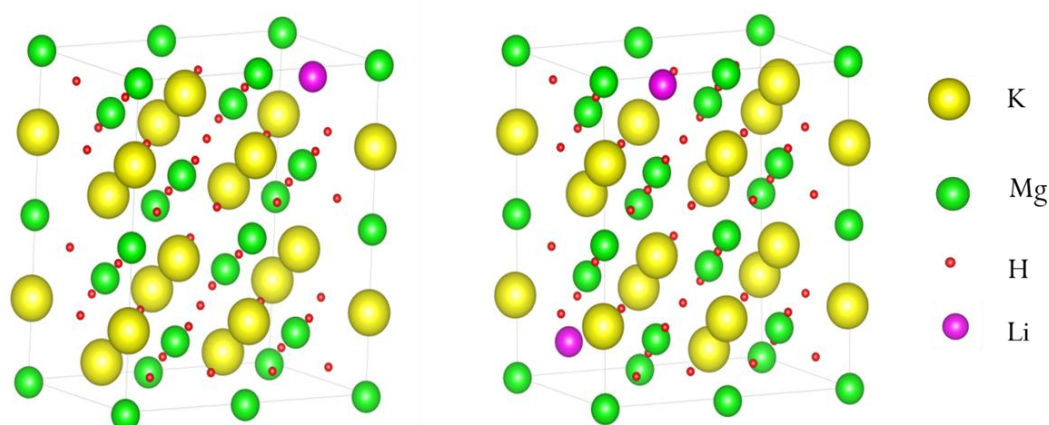


Figure 2. The final stable modified structures of  $K_{1-x}Li_xMgH_3$  ( $x=0.0833, 0.1667$ ) with space group R3c.