



Structure and bonding features of $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) with complex polyhedrons: First-principles calculations



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ABSTRACT

Structure and bonding features of hydride $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) were investigated by first principles calculations. The Ba–H distance in $Ba_6Mg_7H_{26}$ is longer relative to the Sr–H in $Sr_6Mg_7H_{26}$, while the Ba-containing polyhedron with higher symmetry and high coordination numbers possesses high stability reflected by the more negative formation enthalpy obtained for $Ba_6Mg_7H_{26}$. Hydrogen release from $Sr_6Mg_7H_{26}$ would be easier. The electronic structures indicate that the $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) exhibits non-metallic properties and the valence band is primarily dominated by H-s electrons. The chemical bonds in $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) exhibit primary covalent feature with definite ionic component, the covalent feature of Ba–H is more obvious than that of Sr–H. These electronic structures reveal the underlying mechanism for structure and bonding features of the hydride $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$).

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1. Introduction

Today, the energy crisis has become one of the greatly concerning problems [1]. Hydrogen energy is a promising energy due to its abundance, cleanliness, renewal and efficiency [2–5]. The application of hydrogen energy involves in the production, storage, transport, and utilization. Especially, the hydrogen storage is the most challengeable, which is required to possess a high hydrogen capacity, and the good combination of thermodynamics and kinetics [6].

In recent decades, metal hydride is considered to be one of the most promising hydrogen storage materials due to its safety and high hydrogen-storage capacity per unit volume. Magnesium hydride MgH_2 , is a typical and attractive hydrogen storage material with high hydrogen capacity (7.66 wt.%) and low manufacture cost [7–9]. But it is still not applied widely due to its high thermodynamic stability and slow desorption kinetics [10]. To improve the hydrogen storage properties, alloying of magnesium hydride with foreign elements such as transition metal (TM), alkaline earth (Ae) and rare earth (RE) is an effective method [11–14]. Nowadays, the Ae–Mg based hydrogen storage materials are attracting more and more interesting.

In the past decades, a large number of magnesium based ternary alkaline-earth hydrides have been reported, such as Ca–Mg–H series

including $Ca_4Mg_3H_{14}$ and $Ca_{19}Mg_8H_{54}$ [15,16], Ba–Mg–H series including $BaMgH_4$, Ba_2MgH_6 , $Ba_2Mg_3H_{10}$ and $Ba_6Mg_7H_{26}$ [17–20], Sr–Mg–H series including $SrMgH_4$, Sr_2MgH_6 , $Sr_2Mg_3H_{10}$ and $Sr_6Mg_7H_{26}$ [21–24]. Interestingly, $Sr_6Mg_7H_{26}$ and $Ba_6Mg_7H_{26}$ contain complicated cage-like polyhedrons, namely $(Ba_1H_{12})^{-10}$, $(Ba_2H_{12})^{-10}$, $(Sr_1H_{10})^{-8}$, $(Sr_1'H_{11})^{-9}$ and $(Sr_2H_{10})^{-8}$, and the structural symmetry of both hydrides is different because of the smaller atomic radii of Sr [24,25]. Up to now, most studies of the $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) mainly focus on the synthesis of materials and determination of the crystal structures from experiment, the fundamental electronic characteristics has rarely been reported. To reveal the effect of the complex polyhedrons on hydrogen absorption/desorption properties, it is necessary to investigate theoretically electronic characteristics the structure and bonding features of $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$).

In this work, first-principles calculations based on density functional theory (DFT) were performed to systematically study the structure and bonding features of $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$). In Section 2 the method of calculation is briefly described. In Section 3 the structural and bonding feature of $Ae_6Mg_7H_{26}$ ($Ae = Sr, Ba$) are presented and discussed in details. And the conclusions are presented in Section 4.

2. Method of calculation

All calculations were performed with density functional theory using pseudopotentials and a plane wave basis set as implemented in the program VASP [26,27]. The ion core-valence electron

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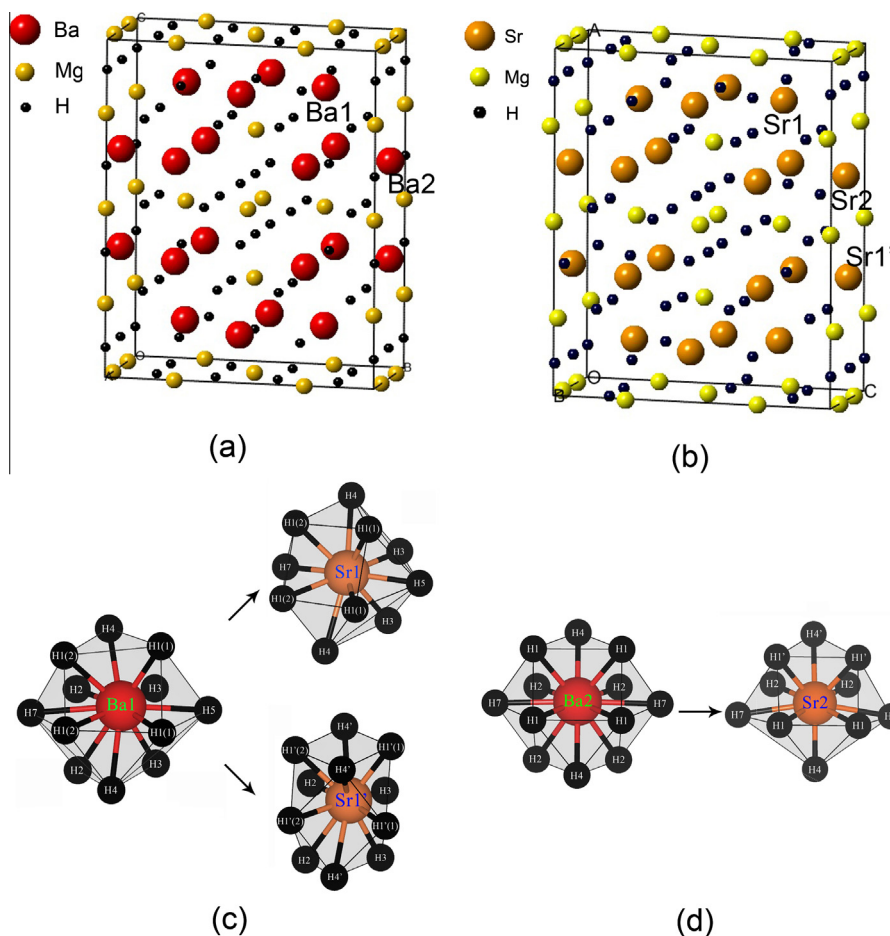


Fig. 1. (a) Crystal structure for $\text{Ba}_6\text{Mg}_7\text{H}_{26}$; (b) crystal structure for $\text{Sr}_6\text{Mg}_7\text{H}_{26}$; (c) the cage-like polyhedrons of Ba1, Sr1 and Sr1'; (d) the cage-like polyhedrons of Ba2 and Sr2.

interaction was described by the projector-augmented wave (PAW) method [28]. The energy cut-off of the plane wave basis set was 400 eV, which is sufficient to full convergence. The exchange-correlation function was treated within generalized gradient approximation of the Perdew–Wang 91 version (GGA-PW91). In the present calculations, the valence electron configuration is Sr-4s4p5s, Ba-5s5p6s, Mg-3s and H-1s. During optimization of crystal structures, the shape and volume of unit cell as well as internal positions of atoms were fully relaxed. The Brillouin zone for $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ and $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ was sampled with a mesh of $4 \times 10 \times 6$, $10 \times 6 \times 4$ k -points generated by the Monkhorst–Pack scheme for geometry optimization. For calculations of the electronic structures, the k -points were sampled by $6 \times 12 \times 8$, $12 \times 8 \times 6$, respectively. The total energy is converged to less than 10^{-5} eV per atom and the Hellman–Feynman forces are converged to less than $0.01 \text{ eV}\text{\AA}^{-1}$.

3. Results and discussions

3.1. Structural feature

$\text{Ba}_6\text{Mg}_7\text{H}_{26}$ possesses orthorhombic structural symmetry with the space group $Immm$ (No. 71) and the unit cell contains 78 atoms [20]. The 12 Ba atoms are located at Wyckoff positions 8l and 4j, the 14Mg atoms are located at Wyckoff positions 4i, 4g, 4e, 2c and the 52 H atoms are located at Wyckoff position 16o, 16n, 8l, 4j, 8i. Due to the smaller radius of Sr [24], $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ crystallizes in monoclinic structural symmetry with the space group $I2/m$ (No. 12, non-standard setting) which is slightly deformed from

the orthorhombic structural symmetry. In the unit cell of $\text{Sr}_6\text{Mg}_7\text{H}_{26}$, the 12 Sr atoms are located at Wyckoff positions 8i, the 14Mg atoms are located at Wyckoff positions 8i, 4g, 2c and the 52 H atoms are located at Wyckoff positions 32j and 20i sites. The crystal structures of $\text{Ae}_6\text{Mg}_7\text{H}_{26}$ ($\text{Ae} = \text{Sr}, \text{Ba}$) are depicted in Fig. 1a and b, respectively.

After structural optimization, the obtained structural parameters are tabulated in Table 1. The calculated lattice parameters and internal coordinate of both $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ and $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ are in good agreement with the experimental values [20,24]. The optimized lattice constants of $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ with $a = 5.7618 \text{ \AA}$, $b = 11.8488 \text{ \AA}$, $c = 14.8466 \text{ \AA}$ are slightly larger than that of $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ with $a = 14.1067 \text{ \AA}$, $b = 5.5932 \text{ \AA}$, $c = 11.4712 \text{ \AA}$. Obviously, the lattice constants of $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ are slightly larger than ones of $\text{Sr}_6\text{Mg}_7\text{H}_{26}$, while the angles β of 90.0° in $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ is smaller than β of 91.1° in $\text{Sr}_6\text{Mg}_7\text{H}_{26}$, this distinction results in lower symmetry and coordination numbers of $\text{Sr}_6\text{Mg}_7\text{H}_{26}$, although the structures of $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ and $\text{Sr}_6\text{Mg}_7\text{H}_{26}$ are closely similar.

With the crystal structure distortion from orthorhombic structural symmetry to monoclinic structural symmetry, the coordination number (CN) is decrease as well. In $\text{Ba}_6\text{Mg}_7\text{H}_{26}$, the both central Ba1 and Ba2 at the Wyckoff positions 8l and 4j have $\text{CN} = 12$. Different from $\text{Ba}_6\text{Mg}_7\text{H}_{26}$, in $\text{Sr}_6\text{Mg}_7\text{H}_{26}$, the CN of central Sr1 and Sr1' at the Wyckoff positions 8i respectively reduces to 10 and 11, and the CN of central Sr2 at the Wyckoff positions 4i reduces to 10. Because of the variation of the coordination number, the regular 18-facet polyhedron of Ba1 is distorted into irregular 15- and 13-facet polyhedron of Sr1 and Sr1', and the regular 18-facet polyhedron of Ba2 is distorted into regular 15-facet

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