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Structural and electronic properties of perovskite hydrides $ACaH_3$ (A=Cs and Rb)

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Abstract

We have performed structural properties, electronic properties, charge density and potential distribution of $CsCaH_3$ and $RbCaH_3$ using TB-LMTO-ASA approach under local density approximation. Our findings show that both $CsCaH_3$ and $RbCaH_3$ are non-magnetic and then insulators with estimated direct band gaps (*M-M)* of 3.15 eV and 3.17 eV respectively. Our estimated values of band gap suggest to both materials as better candidate for the high frequency ultra-violet devices. Furthermore, role of corner atoms in perovskite hydrides are also presented in this study. Present calculations agree well with the previous work.

Keywords: Projected density of states; perovskite; charge density and TB-LMTO-ASA**.**

1. Introduction

Binary alloys of transition and post-transition elements, and also graphene related work have been studied with high effort by many researchers [1-6] but have no band gap. However, various potential applications in optics need significant band gap. The perovskite structure of ternary chlorides is applicable in optics due to their wide band gap [7, 8]. Perovskite compounds and its derivatives are the most popular field owing to their diverse physical properties while going to binary alloy to ternary alloy to perovskite material. Besides this, anomalous dielectric properties of perovskite and phase transition with increasing temperature have made fundamental interest in physics [9-11].

Perovskite hydride compounds belong to Perovskite family, symbolized as ABH_3 (A and B represent lighter metals) are well characterized with their optical properties. Perovskite hydrides have become a source of attraction to experimentalists due to presence of lightweight elements, low production cost and wide range of applications in the industrial area. Alkali and alkaline earth-based complex hydrides are expected to have application for the hydrogen gas storage at certain temperature and pressure [12, 13]. The complexity in structural arrangement of perovskite hydrides and difficulties in establishing proper hydrogen position by x-ray diffraction method in previous attempt [14] motivated us to enter in this burning area of research. As increase in Ca-H distance, narrower the density of states (DOS) on moving from $LiCaH_3$ to $CsCaH_3$, predicted in previous work [15] is insufficient to address the factors for DOS variation and also the compound $NaCaH_3$ has shown absurd behaviour than others in regards to M-H and Ca-H distance. Hence, in the present work efforts have been taken to study the structural, electronic and charge distribution to explore the origin of band gap, contribution of orbitals and role of potentials to bands separation.

Moreover, the crystal structure, shape, size, and surface composition of materials plays vital role to control the hydrogen sorption properties for energy storage applications. For the efficient energy carrier, hydrogen should be absorbed and desorbed in materials easily in sufficient quantities in cheaper price. The complex compound based on Alkali- and alkalineearth hydrides are expected to have potential candidates for storing hydrogen at moderate temperatures and pressures [16-17]. This is another motivation of present work to study the electronic behavior of such materials.

The paper is organized as follows: in section II, the computational details of the present study are included. Results and discussion are presented in section III whereas section IV provides the conclusions of the present study and finally references are listed at the end of the paper.

2. Computational details

The unit cell of the perovskites hydrides $CsCaH_3$ and $RbCaH_3$ crystallize in to the cubic structure with space group Pm-3m. The atomic positions in the elementary cell are at Cs(0.0,0.0,0.0), Rb(0.0,0.0,0.0), Ca (0.5,0.5,0.5) and three hydrogen atoms are at three different positions as H_1(0.5,0.5,0.0) , H_2(0.5,0.0,0.5) and H_3(0.0,0.5,0.5) [8]. With reference to experimental lattice parameter of 4.609 Å for $CsCaH_3$ [18] and 4.547 Å for $RbCaH_3$ [19] unit cell structures thus obtained with the help of xcrysden visualization are shown in figures 1(a) and (b).

Fig. 1: (a) Unit cell of $CsCaH_3$ and (b) Unit cell of $RbCaH_3$.

All the calculations are done based on the density functional theory implemented with TB-LMTO-ASA code to carry out comprehensive analysis of structures along with electronic and magnetic properties. The standard local density approximation (LDA) is used to address exchange correlation potential. The concept of Wigner-Seitz spheres for each atom in the unit cell is taken into account to determine the potential of the crystal [20]. We have only included the energetically higher-lying valence states in the self-consistent calculations of the effective crystal potential [21] according to the norms of the TB-LMTO-ASA approach. The core states are treated fully relativistically while the semi-core and valence states as treated semi-relativistically. All the calculations were iterated to self-consistency along with accuracy of 10^{-6} Rydberg.

3. Results and discussion

The new findings from the calculations of band structures, DOS, charge density and potential distributions are described as follows.

A. Band Structures

The calculated energy bands of perovskites $CsCaH_3$ and $RbCaH_3$ along the high symmetry lines in the Brillouin zone are shown in Fig (2).

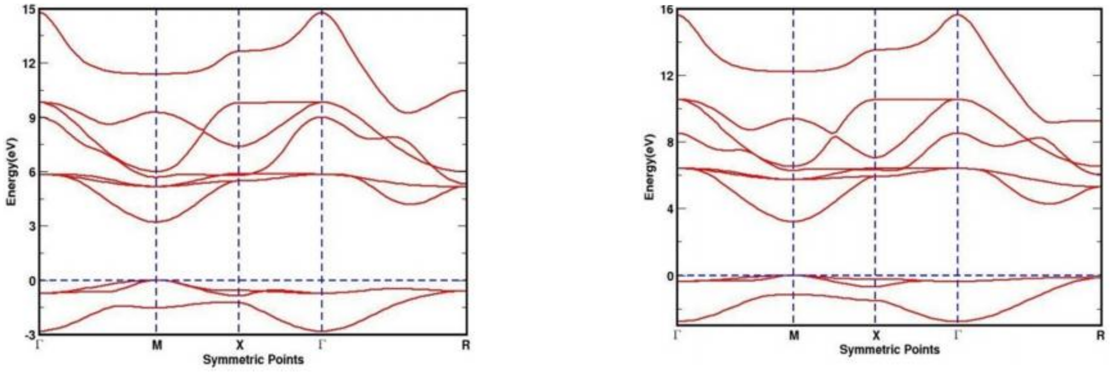

Fig. 2: Band structures of $CsCaH_3$ (left) and $RbCaH_3$ (right).

The horizontal dotted line in the above figures represents the Fermi level. We have found 10 different energy bands in both $CsCaH_3$ and $RbCaH_3$. Zero energy is chosen to coincide with the CBM and VBM both occur at same M point results the direct band gap in both of these perovskite hydrides which indicates that both $CsCaH_3$ and $RbCaH_3$ bear the non-metallic behaviour. Our estimated band gaps of $CsCaH_3$ and $RbCaH_3$ are 3.15 eV and 3.17 eV which indicates that $CsCaH_3$ and $RbCaH_3$ are insulators. Our results of band gap well agree with previous generalized-gradient approximation based theoretical calculations [8]. Resulting band gap of these perovskites meet the requirement for the applications in high frequency ultra-violet device [22].

B. Density of States

To observe the density of states, we have taken same value of the lattice parameter as in band structures calculations. The total DOS and PDOS of $CsCaH_3$ and $RbCaH_3$ are shown below. The total density of states are categorized into four different parts and the contributions of different states can easily be seen from the PDOS analysis.

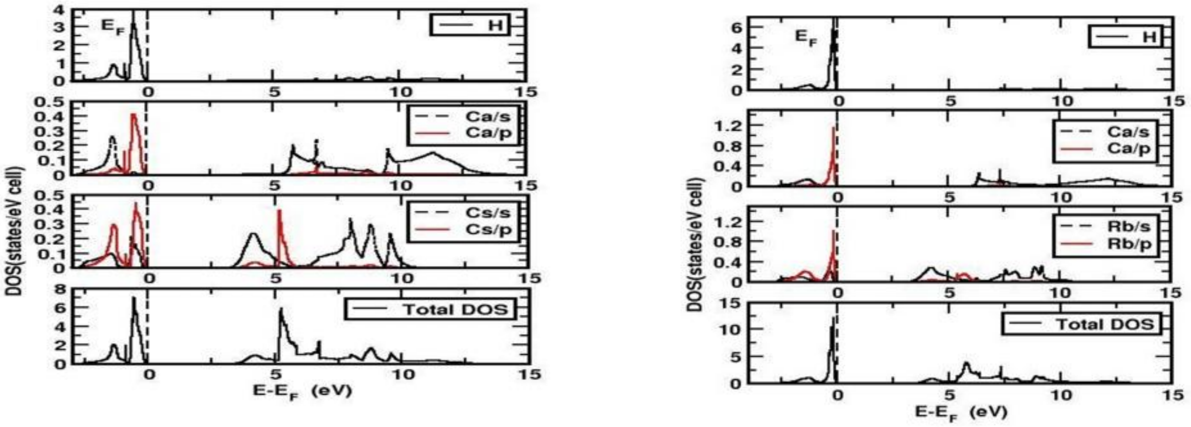

Fig. 3: Total DOS and PDOS of $CsCaH_3$(left) and $RbCaH_3$(right).

The Fermi energy line is in the valence band which supports the non-metallic behaviour. In both $CsCaH_3$ and $RbCaH_3$ Ca-*p* and H-*s* states are located in the vicinity of the Fermi level at the valence band. In $CsCaH_3$ Ca-*s* and $-p$ states are well-separated where as in $RbCaH_3$ Ca-*s* and $-p$ states are not well-separated. The symmetric nature of spin up and spin down DOS indicate the non-magnetic behavior of $CsCaH_3$ and $RbCaH_3$. The contribution to the valance band is maximum by s states of hydrogen and less contributions is seen from Ca and Cs. The contribution of Ca and H atoms to the DOS is major in the valence bands while Cs/s, Cs/p are responsible for that in the conduction band.

Further, one valance electron of Cs (or Rb) in $CsCaH_3$ (or $RbCaH_3$) fill the partially occupied s-orbital of one hydrogen and remaining two partially filled orbitals of hydrogen is filled by two valence electrons of calcium. Since the valence electrons are completely filled, $CsCaH_3$ and $RbCaH_3$ both acts as an insulating materials.

C. Charge density and potential distribution

The charge density distribution and chemical bonding behaviour of $MCaH_3$ is important to check the stability of these materials for hydrogen storage. The charge density plot of $CsCaH_3$ and $RbCaH_3$ obtained by using the same lattice parameters as in DOS and band structures calculations are shown in figure (4).

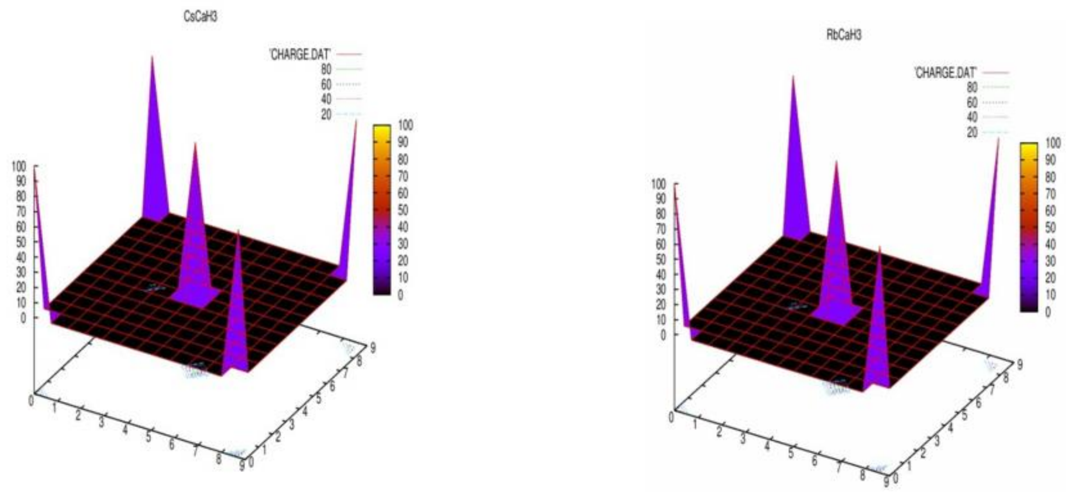

Fig. 4: The charge density distribution of CsCaH_3 and RbCaH_3.

From figure 4, we have found that there are five peaks along the corners and faces which shows the maximum distribution of the charges at the corners and faces. About 10-40 % of total charge occur along the corners and faces which has been shown by a high peaks lines while the distribution of the charges is negligible at other interstitial sites. This is the site at which adsorption and desorption of hydrogen takes place, indicating that such materials can be used for hydrogen storage purposes. The potential distribution plot of CsCaH_3 and RbCaH_3 are shown in figure (5) .

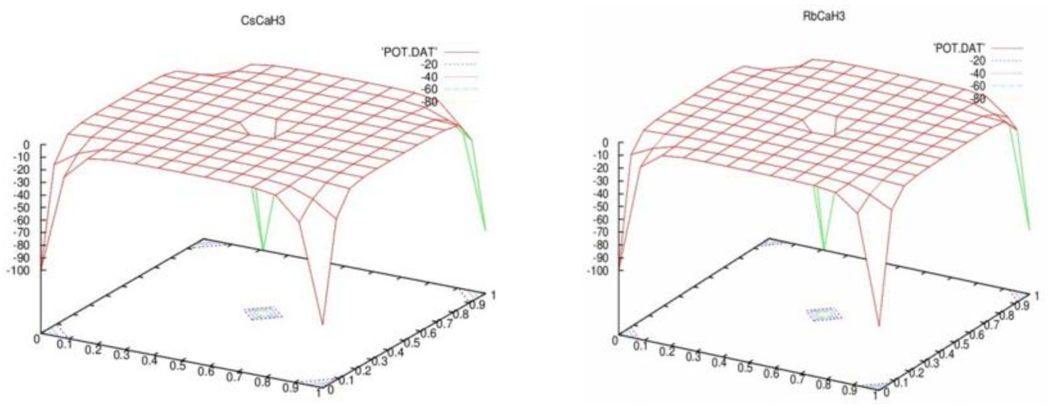

Fig. 5: Potential distribution in CsCaH_3 (left) and RbCaH_3 (right).

From figure 5, we can find that the potential is maximum in the vicinity of core whereas at the interstitial region the potential is found to be constant (flat). Our results agree well with the muffin-tin potential in which the potential is maximum near the core electrons and almost flat in the interstitial space. This kind of potential distribution fully supports the maximum distribution of charge near the corner of crystal structure.

4. Conclusions

In this present work, we studied the band structures, density of states, charge density and potential distribution of perovskite hydrides $CsCaH_3$ and $RbCaH_3$ by using TB-LMTO-ASA. Taking the experimental lattice parameters, we calculated the electronic and magnetic properties of $CsCaH_3$ and $RbCaH_3$. The calculated DOS shows that $CsCaH_3$ and $RbCaH_3$ are non-magnetic. The direct band gap of 3.15 eV found in $CsCaH_3$ and 3.17 eV in $RbCaH_3$ meet the requirement for the application in high frequency ultra-violet device. The charge density plot of $CsCaH_3$ and $RbCaH_3$ indicate that the corner atom contributes mainly to increase charge density which also support from the potential distribution curve. From potential distribution of $CsCaH_3$ and $RbCaH_{3,}$ we found that potential is maximum at core whereas flat at interstitial region. This may be the vital site to store the hydrogen and hence system acts as hydrogen storage materials. Finally we can conclude that TB-LMTO-ASA method can be used as a convenient method for studying the band structures and density of states of different solids. Our results may be useful to study the other various types of elemental solids and perovskites in future.

Acknowledgments

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