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Efficient hydrogen storage in $KCaF_3$ using GGA and HSE approach

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Abstract

Being a renewable and sustainable energy carrier, hydrogen energy has garnered great interest having some technical barriers related to storage aspects. Hydride materials exhibit potential hydrogen storage capacities efficiently and safely. The current study has been performed in the framework of density functional theory to examine structural and optoelectronic properties of KCa $\mathbf{F_{3-x}H_x}$ (x=0, 0.6, 1.2, 1.8, 2.4, and 3) compounds to understand their contribution about hydrogen storage. The mechanical stability of these compounds with elastic constants and negative formation enthalpies suggests these materials are stable and synthesizable. Insertion of impurity into pristine material led to an increase in optimized lattice parameter from 4.31 to 4.48 $\mathbf{\AA}$ where no previous study is available to compare lattice constants other than pristine KCa $\mathbf{F_3}$ that is well consistent with existing literature. Computed and plotted results of plastic properties for different H-inclusions manifestly depict a decrease in elastic moduli, anisotropic and brittle nature of all studied materials. The density of states and band diagrams were drawn utilizing both GGA and HSE03 formalisms, where observations manifest not only an upsurge in bandgap but also shifting from indirect to direct nature. Two effects Burstein -Moss shift and bandgap renormalization were explored to investigate the shifting of absorption edge toward the valence band that results in bandgap narrowing. Optical parameters were also

well explained within the photon energy range of 0–35eV. Startling results of absorption spectra reveal prominent redshift increases in the UV region. Among all H- insertions high value of the static refractive index (n (0)=3.77) and dielectric function with minimum absorption losses possess KCa H_3 only appropriate material for storage aspects. Also, enhancement in optical properties suggests a new end material (KCa H_3) curious for optoelectronic devices. Moreover, H-incorporation has improved hydrogen storage characteristics up to a capacity of 3.6wt% with the challenge of high desorption temperature whose improvement will play a vital role in hydrogen uptake mechanism and will enlighten future studies to make it useful for practical and transportation applications.

Introduction

With the increasing global population and to improve the standard of living the world urged scientists to be focused on two major problems; energy crises and a pollution-free environment. Rapid depletion of fossil fuels, rapid enhancement in energy demand, and global warming have led to a severe energy crisis and environmental pollution on a global scale [1]. Hydrogen is considered an alternative fuel for the future energy industry because of its lightweight, high-energy-density, clean combustion, non-polluting nature, and more production from other renewable sources. Unlike fossil energy fuels; it will be an abundant energy source for both stationary and mobile applications. Besides having many advantages significant challenge that hinders the commercialization of hydrogen-powered vehicles is the lack of a secure and efficient method of storage [[2], [3], [4]]. There are three state storage methods; solid, liquid, and gas. Using these storage states many technologies have been developed for the storage of hydrogen such as liquefaction, compressed gas, in the form of metal hydrides, and complex hydrides but some of these are very expensive. As hydrogen is gas under ambient conditions then for safety cautions high-pressure vessels are required in the gas hydrogen storage method. Not only liquefication but also boiling of hydrogen and cryogenic temperatures are required for the liquid hydrogen storage method that needs additional energy. Physisorption and chemisorption of hydrogen are two categories involved in the solid-state storage method. The physisorption process is mostly used in porous materials like in CNTs While for chemisorption hydrogen is chemically bonded with metal hydrides and complex hydrides. During chemical bonding, the storage of hydrogen in intermetallic phases of various metal hydrides and then its reactions with these metal phases cause absorption of hydrogen in large amounts [5,6]. Among three states solid-state storage method has gained more attention to develop technology in interest. Now recently light-metal perovskite hydrides have gained considerable attention in hydrogen storage applications due to their high hydrogen content by mass and high gravimetric densities. The main hindrance while using hydrides for storage applications is their low hydrogen weight capacity which is due to the low atomic mass ratio of hydrogen to most metals [7].

For efficient hydrogen storage, some requirements must be satisfied such as hydrogen mobility, high gravimetric and volumetric capacities, reversibility, and release at ambient conditions by increasing dehydrogenation properties and decrease in decomposition temperature. Despite a lot of research has been done on hydride materials yet a material that fulfills all requirements has not been discovered [1,6].

A lot of experimental work on perovskite hydrides has been done over the past few years to increase their hydrogen applications. Synthesis of these materials is a very time-consuming effort; there is a need for some theory that tells us about hydrogen storage capacity and predictive power for enthalpies before synthesizing. Density functional theory is a promising approach to studying microscopic characteristics and knowing energetically synthesizable compounds [8]. Most attention was paid to magnesium-based hydrides as these are abundant, lightweight, cheap, and have amazing hydrogenation properties [9]. Among all Mg-based hydrides, NaMg H_3 is the most studied compound for hydrogen storage applications due to large gravimetric and volumetric capacities having values of 6wt% and 88 kg/m^3 respectively [10] that vary with

increase in temperature. Temperature-dependent dehydriding kinetics properties of perovskite-type NaMg H_3 hydride can be improved greatly by substituting K in replacement of Na gradually.

Not only Mg-based perovskites but also a lot of alkali and non-alkali metal hydrides have been studied for future hydrogen storage applications. Transition metal, alkali, and alkaline earth metal hydrides are applicable modes for hydrogen storage at moderate temperatures and pressures. Shafqat Hayat et al. studied structural, optoelectronic, magnetic, mechanical and hydrogen properties of the following novel combination XGa H_3 (X=Rb, Cs, and Fr) [11], LiX H_3 (X=Cr, Zn, Fe, and Co) [12], and XCu H_3 (X=Zn, Co, and Ni) [13] respectively in different papers. New hydride compounds such as XSr H_3 (X=K, and Rb) [14] have also been reported in recent papers to get information about their hydrogen storage abilities. These materials were reported as mechanically and dynamically stable. Hydrogen storage properties of ZrNi H_3 by uniaxial/biaxial strain were examined by Rkhis M et al. [15]. DFT study accomplished for NaX H_3 (X=Fe, Mn, and Co) hydrides presented gravimetric hydrogen storage capacities having values of 3.70, 3.74, and 3.57 wt% [16]respectively. By using dopants from different materials and investigating reactions of two or more hydrides; hydrogen kinetics for desorption and absorption can be enhanced. Furthermore, some other compounds of this structural group such as LiNi H_3, KNi H_3, NaNi H_3, CaTi O_3H_x, MgTi O_3H_x, and BaY O_3H_x were also investigated to study their hydrogen storage properties [5,9,17]. Two mechanically stable perovskite hydrides (LiCa H_3, NaCa H_3) have reached gravimetric hydrogen densities of 5.7 wt% and 4.38 wt% respectively which are reasonable with the goal set by the US Energy Department [18]. Desorption temperatures representing desorption of hydrogen from host materials for these two hydrides are found to be 66.15K and 139.4K respectively. In comparison to some studied alkali and non-alkali metal hydrides; KCa H_3 Possess a low gravimetric ratio that can be improved by having its dependency on temperature. By improving its desorption temperature, it would become vital material for various hydrogen storage applications.

In literature, hydrogen storage capacities have been calculated for many compounds but none of these meet the critical criteria for practical applications showing more need to investigate new materials for high-density hydrogen storage. This paper aims to investigate the hydrogen storage properties of ternary (KCa $F_{3-x}H_x$, x=0, 0.6, 1.2, 1.8, 2.4, and 3.0) compounds. These hydride perovskites synthesized by doping have gained remarkable attention due to some fascinating properties. Heats of formation and decomposition temperatures are two main criteria that were used to verify the stability of these substituted compounds using density functional theory. It was noticed that these substituted materials are mechanically stable and can be synthesizable. The large bandgap of pristine KCa F_3 limits its application indicating the need for further investigation of this crystal structure. Replacements of H with F not only improve its properties as energy fuel carriers but also other physical properties such as tunable bandgap and fascinating optoelectronic and mechanical properties. Reviewing all literature, it is established that very minor work has been done on KCa H_3 both theoretically and experimentally. To the best of our knowledge H-substitution neither at the cationic site nor at the anionic side of c-KCa F_3 has been studied before using first-principles DFT calculations. According to our knowledge, mechanical and optical properties of KCa H_3 also have not been examined previously. Therefore, results obtained in this study of KCa H_3 would provide a valuable contribution to the literature and will motivate scientists for further theoretical and experimental study on this material.

Our work plan in this paper has been deliberated in four sections: in section 2 explanation of computational details and method utilized in these investigations has been elucidated. Results and discussion on optoelectronic, mechanical, and hydrogen storage properties are made assessable in section 3. Finally, in section 4 we have compiled our computed results.

Section snippets

Computational details

Physical properties have been investigated using self-consistent density functional theory (DFT) within the framework of CASTEP (Cambridge Sequential Total Energy Package) for perovskite hydride KCa $F_{3-x}H_x$ (x=0, 0.6, 1.2, 1.8, 2.4, and 3.0). These calculations are performed by using the plane-wave pseudopotential method [17,19]. This method provides faster calculations without affecting efficiency and assuming orbital shape in advance. Here to obtain well-converged results and rapid…

Geometry optimization

At room temperature KCa F_3 is in a cubic phase that is the most stable and does not transform to other phases by adding different substitutions of hydrogen elements. The pseudopotential method based on DFT under the PBE-GGA approach was used to optimize crystal structure and to obtain values of lattice constants at the lowest state [14]. The total energy is minimum at some volume that is named optimized unit cell volume. After optimization of structure Birch Murnaghan's state equation was…

Conclusion

In this study material characteristics of H-incorporated and pristine $KCaF_3$ were investigated through DFT with CASTEP simulation code based on the plane-wave pseudopotential method. Structural investigations under the PBE-GGA approach demonstrate an increase in lattice parameters employing the difference in ionic radii of host and dopant. Negative formation enthalpies, tolerance, and octahedral factors suggest both end materials are structurally and thermodynamically stable to be synthesized…

Author's agreement

Authors are fully agreed with the content of the manuscript and there is no conflict of interest between authors in terms of finance or text.…

Data availability

All data generated or analyzed during this study are included in this published article.…

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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