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Mechanical and Structural Evaluation of $LiSrH_3$ Perovskite Hydride for Solid State Hydrogen Storage Purposes

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Abstract

Increasing catastrophic climate events, energy needs, human population lead to look for clean, cheap and environmentally friendly energy production methods and sources. International agreements have been made to lower carbon emissions and support carbon free way of energy productions. Hydrogen technology is suggested as one excellent way of accomplishing these aims. Hydrogen is an excellent energy carrier with almost zero carbon emission and high efficiency. There are four steps to make hydrogen energy ready for usage: production, transportation, storage and converting it to electricity. Each step has its own obstacles to be overcome. Among the storage methods, solid state storage of hydrogen is very promising since it allows us to store hydrogen in high content and safely. Thus, there are intense ongoing research on this area. Therefore, this study adopts a well proved, time and cost saving method density functional theory to search and evaluate mechanical and electronic properties of $LiSrH_3$ perovskite hydride with space group $Pm\bar{3}m$ (221) for hydrogen storage purposes. Two critical parameters gravimetric hydrogen density and hydrogen desorption temperature along with elastic constants, Poisson's ratio, Shear, bulk, Young modulus are collected and discussed. The mechanical evaluation is demonstrated that $LiSrH_3$ is a mechanically stable material, however, elastic constant evaluation is showed that it is a brittle material which can be an obstacle when handling the material. The electronic band structure is also obtained which demonstrated an indirect band gap of 3.65 eV.

Keywords: Solid state, hydrogen storage, mechanical stability, elastic properties.

1. INTRODUCTION

Our daily lives require energy which depicts a rising pattern due to increasing life standards and world's population. In the current situation, this energy is produced from coal, natural gas and oil. These sources are limited and have been creating pollution which causes catastrophic climate

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changes and disasters such as flood, drought and heat. In addition, the prices of oil, natural gas and oil are going up with the demand. All these reasons are led to search for cheap, safe, carbon free energy sources and methods to decrease climate change effects and prices. International agreements have been made such as Paris Agreement to tackle with high carbon emissions [1]. Several environmentally friendly energy production methods have been suggested and implemented for this purpose. Among them, hydrogen has taken great attention due to being abundant, cheap, and carbon free.

Currently, hydrogen has been produced from steam-methane reforming reactions, coal, natural and water electrolysis [2]. The efficiency of water electrolysis is around 70%. When the excess energy from solar or wind power is used to produce hydrogen via electrolysis, this process can be very effective. Besides production, hydrogen storage and transportation of it, is a critical step, too There are several ways to store hydrogen such as gas, liquid and solid-state storage. Among them, storing hydrogen in a solid host material seems to be much promising compared to compressed gas and liquid storage due to easy transportation, safety, high content, reversibility and high kinetics. Solid state hydrogen storage materials can be used in various applications such as fuel cells which can also be used in stationary or portable devices. These materials include hydrides, alloys and complex materials. ABH_3 materials has taken great interest owing to its perovskite structure. Thus, perovskite hydrides are studied intensely recently. The electronic and elastic behaviors of $KSrH_3$ and $RbSrH_3$ are studied using first principles calculations for hydrogen storage purposes by Raza et al. [3]. Their result suggested a mechanical and thermodynamic stability with a brittle nature for these hydrides. The electronic structures indicated semiconductor nature. The phase stabilities of several hydrides $MBeH_3$ (Li, Na, K. Rb, Cs) are investigated [4]. $LiBeH_3$ and $NaBeH_3$ are reported to be as brittle materials in another study [5]. Elastic, electronic and optical properties of $KMgH_3$ is investigated using density functional theory calculations for different phases and only perovskite structure is reported to be stable [6]. The target for storing hydrogen in solid material is determined as 4 wt. % by the US Energy Department. Materials with higher gravimetric hydrogen density than this value are great of interest such as lithium containing materials. Lithium based host materials are studied extensively since these materials are light and exist in our world in large quantities. $LiSrH_3$ is one of these host materials which is not examined before as host material and its properties are not investigated. Therefore, revealing electronic and elastic features of these hydrides are critical since it is linked to their stabilities. For example, if the host material is brittle, it will be difficult to handle it. Also, the bonding features of host material can affect the bonding of hydrogen to the host material. Thus, this study is adopted first principles calculations to investigate electronic, elastic and hydrogen storage properties of $LiSrH_3$. The stability and bonding properties of $LiSrH_3$ will be examined in great detail.

2. METHOD OF COMPUTATION

All the calculations in this study were done by using Siesta 4.0 package program [7]. First principles calculation was adopted to reveal elastic and electronic features of $LiSrH_3$. Perdew-Burke-Ernzerhof generalised gradient approximation (PBE-GGA) was taken for the exchange correlation potential [8]. A 8x8x8 k-points mash was taken to sample the Brillouin zone. The structure was formed by relaxing all the atoms with residual force smaller than 0.01 eV/Å on each atom. The electronic wave functions were expanded in plane-wave basis to set up a kinetic energy cut off to 35 Ry, while the cut off energy for the electronic charge density was set to 350 Ry. In order to obtain optimized lattice vectors and atomic positions, the stress tolerance and maximum atomic force were taken less than 0.5 GPa and smaller than $0.01 \mathrm{eV\,Å^{-1}}$, respectively.

3. RESULTS AND DISCUSSION

3.1 Elastic Properties

The comprehensive elastic moduli of $LiSrH_3$ have been tabulated in Table 1 and 2 for the first time. To obtain elastic moduli of $LiSrH_3$, the elastic constants C_{ij} need to be calculated, the calculation details have been given in [9, 10]. A material's elastic tensor defines its response to an external stress. For a cubic crystal, there are three elastic constants are defined due to the symmetry, C_{11}, C_{12}, C_{44}. The well-known Born stability condition for this kind of materials is [11]:

$$(C_{11} - C_{12}) > 0,\ C_{11} > 0,\ C_{44} > 0,\ (C_{11} + 2C_{12}) > 0 \quad (1)$$

It can be deduced as;

$$C_{12} < B < C_{11} \quad (2)$$

Based on the equations 1&2, it seen that $LiSrH_3$ meets the stability criteria, thus $LiSrH_3$ can be categorized as a mechanically stable material. C_{11} describes material's resistance to linear compression along the x-axis. By comparing elastic constants, it is noticed that C_{11} is larger than other elastic constants, suggesting a harder compressibility along the x-axis. Also, it seen that the value of C_{11} is higher than that of C_{44}. This suggests that $LiSrH_3$ will show greater resistance to unidirectional compression than shear deformation compression [12].

Cauchy pressure (C_p), Pugh's ratio (B/G), and Poisson's ratio are an indication of material's failure such as ductility/brittleness. Thus, these parameters are also computed. Cauchy pressure tells us about the nature of the materials. Ductile materials can be distorted easily whereas brittle materials can easily change their volumes. It is known that the negative Cauchy pressure implies brittle nature and the positive one implies ductile nature [13]. As Table 1 displays that Cauchy pressure of $LiSrH_3$ has a negative Cauchy pressure of -9.78 and indicates a brittle nature. This can be an obstacle when handling the material in portable applications. Another index that illustrates the nature of the material is that Pugh's ratio. Ductile materials take apart from brittle ones by the ratio of 1.75. The value higher than that indicates ductility and lower value indicates brittleness [14]. In addition to these parameters, Poisson's ratio, $\sigma \sim 0.26$ defines a border line. Lower than this line will be classified as brittle and higher values will be classified as ductile [15]. The obtained Cauchy pressure is negative, the ratio of B/G is lower than 1.75 and Poisson's ratio is around 0.26, thus it can be concluded that $LiSrH_3$ is brittle in nature. This property will not be an issue in stationary applications whereas it can create an obstacle when it is decided to be used in portable applications. Therefore, it will require a great attention when handling it.

Additionally, bonding characteristics within $LiSrH_3$ is assessed using Poisson's ratio. Generally, if the Poisson's ratio is close to 0.1, the solid shows covalent bonding characteristics, if it is close to 0.25, it displays ionic bonding properties [16]. By examining the Poisson's ratio of $LiSrH_3$, it may be anticipated that covalent bonding is dominant for $LiSrH_3$.

Table 1 The calculated lattice constants (*a, Å*), Bulk modulus (*B, GPa*), elastic constants (C_{11}, C_{12}, C_{44}, GPa) and Cauchy Pressure (C_P) of $LiSrH_3$.

Material	a	B	C_{11}	C_{12}	C_{44}	C_{12}-C_{44}
$LiSrH_3$	4.63	7.87	22.55	0.53	10.31	-9.78
Raza et al.[17]	4.58		-	-	-	-

Table 2 The calculated Bulk modulus (B), Shear modulus (G), B/G ratios, Poisson's ratios (σ) and Young's modulus (E) of $LiSrH_3$.

Material	B	G	B/G	σ	E
$LiSrH_3$	7.87	10.59	0.74	0.036	21.93

Bulk modulus, B, is utilised to assess resistance against fracture whereas shear modulus, G, is utilised to assess resistance against plastic deformation. Bulk modulus represents a degree of resistivity towards volume change which is executed by an applied pressure. This can provide substantial information about average bound strength because of having a strong correlation

with cohesive and binding energies of material`s atoms [18, 19]. Higher bulk modulus means higher resistivity against volume change [20]. Also, higher C_{44} value results in higher shear modulus [21]. Moreover, shear modulus is much related to hardness than bulk modulus. Based on the Table 2, it can be predicted that $LiSrH_3$ has a slight hardness and will show resistivity towards volume change. Young modulus, E, reflects the stiffness of materials. Higher Young modulus represents better stiffness of materials [22]. Young modulus of $LiSrH_3$ is 21.93 GPa thus it can be predicted that $LiSrH_3$ shows some stiffness.

3.2 Electronic Properties

The electronic band structure of $LiSrH_3$ along the high symmetry directions in the Brillouin zone using the generalized gradient approximation (GGA) is demonstrated in Figure 1. The Fermi energy level is set to 0 V by extracting Fermi energy value from electronic band energies and displayed as dot lines in Figure 1.

As can be noticed from Figure 1 that a gap exists between the valence and conduction band with the value of 3.65 eV. Thus, it can be concluded that $LiSrH_3$ is a non-metallic material.

In order to assess the electronic features of $LiSrH_3$, total and partial density of states (DOS) is plotted in Figure 2. From total and partial densities of the states, it is noticed that the main contribution to valence band comes from H-1s states.

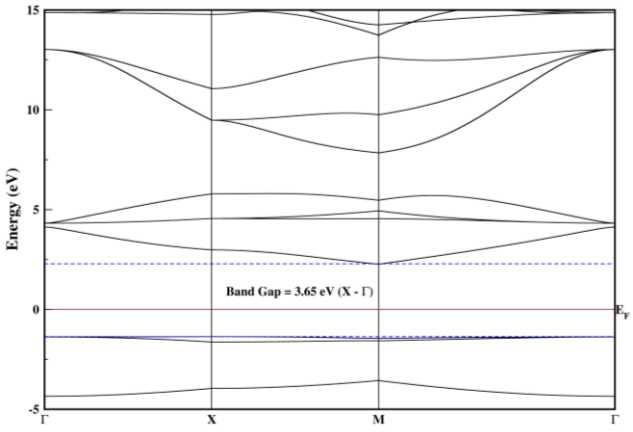

Figure 1 Electronic band structure of $LiSrH_3$.

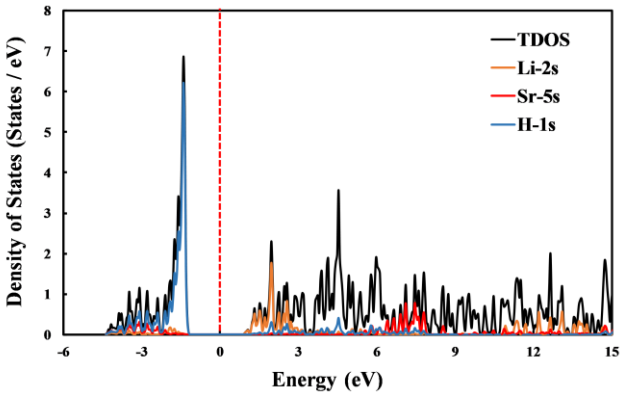

Figure 2 The total and partial density of states of $LiSrH_3$.

3.3 Hydrogen Storage Properties

The gravimetric hydrogen density (GHD) is a critical index for storing hydrogen in a solid host material. The GHD of $LiSrH_3$ is collected using the equation below [16]:

$$C_{wt\%} = \left(\frac{(H/M)M_H}{M_{Host}+(H/M)M_H} \; x \; 100 \right) \% \qquad (3)$$

M_H and M_{host} describes molar mass of the materials and H and M describes the number of atoms of the element. The GHD value of $LiSrH_3$ is obtained as 3.97 wt.% which is in the range of the targeted value by the US Energy Department (4 wt.%). Another critical parameter that needs to be examined that the temperature at which hydrogen can be desorbed from the host material. That is called hydrogen desorption temperature. This temperature is computed as follows [16];

$$\Delta H = T_d \times \Delta S \qquad (4)$$

Where T_d is hydrogen desorption temperature and ΔS is hydrogen entropy change which is 130.7 J/mol. K [23, 24]. Based on this calculation, T_d is found to be as 90 K.

4. CONCLUSION

This research has assessed elastic, electronic and hydrogen storage features of $LiSrH_3$. Several elastic parameters are computed using elastic constants to assess its mechanical stability.

Evaluation of Cauchy pressure, Pugh's ratio and Poisson's ratio demonstrates that $LiSrH_3$ is a brittle material. Ductility and brittleness of the host material is another important parameter that needs to be taken into account when carrying the material. If the material is brittle, it will be difficult to use it in portable devices. Based on our calculations and evaluations, it is found that $LiSrH_3$ is a brittle material and not suitable for portable applications. It might be better to use this material in stationary applications. In addition, the electronic band structures of $LiSrH_3$ displays that this material is non-metallic due to a band gap between valence and conduction band. The hydrogen gravimetric density of $LiSrH_3$ is found to be 3.97 wt.% which is very close to the target value 4 wt.%. Finally,, the hydrogen desorption temperature has been calculated and found to be 90 K.

The Declaration of Conflict of Interest/ Common Interest

We declare no conflict or common interest.

Authors' Contribution

Both authors carried out equal work on this study.

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