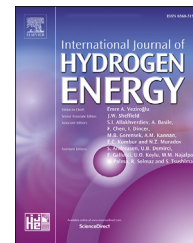




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Theoretical investigations of elastic and thermodynamic properties of LiXH_4 compounds for hydrogen storage

Selgin Al*

Department of Physics, Faculty of Arts and Sciences, Ahi Evran University, Kırşehir, Turkey

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ABSTRACT

The clean and environmentally friendly energy demand increases rapidly over the years. Hydrogen has been recognised as one of the best options to satisfy this demand. Utilisation of hydrogen as an energy carrier requires a number of steps especially for on-board applications, namely, production, transportation and storage. Storage of hydrogen brings a great challenge for the researchers among others. Current technologies include high-pressure compression, liquefaction and solid state storage of hydrogen. Solid state storage of hydrogen seems to be more applicable due to being much safer and denser. Metal hydrides are accepted as good candidates for solid state storage of hydrogen. In this regard, this study focuses on revealing dynamical and mechanical properties of new hydrogen reservoirs with high gravimetric hydrogen density, Li-X-H ($X = \text{C, N}$) using first principle calculations. First principle calculations have been proven to be a great tool to reveal extensive physical and chemical properties of the materials as well as mechanical and dynamical stability without synthesising them. Thus, this study adopts this tool to compute several physical and thermodynamic properties of Li-X-H such as bulk modulus, Young Modules, Shear Modulus, elastic constants, Poisson's ratio, Debye Temperature and so on for the first time. Based on the mechanical stability evaluation of compounds using elastic constants, both compounds are found to be mechanically stable. In addition, according to Pugh's criteria, the compounds have ductile nature. The computation of anisotropy revealed that the compounds are anisotropic at all planes. Also, the specific heat capacities of compounds seem to reach to Dulong-Petit limit at high temperatures.

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Introduction

The world's increasing demand for energy, depletion of fossil fuels and environmental concerns have raised the critical need for searching clean and sustainable energy sources.

Various alternatives are under investigation such as renewable energy sources (wind, solar, tidal, geothermal), nuclear and hydrogen energy in order to produce clean and sustainable energy. Among these sources, hydrogen energy is the most promising technology since it does not bring problems such as nuclear waste, seasonal/locational sensitiveness and

* Corresponding author.

E-mail address: selgin.al@ahievran.edu.tr.<https://doi.org/10.1016/j.ijhydene.2018.11.156>

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noise etc. [1]. Also, hydrogen is highly abundant in nature and a non-toxic element. It is an energy carrier rather than a source and offers advantages in the sense that it burns cleanly and only produces water as a by-product. Owing to these advantages, hydrogen can be adopted as an energy carrier in domestic power plants, fuel cell vehicles and portable electronic devices [2]. However, in spite of listed advantages, hydrogen technology needs to overcome several technical challenges in production, transport and storage of it. Especially, hydrogen storage is a major issue and requires extensive research and development.

The energy density of hydrogen is high by weight (3 times higher than gasoline), however, it is low by volume (4 times lower than gasoline) compared to hydrocarbon fuels [3]. Currently, hydrogen is stored either in compressed tanks in gas form or cryogenic tanks in liquid form on-board applications. Compressed gas tanks raise safety and volumetric issues whilst cryogenic storage requires large amount of energy due to the fact that hydrogen needs to be liquefied which requires ~35% energy content of hydrogen, large liquefaction plants and complex distribution systems [4]. In addition, the saturation temperature of hydrogen is ~20 K that requires usage of special tanks with special insulations to prevent hydrogen from boil-off which is very expensive. Thus, it is ineffective to store hydrogen as gas or liquid. Research has been devoted to explore materials and methods that can allow one to store hydrogen in high gravimetric and volumetric densities with appropriate kinetics and thermodynamics. Recent investigations include solid state storage of hydrogen such as metal or complex hydrides and metal organic frameworks due to being safer and more convenient way compared to compression and liquefaction [5–7]. Metal hydrides have been investigated due to their high adsorption and desorption of hydrogen capacity at different temperatures and pressures [8]. The gravimetric hydrogen storage capacity is set to 4.5% to be applicable by US Department of Energy [1]. This aim can be achieved with lightweight materials having an atomic number up to 20 [9]. Lithium and sodium complex hydrides were studied owing to being lightweight materials to achieve this goal. Sodium alanates showed ~5.6 wt% hydrogen storage capacity, however, these materials have slow kinetics [10,11]. On the other side, lithium alanates exhibited a storage capacity of 10.6 wt%. Unfortunately, these materials are thermodynamically unstable [12]. In addition, borohydrides such as LiBH_4 , NaBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ have been studied extensively by the scientists owing to their high gravimetric and volumetric density [13]. These materials also suffer from thermodynamic instability and formation of unwanted by-products such as diborane. Apart from metal, alkali and alkaline borohydrides, rare earth (RE) borohydrides has been taking a great deal of attention by the researchers lately [14–19]. Humphries et al. [16] prepared $\text{Eu}(\text{BH}_4)_2$ and $\text{Sm}(\text{BH}_4)_2$ and measured hydrogenation capacity of the compounds. $\text{Eu}(\text{BH}_4)_2$ showed up to ~3.5 wt% is reversibly absorbed over three cycles. Erbium borohydride ($\text{Er}(\text{BH}_4)_3$) composite mixture with LiBH_4 and/or LiH were prepared by Heere et al. [19] and desorption-absorption cycle was carried out. The composite desorbed considerable H, however every cycle the desorption rate decreased. Over the last three decades, magnesium-based alloys have been also considered seriously

due to the fact that Mg is cheap, lightweight, abundant and favourable for hydrogenation [20–22]. An electrochemical investigation has been carried out with MgTiX ($X = \text{Ni}$ and Si) by Thirugnasambandam et al. [23] and found Ni is favourable to increase hydrogen storage capacity of this alloy, although dehydrogenation of these alloys remain low. Unfortunately, Mg-based alloys show poor thermodynamic and kinetic properties since a strong bonding establishes between Mg and hydrogen [24]. Recent studies tend to focus on perovskite hydrides for hydrogen storage [25,26]. First principle calculations were adopted by Li et al. [26] to investigate hydrogen storage properties of KMMgH_3 ($M = \text{Li}, \text{Na}, \text{Rb}$ and Cs) with different doping levels to K-sites. Even tough, solid state storage of hydrogen seems to be the best option among other hydrogen storage methods, current materials have disadvantages that can prevent them from being viable for on-board applications. In this sense, further investigations for new materials and improvements for the current materials are essential since there is no material meets the goal that is set by US Department of Energy yet. First principle calculations have been proven to reveal materials' properties accurately with less cost and time, even the materials have not been synthesised. Computational calculations can help to reveal material's crystal structure, elastic, thermodynamic properties, stable phases and so on [27]. From this point of view, the formation energies of series of new compounds including hypothetical LiCH_4 and LiNH_4 compounds with high gravimetric hydrogen density (~17.54 and ~16.14, respectively) were studied by Blanca et al. [28] using ab initio calculations. Their results presented possible combinations of compounds which can be good potential candidates for hydrogen storage materials, however, that requires further theoretical and experimental investigations to reveal their full properties to be utilised as hydrogen reservoir. This study adopts first principle calculations in order to investigate and evaluate the lattice dynamic and thermodynamic properties of LiCH_4 and LiNH_4 compounds for hydrogen storage. Moreover, important physical parameters such as bulk, shear and Young Modulus, specific heat capacity and Debye Temperature have been presented which no theoretical predictions of these values have been found in literature.

Method

The calculations in this paper have been done using an ab initio density functional theory (DFT) [29,30]. The computations in order to obtain minimum energy, equilibrium volumes and structural properties were carried out by using the Quantum-Espresso software package [31]. Perdew-Burke-Ernzerhof, generalised gradient approximation (PBE-GGA) was used for the exchange correlation potential [32]. The position of hydrogen atoms (u) in the hypothetical cubic compounds were determined through the equilibrium volumes. Brillouin zone integration was carried out using a $10 \times 10 \times 10$ k-point mesh. 60 Ry cut off kinetic energy was used to expand electronic wave functions in plane-wave basis whilst 600 Ry was set to for the electronic charge density. Methfessel-Paxton type smearing was applied for integration up to the Fermi surface with $\sigma = 0.02$ Ry smearing parameter [33] in

order to get a smooth density of states. The lattice dynamic calculations were done within the framework of the density functional perturbation theory (DFPT) [34,35].

Elastic constants of a material can give substantial information about its mechanical and dynamical properties [36]. More specifically, its stability and stiffness. There are three independent elastic constants (namely, C_{11} , C_{12} and C_{44}) for a cubic phase. The elastic constants are here obtained from energy difference between distorted and undistorted lattice cell. Once the single crystal elastic constants are calculated, the relevant polycrystalline properties such as Bulk modulus (B), Shear modulus (G), Young's modulus (E) can be obtained. Bulk modulus is defined as the resistance to volume change under applied pressure and given as;

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (1)$$

The shear modulus (G) (resistance of the material towards elastic deformation or resistance to shape change) is the ratio of shear stress to shear strain and given as follows [37];

$$G = \frac{G_V + G_R}{2} \quad (2)$$

where G_V is Voigt's shear modulus and G_R is Reuss's shear modulus. G_V and G_R corresponds to upper and lower bounds of G, respectively and are given as;

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (3)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \quad (4)$$

Young Modulus (E) which is an indication of stiffness of the material can be calculated from Bulk modulus and Shear modulus of the material as follows;

$$E = \frac{9BG}{3B + G} \quad (5)$$

The anisotropy factor (A) demonstrates the degree of anisotropy compared to an isotropic material which is given as;

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \quad (6)$$

As the value of A becomes closer to unity (1), the material becomes isotropic.

The Poisson's ratio (σ) is also relevant and provides information about bonding characteristics of the crystal and can be expressed as [38];

$$\sigma = \frac{1}{2} \left(1 - \frac{E}{3B} \right) \quad (7)$$

Thermodynamic calculations in order to obtain values such as Debye temperature, heat capacity are carried out using the quasi harmonic approximation using Gibbs2 code described in Ref. [39]. Helmholtz free energy is as follows;

$$U = nk_B T \left[\frac{9}{8} \frac{\theta_D}{T} + 3 \ln \left(1 - e^{-\frac{\theta_D}{T}} \right) - D \left(\frac{\theta_D}{T} \right) \right] \quad (8)$$

where, $D \left(\frac{\theta_D}{T} \right)$ function is given by;

$$D \left(\frac{\theta_D}{T} \right) = 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} dx \quad (9)$$

Results and discussion

Structural and elastic properties

The crystal structures of LiXH_4 compounds have been shown in Fig. 1 where a simple cubic system (P23, group number 195) is chosen. Li atoms sit at the origin (0,0,0) whilst X atoms are positioned at the center (1/2,1/2, 1/2) and the positions of H atoms are to be determined for different X. Energy-volume data is fitted to Murnaghan's equation of state [40] in order to obtain their equilibrium lattice constants (a) and bulk modulus (B). The calculated values of u-parameters, lattice constants, bulk modulus and elastic constants of LiXH_4 (X = C and N) are presented in Table 1. The positions of H at the most stable positions (u-parameters) are determined by energy minimisation for the compounds. The obtained u-parameters and lattice constants are presented in Table 1 along with literature values. The results obtained from our calculation is in a good accordance with Blanca et al. [28] that was calculated using a different code within density functional theory. Incompressibility of a compound is described by bulk modulus. In other words, it demonstrates the resistance of the material against volume change under applied pressure or the amount of energy that required to create a deformation. To the best of the author's knowledge, there is no data in literature for comparison, however, it can be said from Table 1 that LiNH_4 is less compressible compared to LiCH_4 and more energy is required to create a deformation.

The mechanical stability of a cubic crystal is determined by examining the three independent elastic constants by the following relations [41];

$$(C_{11} - C_{12}) > 0, C_{11} > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0 \quad (10)$$

The mechanical stability conditions also bring a restriction for bulk modulus B as follows;

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

These parameters can give a good insight of the stability and stiffness of the compounds. As can be seen from Table 1 that both compounds fulfil the stability conditions given in Eqs. (10) and (11). Thus, it can be said that both compounds are mechanically stable in this phase. The resistance to compression along the x-axis can also be predicted from the value of C_{11} [42]. The value of C_{11} for LiNH_4 is higher than that of LiCH_4 , showing that LiNH_4 is less compressible along the x-axis than LiCH_4 .

Shear modulus (G) is defined as the material's resistance to shape change. As can be understood from Table 2 that LiNH_4 has higher G values than that of LiCH_4 which is in accordance with the obtained B values. Further investigations are carried out on mechanical properties of LiXH_4 compounds by examining the ratio of bulk modulus to shear modulus (B/G). This ratio is an indication of the material's ductility or brittleness. According to Pugh [43] if B/G is higher than 1.75, the material is ductile otherwise it is brittle. Based on the data presented in

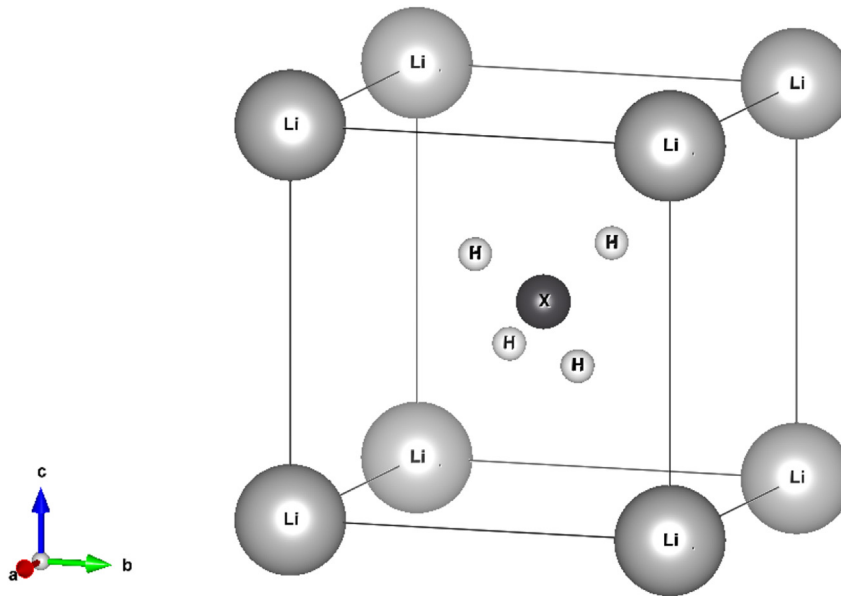


Fig. 1 – Crystal structures of cubic LiXH_4 ($X = \text{C}$ or N).

Table 1 – The calculated values of u -parameters, lattice constants, bulk modulus and elastic constants of LiXH_4 ($X = \text{C}$ and N).

Material	References	u (unit of a)	a (Å)	B (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
LiCH_4	This work	0.3663	4.7678	27.98	30.85	26.55	29.84
	Blanca [28]	0.3656					
LiNH_4	This work	0.3630	4.4556	37.69	46.28	33.40	37.09
	Blanca [28]	0.3625					

Table 2 – The calculated Bulk modulus (B), Shear modulus G (GPa), B/G ratio, anisotropy factor A , Young's modulus E (GPa) and Poisson's ratio of LiXH_4 ($X = \text{C}$ and N).

Material	B	G	G_v	G_R	B/G	σ	A	E
LiCH_4	27.98	11.80	18.76	4.84	2.37	0.31	13.89	31.05
LiNH_4	37.69	18.80	24.83	12.77	2.00	0.28	5.75	48.37

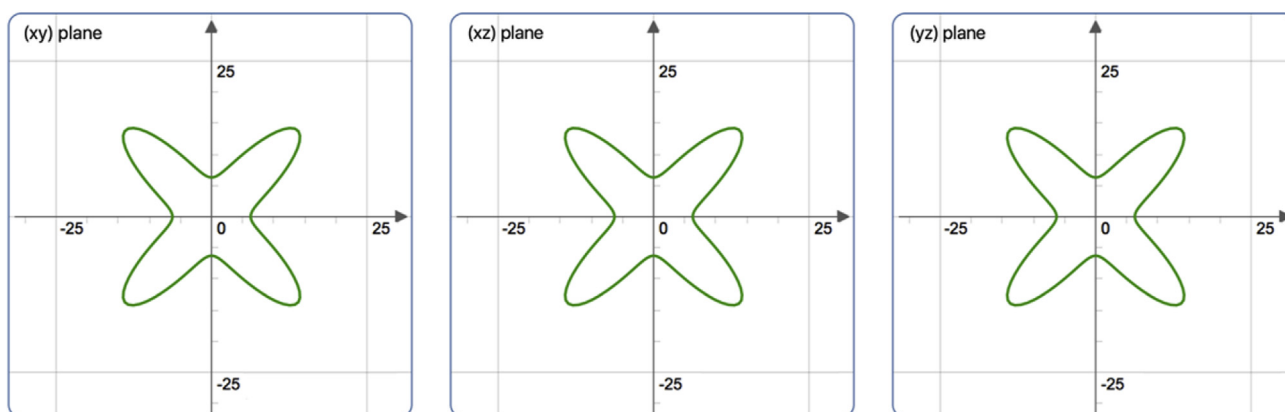
Table 2, both compounds are ductile in nature. In addition to listed properties, Poisson ratios of compounds are computed and examined. Poisson's ratio can be used to predict bonding properties of the material and measure the stability of crystal against shear. As the higher Poisson's ratio, the higher the material's plasticity. Also, Poisson's ratio is suggested as 0.1 for covalent materials and 0.25 for ionic materials in the literature [44]. The values of Poisson's ratio for two compounds are around 0.3 as shown in Table 2, indicating that ionic character is dominant in two compounds.

Young Modulus (E) is the ratio of tensile stress to tensile strain. It provides information about stiffness and tensile elasticity of the material. In other words, higher E means, stiffer material. Young Modulus of LiNH_4 is (48.37) higher than that of LiCH_4 (31.05), meaning that LiNH_4 is the stiffest compound.

The anisotropy factor (A) is an important parameter in terms of determining mechanical and physical properties of

material since it can give information about micro cracks, precipitation, anisotropic plastic deformation, elastic instability and internal friction [45,46]. Thus, these parameters are also computed as a measure of the degree of the elastic anisotropy of the compounds and given in Table 2. If the material is elastically isotropic, this value corresponds to 1. For other values that are greater or lower than 1, the material shows anisotropy. The computed anisotropic factors in this study are 13.89 and 5.75 for LiCH_4 and LiNH_4 , respectively. Since anisotropy factors of two compounds are higher than 1, both compounds are elastically anisotropic. Due to the fact that both compounds are anisotropic, 2D directional dependences of Young Modulus have been calculated using EIAM code [47] and presented in Fig. 2. For an isotropic material, the shape is spherical. Deviation from spherical shape illustrates the degree of anisotropy [48,49]. It can be seen from Fig. 2 that both compounds are anisotropic at all planes.

a)



b)

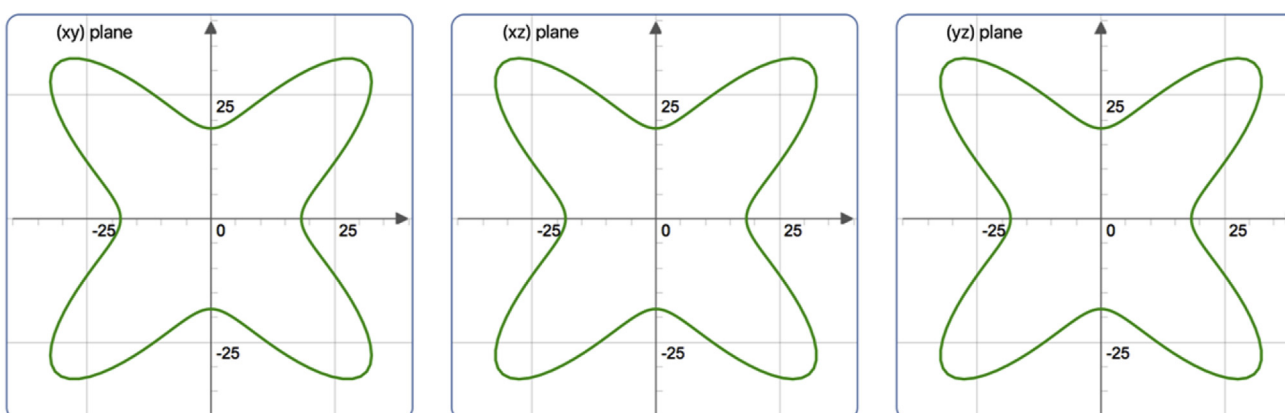


Fig. 2 – 2D directional dependence of Young Modulus of LiCH_4 (a) and LiNH_4 (b).

Thermodynamic properties

The thermodynamic properties of the compounds are obtained within the quasi-harmonic approximation for different temperatures from the energy-volume relation. Debye temperature is one of the important physical parameters of a material which provides information about various properties such as melting temperature, elastic stiffness and specific heat. Fig. 3 illustrates the change in Debye temperature versus temperature. It can be noticed from the figure that Debye temperature shows a slow decreasing trend over the temperature range of 0–1500 K for both compounds. This shows that thermal vibration frequencies of the particles alter with temperature. Moreover, vibrational frequency is proportional to square root of the stiffness within the harmonic approximation, the “stiffness” of materials can also be predicted from Debye temperature and called as ‘Debye stiffness’ [50]. From this point of view, it can be said that Debye stiffness of LiNH_4 is greater than that of LiCH_4 .

The vibrational contributions owing to temperature change to the specific heat capacities of both compounds at a constant volume (C_v) is predicted using ab-initio calculation with the quasi-harmonic approximation, too. The specific heat capacities of compounds versus temperature are given in

Fig. 4. A sharp increase is seen up to about 600 K and then a saturation is observed for both compounds which is called Dulong-Petit limit [51]. Up to 600 K, the specific heat capacities of compounds strongly depend on the temperature and it is

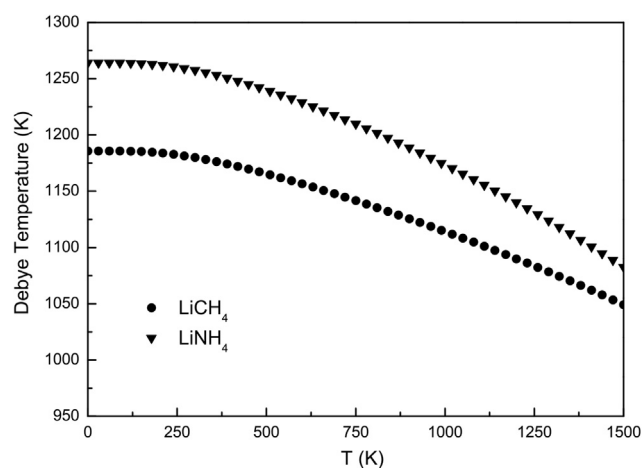


Fig. 3 – The temperature dependence of Debye Temperature for LiCH_4 and LiNH_4 .

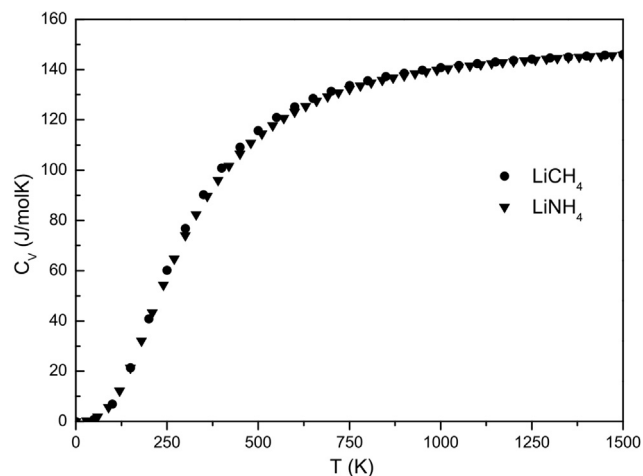


Fig. 4 – The temperature dependence of the specific heat capacities at constant volume (C_v) of LiCH_4 and LiNH_4 .

zero at 0 K. Unfortunately, there is no available data in literature for comparison to best of the author's knowledge.

The change in thermal expansion coefficients of compounds with the temperature is exhibited in Fig. 5. There is a rapid increase in thermal expansion coefficients of both compounds up to 500 K. After this point, a gradual increase is seen with temperature for both compounds. Grüneisen parameter is also computed from the quasi-harmonic approximation. It describes the anharmonic effects in the vibrating lattice and can be used to predict the anharmonic properties of a material.

Grüneisen parameters for both compounds are presented in Fig. 6. As can be easily noticed from the figure that Grüneisen parameters of compounds demonstrate little change with temperature. It is also worthwhile to notice that Grüneisen parameter is not zero at 0 K, suggesting that thermal expansion coefficient and heat capacity approaches zero in the same asymptotic way. Generally, Grüneisen parameter at 0 K is proportional to the logarithmic derivative of T^3 coefficient in the heat capacity with respect to volume [52].

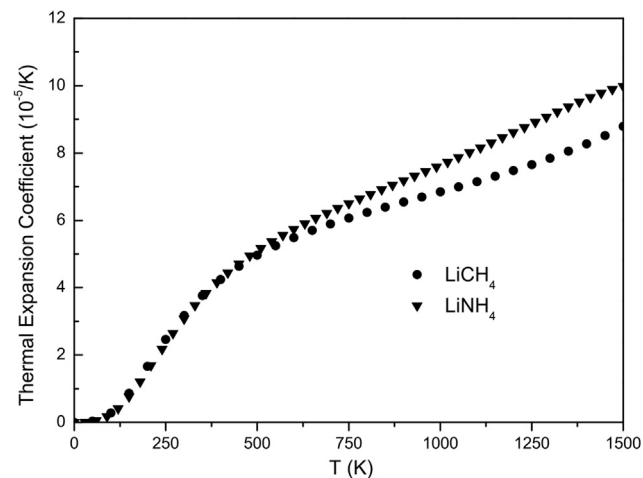


Fig. 5 – Variations of thermal expansion coefficient with temperature for LiCH_4 and LiNH_4 .

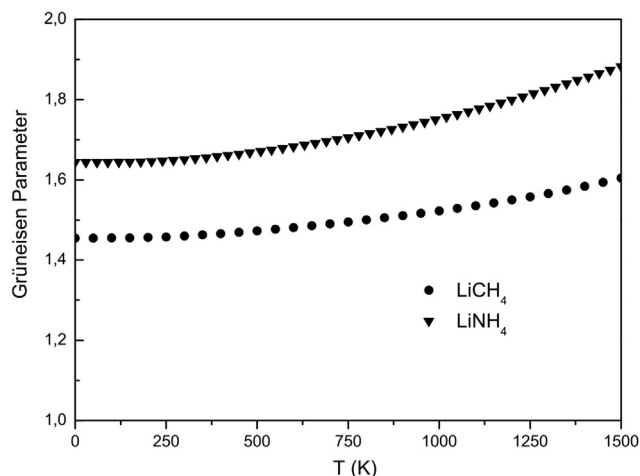


Fig. 6 – Grüneisen parameter change with temperature for LiCH_4 and LiNH_4 .

Conclusion

The main aim of this study is to determine unknown properties of possible compounds with high hydrogen storage capacity for hydrogen storage. Hydrogen storage is a critical step to overcome for practical applications. Therefore, materials with high hydrogen density, fast kinetics and reactivity, good reversibility and moderate thermodynamic and mechanical stabilities are required. In this sense, LiXH_4 ($X = \text{C}$ and N) are chosen which are believed to contribute hydrogen storage. The physical, mechanical and thermodynamic properties of compounds are obtained using first principle calculations. The mechanical stabilities of compounds are analysed via elastic constants. It is observed that both compounds fulfil the mechanical stability criteria. Ductility and brittleness of compounds are examined according to Pugh's criteria and found that both compounds show ductile behaviour. In addition to mechanical properties, thermodynamical properties of both compounds have also analysed. It is seen that specific heat capacities of the compounds reach to Dulong-Petit limit at high temperatures. Unfortunately, there is no available data in literature for comparison. As far as the author's knowledge this is the first thorough theoretical study on these compounds. Thus, it will be a good base work for future theoretical and experimental investigations and comparisons.

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