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Structural electronic and vibrational properties analysis of Li₂CaX (X = Sn, Pb) heusler alloys: a comparative study

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Abstract

This study was focused on structural, electronic and vibrational properties of Li₂CaSn and Li₂CaPb with density functional theory. All properties of these compounds were computed by implementing General Gradient Approximation and using Quantum Espresso software programme. As a result of the calculations, it was found that the lattice parameter is 6.967 Å and bulk modulus is 33.94 GPa for Li₂CaSn. Also, these values are 7.062 Å and 29.574 GPa for Li₂CaPb. The calculated lattice parameters are in good agreement with the available experimental data. There is no previous theoretical calculation for Li₂CaSn and Li₂CaPb compounds. It was calculated that Li₂CaSn and Li₂CaPb have a semi-metal property. The full phonon dispersion curves of Li₂CaSn and Li₂CaPb compounds in the Heusler type structure were examined using the linear response method. Under 0 kbar pressure, Li₂CaPb was unstable while Li₂CaSn was dynamically stable. Calculations showed that when 38.42 kbar pressure is applied to the Li₂CaPb compound, the Li₂CaPb compound becomes dynamically stable. It is believed that this study will shape future studies.

1. Introduction

Heusler type structures were discovered in 1903 by Friedrich Heusler with the addition of the 3rd group element to the CuMn alloy [1]. Heusler type compounds are intermetallic structures and agreed formula is ABC or A₂BC for Heusler type compound. Heusler type compounds contains translation metals (A and B elements) and an element of the III or V group (C element). The composition of Heusler type structures are as A₂BC, where the coordinates of the A atoms are (0.0, 0.0, 0.0) and (0.5, 0.5, 0.5) and the coordinate of the C atom is (0.75, 0.75, 0.75) [2, 3]. Calculations on the electronic band structures of these alloys have shown that these alloys are in semi-metallic ferromagnetic structure [4, 5]. The ability to change the ferromagnetic properties of the atoms that make up the alloy makes the difference between these alloys. Heusler type structures may have the ability to recover their former size and shape with sufficient heat treatment due to their magnetic shape memory effect. Thanks to this important feature, Heusler type alloys are used in many different fields in technology [6]. Hu [7] suggested that full Heusler and half Heusler alloys are ideal for spintronic applications and for Mn₃CoAl alloy. He et al [8] examined the thermal conductivity properties of X₂YZ (X = Ca, Sr, Ba, Y = Au, Hg, Z = Sn, Pb, As, Sb, Bi) alloys. Blum et al [9] reported the phase transitions of the Mn₂NiGa alloy, which is a shape memory material. Liu et al [10] explored the effect of martensitic transformation and shape memory in the Ferromagnetic Heusler alloy Ni₃FeGa. Killian and Victora [11] estimated the transmittance of minority spins in three high-symmetry directions for the Heusler alloy Ni₃MnIn and the semiconductor InAs. Bhattacharya et al [12] showed that the power factors of HfNiSn, ZrNiSn and TiNiSn alloys are higher than 4 W m⁻¹ K⁻¹. For this reason, it proved attractive for potential energy production. Xiao et al [13] investigated the structural and phase transition of Mn₃PtGa using the first principles by pressure effect.

Compounds containing light elements such as Li and Mg have been interesting materials due to their potential to store hydrogen [14]. Structures such as Li₂MgSi, Li₂MgGe, Li₂MgSn, Li₂MgP are known as...
Heusler-type structures and Li$_2$CaSn and Li$_2$CaPb compounds also exhibit a Heusler-type crystal structure [15]. In addition, LiCaN (ordered) [16], α-LiMgN (disordered) [17] and β-LiMgN (ordered) [17] have a Heusler-type crystal structure. Cardoso-Gill et al [18] examined some of the properties of KLi$_2$As. Herbst and Meyer [14] studied the hydrogen storage property of Li$_2$MgSi. Moringa et al [19] investigated the structural properties of the LixSiMg alloy by placing Lithium experimentally in Mg$_2$Si. In recent years, the properties of Li$_4$BN$_3$H$_{10}$ [20, 21], LiNH$_2$ + LiH [22] and LiBH$_4$ + MgH$_2$ [23] have been investigated. Guechi et al [24] computed the effect of pressure on phase transition, electronic and optical properties of LiBeX alloys. Erden Gulebaglan and Kilit Dogan [25] reported the structural, electronic and dynamic properties of Li$_3$Bi and Li$_2$NaBi. They calculated the pressure value that made the Li$_2$NaBi alloy dynamically stable.

The main purpose of this study is to investigate some properties of the experimentally studied Li$_2$CaSn and Li$_2$CaPb compounds and to examine the effect of pressure on the Li$_2$CaPb compound. That is, the novelty of this article is to investigate changes in some physical properties when Li$_2$CaSn is transformed from the Li$_2$CaPb compound by replacing an Sn atom with a Pb atom. In addition, the pressure value stabilizing the Li$_2$CaPb compound will be calculated. Firstly, structural and electronic properties of Li$_2$CaSn and Li$_2$CaPb compounds were investigated. Then, the vibration properties of both Li$_2$CaSn and Li$_2$CaPb compounds were calculated. These results are the first results obtained in the literature.

2. Computational method

Structural, electronic and vibration properties of Li$_2$CaSn and Li$_2$CaPb Heusler-type structure compounds in the ground state were investigated with the Quantum-Espresso [26] software program, which uses density functional theory. General Gradient Approach (GGA) [27] was used in all calculations. In the Perdew–Burke–Ernzerhof scheme [28], the Generalized Gradient Approximation was used. Electron–ion interactions and cut-off energy were determined by these ultrasoft pseudopotentials. From the calculated values, it was seen that the cut-off energy should be 100 Ry. Using the standard special k-point technique, Monkhorst and Pack [29], Brillouin zone investigations were carried out. During this research, k points were taken with $14 \times 14 \times 14$ Monkhorst-Pack grid. The selected plane wave cut-off energy and the number of k points are made to minimize the total energy. At all calculations, spin–orbit interactions were neglected. Because, the pseudopotentials used in calculations are scalar relativistic and there is no spin–orbit coupling. In order not to cause calculation errors, care was taken that the average error value of the energy was less than 1.0 $10^{-8}$ Ry.

3. Results and discussion

The space group of the Li$_2$CaSn and Li$_2$CaPb compounds is $Fm\bar{3}m$ (No: 225). These compounds include four face-centered cubic substrates. Figure 1 shows the prototype of these compounds.

First, in this study, structural and electronic properties of Li$_2$CaSn and Li$_2$CaPb compounds were calculated. Total energies of Li$_2$CaSn and Li$_2$CaPb were calculated as a function of volume using plane wave pseudopotentials. By changing the values of lattice parameters in a certain range, the total energy of the system was calculated with the self-consistent. Among these energies, the lattice parameter corresponding to the minimum energy is the optimum lattice parameter. The energy volume curve was fitted to the Vinet [30] equation (equations (1) and (2)) and the lattice parameters, bulk modulus, and pressure derivative of the bulk modules were computed. The Vinet equation is a state equation that gives relationships between
In Li$_2$CaSn compound, the bond lengths between Li-Ca and Ca-Sn are 3.0178 Å and 3.484 Å, respectively. These values are in good agreement with the experimental results. The values of lattice parameters $a_{Li2CaSn}$ and $a_{Li2CaPb}$ are 6.967 Å and 7.062 Å, respectively. There is a difference of 4.58% and 1.12% between lattice parameters calculated with experimental results for Li$_2$CaSn and Li$_2$CaPb, respectively. These differences can be tolerated. These values are given in table 1.

Pressure as a function of volume using the $P = -\frac{\partial E}{\partial V}$ equation;

$$E(V) = E_0 + \frac{2B_0 V_0}{(B'_0 - 1)^2} \left\{ 2 - \left[ 5 + \frac{V}{V_0} \right]^{1/3} (B'_0 - 1) - 3B'_0 \right\} \times \exp \left\{ -\frac{3}{2} (B'_0 - 1) \left[ \left( \frac{V}{V_0} \right)^{1/3} - 1 \right] \right\}$$

(1)

where, $B_0$ and $B'_0$ are bulk modulus and pressure derivative of the bulk modulus, respectively. $V_0$ is the volume in equilibrium.

Pressure as a function of volume using the $P = -\frac{\partial E}{\partial V}$ equation;

$$P(V) = 3B_0 \left( \frac{V}{V_0} \right)^{-2/3} \left\{ 1 - \left( \frac{V}{V_0} \right)^{1/3} \right\} \exp \left\{ -\frac{3}{2} (B'_0 - 1) \right\}$$

(2)

| compound     | $a$ (Å) | $B$ (GPa) | $B'_0$ |
|--------------|---------|-----------|--------|
| Li$_2$CaSn   | Present work | 6.967 | 33.94 | 4.136 |
| Li$_2$CaSn   | Exp. [8]     | 6.9352 |       |       |
| Li$_2$CaPb   | Present work | 7.062 | 29.574 | 4.231 |
| Li$_2$CaPb   | Exp. [8]     | 6.9835 |       |       |

There are no theoretical study to compare the lattice parameters, however, the calculated lattice parameters are in good agreement with the experimental results. The values of lattice parameters ($a_{Li2CaSn} = 6.967$ Å and $a_{Li2CaPb} = 7.062$ Å) are the lattice parameter values computed for the ground state of Li$_2$CaSn and Li$_2$CaPb compounds. There is a difference of 4.58% and 1.12% between lattice parameters calculated with experimental results for Li$_2$CaSn and Li$_2$CaPb, respectively. These differences can be tolerated. These values are given in table 1.

In Li$_2$CaSn compound, the bond lengths between Li-Ca and Ca-Sn are 3.0178 Å and 3.484 Å, respectively. In Li$_2$CaPb compound, the bond lengths between Li-Ca and Ca-Pb are 3.059 Å and 3.5323 Å, respectively. The angle between Li-Ca-Li in both compounds is 70.529°. Energy band diagram calculation is a non-self consistent account. For Li$_2$CaSn and Li$_2$CaPb alloys, the level of 0 eV is overlap with the Fermi energy level. The energy band gaps calculated for the Li$_2$CaSn and Li$_2$CaPb compounds are $-0.191$ eV and $-0.0278$ eV, respectively. Both crystals are semi-metallic in character. Computed electronic band structures are given in figures 2 and 3 for Li$_2$CaSn and Li$_2$CaPb compounds, respectively. Valence bands and conduction bands of both alloys have been intertwined. The maximum value of the Valence Band is at the X point of the Brillouin zone. The minimum Conductivity Band is at the $\Gamma$ point of the Brillouin zone. Therefore, the compounds Li$_2$CaSn and Li$_2$CaPb have an indirect band structure. As noted in the introduction section, Heusler structure alloys have 18 valence electrons, indicating that they are intermetallic and for these alloys can be adjusted by changing the chemical formula of the band gaps.

Along the $\Gamma \rightarrow X \rightarrow L \rightarrow \Gamma \rightarrow K \rightarrow W \rightarrow U$ high symmetry points, the phonon dispersion curves and phonon density of states of Li$_2$CaSn and Li$_2$CaPb compounds were investigated. There are four atoms in unit cells in both Li$_2$CaSn and Li$_2$CaPb compounds. In this case, there are twelve phonon modes. 3 of these are acoustic mode and 9 are optical mode. 2 of the acoustic modes are Transverse Acoustic (TA) modes and 1 of them is Longitudinal Acoustic (LA) mode. 6 of the optical modes are Transverse optical (TO) mode, and 3 are Longitudinal optical (LO) mode. If we look at figures 4 and 5, the phonon distribution curves and the phonon density of the states can be seen for the Li$_2$CaSn compound. The phonon frequencies of the Li$_2$CaSn compound range is between 0 cm$^{-1}$–485 cm$^{-1}$. The phonon frequencies of the Li$_2$CaSn compound are all positive. Briefly, this compound is dynamically stable because there is no imaginary (negative phonon frequency) phonon modes. This indicates dynamically stability. Looking at the phonon dispersion curve for the Li$_2$CaSn compound, we can say that there are two phonon bands. The frequency of Band1 is between 0 cm$^{-1}$–324 cm$^{-1}$ and the frequency of Band2 is between 367 cm$^{-1}$ and 485 cm$^{-1}$. There is a gap of approximately 43 cm$^{-1}$ between these bands. This comes from the mass difference between the different types of atoms in the unit cell. Acoustic modes are located between 0 and 172.22 cm$^{-1}$ in the phonon dispersion curves for Heusler type Li$_2$CaSn alloy. Transverse acoustic modes degenerate in the high symmetry point ranges between $\Gamma \rightarrow X$ and L $\rightarrow \Gamma$. In addition to this information, at the Gamma high symmetry point of Li$_2$CaSn compound degeneration is observed in modes 4. and 5., in modes 7., 8. and 9., in modes 10. and 11 (of optic modes).
If we look at figures 6 and 7, the phonon distribution curves and the phonon density of the states can be seen for the Li$_2$CaPb compound. The phonon frequencies of the Li$_2$CaPb compound range between $-48.99$ cm$^{-1}$–468 cm$^{-1}$. So, it is noticed that, phonon frequency values take negative values. This indicates that the Li$_2$CaPb compound is dynamically unstable. In short, this compound is not dynamically stable because some phonon frequencies are imaginary. The Li$_2$CaPb compound has two phonon bands, such as the Li$_2$CaSn compound. While frequency of Band1 has negative values, frequency of Band2 is between 348 cm$^{-1}$–468 cm$^{-1}$. Additionally, the lightest of the elements in both compounds are Lithium atoms. Therefore, Lithium atoms oscillate in the upper optical frequency region in the phonon spectrum.

Subsequently, when a proper pressure is applied to the Li$_2$CaPb compound, we expect that this compound may become dynamically stable. Because, the presence of negative values in the phonon distribution curve means that the crystal is not structurally complete. The fact that all the values in the phonon distribution curve are positive indicates that the forces on the atoms forming the crystal are zero Newtons. The crystal is in a stable and is formed structurally. As a result, it is calculated that it will be dynamically stable when 38.42 kbar pressure is applied by using Quantum Espresso software program. Reviews for the Li$_3$Bi and Li$_2$NaBi compounds have shown that dynamic stability can be achieved with the pressure applied to the Li$_3$NaBi compound [25]. This is a

Figure 2. The electronic band structure of Li$_2$CaSn compound.

Figure 3. The electronic band structure of Li$_2$CaPb compound.
similar result in the Li$_2$CaPb compound examined. The phonon dispersion curve and phonon state density at $P = 38.42$ kbar pressure are shown in figure 8 and 9, respectively. At this pressure value, all of the phonon frequency values are positive. Frequencies of Band1 and Band2 take values between $0 \text{ cm}^{-1}$–$319 \text{ cm}^{-1}$ and $419 \text{ cm}^{-1}$–$520 \text{ cm}^{-1}$, respectively. When 38.42 kbar pressure is applied to Li$_2$CaPb compound, degeneration is observed in phonon modes at Gamma high symmetry point as in Li$_2$CaSn compound.

Phonon dispersion curves (figures 4, 6 and 8) show that around X high symmetry point LA and TO modes degenerate. So, there is no gap between optical and acoustic modes for both La$_2$CaSn and La$_2$CaPb (dynamically stable and unstable forms) compounds. For La$_2$CaSn the maximum frequency value for acoustic mode (LA) is $172.22 \text{ cm}^{-1}$ and the minimum value of the optic mode (TO) is $151.27 \text{ cm}^{-1}$. For dynamically stable La$_2$CaPb compound the maximum value of LA is $195.15 \text{ cm}^{-1}$ and the minimum value of TO is $187.30 \text{ cm}^{-1}$. So it is seen that frequency of an optic mode is lower than an acoustic mode (LA) for both of the crystals. Phonons are also very important to understand the thermal conductivity of a material. The main contribution to thermal conductivity comes from the TA modes. But if the low-lying optic modes (TO) are has lower frequency values then TA modes, the low-lying optical phonon modes cause significant scattering of the transverse acoustic modes, leading to decrease the contribution of the TA modes to thermal conductivity and rendering the
transverse branches largely irrelevant in lattice thermal conductance [31]. So, low optical phonons play a role for thermal conductivity. From our graphs we can conclude this subject as, for La$_2$CaSn and La$_2$CaPb compounds, the TO modes cause scattering of acoustic modes, but in La$_2$CaSn the scattering of acoustic modes is more that La$_2$CaPb compound.

Unfortunately, experimental or theoretical phonon frequencies of Li$_2$CaSn and Li$_2$CaPb alloys are not available in literature for comparison.

4. Conclusion

In this work, the structural, electronic and vibrational properties of Li$_2$CaSn and Li$_2$CaPb compounds are calculated. The structural properties of Li$_2$CaSn and Li$_2$CaPb compounds were calculated by implementing General Gradient Approximation and using Quantum Espresso software programme. Then the electronic properties of both compounds were investigated and the band gaps of those compounds were obtained. Lattice parameters were calculated very close to experimental value for Li$_2$CaSn and Li$_2$SnPb. The energy band gaps calculated for the Li$_2$CaSn and Li$_2$CaPb compounds are $-0.1919$ eV and $-0.0278$ eV, respectively. It is seen that both of the crystals are in semi-metallic behaviour. Finally, the phonon dispersion curves and phonon density of
states were discussed. The Li$_2$CaSn compound was found to be dynamically stable, but the Li$_2$CaPb was found to be dynamically unstable in the ground state. When it was seen that Li$_2$CaPb was dynamically unstable for the ground state, it was motivated to find the pressure value at which this crystal was dynamically stable. In addition, it was found that Li$_2$CaPb stabilized dynamically under a pressure of 38.42 kbar. The results obtained are the first calculated values in the literature. This study can provide detailed information and reference for further experimental and theoretical studies.

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**Figure 8.** The phonon dispersion curve for Li$_2$CaPb compound (P = 38.42 kbar). 2 TA modes are represented with red and green lines, LA mode is represented with blue line.

**Figure 9.** The phonon density of states for Li$_2$CaPb compound (P = 38.42 kbar).
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