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Structural Electronic and Dynamic Properties of Li_3Pb

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Abstract

In this study, the structural, electronic and dynamic properties of Li_3Pb compound were examined by using Density Functional Theory within the Generalized Gradient Approximation. The lattice constant and the bulk modulus were calculated and compared with the experimental and theoretical results in the literature and the calculations were found to be consistent. The energy band and the total density of state diagrams of the Li_3Pb compound were generated and it was seen that Li_3Pb compound shows a metallic property. The values of the acoustic and the optical modes of the transverse and longitudinal branches at Γ, X, L, K, W and U high symmetry points were calculated and the phonon distribution curve was plotted against these high symmetry points. These calculations were not previously performed in the literature. It is thought that these calculations will shed light on the studies that will take place in the future.

Keywords: "Li_3Pb, Structural Properties, Dynamic Properties, Electronic Properties, Density Functional Theory"

1. Introduction

In recent years, there has been a focus on the development of nano-oxide materials as an anode material for lithium-ion batteries [1-4]. Lithium-based alloys are currently regarded as promising materials for use as negative electrode materials in Lithium-ion batteries [5]. Martos et al [6] noticed that, (electrochemically or chemically produced) lead (Pb) experiences on electrochemical reaction with lithium (Li) in the potential range 0-1 Volt forming the Li_xPb ($0.5<x<4.4$). Zalkin and Ramsey [7] studied the structural properties of Li_3Pb and Li_7Pb_2 compounds experimentally. Zalkin and Ramsey showed that Li_3Pb was FCC (Face Centered Cubic) and the lattice constant was 6.64 Å. Henry et al [8] reported that the coordinates of the atoms forming the Li_3Pb structure were Pb 0.0 0.0 0.0, Li (1) 0.25 0.25 0.25, Li (2) 0.5 0.5 0.5, Li (3) 0.75 0.75 0.75. Wood [9] examined Li diffusion coefficients for Li_xPb compounds and compared them with 4A group Si and Ge based compounds, using a melt synthesis technique in the study. Wang et al [10] suggested that the electrochemical reaction of PbO with Li was associated with Li_2O and six intermetallic compounds (LiPb, $Li_{2.5}Pb$, $Li_{3.33}Pb$, $Li_{3.5}Pb$ and Li_4Pb). Tericka et al [11] measured the integral mixture enthalpy of liquid Li-Pb alloys using the calorimetric technique. Zhou et al [12] calculated the thermodynamic properties and phase limits of the LiPb system with the first principle calculations. In this study, the structural, electronic and dynamic properties of the cubic Li_3Pb compound were investigated using the Density Functional Theory with Local Density Approximation. Below, in Section 2 we give computation details. Results and discussion and conclusions are given in Sections 3 and 4, respectively.

2. Computational Details

The structural, electronic and dynamic properties of the Li_3Pb compound were investigated using the Quantum Espresso package program. The Quantum Espresso [13] package program is based on the Density Functional Theory and the plane wave theory. In the Perdew-Burke-Ernzerhof (PBE) [14] scheme, the Generalized Gradient Approximation was used and the electron-ion interaction was defined by ultrasoft Vanderbilt pseodopotential. The electronic configurations used for the pseudo potentials were taken as Li ($2s^1$) and Pb ($4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$). It has been extended to the plane wave set with single particle wave functions with a cutoff energy of 70 Ry. The values of cutoff energies used in Li_3Pb are summarized in Table 1. The compound or a system becomes stable at the total energy (Etot) value. In optimizations in order to shorten the procedure with a minimum error, a value of energy should be chosen that is cut off (Ecut) energy. For a state (e.g. ground state) the total energy is fixed but one can chose

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different cut off energies. The bigger values of cut of energy extends the time of the procedure but minimizes errors. In other words, even if the cutoff energy changes, the total energy does not change, so the cutoff energy is 70 Ry. The total energy here is the ground state energy corresponding to the cutoff energy. As seen from Table 1, Li_3Pb compound becomes stable with the value of -9.02025, but one can chose cut off energy as 50, 70 or 80 Ry. Kinetic cutoff energy of 280 Ry is used for electronic density. For the calculations in the Brillouin Region, 14x14x14 k points clusters were selected. 0.02 Ry smearing parameter was used in the calculations. In the phonon distribution curve analysis, 4x4x4 q-points were used by using Monkhorst and Pack technique [15]. The dynamic properties of the Li_3Pb compound have been investigated from the self-consistent solutions of Khon-Sham equations [16].

Table 1. The total energies in the ground states for equilibrium of Li_3Pb with various cutoff energies.

E_{cut} (Ry)	10	30	50	70	80
E_{tot} (Ry)	-8.9868	-9.02023	-9.02025	-9.02025	-9.02025

3. Results and Discussion

In this study, firstly the structural properties of Li_3Pb binary intermetallic compound were investigated. Li_3Pb is in B1 phase and in cubic structure with Fm3m (225) space group [7]. The crystal structure and positions of atoms in a unit cell of Li_3Pb compound is shown in Figure 1. The compound Li_3Pb contains four atoms in its molecule and its unit cell composed of one molecule. The change in the total energy according to the volume was calculated by fitting the values to Birch Murnaghan equation. The Birch Murnaghan equation can be seen in Eq. (1). The Energy versus volume graph of Li_3Pb compound is plotted and displayed in Figure 2. After fit process we have obtained the lattice constant (a), bulk modulus (B_0) and bulk modulus pressure ($B_0^{'}$) of the Li_3Pb compound.

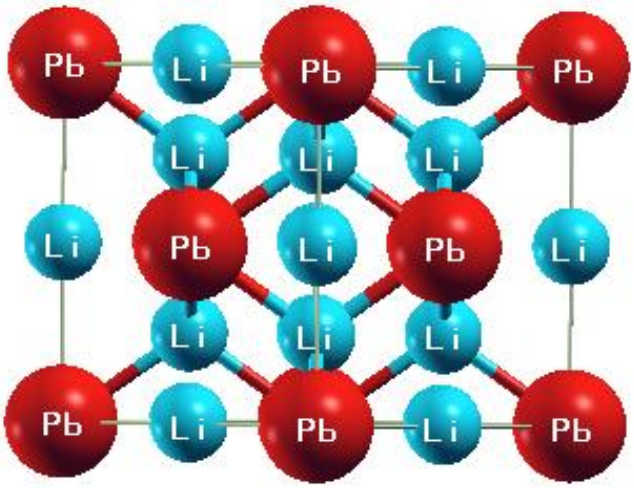

Figure 1. Crystal structure of Li_3Pb compound [16].

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left[(\frac{V_0}{V})-1\right]^3 B_0^{'} + \left[(\frac{V_0}{V})^{\frac{2}{3}}-1\right]^2\left[6-4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right] \quad (1)$$

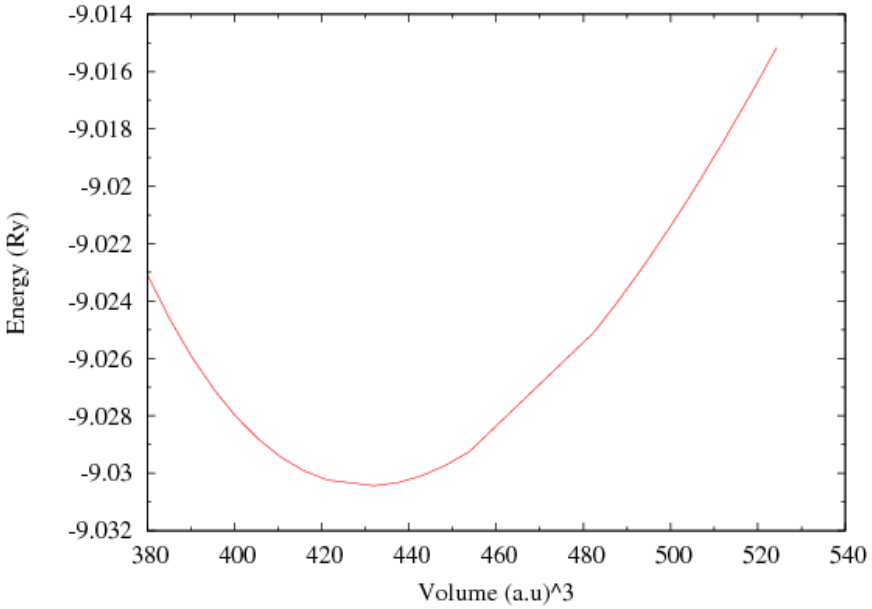

Figure 2. Energy volume of Li_3Pb compound.

E(V) is the total energy as a function of volume, E_0 and V_0 are the equilibrium energy and volume values, respectively. The lattice constant, bulk modulus and pressure derivative values of the bulk modulus are given in Table 2. The lattice constant and bulk modulus obtained from the calculations were compared with the theoretical and experimental results. It is seen that our results are in a good agreement with the literature. The pressure variant of the bulk modulus of Li_3Pb compound was calculated for the first time in this study.

Table 2. The calculated lattice constant (a), bulk modulus (B_0) and bulk modulus pressure ($B_0^{'}$).

	a (Å)	**B_0 (GPa)**	$B_0^{'}$
This work*	6.375	21.50	3.647
Ref [6]	6.697	25.50	
Ref [11]	6.687		

The electronic properties of Li_3Pb compounds were investigated by obtaining the electronic band structure and the total density of states graphs of Li_3Pb compound. The electronic band structure of the Li_3Pb compound was formed using the calculated lattice constants. The energy band diagram along the high symmetry points in the first Brillouin Region is shown in Figure 3. The result of total density of states is plotted for Li_3Pb compound in Figure 4. From both graphs it is seen that there is no forbidden energy band gap at Fermi level. That is, the valance and conduction bands coincide at the Fermi level. It can be said that Li_3Pb compound has a metalic property.

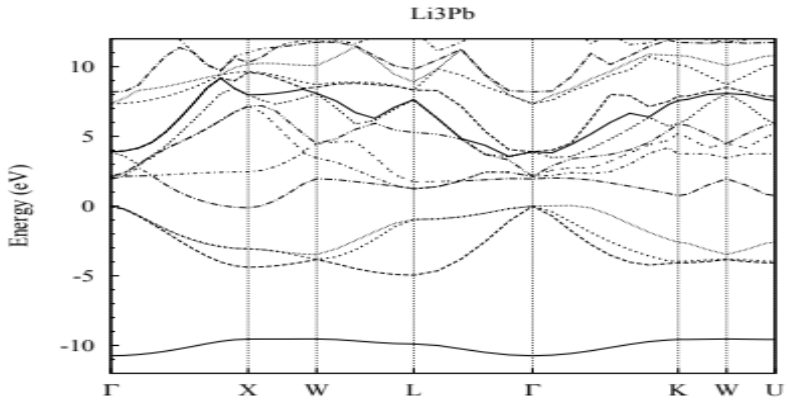

Figure 3. Band structure of Li_3Pb compound.

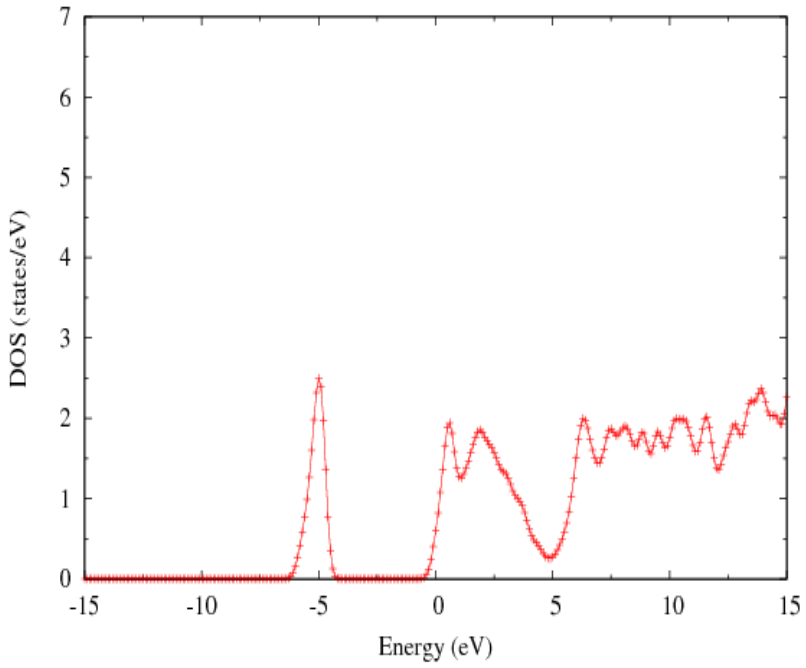

Figure 4. Total density of states of Li_3Pb compound.

Since there are four atoms in the unit cell of the Li_3Pb compound, there are twelve phonon branches. Three of the twelve phonon branches are acoustic and nine are optical branches. Figure 5 and Figure 6 show the phonon distribution curve and phonon density of states, respectively. All phonon branches of Li_3Pb compound have positive frequency values and from these graphs it is noticed that Li_3Pb have stable dynamic structure.

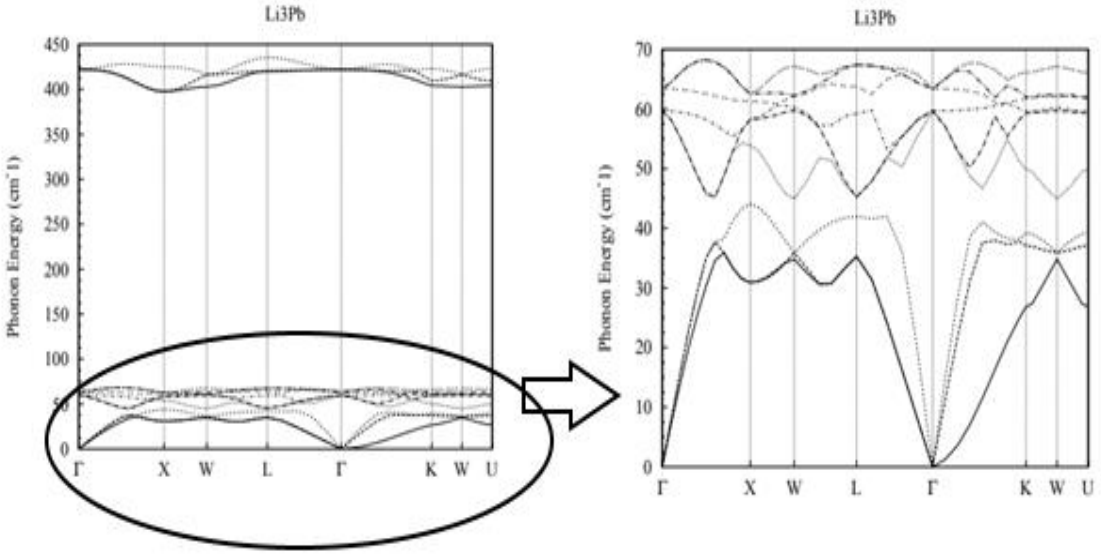

Figure 5. Phonon distribution curve and cross-section of Li_3Pb compound.

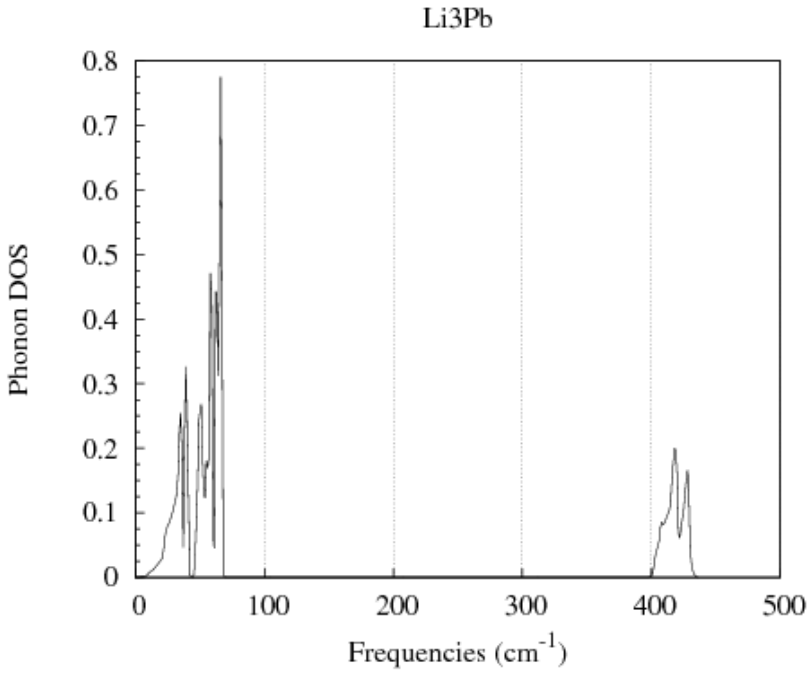

Figure 6. Calculated phonon DOS of Li_3Pb.

Since the mass ratio of the atoms forming the compound is as high as $(m_{Pb}/m_{Li}) = 29.86$, there is a large gap between the optical and acoustic modes. Degeneration is mostly in transverse optical and transverse acoustic modes. The frequency values of transverse and longitudinal acoustic and optical modes for high symmetry points such as Γ, X, L, K, W and U high symmetry points are given in cm^{-1} units.

Since there is no theoretical or experimental data to compare the values of the phonon distribution curve and phonon density of states values of Li_3Pb compound, the results which are found in this study could not have been compared but, these results are thought to be beneficial for future studies.

4. Conclusion

We have performed a first principles study in order to determine the structural, electronic and dynamic properties of Li_3Pb. First we have obtained the total energy values as a function of volume. Fitting the total energy values to the Birch Murnaghan equation, we have examined lattice parameter, bulk modulus and bulk modulus derivation. The electronic band structure and the density of states calculations show that the Li_3Pb is in metalic structure. The electronic band structure is in close agreement with experimental and theoretical results. Next, we have studied the dynamic properties of Li_3Pb and we have calculated the frequency values of transverse and longitudinal acustic and optic modes frequency values and we have also obtained phonon density of states structure of Li_3Pb crystal. From those phonon calculations, we have show that Li_3Pb has a stable dynamic structure. It is believed that this study will be useful for further investigations of researchers on Li_3Pb compound.

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