Structural electronic and dynamic properties of Li$_3$Bi and Li$_2$NaBi

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Abstract

We report a study of structural, electronic and dynamic properties of Li$_3$Bi and Li$_2$NaBi via density functional theory. It is found that Li$_3$Bi and Li$_2$NaBi show semiconducting property with an indirect electronic band gap. The calculated structural and electronic parameters (lattice parameters, bulk modulus, bulk modulus derivation) are in a good agreement with the available experimental data. Full phonon spectra of Li$_3$Bi and Li$_2$NaBi materials in the Rock Salt structure were collected using the linear response method. At 0 GPa pressure, Li$_3$Bi is dynamically stable while Li$_2$NaBi, which can be synthesized from Li$_3$Bi by replacing one Bi atom with Na atom, is unstable. In this study we searched to find the pressure value that makes Li$_2$NaBi dynamically stable. Calculations showed that the Li$_2$NaBi structure becomes stable when 8.62 GPa pressure is applied to the Li$_2$NaBi structure. This study is thought to give direction to the future studies.

1. Introduction

Lithium-based alloys are used as electrodes in lithium-ion batteries remarkably [1]. Rechargeable Li-ion batteries have an important place in the electronics field [2]. Li$_3$Bi, one of the lithium-based compounds, is of greatest interest as it is one of the best performers in lithium ion battery applications [3]. The Li$_3$Bi is a face centered cubic structure and space group is Fm$ar{3}$m (N. 225). There are four atoms in the primitive cell. Li$_2$NaSb and Li$_2$NaBi materials were synthesized by Leonava et al [4]. Temperature and pressure dependence of the phase transitions of Li$_2$NaSb and Li$_2$NaBi materials are examined [5]. Using the Boltzmann transport theory, Yang et al [6] studied the structural, electronic and thermal transport characteristics of Li$_2$Sb and Li$_2$Bi crystals. They showed that these materials have a narrow energy band gap. Zhou et al [1] demonstrated that the oxidized derivatives of Li$_3$Bi are potential composite materials. Klarasse et al [7] investigated the electronic and elastic properties of Li$_3$Sb, Li$_3$Bi, Li$_3$NaSb and Li$_3$NaBi materials using the General Gradient Approach and Local Density Approach within the Wien2k programme. Wang et al [8] synthesized Li$_3$Bi by using thin bismuth film as an anode. Sun [9] investigated the structural, elastic and electronic properties of Li$_3$Bi at pressure of up to 100 GPa. Wappner and Huggins [10] examined the chemical diffusion partial ionic conductivities and other kinetic parameters in Li$_3$Sb and Li$_3$Bi in the temperature range between 360°C and 600°C.

Our motivation is to investigate the alterations on some physical properties when Li$_2$NaBi is synthesized from Li$_3$Bi by changing one Li atom with Na atom and to see the effect of pressure on some physical properties. We searched the changes on structural, electronic and the dynamic properties. Since there are some results on the electronic properties of Li$_3$Bi and Li$_2$NaBi crystals, we used these results to compare our results in order to show how reliable results we have.

It is seen that for the 0 GPa pressure, Li$_2$NaBi is dynamically unstable. We investigated and found the pressure value, at which, this crystal becomes dynamically stable, (that is 8.62 GPa). This calculation and the dynamically stable phonon dispersion curve and phonon density of states graphs are the novelties of this study.

2. Computational details

The structural, electronic and dynamic properties of the Li$_3$Bi and synthesized Li$_2$NaBi crystals in the ground state were investigated by the Quantum-Espresso [11] package program based on the Density Functional Theory
Generalised gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) ultrasoft pseudopotentials were used for calculations. Electron-ion interactions were determined with ultrasoft pseudopotentials and cut-off energy is determined with these pseudopotentials. From the obtained results, the value of cut-off energy is determined as 80 Ryd. Cut-off energy value is used in the calculation of structural, electronic and dynamic properties. Number of k-points is computed using Monkhorst and Pack technique. Brillouin region studies are conducted. During this research, $12 \times 12 \times 12$ mesh was used.

The selected plane-wave cut-off energy and the number of k-points are used to ensure that the total energy is minimized. In addition, Li ($2s^1$), Na ($3s^1$) and Bi ($4f^{14}5d^{10}6s^26p^3$) orbitals are accepted as valence electrons.

During the calculations, spin–orbit interactions were not taken into account. For the accuracy of the calculations, the average error value of the energy is less than $1.0 \times 10^{-8}$ Ry. The DFT method has proven to be one of the most accurate methods for the computation of the electronic structure of solids.

### 3. Results and discussion

Firstly, the structural and electronic properties of Li$_3$Bi and Li$_2$NaBi compounds were investigated. The total energies of Li$_3$Bi and Li$_2$NaBi were calculated as a function of the volume using plane-wave pseudopotentials. The energy versus volume curve is fitted to the Vinet equation and lattice constants, bulk modulus and the pressure variant of the bulk modulus are calculated. The values of those given in table 2. All calculated values are in good agreement with the previous calculations (table 1). The lattice parameters calculated for the ground state of Li$_3$Bi and Li$_2$NaBi are $a_{\text{Li}_3\text{Bi}} = 6.052$ Å and $a_{\text{Li}_2\text{NaBi}} = 5.9856$ Å, respectively. For Li$_3$Bi, the calculated energy band gap is 0.37 eV and is consistent with other theoretical results. The band gap value of the Li$_2$NaBi compound is 0.44 eV, which is greater than the experimental values (table 2). The calculated electronic band structures are given in figures 1 and 2 for Li$_3$Bi and Li$_2$NaBi, respectively.

The dynamic properties such as phonon dispersion curves and phonon density of states for Li$_3$Bi and Li$_2$NaBi compounds are investigated along $\Gamma - X - W - L - \Gamma - K - W - U$ high symmetry points using Quantum-Espresso programme which depends on DFT within the Localized Density Approximation (LDA). In a system, there can be d(p−1) optical modes, where $p$ is the number of atoms in a unit cell and $d=3$ is the possible directions of vibrations. The plane where the vibration occurs is called in-plane and vibration which is perpendicular to this plane is called out-of-plane. So there are two in-plane vibrations (transverse modes) and one out-of-plane vibration (longitudinal mode) [23]. Since both Li$_3$Bi and Li$_2$NaBi crystals have 4 atoms per unit cell, 12 phonon modes appear. Three of them are acoustic and 9 of the are optic modes. For Li$_3$Bi and Li$_2$NaBi compounds 3 of the optic modes are Transverse Optic (TO) in-plane modes, 3 of the are TO out-of-

### Table 1. The calculated lattice constant ($a$), the bulk modulus ($B$) and the pressure variant of the bulk modulus ($B'$).

| Compound | $a$ (Å) | $B$ (GPa) | $B'$ |
|----------|--------|-----------|-----|
| Li$_3$Bi | 6.488  | 32.25     | 3.62|
|          | 6.652  | 30.27     | 4.14|
|          | 6.738  | 28.48     |     |
|          | 6.722  |           |     |
| Li$_2$NaBi | 6.824  | 27.75     | 3.80|
|          | 6.909  | 27.34     | 3.86|
|          | 7.016  | 25.36     |     |

* Present Work.

### Table 2. The comparison of the band gap values of Li$_3$Bi and Li$_2$NaBi with previous studies.

| Indirect Band Gap (eV) | Li$_3$Bi | Li$_2$NaBi |
|-----------------------|----------|------------|
|                       | 0.37$^a$ | 0.44$^a$   |
|                       | 0.34$^6$ |            |
|                       | 0.38$^7$ | 0.36$^7$   |
|                       | 0.45$^9$ |            |
|                       | 0.36$^{22}$ |          |
|                       | 0.35$^{22}$ |          |

* Present Work.
plane modes and 3 of them are Longitudinal Optic (LO) in-plane modes. Totally for both compounds there are 3 LO and 6 TO modes.

The phonon dispersion curves (figure 3) and phonon density of states (figure 4) for the Li$_3$Bi crystal are plotted with 0–500 cm$^{-1}$ frequency interval for the ground state (P = 0 GPa). From figure 3 it can be seen that 3 acoustic modes are located at 0 cm$^{-1}$ frequency value as expected. Between $\Gamma$ – X and L – $\Gamma$ high symmetry point intervals and close to L high symmetry point, transverse acoustic (TA) modes are degenerate. The third acoustic mode with higher frequency value is LO, which is not degenerated with any of acoustic and optic modes. There is a small gap between optical and acoustic modes around at 37 cm$^{-1}$ frequency value. But actually there are two bands of phonon modes, one of them composed of acoustic and some optic modes located between 0–73.1 cm$^{-1}$ frequency values, which can be called as band1 and the second band is composed of the rest of optic modes, located approximately between 330.6–457.9 cm$^{-1}$ frequency values and named by us as band2. These two bands are also can be seen from the density of phonon graph of Li$_3$Bi (figure 4). The values of TO and LO are between approximately 36.8–73.1 cm$^{-1}$ for band1. At band2 TO modes are degenerated and located at 332.5 cm$^{-1}$ and LO mode is located at 429.2 cm$^{-1}$. Also for optical modes in band1 and band2 again between $\Gamma$ – X and L – $\Gamma$ high symmetry point intervals and close to L high symmetry point, there are some
degenerate optic modes. When modes are degenerated then phonon dispersion curves become more symmetrical and when degeneracy dies out then symmetry is broken.

Since there is no modes with negative frequency values which reveals that Li₃Bi compound is dynamically stable. Then phonon dispersion curves (figure 5) and phonon density of states (figure 6) for the Li₂NaBi crystal are plotted with 0–450 cm⁻¹ frequency interval for the ground state (P = 0 GPa). One can see that from figure 5 that the two TA modes have negative frequency values. So it is noticed that Li₂NaBi crystal is not dynamically stable for the ground state. Li₂NaBi crystal has 3 phonon bands as shown in figures 5 and 6. Band1 is located between −22.6 and 56.9 cm⁻¹ interval, band2 is located between approximately 118.4 and 193.3 cm⁻¹ and band3 is between 327.4 and 421.7 cm⁻¹ frequency values. At all bands there are 2 TO and 1 LO individually, but at band1 there are also acoustic bands. As the same with Li₃Bi also for Li₂NaBi, between Γ – X and L – Γ high symmetry point intervals transverse acoustic (TA) modes and some TO modes are degenerated. Also for Li₂NaBi crystal there is no intersection between acoustic and optic modes. But different from Li₃Bi, for Li₂NaBi at 35.4 cm⁻¹ frequency value the two TO modes degenerated through all high symmetry points except for a small part between Γ – K interval.

After this stage, the pressure value at which Li₂NaBi is dynamically stable is searched. After a number of simulations and calculations, that pressure value is found as 8.62 GPa. The phonon dispersion curves (figure 7)
and phonon density of states (figure 8) for the Li$_2$NaBi crystal at $P = 8.62$ GPa are plotted again. From these graphs it is seen that the general structure of phonon dispersion curves and phonon density of states remained same, but only the frequency intervals of bands are changed. Frequency interval of band1 is between 0–70 cm$^{-1}$, band2 is between 158.1–242.5 cm$^{-1}$ and band3 is between 480.5–548.5 cm$^{-1}$ as seen from figures 7 and 8.

It is also known that the elastic constants and elastic properties can be obtained from the slopes of the acoustic phonon dispersion curves [24]. For the further study we want to investigate elastic properties using the phonon dispersion curves of these two compounds.

4. Conclusions

In this study, the structural, electronic and dynamic properties of Li$_3$Bi and Li$_2$NaBi crystals are investigated. Using LDA approximation within the Density Functional Theory using Quantum Espresso computer program the lattice parameters, Bulk modulus and pressure variant Bulk modulus values are calculated. Then the electronic band structures of both crystals are figured out and the band gaps of those crystals are obtained. It is seen that both of the crystals are in semiconductor behaviour with an indirect band gap. Last of all, the phonon dispersion curves and the phonon density of states graphs are obtained. It is realized that Li$_3$Bi is dynamically stable, but the synthesized Li$_2$NaBi is not dynamically stable in the ground state. Then it is found that Li$_2$NaBi

Figure 5. Phonon dispersion curves of the Li$_2$NaBi crystal for the ground state ($P = 0$ GPa).

Figure 6. Phonon density of states graph of the Li$_2$NaBi crystal for the ground state ($P = 0$ GPa).
becomes dynamically stable at a pressure value of 8.62 GPa. The results which can be compared with the literature are in a good agreement with the literature.

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