OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 9, September 2010, p. 1329 - 1331

The structural, mechanical and electronic properties of LiX_6(X=C,B): a first principle study

A. TATAR[*], S. AYDIN
[a]*Physics Department, Faculty of Arts and Sciences, Gazi University, 06500, Teknikokullar, Ankara, Turkey*

The structural, mechanical and electronic properties of LiX_6(X=C,B) compounds have been investigated by using first-principles techniques within density functional theory. Exchange-corelation effects were considered with the generalized gradient approximation (GGA). The single crystal elastic constants were calculated and then, the mechanical stability of LiX_6(X=C,B) compounds were studied. Applying hydrostatic pressure up to 30 GPa, behaviours of them were observed under pressure. The obtaining results were compared to available data.

(Received August 4, 2010; accepted September 15, 2010)

Keywords: LiX_6, First-principles, Mechanical stability, Hexaboride, Bulk modulus, Heat capacity

1. Introduction

Graphite intercalation compounds (GIC's) are formed through a process of electron exchange between the host layers and different types of atoms and molecules [1]. The so-called first-stage lithium intercalated graphite LiC_6 is one of the most thoroughly studied alkali-graphite compounds playing an important role in understanding the performance of carbonbased anodes in rechargeable Li-ion batteries [2]. Upon intercalation of Li ions into graphite, some fraction of the Li 2*s* valence electron density becomes delocalized on the carbon layers [1].

However, lithium graphite intercalated compounds have videly studied to development of rechargeable Li-ion batteries [3]. K. C. Woo et al. investigated phase diagram of these material family experimentally [4]. N. A. W. Holzwarth et al. calculated self-consistent electronic structure for different stages [5]. However, D. A. Morton-Blake et al. studied the migration of Lithium atoms in LiC_6 [6]. As seen from short review above, research of lithium intercalated compounds have considerably important in technologic applications.

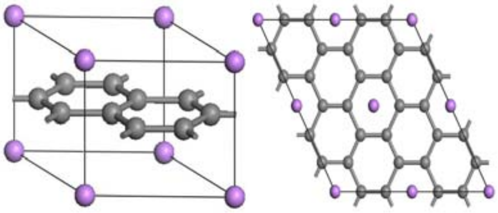


Fig. 1. (a) Unit cell and (b) 2×2 supercell of LiC_6.

In present work, first of all, geometry optimizations of LiX_6(X=C,B) compounds were done. Mechanical stability of them were investigated by means of Born stability criteria using single crystal elastic constants. However, electronic characters of these compounds were determined from calculated band structure and density of states (DOS) graphs. Furthermore, LiX_6(X=C,B) compounds were subjected to hydrostatic pressure up to 30 GPa by step of 5 GPa. So, deviation of volume, lattice parameters, namely, behaviours of these compounds under pressure were studied.

2. Calculation method

All calculations in present work are performed by using density functional theory method within the CASTEP [7] code. K-points of 12×12×12 generated by Monkhorst-Pack scheme were used.

The exchange-correlation functional was taken into account through generalized gradient approximation (GGA) [8] and Perdew Burke Ernzerhof functionals (PBE). The interactions between ions and electrons were described by using the Ultrasoft Vanderbilt pseudopotentials. To speed up convergence with respect to the ultra-fine setup of the code for BFGS minimization, kinetic energy cut-off for the plane wave basis set were chosen as 550 eV. The spin-polarized effects was not considered in the calculations.

3. Results and discussion

The calculated volumes and lattice parameters of LiX_6(X=C,B) compounds on studied pressure range are listed in Table 1 with available data. The calculated results agree well with theoretical and experimental data. For LiB_6, we cannot any comparison due to restricted reference in the literature. Thus, we hope that the presented results for LiB_6 by this work may be provided a helpful information to next experimental and theoretical studies. It is seen from Table 1, lattice parameters (a and c) and volume decrease as pressure increase for LiX_6(X=C,B) compounds. c/a axial ratio of LiC_6 is approximately two times higher than that of LiB_6. To analyse the calculated results easily, we plotted lattice parameters, volume and c/a ratio as a function of pressure in Fig. 2(a), (b), (c), (d) and (e). The a-axis of both compounds decreasing linearly as a function of pressure.

However, c-axis, volume and axial ratio of these compounds decrease obeying to an exponential function. Furthermore, c-axis is more compressible than a-axis for both compounds.

Table 1. The calculated volumes and lattice parameters under pressure for LiX_6*(X=C,B) compounds.*

LiC_6					LiB_6				
P (GPa)	a	c	V	c/a	P (GPa)	a	c	V	c/a
0	4.275	3.702	58.597	0.866	0	5.220	2.210	52.140	0.423
LDA [3] GGA[3]	4.282 4.279	3.690 3.711							
LDA[1] Exp.[1]	4.300 4.305	3.700 3.706							
5	4.257	3.482	54.659	0.818	5	5.193	2.144	50.063	0.413
10	4.242	3.338	52.010	0.787	10	5.164	2.102	48.547	0.407
15	4.228	3.225	49.930	0.763	15	5.138	2.066	47.229	0.402
20	4.215	3.131	48.178	0.743	20	5.113	2.034	46.056	0.398
25	4.204	3.055	46.757	0.727	25	5.089	2.008	45.041	0.395
30	4.192	2.993	45.551	0.714	30	5.065	1.986	44.128	0.392

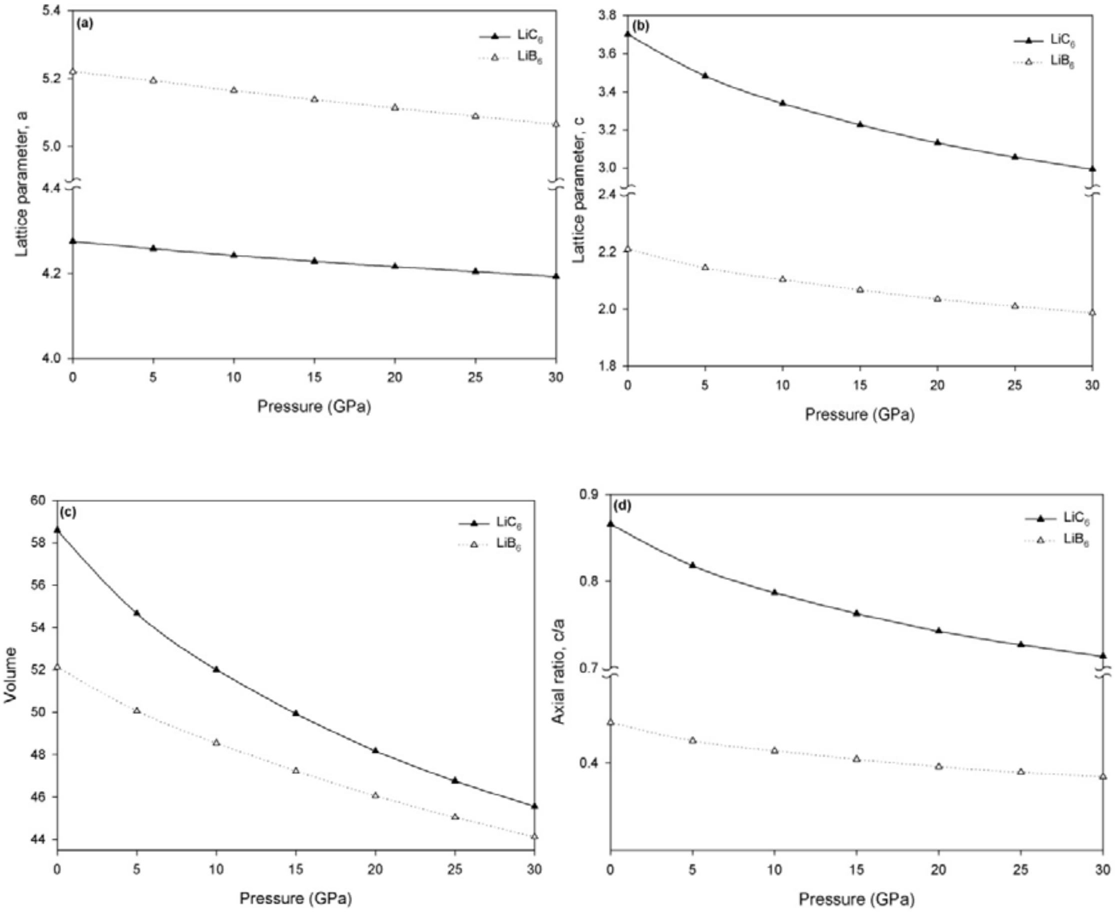
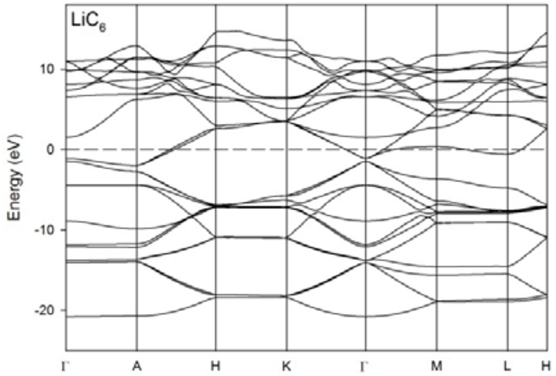
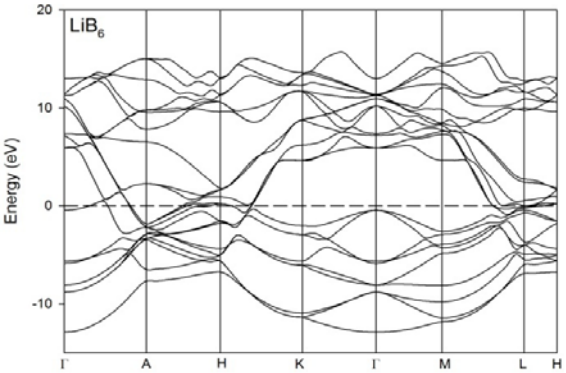


Fig. 2. Plotted lattice parameters, volume and c/a ratio as a function of pressure.

The calculated band structure and partial density of states of LiX_6(X=C,B) compounds are shown in Fig. 3(a), (b) and in Fig. 4(a), (b), respectively. It is seen that, both compounds are metallic. However, calculated density of states of these compounds support this electronic character. When partial density of states are investigated in detail, we conclude that total density of states originated from carbon atoms for LiC_6 and originated from boron atoms for LiB_6.

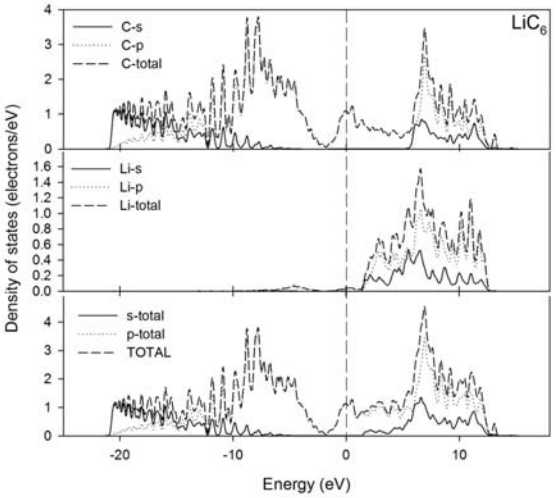


(a)

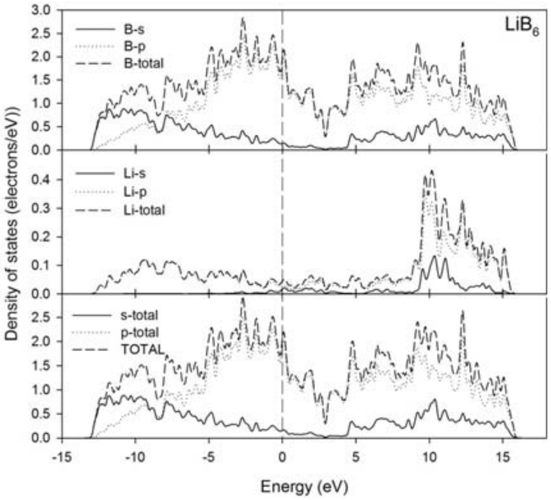


(b)

Fig. 3. Calculated band structure (a) of LiC_6 and (b) of LiB_6.



(a)



(b)

Fig. 4. Calculated partial density of states (a) of LiC_6 and (b) of LiB_6.

The single crystal elastic constants and bulk modulus are listed in Table 2. For mechanically stable hexagonal crystals, single crystal elastic constants satisfy Born stability criteria given as [9]:

$$c_{44} > 0,\ c_{11} > |c_{12}|,$$
$$(c_{11} + 2c_{12})c_{33} - 2c_{13}^2 > 0$$

While LiC_6 satisfies these criteria, LiB_6 don't satisfy. Namely, only LiC_6 is mechanically stable.

Table 2. Single crystal elastic constants and bulk modulus (in GPa) for LiX_6(X=C,B) compounds.

	LiC_6	LiB_6
C_{11}	951.56	385.09
C_{33}	70.94	114.41
C_{44}	16.80	-3913.75
C_{12}	143.21	154.24
C_{13}	-1.01	38.16
C_{66}	404.18	115.43
B	62.59	95.52

References

[1] K. R. Kganyago et al., Phys.Rev. B **68**, 205111 (2003).
[2] J. R. Darn et al., in Lithium Chemistry Library, edited by G.Pistoia, (Elsevier, Amsterdam, 1994), Vol. **5**, p. 1.
[3] Y. Imai et al., J. Alloys and Compounds **439**, 258 (2007).
[4] K. C. Woo et al., Phys. Rev. B **27**, 7831 (1983).
[5] N. A. W. Holzwarth et al., Phys. Rev. B **28**, 1013 (1983).
[6] D. A. Morton-Blake et al, Phys. Rev.B **37**, 4180 (1988).
[7] M. D. Segall, et al., J. Phys.: Cond. Matt., **14**, 2717 (2002).
[8] J. P. Perdew et al., Phys. Rev. B, **46**, 6671 (1992).
[9] Zhi-Jian Wu et al., Phys. Rev. B **76**, 054115 (2007).

---

*Corresponding author: aynur@gazi.edu.tr