



Electronic Structure Study of the LiBC₃ Borocarbide Graphene Material

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Received: 19 December 2019 / Accepted: 19 December 2019 / Published Online: 23 December 2019

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ABSTRACT

The electronic structure properties of the LiBC₃ alloy material, which attracts great interest in both lithium-ion batteries and a possibility to use in medical applications, have been studied by means of the theoretical approach with the commercial code FEFF 8.20 in absorption spectroscopy technique. The analysis results revealed that due to the quantum selection rules no strong coupling between neighboring atoms built in the crystal. Moreover, the lithium atoms were determined to weakly bonded to the BC₃ system and treated as an isolated ion with easily breakable bonded in a weak excitation process. Due to its rich Li-ion content, the material can be a strong candidate for the lithium-ion battery energy storage devices with possibly powerful intercalation properties. Also, the existence of both boron and carbon in the crystal structure with weakly bonded Li⁺ ions provides the material a medical potential in drug designs or medical applications that are related to chemical applications.

Keywords: Borocarbide · Drug Design · Absorption · Li-ion Battery

Introduction

Li-ion batteries and their vast field of applications in the current technology promote the studies on materials that contain lithium atoms. LiBC₃ alloy material has conspiring potential of use in current technology due to its content as lithium, boron, and carbon, which are the key elements of the high technological products. Actually, elemental content of the alloy has been in interest in both lithium-ion batteries, superconducting, and the possibility to use in the medical application of the materials [1]. However, as expected in the early times of the first studies for the superconducting

properties of the LiBC₃ alloy was disappointed in the recent studies that reported no superconducting properties were determined [2]. The inspiring side of this alloy for the Li-ion batteries is the richness of the lithium-ion in the molecule (%23.3), where the amount is %8.7 by weight in LiC₆ materials. The material was first studied by Way in 1994 via the material with the general formula of Li_x(B₂C_{1-z}), for the varying z values between 0.00 and 0.17 [3]. Although the first produced Li-B-C material was determined in hexagonal geometry with the *P63/mmc* space group, where the lattice parameters were

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reported as $a=2.7523 \text{ \AA}$ and $c=7.058 \text{ \AA}$, new crystal structures were also determined apart from the first prepared sample [1]. The crystal structure of the LiBC_3 alloy material was reported as hexagonal geometry with P-6m2 space group and the lattice parameters as; $a=2.5408 \text{ \AA}$ and $c=7.5989 \text{ \AA}$ [1]. The

2D views of the LiBC_3 alloy crystal structure are given in Fig. 1.a. and 1.b. [4].

In this study, the electronic structure properties of the lithium boron tricarbide LiBC_3 material, which is a new material and has not so much studied, was studied by the theoretical calculation approach by the commercial code FEFF 8.2.

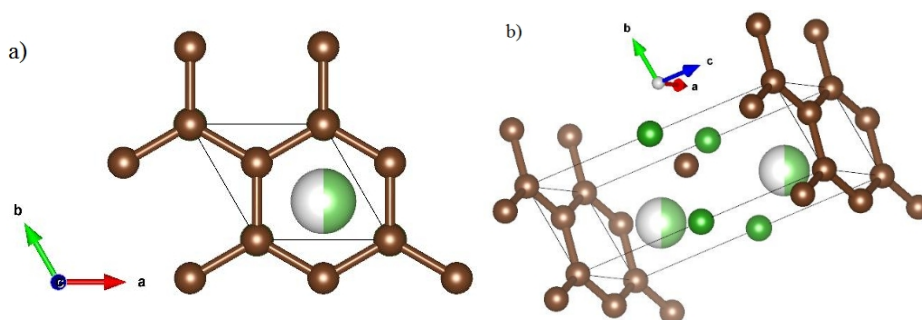


Fig. 1. 2D view of single LiBC_3 alloy a) From the z-axis b) From a different aspect.

Materials and Methods

The electronic structure properties of the LiBC_3 alloy is studied by the performed calculations on the Li, B, and C K-edges with FEFF 8.2 code, where Hedin-Lundqvist exchange correlation potential was used [5]. For the calculations, a FEFF input file was created by the TkATOMS of the IFFFIT package [6]. For the calculations, spherical clusters with 12 angstroms radii were created for the input data of the LiBC_3 alloy for every calculation step of Li, B, and C. The calculations were treated as the full multiple scattering for the LiBC_3 clusters containing 993 atoms (Li, B, C). The calculation was performed on the XAFS (X-ray Absorption Fine Structure) spectroscopy technique; a Li atom in the hexagonal crystal cluster was selected as the absorber and a photoelectron emitter, while two more calculations were also performed where a B atom and a C atom was selected as the absorber. Actually, 993 atoms for the cluster may be thin and the number is so less. However, to understand the background mechanism between their neighboring atoms, the calculations on the electronic properties in coordination with the bonding of the absorbing atom is enough. The

XANES (X-ray absorption near edge) part of the study in a XAFS spectra can provide us fruitful information on the electronic interplays between Li-B-C atoms. Moreover, the extended part (Extended XAFS; EXAFS) can yield crystallographic data via the backscattering and phase shifts with single and multiple scattering paths. The calculations were performed for the room temperature degrees.

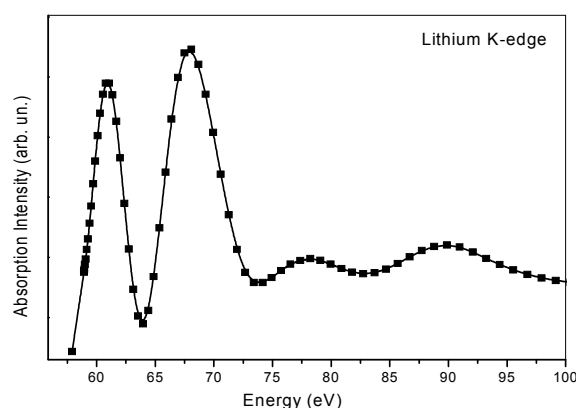


Fig. 2. Calculated Li K-edge XANES spectra of the LiBC_3 alloy.

Results and Discussion

The electronic structure study of the LiBC_3 alloy are were carried with the theoretical calculation of

the XAFS technique. For the analyses, Li, B, and C calculated absorption K-edge spectra were used. Calculated Li K-edge XANES spectra of the LiCB₃ alloy is given in Fig. 2. The ionic state of the Li⁺ has an electronic configuration with an empty 2s levels. The empty 2s level can easily overlap to build up a hybridized molecular band, because, when the neighboring atoms have close energy or in a close distance with each other, they can interact in resonance. In case of such an

interaction, a pre-edge peak structure should appear below the main edge. Lack of such a pre-edge structure on the Li K-edge spectra gives us clues about the LiBC₃ alloy and the weak interaction of the lithium atoms with its neighboring atoms that have unoccupied 2p levels. The peak structures (the sharp peaks) given in Fig. 2 are in good agreement with the results reported in the previous studies [7].

Table 1: Atomic distances from the source B atom in the LiBC₃ sample; R=R ± 0.01 Å

Crystal	Coordination	Radial Distance R(Å)	Degeneracy	Geometry	SG
LiBC ₃	B-C	1.47	3	Hexagonal	<i>P-6m2</i>
	B-Li	2.40	6		
	B-B	2.54	6		
	B-C	2.93	3		
	B-Li	3.50	6		
	B-C	3.80	2		
	B-C	3.88	6		
	B-C	4.07	6		
	B-Li	4.32	12		
	B-B	4.40	6		
	B-C	4.57	12		
	B-C	4.80	6		
	B-B	5.08	6		

The absorption spectra begin to rise at 57.5 eV and have two peaks at 60.95 eV and 67.86 eV, respectively. The smooth spectral feature of the data highlights weakly interacting Li atoms with the BC₃ system. To reveal the electronic interaction between carbon and boron, the XANES spectra of the C and B atoms in the LiBC₃ material are given in Fig. 3 and Fig. 4, respectively.

In Fig. 3, boron K-edge XANES spectra is given.

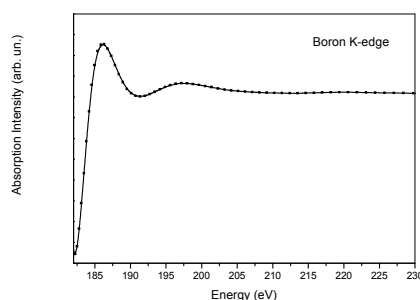


Fig. 3. Calculated B K-edge XANES spectra of the LiBC₃ alloy.

Boron K-edge is a result of the excited 1s electrons' transition to the unoccupied 2p levels. The pure spectral raise below the main edge also confirms no strong coupling between its neighboring atoms via their unoccupied states (p-level). The coupling between p-levels of the B-C systems is forbidden due to the quantum selection rules ($\Delta l = \pm 1$). The K-edge absorption spectra of boron being to rise at 182.2 eV and have a maximum at 186.1 eV.

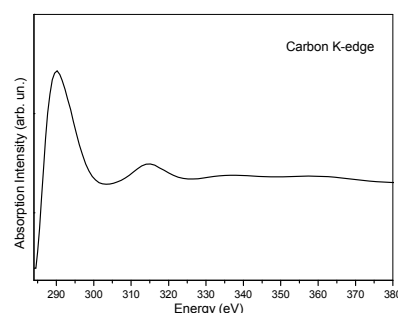


Fig. 4. Calculated C K-edge XANES spectra of the LiBC₃ alloy.

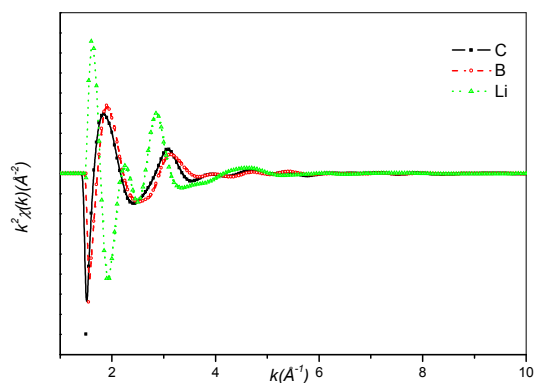


Fig. 5. Calculated EXAFS scattering data of the LiBC₃ alloy.

To have a view from the other side of the BC₃ system, carbon K-edge absorption spectra is given in Fig. 4. Like Li and B K-edges, carbon K-edge spectra also has a smooth pre-edge structure confirming the weakly interacting electronic states. Carbon K-edge is also a result of the 1s electrons' transition to the unoccupied 2p levels above the Fermi level. The spectra begin to rise at 284 eV and has a maximum at 290.2 eV.

The XAFS spectra, apart from the XANES spectra, contain the traces of the photoelectrons' scattering interactions as the fluctuations in the tail part, starting from the energy range of ~50 eV above the main edge and beyond. Thus, the data of the scattering interaction, known as the EXAFS part, can provide us the atomic coordinations, atomic distances to each other and the atomic types. The scattering intensity data, which is extracted from the XAFS spectra is given in Fig. 6. The scattering data is a result of the travel of the photoelectron moving among the atoms with high kinetic energy. To compare the atomic distributions in the vicinity of all atoms (B, C, Li), the scattering data for the same material (LiBC₃) are given in comparison.

In Fig. 5, scattering data aspect from the boron and carbon atoms have a high agreement and confirms the stable BC₃ structure. Besides, the scattering intensities have harmony that emphasizes the similar environment of the boron and carbon atoms. However, lithium atoms have asymmetry

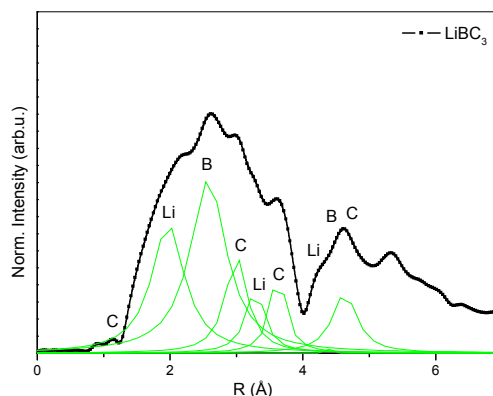


Fig. 6. Calculated atomic displacements from the source boron atoms in the LiBC₃ alloy.

among other atoms' scattering data due to varying chemical environment in the crystal. To reveal the atomic positions in the crystal structure and the distance from each other, Fourier Transform (FT) of the scattering data is given in Fig. 6.

The radial distribution function (RDF) is the known title of the determined distance of the atoms (i.e., FT) from the source atom that is sitting at the origin. The peak features given in Fig. 6 is related to the atoms sitting at the distance and found by the transform of the scattering intensity data from k-space to real space. According to the analyze results, given in Table 1, the closest atom to a boron atom is determined as the three carbon atoms sitting at a distance of 1.47 Å (± 0.01). Just behind the carbon atoms, six lithium atoms were determined to sit at the distance of 2.40 Å (± 0.01) from the boron atom, while six nearest boron atoms were determined to sit at the distance of 2.54 Å (± 0.01).

Conclusion

Within this study, the electronic structure of the LiBC₃ material with potential energy storage and also medical application properties has been studied by means of x-ray absorption spectroscopy calculations. The study was conducted by theoretical approach with the commercial code FEFF 8.20, which is based on real space multiple scattering in absorption spectroscopy technique. The study revealed that,

the lithium atoms are weakly bonded to the BC_3 system and in case of an external excitation, it can easily break its bonds with its neighboring B and C atoms. Besides, due to rich Li ion content, the material can be a strong candidate for the lithium ion battery energy storage devices. Moreover, the

boron and carbon existence in the crystal structure with weakly bonded Li^+ ions, the material can potentially be used for a medical applications of the drug designs or medical applications that are related to the chemical applications.

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How to cite this article: O.M. Ozkendi, S. Gunaydin, M. Mirzaei; Electronic Structure Study of the $LiBC_3$ Borocarbide Graphene Material. *Adv. J. Chem. B* 1 (2019) 37–41 doi: [10.33945/SAMI/AJCB.2019.1.7](https://doi.org/10.33945/SAMI/AJCB.2019.1.7)