First principles calculations to probe electronic response of lithium tetraborate

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Abstract: Electronic structure of thermoluminescent (TL) lithium tetraborate (Li2B4O7) using density functional theory is presented. We have computed the E-k relations and density of states (DOS) by applying ab-initio LCAO and FP-LAPW theories. The band gaps obtained using local density approximation (LDA) within LCAO and FP-LAPW approaches are found to be 6.48 and 5.84 eV, respectively at Γ point of BZ leading to its direct band gap character. Our LCAO based computations give close agreement with experimental value of 7.9 eV. The DOS curves validate the dominance of O-2p states in the top valence band with a minor role of B-2p electrons. The conduction band region consists of dominant contribution of B-2p states.

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1. Introduction
Thermoluminescence (TL) is emission of light by the process of thermal stimulation following the previously absorbed energy from x-rays or gamma-radiations [1]. Thermo-luminescence is produced by some specific materials (may be an insulator or a semiconductor) which persist some time absorbed energy during exposure to radiation. Thereafter, on heating the material the luminescence emission is set off.

Kerikmae et al. [2] have reported trapped-hole centre with a high thermal stability in Li2B4O7:Be and demonstrated a hyperfine splitting due to interaction of the trapped hole with a 9Be nucleus. TL response of lithium tetraborate due to varying concentration of the activators like Cu and B have been analysed by Ozdemir et al. [3]. They have observed that the dose response increases linearly with the β-ray exposure between 0.1 to 20 Gy. First-principles calculations within the density functional theory (DFT) have been undertaken to study the quantum-mechanical effects due to incorporation of the Cu ions at the Li sites in Li2B4O7 crystal by Santos et al. [4]. The luminescence properties of the Eu-doped and Eu-Ag co-doped with Li2B4O7 (Li2O–2B2O3 basic composition) have been studied and analysed by Kindrat et al. [5].
The present paper is devoted to computations of energy bands and density of states (DOS) of Li$_2$B$_4$O$_7$ using linear combination of atomic orbitals (LCAO) method with local density approximation (LDA) based exchange-correlation potential \[6,7\] and also full potential linearized augmented plane wave (FP-LAPW) method \[8,9\]. Electronic response of lithium tetraborate is analysed in the terms of energy bands and DOS.

2. Theoretical computations

2.1 LCAO method

CRYSTAL14 package (which embodies LCAO prescription) facilitates different exchange and correlation potentials within the DFT for computation of electronic response of materials \[6,7\]. We have employed LDA exchange and Perdew-Zunger (PZ) correlation potentials to deduce energy bands and DOS of Li$_2$B$_4$O$_7$. In present computations, we have used experimental lattice parameters as $a=9.610$ Å and $c=10.372$ Å as reported by Senyshyn et al. \[10\]. The all electron local Gaussian-type basis sets for Li, B and O atoms were taken from http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html and were energy optimized for the lowest possible total energy of Li$_2$B$_4$O$_7$ environment using BILLY program \[11\]. The shrinking factor of the commensurate reciprocal space grid was set equal to 8. The self-consistent field (SCF) cycles were iterated till the energy difference between the successive cycles was smaller than $10^{-7}$ atomic units (a.u.). The SCF computations were executed using 59 $k$ point in the irreducible Brillouin zone (BZ).

2.2 FP-LAPW method

Going beyond LCAO method, LDA has been implemented to derive the electronic response of Li$_2$B$_4$O$_7$ using FP-LAPW method as incorporated in WIEN2k code \[8,9\]. In the present FP-LAPW calculations for Li$_2$B$_4$O$_7$, the radii of Muffin-tin (MT) sphere $R_{MT}$ for Li, B and O atoms were chosen to be 1.65, 1.17 and 1.35 a.u., respectively. For SCF convergence of Li$_2$B$_4$O$_7$ system the $K_{\text{max}}$ was set to $7/R_{MT}$ (where $K_{\text{max}}$ is the magnitude of largest wave vector). The cut-off parameter for charge density ($G_{\text{max}}$) was kept equal to 12 a.u. while maximum radial expansion ($l_{\text{max}}$) was fix to 10. In SCF calculations for Li$_2$B$_4$O$_7$, the tolerance in total energy of Li$_2$B$_4$O$_7$ was within $10^{-5}$ Ry. In Figure. 1, we have depicted the crystalline arrangement of constituent atoms in Li$_2$B$_4$O$_7$.

![Figure 1: Crystalline structure of Li$_2$B$_4$O$_7$ with space group $I4_1cd$](image-url)
3. Results and discussion

3.1 Energy bands and DOS

Total and partial DOS and energy bands of Li$_2$B$_4$O$_7$ deduced using FP-LAPW-LDA method are shown in Figs. 2 (a, b), ranging between -2 to 9 eV. The total and partial DOS along with energy bands structure, computed using LCAO-LDA method shown in Figs. 3 (a, b) are found to have similar structure with those of FP-LAPW-LDA method, except change in few fine structures and band gap values. From Fig. 2(a), we observe that the upper valence band (VB) region (below the Fermi level) is primarily constituted due to hybridization of 2p states of O and B atoms. However, 2p states of O have higher contribution in upper VB region than the 2p states of B atom. In contrast, a very small participation of 2s states of B atom is witnessed in the upper VB region. In higher conduction band (CB) region above 5.8 eV, role of 2s states is found to negligible. Further, 2s states of O atoms show minimal contribution in both upper VB and CB regions and 2p states show insignificant contribution in upper CB. From the DOS curves, as indicated in Figs. 2(a) and 3(a), it also concluded that 2p states of B majorly contribute in conduction band and 2p states of O dominate in valence band region as deduced from FP-LAPW-LDA and LCAO-LDA methods. From the energy bands shown in Figs. 2(b) and 3(b), it is observed that the minimum of CB and maximum of VB lie at same $\Gamma$ point of BZ thereby leading to direct band gap in Li$_2$B$_4$O$_7$. From Figs. 2 and 3, it is observed that the energy bands and DOS show a direct band gap of 5.84 eV and 6.48 eV at $\Gamma$ point of BZ of Li$_2$B$_4$O$_7$, using FP-LAPW-LDA and LCAO-LDA methods, respectively, while the experimental value of band gap is 7.9 eV [28].

![Figure 2](image_url)

**Figure.** 2 Total and partial (projected DOS) and (b) energy bands structure of Li$_2$B$_4$O$_7$ computed using FP-LAPW-LDA scheme.
4. Conclusions
We have reported the electronic response of thermoluminescent Li$_2$B$_4$O$_7$ using FP-LAPW and LCAO schemes with LDA. It is observed that B-2p states contribute in conduction band region whereas O-2p states are found dominating in upper valence region using both the approaches. The energy band gaps deduced from LCAO and FP-LAPW are found to be 6.48 and 5.84 eV, respectively at the $\Gamma$ point of BZ, which is close to the reported experimental value 7.9 eV. It is concluded that both FP-LAPW and LCAO schemes with similar type of exchange and correlation potential (LDA) show almost identical topology of energy bands and DOS for Li$_2$B$_4$O$_7$.

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