



Electronic structure and optical properties of lithium tetraborate detector calculated using semi-local exchange correlation potential



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ABSTRACT

Ab-initio calculations based on density functional theory have been employed to study electronic and optical properties of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) detector. Exchange–correlation (XC) effects were simulated by recently developed modified Becke–Johnson (mBJ) potential. It is demonstrated that this, computationally efficient semi-local potential, correctly describes band gap, electron bands and optical properties of the compound. This fact excludes necessity of using hybrid XC potentials in the future theoretical investigations of defects in $\text{Li}_2\text{B}_4\text{O}_7$. Calculated optical response is found to be anisotropic in near ultraviolet region, with a threshold absorption peak dominated by electron transitions within a trigonal boron-oxygen structure motif.

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1. Introduction

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$ – LBT) is a material with many properties useful for applications: it has a high coefficient of electrochemical coupling, low velocity of propagation of surface acoustic waves, high mechanical strength and appreciable pyroelectric coefficient between 100 and 250 K. It is therefore used in electroacoustic devices [1,2], as piezoelectric nonlinear optical device for second harmonic generation [3,4], as pyroelectric sensor [2] and Li^+ ion conductor at high temperatures [5]. Besides, the LBT is well known host material for thermoluminescence (TL) dosimetry applications [6]. The presence of the rare-earth or transition-metal impurities stimulates irradiative processes within it, resulting in bright and well-resolved above-room-temperature TL peaks. The LBT also has potential to be used as neutron detector owing to ^6Li and ^{10}B significant capture-cross-sections for thermal neutrons. Unlike the most other thermoluminescent materials, it is tissue equivalent, having an effective atomic number $Z_{\text{eff}} = 7.3$ very close to that of soft biological tissue ($Z_{\text{eff}} = 7.4$).

During the last decade many experimental works have been conducted over the LBT, studying mostly its photoluminescence [7], thermoluminescence [8], radiation-induced defects [9] and optical properties [10]. Its bulk electronic structure has been experimentally studied from X-ray photoelectron emission spectroscopy [11], while the same technique, together with the inverse photoemission, has been applied to study band structure

of its (100) and (110) surfaces [12]. The structural and electronic properties of the LBT have been theoretically investigated in Ref. [13], whose authors performed a thorough Density Functional Theory (DFT) study testing different types of exchange–correlation (XC) functionals, different basis sets and using different DFT codes. Although the structural properties have been well described regardless of the method, functional or the basis set used, the electronic structure was found to be sensitive on these details. The agreement with the experimentally estimated band gap has been achieved only by using the hybrid XC functionals (combined Hartree–Fock and Plane Wave exchange functionals) which are computationally demanding. The standard local and semi-local functionals, like ones based on Local Density Approximation (LDA) [14] or Generalized Gradient Approximation (GGA) [15], were found to severely underestimate the gap value [13].

Optical properties of materials are closely related to electronic structure details. If a pure compound is studied, then the LDA and GGA “gap deficiencies” can be cured by applying so-called “scissor operator” which shifts the position of the conduction band bottom with objective to make the calculated and experimental band gaps even [16,17]. After this, the theoretical optical response can be directly compared with experimental data. If, however, one studies material with defects, the application of “scissor operator” is not recommended since it changes the position of the bands within the gap (introduced by defects) relative to conduction band bottom. For most applications, especially for dosimeter ones, correct description of the gap and the bands around it is of essential importance. This is because the luminescence of the material originates from the defect centers which introduce electronic

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bands within the gap. Thus, taking into account conclusions of the Ref. [13], the defect contained LBT should be treated only by using computationally expensive hybrid XC functionals.

In this work we present two novelties in relation with the Ref. [13]. Firstly, we calculate electronic structure of the pure LBT by employing computationally efficient, semi-local XC functional and show that it succeeds to reproduce experimental electronic structure and the value of the band gap. Secondly, we calculate linear optical properties of the pure LBT and interpret them in terms of calculated electronic structure. Our study demonstrates that the basic electronic and optical properties of the LBT can be successfully described by usage of semi-local XC potential. This fact can be very useful in the future theoretical investigation of defect centers in the LBT, since permits the calculations with reasonable computational efforts, considering processing power and computer memory.

2. Calculations

Self-consistent band-structure calculations were performed by DFT based, full potential linear augmented plane wave (FP-LAPW) method [18] as embodied in WIEN2k computer code [19]. In this method the electronic wavefunctions, charge density and crystal potential are expanded in terms of partial waves inside the non-overlapping atomic spheres centered at each nuclear position (with radii RMT) and in terms of the plane waves in the rest of the space (interstitial). The choices for the Li, B and O RMTs were 1.61, 1.15 and 1.34 a.u. respectively. The partial waves were expanded up to $l_{\max} = 10$, while the number of plane waves was limited by the cut-off at $K_{\max} = 6.0/\text{RMT(B)}$. As a basis, the augmented plane waves were used. The charge density was Fourier expanded up to $G_{\max} = 12$. K-space summation was performed with a mesh of 12 and 99 k-points in irreducible part of Brillouin zone for the band-structure and optical calculations, respectively. All calculations were converged with respect to total energy and charge transfer criteria: $\Delta E_{\text{tot}} \leq 10^{-5}$ Ry and $\Delta \rho \leq 10^{-5}$ eV/bohr³.

The lattice parameters and all atomic positions within a crystal unit cell have been relaxed in order to reach equilibrium configuration. The relaxation was performed simulating the XC effects by generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) parameterization [20]. Electronic structure and optical calculations were then performed on this, fully relaxed structure simulating the XC effects by semi-local Becke–Johnson functional recently modified and developed by Tran and Blaha (TB-mBJ) [21]. This choice has been made due to the proven fact that the TB-mBJ provides better description of the band gaps and optical properties for a variety of semiconductors and insulators [22–27].

Electronic structure of the LBT has been calculated in a standard way. Its linear optical properties were then calculated by the

WIEN2k optical package [28]. Imaginary part of complex dielectric tensor ε_2 , directly proportional to the optical absorption spectrum, is calculated using the following formula [29]:

$$\varepsilon_{2(\alpha\beta)}(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{if} \int_{\text{BZ}} \frac{2dk}{(2\pi)^3} |\langle \phi_{fk} | P_{\beta} | \phi_{ik} \rangle| |\langle \phi_{fk} | P_{\alpha} | \phi_{ik} \rangle| \delta[E_f(k) - E_i(k) - \hbar\omega],$$

which describes electric dipole allowed transitions from populated Kohn–Sham states $|\phi_{ik}\rangle$ of energy $E_i(k)$ to empty Kohn–Sham states $|\phi_{fk}\rangle$ of energy $E_f(k)$ with the same wave vector k (ω is the frequency of incident radiation, m electron mass, P the momentum operator, and α and β stand for the projections x , y or z). The ε_2 was computed in the range from 0 to 3 Ry (0–40 eV), taking into account electronic transitions between bands from -1.2 to 2.0 Ry. The real part of dielectric tensor ε_1 is then calculated using Kramers–Kronig relations. Owing to its tetragonal symmetry, the LBO's dielectric tensor $\varepsilon = \varepsilon_1 + \varepsilon_2$ is diagonal, with $\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$.

3. Structural optimization

The crystal structure of $\text{Li}_2\text{B}_4\text{O}_7$ is tetragonal with space group number 110 (I41 cd). Conventional unit cell contains 104 atoms. The main crystal motif consists of a boron–oxygen complex B_4O_9 made of two identical planar trigonal $\text{B}_1\text{--O}_3$ ($\text{B}_1 + \text{O}_1 + \text{O}_2 + \text{O}_3$) and two identical tetrahedral $\text{B}_2\text{--O}_4$ ($\text{B}_2 + \text{O}_1 + \text{O}_2 + \text{O}_3 + \text{O}_4$) groups. The Li atoms are located in the interstices of the boron–oxygen motifs (Fig. 1).

In present work the LTB structure was fully optimized, i.e. the lattice parameters and all the atomic positions were relaxed in order to reach the values that correspond to energy minimum. The results are presented in Table 1, from which it can be seen that GGA XC-potential succeeded to reproduce well the experimental structure within the difference of just few percent's.

4. Electronic structure

Band structure of the $\text{Li}_2\text{B}_4\text{O}_7$, as well as its total and partial density of electronic states (TDOS and PDOS respectively), are presented in Figs. 2 and 3. They are calculated using TB-mBJ XC-potential.

The band structure and the DOS calculated in present work look qualitatively the same as the ones calculated in the Ref. [13] using hybrid XC-potential (presented there in Fig. 2a and b). The energy range of principal bands and arrangement of more pronounced peaks are practically the same. The valence panel is dominated by the oxygen's s -states, grouped into the band between -22 and -18 eV, and oxygen's p -states, grouped into the band between -9 and 0 eV. The latter are hybridized with certain amount of the boron's s - and p -states, while the Li contribution is negligible.

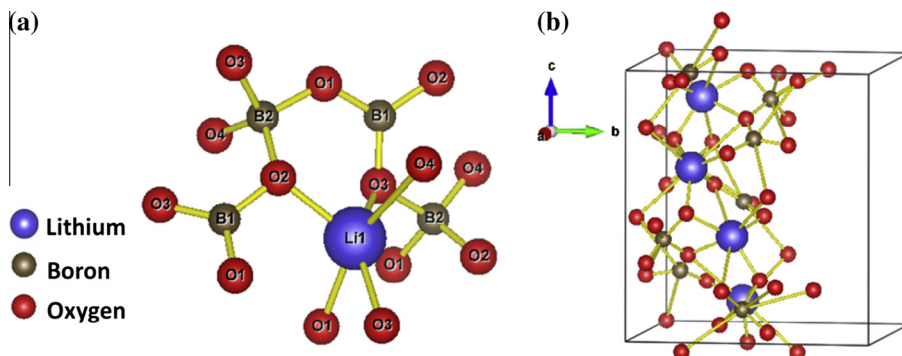


Fig. 1. Schematic representation of (a) the main structure element of the bulk LTB: $[(\text{B}_4\text{O}_9)^{-6}]$ motif consisting of $\text{B}_1\text{--O}_3$ and $\text{B}_2\text{--O}_4$ units, and (b) a portion of the LTB unit cell.

Table 1

Structural characteristics of the $\text{Li}_2\text{B}_4\text{O}_7$ as calculated in this work and compared to experimental data taken from Ref. [30].

Experiment				Theory (this work) GGA		
a , Å	9.4544			9.5141		
b , Å	9.4544			9.5141		
c , Å	10.3236			10.4500		
Atomic coordinates						
	x/a	y/b	z/c	x/a	y/b	z/c
Li	0.0161	0.0174	0.0821	0.0165	0.0181	0.0805
B1	0.0178	0.0092	0.0193	0.0177	0.0090	0.0192
B2	0.1000	0.0119	0.0078	0.0996	0.0118	0.0078
O1	0.0299	0.0147	0.0256	0.0295	0.0143	0.0254
O2	0.0071	0.0187	0.0151	0.0072	0.0186	0.0148
O3	0.0166	0.0997	0.0175	0.0164	0.0989	0.0173
O4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Conduction band consists predominantly of the boron's and lithium's s- and p-states, with contribution of the oxygen's p-states. Peculiar feature is very pronounced trigonal boron (B_1) peak at the conduction band bottom, consisting of its p-states. These states are hybridized with p-states of neighboring oxygens. Empty p-states of tetrahedral boron (B_2) are situated at somewhat higher energies, while the Li p-states dominate the high-energy part of conduction band. Calculated band gap is found to be 9.2 eV and it is indirect (involving $X \rightarrow \Gamma$ k-point transition in Brillouin zone). Hybrid XC-potential calculations in the Ref. [13] result in the gap of 8.9 eV, which is also characterized as indirect one but involving $M \rightarrow \Gamma$ k-point transition in Brillouin zone. To the best of our knowledge, no decisive experimental data about the band gap value of bulk LTB is available. In the Ref. [13] the authors estimate the experimental gap value to be about 9.0 eV, basing their reasoning on the measured fundamental adsorption (FA) energy and experimental and calculated band gaps and FA energies available for other alkali borate crystals. In the more recent Ref. [12] the authors used the angle-resolved photoemission and inverse photoemission spectroscopies to determine gap for LBO's (100) and (110) surfaces, concluding that the bulk band gap certainly exceeds 8.8 eV, being probably more close to the 9.8 eV. In any case, our calculated value falls within this, experimentally predicted, interval. This fact, together with the fact that our calculated

valence-band DOS agrees very well with experimental X-ray photoelectron spectrum data (Fig. 3), permits us to conclude that semi-local TB-mBJ XC-potential correctly describes electronic structure of the $\text{Li}_2\text{B}_4\text{O}_7$ compound.

5. Optical properties

The correctness of calculated electronic structure provides a confidence that the calculated linear optical properties of LTB, derived from the latter, should also be correct (those, of course, do not involve excitons, polarons and other higher order effects beyond DFT description). As, to the best of our knowledge, very few experimental data about linear optical response of the bulk LTB exist in the literature, a major part of our calculations should be understood as theoretical predictions.

Fig. 4 shows real and imaginary part of LTB dielectric tensor in the ultraviolet range of frequencies, as calculated using TB-mBJ XC-potential.

Imaginary part of ϵ is directly proportional to optical absorption spectrum of the LTB. It is characterized by relatively narrow peak, centered at ~ 11 eV, which can be considered as absorption threshold of the compound. This peak is found to be dominated by electronic transitions from populated B_1 and O's p-states to empty B_1 p-states, i.e. by transitions that occur within the trigonal $\text{B}_1\text{--O}_3$ group. The other peak in the absorption spectrum, the broad one and centered at higher energies, was difficult to analyze in terms of electronic transitions. It consists of mixture of them: transitions within the trigonal $\text{B}_1\text{--O}_3$, tetrahedral $\text{B}_2\text{--O}_4$ group and transitions from O's 2p- to the Li 2p-states.

Both imaginary and real parts of ϵ exhibit a clear anisotropy, especially in the near ultraviolet region (9–15 eV). The threshold absorption peak for incident light polarized along the c -axis is much less intense than for the light polarized perpendicularly. The same is valid for the lowest energy peak of ϵ_1 , resulting in different static dielectric constants for the light polarized along the c -axis (2.03) and perpendicularly (2.16). These results are consistent with the fact that the LTB, as pyroelectric material, is expected to exhibit different electrical properties along the axis of electric polarization (which is the c -axis) when compared to other directions [31]. In recent work of Dugan et al. [32] it is demonstrated that the conductivity is much higher along the c -axis of the LTB than along a perpendicular one.

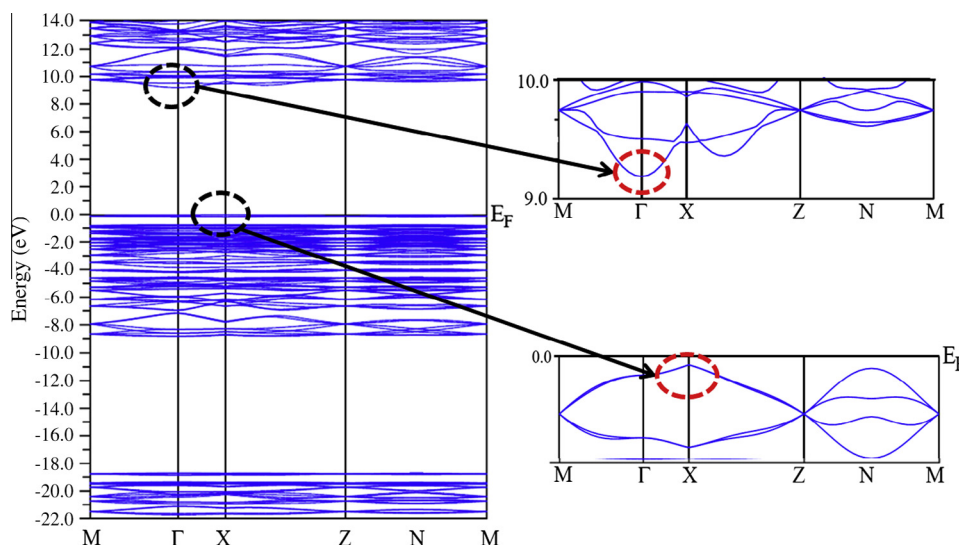


Fig. 2. Band structure of the $\text{Li}_2\text{B}_4\text{O}_7$ as calculated by the FP-LAPW method using TB-mBJ exchange–correlation potential. The top of the valence band is at the k-point X, while the conduction band bottom is at the k-point Γ in the first Brillouin zone.

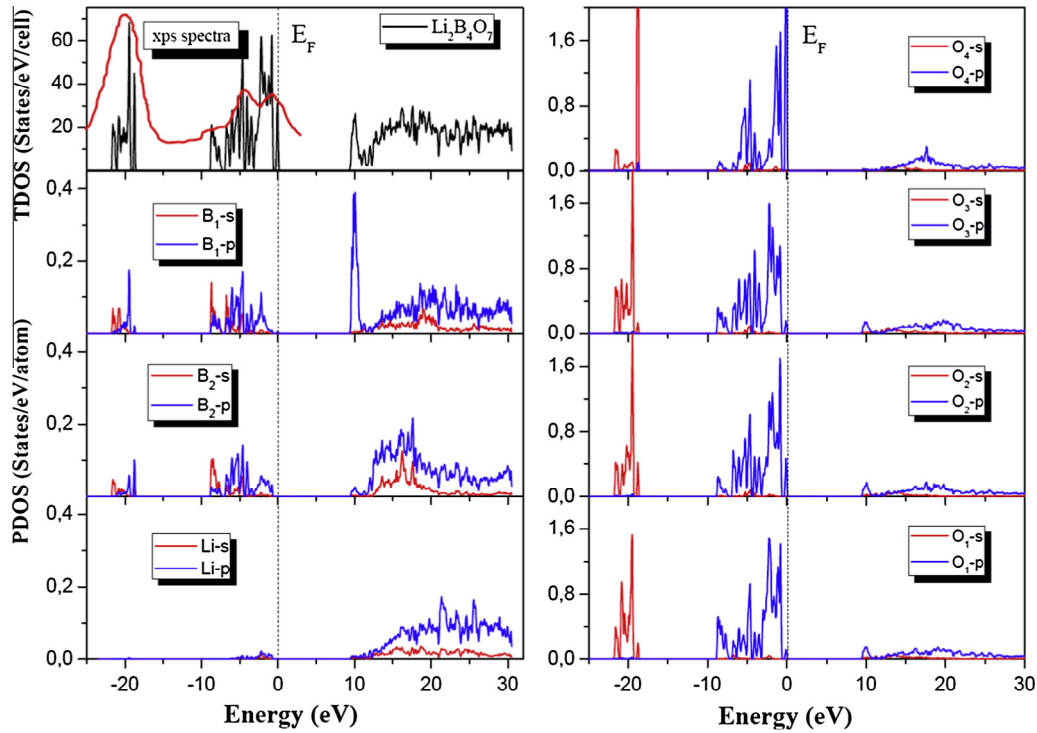


Fig. 3. Total and projected electronic density of states (TDOS and PDOS) of the $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The top of the left graph compares the calculated TDOS with that obtained experimentally from X-ray photoelectron spectrum [11] (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

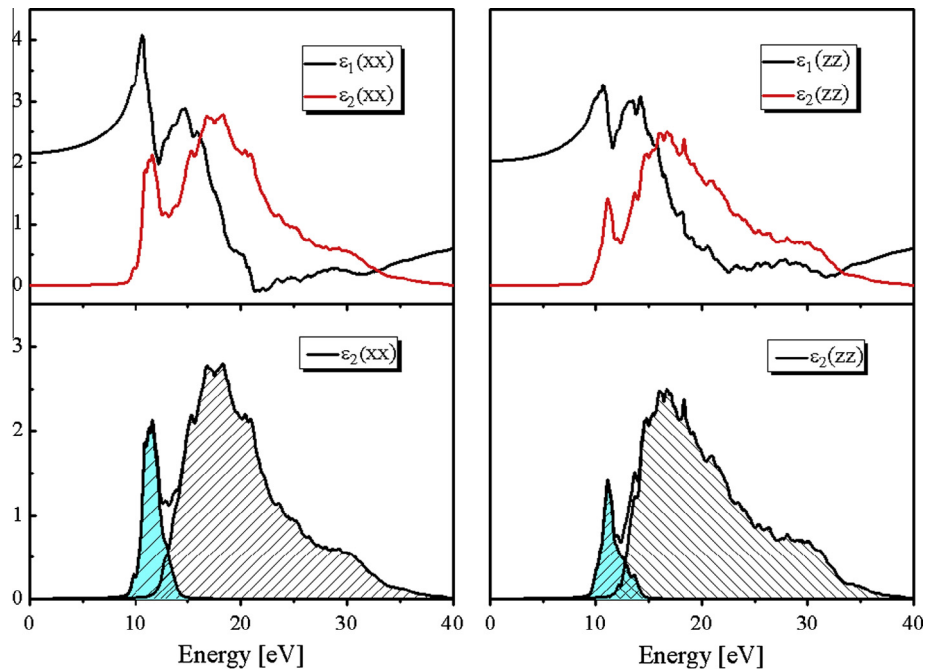


Fig. 4. Calculated real (ϵ_1) and imaginary (ϵ_2) part of ϵ for incident electromagnetic perturbation polarized along crystallographic a - and c -direction (x and z respectively). The lower two graphs interpret the LTB absorption spectrum. Its first peak (blue one) is dominated by electronic transitions within the $\text{B}_1\text{--O}_3$ structure motif (from the occupied O p - to the empty B p -states). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Finally, reliability of presented optical properties can be checked by comparing the calculated refractive indices (derived from combination of ϵ_1 and ϵ_2 , see Ref. [29], for example) with the ones measured at ambient temperature in the range of wave-

lengths from 185 to 2325 nm [4]. As the z -axis is the optic axis for the LBO, the calculated indices n_{zz} and n_{xx} correspond to refractive indices of ordinary and extraordinary rays n_o and n_e , respectively. The results are presented in Fig. 5.

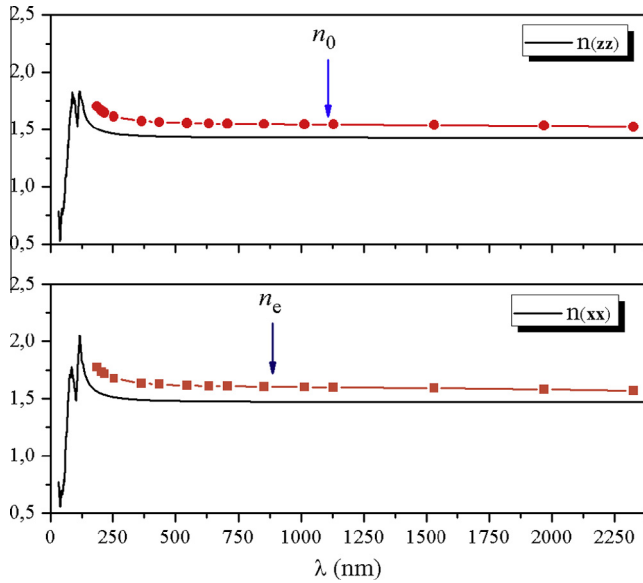


Fig. 5. Calculated refractive indices n_{zz} and n_{xx} (full curves) compared to experimental values (curves with symbols) measured at ambient conditions [4].

Experimental values of n_o and n_e were fitted to following Sellmeyer equation [4]:

$$n^2 = A + B/(\lambda^2 - C^2) + D\lambda^2$$

By this procedure the authors of the Ref. [4] determined Sellmeyer's constants A, B, C, D for LTB. By fitting our theoretical results (excluding the range of wavelengths less than 125 nm absorbed by compound) to the same equation, we extracted theoretical Sellmeyer's constants which are compared to experimental ones in Table 2.

As can be seen from Table 2 and Fig. 5, there is a good overall agreement between theoretical and experimental data. The difference between the calculated and experimental static refractive indices (those at longest wavelengths) is small: experimental values are $n_o(\lambda = 2325 \text{ nm}) = 1.56$ and $n_e(\lambda = 2325 \text{ nm}) = 1.52$, while the theoretical ones are $n_{zz}(\lambda = 2325 \text{ nm}) = 1.43$ and $n_{xx}(\lambda = 2325 \text{ nm}) = 1.47$ respectively. This difference is more or less maintained over the whole range of measured wavelengths. It can be attributed to the fact that the experimental values are recorded at ambient temperature [4], while the calculated ones correspond to the ground state of the LTB (at very low temperatures). The authors of reference [4], however, also measured the temperature derivatives of n_o and n_e in the range of -40°C to 100°C . Their results demonstrate that both n_o and n_e should diminish their values when temperature is lowered, meaning that experimental curves in Fig. 5 should approximate the theoretical ones in that case, improving agreement between them. This fact, together with the fact that theoretical curve starts to increase at the same wavelengths as experimental one (indicating that our calculated band gap is close to experimental), provides additional confidence that linear optical response of the LTB, presented in Fig. 4, is correctly described.

Table 2
Sellmeyer's constants for $\text{Li}_2\text{B}_4\text{O}_7$ compound: calculated ones (n_{zz} and n_{xx} , this work) and experimentally determined ones (n_o and n_e , Ref. [4]).

	A	B (μm) ²	C (μm)	D (μm) ⁻²
n_o	2.56431	0.01234	0.11445	-0.01907
n_{zz}	2.03889	0.00501	0.10344	-0.00001
n_e	2.38651	0.01066	0.11348	-0.01281
n_{xx}	2.16409	0.00646	0.10186	-0.000005

6. Conclusions

In this paper we investigated electronic and linear optical properties of lithium tetraborate crystal ($\text{Li}_2\text{B}_4\text{O}_7$ – LTB), using DFT based FP-LAPW method with TB-mBJ exchange–correlation (XC) potential. We demonstrated that this, computationally efficient semi-local potential, correctly describes the band gap of the LTB. Our calculated band gap value is 9.2 eV, the previous DFT calculations with hybrid XC-potential result in 8.9 eV, while experimental estimates are 8.8–9.8 eV. Besides the gap, the calculated electronic structure is also found to agree well with experimentally findings obtained from X-ray photoelectron spectrum. These facts exclude necessity of using hybrid XC potentials in the future theoretical investigations of defects in $\text{Li}_2\text{B}_4\text{O}_7$. Calculated linear optical response is found to be anisotropic in near ultraviolet region, with a threshold absorption peak dominated by electron transitions within a trigonal boron-oxygen structure motif.

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