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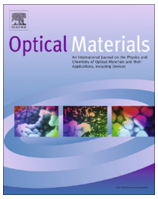

Mixed alkali and alkaline-earth borate $Li_2Sr_4B_{12}O_{23}$ single crystal

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ABSTRACT

A comprehensive theoretical investigation of the electronic band structure, density of states, electron charge density distribution and the optical properties for mixed alkali and alkaline-earth borate $Li_2Sr_4B_{12}O_{23}$ (LSBO) single crystals were performed. The experimental geometrical structure was optimized by minimizing the forces acting on each atom. Calculations were performed using the full potential linear augmented plane wave plus local orbitals (*FPLAPW* + *lo*) method within the local density approximation (*LDA*), generalized gradient approximation (*GGA*) and the recently modified Becke–Johnson potential (*mBJ*). Our calculations show that LSBO crystal is a direct band gap semiconductor. The calculated band gap is 4.64 eV (*LDA*), 4.92 eV (*GGA*) and 5.51 eV (*mBJ*). An earlier calculation using the CASTEP code within *LDA* obtained a band gap of about 4.66 eV. To overcome the well-known *LDA* underestimation of the energy gap we have used *GGA* and *mBJ*. We find that *mBJ* succeed by large amount in bringing the calculated bond lengths in good agreement with the experimental data. Also we found that using *mBJ* to calculate the optical properties gives a birefringence of about 0.068 (at $\lambda = 586.5$ nm) in excellent agreement with the experimental data (0.068 at $\lambda = 586.5$ nm). Therefore, we believe that the *mBJ* calculations reported here show excellent agreement with the experimental data.

1. Introduction

The formation of a large variety of borates is a consequence of two unique coordination of B atoms BO_3 and BO_4. Borates are promising candidates for several applications. Several borates materials considered to be as potential candidates for generating second harmonic in the ultra-violet region [1–3] among them is the alkali or alkaline-earth metal borates. The cations of these alkali or alkaline-earth metal borates favor excellent optical transparency in the ultra-violet region [4]. Some alkali/alkaline earth metal borates, $Li_2Sr_4B_{12}O_{23}$ (LSBO) [5,6], have a three-dimensional framework and can be used as micro-porous materials. Recently Zheng and Li [7] have used the high-temperature solid state reaction to synthesize a pure mixed alkali–alkaline earth metal borate of $Li_2Sr_4B_{12}O_{23}$ with micro-porous structure. The single crystal was characterized by XRD, FT-IR, TG techniques, and chemical analysis. Zhang et al. [6] have used the top-seeded solution growth method below 730 °C to grow ternary lithium strontium borate $Li_2Sr_4B_{12}O_{23}$ single crystals with size $20 \times 10 \times 4$ mm. They found that $Li_2Sr_4B_{12}O_{23}$ crystallizes in the monoclinic space group P21/c. Using the IR spectrum they confirm the presence of both BO_3 and BO_4 groups. Furthermore, they calculate the electronic band structure and the density of states using the *ab initio* density functional theory (DFT) method implemented in the CASTEP package within the local density approximates (LDA). It has been found that the calculated energy band gap of LSBO is about 4.66 eV. Also they have calculated the birefringence, imaginary and real parts of the optical dielectric function using LDA.

It is well-known that in calculating the self-consistent band structure within DFT, the LDA approximation underestimates the energy band gap by around 10–30% [8–10]. This is mainly due to the fact that LDA has simple forms that are not sufficiently flexible to accurately reproduce both the exchange–correlation energy and its charge derivative. Therefore, we thought it is worthwhile to do more accurate calculations using full potential method with different exchange and correlation potentials. We would like to mention that we are not aware of experimental data for the energy gap of LSBO crystal. However, since there is an experimental value for the birefringence of LSBO therefore, we have performed calculations using three different exchange-correlation potentials in order to ascertain which one gives the birefringence in close agreement with the experimental value. We feel that the exchange- correlation which will succeed in bringing the calculated birefringence in close agreement with the experimental value, would also give the correct band gap. First-principles calculation is one powerful and useful tool to predict the crystal structure and

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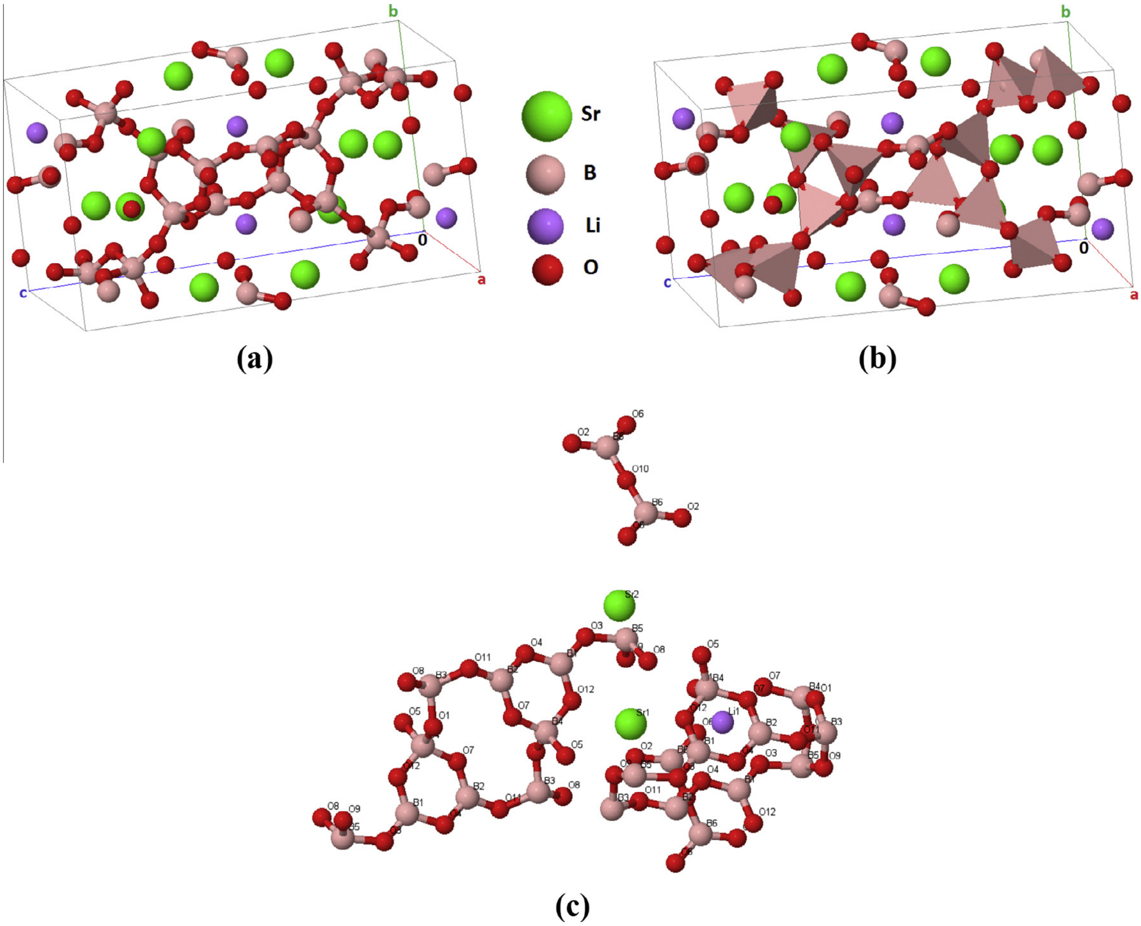
properties related to the electron configuration of a material before its synthesis [11–15].

2. Details of calculations

$Li_2Sr_4B_{12}O_{23}$ (LSBO) single crystal is alkali and alkaline-earth metal mixed borate with $[B_{10}O_{18}]^{6-}$ network and isolated $[B_2O_5]^{4-}$ unit. LSBO crystallizes in a monoclinic structure, space group, $P2_1/c$. The unit cell parameters are a = 6.4664(4) Å, b = 8.4878(4) Å and c = 15.3337(8) Å, β = 102.02(3)°, V = 823.13(8) Å^3, Z = 2 [6]. The crystal structure of LSBO is shown in Fig. 1(a)–(c). In this calculation we have used the crystallographic data obtained by Zhang et al [6]. Using *GGA* [16] the atomic coordinates of LSBO were optimized by minimization of the forces acting on each atom. We assume that the structure is fully relaxed when the forces on the atoms reach values less than (1 mRy/a.u.). The optimized atomic positions along with those obtained from the crystallographic data [6] were listed in Table 1, good agreement was found. Once the forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency. From the obtained relaxed geometry the electronic structure, chemical bonding, electronic charge density and the optical properties have been determined and compared with the available experimental data.

The calculation were performed using *DFT* within the full potential linear augmented plane wave plus local orbitals (*FPLAPW* + *lo*) method in a scalar relativistic version as embodied in the *WIEN2k* code [17]. The exchange-correlation (*XC*) potential was solved using three different possible approximations. The *XC* are described by *LDA* [18] and *GGA*, which is based on exchange-correlation energy optimization to calculate the total energy. In addition, we have used the recently modified Becke–Johnson potential (*mBJ*) [19] which optimizes the corresponding potential for electronic band structure calculations. It is well-known that in calculating the self-consistent band structure within DFT, the LDA approximation underestimates the energy band gap by around 10–30% [8–10]. This is mainly due to the fact that LDA has simple forms that are not sufficiently flexible to accurately reproduce both the exchange–correlation energy and its charge derivative. To overcome this drawback we proposed *mBJ*. The *mBJ*, a modified Becke–Johnson potential, allows the calculation of band gaps with accuracy similar to the very expensive *GW* calculations [19,15]. It is a local approximation to an atomic "exact-exchange" potential and a screening term. Since the exact value of the experimental band gap is not reported in the literature, therefore based on our previous calculation [20–22] of the band gap using *mBJ* for several systems whose energy band gap are known experimentally, in those previous calculations we found very good agreement with the experimental data. Thus, we believe that our calculations reported in this paper would produce very accurate and reliable value of the energy band gap.

The Kohn–Sham equations are solved using a basis of linear *APW′s*. The potential and charge density in the muffin-tin (*MT*) spheres are expanded in spherical harmonics with $l_{\max} = 8$ and non-spherical components up to $l_{\max} = 6$. In the interstitial region the potential and the charge density are represented by Fourier series. Self-consistency is obtained using 300 $\bar{k}$ points in the



(a)
(b)
(c)

Fig. 1. (a) and (b) Different view for the unit cell of LSBO single crystal; (c) LSBO molecule.