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# Electronic structure and optical properties of $LiB_3O_5$

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The band structure and the interband optical conductivity of a $LiB_3O_5$ crystal with excellent nonlinear optical properties are studied by means of a first-principles method. The electronic structure is characterized by highly localized bands with a direct gap of 7.37 eV at Γ and a very low static dielectric constant of 2.7. The optical absorption curve shows several prominent structures but with very small directional anisotropy. The calculated frequency-dependent refractive index is in good agreement with experimental data.

Recently, the discovery of a new optical crystal $LiB_3O_5$ with excellent nonlinear optical properties was reported.[1,2] This boron oxide compound has some of the best optical qualities such as chemical stability, high damage threshold, a large gap, and a small dielectric constant; and most importantly, it has a nonlinear optical (NLO) coefficient much larger than that of $KTiOPO_4$ (KTP), another excellent NLO crystal discovered earlier.[3] Since the discovery of $LiB_3O_5$ was claimed to be guided by theoretical considerations,[1] it is important to understand the fundamental electronic structure and bonding in this material and to see if its unusual NLO properties can be explained. In this paper, we present the results of a self-consistent band-structure calculation of $LiB_3O_5$ using the orthogonalized linear-combinations-of-atomic-orbitals method (OLCAO). Furthermore, we have calculated the linear optical properties of this crystal using the wave functions obtained from the band calculation. Our results will be compared with very limited experimental data on this crystal. Some comments on the possible connection of electronic structure and the NLO properties of $LiB_3O_5$ are made.

$LiB_3O_5$ crystallizes in a complex orthorhombic cell with four formula units per cell.[4] The space group is $Pn2_1a(C^9_{2v})$, with crystal parameters of $a=8.46$ Å, $b=5.13$ Å, and $c=7.38$ Å. Two of the three inequivalent B atoms B(1) and B(3) are threefold bonded similar to $B_2O_3$ with an average nearest-neighbor (NN) distance of 1.368 and 1.373 Å, respectively. The B(2) site is fourfold bonded in the form of a distorted tetrahedron with an average NN distance of 1.476 Å. There are five inequivalent O sites. The NN B—O bonding distances range from 1.349 to 1.493 Å. The four NN Li—O bonding distances are much larger, ranging from 1.983 to 2.178 Å. The structure can be viewed as an open B-O network with the Li atoms located at the open interstices of the network. The structure is similar to but not isotropic to that of cesium triborate, $Cs_2B_2O_3$.[5]

The band structure of $LiB_3O_5$ is calculated using the self-consistent OLCAO method in the local-density approximation. The OLCAO method is particularly effective for complex crystals with open structures, such as $LiB_3O_5$ with 36 atoms in the unit cell. The basis function consists of 1*s*, 2*s*, 3*s*, 2*p*, and 3*p* orbitals of Li, B, and O atomic waves with all the 1*s* orbitals treated as core states. The potential and the charge density of the crystal are linearly fitted to a superposition of atom-centered functions which are expressed as linear combinations of Gaussians with a fixed set of exponentials. The accuracy of the calculation depends on the quality of the fit. In the present calculation, we have achieved a fitting error of less than 0.0015 electron per valence electron. Past experience indicates that such an accuracy is more than adequate for band-structure studies.

The calculated conduction-band (CB) and valence-band (VB) structures of $LiB_3O_5$ along lines of high symmetry are shown in Fig. 1. It has a direct band gap of

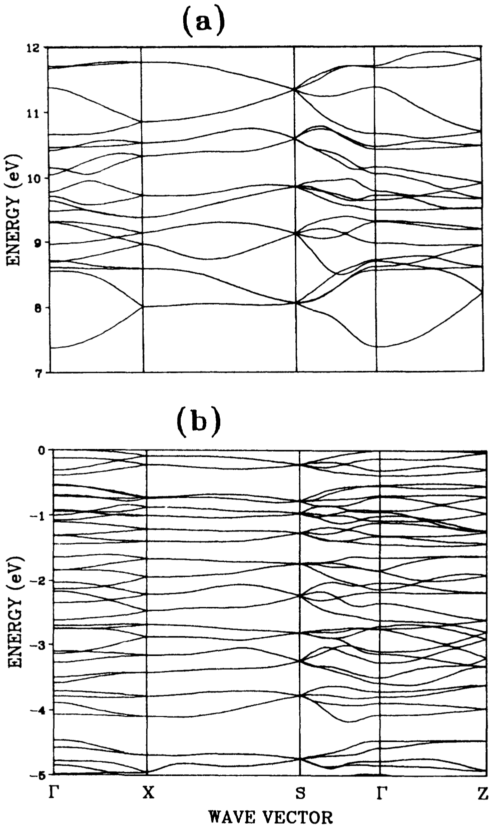

FIG. 1. Calculated band structure of $LiB_3O_5$. (a) Conduction band and (b) valence band.

7.37 eV at Γ, very close to the reported experimental gap of 7.75 eV.[1] The VB are characterized by a lack of dispersion and there are minigaps all over the VB region. This type of band structure signifies that the electronic states are more or less dictated by the localized B—O bonding units. As a result, the hole effective masses are very large, typical of wide-gap insulators. The CB electron effective masses are estimated to be $0.73m_e$, $0.89m_e$, and $0.69m_e$, respectively, along the $\Gamma \rightarrow X$, $\Gamma \rightarrow S$, and $\Gamma \rightarrow Z$ directions. The total density of states (DOS) and orbital-resolved partial DOS (PDOS) are shown in Fig. 2. The DOS calculation is based on the energy eigenvalues and wave functions at the 80 $k$ points of the irreducible portion of the Brillouin zone (BZ) and the use of an analytic linear tetrahedron method.[6] The DOS spectrum is full of sharp spikes in the VB region due to flat bands, and the presence of minigaps is also evident. The O 2$s$ and O 2$p$ levels interact strongly with both the B 2$s$ and B 2$p$ orbitals. This is, of course, the consequence of the short O—B bond in the localized B-O units. The O 2$s$ band spans over a 3.0-eV region, indicating a random network-like binding structure for $LiB_3O_5$. The upper VB which is dominated by the O 2$p$ orbitals while the states near the CB minimum involve orbitals of all three elements.

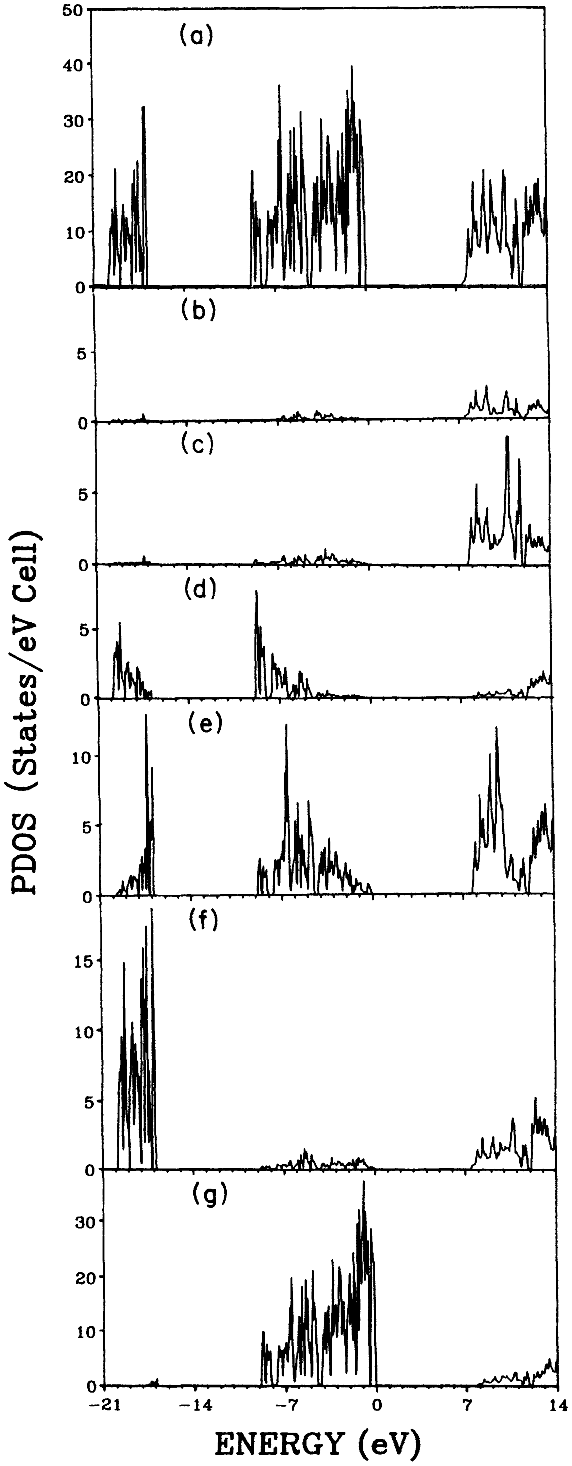

FIG. 2. Calculated DOS and PDOS: (a) total, (b) Li 2$s$, (c) Li 2$p$, (d) B 2$s$, (e) B 2$p$, (f) O 2$s$, and (g) O 2$p$.

The effective charges (EC) $Q^*$ on each atom as calculated by the Mulliken analysis are listed in Table I together with the EC obtained from similar calculations[7] for $Li_2O$ and $B_2O_3$ crystals. The $Q^*$ of Li is 0.94 electron as compared to 0.74 electron in the $Li_2O$ case. This is due to the fact that the Li atoms are in the center of large interstices of the B-O network with a relatively large Li-O distance. The average EC on the O atoms is 6.22 electrons, less than 6.53 electrons in $Li_2O$ and 6.35 electrons in $B_2O_3$. The EC for B(1), B(2), and B(3) are 2.58, 2.74, and 2.62 electrons, respectively, compared to an average $Q^*$ of 2.48 electrons in $B_2O_3$. The larger $Q^*$ for B(2) is due to its relatively larger B-O NN distances mentioned earlier. Thus both Li and B act as electron donors in $LiB_3O_5$, but to a lesser extent than in the $Li_2O$ and $B_2O_3$ crystals. The calculated band gaps for the $Li_2O$ and $B_2O_3$ crystals are 5.38 and 4.64 eV, respectively; both are smaller than $LiB_3O_5$.

We have also calculated the interband optical conductivity of $LiB_3O_5$ using the energy eigenvalues and wave functions at the same 80 $k$ points in the BZ according to the Kubo-Greenwood formula.[8] The contribution from the dipole matrix elements are explicitly calculated and

TABLE I. Calculated effective charges $Q^*$ (electrons) in $LiB_3O_5$, $Li_2O$, and $B_2O_3$.

| Atoms | $LiB_3O_5$ | $Li_2O$ | $B_2O_3$ |
|---|---|---|---|
| Li | 0.94 | 0.74 | · · · |
| B(1) | 2.58 | · · · | 2.54 |
| B(2) | 2.74 | · · · | 2.41 |
| B(3) | 2.62 | · · · | |
| Average | (2.65) | | (2.48) |
| | | | |
| O(1) | 6.34 | | 6.55 |
| O(2) | 6.20 | | 6.22 |
| O(3) | 6.13 | | 6.28 |
| O(4) | 6.23 | | |
| O(5) | 6.22 | | |
| Average | (6.52) | (6.52) | (6.35) |
| $E_g$ (eV) | 7.37 | 5.38 | 4.64 |

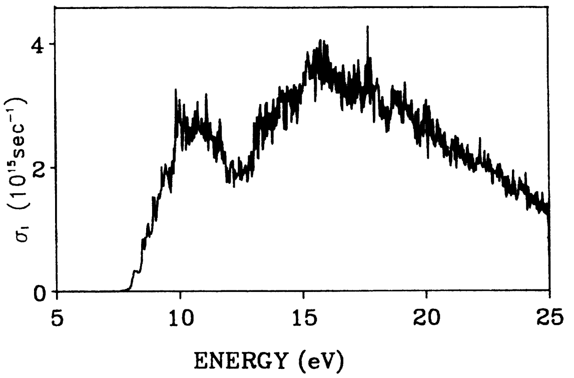

FIG. 3. Calculated interband optical conductivity of $LiB_3O_5$.

fully taken into account. The directionally averaged conductivity curve $\sigma(\omega)$ up a photon energy of 25 eV is shown in Fig. 3. The optical absorption increases rapidly immediately above the direct-gap threshold. This is in sharp contrast to some other oxides where the transition is symmetry forbidden at the band extremes and the optical absorption becomes appreciable only at a photon energy way above the minimum gap.[9] $\sigma$ reaches a maximum at 10.0 eV, a second maximum at 11.2 eV, drops to a minimum at 12.4 eV, and then raises to a broader maximum at 15.7 eV. Beyond 15.7 eV, $\sigma$ decreases more or less monotonically. There appears to be a shoulder at 13.2 eV. We also find the anisotropy in $\sigma$ along the three crystal-axis directions to be small.

From the interband optical conductivity curve, both the real and the imaginary parts of the frequency-dependent dielectric function, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, can be evaluated using the Kramers-Kronig relation. The direction-resolved $\epsilon_1(\omega)$ curve up to 10 eV is shown in Fig. 4. Our calculation shows that $LiB_3O_5$ has a very low static dielectric constant $\epsilon(0)$ of about 2.7. In the inset of Fig. 4, we show in more detail of the frequency dependence of $\epsilon_1(\omega)$ in the three directions. Also shown are the experimental data of frequency-dependent refractive index along the three principal axes of the crystal from Ref. 1. The squares of the refractive index values are directly comparable to $\epsilon_1(\omega)$ in the frequency range of the wide gap; the converted data are shown in the inset of Fig. 4. Although an absolute agreement is not achieved, the relative small anisotropy, the trend of frequency dependence and the general magnitudes are all well reproduced. The theoretical curves are slightly above the experimental data points. This is probably due to the fact that the band gap is slightly underestimated. It is quite rare that first-principles calculation of optical properties on wide gap insulators can get results that close to the experimental data.

To have a better understanding of the NLO properties of $LiB_3O_5$, nonlinear optical parameters need to be calculated and analyzed. Unfortunately, such a calculation based on first-principles band-structures results is very complicated, especially for a crystal as complex as $LiB_3O_5$. Even in the case of structurally simpler cubic semiconductors, nonlinear susceptibility calculation based on realistic band structures can differ from experimental data substantially.[10] Nevertheless, the linear optical properties we calculated provides a starting point to understand the nonlinear optical properties of this unique system. Since our calculation shows the electronic structure of $LiB_3O_5$ is dominated by the localized planar $B\text{-}O_3$ and tetrahedral $B\text{-}O_4$ units, the use of anionic group theory[1] which is based on the use of approximate electron wave functions of molecular subgroups to calculate the NLO parameters seems to be justified.

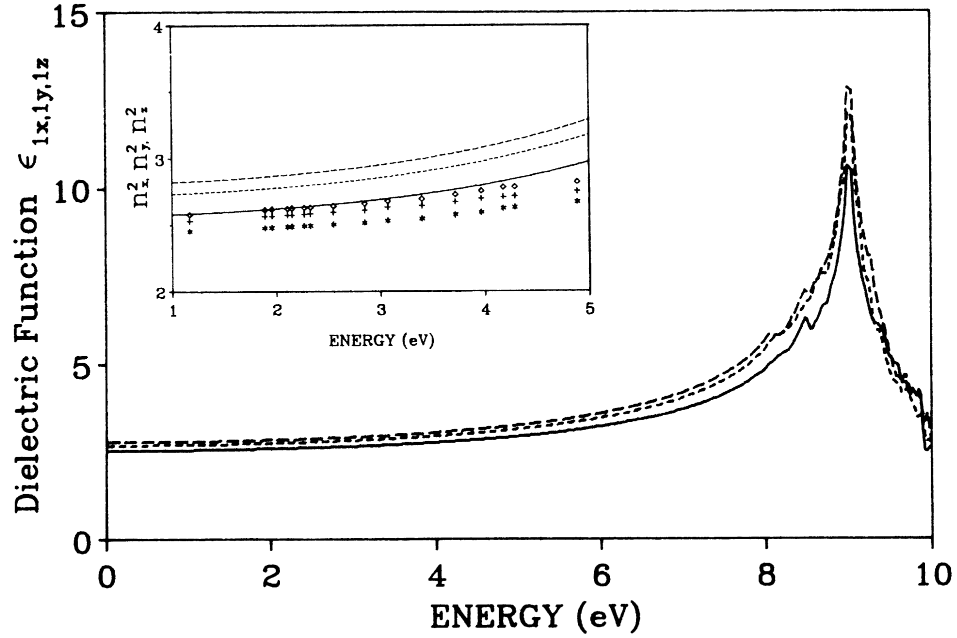

FIG. 4. Calculated real part of the dielectric function. Inset: solid line, $\epsilon_{1x}$; dashed line, $\epsilon_{1y}$; dotted line, $\epsilon_{1z}$. ◇, +, and * are converted experimental data from Ref. 1 for $n_x^2$, $n_y^2$, and $n_z^2$, respectively.

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