

Electronic properties of compounds of the $\text{Li}_2\text{O-B}_2\text{O}_3$ system

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The electronic properties of $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ ($x=0.0, 0.25, 0.33, 0.5, 0.75,$ and 1.0) compounds were studied by periodic quantum-chemical calculations at density functional theory level using localized atomic basis functions. A good agreement between calculated and measured values of the band gap was obtained for Li_2O . The band gaps were predicted for other compounds of the $\text{Li}_2\text{O-B}_2\text{O}_3$ system where less reliable experimental data are available. The calculated band gap of $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ decreases with increasing mole fraction x of Li_2O . This was interpreted by the decreasing bonding interaction between BO_n groups. By an analysis of the electron density distribution, it was shown that in all systems under consideration the B-O bonds are mainly covalent, and that B-O bonds in BO_3 units are stronger than in BO_4 . The Li-O interaction is predominantly ionic.

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I. INTRODUCTION

The $\text{Li}_2\text{O-B}_2\text{O}_3$ phase diagram contains eight stoichiometric compounds.¹⁻³ Only five of these are stable at room temperature, namely LiB_3O_5 (lithium triborate), $\text{Li}_2\text{B}_4\text{O}_7$ (lithium tetraborate, LTB), LiBO_2 and $\text{Li}_6\text{B}_4\text{O}_9$ (lithium metaborates), and Li_3BO_3 (lithium orthoborate). These stoichiometries correspond to $x=0.25, 0.33, 0.5, 0.6,$ and $0.75,$ respectively, in the general formula $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$. Single crystals of the $\text{Li}_2\text{O-B}_2\text{O}_3$ system are of considerable interest, not only for practical use but also for fundamental investigations. A large number of possible applications is known for these crystals. Namely, LiB_3O_5 single crystals are suitable for the second and third YAG:Nd laser harmonic generation,⁴⁻⁶ the development of parametric light generators,⁷ and as wave-guides.⁸ $\text{Li}_2\text{B}_4\text{O}_7$ single crystals can be used as substrates for thermostable surface⁹⁻¹¹ and bulk¹² acoustic wave-based devices, as pyroelectric temperature sensors,¹³ as nonlinear optical devices for the fourth and fifth YAG:Nd single crystal laser harmonics generation,¹⁴ and for thermoluminescent dosimetry of x-ray, gamma, and neutron radiation.¹⁵⁻¹⁷ Li_2O has possible applications in deuterium-tritium fusion reactors as blanket breeding material¹⁸ and in solid state batteries.¹⁹ A promising material for Li batteries is a composite of Li_2O and B_2O_3 nanocrystallites.²⁰

Despite the large number of experimental and theoretical studies on compounds of the $\text{Li}_2\text{O-B}_2\text{O}_3$ system, information about their optical spectra is scarce, except for Li_2O . In general, it is well known that optical absorption spectra are very sensitive to small amounts of impurities and defects in the sample. Theoretical predictions of band widths and band gaps (E_g) show substantial variations depending on the method of investigation and the choice of the basis set.

So far, electronic properties have been investigated extensively only for Li_2O .²¹⁻²⁸ A value of 7.99 eV was found for E_g ²¹ in an investigation of different quality samples using a

Wannier-excitation model for experimental adsorption and reflection spectra. This value is larger than those obtained by photoemission and electron energy loss spectroscopy (EELS), 7.0-7.5 eV,²² and optical absorption spectroscopy, 7.02 eV,²³ 6.6 eV,²⁴ and 6 eV.²⁵ A number of theoretical studies on the electronic properties of Li_2O exist in the literature. It is important to note that band gaps and bandwidths are generally overestimated by the *ab initio* Hartree-Fock (HF) method^{26,28} and underestimated by density functional theory (DFT), in particular within the local density approximation (LDA).^{27,28} DFT methods based on the generalized gradient approximation (GGA), and hybrid DFT methods incorporating exact HF exchange²⁸ improve the agreement of calculated electronic properties with experiment.

Only a few investigations have been performed for compounds of the $\text{Li}_2\text{O-B}_2\text{O}_3$ system. Recently, a value of 9.5 eV has been obtained for the band gap of LiB_3O_5 .³⁴ This has to be compared to the value reported previously by Chen *et al.*, 7.75 eV,³⁵ and to the measured fundamental absorption (FA) energy (E_a), 7.8 eV.³⁴ Theoretical calculations of the LiB_3O_5 band gap at different DFT levels yield 6.95 eV,³¹ 7.26 eV,³³ and 7.37 eV.³⁰ These calculated band gaps are considerably lower than the most recent experimental value. Practically the same situation is present for the related $\beta\text{-BaB}_2\text{O}_4$ crystal, which is known as nonlinear optic material. The value of its band gap (7.5 eV) was reliably measured for the direct $\Gamma\text{-}\Gamma$ transition from the data obtained by low-temperature optical-luminescence visible UV spectroscopy.²⁹ A comparison of this value with DFT results (5.61 eV,³⁰ 4.88 eV³¹) and the energy E_a at the FA edge (6.43 eV³²) reveals that DFT calculations underestimate the experimental band gap. Their results for the energy difference between the one-electron levels of occupied and unoccupied bands are more comparable with E_a than with E_g .

Less information is available for $\text{Li}_2\text{B}_4\text{O}_7$. Only E_a (7.3³⁴ and 7.9 eV³⁶) has been measured. For Li_3BO_3 , $\text{Li}_6\text{B}_4\text{O}_9$, and LiBO_2 , no experimental and theoretical data of electronic properties could be found. The electronic properties of boron

oxide in high- and low-pressure phases were calculated using the LDA.³⁷ It was reported that the band gap of the low-pressure phase is 6.2 eV. Only one experimental study of the electronic properties of B_2O_3 was found, based on x-ray emission spectroscopy (XES) and photoelectron spectroscopy (PES).³⁸

In the present work, a theoretical investigation of the structural and electronic properties and electron charge distribution was performed for the crystals of $(Li_2O)_x(B_2O_3)_{1-x}$ ($x=0, 0.25, 0.33, 0.5, 0.75, \text{ and } 1$). Since no experimental information was found for the crystal structure of $Li_6B_4O_9$, this compound was not considered. A HF-DFT hybrid method was employed for the calculations in order to overcome the deficiencies of pure HF and DF theory. The calculated structural properties obtained at PW1PW level were compared to pure LDA (Vosko–Wilk–Nusair) and pure PWGGA (Perdew–Wang GGA) methods. In this way, the reliability of the PW1PW approach for describing the structural properties of Li_2O - B_2O_3 compounds was examined. The solids were represented by periodic three-dimensional models. The crystalline orbitals were chosen as linear combinations of localized basis functions. The effect of the basis set size on calculated structural and electronic properties was investigated for all compounds of the $(Li_2O)_x(B_2O_3)_{1-x}$ system ($x=0, 0.25, 0.33, 0.5, 0.75, \text{ and } 1$).

II. COMPUTATIONAL METHOD

All calculations were performed with the crystalline orbital program CRYSTAL03.³⁹ The Bloch functions are linear combinations of atom-centered functions. The quality of the results is affected by the choice of the atomic basis sets. For this reason we performed basis set convergence tests as described in detail below. Three different DFT type approaches were employed. The first method is a HF-DFT hybrid approach which is denoted as PW1PW. In this approach, the exchange functional is a linear combination of the HF expression (20%) and the Perdew–Wang PWGGA⁴⁰ exchange functional (80%). The electron correlation is described with the PWGGA correlation functional.⁴⁰ This approach was parametrized to reproduce structural, energetic, and electronic properties of main group and transition metal oxides,⁴¹ namely MgO, NiO, and CoO. But also for other compounds like TiO_2 ,⁴² LTB⁴³ and $MgSO_4 \cdot H_2O$ ⁴⁴ good agreement between calculated and experimental electronic properties was obtained. The second approach is a pure DFT method within the LDA. The local exchange functional of Dirac⁵² is combined with the Vosko–Wilk–Nusair (VWN)⁵³ correlation functional. The third approach is the original PWGGA DFT method.⁴⁰

In the present study, two different basis sets were used in order to investigate the basis set dependence of calculated properties. We started from Li and B basis sets that have been optimized in previous CRYSTAL studies.⁴⁶ A 6-11G⁴⁷ basis set was used for Li, where the outer exponent has been optimized for $Li(OH) \cdot H_2O$. For boron, a 6-21G* basis⁴⁸ was used, where the outer sp exponent has been optimized for BN. In a second step a 7-11G* basis set for Li⁴⁹ from the literature was extended to 7-11G(2d) in the present study.

The inner s and sp shells remained unchanged while the outer sp and d orbitals were optimized with respect to the Li_2O total energy. The lattice parameter was fixed at 4.573 Å. This value was obtained by extrapolation of measured values^{50,51} to the athermal limit. The optimized exponents of Li 3 sp and d orbitals were 0.1539 and 0.489, respectively. The 6-21G* basis set of B was augmented with a second d shell, 6-21G(2d). An 8-411G* basis set⁴⁵ was taken for oxygen throughout. Further extension of the O basis set by including a second d shell did not change the calculated results significantly, but led to severe convergence problems of the self-consistent field procedure.

In the following we will use the notation basis set (BS) I for the combination 6-11G (Li), 6-21G*(B), 8-411G*(O), and BS II for 7-11G(2d)(Li), 6-21G(2d)(B), 8-411G*(O).

A grid of 64 k -points was used in the irreducible Brillouin zone for integration in the reciprocal space. For high accuracy of the calculation of bielectronic Coulomb and exchange series, small values of overlap thresholds were used (10^{-9} , 10^{-9} , 10^{-9} , 10^{-9} , and 10^{-18}).³⁹

III. RESULTS AND DISCUSSION

A. Structural properties

A common feature of all anhydrous lithium borate crystalline structures is the boron–oxygen anion subsystem. This subsystem forms a covalent anionic framework where the boron atoms are in different hybridization states, namely sp^2 (in BO_3) and sp^3 (in BO_4). The crystal system, space group, point group, number of atoms per unit cell, and atomic positions in the Wyckoff notation of the investigated crystals are given in Table I.

A full optimization of structures was performed in two steps. First, the atomic fractional coordinates were optimized using experimental lattice parameters. Then optimization of lattice parameters was performed with fixed fractional coordinates. This procedure was repeated until convergence of total energies and lattice parameters was achieved. The optimized lattice parameters of the $(Li_2O)_x(B_2O_3)_{1-x}$ ($x=0, 0.25, 0.33, 0.5, 0.75, \text{ and } 1.0$) crystals are compared with experimental data in Table II. It is observed that the PW1PW approach gives the best agreement with experiment. For all crystals, the deviation of lattice parameters from experimental values was less than 0.04 Å for lattice vectors and 1° for angles. Both LDA and PWGGA methods show larger deviations from experiment compared to PW1PW results. Except for Li_2O , LDA gives too small values of lattice parameters for all the crystals, whereas PWGGA gives too large values. For cubic Li_2O , both LDA and PWGGA approaches overestimate the lattice parameter a .

The extension of the Li and B basis set from BS I to II has only a small effect on the calculated lattice parameters. The exception is Li_2O where a is increased by 0.011 Å due to the additional sp and d shell at Li. The smaller effect of basis set extension on the lattice parameters of the other compounds can be explained by the fact that their structures are formed by B-O frameworks and not by Li-O bonds.

B. Electronic structure and density of states

In this section, results of PW1PW calculations for the band structure and electronic density of states for all crystals

TABLE I. Crystal system, space group, point group, number of atoms per unit cell, and atomic positions of the systems $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ investigated in this study.

	B_2O_3 ($x=0$)	LiB_3O_5 ($x=0.25$)	$\text{Li}_2\text{B}_4\text{O}_7$ ($x=0.33$)	LiBO_2 ($x=0.50$)	Li_3BO_3 ($x=0.75$)	Li_2O ($x=1$)
Crystal system	Trigonal	Orthorhombic	Tetragonal	Monoclinic	Monoclinic	Cubic
Space group	$P3_121$ (No.: 152)	$Pna2_1$ (No.: 33)	$I4_1cd$ (No.: 110)	$P2_1/c$ (No.: 14)	$P2_1/c$ (No.: 14)	$Fm-3m$ (No.: 225)
Point group	321	$mm2$	$4mm$	$2/m$	$2/m$	$m-3m$
Atoms per cell	15	36	52	16	28	3
Atomic positions	B(6c), O(6c)	Li(4a),B(4a),O(4a)	Li(16b),B(16b),O(8a,16b)	Li(4e),B(4e),O(4e)	Li(4e),B(4e),O(4e)	Li(8c),O(4a)

of the Li_2O - B_2O_3 system are presented. For brevity the figures contain only results obtained with the larger BS II.

I. Li_2O

The band structure of Li_2O was computed along the way that contains the largest number of high-symmetry points of

the Brillouin zone (BZ),⁶⁰ namely $W \rightarrow L \rightarrow \Gamma \rightarrow X \rightarrow W$. In agreement with experimental observations, we found that Li_2O is a wide-gap insulator with a Γ - Γ transition at 8.02 eV (BS II). The upper part of the valence band (VB) and the lower part of the conduction band (CB) are shown in Fig. 1(a). Our value of the band gap, 8.02 eV, agrees well with

TABLE II. Calculated lattice parameters of compounds of the Li_2O - B_2O_3 system in comparison with experimental data.

	Li_2O			B_2O_3	
	Exp.	Calc.		Exp. ⁵⁵	Calc.
a, Å	4.573 ^{50,51}	4.567 ^a /4.578 ^b	a, Å	4.336	4.351 ^a /4.359 ^b
	4.619 ⁵⁴	4.587 ^c /4.646 ^d			4.333 ^c /4.379 ^d
			c, Å	8.34	8.332 ^a /8.351 ^b 8.290 ^c /8.357 ^d
	Li_3BO_3			LiBO_2	
	Exp. ⁵⁶	Calc.		Exp. ⁵⁷	Calc.
a, Å	3.265	3.245 ^a /3.245 ^b	a, Å	5.845	5.848 ^a /5.857 ^b
		3.145 ^c /3.289 ^d			5.808 ^c /5.858 ^d
b, Å	9.180	9.160 ^a /9.163 ^b	b, Å	4.353	4.363 ^a /4.363 ^b
		9.087 ^c /9.189 ^d			4.325 ^c /4.363 ^d
c, Å	8.316	8.306 ^a /8.301 ^b	c, Å	6.454	6.444 ^a /6.434 ^b
		8.339 ^c /8.324 ^d			6.084 ^c /6.538 ^d
β , °	101.1	100.7 ^a /100.8 ^b	β , °	115.1	115.0 ^a /114.8 ^b
		101.1 ^c /100.5 ^d			114.6 ^c /114.4 ^d
	$\text{Li}_2\text{B}_4\text{O}_7$			LiB_3O_5	
	Exp. ⁵⁸	Calc.		Exp. ⁵⁹	Calc.
a, Å	9.479	9.499 ^a /9.503 ^b	a, Å	8.447	8.468 ^a /8.465 ^b
		9.466 ^c /9.549 ^d			8.408 ^c /8.483 ^d
c, Å	10.290	10.315 ^a /10.325 ^b	b, Å	7.379	7.390 ^a /7.390 ^b
		10.179 ^c /10.300 ^d			7.340 ^c /7.389 ^d
			c, Å	5.141	5.146 ^a /5.143 ^b 5.136 ^c /5.158 ^d

^aPW1PW/BS I

^bPW1PW/BS II

^cVWN/BS II

^dPWGGGA/BS II

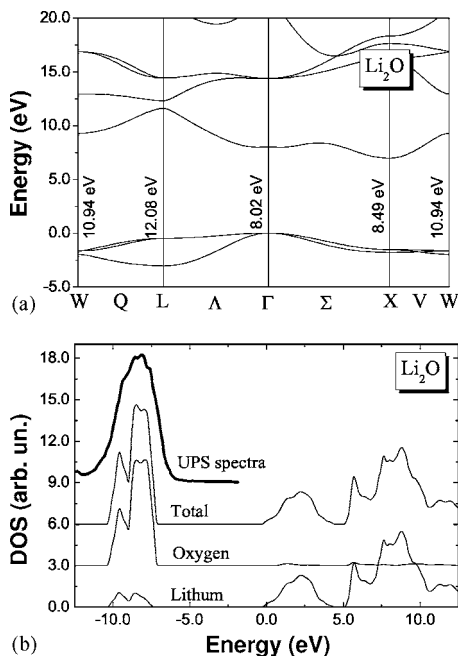


FIG. 1. Band structure (a) and density of states (b) of Li_2O .

the experimental value of 7.99 eV.²¹ The PW1PW band structure is similar to our DFT-LDA and DFT-GGA calculations and previous DFT-LDA calculations²⁷ based on the Car-Parrinello method, and to Hedin's *GW* approximation (there the band gap at Γ is 5.3 and 7.4 eV with correction, respectively). The analysis of the band structure shows that the lowest interband transition of Li_2O is indirect. The difference between the minimal direct (Γ - Γ , 8.02 eV) and minimal indirect (Γ -X, 6.97 eV) transition is significant.

In Fig. 1(b) the calculated electronic density of states (DOS) is compared with an ultraviolet photoemission spectrum (UPS).²² The experimental UPS was shifted to the calculated Fermi level which corresponds to the top of the VB in the present case. Good agreement was found between the VB widths of the calculated and the experimental spectra. The positions of the two main peaks at -8 eV and of the shoulder at -9 eV are well reproduced. The lithium DOS projection (PDOS) shows that the CB is dominated by lithium states [see Fig. 1(b)].

2. Li_3BO_3 and LiBO_2

To our knowledge, the electronic properties of Li_3BO_3 and LiBO_2 have not been investigated. Figures 2(a)–2(d) depict the electronic structure and DOS of those crystals calculated with BS II.

Both Li_3BO_3 and LiBO_2 are predicted to be wide-gap insulators. The lowest direct transition energies are 7.84 and 8.25 eV, respectively. For LiBO_2 , the VB top is at the Γ point and the CB bottom is at the B point. The Γ - B transition (8.19 eV) is slightly smaller than the Γ - Γ transition. The VB has a small dispersion indicating a large effective hole mass, which is typical for wide-gap insulators.³³ For Li_3BO_3 the Γ - Γ transition has the smallest value.

The PDOS [see Figs. 2(b) and 2(d)] reveals that the occupied states consist of $2p$ orbitals of oxygen atoms like in

the case of Li_2O . For Li_3BO_3 the main contribution to the total CB DOS is made by Li atoms, while for LiBO_2 , in turn, the states of B atoms dominate the CB.

3. $\text{Li}_2\text{B}_4\text{O}_7$ and LiB_3O_5

Experimental data for the band gap E_g of $\text{Li}_2\text{B}_4\text{O}_7$ (LTB) are lacking. Only an experimental value of the fundamental adsorption (FA) edge, $E_a=7.9$ eV, is present.³⁶ The LiB_3O_5 (LBO) band gap ($E_g=9.5$ eV) has been estimated from the measured FA edge, $E_a=7.3$.³⁴ If one takes into account the close relationship between LTB and LBO for luminescence properties,^{61,62} the E_g of LTB can be estimated as about 9 eV from the difference between the two E_a values.

The calculated band structure of LTB and LBO along selected high-symmetry lines within the first Brillouin zone⁶⁰ is given in Figs. 2(e) and 2(g). Both the VB and the CB have only small dispersion indicating the large effective masses for the charge carriers as found before for other crystals of the Li_2O - B_2O_3 system. The lowest interband transition is indirect for both LTB and LBO. The VB top of LTB (LBO) is at point M (Γ) and the CB bottom of CB is at point Γ (Z). The value of the smallest vertical Γ - Γ transition is 8.87 and 9.00 eV for LTB and LBO, respectively. These values are in reasonable agreement with the estimated E_g values from experimental data, 9 and 9.5 eV, respectively.

The shape of the calculated conduction band for LBO agrees with a previous LDA-DFT calculation⁶³ where the CB bottom is at Z point, but disagrees with the result of a plane-wave DFT calculation⁶⁴ where the CB bottom is found at Γ point. A possible explanation for the observed difference is the replacement of inner electrons of Li, B, and O by effective core potentials in the plane wave calculations,⁶⁴ while in the present PW1PW calculations all electrons are treated explicitly. In order to investigate this possibility we performed a PW1PW CRYSTAL calculation where the inner $1s$ electrons of Li, B, and O were replaced by an effective core potential (Durand and Barthelat⁶⁵). The valence electrons were described with the corresponding standard basis sets. In this case the calculated CB has a similar shape as found in Ref. 64. This indicates a possible effect of the approximate description of the core electrons on the band structure of LBO.

The comparison of the calculated DOS with experimental data^{32,66} from X-ray photoelectron spectroscopy (XPS) are shown in Fig. 2(f) for $\text{Li}_2\text{B}_4\text{O}_7$ and in Fig. 2(h) for LiB_3O_5 . The XP spectra were shifted to the calculated Fermi level which corresponds to the top of VB. A good agreement with experiment was obtained for the band widths and the relative positions of the main peaks. LTB and LBO have very sharp VB and CB edges. The top of the VB mainly consists of oxygen $2p$ states for both crystals. The contributions of other atoms [Li, B_1 (boron in BO_3 units), and B_2 (boron in BO_4 units)] are ten times smaller than the oxygen PDOS. The valence band width is about 10 eV for both LTB and LBO. The states between -24 and -30 eV correspond to O $2s$ orbitals. The CB bottom of both crystals is dominated by the contributions from B_1 atoms. It should be noted that states of Li and B_2 atoms are not involved in band-band transitions

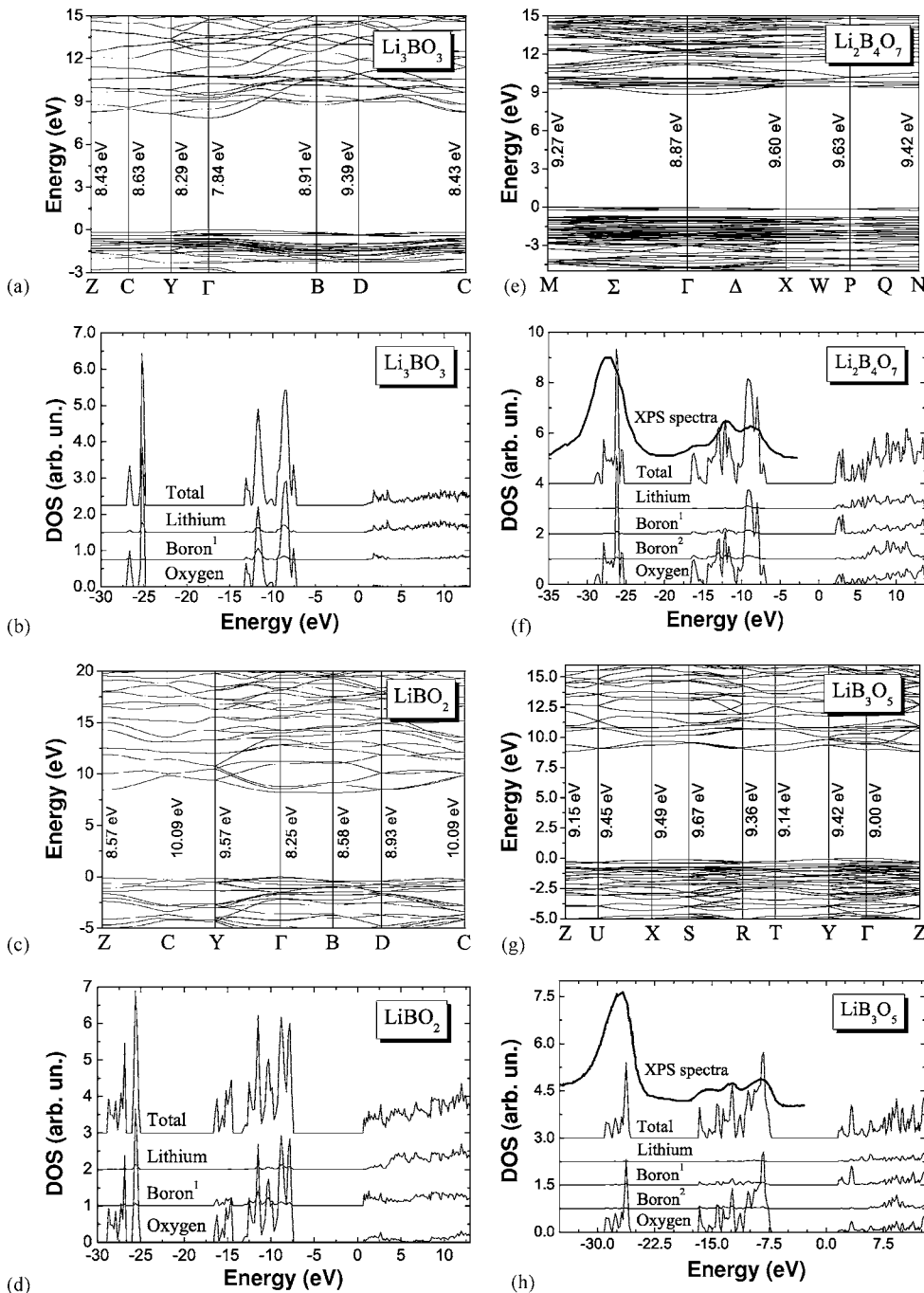


FIG. 2. Band structure (a),(c),(e),(g) and density of states (b),(d),(f),(h) for $\text{Li}_2\text{O-B}_2\text{O}_2$ compounds.

since the contribution in the lower part of CB of these atoms is very small.

4. B_2O_3

The calculated band structure (PW1PW results, BS II) along the high-symmetry axes of the BZ⁶⁰ for B_2O_3 is shown in Fig. 3(a). This system is a wide-gap insulator. The top of the VB is at a point along A - L direction and the bottom of CB is at A . The minimal direct transition corresponds to A - A with 9.05 eV and the smallest indirect transition is 8.81 eV. Both bands are very flat with small dispersion. Our calculated band gap, 9.05 eV, is larger than the result of a previous LDA study (6.2 eV).³⁷ This difference is due to the

different level of theory and not to other computational details of the two studies. If we use the BS I with LDA exchange and VWN correlation,⁵³ we receive a band gap of 6.29 eV which is close to the previous LDA result. Since it is known that one-electron energies computed at LDA level strongly underestimate the band gap, we conclude that the PW1PW value is more accurate.

The DOS and PDOS of B_2O_3 together with an experimental PE spectrum are given in Fig. 3(b). As for the other systems there is good agreement of the band widths and the relative positions of main peaks between the theoretical (PW1PW) and the experimental spectra. The oxygen 2p states have the major contribution in the VB, similar to Li_2O .

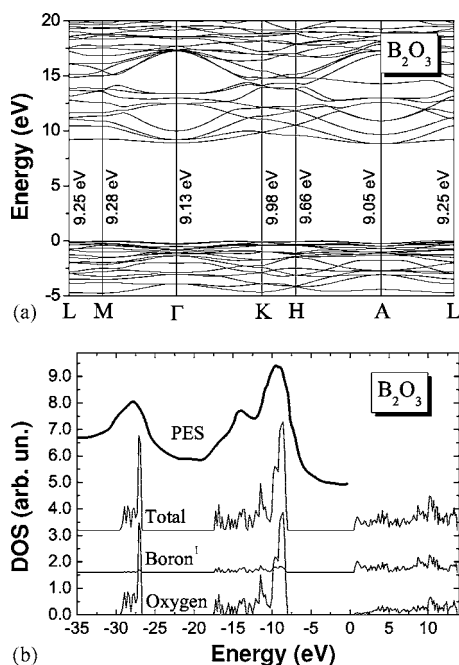


FIG. 3. Band structure (a) and density of states (b) of crystalline B_2O_3 .

The CB consists of boron $2p$ states. The semicore states at about -27 eV correspond to $2s$ oxygen orbitals.

C. General trends for electronic properties of the compounds in the Li_2O - B_2O_3 system

After analysis of all electronic spectra of the systems $(Li_2O)_x(B_2O_3)_{1-x}$ with $x=0.0, 0.25, 0.33, 0.5, 0.75,$ and 1.0 it is possible to draw the following conclusions:

The PW1PW approach in connection with the extended BS II gives reasonable values for the band gaps of all crystals of the Li_2O - B_2O_3 system where comparison with experiment is possible.

The upper part of the VB of all compounds of the Li_2O - B_2O_3 system mainly consists of oxygen $2p$ states. The major contribution to the CB is from the $2p$ states of boron atoms. Only for Li_2O and Li_3BO_3 the contribution of Li $2p$ is essential, because the concentration of Li atoms is large.

TABLE III. Basis set dependence of minimal vertical electronic transition (MVT) and minimal transition (MT) energies ΔE (eV) for the systems $(Li_2O)_x(B_2O_3)_{1-x}$ ($x=0, 0.25, 0.33, 0.5, 0.75,$ and 1).

	B_2O_3 ($x=0$)	LiB_3O_5 ($x=0.25$)	$Li_2B_4O_7$ ($x=0.33$)	$LiBO_2$ ($x=0.50$)	Li_3BO_3 ($x=0.75$)	Li_2O ($x=1$)
MVT	A-A	Γ - Γ	Γ - Γ	Γ - Γ	Γ - Γ	Γ - Γ
ΔE^a	9.08	9.20	9.41	8.40	8.67	8.37
ΔE^b	9.05	9.00	8.87	8.25	7.84	8.02
MT	AL-A	Γ -Z	M- Γ	Γ -B	Γ - Γ	Γ -X
ΔE^a	8.86	8.93	9.35	8.32	8.67	7.58
ΔE^b	8.81	8.85	8.81	8.19	7.84	6.97

^aPW1PW/BS I

^bPW1PW/BS II

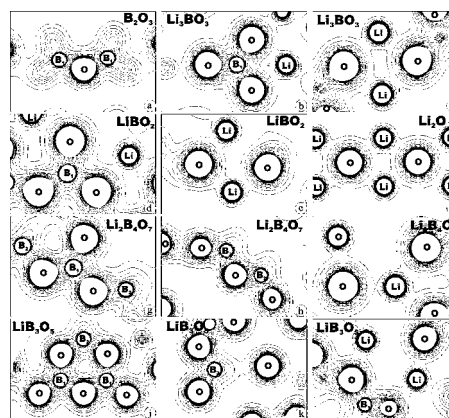


FIG. 4. Electronic charge density distribution for compounds of the Li_2O - B_2O_3 system. The contour lines are in the range from 0.0 to $0.3 e/\text{\AA}^3$ with steps of $0.02 e/\text{\AA}^3$.

Practically all $(Li_2O)_x(B_2O_3)_{1-x}$ compounds (except Li_3BO_3) are indirect insulators.

The minimum value of the vertical transition (see Table III) decreases with increasing Li_2O concentration. This can be the result of increasing B-B distances which reduces the interaction between B atoms or in general between BO_n ($n=3$ or 4) units;

D. Charge distributions

In the following the bonding picture of the systems $(Li_2O)_x(B_2O_3)_{1-x}$ is illustrated by charge density distribution maps along specific crystallographic planes. We choose three types of planes which describe the three main types of bonds, B₁-O, B₂-O, and Li-O. B¹ and B² represent the boron atoms in BO_3 and BO_4 units, respectively. The charge density distribution maps for compounds of the Li_2O - B_2O_3 system are shown in Fig. 4.

In Figs. 4(a), 4(b), 4(d), 4(g), and 4(j) the charge density distributions in the O-B₁-O or B₁-O-B₁ planes are shown for B_2O_3 , LiB_3O_5 , $LiBO_2$, $Li_2B_4O_7$, and Li_3BO_5 . The charge density distributions are similar for all compounds. The same situation is present for other planes, O-Li-O [Figs. 4(c), 4(e), 4(f), 4(i), and 4(l)] and O-B₂-O [Figs. 4(h), 4(j), and 4(k)]. For all B₁-O and B₂-O bonds, the charge distribution of O is

TABLE IV. Averaged Mulliken charges for the compounds of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system obtained with different basis sets BS.

Atoms BS	Li_2O		Li_3BO_3		LiBO_2		$\text{Li}_2\text{B}_4\text{O}_7$		$\text{Li}_2\text{B}_4\text{O}_7$ (Exp. ^a)	LiB_3O_5		B_2O_3	
	I	II	I	II	I	II	I	II		I	II	I	II
Li	0.70	0.57	0.79	0.55	0.86	0.60	0.85	0.63	0.8 ± 0.1	0.83	0.59		
B			1.36	1.74	1.48	1.73	1.39	1.60	1.23 ± 0.05	1.38	1.60	1.44	1.68
O	-1.39	-1.14	-1.24	-1.13	-1.17	-1.16	-1.04	-1.09	-0.93 ± 0.01	-1.00	-1.08	-0.96	-1.12

^aReference 69.

deformed towards the boron atoms. This, according to Bader analysis,⁶⁷ shows that the bonds in the triangular BO_3 and tetrahedral BO_4 groups have covalent character. The Li-O bonds show a different behavior. The charge distribution of both Li and O atoms is almost spherical and the magnitude of the charge density between these two atoms is small which indicates that the interaction is mainly ionic.

An investigation of critical points (in our case saddle points) of the electron density⁶⁷ for the $\text{B}_1\text{-O}$ and $\text{B}_2\text{-O}$ bonds yields that the $\text{B}_1\text{-O}$ bond is stronger than the $\text{B}_2\text{-O}$ bond for all exchange-correlation functionals. The electron density along the line $\text{B}_1\text{-O}$ is larger than that along $\text{B}_2\text{-O}$ at the corresponding critical points by 0.033 a.u. for PW1PW, 0.032 a.u. for PWGGA and 0.030 a.u. for VWN. This trend was expected because the sp^2 hybridization (B_1) is more natural than the sp^3 hybridization (B_2) for boron.

The calculated atomic Mulliken charges⁶⁸ for Li_2O , Li_3BO_3 , LiBO_2 , $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 , and B_2O_3 obtained with PW1PW using the two basis sets I and II are given in Table IV. The atomic charges obtained with BS II and PWGGA and VWN are comparable with PW1PW/BS II results. The Mulliken charges of $\text{Li}_2\text{B}_4\text{O}_7$ agree with charges derived from the longitudinal optical and transverse optical splitting (LO-TO) in Raman spectroscopy.⁶⁹ The charge of the oxygen atom, obtained with the less diffuse BS I, increases with increasing mole fraction of Li_2O . The same tendency was obtained with a simple pair potential model.⁷⁰ A correlation exists between q_{O} and q_{Li} , which expresses qualitatively the charge transfer between different ions. We suggest that the q_{O} dependence on $x(\text{Li}_2\text{O})$ is the result of a change in oxygen coordination by lithium atoms, which decreases from 8 for LiBO_2 to 5 for LiB_3O_5 , and becomes zero for B_2O_3 . The only exception is for Li_2O where the oxygen atoms are not connected with B atoms, and Li_3BO_3 where they do not connect two BO_i ($i=3$ or 4) units, respectively. Therefore, oxygen interacts more with the Li_2O atoms in Li_2O and Li_3BO_3 than in the other crystals. Hence, the charges q_{O} and q_{Li} are smaller for these compounds. The absence of q_{O} dependence from mole fraction of Li_2O obtained with the larger BS II can be explained by the known deficiencies of the Mulliken analysis for diffuse basis functions.

IV. SUMMARY

A systematic study of the geometry, the band structure, electronic density of states, and charge density distribution

was performed for six compounds of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system. The basis set effect on structural and electronic properties was investigated. It was found that the addition of polarization and diffuse basis functions to Li and B atoms leads to a significant improvement of the calculated electronic spectra, while the effect on structure parameters is small.

In particular, the small effect of Li basis extension on optimized lattice vectors and fractional coordinates for all $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ with $x < 1$ is in line with the fact that these crystal structures are dominated by B-O frameworks. This also agrees with the analysis of electron charge density distribution. It was observed that the charge distribution for the main types of bonds in all compounds is similar. According to a Bader analysis of critical points along the B-O bonds, the $\text{B}_1\text{-O}$ and B-O bonds have a predominantly covalent character while Li-O is an ionic bond. Moreover, the $\text{B}_1\text{-O}$ bond is stronger than the $\text{B}_2\text{-O}$ bond. Due to the observed similarity of the charge distribution for all $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ compounds we suggest that for other alkali and alkali-earth borates, the main structural unit is the B-O subsystem and the metal-oxygen bond might also have an ionic character.

A good agreement between theory and experiment was obtained for the band gap of Li_2O (calc. 8.02 eV, exp. 7.99 eV). We also predict the band gaps of the $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ ($x=0, 0.25, 0.33, 0.5, \text{ and } 0.75$) compounds. The observed monotonous dependence of the minimum electron transition energy from $x(\text{Li}_2\text{O})$ allows to estimate the band gap for other compounds of the binary system. The dependence is supposed to be a result of decreasing $\text{BO}_i\text{-BO}_j$ ($i, j=3$ or 4) interaction due to increasing boron-boron distance. A good agreement between calculated charges and charges derived from the LO-TO splitting in Raman spectra for $\text{Li}_2\text{B}_4\text{O}_7$ crystal has been obtained.

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