



# Role of oxygen on the optical properties of borate glass doped with ZnO

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## ABSTRACT

Lithium tungsten borate glass  $(0.56 - x)\text{B}_2\text{O}_3 - 0.4\text{Li}_2\text{O} - x\text{ZnO} - 0.04\text{WO}_3$  ( $0 \leq x \leq 0.1$  mol%) is prepared by the melt quenching technique for photonic applications. Small relative values of ZnO are used to improve the glass optical dispersion and to probe as well the role of oxygen electronic polarizability on its optical characteristics. The spectroscopic properties of the glass are determined in a wide spectrum range (200–2500 nm) using a Fresnel-based spectrophotometric technique. Based on the Lorentz–Lorenz theory, as ZnO content increases on the expense of  $\text{B}_2\text{O}_3$  the glass molar polarizability increased due to an enhanced unshared oxide ion 2p electron density, which increases ionicity of the chemical bonds of glass. The role of oxide ion polarizability is explained in accordance with advanced measures and theories such as optical basicity, O 1s binding energy, the outer most cation binding energy in Yamashita–Kurosawa's interionic interaction parameter and Sun's average single bond strength. FT-IR measurements confirm an increase in bridging oxygen bonds, as a result of replacement of ZnO by  $\text{B}_2\text{O}_3$ , which increase the UV glass transmission window and transmittance.

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## 1. Introduction

Beside the high transparent window in the region from 370 nm to 2.2  $\mu\text{m}$  [1], zinc borate glasses are attractive host materials to incorporate rare earth elements for optoelectronics and optical fibers, which have a large core diameter. Zinc borate glass fibers can be integrated in telecommunication systems between expensive quartz fibers and high-loss polymer fibers. The spectral properties of zinc borate glasses are different than that of crystal [2], where the glass is containing a relative small fraction of tetrahedral coordinated boron.

$\text{W}^{5+}$  ion is a paramagnetic ion used in borate glasses for photonic devices, where the glasses exhibit photochromism and electrochromism properties [3]. The structural groups of  $\text{WO}_3$  are expected to alternate with  $\text{BO}_3$  and  $\text{BO}_4$  structural groups influencing the physical properties of borate glasses to a large extent [4]. The tungsten ions exist in different valence states such as  $\text{W}^{6+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{4+}$  state as per the following thermo-reversible disproportionate reaction [5,6]:  $\text{W}^{5+} + \text{W}^{5+} \rightleftharpoons \text{W}^{4+} + \text{W}^{6+}$ . The presence of  $\text{WO}_3$  in ZnO mixed borate glasses provides the highest forming ability with the highest covalent environment for tungsten ions [4].

Lithium oxide increases the glass forming ability with increasing the non-bridging oxygen bonds.  $\text{Li}_2\text{O}$  ions are also lowering the glass transition temperature, which in turn increases the

thermal stability of the glass and increases its transmission [7]. In comparison to all other alkali ions,  $\text{Li}_2\text{O}$  ions could also increase the luminescence intensity in zinc borate glasses doped with rare earth metals [8] due to the smallest  $\text{Li}^+$  ionic radius  $r$  (0.78 Å). The ratio  $r(\text{Li}^+)/r(\text{O}^{2-})=0.59$  shows the possibility that lithium may present the coordination numbers (CN)=4 and 6 in relation with oxygen [9], where for other alkali ions  $\text{CN} \geq 6$ . Lithium ion has also the biggest field strength (0.23) for single bond strength Li–O (150.5 kJ/mol), the smallest cation–anion distance (2.1 Å) for CN=6 and the highest electronegativity (Pauling), therefore, the Li–O bond presents the most prominent covalent character.

Furthermore, compounds containing cations with an outer electron shell of 18 ( $\text{Zn}^{2+}$ ) or 18+2 electrons ( $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Bi}^{3+}$ ) have higher polarizability and lower melting temperatures [10]. Thus many studies on the structure and properties of ZnO-containing lithium borate glasses have been reported [2,10–12]. However, information on the role of oxide ion on the optical properties of these glasses is actually poor.

In the present work, zinc oxide is used to probe the role of oxygen on the optical characteristics of the lithium tungsten borate glasses. The probing process is done through the investigation of optical basicity, the O 1s binding energy and outer most cation binding energy in Yamashita–Kurosawa's interionic interaction parameter, and the average single bond strength of the charge overlapping between electronic shells of the oxide ion and cation. The enhanced unshared oxide ion 2p electron density for donation increased the ionicity of the chemical bonds and hence the refractive index of the oxide glasses. FT-IR absorption spectra

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are used to analyze the glass structure as a result of replacement of ZnO by B<sub>2</sub>O<sub>3</sub>, and to explain the change in the glass transmittance through determination non-bridging oxygen bonds (NBO).

## 2. Experimental

### 2.1. Glass preparation

A series of zinc lithium tungsten borate glasses of composition  $(0.56-x)\text{B}_2\text{O}_3-0.4\text{Li}_2\text{O}-x\text{ZnO}-0.04\text{WO}_3$  ( $0 \leq x \leq 0.1$  mol%) is prepared. The materials used are of chemically pure grade, in the form of H<sub>3</sub>BO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, WO<sub>3</sub> and ZnO. The amount of the glass batch is 50 g melt<sup>-1</sup>. The glass is prepared by melt quenching technique using platinum 2% rhodium crucibles in an electric furnace. The batch is pre-heated at 500–600 °C for almost an hour to evaporate the carbonates. The temperature of melting is 950–1000 °C, the duration of melting is one hour after the last traces of batches are disappeared. To avoid the presence of bubbles the glasses were continue stirred during the glass preparation. Then the melt is poured onto stainless steel mold and then annealed at around 350 °C to remove thermal strains. Optical slabs are prepared by grinding and polishing of the prepared samples with paraffin oil and minimum amount of water. The thickness of the glass slabs is about 3 mm. Polishing is completed with stannic oxide and paraffin reaching a surface roughness less than  $\lambda/3$ , which is tested by interferometric method. The homogeneity of the glasses is examined using two crossed polarizers.

### 2.2. Spectrophotometric measurements

Computer aided two-beam spectrophotometer (Shimadzu 3101PC UV–vis NIR) was used to record the reflectance,  $R$ , and the transmittance,  $T$ , data of the slab plane-parallel glass samples. A resolution limit of 0.2 nm and a sampling interval of 2 nm were used for the different 1401 measuring points. The accuracy of measuring  $R(\lambda)$ , and  $T(\lambda)$  is 0.003 with the incident beam making an angle of  $5.0^\circ \pm 0.1^\circ$  to the normal to external slab faces. The measurements were carried out at room temperature for the entire spectral range 0.2–2.5  $\mu\text{m}$ .

### 2.3. Measurement of density

The density of the glasses at room temperature is measured by the Archimedes principle using a sensitive microbalance with xylene as an immersion liquid. The density,  $D$ , is calculated using the formula

$$D = \frac{W_1}{W_1 - W_2} \times 0.864 \quad (1)$$

where  $W_1$  is the weight of sample in air,  $W_2$  the weight of sample in xylene and 0.864 is the density of xylene. Table 1 lists the measured density values for the different prepared glass samples. The error in measuring the glass density is 0.001 g/cm<sup>3</sup>.

### 2.4. FT-IR absorption measurements

Infrared absorption measurements are recorded for the present glass compositions in the range of (4000–400 cm<sup>-1</sup>) using a Jasco FT/IR-300E infrared spectrophotometer. Alkali halide disk-technique at room temperature was used. Well-dried and ground glasses were mixed with well-dried infrared grade potassium bromide and then sufficiently ground to obtain a homogeneous mixture of minimum particle size. The mixture was mechanically pressed at 70-MPa pressure in the form of disks.

## 3. Results and discussion

### 3.1. Density and molar volume

It can be seen from Table 1 that, increasing ZnO content leads to a gradual increase in the glass density. So addition of ZnO to the lithium tungsten borate network causes some type of structural rearrangement of the atoms. There is a possibility for the alteration of the geometrical configuration upon substitution of ZnO into the glass network. Since the density of ZnO is 5.606 g/cm<sup>3</sup> while for B<sub>2</sub>O<sub>3</sub> is 2.55 g/cm<sup>3</sup>, so the replacement of zinc oxide by boron oxide explains obviously such increase in the glass density with increasing ZnO content in glass. Such increase in glass density gives evidence to the subsequent increase in glass refractive index [13], as it will be seen later.

The molar volume,  $V_m$ , of a given glass composition can be calculated using the following expression:

$$V_m = \sum_i \frac{M_i}{C_i} \quad (2)$$

where  $M_i$  denotes the molar mass of the glass, which is equal to  $C_i A_i$ . Here  $C_i$  and  $A_i$  are the molar concentration and the molecular weight of the  $i$ th component, respectively. As shown in Table 1, a decrease in the value of molar volume of the glass as the ZnO content increases, this means that the glass becomes more compact. This indicates that Zn<sup>2+</sup> has a contracting effect leading to the increase in the glass density. The decrease in the bond length or inter-atomic spacing between the atoms may be attributed to the increase in the stretching force constants of the bonds inside the glass network.

The average boron-boron separation  $\langle d_{B-B} \rangle$  is calculated to give more insight on the modification of the glass network due to the presence of ZnO. The boron atoms are the central atoms BO<sub>3/2</sub> with negatively charged tetrahedral BO<sub>4/2</sub> units, thus the volume  $V_m^B$ , which corresponds to the volume that contains one mole of boron atoms within the given glass structure is fined as [14]

$$V_m^B = \frac{V_m}{2(1-x_B)} \quad (3)$$

where  $x_B$  is the molar fraction of B<sub>2</sub>O<sub>3</sub> oxide. The average boron-boron separation  $\langle d_{B-B} \rangle$  is calculated using the expression [14]

$$\langle d_{B-B} \rangle = \left( \frac{V_m^B}{N_A} \right)^{1/3} \quad (4)$$

where  $N_A$  is Avogadro's number ( $6.0228 \times 10^{23}$  g/mol). Table 1 lists the calculated values of average boron-boron separation. Since  $V_m^B$

**Table 1**

Table lists glass compositions, glass density, molar volume, boron-boron separation, cutoff wavelength, refractive index and Cauchy's dispersion parameters.

S	D (g/cm <sup>3</sup> )	V <sub>m</sub> (cm <sup>3</sup> /mol)	d <sub>B-B</sub> (nm)	λ <sub>cuf</sub> (nm)	n at λ=587.56 nm	A	B (nm <sup>2</sup> )
0.56B <sub>2</sub> O <sub>3</sub> -0.4Li <sub>2</sub> O-0.04WO <sub>3</sub>	2.551	23.60	0.354	396	1.415	1.41	1838.5
0.52B <sub>2</sub> O <sub>3</sub> -0.4Li <sub>2</sub> O-0.04ZnO-0.04WO <sub>3</sub>	2.602	23.31	0.343	362	1.466	1.43	12400
0.48B <sub>2</sub> O <sub>3</sub> -0.4Li <sub>2</sub> O-0.08ZnO-0.04WO <sub>3</sub>	2.673	22.87	0.332	336	1.490	1.4442	14158.9
0.46B <sub>2</sub> O <sub>3</sub> -0.4Li <sub>2</sub> O-0.12ZnO-0.04WO <sub>3</sub>	3.064	20.03	0.313	328	1.581	1.5447	12826

depends on cation species, therefore, with the increase in the ZnO content a decrease in the average boron-boron separation is obtained. Thus, the incorporation of ZnO on expense of B<sub>2</sub>O<sub>3</sub> leads to a substantial densification of the glass structural network, which confirms the obtained density and molar volume values. Such densification can also explain the prospect increase in the values of refractive index with the addition of ZnO.

### 3.2. Transmittance and reflectance

The wide range spectra of the measured transmittance  $T$  and reflectance  $R$  for the different glass composition are shown in Fig. 1. The transmittance exhibits two steep depressions around 300 nm and 2500 nm indicating the existence of two strong absorption bands at UV (representing electronic excitation) and at IR region of spectrum for structural vibrational modes. Through the reflectance two shallow depressions exist. The transmission is increased up to more than 90% in sample 4 (0.46B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O–0.1ZnO–0.04WO<sub>3</sub>). The variation in the transmittance and reflectance values with the change of ZnO/B<sub>2</sub>O<sub>3</sub> ratio of glass-forming agent (B<sub>2</sub>O<sub>3</sub>) can be attributed to a variation in the ratio between trigonal BO<sub>3/2</sub> and anionic tetrahedral BO<sub>4/2</sub> units of the glass network [14,15].

The UV cutoff wavelengths,  $\lambda_{\text{cuf}}$ , of the different glasses are listed in Table 1. Such decrease in  $\lambda_{\text{cuf}}$  values with the increase of ZnO content on the expense of B<sub>2</sub>O<sub>3</sub> content could be attributed to variation in the density of bridging oxygen's bonds (BO) [16], as will be seen hereinafter from the FT-IR absorption measurements. Since ZnO has a relative small ionic cation radius (0.074 nm), it should facilitate the transformation of part of BO<sub>4</sub> groups into BO<sub>3</sub> groups, which produces a certain decrease in the number of non-bridging oxygen bonds NBO relative to (BO). This manifests itself by the blue shift in  $\lambda_{\text{cuf}}$  value. With a continuous increase in the ratio of ZnO/B<sub>2</sub>O<sub>3</sub>, zinc oxide is capable of forming its own structure of zinc–borate complexes with an increase in BO's density, which is accomplished by the blue shift for the UV cutoff wavelengths (UV absorption edge). Thus, ZnO has increased the glass transmittance and widen its transmission window.

### 3.3. Dispersion and quantum parameters of glasses

The different linear and nonlinear optical applications of the glass require information about its refractive index and dispersion

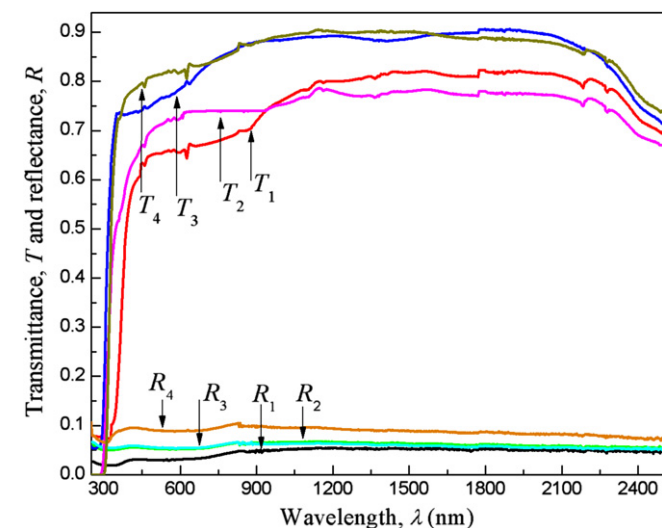


Fig. 1. Transmittance,  $T$ , and reflectance,  $R$ , of the studied glass system (0.56– $x$ )B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O– $x$ ZnO–0.04WO<sub>3</sub>. In sample 1 the ZnO content in mol%  $x=0$ , sample 2:  $x=0.04$ , sample 3:  $x=0.08$  and in sample 4:  $x=0.1$ .

[17]. Applying Fresnel's theory, the glass refractive index,  $n$ , is determined by means of an iteration technique [18] using the transmittance and reflectance recorded data. The estimated error in the index of refraction is  $\pm 0.005$ . The portion of the dispersion curve in-between the anomalous-dispersion branches are known to present a normal dispersion obeying, as good approximation, the empirical Cauchy dispersion relation [18]

$$n^2 = A + B/\lambda^2 \quad (5)$$

where  $\lambda$  is the wavelength, and  $A$ ,  $B$  are the Cauchy coefficients, which characterize the material. These coefficients are defined as

$$A = 1 + \sum_{j=i+1}^{\infty} a_{ij}, \quad B = \sum_{j=i+1}^{\infty} a_{ij} \lambda_{ij}^2 \quad (6)$$

where  $a_{ij} = r_e N f_{ij} \lambda_{ij}^2 / 2\pi$  and  $r_e = 2.818 \times 10^{-13}$  cm is the radius of an excited electron experiencing a transition from a lower energy level,  $i$ , to a higher level,  $j$ , by absorbing a photon associated with a transition wavelength  $\lambda_{ij}$ .  $N$  is the atomic number density. The oscillator strength,  $f_{ij}$ , is a fraction of  $N$ , which takes part in a given  $i \rightarrow j$  transition. Fig. 2 illustrates the calculated refractive indices and their dispersion in a very wide range of spectrum. An increase in the glass refractive index is seen as the ratio of ZnO/B<sub>2</sub>O<sub>3</sub> increases. The glass refractive indices at the standard sodium  $d$ -line ( $\lambda=587.56$  nm) in comparison with the equivalent fraction of ZnO and the Cauchy parameters of the studied glasses are listed in Table 1. As shown in Fig. 3 the refractive index is increased up to 11.7% with 0.1 mol% of ZnO or with ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%. This reveals the large effect of zinc oxide on the lithium tungsten borate glass index of refraction and dispersion.

### 3.4. Molar polarizability

The B<sup>3+</sup> ion has 0.27 Å cation ionic radius and 0.008 Å<sup>3</sup> bond polarizability; whereas the ionic radius of Zn<sup>2+</sup>=0.74 Å with 0.8 Å<sup>3</sup> bond polarizability [19]. The field strength of the divalent modifier ion, Zn<sup>2+</sup>, is 54.78 Å<sup>–2</sup>, which is less than that of the trivalent former ion, B<sup>3+</sup>, 68.59 Å<sup>–2</sup>. This means that Zn<sup>2+</sup> ion is much more polarizable than B<sup>3+</sup> ions and thus Zn<sup>2+</sup> increases directly the glass index of refractive.

Furthermore, the refractive index is related to the density and molar electronic polarizability ( $\alpha_m$ ) through the Lorentz–Lorenz

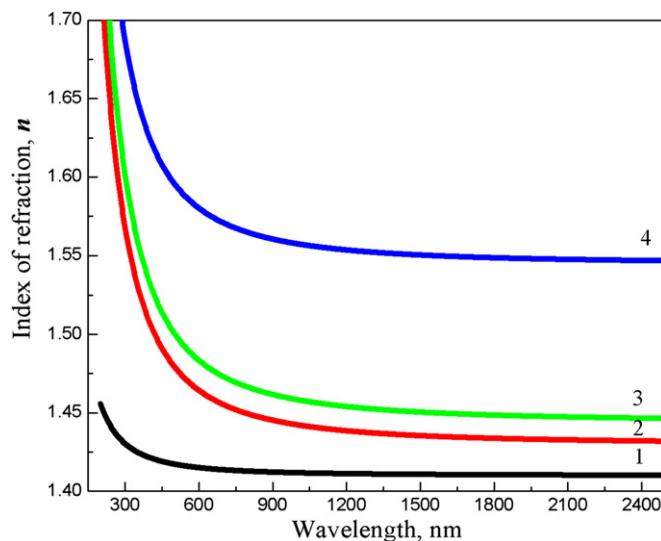


Fig. 2. Dispersion of refractive index versus wavelength for the investigated glass system (0.56– $x$ )B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O– $x$ ZnO–0.04WO<sub>3</sub>. In case of sample 1 the ZnO content in mol%  $x=0$ , sample 2:  $x=0.04$ , sample 3:  $x=0.08$  and in sample 4:  $x=0.1$ .

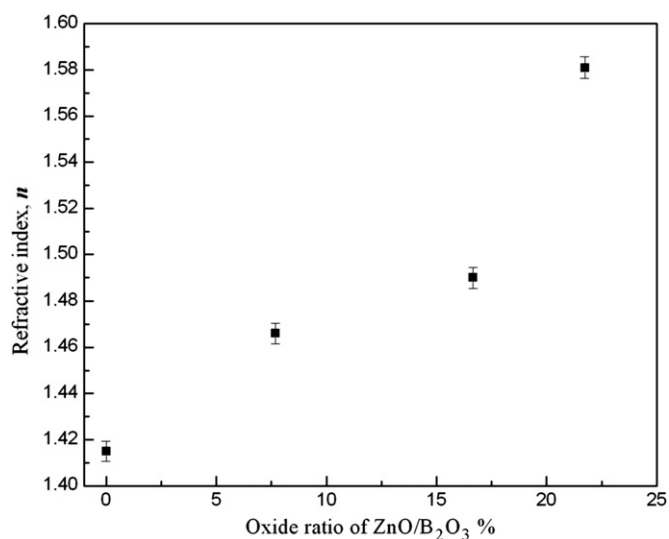


Fig. 3. The increase in glass index of refraction variation versus the increase in the ratio of ZnO/B<sub>2</sub>O<sub>3</sub> content.

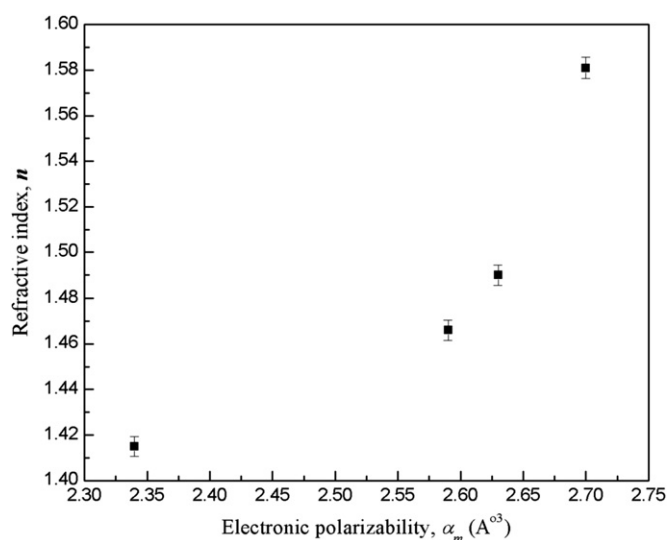


Fig. 4. Variation of refractive index of the glass with the change in glass molar polarizability. The index is increased up to 1.581 with the increase in molar polarizability to 2.7 Å<sup>3</sup> at ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%.

equation [20]

$$\frac{(n^2-1)}{(n^2+2)} = \frac{4\pi}{3} N_A \alpha_m \frac{D}{M} \quad (7)$$

where *M* is the molar mass of glass composition and *D* is the glass density. The molar reflectivity term  $(n^2-1)/(n^2+2)$  increases with increasing the value of refractive index where *n* > 1. As shown in Fig. 4, with addition of ZnO instead of boron oxide up to 0.1 mol% or with ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%, the value of glass molar polarization  $\alpha_m$  increased to be 15.4%.

### 3.5. Electronic polarizability of oxygen in the glass system

Electronic polarizability or the oxide ion polarizability is one of the most important properties of materials in the field of optics and opto-electronics. Since the molar polarizabilities are additive quantities for a multi-component system, so the molar electronic polarizability can also be expressed as the sum of the electronic

polarizabilities of contributed ions by the following equation:

$$\alpha_m = N_O \alpha_O^{2-} + \sum_i N_i \alpha_i \quad (8)$$

where *N<sub>O</sub>* and *N<sub>i</sub>* are the numbers of oxygen ions and cations, respectively. Also  $\alpha_O^{2-}$  and  $\alpha_i$  are the electronic polarizabilities of an oxygen ion and a cation. The values of *N<sub>O</sub>* and *N<sub>i</sub>* can be obtained from chemical compositions. The required values of  $\alpha_i$  are 0.024 Å<sup>3</sup> for Li<sup>+</sup>, 0.002 Å<sup>3</sup> for B<sup>3+</sup>, 0.283 Å<sup>3</sup> for Zn<sup>2+</sup> and for 0.147 Å<sup>3</sup> for W<sup>6+</sup> [19,21]. Thus, a value for  $\alpha_O^{2-}$  of the glass can be calculated using Eq. (8). As the ratio of ZnO/B<sub>2</sub>O<sub>3</sub> in the studied glasses composition increases the electronic polarizability of the oxygen ion increases as well, see Fig. 5. It can be seen that the oxide ion polarizability,  $\alpha_O^{2-}$ , is increased to reach 25.7% with 0.1 mol% ZnO or with the maximum ratio of ZnO/B<sub>2</sub>O<sub>3</sub>=21.7% in the glass composition.

### 3.6. Optical basicity

Duffy et al. [22] proposed the concept of optical basicity, which permits a comparison of the acid–base character of oxides. The optical basicity, *A*, of an oxidic medium, is the average electron donor power of all the oxide atoms comprising the medium. Increasing basicity results in increasing the negative charge on the oxygen atoms and, accordingly, increasing covalency in the oxygen–cation bonding. The optical basicity can be calculated from the glass composition and from the basicity moderating parameters of the different cations present. The theoretical optical basicity, *A<sub>th</sub>*, is calculated using the following expression [23]:

$$A_{th} = \sum_i x_i A_i \quad (9)$$

where *x<sub>1</sub>*, *x<sub>2</sub>*, ..., *x<sub>n</sub>* are equivalent fractions (mol%) of different oxides, i.e., the amount of oxygen each oxide contributes to the overall glass stoichiometry and *A<sub>1</sub>*, *A<sub>2</sub>*, ..., *A<sub>n</sub>* are the optical basicity values assigned to the constituent oxides. Taking sample 1 (0.56B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O–0.04WO<sub>3</sub>) as an example, the number of oxygen is (40+4×3+56×3)=220. It follows that *x<sub>1</sub>* for Li<sub>2</sub>O is 40/220, *x<sub>2</sub>* for WO<sub>3</sub> is (4×3)/220 and *x<sub>3</sub>* for B<sub>2</sub>O<sub>3</sub> is (56×3)/220. The used values of optical basicity for the different constituent oxides in the present glass are: 0.43, 1.00, 0.95 and 1.045 for B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, ZnO and WO<sub>3</sub>, respectively [21]. The calculated optical basicity of

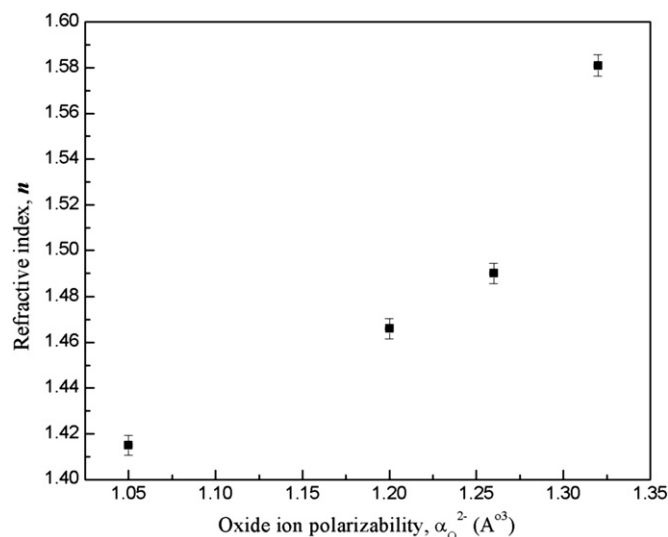
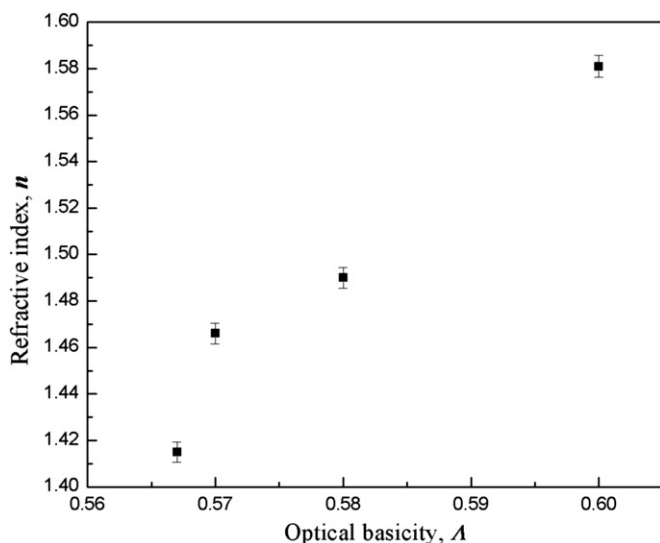


Fig. 5. The increase in glass index of refraction as a function of oxide ion polarizability. Maximum refractive index (1.581) is obtained with oxide ion polarizability=1.32 Å<sup>3</sup> at ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%.





**Fig. 6.** The effect of change glass optical basicity on its index of refraction. The glass refractive index (1.581) is gained with optical basicity=0.6 with ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%.

investigated glasses is shown in Fig. 6. The insertion of ZnO oxide on the expenses of B<sub>2</sub>O<sub>3</sub> increased the optical basicity to be 5.8% with ZnO/B<sub>2</sub>O<sub>3</sub>=21.7%. Because B<sub>2</sub>O<sub>3</sub> is a strong acidic oxide with low optical basicity, 0.34, while ZnO is an oxide with a significant basicity, 0.95, the increase in optical basicity of the glass is expected with increasing ZnO content. This reveals that the acid–base properties of ZnO have a great effect on the optical properties of the glass, which possesses an increase in its refractive index values.

The oxygen (oxide ion) polarizability is an expression of the degree of negative charge borne by oxygen atoms. Moreover, optical basicity is a measurement of this charge, which follows that there should be a relationship between optical  $A$  and  $\alpha_{O^{2-}}^2$ . Duffy [23] has established a relationship between the optical basicity and the electronic polarizability of the oxide ion as follows [23]:

$$A = 1.67 \left( 1 - \frac{1}{\alpha_{O^{2-}}^2} \right) \quad (10)$$

This relationship confirms the obtained increase in the oxide ion polarizability along with the increase in optical basicity of the studied glass system. This could also explain the tendency of consistently increase in the glass refractive index with the increase of ZnO content on the expense of B<sub>2</sub>O<sub>3</sub>.

### 3.7. O 1s binding energy

X-ray photoelectron spectroscopy (XPS) is a chemical analysis technique deals with elements having atomic number  $\geq 3$  for the direct estimation of optical basicity. The O 1s chemical shift in XPS spectra can be used for an adequate relation between peak position and optical basicity in some oxides and borate glasses [24–26]. The O 1s chemical shift corresponds to the different degree of ionicity in the M–O bonds where O 1s binding energy of the different oxides varies in 528.0–533.5 eV. The O 1s binding energy is related to the optical basicity of simple basic oxides (basic oxides are those with the least cationic character in the bonding orbitals) by the Mulliken occupation number of the metal orbital.

Categorization of simple oxides among O 1s binding energy provides separation of in three groups: (a) semicovalent oxides

with O 1s binding energy in the range of 530.5–533.0 eV; (b) normal ionic oxides with O 1s binding energy at  $530 \pm 0.4$  eV and (c) very ionic oxides with O 1s binding energy in the range of 529.5–528.0 eV [27].

We used the reported XPS data of the different constituent glass oxides to estimate the decrease in the O 1s binding energy in the studied glasses with increasing the ZnO content. It was shown that a decrease of the O 1s binding energy in the XPS of Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses corresponds to an increase of the calculated optical basicity [25,26]. Since the binding energy of B<sub>2</sub>O<sub>3</sub> oxide is 533.5 eV whereas for ZnO oxide is 530.3 eV [21], therefore it is expected that present glasses acquire also a decrease in the O 1s binding energy, which explains the increase in the recorded glass optical basicity and hence refractive index values with the increase in the ZnO content.

Decreased O 1s binding energy means increased electronic polarizability of oxygen,  $\alpha_{O^{2-}}^2$ , that is, stronger electron donor ability of the oxide ion. The valence band in the oxides is composed basically from O 2p orbitals. Therefore the O 1s chemical shift to a lower binding energy is a result of an O 2p chemical shift in the valence band of the oxide. From polarization point of view, this means an increase in the polarizability of both oxide ions and cations, which provides in turn an increase in the glass refractive index. The reason for the low energy shift of O 2p band is probably due to the interaction between the outermost filled cation orbital and the 2p electrons of the oxide ion [28].

### 3.8. Yamashita–Kurosawa's interionic interaction parameter

The interaction parameter ( $A$ ), proposed in Yamashita–Kurosawa's theory of dielectric constant in ionic crystals [29], is a measure for the interionic interaction of 2p electrons of negative ions such as O<sup>2–</sup> with the neighbor cations. The parameter describes the polarizability of an average oxide ion in simple oxides and borate glasses [11,30,31] and its ability to form an ionic-covalent bond with the cation. Therefore, the interaction parameter expresses the decrease in polarizability of oxide ion placed in a crystal lattice with respect to the free-ion polarizability. Accordingly the interaction parameter is closely related to the optical basicity. That is the larger the oxide ion polarizability and optical basicity, the smaller interaction parameter.

According to the analysis performed by Diskhit and Kumar [32] based on Yamashita–Kurosawa's theory to obtain the interaction parameter of a given cation–anion pair, the interaction parameter  $A$  of simple oxides can be estimated using the following expression, which is proposed by Dimitrov and Komatsu [33]:

$$A = \frac{(\alpha_f^- - \alpha_{O^{2-}}^2)}{2(\alpha_f^+ + \alpha_f^-)(\alpha_f^+ + \alpha_{O^{2-}}^2)} \quad (11)$$

where  $\alpha_f^-$  and  $\alpha_f^+$  are the electronic polarizabilities of the free oxide and positive ions in the free state, respectively. A value of  $3.921 \text{ \AA}^3$  for the electronic polarizability of the free oxide ion  $\alpha_f^-$  is used taking into account the value of ionic refraction of O<sup>2–</sup> theoretically determined by Pauling [34]. Since the polarizability and optical basicity are additive quantities for a multi-component system, so it is reasonable to assume that interaction parameter  $A$  is also additive quantity in glasses.

To describe the polarizability state of an average oxide ion in oxide glasses and its ability to form an ionic covalent bond with the cation, we have to calculate what is called the theoretical interaction parameter with introducing ZnO to the glass network. Similar to the theoretical optical basicity, the so-called theoretical interaction parameter ( $A_{th}$ ) for the glass can be expressed as a sum from the parts each cation with the given oxide ion contributes to the total interaction for an averaged cation–anion

pair in the glass matrix [33]:

$$A_{th} = \sum x_{A_n B_m} A_{A_n B_m} \quad (12)$$

where  $x_{A_n B_m}$  is equivalent fraction based on the amount of oxygen each oxide contributes to overall glass stoichiometry and  $A_{A_n B_m}$  is the value of the interaction parameter of oxides in the form  $A_n B_m$ . The values  $A_{B_2O_3} = 0.244 \text{ \AA}^{-3}$ ,  $A_{ZnO} = 0.040 \text{ \AA}^{-3}$ ,  $A_{Li_2O} = 0.110 \text{ \AA}^{-3}$  and  $A_{WO_3} = 0.055 \text{ \AA}^{-3}$  were taken from Ref. [27]. Since ZnO has lower interaction parameter value than that of  $B_2O_3$ , therefore with the replacement of ZnO by  $B_2O_3$  the glass exhibits low theoretical interaction parameter, which decreases with increasing ZnO content, as shown in Fig. 7. It can be seen that the interionic interaction parameter is decreased to be 15.7% with increasing the ratio of Zn/ $B_2O_3$  to 21.7%.

The decrease of interacting parameter due to the existence of ZnO correlates the charge overlap and large cation and oxide ion polarizabilities, which thus enhances the unshared oxide ion 2p electron density available for donation. The result is an increase in the glass polarizability and hence its refractive index. Therefore the interionic interactions are strong in glasses formed by acidic oxides (as  $B_2O_3$ ) and they become weaker in glasses produced by a mixture of acidic and basic (as ZnO) or totally basic oxides.

### 3.9. Average single bond strength of $B_{M-O}$ of the glass system

According to the Krogh–Moe model [35] for structural groupings in alkali borate glasses, Fig. 8, which is supported by the experimental results of Bray and O'Keefe [36], the mole fraction,  $N_4$ , of four-coordinated boron is defined as the amount of  $B_4$  divided by the total boron content. For alkali borate glasses of the composition  $yLi_2O-zWO_3-(1-y-z)B_2O_3$  (sample 1, i.e.,  $x=0$ ), the total number of boron ion is  $2(1-y-z)$ . Since every modifier ion converts one boron ion from  $B_3$  to  $B_4$ , the number of  $BO_4$  structural unit is  $2(y+z)$ , and hence  $N_4 = (y+z)/(1-y-z)$  and thus the mole fraction of  $BO_3$  structural unit of three-coordinated boron is  $N_3 = [(1-y-z)-(y+z)]/(1-y-z)$ . The calculated values  $N_4$  and  $N_3$  of the glass are 0.786 and 0.214, respectively.

In the structure of zinc lithium tungsten borate glasses, the  $ZnO_4$  structure unit would be probably the most preferable groups. Moreover, tungsten ions exist in three possible valences;  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$ . The first two states are predominate with structural units  $WO_4(Td)$  and  $WO_6(Oct)$  of hexavalent  $W^{6+}$  ions

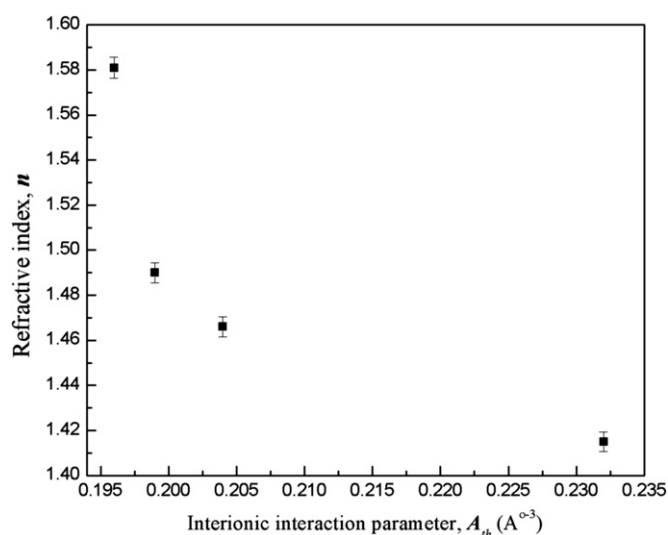


Fig. 7. Correlation between interionic interaction parameter of the glass and its refractive index. The refractive index is increased to 1.581 with decreasing the value of interionic interaction parameter to be  $0.196 \text{ \AA}^{-3}$  at ZnO/ $B_2O_3$ =21.7%.

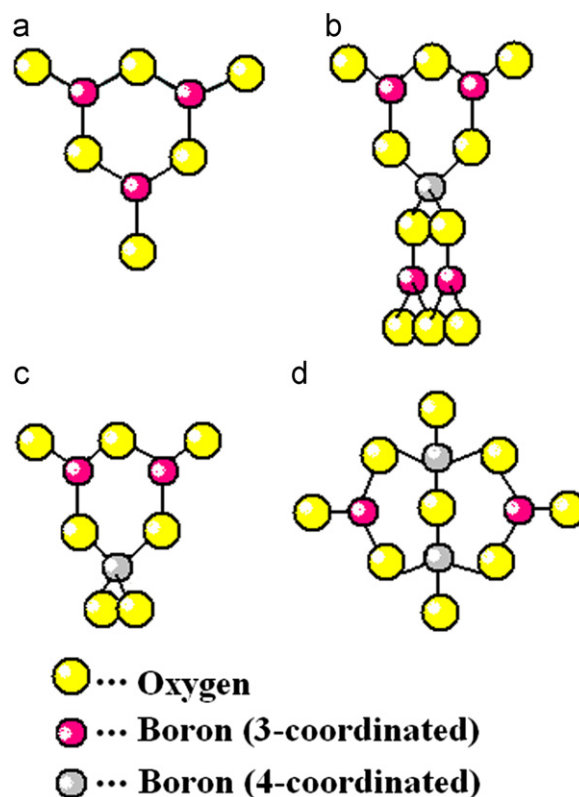


Fig. 8. Structural groupings present in alkali borate glasses as proposed by Krogh–Moe: (a) boroxol, (b) pentaborate, (c) triborate and (d) diborate groupings.

and  $W^{5+}O_3$  (Oct) of pentavalent  $W^{5+}$  ions [4,5]. The small content  $WO_3$  in the glass composition initiates the existence of hexavalent  $WO_6$  structural unit for tungsten oxide ions.

The formation of one  $MO_4$  tetrahedron requires an additional oxygen atom or two single bonded oxygen ions, which can be provided by the alkali molecules such as  $Li^+$ . The boric oxide is built up of  $BO_3$  triangles and upon adding divalent oxides, such as  $Zn^{2+}$ , the coordination number of the boron changes from  $SP^3$  tetrahedral  $BO_4$  to from  $SP^2$  planar  $BO_3$ , preserving the B–O bonding without the creation of non-bridging oxygen ions. It means that the introduction of divalent oxides causes a significant formation of the  $BO_3$  groups with a lower coordination number, pursuing an equilibrium reaction  $BO_3 \leftrightarrow BO_4 + NBO$ . When the divalent ions are present in amounts greater than the number of the interstices available, they will act partly as bridges between the adjacent  $BO_4$  tetrahedral. The  $Zn^{2+}$  ions will thus become enclosed in the structural interstices or will act as bridges between the network forming units.

On the other side, Sun [37] have proposed bond energy criterion for glass formation based on the dissociation energy of the oxides. The single bond strength  $B_{M-O}$  of a chemical bond M–O in an oxide  $MO_x$  is obtained by dividing the dissociation energy of the oxide by the coordination number of the metal (CM). The data reported by Sun provide for the glass scientists a good basis for separating oxides into glass-formers, intermediates and modifiers. Based on Sun's approach, Dimitrov and Komatsu [38] proposed what is called the average single bond strength  $B_{M-O}$  of the glasses which, therefore, could be expressed in our glasses as follows:

$$B_{M-O} = yB_{Li-O}^{(4)} + zB_{W-O}^{(6)} + xB_{Zn-O} + (1-x-y-z) \times [(x)N_3B_{B-O}^{(3)} + (1-x)N_4B_{B-O}^{(4)}] \quad (13)$$

where  $x$ ,  $y$  and  $z$  are the mole fractions of ZnO, Li<sub>2</sub>O and WO<sub>3</sub>, respectively.  $B_{\text{Li-O}}^{(4)}$ ,  $B_{\text{W-O}}^{(6)}$  and  $B_{\text{Zn-O}}^{(4)}$  are the single bond strength of Li–O, W–O and Zn–O bonds in the LiO<sub>4</sub>, WO<sub>6</sub> and ZnO<sub>4</sub> groups, respectively.  $B_{\text{B-O}}^{(3)}$  and  $B_{\text{B-O}}^{(4)}$  are the single bond strength of B–O bond in BO<sub>3</sub> and BO<sub>4</sub> groups, respectively. According to Sun [37], the single bond strength of B–O bond in B<sub>2</sub>O<sub>3</sub> oxide,  $B_{\text{B-O}}$ , is 498 kJ/mol for BO<sub>3</sub> structural units and 373 kJ/mol for BO<sub>4</sub> structural units that of Zn–O bond in ZnO,  $B_{\text{Zn-O}}^{(4)}$  is 150.6 kJ/mol for ZnO<sub>4</sub> units and of Li–O bond in  $B_{\text{Zn-O}}^{(4)}$  is 150 kJ/mol. Furthermore, the single bond strength W–O in WO<sub>3</sub>, i.e., for  $B_{\text{W-O}}^{(6)}$  is assumed to be 112 kJ/mol, because the dissociation energy of WO<sub>3</sub> is 672 kJ/mol. The coordination number of the cation is shown in the brackets as superscript. The average single bond strength  $B_{\text{M-O}}$  of the glass system is calculated using Eq. (13) and the results are shown in Fig. 9. It can be seen that the glass average bond strength decreases with increasing of the ZnO content. The glass average single bond strength is decreased to 11.6% with increasing the ratio of Zn/B<sub>2</sub>O<sub>3</sub> up to 21.7%.

Dimitrov and Komatsu [38] demonstrated that there is a good correlation among electronic oxide polarizability and average single bond strength of several oxide glasses. That is, in general, electronic oxide polarizability increases with decreasing the average single bond strength in glasses. This in turn explains well the recorded increase in the glass index of refraction with the increase in ZnO content. This calculated weakness in chemical bond with the increase in glass refractive index is also reported for ZnO–Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses [39,40].

### 3.10. FT-IR absorption spectra analysis

The FT-IR absorption spectra of the glasses are generally characterized by three distinguished absorption regions. The first one is extending from 1200 to 1600 cm<sup>−1</sup> due to B–O stretching of BO<sub>3</sub> units and the second one extends from 800 to 1200 cm<sup>−1</sup> due to B–O stretching of BO<sub>4</sub> units. The third region lies around 700 cm<sup>−1</sup> due to bending of B–O–B linkages in the borate network.

The effect of zinc oxide content on the infrared absorption spectra of the lithium tungsten borate glasses is shown in Fig. 10, from which it can be seen as follows:

1. Several absorption bands were observed in the FT-IR absorption spectra given by the base glass of the composition

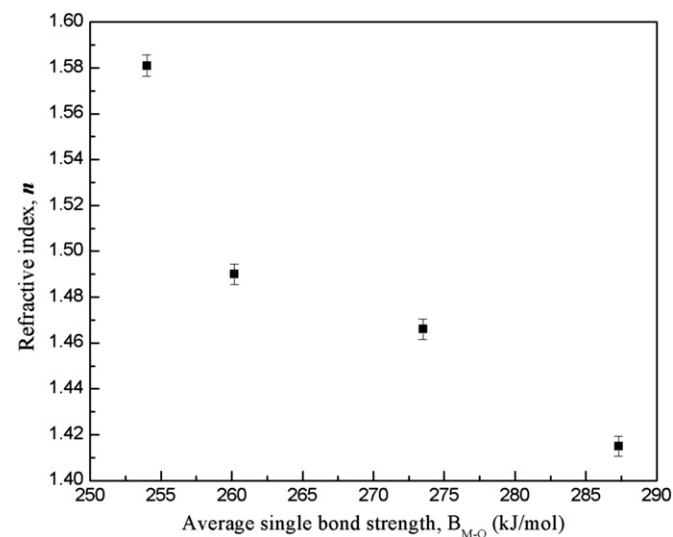


Fig. 9. The increase in glass index of refraction up to 1.581 with decreasing average single bond strength to be 254 kJ/mol associated with increasing the ZnO/B<sub>2</sub>O<sub>3</sub> reaching 21.7%.

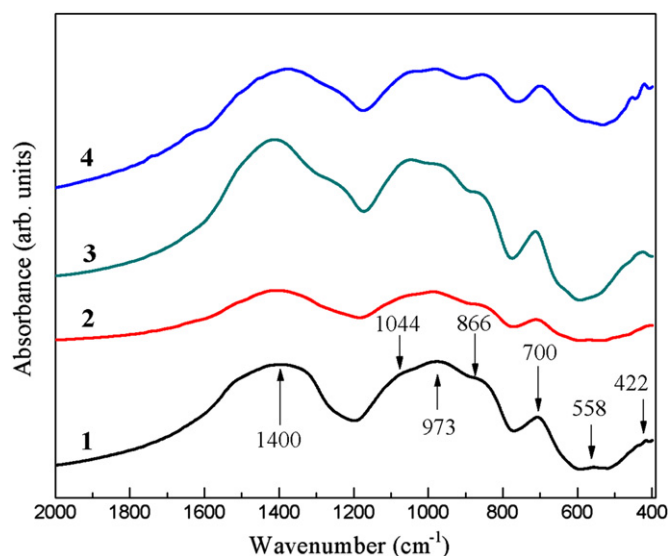


Fig. 10. FT-IR spectra of the investigated glass system (0.56– $x$ )B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O– $x$ ZnO–0.04WO<sub>3</sub>. In sample 1 the ZnO content in mol%  $x=0$ , sample 2:  $x=0.04$ , sample 3:  $x=0.08$  and in sample 4:  $x=0.1$ .

- 0.56B<sub>2</sub>O<sub>3</sub>–0.4Li<sub>2</sub>O–0.04WO<sub>3</sub> (mol%) at about 422, 558, 700, 866, 973 and 1044 cm<sup>−1</sup>.
2. Band at 422 cm<sup>−1</sup> may be attributed to the vibration of metal cations in their oxygen sites [41,42] and to RO<sub>4</sub> tetrahedra [43].
3. Band at 558 cm<sup>−1</sup> represents deformation modes of network structure and vibration of chemical bond (Zn<sup>2+</sup>–O<sup>2−</sup>) in a location of the tetrahedron [44–47].
4. Band at 700 cm<sup>−1</sup> stands for B–O–B bond bending vibrations of bridging oxygen atoms [44–47].
5. Band at 866 cm<sup>−1</sup> is stretching vibration of tri-, tetra- and penta-borate groups also due to stretching vibration of non-bridging oxygens of BO<sub>4</sub> groups overlapping with stretching vibrations of WO<sub>3</sub> units [48].
6. Band at 973 cm<sup>−1</sup> represents vibration of diborate groups B–O and major component of asymmetric stretching of BO<sub>4</sub> tetrahedron.
7. Band at 1044 cm<sup>−1</sup> corresponds to B–O stretching vibration of tetragonal BO<sub>4</sub> units in tri-, tetra- and penta-borate groups [44–47].
8. Band at 1400 cm<sup>−1</sup> is attributed B–O stretching vibrations of trigonal BO<sub>3</sub> units in different borate groups [44–47].

Therefore, the progressive increase in ZnO content makes the absorption bands observed at about 700, 1044 and 1400 cm<sup>−1</sup> in the base glass became more pronounced. This means that the BO<sub>3</sub> groups and hence the bridging oxygen contents are increased with increasing of ZnO content on the expenses of borate oxide content. Such increase in bridging oxygen ions with increasing ZnO content is in accordance with previously observed blue shift in the UV transmission edges explaining the increase in transmittance and transmission window of the lithium tungsten borate glasses.

### 4. Conclusion

Zinc lithium tungsten borate glass system prepared for IR photonic applications, such as optoelectronic devices, solar energy converter and for UV-emitting lasers [1,3,8], shows a good correlation between refractive index and oxide ion electronic polarizabilities among with the insertion of a small ZnO content

on the expense of boric oxide. It gives rise to the formation of very ionic chemical bonds and hence large electronic polarizabilities of both cation and oxide ions. ZnO increased the transmission window of the studied glass and also its transmittance. Zinc oxide is used to probe the oxide ion electronic polarizability and its role on the glass dispersion properties through applying theories such as optical basicity, O 1s binding energy, interionic interaction parameter and average single bond strength. The increase in the glass transmission range is explained by the FT-IR results, which confirm an increase in bridging oxygen bonds as a result of replacement of ZnO by B<sub>2</sub>O<sub>3</sub>. The results may provide knowledge about what types of oxides should be used and what are their bond characteristics, which are needed to tailor the glass refractive indices. Furthermore, such approach may explain the relation between glass-forming substances and the functional connections between their compositions and properties through oxygen electronic polarizability.

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