

## POLARIZABILITY AND OPTICAL BASICITY OF $\text{Er}^{3+}$ IONS DOPED TELLURITE BASED GLASSES

M. N. AZLAN, M. K HALIMAH\*, S. Z SHAFINAS, W. M. DAUD

*Physics Department, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

The refractive indices ( $n$ ) and densities ( $\rho$ ) of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses with  $y = 0.00, y = 0.005, y = 0.01, y = 0.02, y = 0.03, y = 0.04, y = 0.05$  were measured at room temperature. The theoretical value of average electronic polarizability and oxide ion polarizability were calculated by using Lorentz-Lorenz equation on the basis of refractive index and band gap energy. The value of electronic polarizability and oxide ion polarizability is found to be increased with increasing refractive index and decreasing band gap energy. The optical basicity was measured on the basis of oxide ion polarizability and calculated from refractive index and band gap energy. The value of optical basicity was found to be increased with increasing refractive index and band gap energy. The metallization criterion has been calculated on the basis of refractive index and band gap. It was found to be decreased with increasing refractive index and decreasing band gap. The large value of metallization criterion indicates that the glass materials are an insulators.

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*Keywords:* Tellurite based glass; Polarizability; Optical basicity; Metallization criterion

### 1. Introduction

Tellurite-based glass is a good candidate for designing the photonic system because of its valuable properties such as high dielectric constant, high refractive index, low melting temperature and low phonon energy. The recent research on tellurite-based glass is extensively conducted by doping with heavy metal to alter the physical and optical properties which show remarkable changes [1].

The Photonic - based system is an excellent application to be used in ultra-high speed transfer and processing. Glass is one of the examples for the system application because of its superior properties of tunable nonlinear optical (NLO) properties and low phonon cut energy [2]. The demand of such properties increases the development of photonic materials. Designing the photonic-based systems require the application of nonlinear optical (NLO) properties. One of the most important properties in the field of optical and electronic is the electronic polarizability of ions [2].

Nonlinear optical (NLO) properties are monitored by electronic polarization of material in exposure of intense light beams which can be related to several properties of materials such as electro-optical effect, conductivity and refractivity [3]. The new kind of materials in which possesses excellent nonlinear optical (NLO) properties has to be found in order to design the photonic based system, which are accessible and understandable. Hence, the approach of the electronic polarizability of new materials would be valuable for optical and electronic development.

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\*Corresponding author: halimah@science.upm.edu.my

Recently, Dimitrov and Komatsu have investigated the polarizability approach of numerous oxide glasses by estimating the electronic oxide ion polarizability, optical basicity and metallization criterion based on their refractive index and band gap energy [4]. The research on the electronic polarizability of tellurite-based doped with rare earth has not yet been well investigated. Thus, further research on the polarizability properties of tellurite based glass doped with erbium is extremely required.

## 2. Experimental Section

The glass sample was prepared by using the melt quenching method. The composition of erbium zinc borotellurite  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glass for  $y=0.005, 0.01, 0.02, 0.03, 0.04, 0.05$  mol% were fabricated from the reagent grade of erbium (III) oxide,  $\text{Er}_2\text{O}_3$  (99.9%, Reacton, Alfa Aesar), tellurium (IV) oxide,  $\text{TeO}_2$  (99.99%, Puartronic, Alfa Aesar),  $\text{ZnO}$  (99.99%, Assay, Alfa Aesar) and boron oxide,  $\text{B}_2\text{O}_3$  (99.98%, Assay, Alfa Aesar). The chemical powder of  $\text{Er}_3\text{O}_2$ ,  $\text{TeO}_2$ ,  $\text{ZnO}$  and  $\text{B}_2\text{O}_3$  were prepared at appropriate amount. The chemical powder of  $\text{Er}_3\text{O}_2$ ,  $\text{TeO}_2$ ,  $\text{ZnO}$  and  $\text{B}_2\text{O}_3$  were weighed by using a digital weighing machine with accuracy of  $\pm 0.0001$ g and mixed together thoroughly. The mixtures in alumina crucible were then put in electric furnace and preheat it at  $400^\circ\text{C}$  for 30 minutes as to remove water content in the mixture.

After pre-heat process, the crucible was transferred to the second furnace at  $900^\circ\text{C}$  for a period of 2 hours. During the heating process, the cylindrical stainless steel was put in the first furnace at  $400^\circ\text{C}$  for a period of 1 hour. After 2 hours, the molten liquid was quenched rapidly into cylindrical stainless steel split mold which had been pre-heated at  $400^\circ\text{C}$ . The sample was immediately transferred to annealing process held at  $400^\circ\text{C}$  for a period of 60 minutes and the furnace was turned off.

After annealing process, the glass sample was formed. The glass sample was cut at a thickness of about 2 mm by using low speed saw machine for the required measurements by using Isomet Buehler low speed saw machine. The sample was polished with various types of sand papers, 1500 grid, 1200 grid and 1000 grid to obtain flat and smooth surface.

The density of glass sample was measured at room temperature by using the Archimedes principle and distilled water was utilized as the immersion liquid. The weight of glass sample in the air and distilled water was weighed by using a digital weighing machine with accuracy of  $\pm 0.0001$ g.

### Optical measurement

To determine the optical measurements, the sample surfaces were polished by various types of sand papers to obtain the smooth and clear surface.

1. Single side polished surface-for refractive index measurement
2. Both sides polished surface-for optical absorption measurement

After the sample was cut and polished, the refractive index was measured by using EL X-02C high precision Elipsometer. The optical absorption was obtained by using UV-1650PC UV-Vis Spectrophotometer (Shimadzu) with the wavelength of 190-1100 nm. The angle of incident is  $70^\circ$  whereas the wavelength of light source is 632.80 nm. Both refractive index and optical absorption measurement were carried out at room temperature with dark surrounding for better result. All data were analyzed automatically and controlled by a CPU. The data of measurement were calculated by using different equation for their optical energy gap and absorption coefficient.

## 3. Results and Discussion

### 3.1 X-ray Diffraction (XRD) and Fourier transform analysis (FTIR)

The amorphous structural arrangement was confirmed by using X-ray diffraction (XRD) analysis in the  $2\theta$  range  $20^\circ - 80^\circ$  at a scanning rate of  $2^\circ/\text{min}$ . The XRD spectra of erbium doped zinc borotellurite glasses with 0.5-5% mol concentration of erbium oxide is shown in Figure 1. It

can be seen from the figure that the XRD pattern exhibit broad diffusion at a lower scattering angle indicating their long range disorder arrangement. There are absent of sharp peaks from the spectra which shows the non-existence of crystalline phase. This result corresponds to the characteristic of glass materials which exhibit random and disorder arrangement.

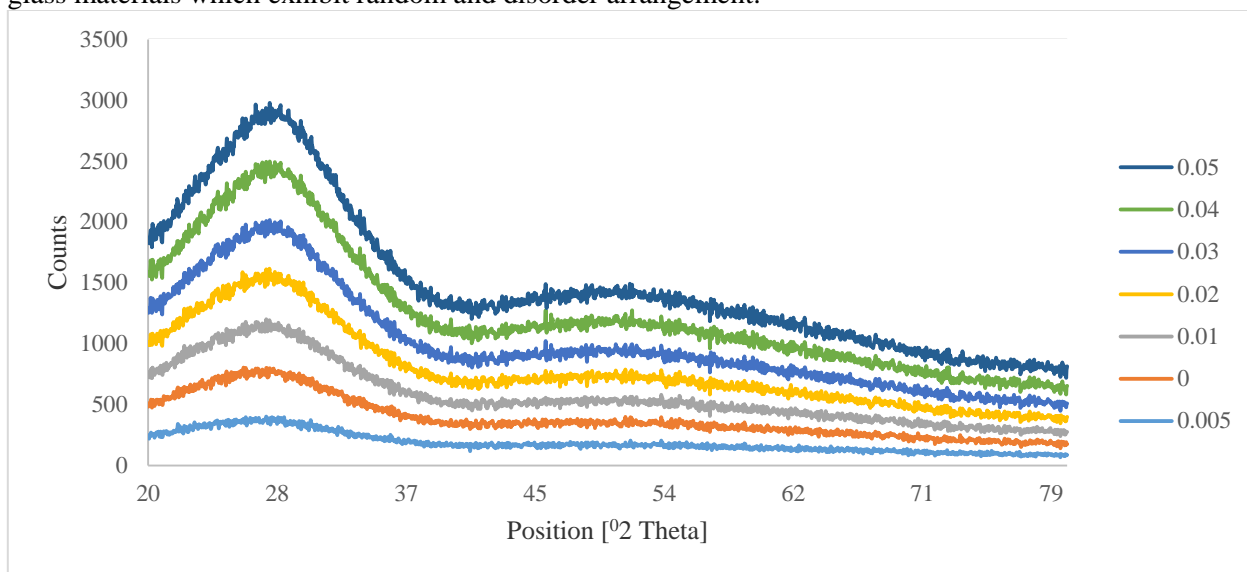


Fig. 1. X-ray diffraction pattern of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

Fourier transform infrared (FTIR) analysis was used to acquire deeper insight into the glass samples and a possible mechanism for non-bridging oxygen formation. The FTIR spectra is presented in Figure 2 and the possible mechanism bands was tabulated in Table 1. It can be seen from Figure 2 that there are several bands appeared indicating their local structure. The transmission bands are positioned in the range of  $656 - 664\text{ cm}^{-1}$ ,  $1233 - 1252\text{ cm}^{-1}$  and  $1327 - 1343\text{ cm}^{-1}$ . In addition, some shoulders were recorded at  $414\text{ cm}^{-1} - 421\text{ cm}^{-1}$  and  $2000 - 3744\text{ cm}^{-1}$  in the glass system.

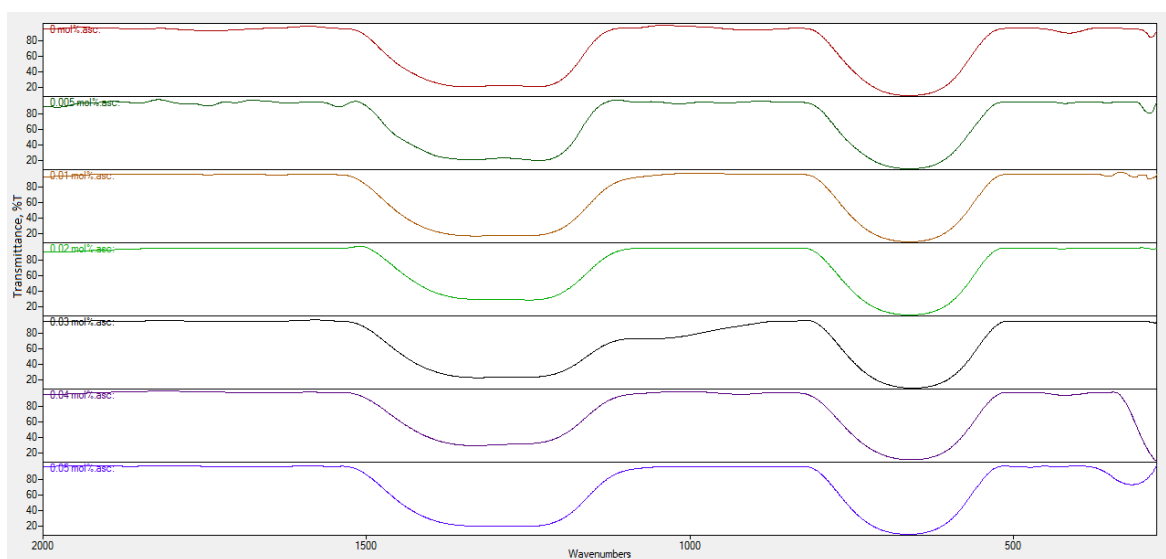


Fig.2. FTIR spectra of zinc oxide, boron oxide, tellurite oxide, erbium oxide and  $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{70}(ZnO)_{30}\}_{100-y}(Er_3O_2)_y$  glass system

Table 1. Assignment of infrared transmission bands of sample glass

Peak position (cm <sup>-1</sup> )	Assignment
414 -421cm <sup>-1</sup>	ZnO participate in the glass network with ZnO <sub>4</sub> structural units and alternate TeO <sub>4</sub> units [6]
656 – 664 cm <sup>-1</sup>	TeO <sub>3</sub> group are exists in all tellurite containing glass [6]
1233 – 1252 cm <sup>-1</sup>	Trigonal B-O bond stretching vibrations of BO <sub>3</sub> units from boroxyl groups [6]
1327 – 1343 cm <sup>-1</sup>	Trigonal B-O bond stretching vibrations in isolated trigonal BO <sub>3</sub> units [6]
2000 – 3744 cm <sup>-1</sup>	Indication of OH groups [6]

The active network of pure tellurite oxide, TeO<sub>2</sub> was positioned at 640 cm<sup>-1</sup>. Tellurite oxide exhibit two types of structural units which is trigonal pyramid, TeO<sub>3</sub> and trigonal bipyramid, TeO<sub>4</sub>. The position of trigonal pyramid, TeO<sub>3</sub> was located in the range 600-650 cm<sup>-1</sup> meanwhile trigonal bipyramid, TeO<sub>4</sub> was located in the range 650-700 cm<sup>-1</sup>. The first group of band observed was located in the range 656 – 664 cm<sup>-1</sup> which corresponds to the trigonal pyramid, TeO<sub>3</sub> structural units. As the Er<sup>3+</sup> ion content increases, bismuth oxide as the network modifier ion modifies the glass structure and enhances the breaking of axial Te–O–Te linkages in the trigonal bipyramids [TeO<sub>4</sub>] (tbp) and creates the formation of trigonal pyramid [TeO<sub>3</sub>] (tp) units and non-bridging oxygen [5].

The transmission band of pure borate oxide, B<sub>2</sub>O<sub>3</sub> was located at 806 cm<sup>-1</sup> indicating the boroxyl ring structural units. After the glass formation this band disappears, which is due to the substitutions of BO<sub>3</sub> and BO<sub>4</sub> units. The vibrational modes of borate network are mainly active in the two transmission band, which are similar to the previous report [6,7]. The first group of band which is due to the asymmetric stretching vibrations of trigonal BO<sub>3</sub> units occurs at 1233 – 1252 cm<sup>-1</sup>. The second group of band lies in between 1327 – 1343 cm<sup>-1</sup> is due to the trigonal B-O bond stretching vibrations in isolated trigonal BO<sub>3</sub> units. The group of band positioned at 2000 - 3744 cm<sup>-1</sup> is attributed to the fundamental stretching of the O-H group. The appearance of transmission band centered in between 414 cm<sup>-1</sup> - 421cm<sup>-1</sup> ascribed to the ZnO<sub>4</sub> structural units. However, this band disappears after introducing the Er<sup>3+</sup> ions indicating the zinc lattice is completely broken down. The absence of Er<sup>3+</sup> in the FTIR spectra is due to the low concentration of erbium ions that could not be detected by the device.

### 3.2 Refractive index and optical band gap energy

The refractive index is used to determine the suitability of glass materials to be optical devices. Factors which affect the refractive index are: a) polarizability of the first neighboring ions coordinated with it (anion); b) coordination number of the ion; c) electronic polarizability of the oxide ion; d) optical basicity of the glasses. Based from these factors, refractive index of the glass samples can be explained. The effect of erbium concentration on refractive index is shown in Figure 3 and tabulated in Table 2. The value of refractive index lies in between 1.700 – 1.740. It can be seen from the Figure 3 that the refractive index increases with the increasing number of erbium concentration. Erbium ions, Er<sup>3+</sup> consist of empty unfilled d-orbital (outer electronic configuration; 5d<sup>0</sup>) which contributes to linear polarizability. This will result to the increasing number of refractive index. Increase of the Er<sub>2</sub>O<sub>3</sub> indicates an increasing concentration of erbium ions that take part in the network modifying positions, and the conversion of TeO<sub>4</sub> tetrahedral to TeO<sub>3</sub> triangular in the structure [8]. This will create more non-bridging oxygen in the glass samples. Non-bridging oxygen possess a greater number of polarizability compared to bridging oxygen which results to the increasing number of refractive index. Another possibility is that, high coordination number of erbium ions, Er<sup>3+</sup> leads to the higher number of refractive index.

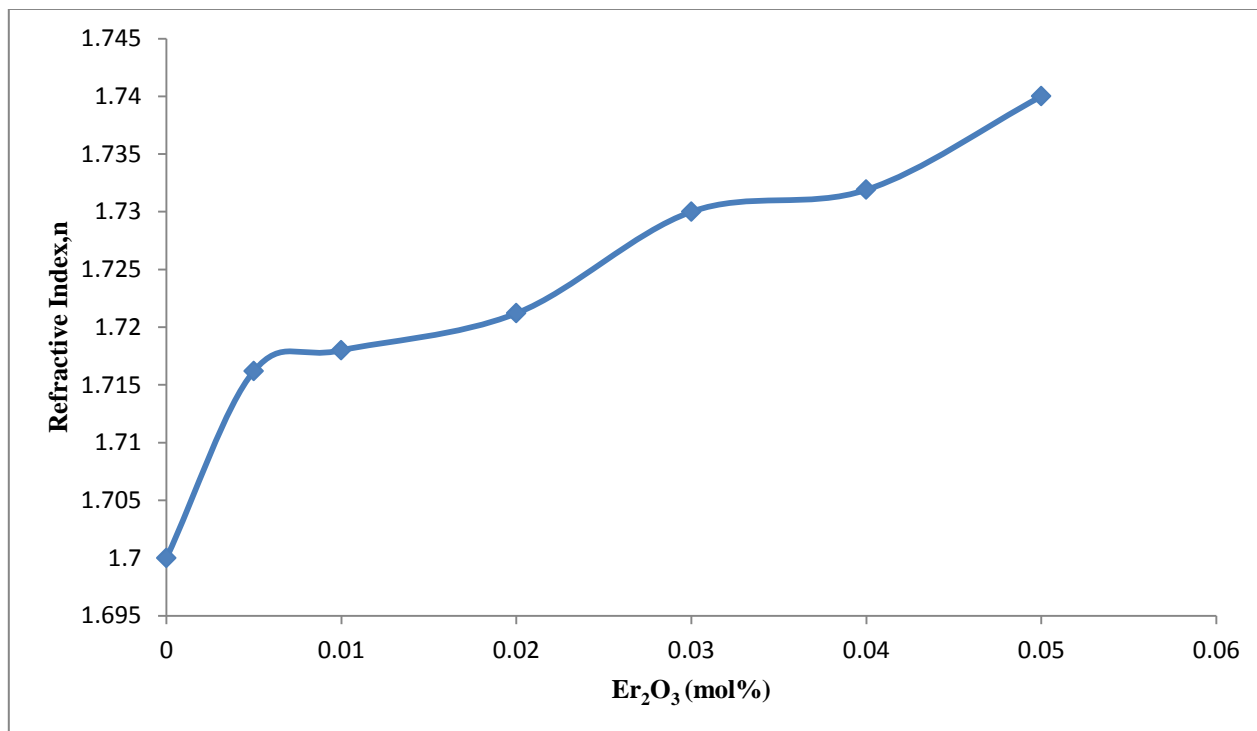


Fig. 3. Refractive Index of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses

Table 2. Refractive indices of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses

Mole %	Refractive Index (n)
0.000	1.7000
0.005	1.7162
0.010	1.7180
0.020	1.7212
0.030	1.7300
0.040	1.7319
0.050	1.7400

The optical absorption spectra of Er<sup>3+</sup> doped zinc borotellurite glasses in the UV-visible (400-2500nm) region are shown in Figure 4. There are few absorption bands observed from the figure and absorption edge is clearly observed in the UV region. These absorption bands indicate the characteristic of Er<sup>3+</sup> ions. Such bands arise from the intra-configurational (f-f) transition from the ground state <sup>5</sup>I<sub>8</sub> to the excited states <sup>4</sup>F<sub>7/2</sub> + <sup>2</sup>H<sub>11/2</sub> + <sup>4</sup>S<sub>3/2</sub> + <sup>4</sup>F<sub>9/2</sub> + <sup>4</sup>I<sub>9/2</sub> + <sup>4</sup>I<sub>11/2</sub>. The 4f electrons are shielded by the outer 5s and 5p bonding electrons, which leads to sharp absorption and emission bands [9]. The absorption edge depends on the oxygen bond strength in the glass forming network. The obtained data shows that there is a change in oxygen bond strength which affects to the absorption characteristics of the glass samples. There is no sharp edge (Urbach edge) appeared which indicates the amorphous nature of the glass samples.

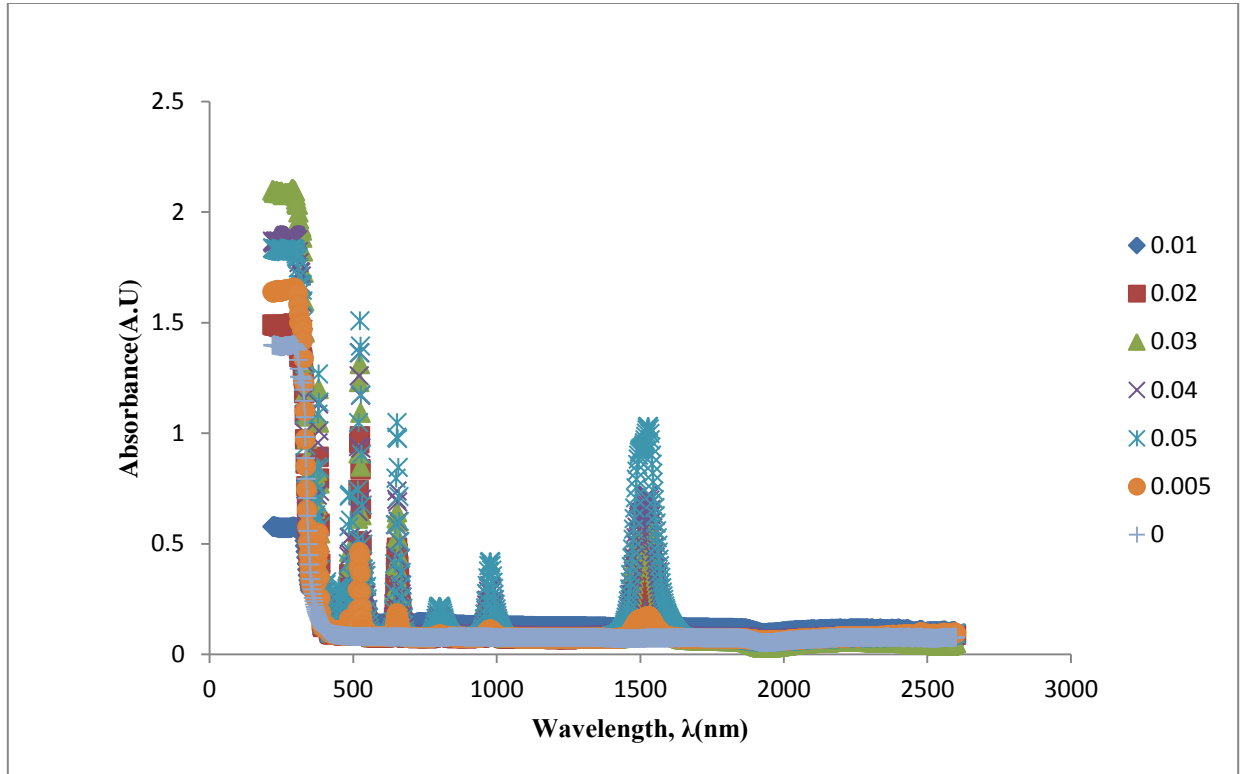


Fig. 4. Optical density spectra for  $\{[(TeO_2)_{0.70} (B_2O_3)_{0.30}]_{1-x} (ZnO)_x\}_1 (Er_3O_2)_y$  glasses

Davis and Mott [10] proposed the relation between absorption coefficient,  $\alpha(\omega)$  and photon energy,  $\hbar\omega$  of the incident radiation, this can be written generally as follows:

$$\alpha(\omega) = \frac{B(\hbar\omega - E_{opt})^n}{\hbar\omega} \quad (1)$$

$\hbar = 4.14 \times 10^{-15}(\text{eVs})$

$n=2$  for indirect transition and  $n=1/2$  for allowed direct transitions. In both cases, electromagnetic waves interact with the electrons in the valance band, which are raised across the fundamental gap to the conduction band. The values of indirect optical band gap  $E_{opt}^1$  and direct optical band gap  $E_{opt}^2$  can be obtained by extrapolating the straight line on the curve in Figure 5 (a) and Figure 5 (b) to the  $h\omega$  axis at  $(\alpha\hbar\omega)^{1/2}$  and  $(\alpha\hbar\omega)^2=0$  respectively.

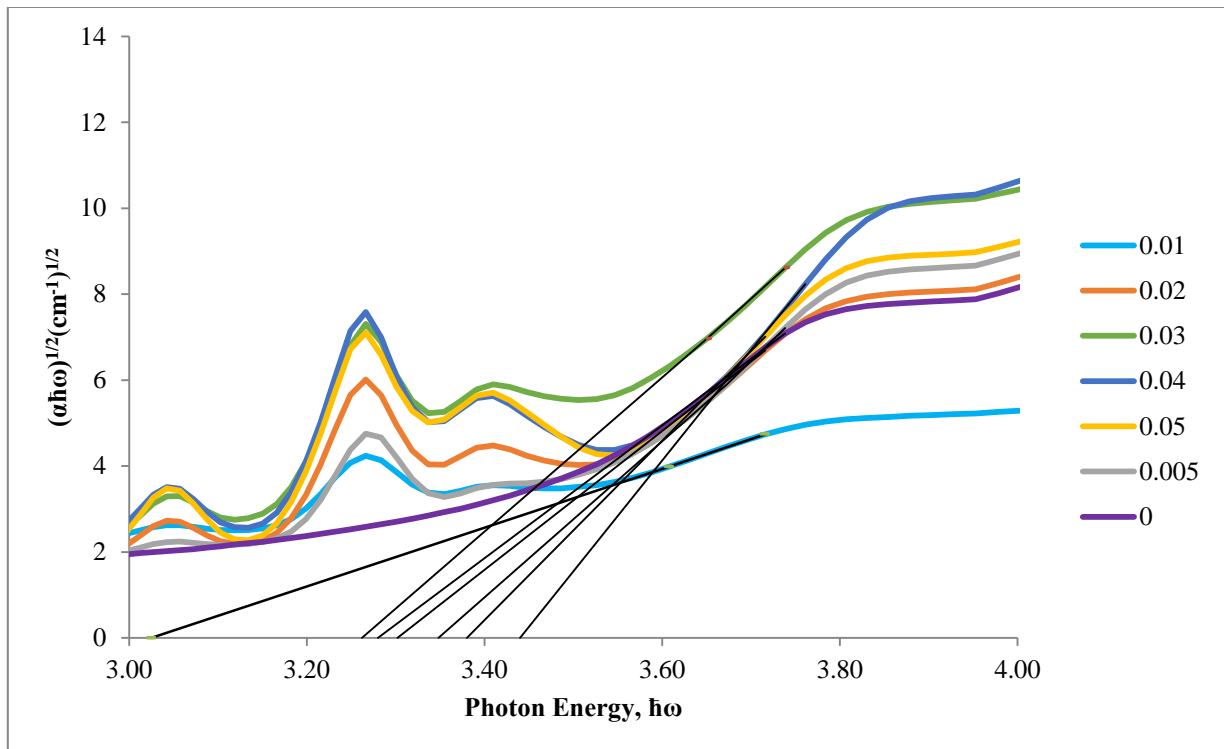


Fig. 5(a). Plot of  $(\alpha\hbar\omega)^{1/2}$  against photon energy  $\hbar\omega$  for indirect band gap measurement

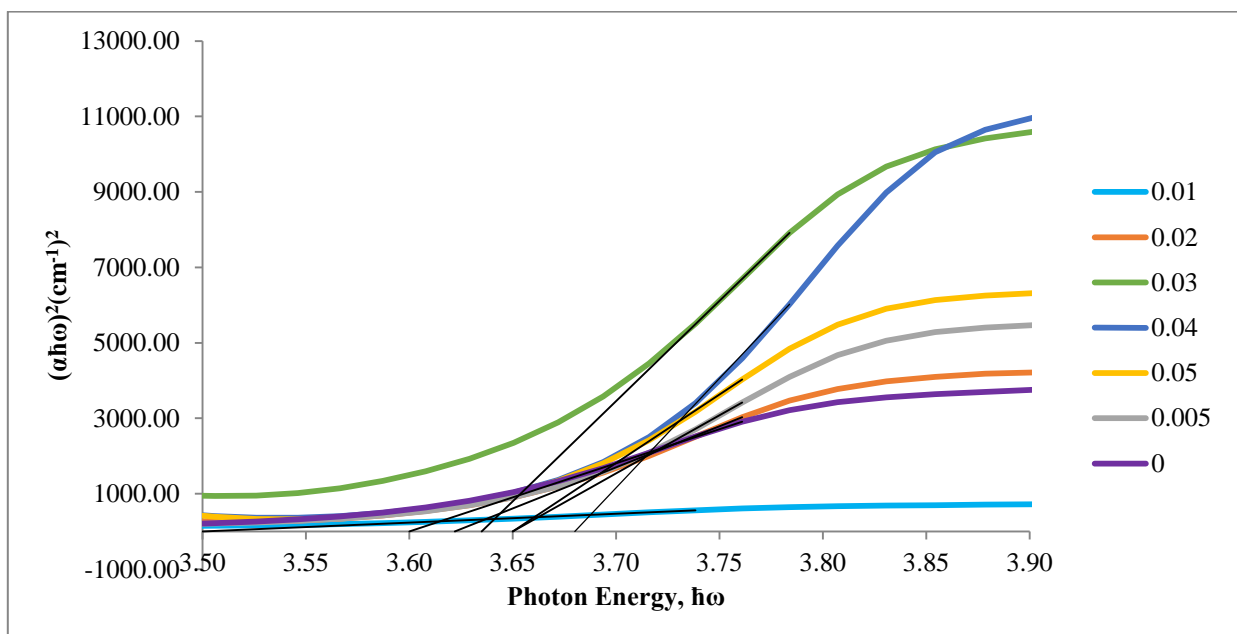


Fig. 5(b). Plot of  $(\alpha\hbar\omega)^2$  against photon energy  $\hbar\omega$  for direct band gap measurement

The values of direct and indirect optical band gap energy for the studied glass are shown and tabulated in Figure 6 and Table 3. It can be seen that the values of optical band gap energy decreases with the increasing concentration of erbium ions,  $\text{Er}^{3+}$ . The decreasing value of optical band gap energy by increasing the erbium content can be understood in terms of the structural change that are taking place. The weaker bond strength of erbium oxide, Er–O (147.0 kcal/mol) compared to boron oxide, B–O (192.7 kcal/mol) are responsible for the decrease of optical band gap energy. The increasing number of non-bridging oxygen indicates the increasing number of free electrons. This will contribute to the decreasing number of optical band gap energy.

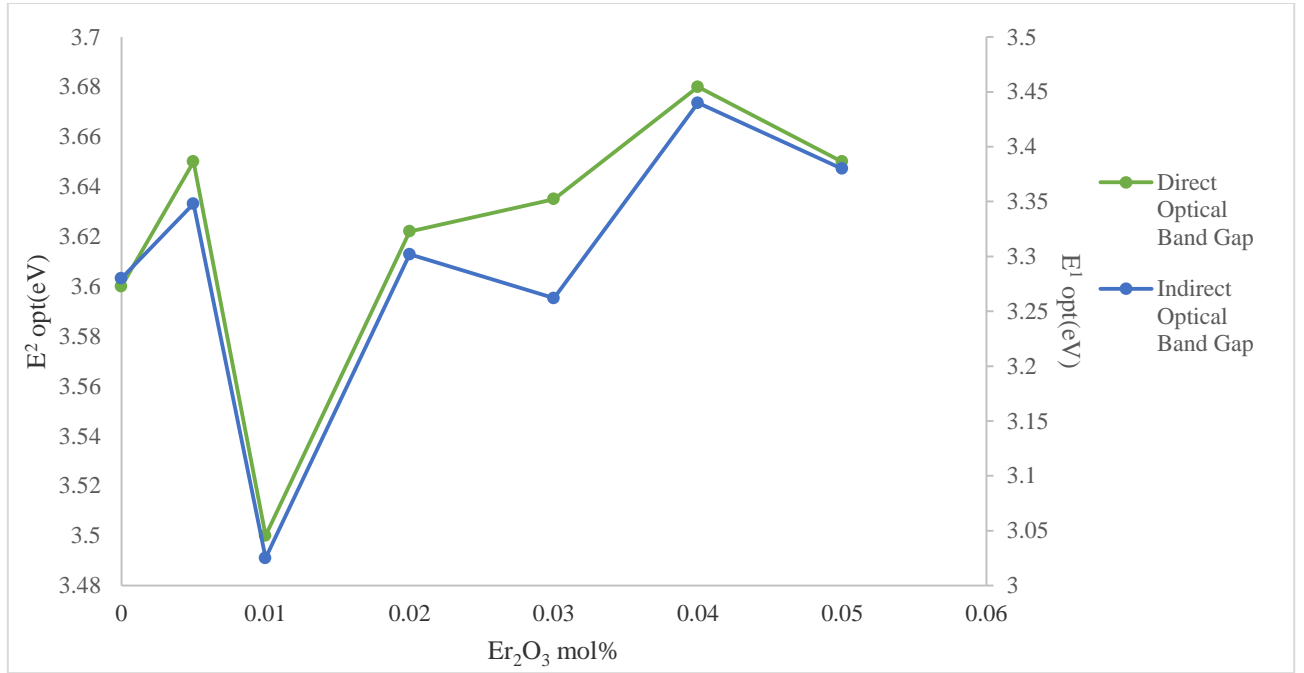


Fig. 6. Variation of direct optical band gap with glass composition for indirect transition for  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses

Table 3. Indirect optical band gap ( $E^1_{opt}$ ), Direct optical band gap ( $E^2_{opt}$ ) and Urbach energy ( $\Delta E$ ) of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses

Sample, y	$E^1_{opt}$ (eV)	$E^2_{opt}$ (eV)
0.000	3.280	3.600
0.005	3.348	3.650
0.010	3.025	3.500
0.020	3.302	3.622
0.030	3.262	3.635
0.040	3.440	3.680
0.050	3.380	3.650

### 3.3 Refractive index-based electronic polarizability

The relationship between molar refraction to refractive index and molar volume of a glass is described by the following Lorentz-Lorenz equation:

$$R_m = \frac{(n_0^2 - 1)}{(n_0^2 + 2)} V_m \quad (2)$$

Where  $R_m$  is the molar refraction,  $n_0$  is the linear refractive index and  $V_m$  is the molar volume. This relationship gives the average value of molar refraction for isotropic substances such as glasses and polycrystalline materials [11].

The structure of the glass material is related to the molar refraction. The electronic polarizability is proportional to the molar refraction by introducing the Avogadro's number through the following equation:



$$\alpha_m = \frac{3}{4\pi N_A} R_m \quad (3)$$

The electronic polarizability is based on the magnitude of electrons responds to an electrical field represented by the Lorentz-Lorenz equation. With  $\alpha_m$  in ( $\text{\AA}^3$ ) in Equation (3) can be transformed to the following expression:

$$\alpha_m = \frac{R_m}{2.52} \quad (4)$$

The obtained data of electronic polarizability are shown in Table 4. The plotted graph of electronic polarizability versus refractive index is shown in Figure 7. The increasing value of electronic polarizability shows the effect of  $\text{Er}_2\text{O}_3$  concentration on the polarizability. The addition of  $\text{Er}_2\text{O}_3$  in the glasses increases the number of non-bridging oxygen, which tends to make the glasses become more polarized.

Table 4. Values of molar percentage, refractive index and electronic polarizability of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses

Mole %	Refractive Index ( $n_0$ )	Electronic polarizability ( $\alpha_m$ )
0.000	1.7000	4.9535
0.005	1.7162	5.0706
0.010	1.7180	5.1232
0.020	1.7212	5.1558
0.030	1.7300	5.2322
0.040	1.7319	5.2160
0.050	1.7400	5.2740

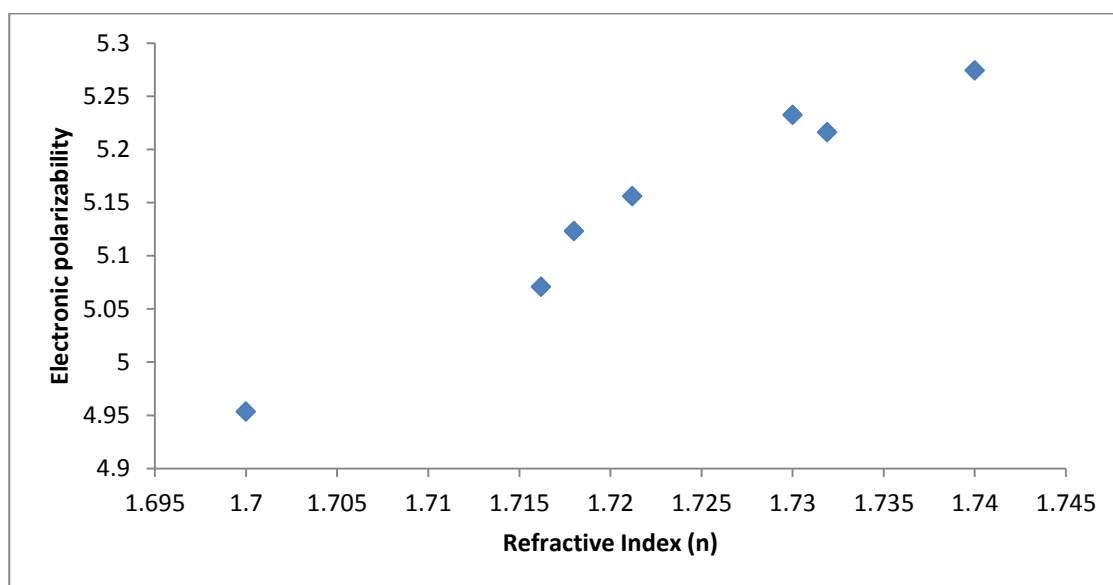


Fig. 7. Refractive index-based electronic polarizability of  $\{[(\text{TeO}_2)_{0.70}(\text{B}_2\text{O}_3)_{0.30}]_{1-x}(\text{ZnO})_x\}_{1-y}(\text{Er}_3\text{O}_2)_y$  glasses.

The existence of  $\text{Er}^{3+}$  trivalent ion increases the number of non-bridging oxygen by capturing one electron from oxygen that leads to increase the number of outer electrons which then forming bonds with oxygen atoms [1]. Based on the results, the refractive index is not only depends on the density, but also depends on the polarizability of the glass materials. [12].

### 3.4 Refractive index-based oxide ion electronic polarizability

The calculation of electronic oxide ion polarizability was described by Dimitrov and Sakka on the basis of refractive index and energy gap with various single component oxides [13]. The Lorentz-Lorenz equation is used to calculate the oxide ion polarizability by subtracting the cation polarizability as shown in the following equation:

$$\alpha_{\text{O}_2^-}(\text{n}) = \left[ \frac{R_m}{2.52} - \sum \alpha_i \right] (\text{N}_{\text{O}_2^-})^{-1} \quad (5)$$

Where  $\sum \alpha_i$  denotes molar cation polarizability and  $\text{N}_{\text{O}_2^-}$  denotes the number of oxide ions in the chemical formula.  $\sum \alpha_i$  is given by  $x_1 k \alpha_A + x_2 m \alpha_B + x_3 n \alpha_C + x_3 o \alpha_D$  and  $\text{N}_{\text{O}_2^-}$  is given by  $x_{1j} + x_{2k} + x_{3l} + x_{4m}$ . The molar cation polarizability is calculated from Dimitrov and Komatsu data of cation polarizability having the following values;  $\text{Er}^{3+} = 2.253$ ,  $\text{Te}^{4+} = 1.595$ ,  $\text{Zn}^{2+} = 0.283$ ,  $\text{B}^{3+} = 0.002$  [4]. The obtained data of oxide ion polarizability are shown in Table 5 by using Equation (5) and the graph of oxide polarizability versus refractive index is plotted in Figure 8.

Table 5. Values of molar percentage, refractive index and refractive index based-oxide ion polarizability of  $\{(TeO_2)_{0.70}(B_2O_3)_{0.30}\}_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

Mole %	Refractive Index ( $n_o$ )	Oxide ion polarizability $\alpha_{\text{O}_2^-}(\text{n})$
0.000	1.7000	2.1394
0.005	1.7162	2.1850
0.010	1.7180	2.1965
0.020	1.7212	2.2048
0.030	1.7300	2.1899
0.040	1.7319	2.1496
0.050	1.7400	2.1481

The values of oxide ion polarizability plotted in Figure 8 shows  $\alpha_{\text{O}_2^-}$  increases from 1.700 to 1.721 of refractive indices while from 1.730 to 1.740 of refractive index decreases. The decreasing value of oxide ion polarizability in between 1.730 – 1.74 of refractive index is due to the dual nature of zinc oxide, ZnO which tends to be glass former at certain mol percentage.

The tellurite-based glass,  $\text{TeO}_2$  consists of  $\text{TeO}_4$  trigonal bipyramidal and  $\text{TeO}_3$  trigonal bipyramidal. The fraction of  $\text{TeO}_3$  structural units with nonbridging oxygen (NBOs) increases with increasing the alkali content [14]. The high value of both refractive index and polarizability is expected due to the increasing number of non-bridging oxygen (NBOs) in the glass system.

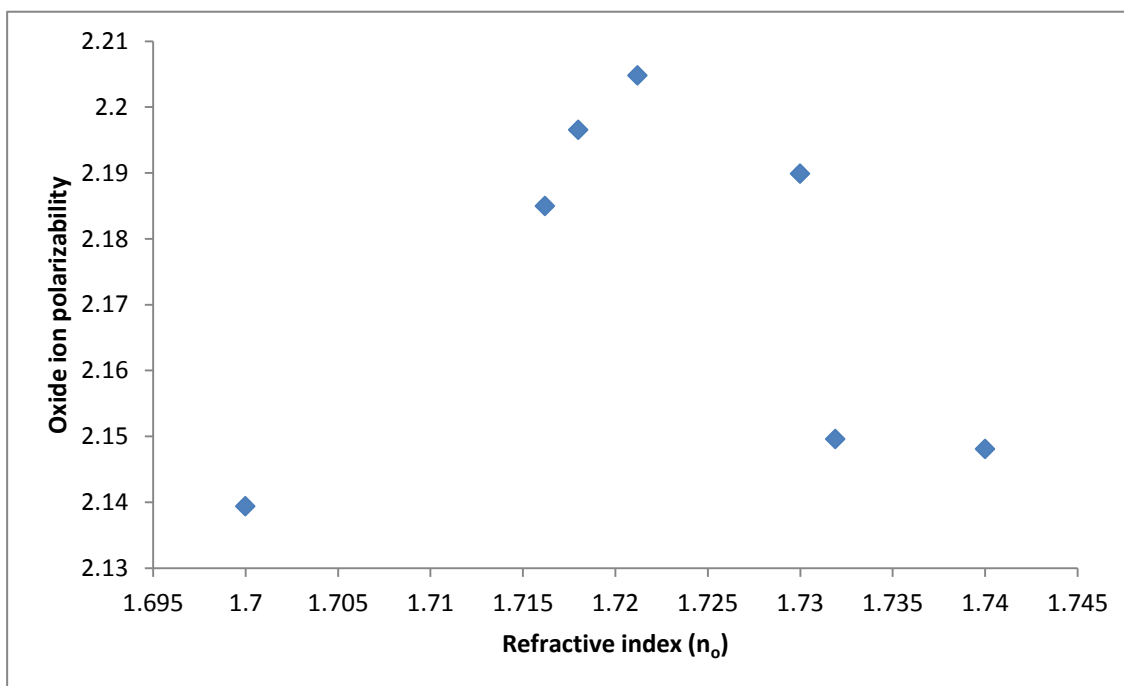


Fig. 8. Refractive index-based oxide ion polarizability of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_2O_3)_y$  glasses.

### 3.5 Energy gap-based oxide ion electronic polarizability

Based on the theory of metallization of condensed matter explained by Herzfeld, refractive index turn to be infinite in the condition of  $R_m/V_m = 1$  from the Lorentz-Lorenz equation. This is in accordance to the metallization of covalent solid materials [4]. Dimitrov and Komatsu explained on predicting the nature of solids which is metallic or non-metallic based on the condition of  $R_m/V_m < 1$  (non-metal) and  $R_m/V_m > 1$  (metal). Subtracting by 1 gives the metallization criterion

$$M = 1 - \frac{R_m}{V_m} \quad (6)$$

Duffy has proposed that there is a correlation between the energy gap of the oxides and their molar refraction by plotting  $\sqrt{E_g}$  against  $1 - R_m/V_m$  gives the relation

$$E_g = 20 \left( 1 - \frac{R_m}{V_m} \right)^2 \quad (7)$$

By substituting the Equation (6) to the Equation (5) gives the oxide ion polarizability of rare earth material

$$\alpha_{O_2^-}(E_g) = \left[ \frac{V_m}{2.52} \left( 1 - \sqrt{\frac{E_g}{20}} \right) - \sum \alpha_i \right] (N_{O_2^-})^{-1} \quad (8)$$

The equation gives the average value of the polarizability of oxide ion based on the energy gap, molar volume and cation polarizability of the materials. This equation has a good compatibility with the heavy metal oxide glasses. The obtained data of oxide ion polarizability based on the energy gap is listed in the Table 6. It is clear from the plotted data in Fig. 9 that the oxide ion polarizability decreases with an increasing energy gap of the glass materials.

Table 6. Values of molar percentage, energy gap and energy gap based-oxide ion polarizability of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

Mole %	Energy gap ( $E_g$ )	Oxide ion polarizability $\alpha_{O_2^-}(E_g)$
0.000	3.280	3.4091
0.005	3.348	3.3956
0.010	3.025	3.4723
0.020	3.302	3.4301
0.030	3.262	3.3760
0.040	3.440	3.3158
0.050	3.380	3.3060

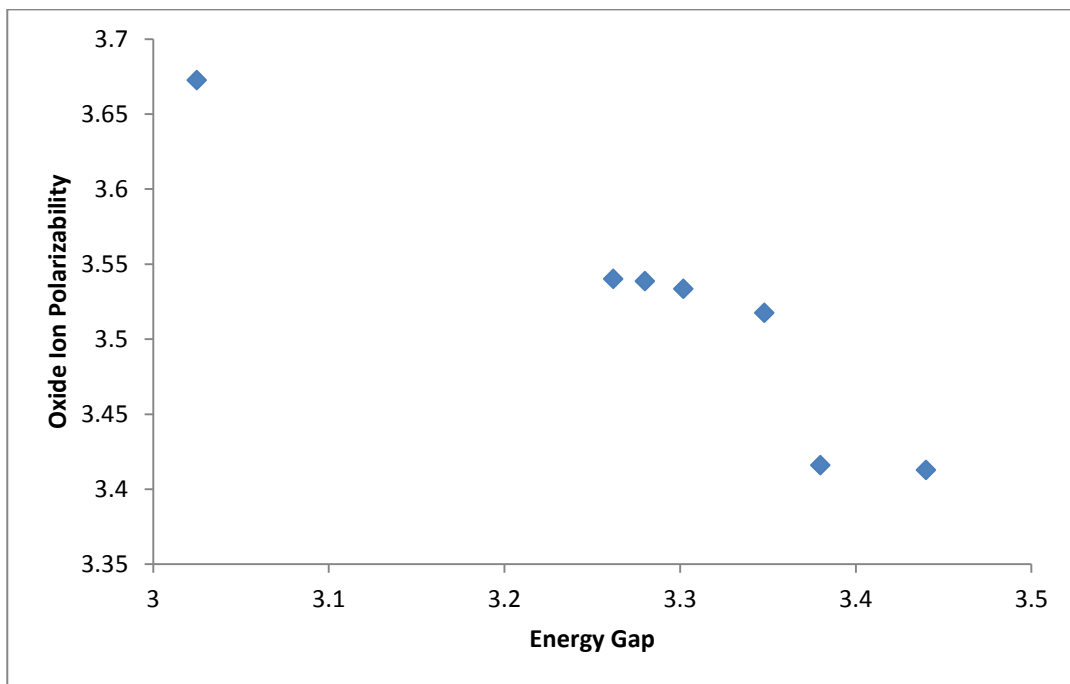


Fig. 9. Energy gap-based oxide ion polarizability of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

It was shown that the value of  $\alpha_{O_2^-}(E_g)$  is bigger than those obtained values of  $\alpha_{O_2^-}(n)$ . The differences between value of  $\alpha_{O_2^-}(E_g)$  and  $\alpha_{O_2^-}(n)$  can be explained by the existence of the localized density states in band gap energy based from the theory of conduction in non-crystalline [4].

### 3.6 Optical basicity of the glasses

Duffy and Ingram explained the theory of optical basicity of an oxide medium as the numerical expression of the average electron donor power of the oxide species constituting the medium [15]. The increasing number of oxide ion polarizability indicates the stronger ability of electron donor of the oxide ion. The optical basicity values give information about the acid-based properties of oxides, glasses, alloys, slags, molten salts etc.

The theoretical value of optical basicity,  $\Lambda$  of multi-component glasses can be calculated by the following expression as proposed by Duffy and Ingram

$$\Lambda = X_1\Lambda_1 + X_2\Lambda_2 + \dots + X_n\Lambda_n \quad (9)$$

where  $X_1, X_2, \dots, X_n$  denotes as the equivalent fractions of each oxides in which contributes to the overall material stoichiometry and  $\Lambda_1, \Lambda_2, \dots, \Lambda_n$  denotes as the optical basicity of each individual oxides in the glass system. The experimental value of optical basicity can be obtained by the measurement of the ultraviolet frequency shift from the metal ion probes and changes in  $O1_s$  binding energy [2]. The limitation of ultraviolet measurement which is due to the impairment of many glasses results the method to be not applicable.

The optical basicity can be alternatively calculated from the relationship of basicity and refractivity. Duffy explained that there is an intrinsic relationship between oxide ion polarizability  $\alpha_{O^{2-}}$  and optical basicity of the glass medium  $\Lambda$  by the following correlation

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

This equation indicates the optical basicity increases with increasing oxide ion polarizability. The obtained data of optical basicity are shown in Table 7 and plotted in Figure 10 and Figure 11. The large value of optical basicity in the glass system shows that the glass system is basic in nature.

Table 7. Values of refractive index, energy gap and refractive index based-optical basicity and energy gap-optical basicity of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

Refractive Index ( $n_0$ )	Energy gap ( $E_g$ )	Optical basicity $\Lambda(n_0)$	Optical Basicity $\Lambda(E_g)$
1.7000	3.280	0.8900	1.180
1.7162	3.348	0.9057	1.178
1.7180	3.025	0.9010	1.189
1.7212	3.302	0.9126	1.183
1.7300	3.262	0.9074	1.175
1.7319	3.440	0.8931	1.166
1.7400	3.380	0.8926	1.165

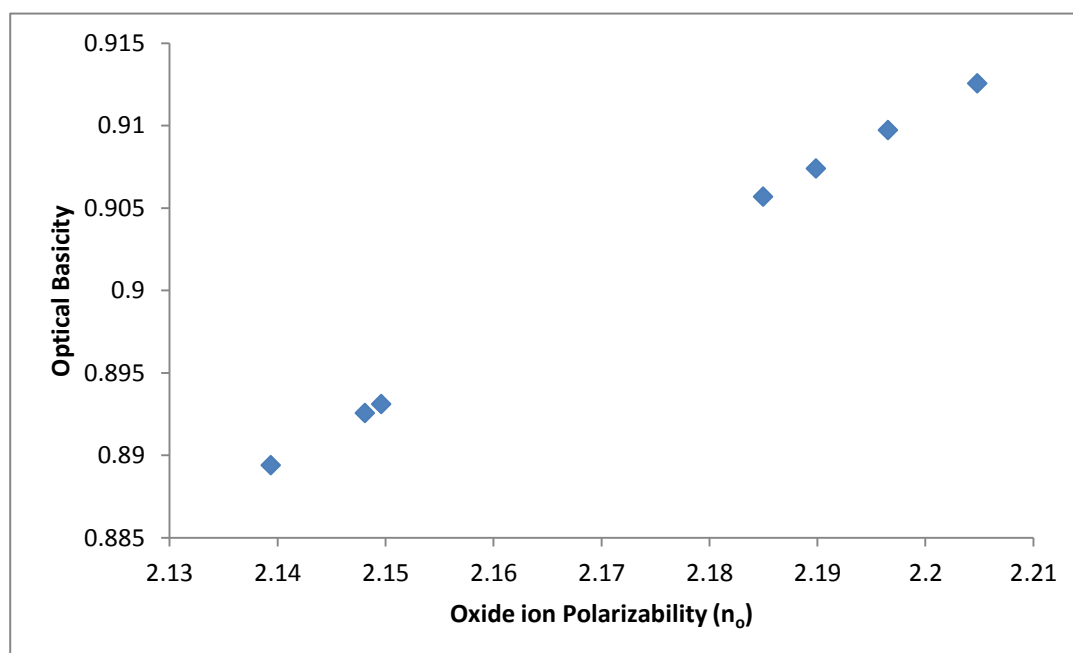


Fig. 10. Refractive index-based optical basicity of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

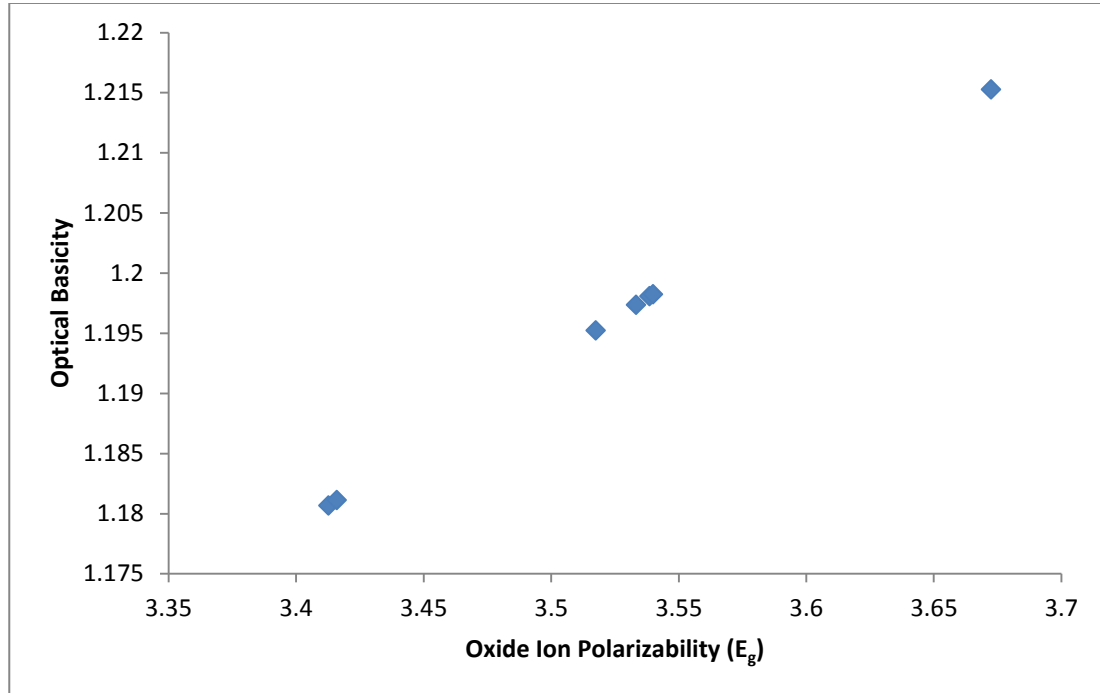


Fig. 11. Energy gap-based optical basicity of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses.

In conditions of glass former and modifier, former oxides should be less basic compared with modifier oxides. The addition of modifier oxide to former oxide results in the modification reaction to be an acid-base reaction in which the acidic region of the former oxide is approached by the modifier oxide ion in order of decreasing acidities [12]. The increasing of optical basicity indicates the decrease in covalency.

Based on the data, it indicates that the addition of modifier oxide reduces the acidity of the former oxide and increases the basicity of the glass. The values of optical basicity of each oxide are:  $\Lambda(Er_2O_2) = 0.929$ ,  $\Lambda(TeO_2) = 0.93$ ,  $\Lambda(ZnO) = 0.82$ ,  $\Lambda(B_2O) = 0.425$  [4]. As can be seen, the optical basicity of borate oxide is small and it is below 0.75.

The mixture of former and modifier oxides results in the optical basicity of borate oxide to increase. This is due to the higher number of optical basicity in erbium oxide (0.929), tellurium oxide (0.93) and zinc oxide (0.82). Tellurite as the glass former is the main role of acid-base property of the glasses has a significant effect [4]. The increasing number of optical basicity means that the ability of oxide ions to donate electrons to surrounding cations is increased.

### 3.7 Metallization criterion of the glasses

Based on the metallization criterion explained by Dimitrov and Komatsu, the nature of metallic and non-metallic of oxide glasses can be predicted by the following conditions:  $R_m/V_m < 1$  (non-metal) and  $R_m/V_m > 1$  (metal) [4]. The calculation of the metallization criterion can be computed from Equation (6). By means of the Lorentz-Lorenz equation, the metallization criterion on the basis of refractive index and band gap energy can be calculated from the expression:

$$M = 1 - \frac{(n_0^2 - 1)}{(n_0^2 + 2)} = \left(\frac{E_g}{20}\right)^{\frac{1}{2}} \quad (11)$$

The transition to a metal state occurs when Equation (11) and energy gap ( $E_g$ ) equals to zero. Based on the similarity of both quantities tending to be zero, Duffy proposed that there is a correlation between energy gap and molar refraction of the glass oxide [16]. Dimitrov and Sakka calculated the metallization criterion for numerous simple oxides and found that oxides with a large refractive index and small energy gap possess a small metallization criterion compared with the

small refractive index and large energy gap [13]. The materials in which possesses large metallization criterion, M value close to 1 is said to be insulators.

The obtained value of metallization criterion is tabulated in Table 8. It can be seen that the metallization criterion of ternary glasses on the basis of refractive index is in the range of 0.597-0.614. Metallization criterion on the basis of band gap energy is in the range of 0.389 – 0.415. Figure 12 shows that the increasing concentration of erbium will reduce metallization criterion of the glasses. This is due to the increasing number of refractive indices and decreasing number of energy gap.

Table 8. Values of molar percentage and metallization criterion of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses

Mole %	Metallization criterion $M(n_0)$	Metallization criterion $M(E_g)$
0.000	0.6135	0.4050
0.005	0.6066	0.4091
0.010	0.6059	0.3890
0.020	0.6046	0.4063
0.030	0.6009	0.4039
0.040	0.6001	0.4147
0.050	0.5967	0.4111

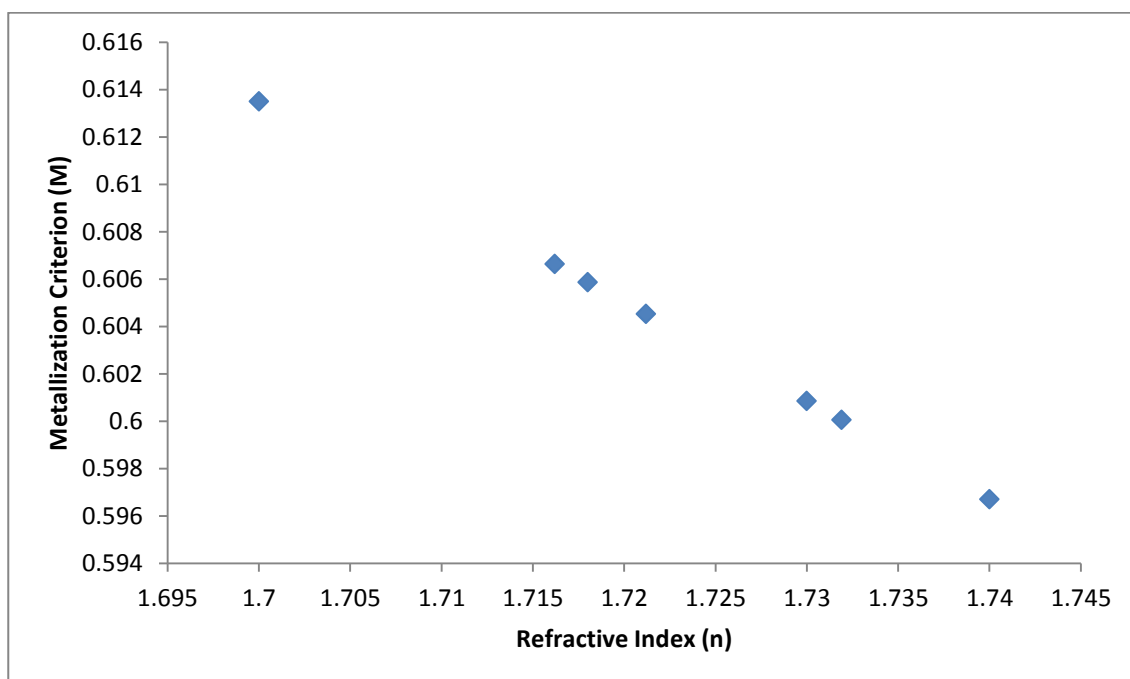


Fig. 12. Metallization criterion,  $M(n_0)$  of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses.

On the other hand, Figure 13 reveals that the value of the metallization criterion on the basis of band gap energy increases with the increasing number of band gap energy. This is due to the increasing value of the band gap in which decreases the conduction band. The decrease in metallization criterion means that the glass sample is metalizing. This suggests that the conduction band and valence band are broadened [17].

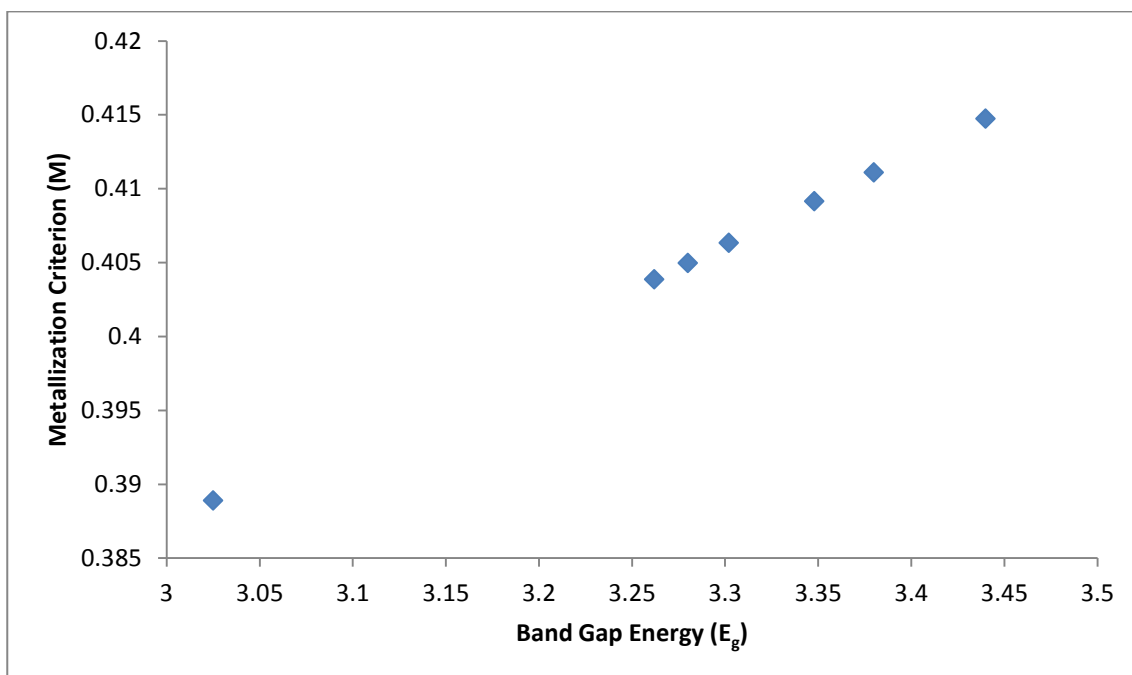


Fig. 13. Metallization criterion,  $M(E_g)$  of  $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{1-x}(ZnO)_x\}_{1-y}(Er_3O_2)_y$  glasses.

The result is in accordance with metallization criterion calculated by Dimitrov and Sakka. The small value of metallization criterion means that the width of conduction band becomes large which increased the tendency for metallization of the glasses [18].

#### 4. Conclusions

The average electronic polarizability, optical basicity and metallization criterion of zinc borotellurite doped erbium have been analyzed and investigated on the basis of refractive index and band gap energy. The electronic polarizability shows a general trend of increase with increasing refractive index and decreasing band gap energy. It is found that the oxide ion polarizability value increases with increasing refractive index and decreases with decreasing band gap energy. Higher value of oxide ion polarizability indicates that the increasing number of non-bridging oxygen (NBOs) in the glass material. The optical basicity of the glass materials shows a linear increase with increasing number of oxide ion polarizability. The value of optical basicity obtained from the data shows that the glass materials are more basic. It is suggested that the ability of oxide ion to donate electrons to surrounding cations increases. The metallization criterion of the glass material linearly decreases with increasing concentration of erbium. This is due to the increasing number of refractive indices and decreasing number of band gap energy. The decrease value of metallization criterion indicates that the glass material is metalizing.

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