Borate Glasses for Low Loss Optical Fibre

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Abstract. Borate glasses with composition 50B₂O₃ – (25-x) Bi₂O₃ – 25ZnO – xTiO₂ where x = 0, 1, 2, 3, 4 (mol%) were successfully fabricated using a conventional melt-quenching technique aimed at tailoring glass suitable for a low loss optical fiber fundamental. For this purpose, glasses were characterized for their density, refractive index, reflectance, UV-Vis absorption and FTIR spectra. Density measurement was carried out by applying Archimedes principle. Refractive index was measured using Brewster’s angle method. UV-Vis spectrum was recorded within the range of 200-1100 nm and FTIR measurement was measured at IR range. Combining the spectra data recorded both from UV-Vis–NIR and FTIR, the theoretical minimum loss of the glass was obtained. In addition, the band gap energy of the present glasses was also calculated. From these data, it can be derived many other glass properties such as Oxygen Packing Density (OPD), ionic radius, and polaron radius.

1. Introduction
Borate glass (B₂O₃) has been extensively studied and applied in various applications [1]. Borate glass has optical properties such as high solubility of rare-earth ions, good thermal stability, and high chemical properties. Borate glass has very high phonon energy around 1300 cm⁻¹ can cause non-radiation losses and reduce effective radiation emissions [2]. To form a glass, however, B₂O₃ cannot stand alone without the addition of alkali, alkaline earth or the addition of other glass formers [3]. Therefore, borate glass must be added to other glass formers to produce glass such as Bi₂O₃, ZnO, and TiO₂.

The addition of alkali, alkaline earth or other glass-forming in this borate glass have been reportedly produced glass with very high transparent. Bi₂O₃ is a chemical oxide which has a high electron valence but has low field strength and high polarization [4]. The addition ZnO into the glass reduces the glass melting point and increases glass stability against crystallization, refractive index and ability to form glass [5]. Apart from the addition of Bismuth (Bi₂O₃) and Zinc Oxide (ZnO), the addition of other oxides is Titanium (TiO₂). In borate glass the addition of TiO₂ can increase the ability of glass formation, glass stabilization, chemical resistance, and tissue formation [6]. In this paper, borate glasses with compositions: 50B₂O₃ – (25-x) Bi₂O₃ – 25ZnO – xTiO₂ where x = 0, 1, 2, 3, 4 (mol%) will be fabricated and characterized for their densities, refractive indices, reflectance, absorption spectra both in UV-VIS-NIR wavelength range and IR range.

2. Experiment
Borate glasses with compositions: 50B₂O₃ – (25-x) Bi₂O₃ – 25ZnO – xTiO₂ where x = 0, 1, 2, 3, 4 (mol%) were fabricated by applying melt-quenching method. The starting materials were weighed using a digital scale a nitrogenized glove box and then mixed evenly using mortar for 10 minutes.
Mixture was then transfer into an platinum crucible melted in electrical furnace at 900 °C for 1 hour. Casting was carried out by pouring the molten into a preheated mold and subsequently annealed at temperature of 300°C for approximately 9 hours and cooled to room temperature at a cooling rate of 1°C/minute. For optical characterization purpose, glasses were polished to optical standard. Density and optical characterization, i.e., refractive index, absorption spectra (UV-VIS-NIR and FTIR), were carried out using methods as has been presented in our previous papers [7, 8, 9].

3. Results and Discussion

3.1. Density

Figure 1-a shows how TiO$_2$ concentration affects the average molecular weight, density and molar volume of the investigated glasss. Density of a glass is affected by average molecular weight and molar volume as expressed by

$$\rho = \frac{\sum x_i M_i}{V_m}$$  \hspace{1cm} (1)

where $\rho$ is the density value of glass, $x_i$ is the molar fraction and $M_i$ is the molecular weight of the oxides that make up the glass. This competing factor as shown in Figure 1 shows a trend that according to equation (1) causes increasing value of density. The increase of glass density with increasing TiO$_2$ concentration means that slow rearrangement during glass formation process occur as TiO$_2$ was added into the mixture [10,11].

![Figure 1](image1.png)

**Figure 1.** (a) Average molecular weight of borate glass (b) Variation of glass density and molar volume of pure borate glass (B$_2$O$_3$) with TiO$_2$ content content where $x = 0, 1, 2, 3, 4 \text{ (mol\%)}$.

3.2. Oxygen Packaging Density

Oxygen Packaging Density (OPD) is a closeness measure of oxygen atoms making up the glass. Oxygen Packaging Density (OPD) can be used to measure variations in density and temperature of glass transition characterized by a glass matrix with spatial oxygen dispersion and can be related to molar volume [11,12]. Oxygen Packaging Density (OPD) can be calculated using the equation:

$$OPD = \frac{\sum N_i}{V_m}$$  \hspace{1cm} (2)

where $N_i$ is the number of oxygen atoms in the glass and $V_m$ is the molar volume cm$^3$/mol. As shown in Figure 2-a, OPD of the glass increases with increasing TiO$_2$ ions into the glass. Polaron radius which increases with the increase of TiO$_2$ as shown in Figure 2-b resulting in decreasing electrical conductivity of glass [13].
Figure 2. (a) Oxygen Packing Density (OPD) of borate glasses with different concentrations of TiO\textsubscript{2} ions. (b) Polaron Radius of TiO\textsubscript{2} doped borate glass.

3.3. Absorption Spectra and refractive index

The bandgap of the amorphous glass system is very effective when investigated using the UV-Vis method [14]. The absorption spectrum of TiO\textsubscript{2} doped borate glass was identified at a wavelength of 200-1100 nm and is shown in Figure 3. The absorption edge began to occur at a wavelength of 400 nm. As the TiO\textsubscript{2} concentration increases, the absorption edge experiences a shift in wavelength. This is due to the increased concentration of non-bridging oxygen [15,16]. Using According to Davis and Mott optical absorption is a method that can be used to confirm optical transitions and optical band gaps [17]. Optical energy bandgap can be determined using the equation (3):

\begin{equation}
(ahv)^{\frac{1}{2}} = C(hv - E_{opt})
\end{equation}

Figure 3. Absorption coefficient of borate glass as a function of TiO\textsubscript{2} content.

The decrease of bandgap energy as function of the change in TiO\textsubscript{2} is shown in Figure 4a. The reduction in the energy band gap is caused by the addition of TiO\textsubscript{2} ions to the B\textsubscript{2}O\textsubscript{3} glass. The reduction occurred due to structural changes after the addition of TiO\textsubscript{2} ions. According to Villegas &
Fernandez, changes induced by the TiO$_2$ ion glass structure as a result of an increase in the amount of non-bridging oxygen [18]. Therefore, the addition of TiO$_2$ in glass can reduce the optical bandgap.

As seen in Figure 4b, the refractive index of borate glass increases with increasing TiO$_2$ ion concentration. The Ti ion in this glass is Ti$^{4+}$ [14]. The addition of Ti$^{4+}$ ions can increase the amount of Non-Bridging Oxygen (NBO). Since NBO is more polarizable than BO, this addition causes the increase in refractive index [19].

![Figure 4](image1.png)

**Figure 4.** (a) The Tauc’s Plot for borate glass with 0% TiO$_2$ (b) Measured and predictive refractive index of all samples

| Glass Sample | Optical Band Gap Energy $E_{\text{opt}}$ (eV) |
|--------------|------------------------------------------|
| BBiZTi (0)   | 2.7217                                   |
| BBiZTi (1)   | 2.6939                                   |
| BBiZTi (2)   | 2.7093                                   |
| BBiZTi (3)   | 2.7433                                   |
| BBiZTi (4)   | 2.7304                                   |

3.4. Reflectance
Reflectance is the ratio of light reflected from sample glass and aluminum mirror [20]. Aluminum mirror is used for comparison because of its greater light transfer. From the results of the study that the reflectance of B$_2$O$_3$ glass increases with the increase of TiO$_2$ ions concentrations (Figure 5).
3.5. FTIR

The FTIR absorption spectrum of borate glass with TiO$_2$ doped has been analyzed, the absorption peaks formed occurred in the range 400-4000 cm$^{-1}$ as shown in Figure 6 (a). Borate glass contains structural units such as BO$_3$, BO$_4$, triborate, and diborate. This structure shows the information of the boroxol ring in the glass system, this explains that the glass containing the structure BO$_3$ and BO$_4$ is connected randomly [21,22,23].

Figure 6-a is FTIR data for all the investigated samples. To see the exact location of the absorption peaks and to provide information about the bonds forming the peaks, all samples were deconvoluted. Nevertheless, only one sample is shown here, namely the BBiZTi sample with x = 3. Deconvolution was carried out within the range 400 - 1500 cm$^{-1}$ (Figure 6-b). As can be seen from Figure 6-b, the absorption spectra within this range is better regarded as a superposition of 13 absorption bands. The spectrum of each band shows the different locations, the exact location of the bands are 387.11; 608.01; 689.66; 793.17; 871.24; 987.32; 1070.66; 1070.68; 1215.49; 1331.63; 1404.98; and 1452.20 cm$^{-1}$. The position of the glass sample bands and the bonding function are shown in Table 2.

![Figure 5](image1.png)

**Figure 5.** The reflectance spectra of TiO$_2$ doped B$_2$O$_3$ glass.

![Figure 6](image2.png)

**Figure 6.** (a) FTIR spectra of borate glass at range 500-3750 cm$^{-1}$. (b) Deconvolution of FTIR spectra for BbiZTi glass where x=3 mol%.
Table 2. Absorbance peak position of BBiZTi (3) doped TiO2 glass

| Peak (cm⁻¹) | Assignments | References |
|-------------|--------------|------------|
| 345 – 392   | Vibration Bi-O-Bi of BiO₃ pyramidal or BiO₆ octahedral units and assigned to bending mode of BO atoms. | [19,24] |
| 601 – 623   | TeO₄ containing tellurite in a glass. | [25] |
| 680 – 700   | The vibration of B-O-B in the borate network and TeO₄ trigonal pyramids. | [21,22] |
| 773 – 793   | Vibration stretching TeO³ of TeO₃+5 polyhedra units and vibration continuous network of TeO₄. | [26] |
| 817 – 1121  | Vibration stretching B-O of BO₃ units. | [19] |
| 959 – 988   | Vibration stretching for all glass of B-O-Bi. | [27] |
| 1061 – 1105 | Vibration stretching B-O and overlapping of BO₄ structural units due to various boroxol rings and penta-borate, tetra-borate, tri-borate groups. | [21,28] |
| 1214 – 1272 | Vibration stretching B-O bonds of BO₃ trigonal groups on boroxol rings. | [29] |
| 1212 – 1370 | Vibration stretching B-O in BO₃ units of the boroxol rings containing planar the six member borate groups. | [30,31] |
| 1315 – 1410 | Vibration stretching asymmetric of BO₃ triangular units in meta-borate, pyro-borate, and ortho-borate groups. | [27] |
| 1443 – 1460 | B-O³ is isolated pyroborate groups. | [32] |

4. Conclusions

The optical properties and physical properties of borate glass have been investigated, with the composition of 50B₂O₃ – (25-x)Bi₂O₃ – 25ZnO – xTiO₂ where x = 0, 1, 2, 3, 4 (mol%) using the melt-quenching method. The data generated based on research states that the physical properties which include Density, Molar Volume, Oxygen Packing Density (OPD), and Ionic Radius with the addition of TiO₂ ion concentration on B₂O₃ glass are increasing in the graph. While the optical properties which include absorption spectra, refractive index, bandgap, and reflectance of the resulting graphs are increasing. Whereas in deconvolution it produced 13 absorption bands. This is due to the influence of the addition of TiO₂ ion concentration on B₂O₃ glass.

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