Effect of TiO$_2$ Addition on Optical Properties of TeO$_2$-ZnO-PbO Glasses

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Abstract. Glasses with composition (in mol%): 60TeO$_2$-(30-x)ZnO-10PbO-xTiO$_2$ (TZPb:Ti) (where x = 0, 1, 2, 3 and 4) have been fabricated and characterised in order to study their physical and optical properties. Density and refractive index of glasses were measured at room temperature by applying Archimedes’s principle and Brewster’s angle method, respectively. Absorption spectra within range of UV-VIS-NIR were measured at room temperature using UV-VIS Spectrophotometer while those at IR range using FTIR. We have shown that density decreases with the increase of TiO$_2$ while refractive index and optical energy band gap behave conversely.

Keywords: Tellurite glasses, TiO$_2$ doped glasses, IR absorption spectra, UV-VIS absorption spectra, refractive index.

1. Introduction

In the last few decades, tellurite glasses has received more attention among other glass families [1] especially due to its potential applications such as optical amplifier, fiber sensors, and lasing materials [2, 3, 4], i.e., utilizing their unique properties such as low melting point, relatively stable against crystallization, large transparency window, high refractive index and large rare earth ion solubility [5,6,7,8,9]. Tellurium oxide, however, is an intermediate glass former, glass cannot be formed by itself. In order to form a glass, addition of alkali oxides or alkaline earth oxide and heavy metal oxides is required [10].

Effect of addition of heavy metal oxide on the glass structure, thermal stability and optic have been carried [11,12]. TiO$_2$ is one of metal oxides that have been widely used in many applications [13]. In glass technology, TiO$_2$ addition were studied from different point of view, such as structural change, crystallization tendency and optical properties [14, 15]. In this paper, TiO$_2$ were added to TeO$_2$-ZnO-PbO glass aimed at investigating its effect on molar volume, glass density, refractive index, absorption spectra within UV-VIS-NIR and IR range.

2. Experiment

Tellurite glass used as a base have compositions: 60TeO$_2$-(30-x)ZnO–10PbO–xTiO$_2$ (x = 0, 1, 2, 3, 4 mol%). Powders of all components (TeO$_2$, ZnO, PbO, and TiO$_2$) were mixed in agate mortar. The mixture was then poured into platinum crucible and melted in electrical furnace at 900°C for 35 min. Stirring was carried out to obtain a bubble-free melt. Casting was carried out by pouring the melt into a preheated square brass mold and subsequently annealed at temperature of 250°C for 6 hours and then cooled very slowly to room temperature (cooling rate 1 min/sec). The glasses were then optically polished for the purpose of optical characterizations.
Glass density ($\rho_g$) of all glasses were measured by applying Archimedes principle using pycnometer. The immersion liquid for this measurement was distilled water ($\rho_d = 1.000 \text{ g/cm}^3$ at room temperature). Measurements were carried out based on the following equation:

$$\rho_g = \frac{\rho_d (w_{ga} - w_{la})}{(w_{ga} - w_{la}) - (w_{gt} - w_{lt})}$$  \hspace{1cm} (1)

where $w_{ga}$ is mass of empty glass, $w_{gt}$ is mass of distilled water filled in the glass, whilst $w_{la}$ and $w_{lt}$ are weights in open air and destilled water. Molar volumes were then calculated based on density data using equation:

$$V_m = \frac{\sum x_i M_i}{\rho_g}$$  \hspace{1cm} (2)

where $x_i$ is mole fraction for each glass component $i$ which has molecular weight ($M_i$).

Refractive index for all samples were obtained from measurement Brewster’s angle method using setup as reported in [16]. Absorption spectra within UV-Vis-NIR range (from 200-900 nm) were obtained from UV-Vis Spectrometer Perkin Elmer Lambda 25 while for that within IR area (400-4000 cm$^{-1}$) were obtained from Shimadzu Prestige IR 21 Spectroscopy. All the above experiments were carried at room temperature.

3. Results and Discussion

3.1. Density and refractive index

Table 1 shows the density and molar volume which change as the TiO$_2$ concentration change. It can be seen from Figure 1 that the density of glass decreases with increasing TiO$_2$ concentration. This result can be easily understood as Zn has higher atomic mass (65.387 amu) compared to that of Ti (47.867 amu). Increasing molar volume as more TiO$_2$ was added might be easily linked to the atomic radius of Zn (139 pm) compared to that of Ti (147 pm). In addition, this increase might also be linked to the increase of the ratio between nonbridging oxygen (NBO) to bridging oxygen (BO).

| Composition Code | Density (g/cm$^3$) | Molar Volume (cm$^3$/mol) |
|------------------|--------------------|---------------------------|
| TZPbTi 0         | 6.1921             | 23.0120                   |
| TZPbTi 1         | 6.0877             | 23.4044                   |
| TZPbTi 2         | 5.9338             | 24.0087                   |
| TZPbTi 3         | 5.9270             | 24.0337                   |
| TZPbTi 4         | 5.6993             | 24.9911                   |

Figure 1. Relations between Density and Molar Volume with TiO$_2$ concentration.

Figure 2. Relations between Refractive Index with TiO$_2$ concentration.
Refractive index change as function of TiO₂ addition is tabulated in Table 2 and visualized in Figure 2. It is seen that refractive index increases with the increase of TiO₂ concentration. Linked to the increasing molar volume as discussed above, this result might be related to the increasing number of new non-bridging oxygen (NBO). It was reported that the increase of NBO/BO ratio can raise the glass polarizability and result in increasing refractive index [17]. From view point of ionic polarizability, Ti ions have greater ionic polarizability (Ti²⁺ = 0.7012871, Ti³⁺ = 0.6242542 or Ti⁴⁺ = 0.3912914) than Zn ions (Zn²⁺ = 0.1752656, Zn⁴⁺ = 1.1759126). Consequently, glass polarizability increases with the increase of Ti ions contents and therefore increase glass refractive index.

**Table 2. Refractive Index (n) and Optical Band Gap Energy value (E_g) of TZPb:Ti Glasses**

| Composition Code | n     | E_g (eV) |
|------------------|-------|----------|
| TZPbTi 0         | 1,8265| 2,63     |
| TZPbTi 1         | 1,8673| 2,62     |
| TZPbTi 2         | 1,9210| 2,60     |
| TZPbTi 3         | 1,9350| 2,55     |
| TZPbTi 4         | 1,9626| 2,52     |

**Figure 3. Absorbance of TZPb:Ti Glasses**

**Figure 4. Band gap energy determination of TZPb:Ti glasses**

### 3.2. UV-VIS and IR Absorption Spectra

Absorption spectra of all samples are shown in Figure 3. It can be seen that absorption spectra of samples increases with increasing the TiO₂ content. Absorption peak at around 400 nm is shown in Table 3, the same result was also reported by Rao, et al. 2018 [18] which is resulted for electronic transition in Ti³⁺ ions assigned to ²B₂g→²B₁g transition.

**Table 3. Refractive Index and Optical Band Gap Energy value of TZPb:Ti Glasses**

| Composition Code | Wavelength (nm) | Absorptivity coefficient (1/cm) |
|------------------|-----------------|---------------------------------|
| TZPbTi 0         | 384             | 5,42                            |
| TZPbTi 1         | 407             | 8,32                            |
| TZPbTi 2         | 412             | 8,75                            |
| TZPbTi 3         | 414             | 9,68                            |
| TZPbTi 4         | 420             | 9,07                            |
Figure 4. shows the band gap energy determination by applying Tauch's plot method. Firstly, graph relating \((\alpha h\nu)^{1/2}\) and photon energy \((h\nu)\) was constructed. Defining band energy as the energy boundary determining the range of energy transmitted or absorbed by the materials of interest, the energy band gap can be obtained by taking extrapolation of the linear part of the curve indicating the boundary between transmission and absorption area. It is shown that the band gap energy decreases with the increase of TiO\(_2\) content.

Figure 5. Transmittance at IR region of TZPbTi Glasses

Figure 5 shows the IR transmittance spectra of all samples within the range of 400-4000 cm\(^{-1}\). The O-H stretching group was identified in the range of wavenumbers 3400 cm\(^{-1}\) [19]. The Te-O group is in the range of wavenumbers 650 cm\(^{-1}\) [20]. Zn-O group is in the range of wavenumbers of around 673 cm\(^{-1}\) which corresponds to asymmetric vibrations of TiO\(_6\) [22] is stronger for the glass with higher content of TiO\(_2\).

4. Conclusions
Glasses with composition (in mol%): 60TeO\(_2\)-(30-x)ZnO-10PbO-xTiO\(_2\) (TZPb:Ti) (where x = 0, 1, 2, 3 and 4) have been studied and characterized in terms of density, refractive index, UV-VIS and IR absorption spectra. Addition of TiO\(_2\) ions causes decrease in density and optical band gap energy. Refractive index of glasses increases due to the increase NBO/NO ratio. Asymmetric vibrations of TiO\(_6\) is found stronger as the content of TiO\(_2\) increases.

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