Physical and optical properties of lead doped tellurite glasses

Riyatun¹, Lita Rahmasari² and Ahmad Marzuki¹*

¹Department of Physics, Sebelas Maret University, Jl. Ir. Sutami 36 A Surakarta 57126 Indonesia
²Department of Physics Education, Sebelas Maret University, Jl. Ir. Sutami 36 A Surakarta 57126 Indonesia
*E-mail: amarzuki@mipa.uns.ac.id

Abstract. Physical and optical properties of lead telluride (Pb:TZBN) glasses with composition 55TeO₂-(41-x)ZnO-2Bi₂O₃-2Na₂O-xPbO where x = 1.0, 1.5, 2.0, 2.5% mol are presented. UV-VIS-NIR spectra of the glasses in the range of 300 – 800 nm along with their densities and refractive indices at 746 nm were recorded at room temperature. The optical bandgap energy ($E_g$) has been calculated from the fitting of Tauc plot. On the basis of these results we found that with the increase of Pb²⁺ content, their refractive indices are increased while their optical bandgaps are decreased. From this experiment, no distinct relationship between the Pb²⁺ content variation and the electronic polarizability ($\alpha_{O2-}$) as well as their optical basicity values (A) were observed.

1. Introduction
In the last view decades, tellurite glasses have received considerable attention due to their unique properties, i.e., they have high glass transition temperature, high refractive index, wide infrared transmissions, relatively low melting point (725 °C), and high rare earth ion solubility [1,2,3]. Considering these properties, tellurite glasses have been widely researched and applied to the laser, photonic, communications and nonlinear applications [4,5].

Possessing high refractive index is one of the main reason tellurite glasses are considered as the important material for non-linear optical (NLO) applications. It has been shown that incorporating heavy metals oxides of Bi²⁺ or Pb²⁺ into TeO₂ glass enhances NLO properties [6].

This paper presents physical and optical properties of Pb:TZBN glasses with composition 55TeO₂-(41-x)ZnO-2Bi₂O₃-2Na₂O-xPbO where x = 1.0, 1.5, 2.0, 2.5% mol to predict the NLO properties.

2. Experiment
Tellurite glasses that we call Pb:TZBN with composition 55TeO₂-(41-x)ZnO-2Bi₂O₃-2Na₂O-xPbO) here x = 1.0, 1.5, 2.0, 2.5% mol were obtained by melting 10 g batches in platinum crucible at temperature of 900 °C for 30 minutes in air atmosphere. The melt was poured onto a pre-heated stainless steel parallel plates and then annealed at a temperature of 350 °C for 6 hours allowing the glass to release its thermal and mechanical stress followed by cooling to room temperature at the cooling rate of 1 °C/min. The densities of all the glass samples ($\rho$) were measured based on Archimedes method carried out at room temperature using pycnometer. Glasses refractive indices (n) were calculated from Brewster Angle $\theta_p$ using the equation (1).
The optical absorption of the samples was measured at wavelength range 300 - 800 nm at room temperature in order to calculate the optical bandgap energies ($E_g$). The results were then compared to those predicted by following Lorentz-Lorenz equation (2).

$$E_g = 20(1 - R_m/V_m)^2$$  \hspace{1cm} (2)

The value of the electronic glass polarizability ($\alpha_{O_2^-}$) determined based on the measured density and the refractive index was calculated using equation (3).

$$\alpha_{O_2^-}(n_o) = \left[\frac{V_m}{252}\right]^{\frac{1}{2}} - p\alpha_i q^{-1}$$  \hspace{1cm} (3)

$$\alpha_{O_2^-}(E_g) = \left[\frac{V_m}{252}\right]^{\frac{1}{2}} \left(1 - \frac{E_g}{20} - p\alpha_i\right) q^{-1}$$  \hspace{1cm} (4)

Similarly, their corresponding value of optical basicity ($\lambda$) was calculated using equation (5).

$$\lambda(n_o) = 1.67\left(1 - \frac{1}{(V_m/252)(n_o^2 - 1)/(n_o^2 + 2) - p\alpha_i q^{-1}}\right)$$  \hspace{1cm} (5)

$$\lambda(E_g) = 1.67\left(1 - \frac{1}{(V_m/252)(1 - \sqrt{E_g/252} - p\alpha_i) q^{-1}}\right)$$  \hspace{1cm} (6)

Where $p$ is the cation number, $q$ is the number of oxide ions, and $\alpha_i$ is the cationic polarizability.

3. Results and Discussion

3.1. Density and Molar Volume

The experimental values of the density and molar volume of all the glasses are given in Figure 1. Density and molar volume of the glasses increase with an increase in Pb$^{2+}$ content. These results may be attributed to the change of the atomic mass content and interatomic interspacing between atoms in the glass. The increase of the molar volume and density with the addition of the heavy and large ionic radius Pb$^{2+}$ into the glass network indicates that the glass network is shrinkage and creation of non-bridging oxygen is resisted.

![Figure 1. Effect of Pb$^{2+}$ on the glass densities (a) and molar volumes (b).](image-url)
3.2. Refractive index

The values of refractive index as shown in Figure 2 indicate that addition of Pb$^{2+}$ to TZBN glasses increases their refractive index. Similar results were also obtained if Pb$^{2+}$ ions were added to other glasses. These results can be understood by applying Lorentz-Lorentz equation that can be expressed as equation (7).

\[ n = \sqrt{\frac{V_m + 2R_m}{V_m - R_m}} \]  

where $R_m$ is the molar refractivity and $V_m$ is the molar volume. Molar refractivity can be expressed as a function of polarizability of a molecule ($\alpha_m$) as given by equation (8).

\[ R_m = \frac{4\pi\alpha_m N_A}{3} \]  

where $N_A$ is the Avogadro number. For a multi-component glass, total molar refractivity ($R_m$) is an additive function of its individual component molar refractivity ($R_{mi}$)

\[ R_m = \sum f_i R_{mi} \]

where $f_i$ is a molar fraction of a component composing the glass. Tellurite glass is an oxide glass composed of many individual oxides $A_pO_q$ each has molar refractivity

\[ R_m = pR_{m-A^{2+}} + qR_{m-O^{2-}} = 2.52(p\alpha_{m-A^{2+}} + q\alpha_{m-O^{2-}}) \]

Where $\alpha_{m-O^{2-}}$ and $\alpha_{m-A^{2+}}$ are polarizability of the cation and the anion, respectively. Among the cationic component in the glass, the cationic polarizability of Pb$^{2+}$ is the highest. Their values are Te$^{4+} = 0.242$ Å$^3$, Zn$^{2+} = 0.283$ Å$^3$, Bi$^{3+} = 1.508$ Å$^3$, Na$^{+} = 0.175$ Å$^3$, and Pb$^{2+} = 3.623$ Å$^3$ [7]. Looking back to equation (10) and (7), it is easily understood that incorporating Pb$^{2+}$ into the glass can increase the glass refractive index significantly.

![Figure 2](Image)

**Figure 2.** Refractive index change in TZBN glass as a function of Pb$^{2+}$ content.

3.3. Optical energy bandgap

Figure 3 is absorption spectra of Pb-incorporated TZBN glasses at 200 – 400 nm measured at room temperature. The Higher absorption coefficient was observed for a glass with higher Pb$^{2+}$ concentration. Red shifted UV edge was also observed as Pb$^{2+}$ ions were added to the glass. Converting the graph shown in Figure 3 into $(\alpha h\nu)^{1/2}$ versus $h\nu$ where $\alpha$, $h$, and $\nu$ are absorption coefficient, Plank constant, and light frequency, respectively; optical energy bandgap can be calculated. The typical graph obtained for this purpose is shown in Figure 4. Optical energy bandgaps obtained in this way along with those obtained from equation (2) are given in table 1. It can be seen that the optical energy bandgap decreases with respect to increasing the Pb$^{2+}$ content.
Figure 3. Absorption spectra of Pb-incorporated FTZBN glass at 200 – 400 nm.

Figure 4. Calculating optical energy bandgap using Tauc Plot.

### Tables

| Samples  | Calculation (eV) | Measurement (eV) | Relative difference (%) |
|----------|------------------|------------------|--------------------------|
| 1.0 mol% | 3.759            | 3.277            | 12.82                    |
| 1.5 mol% | 3.741            | 3.269            | 12.62                    |
| 2.0 mol% | 3.723            | 3.248            | 12.76                    |
| 2.5 mol% | 3.707            | 3.227            | 12.95                    |

| Pb$^{2+}$ content (mol%) | 1.0  | 1.5  | 2.0  | 2.5  |
|--------------------------|------|------|------|------|
| $\alpha_{\text{O2}^-}$ ($\text{Å}^3$) | 2.486 | 2.485 | 2.491 | 2.461 |
| Optical basicity (Å)     | 0.978 | 0.9775 | 0.981 | 0.9725 |

From the value of the refractive index and optical energy bandgap and by applying equation (3) – (6) we can predict the glass electronic polarizability optical and optical basicity (Table 2) [8]. Typical oxide electronic polarizabilities of common oxide glasses are within the range of 1.4-1.6 Å$^3$ ) while their corresponding optical basicity values are in the range of 0.4-0.6. Since electronic polarizability represents an ability to donate electrons to the surrounding cations, an increase in electronic oxide polarizability means that an oxide ion has a stronger electron donor ability and thus easily be polarized. High values of oxide electronic (ionic) polarizability, as well as optical basicity as shown in Table 2, indicate that Pb-incorporated TZBN glasses are potentially used as the important material for non-linear optical (NLO) applications. High optical basicity of the glasses means that the glasses have the small single bond strength and thus easily polarized.

### 4. Conclusions

We have investigated the physical and optical properties of Pb:TZBN glasses with composition 55TeO$_2$-(41-x)ZnO-2Bi$_2$O$_3$-2Na$_2$O-xPbO where x = 1.0, 1.5, 2.0, 2.5% mol. We found that refractive index and molar volume of the glass increases with the increase of Pb$^{2+}$ content. We also calculated
the oxide ion polarizability ($\alpha_{\text{O}2^-}$) as well as their optical basicity value ($\Lambda$). The way their values change as a function of Pb$^{2+}$ addition in the glass is not obvious. High values of $\alpha_{\text{O}2^-}$ and $\Lambda$ obtained in the experiment here in shows that these glasses have potential use in non-linear optical (NLO) applications.

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