Effect of TiO$_2$ Addition on Physical and Spectroscopic Properties of TeO$_2$-ZnO-Na$_2$O Glasses

Ahmad Marzuki*, Devara Ega Fausta
Department of Physics, Sebelas Maret University, Surakarta 57126, Indonesia
*E-mail: amarzuki@mipa.uns.ac.id

Abstract. This paper presents the effect of TiO$_2$ addition on the physical and optical properties of TeO$_2$-ZnO-Na$_2$O glasses. For this study, glasses with the compositions of 63.16TeO$_2$ - (31.57-x) ZnO – 5.26 Na$_2$O – xTiO$_2$ (where x = 1.06, 2.11, 3.16, and 4.22 mol%) were prepared with melt quenching technique. Glasses were characterized in order to obtained glass density, refractive index, and absorption spectra ranging from UV to IR regions. From these basic data, we have evaluated the values of molar volume, oxygen packed density, polaron radius, inter-ionic distance, field strength, and optical band gap. It was observed that incorporating TiO$_2$ into the glasses to substitute ZnO have resulted in decreasing the values of density, inter-ionic distance, and field strength; and yet increasing molar volume, oxygen packed density and polaron radius. The structural units building the glass networks have also been evaluated.

Keywords: Tellurite glasses, optical bandgap, refractive index, oxygen packed density, polaron.

1. Introduction
First tellurite glass was synthesized by Burger H., et al. at 1985 [1]. Since then, tellurite glasses have received more attention and researched for various applications by employing their properties such as: low melting point, good thermal stability, high refractive index, low phonon energy, wide transmission window, high rare-earth ions solubility and theoretically possess low minimum loss [2, 3, 4, 5, 6]. Several important applications employing these properties are intended to tailor optical devices such as optical amplifiers, fiber laser, photonic nanowires and sensors [7, 8].

TiO$_2$ has many unique optical and electrical characteristics and therefore has been researched for many different applications such as: sunscreen [9], self-cleaning coating [10] and solar cell [11]. It is well known that TiO$_2$ is a nucleating agent [12, 13]. Addition of TiO$_2$ into a glass can therefore enhance crystallization [14]. TiO$_2$ addition into a glass has also been studied because of its role in modifying glass refractive index [15]. Glass refractive index generally increase with increasing TiO$_2$ content. In addition
of that, it was also shown that addition of TiO$_2$ can increase glass chemical durability and nonlinear refractive index which is useful for nonlinear optical devices.

This present work reports the effect of TiO$_2$ addition on the physical and spectroscopic properties of TeO$_2$-ZnO-Na$_2$O glasses. Physical studies are performed by evaluating glass density, molar volume, oxygen packing density (OPD), ionic concentration, polaron radius, inter-ionic distances, and field strength. While the spectroscopic studies will include investigation glass absorption in UV-Vis and IR regions.

2. Experiment

Tellurite glasses with composition (in mol%): 63.16 TeO$_2$-(31.57-x) ZnO–5.26 Na$_2$O–xTiO$_2$ (where x = 1.06, 2.11, 3.16 and 4.22) were synthesized using melt quenching technique. For this purpose, appropriate amount of each chemical was weighed and then mixed thoroughly in an agate mortar. The prepared mixture was then placed in platinum crucible and then melted in an electrical furnace at temperature of 900°C for about 35 minutes. Casting was carried out by pouring the molten glass into a pre-heated brass mould. In order to release any thermal and mechanical stress that might occur during fabrication process, the obtained glass was then annealed at 265°C for 6 hours and subsequently cooled to room temperature at cooling rate of 10°C/minute. The obtained glasses were then cut into the size of 1.5 cm x 1.5 cm and then optically polished to meet the requirement for further optical characterization.

Density of all glasses were measured by applying Archimedes principles that is by immersing glass into distilled water contained in a pycnometer at room temperature. Using the obtained density, several other physical quantities are calculated. Among them are:

a. Molar volume ($V_m$)

$$V_m = \frac{\sum x_i M_i}{\rho_g}$$

b. Oxygen Packed Density (OPD)

$$OPD = \frac{1000 N_O \rho_g}{M_g}$$

c. Polaron radius ($r_p$)

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{1/3}$$

d. Field strength ($F$)

$$F = \frac{z}{r_p^2}$$

In the above equation, $\rho_g$ is glass density, $x_i$ and $M_i$ are molar fraction and molecular weight of the $i^{th}$ component of glass, $N_O$ is number of oxygen atom for each composition, $N$ is number of site density and $z$ is atomic number of Ti.

Refractive indices of all samples were measured using Brewster angle method at room temperature. Optical absorption spectra at UV-Vis-NIR range were measured at room temperature using UV-Vis Spectrometer Perkin Elmer Lamda 25 in the wavelength 200-1000 nm while thorecorded using Shimadzu Prentige IR 21 Spectroscopy by KBr disc technique.

3. Results and Discussion

3.1. Physical analysis

Figure 1 shows the change in density and molar volume as function of TiO$_2$ content and Table 1 tabulates the value of density, molar volume, OPD, polaron radius, ionic concentration, inter-atomic distance and field strength. Decreasing glass density as TiO$_2$ content increase can be linked to atomic mass of Ti (47.87 sma) compared to that of Zn (65.39 sma) as well as atomic radius of Ti atom (2.0 Å) as
compared to that of Zn atom (1.53Å). This substitution can therefore make the glass lighter while at the same time its volume is decreased. In other words the glass molar volume increases with the increases of TiO$_2$ content. This increase in molar volume can be linked to the increase in volume which also means an increase in the amount Non-Bridging Oxygen (NBO) inside the glass network [16, 17, 18]. It can also be seen from Table 1 that the increase of TiO$_2$ content leads to increasing OPD, ionic concentration, and polaron radius, while decreasing the value of interatomic distance and field strength.

![Figure 1. Variation of density and molar volume of all samples as function of TiO$_2$ content](image)

| Composition Code | Density (g/cm$^3$) | Molar Volume (cm$^3$) | OPD (mol/L) | Ionic Concentration (x10$^{22}$ ions/cm$^3$) | Polaron Radius (Å) | Inter Ionic Distance (Å) | Field Strength ($10^{-15}$ cm$^2$) |
|------------------|--------------------|-----------------------|-------------|---------------------------------------------|-------------------|------------------------|-------------------------------|
| TZNT1            | 5.4906             | 23.63                 | 69.49       | 2.7017                                      | 2.356             | 0.0123                 | 1.438                         |
| TZNT2            | 5.4842             | 23.65                 | 69.86       | 5.3724                                      | 4.685             | 0.0062                 | 0.368                         |
| TZNT3            | 5.4570             | 23.77                 | 69.97       | 8.0069                                      | 6.983             | 0.0041                 | 0.164                         |
| TZNT4            | 5.4269             | 23.89                 | 70.03       | 10.635                                      | 9.276             | 0.0031                 | 0.092                         |

3.2. Optical Band Gap Energy and Refractive Index

Optical band gap energy is a measure of energy range separating valence band and conduction band energies and its value is sensitive to structural change. Optical band gap energy can be calculated using equation:

$$\alpha \nu = B \left( \frac{\nu - E_g}{\nu} \right)^n$$

(5)

where $\alpha$ is absorption coefficient, $\nu$ is photon energy, $B$ is constant, $E_g$ is the optical band gap energy and $n$ is a constant ($n$ equals 2 for indirect band gap and equals $\frac{1}{2}$ for direct optical band gap). In the present work, the absorption edge indicates that it is indirect optical band gap [19] and therefore $n$ is taken equals $\frac{1}{2}$. 

---

Table 1. Density, Molar Volume, OPD, Ionic Concentration, Polaron radius, Inter Ionic Distances, Filed Strength of all Glasses

| Composition Code | Density (g/cm$^3$) | Molar Volume (cm$^3$) | OPD (mol/L) | Ionic Concentration (x10$^{22}$ ions/cm$^3$) | Polaron Radius (Å) | Inter Ionic Distance (Å) | Field Strength ($10^{-15}$ cm$^2$) |
|------------------|--------------------|-----------------------|-------------|---------------------------------------------|-------------------|------------------------|-------------------------------|
Figure 2 shows a plot of \((ahv)^{\frac{1}{2}}\) agains \(hv\) for all samples. The value of \(E_g\) was obtained by extrapolating the linear part of the curve to intercept the \(hv\)-axis. The optical band gap obtained by extrapolating the linear region from the curve which \((ahv)^{\frac{1}{2}} = 0\). The values of \(E_g\) along with refractive index measured using Brewster angle’s method are presented in Table 2. While the Optical band gap energy decreases with the increase of the TiO\(_2\) content, the glass refractive index increase with the increase of TiO\(_2\) content. This result may be resulted from reconstruction of tellurite network cause by incorporating of Ti\(^{4+}\) ions that increases the number of NBO and thus increases polarizability which in turn raise refractive index [19].

| Composition Code | \(E_g\) (eV) | \(n\)   |
|------------------|-------------|--------|
| TZNT1            | 2.86        | 1.911  |
| TZNT2            | 2.82        | 1.961  |
| TZNT3            | 2.75        | 1.976  |
| TZNT4            | 2.71        | 2.005  |
3.3. Absorption Spectra

Figure 4. shows optical absorption spectra of all the investigated glass recorded at room temperature at wavelength ranging from 400- 800 nm. It can be seen that the UV-edge is red-shifted as TiO$_2$ concentration is increased, so is the absorption coefficient. This red-shifting is explained in the same way of decreasing $E_g$ with the increase of TiO$_2$. 
Figure 5 shows the FTIR absorption spectra of all glass samples. Several peaks within the range of 400-4000 cm$^{-1}$ were observed. High similarity as can be seen for all spectrum indicates that all glass samples have similar glass network [20]. The peaks around 3426 cm$^{-1}$ can be assigned as a peak originated from absorption of hydroxyl which might be arise from the fact that the absorption spectra were recorded in situ and, due to high humidity, re-adsorption of water might be occurred [21] [22] [23]. The peaks at 1636 cm$^{-1}$ is assigned to vibrations of hydroxyl group [24]. According to [25] the modifier cations like Na$_2$ possess vibrational sites below 500 cm$^{-1}$. Broad band which centered between 500 to 600 cm$^{-1}$ are related to TiO$_2$ components [24]. In this work, that band slightly increased from 513 to 543 cm$^{-1}$ as the higher addition of TiO$_2$ components.

Otherwise, the last strong band occurred between 647 to 670 cm$^{-1}$. According to [26] the shift of band, near 640 cm$^{-1}$ towards higher frequencies (690 cm$^{-1}$) due to vibration between TeO$_2$-ZnO. It was shown that increase of TiO$_2$ composition does not strongly affect the characteristic vibrational band of pure TeO$_2$. It can be explained because both lengths of Te-O and Ti-O bonds are 1.9-2.0 Å. In this bond there is also vibration of Te-O bond in the TeO$_2$ pyramidal units which exhibiting strong infrared absorption [27]. For the further investigation, deconvolution was performed between 500 to 800 cm$^{-1}$ in all glass samples. Figure 6. shows deconvoluted peak from TZNT Glasses. It was shown that, there are several peaks which constructed the strong peak between 500 to 800 cm$^{-1}$. 

![Figure 5. FT-IR Spectra of TZNT Glass](image-url)
4. Conclusion

TeO$_2$-ZnO-Na$_2$O glasses doped with various concentration of TiO$_2$ have been fabricated and characterized for physical and spectroscopies studies. It was shown that addition of TiO$_2$ causes decreasing in density, inter-ionic distance, field strength and optical band gap energy. In addition, the increase in TiO$_2$ content caused an increase in refractive index and shifts the UV-edge to longer wavelength.

References

[1] M Burger H, Vogel W and Kozhukharov V 1985 Infrared Phys. 25 395-409. (https://doi.org/10.1016/0020-0891(85)90114-9).

[2] Marzuki A, Fausta D E 2018 IOP Conf Ser Mater Sci Eng 333 (1) 012015. (DOI: 10.1088/1757-899X/333/1/012015).
[3] Marzuki A, Yunianto M, Riyatun, Purwanto H 2018 KEM 772 85-89. (DOI: 10.4028/www.scientific.net/KEM.772.85).
[4] Zhu Y, Shen X, Su X, Zhou M, Zhou Y 2019 Mater. Lett. 244 175-177 (DOI: https://doi.org/10.1016/j.matlet.2019.02.078).
[5] Fu W, Zhang C, Hou G, Xia J, Li G, Ping Y, 2019 Optik 182 308-313. (DOI: https://doi.org/10.1016/j.ijleo.2019.01.034).
[6] Yang Z, Wu Y, Yang K, Xu P, Zhang W, Dai S, Xu T 2017 Opt. Mat. 72 524-528. (DOI: https://doi.org/10.1016/j.optmat.2017.06.057).
[7] Tong L, Hu L, Zhang J, Qiu J, Yang Q, Lou J, Shen Y, He J, Ye Z 2006 Opt. Express 14 (1) 82-87. (DOI: https://doi.org/10.1364/OPEX.14.0000082).
[8] Azlan M N and Halimah M K 2018 Results in Physics 11 58-64. (DOI: https://doi.org/10.1016/j.rinp.2018.08.017).
[9] Lewicka Z A, Yu W W, Oliva B L, Contreras E Q, Colvin V L 2013 J. Photochem. Photobiol, 263 24-33. (DOI: https://doi.org/10.1016/j.jphotochem.2013.04.019).
[10] Chen P, Wei B, Zhu X, Gao D, Gao Y, Cheng J, Liu Y 2019 Ceram. Int. 45 (5) 6111-6118. (DOI: https://doi.org/10.1016/j.ceramint.2018.12.085).
[11] Deng X, Wang Y, Cui Z, Li L, Shi C 2018 Superlattices Microst 117 283-287 (DOI: https://doi.org/10.1016/j.smicro.2018.03.051).
[12] Krz´manc M M, Dos’ler U, and Suvorov D 2012 J. Am. Ceram. Soc. 1–7 (DOI: 10.1111/j.1551-2916.2012.05216.x).
[13] Mukherjee D P, Das S K 2016 Journal of Asian Ceramic Societies 4 (1) 55-60 (DOI: https://doi.org/10.1016/j.jascer.2015.11.004).
[14] Zhang L, Liu S 2018 J. Non-Cryst. Solids 500 366-370 (DOI: https://doi.org/10.1016/j.jnoncrysol.2018.08.023).
[15] Karlsson S, Bäck L G, Kidkhunthod P, Lundstedt K, & Wondraczek L (2016 Opt. Mater. Express, 6 (4) 1198. (https://doi.org/10.1364/OME.6.001198).
[16] Altaf M and Chaundry M.A, 2010 J. Mod. Phys.1 201-205. (DOI: https://doi.org/10.4236/jmp.2010.14030).
[17] Ruengsri S., Kaewkhao, J., Limsuwan, P, 2012 Procedia Engineering32 772-779. (DOI: https://doi.org/10.1016/j.proeng.2012.02.011).
[18] Edukondaki A., Kavitha, B., Hameed, A., Kumar, K.S, 2012 IOP Conf. 73 012127. (DOI: 10.1088/1757-899X/73/1/012127).
[19] Stambouli W., Elhouichet, H., Ferid, M, 2012 J. Mol. Struc 1028 39-43. (DOI: https://doi.org/10.1016/j.molstruc.2012.06.027).
[20] Souri, D, 2010 Mid. East J. Sci. Research5 44-48. (DOI: http://dx.doi.org/10.4236/mep.2010.40301).
[21] Perumal, S., Sambandam, C.G., Prabu, K.M., Anathakumar S, 2014, IJRET 3 651-657. (DOI: 10.15623/IJRET.2014.0304116).
[22] Sahar, M R., Rohani M.S. and Kasim, A, 2009 S. State Sci. and Tech.1 27-30. ISSN 0128-7389.
[23] Beranek, R and Kisch, H, 2008, Photochemical and Photobiological Science 7 40-48. (DOI: 10.1039/b711658f).
[24] Burger, H., Kneipp, K., Hobert, H., Vogel, W. 1992 J Non-Cryst. Solid151 134-142. (DOI: https://doi.org/10.1016/0022-3093(92)90020-K).
[27] Heo, J., Lam, D., Sigel, H.S., Mendoza, E.A., Hensley, D.A, 1992 J. Am. Ceram. Soc 2 277-281 (DOI: 10.1111/j. 1151-2916.1992. tb08176.x).