EFFECT OF Fe₂O₃ ON OPTICAL AND STRUCTURAL PROPERTIES OF 80TeO₂–(20−x)ZnO–xFe₂O₃ TELLURITE GLASS SYSTEM

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Ternary 80TeO₂–(20−x)ZnO–xFe₂O₃ glass system was prepared using conventional melt quenching technique to investigate the effect of Fe₂O₃ on structural, thermal and optical properties of the glass system. FTIR analysis shows domination of bridging oxygen (BO) as indicated by intensity of TeO₄ assigned peak (~650cm⁻¹) relative to intensity of TeO₆ assign peak (780cm⁻¹). Shifting of FeO₆ assign peak (~460cm⁻¹) to a higher wavenumber indicates hardening which may be due to increase in rigidity as corroborated by the increase of Tg of the glass system. Direct and indirect optical energy gap, (E_{opt}^{D} and E_{opt}^{I}) obtained from UV-Vis spectra analysis showed both values displayed large drop with initial addition of Fe₂O₃ (x=5 mol%) before decreasing at slower rate for x>5 mol%. Both E_{opt} are suggested to decrease with increase of TeO₄ since the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) of TeO₄ is smaller compared to that of TeO₃.

(Received August 20, 2019; Accepted November 11, 2019)

Keywords: Optical properties, Tellurite glass, HOMO, LUMO

1. Introduction

Tellurium oxide (TeO₂), a well-known oxide based glass are considered as a very promising material due to electrical [1, 2], optical [3-8], magnetic [9] and elastic [10, 11] properties and possesses advantageous properties such as chemical stability, high reflective index and malleability, low phonon energy and high dielectric constant which is good candidate for optical switching and gas sensing material. More interestingly, tellurite glass is non-hygroscopic compare to phosphate glass and borate glass. On the other hand, TeO₂ are known as a conditional glass former which can form a glass network in conjunction with a glass modifier such as WO₃ [12, 13], ZnO [5, 7, 8, 10, 14] iron-oxides [4, 15] or any alkali metal or transition metal oxides. Previously, studies on tellurite glass doped with metal-basis oxides were being widely conducted. Addition of metal oxides in the tellurium glasses shows significant changes not only in physical but also optical properties [5-7, 16, 17].

Study on tellurite glass doped with transition metal oxide shows significant effects on some properties such as structural, electrical, thermal and optical in both binary and ternary glass system [2, 5-8, 11, 16, 18-21]. Previous studies on binary ZnO-TeO₂ [22] or zinc tellurite glass shows that physical properties such as density increase linearly while molar volume decreases with the increament of ZnO content which was suggested to be due to decreases in average interatomic spacing. In addition, optical band gap, E_{opt} decreased while refractive index, n increased suggested due to presence of more non-bridging oxygen (NBO) since NBO has much greater ionic character and lower bond energies. In contrast, studies on temperature dependence of electronic polarizability and optical basicity by V. Dimitrov and T.Komatsu et. al. [23] shows decrease in density with increase in mole fraction of ZnO in xZnO–(100 – x)TeO₂. Furthermore, at room temperature for x>20 mol% optical properties such as refractive index n, molar polarizability α_m, electronic polarizability of oxide ion α_e, and optical basicity Λ decreased. It is suggested that fraction of TeO₃ structural units with NBO content increased as a function of ZnO. Meanwhile, Manning et. al [24] found that refractive indices decrease with the increase of ZnO content and

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proposed conversion of TeO\textsubscript{4} units into TeO\textsubscript{3} units reduced polarizability, hence refractive index, \( n \) reduced. Coincidentally, same behavior on physical and optical properties also found in zinc-tellurite glass by J.G Thorbhan and J.W Zwanziger et. al [25] and Kaur et. al [26]. They suggested that at high concentration of ZnO, networks of ZnO\textsubscript{4} are formed and at low concentration of ZnO acts as network modifier, breaking the Te–O–Te linkages.

On the other hand, several reports on Fe\textsubscript{2}O\textsubscript{3} – TeO\textsubscript{2} binary glass system shows an interesting behavior in both physical and chemical properties [27, 28]. Increasing of Fe\textsubscript{2}O\textsubscript{3} by concurrent reduction of TeO\textsubscript{2} strongly influenced the magnetic susceptibility but not change the basic TeO\textsubscript{4} trigonal bipyramidal structure units to local TeO\textsubscript{3} indicating the dominance of BO [13]. On the contrary, other study on binary Fe\textsubscript{2}O\textsubscript{3}–TeO\textsubscript{2} glass system has shown that incorporating Fe\textsubscript{2}O\textsubscript{3} in the TeO\textsubscript{2}-rich glass network strongly induced depolymerization of TeO\textsubscript{4} units into TeO\textsubscript{3} and TeO\textsubscript{3} units [29] and decreases the density upon adding Fe\textsubscript{2}O\textsubscript{3} content.

Previously we reported on the elastic and structural properties of ternary 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3} tellurite glass system which shows non-linear increase in elastic constants (longitudinal, \( C\textsubscript{l} \), shear, \( C\textsubscript{s} \), bulk modulus, \( K \) and Young’s modulus, \( E \)) as well as Debye temperature, \( \theta\textsubscript{D} \). It was found that both \( K \) and \( E \) has a large increase at \( x=0 \) mol\% to \( x=5 \) mol\% followed by small increase for \( x>5 \)mol\%. Furthermore, Fourier transform infrared (FTIR) studies on 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3} glass system reported that formation of BO is more dominant than NBO. In addition, both increment in elastic moduli and \( \theta\textsubscript{D} \) show that additions of Fe\textsubscript{2}O\textsubscript{3} strengthen the compound structure by producing more BO as Fe\textsubscript{2}O\textsubscript{3} increase. On the other hand, for 20ZnO–(80–\( x \))TeO\textsubscript{2}–\( x \)Fe\textsubscript{2}O\textsubscript{3} [30] reported that the glass transition temperature, \( T\textsubscript{g} \) and thermal stability \( \Delta T \) increased. It was suggested that the addition of Fe\textsubscript{2}O\textsubscript{3} increased the average coordination number and creates strongly bonded network which is also responsible for the increase in thermal stability. Such change brought about by iron on 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3} may also influence optical properties of the glass system as reported in other ternary glass such as TeO\textsubscript{2}–WO\textsubscript{3}–PbO\textsubscript{2} [31, 32], TeO\textsubscript{2}–La\textsubscript{2}O\textsubscript{3}–TiO\textsubscript{2} [33, 34] and WO\textsubscript{3}–Ag\textsubscript{2}O–TeO\textsubscript{2} [35] glass systems where substitution of transition metal oxides (TMO) influenced the elastic and optical properties of the glass systems. However, for 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3}, such study on optical properties has not been carried out.

The aim of this present work is to determine the effect of Fe\textsubscript{2}O\textsubscript{3} in 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3} tellurite glass system on its structural and optical properties using FTIR spectroscopy and UV-Vis spectroscopy, respectively. Urbach energy (\( E\textsubscript{U} \)) of the glass system was also calculated in order to elucidate structural disorder of the glass structure. In addition, in order to relate rigidity with the effect of Fe\textsubscript{2}O\textsubscript{3} addition, results of DSC study have been presented and discussed.

2. Experiment details

The 80TeO\textsubscript{2}–(20–\( x \))ZnO–\( x \)Fe\textsubscript{2}O\textsubscript{3} glass system with \( x=0, 5, 10, 15 \) and 20 mol\% were synthesized by melt-quenching technique. The powder of Fe\textsubscript{2}O\textsubscript{3} (99.99\% purity), ZnO (99.99\% purity) and TeO\textsubscript{2} (99.995\% purity) were mixed and ground in agate mortar in an hour to reach homogeneity and fined grained mixture. The mixed batches were then melted at 900°C in an hour. The melt was quickly quenched by pouring it on stainless steel plate before annealed at 150°C for 3 hours. The glasses were then ground into powder to meet the requirement of X-ray diffraction (XRD), IR spectra (FTIR), UV-Vis and differential scanning calorimeter (DSC) measurements. XRD analysis was performed to confirm the amorphous nature of the glass samples by using X’Pert Pro Panalytical diffractometer. The density, \( \rho \) of the glass samples were determined using Archimedes principle with xylene as an immersion medium and the relation is:

\[
\rho = \left( \frac{W_a}{W_a-W_b} \right) \rho_b
\]

where \( W_a \) is the glass sample weight in air, \( W_b \) is the glass sample weight in xylene and \( \rho_b \) is the density of xylene (0.865 g/mL). The corresponding molar volume was calculated using formula:
\[ V_m = \frac{M}{\rho} \]  
(2)

where \( M \) is the molar volume and \( \rho \) is density.

Infrared (IR) absorption analysis was performed in the region of 400-1000 cm\(^{-1}\) with NICOLET 560 spectrometer, using KBr pellets at room temperature. On the other hand, the glass transition temperature, \( T_g \) was measured using DSC (NETZSCH DSC 200 F3 model). All samples were heated in porcelain crucible from 100°C to 500°C at the rate of 10°C min\(^{-1}\).

Optical absorption spectra were recorded using Varian Cary 5000 UV-VIS-NIR spectrometer with wavelength range between 200-1000 nm at room temperature. Optical energy band gap for both direct and indirect was obtained from the graph. The optical absorption coefficient \( \alpha(l) \) for each photon energy, below and near the edge of each curve is calculated by

\[ \alpha(\lambda) = \frac{2.303A}{d} \]  
(3)

where \( A \) is the absorbance and \( d \) is thickness of the sample.

The optical absorption coefficient \( \alpha(\nu) \) as a function of photon energy \( h\nu \) can be expressed using the Davis and Mott equation that yields the optical energy band gap:

\[ \alpha(\nu) = A[(h\nu - E_{opt})^p/h\nu] \]  
(4)

where \( \alpha \) is absorption coefficient near the fundamental absorption edge of each spectrum, \( E_{opt} \) is optical band gap in eV, \( A \) is constant and \( p \) is an index which can be assumed to have 1/2, 3/2, 2 or 3, depending on the nature of the electronic transition responsible for absorption. Here \( p \) is equal to 1/2 for direct allowed transition, 3/2 for direct forbidden transitions, 2 for indirect allowed transitions and 3 for indirect forbidden transitions. \( n \) is determined through a following empirical relation:

\[ \frac{n^2 - 1}{n^2 + 2} = 1 - \frac{E_{opt}}{2\nu} \]  
(5)

Relation between molar refraction, refractive index and molar volume is described by the Lorentz-Lorenz equation:

\[ R_m = \frac{(n^2-1)}{(n^2+2)} V_m \]  
(6)

where \( R_m \) is molar refraction. The molar refraction is related to structure of the glass and it is proportional to molar electronic polarizability of the material \( \alpha(m) \) through the following relation:

\[ \alpha(m) = \frac{4}{3\pi NA} R_m \]  
(7)

with \( \alpha_m \) in (Å\(^3\)) in Equation (7) can be transformed to the following expression:

\[ \alpha(m) = \frac{R_m}{2.52} \]  
(8)

3. Result and analysis

The XRD pattern for all samples of 80TeO\(_2\)-(20-\(x\))ZnO-\(x\)Fe\(_2\)O\(_3\) (\(x=0, 5, 10, 15, 20\) mol \%) glass system confirm the amorphous nature of the glass system (Fig. 1). Table 1 gives the values of density (\( \rho \)), and molar volume (\( V_m \)). Fig. 2 shows the variation of \( \rho \) and \( V_m \) with increments of Fe\(_2\)O\(_3\) content for 80TeO\(_2\)-(20-\(x\))ZnO-\(x\)Fe\(_2\)O\(_3\) glass system. The figure clearly shows that the value of \( \rho \) decreases gradually with addition of Fe\(_2\)O\(_3\) content from 6174 kg m\(^{-1}\) (\(x = 0\) mol \%) to 4638 kg m\(^{-1}\) (\(x = 20\) mol \%). Meanwhile, as addition of Fe\(_2\)O\(_3\) increasing from \(x = 0\) to \(x = 20\) mol\%, the
molar volume \((V_a)\) of the glasses also steadily decrease from \(2.33 \times 10^{-3}\) m\(^3\) mol\(^{-1}\) to \(3.44 \times 10^{-3}\) m\(^3\) mol\(^{-1}\).

Meantime, Fig. 3 shows the FTIR spectroscopy for 80TeO\(_2\)-(20-\(x\))ZnO-\(x\)Fe\(_2\)O\(_3\) glass system. Four major bands IR absorption bands were observed, namely, 452-456, 578-580, 632-660 and 747-794 cm\(^{-1}\). An abruptly appear peak for \(x>5\) mol\% at 452-456 cm\(^{-1}\) is assign to vibration of FeO\(_6\) octahedral group [36] while 578-580 cm\(^{-1}\) peak is assign to stretching vibration of TeO\(_3\)\(^{+1}\) [37]. Meantime, band 632-660 cm\(^{-1}\) peak is assign to bending and stretching vibration of TeO\(_4\) trigonal bipyramidal (tbp) group. Wavenumber of 747-794 cm\(^{-1}\) is assign to stretching vibration of TeO\(_3\) bipyramidal (bp) unit. Additionally, peak 455 cm\(^{-1}\) is assign to vibration of zinc - oxygen bonding respectively [10]. The assignment for the FTIR peak was shown in Table 2. Deconvoluted diagram for \(x=5\) mol\% using Guassian function (Fig. 4) shows the four-major peak intensity of FeO\(_6\), TeO\(_3\)\(^{+1}\), TeO\(_4\) and TeO\(_3\) respectively.

The DSC curves for 0 \(\leq x \leq 20\) mol\% of the glass system are shown in Fig. 5. The values of glass transition temperature \((T_g)\), onset crystallization temperature, \((T_o)\), temperature of the first crystallization peak \((T_x)\) and thermal stability, \((\Delta T = T_o - T_g)\) are tabulated in Table 3. The replacement of ZnO by Fe\(_2\)O\(_3\) leads to an increase of \(T_g\) in glass from 317 \(^\circ\)C \((x=0\) mol\%) to 412\(^\circ\)C \((x=20\) mol\%). The graph of thermal behavior of \(T_g\) was illustrated in Fig. 6. Calculated values of \(\Delta T\) Shows increasing in temperature at \(x=0\) mol\% (67\(^\circ\)C) to \(x=10\) mol\% (143\(^\circ\)C) before slightly decreases at \(x>10\) mol\% (143\(^\circ\)C - 129\(^\circ\)C) respectively.

**Table 1.** Density, \(\rho\) and molar volume, \(V_a\) of 80TeO\(_2\)-(20-\(x\))ZnO-\(x\)Fe\(_2\)O\(_3\) \((x=0, 5, 10, 15, 20\) mol\%) glass system.

<table>
<thead>
<tr>
<th>(x) (mol%)</th>
<th>(\rho) (± 20 kg/m(^3))</th>
<th>(V_a) (± 0.003 m(^3)/mol) (\times 10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6174</td>
<td>2.33</td>
</tr>
<tr>
<td>5</td>
<td>5715</td>
<td>2.58</td>
</tr>
<tr>
<td>10</td>
<td>4955</td>
<td>3.06</td>
</tr>
<tr>
<td>15</td>
<td>4702</td>
<td>3.31</td>
</tr>
<tr>
<td>20</td>
<td>4638</td>
<td>3.44</td>
</tr>
</tbody>
</table>
Fig. 2. Density, $\rho$ and molar volume, $V_0$ of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Fig. 3. The FTIR spectroscopy of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Table 2. Wavenumber and their assignments for IR spectra for 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol%) glass samples.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>~452-456</td>
<td>Vibration of FeO$_6$ octahedral group</td>
</tr>
<tr>
<td>~578-587</td>
<td>Stretching vibration of TeO$_{3n+1}$</td>
</tr>
<tr>
<td>~632-681</td>
<td>Bending and stretching vibration of TeO$_3$ trigonal bipyramidal (tbp) group</td>
</tr>
<tr>
<td>~747-794</td>
<td>Stretching vibration of TeO$_3$ bipyramidal (bp) unit</td>
</tr>
</tbody>
</table>

Fig. 4. Deconvoluted IR spectra of the 80TeO$_2$-15Fe$_2$O$_3$-5ZnO glass sample using a Gaussian type function.
Fig. 5. DSC curves of $\text{80TeO}_2-(20-x)\text{ZnO-xFe}_2\text{O}_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Table 3. Values of temperature glass transition temperature ($T_g$), onset crystallization temperature, ($T_o$), temperature of the first crystallization peak ($T_x$) and thermal stability, ($\Delta T$) of $\text{80TeO}_2-(20-x)\text{ZnO-xFe}_2\text{O}_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

<table>
<thead>
<tr>
<th>x (mol%)</th>
<th>$T_g$ (°C)</th>
<th>$T_o$ (°C)</th>
<th>$T_x$ (°C)</th>
<th>$\Delta T = T_o - T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>317</td>
<td>384</td>
<td>403</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>348</td>
<td>433</td>
<td>457</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>374</td>
<td>517</td>
<td>539</td>
<td>143</td>
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<tr>
<td>15</td>
<td>393</td>
<td>527</td>
<td>596</td>
<td>134</td>
</tr>
<tr>
<td>20</td>
<td>412</td>
<td>541</td>
<td>585</td>
<td>129</td>
</tr>
</tbody>
</table>

Fig. 6. Graph of $T_g$ behavior of $\text{80TeO}_2-(20-x)\text{ZnO-xFe}_2\text{O}_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

The absorption spectra taken at room temperature for all glass system are shown in Fig. 7. The absorption edges are shifting as addition iron content increases. The calculated values of optical energy gap ($E_{opt}$) for direct ($E_{D\text{opt}}$) and indirect ($E_{I\text{opt}}$), Urbach energy ($E_u$), refractive index ($n$), molar fraction ($R_m$) and electronic polarizability, ($\alpha_m$) was tabulated in Table 4.

Optical energy gap was determined from Eq. (4) by extrapolating the $\alpha$ to zero absorption in the $(\alpha h\nu)^{1/2}$ vs $h\nu$ for $E_{D\text{opt}}$ and $(\alpha h\nu)^{3/2}$ vs $h\nu$ for $E_{I\text{opt}}$ as shown in Fig. 8 and Fig. 9 respectively. The comparison graph of calculated value between those two are shown in Fig. 10. Both the gaps for the glass systems shows a large drop from $x=0$ mol% to $x=5$ mol% before slightly decreases at $x>5$ mol%.

Refractive index, $n$ is one of important properties of optical glass and can be obtained using Eq. (5). The calculated $n$ shows an opposite trend to $E_{D\text{opt}}$ (Fig. 11) where it was initially increase from 2.62 ($x=0$ mol%) to 3.05 ($x=5$ mol%) followed by slightly increase to 3.53 at $x=20$.
mol%. On the other hand, molar fraction, $R_m$ can be described by Lorentz-Lorentz equation (Eq.6). The equation gave the average molar refraction for isotropic substance, which co-relate with structure of the glass by $V_m$ and it is proportional to molar electronic polarizability, $\alpha_m$ (Eq. 7 and Eq. 8). The $\alpha_m$ was gradually increase from 6.12Å$^3$ at $x=0$ mol% to 10.83Å$^3$ at $x=20$ mol% (Fig. 13). Meantime, the $E_u$ can be obtained by extrapolating the graph lnα vs $hv$ as shown in Fig. 12. The Urbach energy, $E_u$ has the lowest value at $x=0$ mol% (0.26eV). The values tend to increase as Fe$_2$O$_3$ content increased as shown in Fig. 13 above.

Table 4. Direct optical energy band gap, $E^D_{opt}$, Indirect optical energy band gap, $E^I_{opt}$ Urbach energy, $E_u$, Refractive index, $n$, Molar fraction, $R_m$ and Electronic polarizability, $\alpha_m$ of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

<table>
<thead>
<tr>
<th>x</th>
<th>$E^D_{opt}$ (eV)</th>
<th>$E^I_{opt}$ (eV)</th>
<th>$E_u$ (eV)</th>
<th>$N$</th>
<th>$R_m$ ($cm^3 mol^{-1}$)</th>
<th>$\alpha_m$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.29</td>
<td>3.41</td>
<td>0.27</td>
<td>2.62</td>
<td>15.43</td>
<td>6.12</td>
</tr>
<tr>
<td>5</td>
<td>1.41</td>
<td>2.38</td>
<td>0.75</td>
<td>3.05</td>
<td>18.93</td>
<td>7.51</td>
</tr>
<tr>
<td>10</td>
<td>1.32</td>
<td>2.26</td>
<td>0.81</td>
<td>3.11</td>
<td>22.77</td>
<td>9.04</td>
</tr>
<tr>
<td>15</td>
<td>1.04</td>
<td>2.14</td>
<td>0.99</td>
<td>3.34</td>
<td>25.58</td>
<td>10.15</td>
</tr>
<tr>
<td>20</td>
<td>0.86</td>
<td>2.00</td>
<td>1.23</td>
<td>3.53</td>
<td>27.29</td>
<td>10.83</td>
</tr>
</tbody>
</table>

Fig. 7. Optical absorption spectra taking at room temperature of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Fig. 8. Plot of $(\alpha h \nu)^2$ as a function of $h \nu$ for 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.
Fig. 9. Plot of $(\alpha h \nu)^{1/2}$ as a function of $h \nu$ for 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Fig. 10. Direct optical energy band gap, $E_{D_{\text{opt}}}$ and indirect optical energy band gap, $E_{I_{\text{opt}}}$ of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Fig. 11. Indirect optical energy band gap, $E_{I_{\text{opt}}}$ and refractive index, $n$ of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.

Fig. 12. Determining Urbach energy, $E_u$ of 80TeO$_2$-(20-x)ZnO-xFe$_2$O$_3$ (x=0, 5, 10, 15, 20 mol %) glass system.
4. Discussions

Density analysis is one of the important physical studies to indicate the structural compactness of a glass system. In our present study, increasing Fe$_2$O$_3$ content results in decreasing of $\rho$ while $V_m$ increased. The behavior of $\rho$ can be due to either change in molar mass ($M_a$) or molar volume $V_a$ but the substitution of heavier Fe$_2$O$_3$ (molecular mass 159.69 g/mol) compared to lighter ZnO (molecular mass 81.408 g/mol) caused density to decrease suggesting that the increase in $V_a$ is larger in comparison to the increase in $M_a$ [10]. It is also suggested that shorter Zn – O bonds were replaced by longer Fe – O bonds, leading to formation of more open network structure [32]. The glass transition temperature ($T_g$) is well known to be a structural parameter depending on the bond strength, degree of cross-link density and closeness of packing [43]. The increase in $T_g$ (Fig. 6) could be caused by the replacement of ZnO by Fe$_2$O$_3$ which has greater bond strength (409 kJmol$^{-1}$) than ZnO (151 kJmol$^{-1}$) [43, 44]. Moreover, the increase in the value of $T_g$ can be corroborated to support the increase in rigidity of the glass system.

Our result on increase in rigidity due to increase of Fe$_2$O$_3$ was evidenced by FTIR analysis where it was observed that FeO$_6$ assigned peak was shifted to higher wavenumbers. Meantime, peak intensity of TeO$_4$ $tbp$ at 661cm$^{-1}$ ($x=15$mol%) which was higher compared to peak intensity of TeO$_3$ $tp$ at 782cm$^{-1}$ indicates the ascendancy of BO as shown in the deconvoluted diagram (Fig. 4). In addition, the shifting of TeO$_3$ assigned peak as well as the increase its intensity at around 631-681cm$^{-1}$ for $x=0$mol% to $x=20$mol% samples indicates the formation of BO. Meanwhile, formation of NBO was indicated by TeO$_3$ $tp$ assigned shoulder at around 780cm$^{-1}$. The presence of both BOs and NBOs indicates some form of competition may be present between them. However, in our studies, the intensity of TeO$_4$ assigned peak was more abundant which indicates the dominance of BO compared to NBO on the glass system. Our suggestion of more dominant BO was supported by the increase in rigidity from the DSC studies and the result in rigidity was collaborated by increase in elastic modulus studies reported by Azianty et. al [10].

Optical absorption of photon in the glasses can take place by direct or indirect transition. Many studies reported that the indirect transition which involves both photon and phonon are more prominent in amorphous materials [12, 13, 39]. However, here, for a comparison, both direct and indirect transitions were taken into consideration in order to determine the most suitable transition for this glass system. Generally in oxide glasses, increasing BO usually leads to increasing $E_{opt}$ as electrons are bound more tightly for BO and are harder to excite compared to NBO [23, 40]. However, for this glass system, we observed that $E_{opt}$ for $x=0$-20 mol % (Fig. 10) decreased as BO content increased as shown in FTIR analysis. Such behavior could be understood by considering previous report on ab-initio molecular orbital calculation results which showed that the energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) state of TeO$_4$ is smaller than those of TeO$_3$ [41].

The increase in $n$ (Table 4) is essentially a consequent of the decrease in $E_{opt}$ as calculated using Eq.5. The increase could also be understood due to the increase in total electronic
polarizability as shown in Fig. 13 since Fe$_2$O$_3$ has larger electronic polarizability (2.647Å$^3$) compared to ZnO (2.612Å$^3$). Our result of the increase in $n$ with the increase in BO is not unique to the present glass system but has also been reported for several glass systems such as TeO$_2$–Nb$_2$O$_5$–ZnO[8] and TeO$_2$–Nb$_2$O$_5$–ZnO–PbO [42] glass systems. On the other hand, the increasing behavior of Urbach energy (Fig. 13) indicates the increase in defect of the glass network. In glass, the presence of defect has been suggested to be closely related to the amount of NBO [3, 4, 13].

5. Conclusions

Fe$_2$O$_3$ substitution in 80TeO$_2$-(20-x)Fe$_2$O$_3$–xZnO glass system has caused larger number of TeO$_4$ tbp over TeO$_3$ tbp which indicate the dominance of BO on the glass system as indicated by FTIR analysis. Optical band gap shows a decreasing behaviour and was suggested be due to smaller energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) of TeO$_4$ compared to that of TeO$_3$. Refractive index, $n$ calculated from $E_{opt}$ values shows an increase with Fe$_2$O$_3$ which may be due to the increase in electronic polarizability. Urbach energy, $E_u$ increased suggesting that defects in the glass system increased with increasing Fe$_2$O$_3$.

Acknowledgements

The authors express gratitude to the Institute of Research Management and Innovation (IRMI) and Universiti Teknologi MARA, Selangor, Shah Alam, Malaysia for funding this research under the BESTARI Grant (600-IRMI/DANA 5/3/BESTARI (130/2018)).

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