Abstract—The changes of the optical and structural properties of Bismuth-Boro-Tellurite glasses before and after gamma irradiation were studied. Six glass samples, with different composition \([\text{TeO}_2]_{0.7} (\text{Bi}_2\text{O}_3)_{0.3}]_{1-x} (\text{Bi}_2\text{O}_3)x\) prepared by melt quenching method were irradiated with 25kGy gamma radiation at room temperature. The Fourier Transform Infrared Spectroscopy (FTIR) was used to explore the structural bonding in the prepared glass samples due to exposure, while UV-VIS Spectrophotometer was used to evaluate the changes in the optical properties before and after irradiation. Gamma irradiation causes profound changes in the peak intensity as shown by FTIR spectra which is due to the breaking of the network bonding. Before gamma irradiation, the optical band gap, \(E_g\) value decreased from 2.44 eV to 2.15 eV with the addition of Bismuth content. The value kept decreasing (from 2.18 eV to 2.00 eV) following exposure to gamma radiation due to the increase of non-bridging oxygen (NBO) and the increase of defect in the glass. In conclusion, the glass with high content of Bi2O3 (0.30Bi) give smallest \(E_g\) and show less changes in FTIR spectra after gamma irradiation which indicate that this glass is more resistant to gamma radiation compared to other glasses.

Keywords—Boro-Tellurite, bismuth, gamma radiation, optical properties.

I. INTRODUCTION

In recent years there have been numerous studies about the effect of gamma radiation on the structural and optical properties of borotellurite glasses using well-known analytical techniques such as UV-VIS, XPS, EPS and Raman spectroscopy. Since the optimal engineering performance of glasses is dominated by its structure and the change in the specification within the glass network, with even a small change in composition or processing can have significant effect on the properties, it is therefore important to study the influence of various external factors on the glass system. Gamma irradiation affects the optical properties of various glasses with varying degrees depending on the type and composition of glass including the presence of transition metal ions even if present as impurities. The knowledge of the glass structure before and after irradiation is a prerequisite for understanding the structural evolution of glasses under long term radiation. Boro-tellurite glasses show highly marked shielding towards successive gamma irradiation. This type of glass which contains heavy metal oxides is extensively used in radiation shielding because of their resistance to high radiation, high absorption cross-section for radiation and, at the same time, small irradiation effects on their mechanical and optical properties [1]. It has been proven to be the best radiation shielding candidate when comparing the combined spectral results after successive gamma irradiation. Recent spectral optical and FTIR studies by various glass scientists have arrived to the conclusion that heavy metal oxides in glasses have potential effects on gamma irradiation causing some shielding behavior because of their high radiation and, at the same time, small irradiation effects on their mechanical and optical properties [3]. Irradiation effects on the optical and structural properties of heavy metal oxides are important because of interesting applications as a host for rare-earth scintillators and a calorimeter medium for the superconducting super collider [4].

The objectives of this study are: (i) to study the structural changes of \([\text{TeO}_2]_{0.7} (\text{Bi}_2\text{O}_3)_{0.3}]_{1-x} (\text{Bi}_2\text{O}_3)x\) before and after gamma radiation, (ii) to investigate the relation between glass density and gamma radiation (iii) to calculate the band gap values before and after gamma radiation. In previous study done by our group research, the optical properties of Bismuth-Boro-Tellurite glasses have been reported [5] but without exposing the glasses to gamma radiation. Therefore this research which exposes the glasses to gamma radiation will lead to a fundamental understanding of gamma irradiation induced structural modifications and optical in Bismuth-Boro-Tellurite glasses.

II. EXPERIMENTAL DETAILS

Six glasses of \([\text{TeO}_2]_{0.7} (\text{Bi}_2\text{O}_3)_{0.3}]_{1-x} (\text{Bi}_2\text{O}_3)x\) (where \(x = 0.05, 0.10, 0.15, 0.20, 0.25\) and 0.3 mol%) were prepared by using a melt quenching technique. The chemicals such as tellurium (IV) dioxide TeO2, boron oxide B2O3 and bismuth oxide Bi2O3 from Assay, Alfa Aesar were mixed together and ground thoroughly by using an agate mortar for about 20 minutes. The mixture was preheated at 350°C for 30 minutes and then melted at 400°C for 1 hour. The molten glass was poured into a stainless steel mould which was preheated at 400°C and annealed at 400°C for 1 hour. All glasses were cut (about 2 mm thickness) and then polished until its surfaces become smooth. The glasses were also prepared in powder.
form for the Fourier Transform Infrared (FTIR) analysis in the range of 200–2000 cm⁻¹. The glass density, \( p_g \), was determined using Archimedes principle.

A UV-Visible spectroscopy SIMADSU Model UV-1650PC was used to observe the optical absorption at the range of 200-800 nm. Optical absorption coefficient, \( \alpha \), was determined using:

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

where \( d \) is thickness of glass sample and \( A \) is absorbance. The band gap energy, \( E_{\text{opt}} \) (indirect transition) was measured using:

\[
(e\omega)^{1/2} = B(h\omega - E_{\text{opt}})
\]

where \( B \) is a constant and \( h\omega \) is the photon energy. Urbach energy, \( \Delta E \) is define as the width of tailed of localized states in the band gap and was determined by taking the reciprocal of the slope of the plot \( \ln \alpha \) against \( h\omega \) curve. The decrease or increase value of \( \Delta E \) can describe defect in the glass network.

The gamma irradiation process was conducted using \(^{60}\text{Co} \) gamma rays source with a dose rate of 5.52 kGy/h at Malaysia Nuclear Agency. All glasses placed at 100 cm from the source were subjected to the same gamma dose, 25 kGy.

### III. RESULTS AND DISCUSSION

#### A. Physical Properties

Six ternary Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\)-Te\(_2\)O\(_3\) glasses were prepared using melt quenching technique. All glasses were transparent, yellow in color and without bubbles. The data for density and molar volume measurement for all glasses were shown in Table I where the density and molar volume increased from 4.29 g.cm\(^{-3}\) to 6.24 g.cm\(^{-3}\) and 33.05 cm\(^3\).mol\(^{-1}\) to 37.31 cm\(^3\).mol\(^{-1}\) respectively. A graph was plotted for the density and molar volume of the present glass as shown in Fig. 1. The density and molar volume increases due to the increase of Bi\(_2\)O\(_3\) content. The highest content of Bi\(_2\)O\(_3\) in the glass gives the highest density and molar value compared to other glasses.

The increase of glass density can be explained by: 1) high density of Bi\(_2\)O\(_3\), 2) high molecular weight of Bi\(_2\)O\(_3\), and 3) production of non-bridging oxygen (NBO). In this study the increasing density refers to the replacement of low density of B\(_2\)O\(_3\) (2.46 g/cm\(^3\)) and Te\(_2\)O\(_3\) (5.67 g/cm\(^3\)) with high density of Bi\(_2\)O\(_3\) (8.99 g/cm\(^3\)). From previous reports, the addition of Bi\(_2\)O\(_3\) content in glasses will modify the glass structure which will break up the continuous network and produce non-bridging oxygen (NBO) [6]. When Bi\(_2\)O\(_3\) content increases, formation of NBO also increases and causes the glass to be denser.

The molar volume values from Table I show the same behavior with the increasing density values when the Bi\(_2\)O\(_3\) content increases. This is due to the high molecular weight of Bi\(_2\)O\(_3\) (465.96 g/mol), which is twice as big compared to B\(_2\)O\(_3\)-Te\(_2\)O\(_3\) (229.2 g/mol). In addition, the increase of the molar volume maybe due to the ionic radii of Bi\(^{3+}\) (1.70 Å) which is higher than boron (1.44 Å) and tellurite (1.60 Å) [7].

Previous research reports that the molar volume can be used as a parameter to identify an open structure where the highest value of molar volume corresponds to the maximum open structure [8]. This research shows that 0.30Bi glass has maximum open structure compared to the other glasses.

#### B. FTIR Analysis

The FTIR spectra for all glasses before and after exposure to gamma ray are illustrated in Figs. 2-7 in the range of 200–4000 cm\(^{-1}\). The IR spectra of Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\)-Te\(_2\)O\(_3\) glasses before irradiation indicates several changes as the Bi\(_2\)O\(_3\) content increases and is shown below:

- a) The absorption band ~ 610 cm\(^{-1}\) assigned to Bi-O stretching in BiO\(_6\).
- b) The component peak 639-645 cm\(^{-1}\) attributed to the vibration of TeO\(_4\).
- c) The intensity of absorption band at 720-780 cm\(^{-1}\) as the Bi\(_2\)O\(_3\) content increases maybe due to stretching mode of TeO\(_4\) with non-bridging oxygen.
- d) The shoulder form at 860-890 cm\(^{-1}\) may be attributed to vibration of Bi-O in BiO\(_6\) units.
- e) The small peak range at 1019-1027 cm\(^{-1}\) is due to B-O stretching vibration of BO\(_3\). This band is observed for 0.05Bi-0.20Bi glass, but absent in 0.25Bi and 0.30Bi glasses.
- f) The intensity peak at 1200 cm\(^{-1}\) increase as Bi\(_2\)O\(_3\) content increases and is attributed to the increase of B-O bond stretching vibration of BO\(_3\) group.

### Table I

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density (g/cm(^{3}))</th>
<th>Molar Volume (cm(^3).mol(^{-1}))</th>
<th>Optical Band Gap, ( E_{\text{opt}} ) (eV)</th>
<th>Urbach Energy, ( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05Bi</td>
<td>4.29</td>
<td>33.05</td>
<td>2.50</td>
<td>2.18</td>
</tr>
<tr>
<td>0.10Bi</td>
<td>4.81</td>
<td>34.49</td>
<td>2.43</td>
<td>2.17</td>
</tr>
<tr>
<td>0.15Bi</td>
<td>5.20</td>
<td>35.10</td>
<td>2.42</td>
<td>2.13</td>
</tr>
<tr>
<td>0.20Bi</td>
<td>5.56</td>
<td>35.83</td>
<td>2.35</td>
<td>2.10</td>
</tr>
<tr>
<td>0.25Bi</td>
<td>5.85</td>
<td>36.95</td>
<td>2.30</td>
<td>2.05</td>
</tr>
<tr>
<td>0.30Bi</td>
<td>6.24</td>
<td>37.31</td>
<td>2.17</td>
<td>2.00</td>
</tr>
</tbody>
</table>

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g) The intensity peak around 1300 cm\(^{-1}\) decrease as Bi\(_2\)O\(_3\) content increases which may be due to the asymmetric stretching vibration of B-O in BO\(_3\) group.

The obvious changes of FTIR spectra for Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\)-TeO\(_2\) glass after exposed to gamma ray can be seen at Figs. 2-7. There are several main changes in absorption band for 0.05Bi-0.20Bi glasses, which are ~1200 cm\(^{-1}\), ~1300 cm\(^{-1}\), 720-780 cm\(^{-1}\) and 1010-1030 cm\(^{-1}\). The intensity of these absorption bands are seriously increased after irradiation while, the FTIR spectra after radiation for 0.25Bi and 0.30Bi glasses show very small changes compared before irradiation. This indicates that 0.25Bi and 0.30Bi glasses are resistant to gamma radiation compared to other glasses.

C. Optical Properties

The optical band gap energy, \(E_{opt}\) (indirect) was obtained by extrapolating the straight line on the curve to the axis at \((\alpha \cdot \omega)^{1/2} = 0\) as shown in Fig. 8. The optical band gap value for indirect transition of all glasses before and after irradiation is shown in Table I. These \(E_{opt}\) values were also plotted in a graph as shown in Fig. 9. It is shown that \(E_{opt}\) before and after radiation decrease as Bi\(_2\)O\(_3\) content increases. Before irradiation, the decreasing of optical band gap is due to the structural rearrangement in the glass network after the addition of glass modifier Bi\(_2\)O\(_3\). In binary B\(_2\)O\(_3\)-TeO\(_2\) glass, non-bridging oxygen (NBO) atoms are already present [9], and with the addition of Bi\(_2\)O\(_3\) in the glass, cause the transformation of TeO\(_4\) to TeO\(_3\) along with non-bridging oxygen. Increasing amount of Bi\(_2\)O\(_3\) will produce more NBO atom in the glass network. The large magnitude of negative charges on NBOs may rise up the top of valence band and resulting in reduction of the optical band gap. The decreasing value of \(E_{opt}\) about 7-12% after irradiation is due to the increase in the degree of network disorder. Gamma irradiation is expected to create atoms displacement, ionizing electron and break network bonding in glass structure. Previous research reports that gamma irradiation effect on glasses depends on several factors such as radiation dose, type of glass and the essential defects which are already present in the glass before irradiation [10]. An increase in the modifier content shows less decrease in the band gap value with irradiation. This means that the glass system becomes resistant to radiation with the addition of modifier [11].

![Fig. 2 FTIR spectra for 0.05Bi glass before and after gamma irradiation](image1)

![Fig. 3 FTIR spectra for 0.10Bi glass before and after gamma irradiation](image2)

![Fig. 4 FTIR spectra for 0.15Bi glass before and after gamma irradiation](image3)

![Fig. 5 FTIR spectra for 0.20Bi glass before and after gamma irradiation](image4)

![Fig. 10 shows the variation of Urbach energy, \(\Delta E\) value for different concentration of Bi\(_2\)O\(_3\). The \(\Delta E\) value increases from 0.36 to 0.46 eV before gamma irradiation, and also increases from 0.45 to 0.57 eV as the Bi\(_2\)O\(_3\) content increases after gamma irradiation. It is clearly shown in Fig. 10 that \(\Delta E\) value of each glass is increases after radiation. The increasing \(\Delta E\) before irradiation is due to the defect within the glass network such as increasing number of NBOs and cation-anion vacancy pair. After gamma irradiation, the increasing of \(\Delta E\) values is due to the glass defect which was generated through atomic
displacement, ionization and charge trapping, and photochemical effect.

Fig. 6 FTIR spectra for 0.25Bi glass before and after gamma irradiation

Fig. 7 FTIR spectra for 0.30Bi glass before and after gamma irradiation

Fig. 8 Graph of \((\alpha\hbar\omega)^{1/2}\) against photon energy of 0.30Bi glass before and after gamma irradiation

Fig. 9 Variation of optical band gap energy, \(E_{opt}\) of all glasses before and after gamma irradiation

Fig. 10 Variation Urbach energy, \(\Delta E\) of all glasses before and after gamma irradiation

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