THERMAL STABILITY, STRUCTURAL AND OPTICAL PROPERTIES OF RICE HUSK SILLICA BOROTELLURITE GLASSES CONTAINING MnO₂

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The quaternary glass system \[\{(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}\text{SiO}_2\}_{1-x}\text{[MnO}_2\text{]}_x\], where \(x = 0.00, 0.01, 0.02, 0.03, 0.04\) and \(0.05\) molar fraction was prepared by melt quenching technique. The amorphous nature of the glass is confirmed by X-ray diffraction patterns and Scanning Electron Microscopy (SEM). The prepared glass samples had also been characterized by Differential Scanning Calorimetry (DSC). The glass transition (\(T_g\)), onset glass transition (\(T_{o} \)), crystallization (\(T_c\)) and melting temperature (\(T_m\)) values were measured from DSC thermo-gram. Results from DSC indicate good thermal stability and low value of fragility (\(F\)) of the prepared glass samples. Thermal stability (\(T_s\)), Hurby parameter (\(K_{gl}\)), fragility (\(F\)) and activation energy (\(E_a\)) were calculated for every glass composition. It is observed that the optical band gap decreases with the concentration of MnO₂. On the other hand, the refractive index (\(n\)) is observed to increase as the concentration of MnO₂ increases. Fourier Transform Infrared (FTIR) spectroscopy has been done to identify the functional group in glass sample.

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1. Introduction

Recently, tellurite glass has gained significant research interest due to its possibility to be made as a network former because of its various application such as in the field of laser, non-linear applications, optoelectronic and photonics. Tellurite glass shows high refractive index (~2.0), low phonon energy (~700 cm⁻¹), high dielectric constant, good corrosion resistance and thermal and chemical stability [1-4]. Inorganic borate glasses have been widely used in recent application such as in photonic field.

Borate glasses are advantageous material for radiation dosimetry, infra-red studies, dielectric and insulating materials. Borate glass is usually used in forming system because of its unique and various structural units [5-7]. The pure borate glass contains boroxol ring \(\text{B}_2\text{O}_6\) that has high bond strength and low cation size. Borate glass also has low refractive index, high melting point and large phonon energy [8].

Silicate glass has high viscosity which can be considered to be used as waveguides in optical communications systems [9]. This silicate glass shows low thermal expansion coefficient, and is chemically durable [10]. Silicate glass is also used as mixed network such as boro-silicate, alumino-silicate, phospho-silicate, sodium-silicate bismuth-silicate glasses or three or more network formers because of its unique ability to infuse into the overall glass structure [11-13].

In this work, silica powder was extracted from the rice husk or rice paddy. Due to the high silica content, rice husk can be processed to extract silicon compounds [14]. Silica extracted from rice husk can reduce disposal problems and can be a cheap raw material rather than buying a commercial silica powder. Main contain of this rice husk contains large amount amorphous silica

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and other metal impurities such as in a minimum amount. There are many methods to extract silica from the rice husk depending on temperature and duration of burning process [15-17].

The optical, structural and thermal properties of silica borotellurite doped with MnO₂ glass system contain varying concentrations of MnO₂ from 0.00 to 0.05 molar fraction have been studied in this paper. The values of optical band gap energy (E_{\text{gap}}) and refractive index (n) are determined to explore the optical behavior of the silica borotellurite glass doped with manganese oxide. Thermal properties of the glass network are measured to investigate the fragility index (F) and activation energy (E_a) of the glass system.

The use of silica from rice husk contribute to a much stronger glass as can be seen in fragility index (F) aside from discovering a new purpose for rice husk waste. About 98.85% of silica were being extracted from the waste utilization of rice husk. No work has been done on optical properties and thermal stability of silica borotellurite doped with manganese.

2. Experimental methods

Glasses with compositional formula \{[(TeO_2)_{x}B_2O_3]_{0.8}[SiO_2]_{0.2}\}_{x=1-5}MnO_2, where x = 0.00, 0.01, 0.02, 0.03, 0.04 and 0.05 molar fraction were prepared by melt quenching technique. The glasses were fabricated by mixing thoroughly the chemicals consisting of tellurium (IV) oxide – TeO₂ (Alfa Aesar, 99.99%), boron oxide – B₂O₃ (Alfa Aesar, 98.5%), rice husk ash as silica source – SiO₂ (97.94%) and manganese (IV) oxide – MnO₂ (Alfa Aesar, 99.99%).

Rice husk which was a common agriculture waste was utilized in this project in order to extract silica. The rice husk was washed with distilled water to remove dirt and any other contaminants in the raw material. For the sake of obtaining high purity of silica, the washed rice husk was leached with 2.0 M of hydrochloric acid (HCl) and stirred for 20 minutes. After that, the rice husk was heated at 110 °C for 3 hours. The heated rice husk was rinsed with distilled water in order to get the HCl acid off from rice husk. The rice husk was then dried in an oven at 110 °C for 3 hours. Finally, the rice husk was burned at 600 °C for 6 hours to get white rice husk ash (silica).

The glasses were prepared by mixing all the chemicals in alumina crucible for 30 minutes before being transferred to its first furnace for 1 hour for pre-heating at 400 °C. After that, the crucible was transferred to a second furnace and was heated at 1100 °C for 3 hours to aid the melting process. The molten liquid was quenched onto a stainless steel cylindrical shape mould and sent to the first furnace to undergo annealing process for 2 hours at 400 °C. The furnace was then turned off and the sample was left in the furnace overnight to be cooled to room temperature. The rice husk was tested using X-Ray Fluorescence (XRF) spectrometer for elemental analysis.

The X-ray diffractograms were recorded via a PW 3040/60 MPD X’pert high pro panalytical (Philips) in the range of 20° ≤ θ ≤ 80°. Optical absorption spectra of all glasses were recorded using UV-Vis spectrophotometer in the spectral range between of 200-800 nm at room temperature. The IR spectra of the glasses were obtained using Perkin Elmer in the range of 280-4000 cm⁻¹. A spectral resolution of FTIR spectroscopy was ±1 cm⁻¹. The thermal characteristic of the glass samples was characterized by differential scanning calorimetry (DSC) at heating rate of 10 °C/min from room temperature to 1200 °C using Thermo Gravimetric Analyzer, (1HT). The microstructure surface of the glass sample was observed by using SEM (LEO 1455 VPSEM) operated at 15 kV and linked with Oxford Inca EDX (energy dispersive X-ray). All the samples were coated with gold using a Bal-Tec coating unit model SCD 005 Sputter Coater.

3. Result and discussion

3.1. XRF analysis

The purity of silica extracted from rice husk in this research was 98.85 %. The purity of the extracted silica depends on the methods of extraction, which includes HCl concentration, burning and leaching temperature. Table 1 unveiled the test result of the purity of extracted silica as well as the percentage of other elements found in the silica that originated from the rice husk.
Table 1. The XRF analyzed result of elements(oxides) and concentrations in white rice husk (silica)

<table>
<thead>
<tr>
<th>Element (oxide)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>98.85</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.75</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe$_3$O$_3$</td>
<td>0.07</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
</tr>
<tr>
<td>CuO</td>
<td>0.03</td>
</tr>
</tbody>
</table>

3.2. XRD studies
X-ray diffraction spectroscopy studies of the silica borotellurite glass were performed at room temperature. Fig. 1 shows the XRD patterns of the glass samples whereby no discrete or continuous sharp peaks can be observed. All XRD patterns exhibit no sharp Bragg’s peak indicating amorphous nature of glass system. The only observable hump is indicated by a broad diffuse scattering which can been seen around low angle between 20º and 35º [18-19]. This clearly proves that the glass samples possess amorphous nature without the presence of a long-range atomic arrangement.

3.3. SEM Studies
The SEM micrograph of the glass sample is shown in Fig. 2(a) for the undoped glass and Fig. 2(b) for the glass doped with 0.05 mol fraction of MnO$_2$. Both SEM images in Fig. 2(a) and 2(b) do not indicate any agglomeration or crystal line occurring in the sample. This proves that the samples are amorphous as confirmed by the XRD pattern. As the concentration of MnO$_2$ increases, more numbers of micro size grains can be detected, indicating that the glass samples are becoming lighter. It is worth to mention that the prepared glasses are homogeneous without particle aggregate ion. SEM-EDX is a method used to monitor the elements that are present in the glass system. The SEM-EDX spectrum of undoped glass sample is shown in Fig. 3(a) and Fig. 3(b) shows glass sample doped with 0.05 molar fraction of MnO$_2$. Based on the spectrum in Fig. 3(a), it can be deduced that the elements which exist in the undoped glass consists of B, Si, O and Te. On the other hand, the elements which exists in the doped glass consists of B, Si, O, Te and Mn, as can be seen from the spectrum in Fig. 3(b). In general, the SEM results confirmed that there are no addictive impurities in the glass sample. The concentration of every element in the glass sample as obtained from the EDX results for 0% and 0.05% molar fraction of MnO$_2$ is summarized in Table 2. Based on the table, Te element has the highest concentration since the highest element composition in the glass system is formed by Te.
Fig 2. (a) SEM micrograph of undoped silica borotellurite glass

Fig 2. (b) SEM micrograph of silica borotellurite glass doped with 0.05 mol fraction of MnO$_2$

Fig 3. (a) EDX spectrum of undoped silica borotellurite glass

Fig 3. (b) EDX spectrum of silica borotellurite glass doped with 0.05 molar fraction of MnO$_2$

Table 2. EDX results of undoped and 0.05 molar fraction of MnO$_2$ in silica borotellurite glass
DSC studies
Differential scanning calorimetry (DSC) is a thermal technique in which the difference in heat flow into a substance and a reference is measured as a function of the sample temperature while the two are subjected to a controlled temperature program [20]. Fig. 4 shows the typical DSC scans at a heating rate of 10 °C/min. DSC curves of all samples are recorded in the range of 0 - 1200 °C. The endothermic hump as revealed by the DSC curves originated from the glass transition whereas the existence of the exothermic peaks in the curves is due to the crystal [21]. The glass transition temperature ($T_g$), onset crystallization temperature ($T_o$), crystallization temperature ($T_c$), melting temperature ($T_m$), thermal stability ($T_s$), thermal stability ($\Delta T$), Hurby value ($K_{gl}$), fragility index ($F$), and activation energy ($E_a$) were determined from Fig. 4. The obtained thermal parameters are summarized in Table 3.

Table 3. Value of glass transition temperature ($T_g$), onset crystallization temperature ($T_o$), crystallization temperature ($T_c$), melting temperature ($T_m$), thermal stability ($T_s$), thermal stability ($\Delta T$), Hurby value ($K_{gl}$), fragility index ($F$), and activation energy ($E_a$) for DSC curves of silica borotellurite glass doped with MnO$_2$ at heating rate of 10 °C/min

<table>
<thead>
<tr>
<th>X (mol %)</th>
<th>$T_g$ (± 1°C)</th>
<th>$T_o$ (± 1°C)</th>
<th>$T_c$ (± 1°C)</th>
<th>$T_m$ (± 1°C)</th>
<th>$T_s$ (± 1°C)</th>
<th>$\Delta T$ (± 1°C)</th>
<th>$K_{gl}$ (± 0.05)</th>
<th>$F$ (± 0.5)</th>
<th>$E_a$ (±5 kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>394</td>
<td>495</td>
<td>542</td>
<td>1118</td>
<td>101</td>
<td>12.05</td>
<td>0.26</td>
<td>0.89</td>
<td>11.31</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>510</td>
<td>564</td>
<td>1059</td>
<td>110</td>
<td>14.85</td>
<td>0.33</td>
<td>0.88</td>
<td>11.31</td>
</tr>
<tr>
<td>2</td>
<td>407</td>
<td>523</td>
<td>578</td>
<td>1081</td>
<td>116</td>
<td>15.68</td>
<td>0.34</td>
<td>0.87</td>
<td>11.31</td>
</tr>
<tr>
<td>3</td>
<td>411</td>
<td>530</td>
<td>586</td>
<td>1063</td>
<td>119</td>
<td>16.21</td>
<td>0.37</td>
<td>0.86</td>
<td>11.31</td>
</tr>
<tr>
<td>4</td>
<td>414</td>
<td>538</td>
<td>596</td>
<td>1071</td>
<td>124</td>
<td>17.37</td>
<td>0.38</td>
<td>0.86</td>
<td>11.31</td>
</tr>
<tr>
<td>5</td>
<td>420</td>
<td>546</td>
<td>606</td>
<td>1078</td>
<td>126</td>
<td>18.00</td>
<td>0.39</td>
<td>0.85</td>
<td>11.31</td>
</tr>
</tbody>
</table>

The $T_g$ values show an increment from 394 °C to 420 °C. The increasing trend in $T_g$ values against the MnO$_2$ concentration with respect to the increase of the MnO$_2$ concentration in the rigidity of the glass network as opposed to previous studies in references [22-23]. The change...
in \( T_g \) clearly shows that the \( \text{MnO}_2 \) affects the structure of the glass systems. A sample with 0.05 molar fraction of \( \text{MnO}_2 \) shows the highest stability among all the samples. On the other hand, the undoped glass sample shows the highest \( T_m \). This is probably due to the high concentration of silica whereby the melting point of silica is the highest among all other elements in the glass.

Thermal stability (\( T_s \)) of glasses is a measure of disorder of glass network [24]. \( T_s \) can be determined by the difference between \( T_g \) and \( T_o \) values using Dietzel criterion [25], \( T_s = T_o - T_g \). A larger \( T_s \) value leads to high thermal stability as well as high kinetic resistance of the glass system towards crystallization. In addition, a large value \( T_s \) value also retards the nucleation process [26-27]. Another thermal stability (\( \Delta T \)) equation that is proposed by Saad and Poulin [28] is defined as:

\[
\Delta T = \frac{(T_c - T_o)(T_o - T_g)}{T_g} \tag{1}
\]

According to the previous research [29] thermal stability is greater when the values of criterion parameters is higher. According to Table 2, sample with 0.05 molar fraction of \( \text{MnO}_2 \) shows the highest value of \( \Delta T \) which implies that the sample is most thermally stable. Hruby value (\( K_{gl} \)) is a strong indicator of glass forming ability [21,30-31] which is defined as follows:

\[
K_{gl} = \frac{T_c - T_g}{T_m - T_c} \tag{2}
\]

In this study, the heating rate for all samples was kept constant at 10 °C/min. The \( K_{gl} \) value for all samples is found to be more than 0.1 implying that the samples are stable and easy to form a glass [32-33].

Fragility index is a measure of the rate at which the relaxation time decreases with the temperature around \( T_g \) using the following relationship [34-36]:

\[
F = \frac{E_g}{RT_g \ln 10} \tag{3}
\]

where \( R \) stands for gas constant, \( E_g \) is the activation energy for glass transition which can be calculated using Kissinger formula [37]:

\[
\ln \left( \frac{T_g^2}{a} \right) = \frac{E_g}{RT_g} + \text{const.} \tag{4}
\]

where \( a \) is the heating rate of DSC. In this equation, \( E_g \) can be calculated from the slope of \( \ln(T_g^2/a) \) and 1000/\( T_g \) as shown in Fig. 5. A linear relationship is observed between the \( \ln(T_g^2/a) \) and 1000/\( T_g \) and the value of \( E_g \) for every sample is 11.31 kJ/mol. This is attributed to the similar heating rate of each of the sample.

\[\text{Fig. 5. Plot of } \ln(T_g^2/a) \text{ vs. } 1000/T_g (K^{-1}) \text{ for silica borotellurite glass doped with } \text{MnO}_2\]
The values of fragility index and the activation energy of the glass system are shown in Table 2. Glass forming liquid that exhibits an approximately Arrhenius temperature dependence of the viscosity is defined as strong glass with a low value of F (F ≈ 16) [38] and the limit for kinetically fragile glass is characterized by a high value of F (F ≈ 200) [39]. Since the value of fragility index for all glass samples does not exceed 16, the glass samples fabricated can be categorized in the strong glass forming systems.

3.5 Optical spectroscopy

Optical absorption spectra, $\alpha(w)$ of the fabricated samples is determined using the following equation [40-41]:

$$\alpha(w) = 2.303 \frac{A}{d}$$  \hspace{1cm} (5)

where $A$ represents the absorbance and $d$ stands for the thickness of the prepared glasses. The relation between $\alpha(w)$ and photon energy, $hw$ is given by the relation [42]:

$$\alpha(w) = \frac{B(hw - E_{opt})^n}{hw}$$  \hspace{1cm} (6)

where $B$ is a constant, $n = \frac{1}{2}$ for direct transition, $E_{opt}$ is the optical band gap energy in eV. In amorphous glass systems, the optical band gap is the energy gap between the valence and conduction band. Equation (6) is employed to calculate the direct and indirect transition that occur in the band gap. The value of indirect $E_{opt}$ can be obtained by extrapolating the absorption coefficient to zero absorption in the plot of $(\alpha hw)^{\frac{1}{2}}$ vs $hw$ shown in Fig 6. [43-45].

![Plot of $(\alpha hw)^{\frac{1}{2}} \times 10^3$ vs. photon energy for silica borotellurite glass doped with MnO$_2$](image)

The calculated $E_{opt}$ values are summarized in Table 3. These $E_{opt}$ values show a decreasing pattern from 2.72 eV to 2.62 eV as the concentration of the MnO$_2$ increases. The decrease in the $E_{opt}$ value might be due to the rise of non-bridging oxygen(NBO) as well as the drop of bridging oxygen(BO) number in the glass system. NBO which is more polarizable and bounds an excited electron less tightly than the BO has contributed to the decrement of energy that is essential for an electron to jump from valence band to conduction band. More likely, MnO$_2$ enters the glass network by breaking up the Te-O-Te and B-O-B bonds and introduces coordinate defect known as dangling bonds along with NBO [32]. The oxygen in MnO$_2$ will break the local symmetry whereas the Mn$^{2+}$ ions will occupy the interstitial positions. The decrement in $E_{opt}$ value is also due to the increment in BO$_3$ units at the expense of BO$_4$ as MnO$_2$ content increases in the glass system. MnO$_2$ enters the glass network as a modifier and changes in the structure of the glass system.

However, as in the case of adding 0.01 and 0.04 molar fraction of MnO$_2$ into the glass system, the $E_{opt}$ value seems to increase. The increasing trend might be the consequence of the role of MnO$_2$ as a glass former rather than as a glass modifier that creates NBO instead of BO in the
glass system. The rise in amount of BO in the form of \( \text{TeO}_4 \) in glass samples with 0.01 and 0.04 molar fraction of MnO\(_2\) can be validated via structural studies of the FTIR spectra.

The relationship between the optical band gap \( (E_{\text{opt}}) \) and refractive index \( n \) is measured by the relation proposed by Dimitrov and Sakka [46]:

\[
\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{\text{opt}}}{20}}
\]  

(7)

The calculated values of the refractive index of the glass samples are presented in Table 4.

**Table 4. Optical band gap \( (E_{\text{opt}}) \) and refractive index\( (n) \) for silica borotellurite glass doped with MnO\(_2\)**

<table>
<thead>
<tr>
<th>Molar fraction MnO(_2) (x)</th>
<th>Optical band gap ( (E_{\text{opt}}) ) (eV)</th>
<th>Refractive index (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.72</td>
<td>2.48</td>
</tr>
<tr>
<td>0.01</td>
<td>3.17</td>
<td>2.35</td>
</tr>
<tr>
<td>0.02</td>
<td>3.14</td>
<td>2.36</td>
</tr>
<tr>
<td>0.03</td>
<td>3.06</td>
<td>2.38</td>
</tr>
<tr>
<td>0.04</td>
<td>3.25</td>
<td>2.33</td>
</tr>
<tr>
<td>0.05</td>
<td>2.62</td>
<td>2.51</td>
</tr>
</tbody>
</table>

The increasing pattern in refractive index as shown in Fig. 7 is attributed to the replacement of \( \text{TeO}_4^{2-} \) ions by \( \text{Mn}^{2+} \) ions which has a lower cation polarizability [47]. Moreover, the increase of the number of high polarizability NBO in the glass system owing to the formation of BO\(_3\) can be verified through the FTIR spectra. The decrease in the refractive index value in 0.02 and 0.04 molar fraction of MnO\(_2\) is due to the dual nature of MnO\(_2\) which acts as modifier and may occupy the network former position [48]. In addition, the decrease of the number of NBO as TeO\(_4\) is formed in the glass system is another factor that may contribute to the decrease of the refractive index values.

**Fig. 7. Optical band gap and refractive index of silica borotellurite glass doped with MnO\(_2\)**

**3.6 FTIR Studies**

The effect of doping of MnO\(_2\) on structural properties of \( [(\text{TeO}_2)_{0.7}\text{(B}_2\text{O}_3)_{0.3}]_{0.8}[\text{SiO}_2]_{0.2} \) \( x \{\text{MnO}_2\} \) glass composition has been investigated based on the FTIR spectra obtained from FTIR spectroscopy. FTIR spectra of the prepared glass samples were recorded in the spectral range of 280 cm\(^{-1}\) – 4000 cm\(^{-1}\) as shown in Fig. 8. The absorption peak in the region of 600 cm\(^{-1}\) – 656 cm\(^{-1}\) is attributed to the stretching vibration of equatorial and axial Te-O bonds in TeO\(_4\) trigonal bipyramidal unit [47]. It is observed that there is an IR peak in between 671 cm\(^{-1}\) -701 cm\(^{-1}\). The
presence of the IR peak in this range is probably due to Te-O vibrations in trigonal pyramid TeO$_3$ groups [49] and or the presence of B-O-B bridges in various bonding environments [50]. The peak observed around 725 cm$^{-1}$ – 780 cm$^{-1}$ in IR spectra is assigned to B-O-B linkages in borate network and bending vibration of bridges containing one trigonal and one tetrahedral boron [51-52]. The intensity of this peak remains almost the same for all glass samples. Another IR peak observed between 801 cm$^{-1}$-828 cm$^{-1}$ is assigned to B-O-B bridge linking in borate network and bending vibration of bridges containing one trigonal and one tetrahedral boron [53-54].

The fundamental IR spectra of the prepared glass sample with different concentration of MnO$_2$ is shown in Fig. 8. FTIR spectra of the prepared glass sample with different concentration of MnO$_2$

4. Conclusion

Silica borotellurite glass doped with manganese with composition {[(TeO$_2$)$_{1-x}$(B$_2$O$_3$)$_{0.7}$SiO$_2$]$_{0.8}$[MnO$_2$]$_x$}, where $x = 0.00, 0.01, 0.02, 0.03, 0.04$ and $0.05$ molar fraction was prepared by melt quenching technique. The XRD measurement of the glass samples exhibits a broad band, proving the amorphous nature of the glass system. The image from SEM measurement shows no crystalline structure which confirms that the glass systems are amorphous. Result from EDX shows no impurities in the glass network. From analysis of DSC, it is found that the prepared glass samples have low value of fragility ($F \approx 16$) and good thermal stability. The IR spectra show that the glass network contains TeO$_4$, TeO$_3$, BO$_4$, BO$_3$, Si-O-Si structural units. Optical band gap energy calculated from Mott and Davis formula with respect to the experimentally observed absorption spectra has shown a non-linear behaviour. As the MnO$_2$ concentration increases, the optical band gap value shows a decreasing trend, which is opposed to the refractive index. This is due to the formation of NBO that governs linear optical parameters such as optical band gap and refractive index.

Acknowledgments

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References