MAGNETIC BEHAVIOUR OF \( (\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x} \) GLASS SYSTEM DUE TO IRON OXIDE

N.A. ZARIFAH*, M. K. HALIMAH, M. HASHIM, B. Z.AZMI, W. M. DAUD  
Department of Physics, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Homogeneous \((\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}\) were synthesis using melt- quenching technique for \(x=0.1-0.3\) in the interval of 0.05. The binary glasses were dark brown in colour. The amorphous structure of glasses was confirmed by the X-ray diffraction spectrum. The physical properties such as density and molar volume have been determined in room temperature and were found decrease with \(\text{Fe}_2\text{O}_3\) contents increase. From the vibrating-sample magnetometer (VSM) measurement it was observed that that magnetization of glass increase almost linearly with applied fields and shows paramagnetic materials behavior.

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1. Introduction

Telluride based glass have physical properties that important for both fundamental and practical applications which is low melting temperature, high dielectric constant, high refractive index, good infrared transmittance and high chemical durability [1]. Telluride glasses are important for practical applications due to nonlinear optical properties for example optical modulators and memories [2] while oxide glass with iron oxide important due to their magnetic, optical and electrical properties [3]. Glass with transition metal ions is vital in electronic properties; this is because of the presence of multivalence states. It was reported that glasses containing transition metal ions are used as elements in memory switching devices and cathode material in batteries [4].

IR spectroscopy is used to investigate the structural of the glass studies. In telluride glass \(\text{Te}\) ions form in a structure of trigonal bipyramidal (tbp) with \(\text{TeO}_4\) structure units. In this structure there are two oxygen ions are located in the axial vertices while in the equatorial positions there are two oxygen ions and lone electron pair of tellurium, where axial \(\text{Te}-\text{O}\) bonds are longer than equatorials bonds [5]. Effect of \(\text{Fe}_2\text{O}_3\) in the glass studied has been reported before [6] that \(\text{Fe}_2\text{O}_3\) influences IR absorptions spectra of \(\text{Fe}_2\text{O}_3 (1-x)\) [3B2O3.MO] where (MO=CaO or CaF2) glasses indirectly.

In the previous study was found that magnetic properties are related with the iron oxide content in the glass series [7,8]. An earlier report [9] on \(\text{CaO-\text{SiO}_2-P_2\text{O}_5-Na_2\text{O-Fe}_2\text{O}_3}\) glass ceramics stated that samples with composition of iron oxide \(x \geq 2\) mol% exhibit magnetic behaviors similar to soft material which has low coercivity and narrow hysteresis loop.

The main objective of this work is to study magnetic properties and structural properties of \((\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}\) glass system with different composition of \(\text{Fe}_2\text{O}_3\)

* Corresponding author: zarifah_alassan@yahoo.com
2. Experimental

Sample of binary glass system (Fe$_2$O$_3$)$_x$ (TeO$_2$)$_{1-x}$ were prepared using Fe$_2$O$_3$ (99.5% purity) and TeO$_2$ (99+%, purity) with different composition of iron ($x = 0.1$ to 0.3 with interval of 0.05). The chemicals were weight accurately using an electronic balance and manually mixed and ground in agate mortar and pestle to fine powder. The chemical were placed in platinum crucible and preheat in electrical furnace at temperature of 350°C for 30 minutes to evaporate water from the batch which may be absorbed during weighing and mixing process. After that, the crucible was transferred to second furnace and melted at temperature of 950°C. After 2 hours, the melt in the crucible was cast into preheat stainless steel mold. The mold was preheated first at temperature 350°C to reduce thermal stress during casting process. After it solidified, the glass sample was put into first furnace at temperature 350°C for annealing process. After 3 hours, the furnace was switched off and the glass was allowed to cool to room temperature. The samples were then cut and polished to desired dimension. Some of the samples were crushed into fine powder using agate mortar and pestle for DTA, XRD and FTIR measurement.

The densities of these glasses were determined using Archimedes’s method with acetone as the immersion liquid. The density of the sample was then calculated using the relationship

$$\rho_{glass} = \rho_{acetone} \times \frac{\text{weight of glass in air}}{\text{weight of glass in acetone}}.$$ 

The amorphous nature of the glass was determined by X-ray Diffractometer (PANalytical (Philips) X’Pert Pro PW 3040/60).

Infrared (IR) spectra were recorded using Fourier Transform Infrared Spectroscopy (FTIR) in the frequency range 280-4000 cm$^{-1}$ at room temperature.

The magnetic properties of samples were measured at room temperature by a vibrating-sample magnetometer (VSM) in a field of 15 kOe.

3. Results and discussion

The prepared glass samples were free from bubbles and dark brown in colour. The composition dependencies on the density, d and molar volume, Vm of the glass samples are shown in Fig 1. The density of Fe$_2$O$_3$-TeO$_2$ glass shows the trend of decrement when the mole fraction of Fe$_2$O$_3$ increases. The decrement of density by introducing the transition metal oxide (TMO) into telluride system is mainly due to the density of Fe$_2$O$_3$, which is lower than the primary forming glass system. When Fe$_2$O$_3$ is introduced into the glass, the content of TeO$_2$ is relatively reduced as Fe$_2$O$_3$ increased. The density of Fe$_2$O$_3$ which has lower density dominates the density of glass system. The decrement of density might be related with the changes of concentration of FeO$_4$ and FeO$_6$ units and attribute to the increase in the fraction of FeO$_4$ tetrahedral when Fe$_2$O$_3$ increases [7] and changes from packed trigonal bipyramidal TeO4 into TeO3 trigonal pyramid open the glass network. The presence of non bridging oxygen also effect density of the glass system, as modifier content increase, amount of non bridging oxygen decrease as well as the density [10].
Fig. 1. Composition dependence of density and Molar volume for Fe$_2$O$_3$–TeO$_2$ glasses.

The result of X-ray diffraction (XRD) is shown in Fig. 2. X-Ray diffraction shows that no sharp peaks observed from the spectra of Fe$_2$O$_3$–TeO$_2$ with only the presence of a hunch for 2$\theta$ around 15°-35°, indicating that the prepared samples are fully amorphous.

Fig. 2. XRD pattern of (Fe$_2$O$_3$)$_x$(TeO$_2$)$_{1-x}$ glass.

Fig. 3 shows DTA curve for glass sample Fe$_2$O$_3$–TeO$_2$. From the curve, glass transition temperature $T_g$, the exothermal peaks, $T_c$ and melting endothermic peaks, $T_m$ are summarized in Table 1. The Glass transition temperature or glass transformation temperature, $T_g$ is critical temperature where amorphous material changes its behavior which is from glassy to rubbery. The value of $T_g$ are in the range of 364-531 °C. It can be seen that there are two exothermic peak for composition of $x=0.10$ and for others composition only have one peak. For endothermic peak, only one peak has been observed for $x=0.10$, two endothermic peaks for $x=0.15,0.20$ and 0.30, and three peaks for $x=0.25$. 
In Table 1, it can be observed that $T_g$ values depend on the composition of Fe$_2$O$_3$. $T_g$ values increases linearly with increasing of Fe$_2$O$_3$ content in the glass series. This dependence is shown in Fig. 4. Increasing of $T_g$ value indicate that the glass sample become more stable and this indicate that Fe$_2$O$_3$ contribute to the increase of glass transition temperature. Thermal stability of glass depends on $\Delta T$ which is increased as Fe$_2$O$_3$ increases.

**Table 1.** Table of Transition Temperature $T_g$, Crystallization Temperature, $T_c$, and Melting Temperature, $T_m$ determine from DTA for (Fe$_2$O$_3$)$_x$(TeO$_2$)$_{1-x}$ glass system.

<table>
<thead>
<tr>
<th>Composition of Fe$_2$O$_3$</th>
<th>$T_g$</th>
<th>$T_{c1}$</th>
<th>$T_{c2}$</th>
<th>$T_{m1}$</th>
<th>$T_{m2}$</th>
<th>$T_{m3}$</th>
<th>$\Delta T=T_c-T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>364.519</td>
<td>449.692</td>
<td>531.055</td>
<td>622.965</td>
<td>-</td>
<td>-</td>
<td>166.536</td>
</tr>
<tr>
<td>0.15</td>
<td>394.906</td>
<td>524.526</td>
<td>-</td>
<td>613.119</td>
<td>655.775</td>
<td>-</td>
<td>129.620</td>
</tr>
<tr>
<td>0.20</td>
<td>460.055</td>
<td>527.267</td>
<td>-</td>
<td>631.486</td>
<td>700.966</td>
<td>-</td>
<td>67.212</td>
</tr>
<tr>
<td>0.25</td>
<td>485.137</td>
<td>545.562</td>
<td>-</td>
<td>613.617</td>
<td>646.624</td>
<td>704.357</td>
<td>60.425</td>
</tr>
<tr>
<td>0.30</td>
<td>531.208</td>
<td>545.108</td>
<td>-</td>
<td>608.544</td>
<td>702.912</td>
<td>-</td>
<td>31.900</td>
</tr>
</tbody>
</table>

![Fig. 3. DTA curve of (Fe$_2$O$_3$)$_x$(TeO$_2$)$_{1-x}$ glass.](image1)

![Fig. 4. Glass transition temperatures ($T_g$) with different composition of Fe$_2$O$_3$.](image2)
Fig. 5. shows the FTIR Spectra of \((\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}\) glasses recorded between 280-4000 cm\(^{-1}\) where the bands are assigned. It can be seen that there are two strong bands at ~450 and ~660 cm\(^{-1}\). Furthermore, there are two weak bands at ~1240 and ~1750 cm\(^{-1}\). Obviously it can be seen that changes in FTIR spectra are due to Fe\(_2\)O\(_3\) composition. These bands and their assignments are summarized as follow:

i. The bands at ~450 are assigned to vibrations of Fe-O bonds that occur in FeO\(_6\) units. The intensities of these band increase up to \(x=0.25\) and decrease after that, this may attribute to the structural disorder of the glass system where in these case iron ion behave dissimilar with Fe\(_2\)O\(_3\) [6].

ii. The bands at ~660 are assigned stretching modes Te-O bonds of the trigonal bipyramidal [TeO\(_4\)] structural units with bridging oxygens. [5,11,12]. The shoulder bands at ~750 assigned trigonal pyramidal [TeO\(_3\)] structural units with non-bridging oxygen [11,12]. The bands at ~660 are due to axial symmetric vibrations of Te–Oax bonds, and equatorial asymmetric vibrations of Te–Oeq bonds are situated at ~750 which is [TeO\(_3\)] structural units.

iii. The weak bands at ~1240 and ~1750 cm\(^{-1}\) is due to the vibrations bands Te-O non bridging bonds of [TeO\(_3\)] structural units. Increasing composition of Fe\(_2\)O\(_3\) in the glass system changes the vibration intensity of [TeO\(_3\)] and [TeO\(_3\)]. The existing iron ions in telluride system may be due to the influence of lone pair electron in telluride system. [7, 12]

![Fig. 5. FTIR Spectra of (Fe\(_2\)O\(_3\))\(_x\) (TeO\(_2\))\(_{1-x}\) glass system.](image)

The results from vibrating sample magnetometer (VSM) are shown in Fig. 6. The magnetization of glass increase almost linearly with applied fields, this behavior exhibits characteristic of paramagnetic materials [8]. The characteristic of material can determine by magnetization curves where for paramagnetic material magnetization increase linearly with field [8]. The graph of magnetization does not show any regular trend with increasing of Fe\(_2\)O\(_3\), this can be explained with position of magnetic moments in glass system. Large dispersion occurred at \(x=0.2\), this may be due to position of magnetic moments that situated far to each other, at this situation the magnetic moments are easier to aligned when external magnetic field is applied while for the sample that shows smaller dispersion, this may due to the magnetic moment that are closer together, this will cause magnetic moment to cancel each other.
Fig. 6. Magnetic properties of \((\text{Fe}_2\text{O}_3)_{x} (\text{TeO}_2)_{1-x}\) glass with different composition of iron.

The magnetic susceptibly of the glass system are calculated with this relationship

\[ M = \chi_m H \]

where \(\chi_m\) is magnetic susceptibility, \(M\) is a magnetization and \(H\) is a field. Through this relationship, magnetization is proportional with applied field gives magnetic susceptibility which is slope of the graph. Fig. 7 shows the relationship of magnetic susceptibility with different composition of \(\text{Fe}_2\text{O}_3\) in glass samples. The graph shows that magnetic susceptibility increases as \(\text{Fe}_2\text{O}_3\) increases. The iron telluride glass system has paramagnetic behavior because the glass has very small magnetic susceptibility value with magnetization curves that increase linearly with external magnetic field.

Fig. 7. Magnetic susceptibility of \((\text{Fe}_2\text{O}_3)_{x} (\text{TeO}_2)_{1-x}\) glass with different composition of iron

4. Conclusions

A series of binary glass \((\text{Fe}_2\text{O}_3)_{x} (\text{TeO}_2)_{1-x}\) has been successfully synthesized with different composition of \(\text{Fe}_2\text{O}_3\) and their magnetic behavior were studied. From density results, density decreases with increasing of \(\text{Fe}_2\text{O}_3\) composition due to changes of Te-O structural units which is
from packed TeO$_4$ tp into TeO$_3$ tp and was confirmed with FTIR results. From VSM, the glasses are found to exhibit paramagnetic behavior and have small magnetic susceptibility

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References