Effect of Heat Treatment on Structural Properties of Silica Borotellurite Glasses Containing MnO

Zaitizila I. 1,a, Halimah M.K. 1,b*, Muhammad F.D. 1,c, Nurisya M.S. 1,2,d

Glass and Dielectric Lab, Department of Physics, Faculty of Science, University Putra Malaysia
^2Lab. of Comp. Sciences & Mathematical Physics, Institute for Mathematical Research (INSPEM), University Putra Malaysia
^a)zaitizila@yahoo.com, ^bhmk6360@gmail.com, ^cfarahdiana@upm.edu.my, ^d)risya@upm.edu.my

Abstract. \({\left( {\text{TeO}_2}\right)^0.7\left( {\text{B}_2\text{O}_3}\right)^{0.3}\left[ {\text{SiO}_2}\right]^{0.2}}\)\(_{1-x}{\text{MnO}_2}\)\(_x\) where \(x = 0.00, 0.01, 0.02, 0.03, 0.04\) and 0.05 molar fraction were prepared by using melt quenching technique. Heat treatment of the glass sample was performed at 600 °C for 3 hours. The structure of the glass samples was characterized by using Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD). Crystalline phase was recorded after parent glass went through heat treatment process. The FTIR spectra for parent glass and heat treated glass samples validate the presence of TeO\(_4\), TeO\(_3\), BO\(_4\), BO\(_3\) and Si-O(Si) in the glass network. After the samples were heat treated, vibration from manganese group were detected in FTIR spectra.

1. Introduction
Tellurite based glasses have attracted much attention from researches due to their high refractive index, low melting point, good infrared transmission, high dielectric constant, low phonon maxima and excellent transparency in the far infrared region [1-2]. Borate glasses have been known to have the nature of amorphous materials according to the specific structure and physical properties [3]. As reported earlier, the borate glasses can be used as inorganic hosts for transition metal and increase the glass forming ability [4-5]. The purpose of this research is to study the crystallization and structural changes in the glass network. For this purpose, XRD and FTIR were used as combined technique to investigate the changes that occur in the glass system before and after the heat treatment process. This research attempts to study the effect of heat treatment on FTIR and XRD of the glass system. There is also less research done on glass system doped with transition metal oxide to be applied as UV absorbance glass.

2. Experimental methods
Glasses of different compositions in the system \({\left( {\text{TeO}_2}\right)^0.7\left( {\text{B}_2\text{O}_3}\right)^{0.3}\left[ {\text{SiO}_2}\right]^{0.2}}\)\(_{1-x}{\text{MnO}_2}\)\(_x\) where \(x = 0.00, 0.01, 0.02, 0.03, 0.04\) and 0.05 molar fraction were fabricated via the melt quenching technique. The mixed chemicals were pre-heated in alumina crucible at 400°C for 1 hour and then melted at 1100°C for 3 hours in an electric furnace (Carbolite). The glass sample was quench into a stainless steel cylindrical shape mould before being transferred for annealing process at 400°C for 2 hours. The fabricated glass samples were heat-treated at 600 °C for 3 hours. The infrared spectra were measured using FTIR spectrometer (Perkin Elmer) in the region of between 280-4000 cm\(^{-1}\). X-ray diffraction
(XRD) studies were performed at room temperature on the as-quenched and heat-treated samples to confirm their amorphous and crystalline states.

3. Result and discussion

3.1 FTIR

The IR spectra for unheated and heat-treated glass samples are shown in Fig. 1 and Fig. 2 respectively. Based on Fig. 1, it can be seen that there are three obvious absorption bands for all glass samples. The bands are assigned to tellurite, borate and silica glass network. Two conventional regions for tellurite group can be observed, whereby the first region from 600 to 650 cm\(^{-1}\) exists due to vibrations of TeO\(_4\) tetragonal pyramids [6]. On the other hand, the second region which is observed from 671 to 714 cm\(^{-1}\) occurs due to the stretching vibration of equatorial and axial Te-bonds in the TeO\(_4\) and TeO\(_3\) unit [7]. As for the borate groups, three bands are observed at 820 cm\(^{-1}\), 1234cm\(^{-1}\) and 1380 cm\(^{-1}\) which are assigned to the B-O bond stretching of BO\(_4\) units [8], BO\(_3\) unit with non-bridging oxygen existing in boron-oxygen network and the stretching of B-O bonds of various borate arrangements [9-10]. The band at 1070 cm\(^{-1}\) is attributed to Si-O(Si) anti-symmetric stretching [11]. The bands around 3090-3120 cm\(^{-1}\) correspond to the hydroxyl groups and hydrogen bonds [12].

The heat-treated glasses show remarkable changes in FTIR spectra. There is addition of the bands in heat-treated glass. The new absorption bands that appear at 310-327 cm\(^{-1}\) and 514-540 cm\(^{-1}\) are assigned to vibration of Mn\(^{2+}\) and Mn\(^{3+}\) as well as Mn-O stretching mode respectively [13-14]. Moreover, the presence of small kinks at 470 cm\(^{-1}\) can be explained by the symmetric stretching mode of Te-O-Te chain unit [12].

In the FTIR spectra, it can be seen that the presence of additional bands and sharp peaks in heat-treated glasses when compared to room temperature glass. This might be due to strong vibrational frequency of the various groups present in glass network as the samples were heat-treated. Moreover, increasing the concentration of the dopant might have resulted in glass structure that is more open as the MnO breaks the network structure of the glass former and consequently produces NBO. As the amount of MnO in the glass system increases, the absorption bands of the FTIR spectra become deeper as can be clearly seen at 1070 cm\(^{-1}\) band. According to Central Force Model, the increasing intensity of Si-O(Si) absorption band may be caused by the structural changes and structural rearrangement that occur in the glass system [15-16]. In this regards, the detection of Mn and Te-O-Te functional group in the heat-treated samples might be the result of the rearrangement of the glass structure after the heat treatment process.
FIG. 1. FTIR spectra for glass samples at room temperature corresponding to: (a) undoped MnO₂, (b) 0.01 MnO₂, (c) 0.02 MnO₂, (d) 0.03 MnO₂, (e) 0.04 MnO₂, (f) 0.05 MnO₂.

FIG. 2. FTIR spectra for glass samples at the heat treated glass at 600°C for 3 hours corresponding to: (a) undoped MnO₂, (b) 0.01 MnO₂, (c) 0.02 MnO₂, (d) 0.03 MnO₂, (e) 0.04 MnO₂, (f) 0.05 MnO₂.
3.2 XRD

Fig. 3 and Fig. 4 show the XRD patterns for as-quenched and heat treated glass samples respectively. No discrete or continuous sharp peaks can be observed from the XRD spectra, as shown in Fig 3. Broad hump with the absence of sharp line spectra in the XRD pattern indicates the presence of long-range structural disorder and amorphous characteristic of the glass samples.

The glass samples tend to show crystalline peaks after being heated at 600 °C. However, only undoped glass sample and glass samples with 0.01 and 0.02 molar fraction show crystalline peaks. These crystalline peaks show a decreasing intensity as concentration of the dopant increases. Glass samples with undoped manganese oxide have three phases ($\beta$-Boron, SiO$_2$ and B$_2$O$_3$) which appear for $2\theta$. The crystalline size of the undoped sample is 88 nm. On the other hand, the heated-treated glass with 0.01 molar fraction of manganese only has one phase which is tellurium silicon (Te$_{16}$Si$_{38}$). The crystallization peaks appear at around 20.87°, 32.00°, 34.33° and 53.90°. The crystalize size for this sample has decreased to 37 nm.

From Fig. 4, it can be observed that the heated glass samples with 0.02 molar fraction of manganese is still in glassy nature with small crystalline traces of SiO$_2$. The crystalline size of this sample decreases to 24 nm with the addition of manganese oxide. Glass samples with 0.03 – 0.05 molar fraction of manganese oxide are also still in the glassy state. Nucleation temperature of the glass samples that lies within and near to the heat treatment temperature range as well as the addition of manganese that will reduce the ionic potential and decrease the amount of crystallization might have led to the glassy nature of the samples [3].

![XRD patterns](image_url)

**FIG. 3.** The XRD for glass samples at room temperature corresponding to: (a) undoped MnO$_2$, (b) 0.01 MnO$_2$, (c) 0.02 MnO$_2$, (d) 0.03 MnO$_2$, (e) 0.04 MnO$_2$, (f) 0.05 MnO$_2$. 

- a  M$n$O-RT
- b  $0.01$ M$n$O-RT
- c  $0.02$ M$n$O-RT
- d  $0.03$ M$n$O-RT
- e  $0.04$ M$n$O-RT
- f  $0.05$ M$n$O-RT
4. Conclusion

Silica boro tellurite glass doped with manganese has been successfully fabricated by using melt quenching method. The results from FTIR spectra show that the pristine glasses consist of BO₄, BO₃, TeO₄, TeO₃, Si-O(Si) functional group. After the heat treatment process, Mn²⁺, Mn³⁺, Mn-O as well as Te-O-Te functional groups were detected. The XRD spectra analysis reveals a crystallization peaks after the heat treatment process only for undoped sample and sample with 0.01 and 0.02 molar fraction of manganese oxide. On the other hand, the glass samples that did not undergo heat treatment process present an amorphous characteristic. The potential application of this material system is as a UV absorbance glass.

Acknowledgement

The authors appreciate the financial support for the work from University Putra Malaysia (UPM) through GP-IPS (grant number: 9504400).

References

[1] A.K. Yakhkind (1966). Tellurite glasses. Journal of the American Ceramic society, 49(12), 670-675.
[2] G.V. Prakash, D.N. Rao, A.K. Bhatnagar. Linear optical properties of niobium-based tellurite glass. Solid State Comm. 2001, 119, 39–44.
[3] I. Kashif, A.A. Soliman, E.M. Sakr, A. Ratep. (2013). XRD and FTIR studies the effect of heat treatment and doping the transition metal oxide on LiNbO₃ and LiNb₅O₁₆ nano-crystallite phases in lithium borate glass system, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 113, 15-21.
[4] A. Terczyńska-Madej, K. Cholewa-Kowalska, M. Łączka. (2011). Coordination and valence state of transition metal ions in alkali-borate glasses. Optical Materials, 33(12), 1984-1988.
[5] L. Hasnimulyati, M.K. Halimah, A. Zakaria, S.A. Halim, M. Ishak, A comparative study of the experimental and the theoretical elastic data of Tm³⁺ doped zinc borotellurite glass, Mater. Chem. Phys. 192 (2017) 228–234.
[6] H.A.A. Sidek, S. Rosmawati, Z.A. Talib, M.K. Halimah, W.M. Daud, Synthesis and optical
properties of ZnO-TeO₂ glass system, Am. J. Appl. Sci. 6 (2009) 1489.

[7] El-Mallawany, R.A., 2002. Tellurite Glasses Handbook, Physical Properties and Data. CRC Press, Baca Raton, FL., ISBN: 0849303680, pp: 540.

[8] B. Karthikeyan, C.S. Suchand Sandeep, J. Cha, H. Takebe, R. Philip, S. Mohan, Optical properties and ultrafast optical nonlinearity of Yb³⁺ doped sodium borate and bismuthate glasses, J. Appl. Phys. 103 (2008).

[9] G. Padmaja, P. Kistaiah, Infrared and Raman Spectroscopic Studies on Alkali Borate Glasses : Evidence of Mixed Alkali Effect, (2009) 2397–2404.

[10] V. Naresh, S. Buddhudu. Structural, thermal, dielectric and ac conductivity properties of lithium fluoro-borate optical glasses, Ceram. Int. 38 (2012) 2325–2332.

[11] M. Sitarz. Influence of modifying cations on the structure and texture of silicate – phosphate glasses, 887 (2008) 237–248.

[12] Z.A. Said Mahraz, M.R. Sahar, S.K. Ghoshal, M. Reza Dousti. Concentration dependent luminescence quenching of Er³⁺ doped zinc boro-tellurite glass, J. Lumin. 144 (2013) 139–145.

[13] D. Moncke, E.I. Kamitsos, D. Palles, R. Limbach, A. Winterstein-Beckmann, T. Honma, Z. Yao, T. Rouxel, L. Wondraczek. Transition and post-transition metal ions in borate glasses: Borate ligand speciation, cluster formation, and their effect on glass transition and mechanical properties, J. Chem. Phys. 145 (2016).

[14] K.S. Pugazhvadivu, K. Ramachandran, K. Tamilarasan, Synthesis and characterization of cobalt doped manganese oxide nanoparticles by chemical route, Phys. Procedia. 49 (2013) 205–216.

[15] E.G. Parada, P. González, J. Pou, J. Serra, D. Fernández, B. León, M. Pérezamor, J. Pou, J. Serra, D. Ferna. Aging of photochemical vapor deposited silicon oxide thin films Aging of photochemical vapor deposited silicon oxide thin films, 436 (1996) 1–6.

[16] G. Kaur, M. Kumar, A. Arora, O.P. Pandey, K. Singh. Influence of Y₂O₃ on structural and optical properties of SiO₂–BaO–ZnO–xB₂O₃–(10–x) Y₂O₃ glasses and glass ceramics, 357 (2011) 858–863.