

## **FTIR SPECTROSCOPY STUDY ON TELLURITE DOPED $\text{Eu}_2\text{O}_3$ GLASS**

Ramli Arifin, Md. Rahim Sahar and Sulhadi

*Physics Department, Faculty of Science,  
Universiti Teknologi Malaysia, 81310 Skudai, Johor DT, Malaysia.*

### **ABSTRACT**

A series of tellurite glass based on  $\text{TeO}_2$ - $\text{ZnO}$ - $\text{ZnCl}_2$ - $\text{Li}_2\text{O}$ - $\text{Eu}_2\text{O}_3$  were successfully prepared by the melt-quenching technique. Fourier Transform Infrared (FTIR) studies for each sample has been carried out in the range of  $400 - 4000 \text{ cm}^{-1}$ . Differential Thermal Analysis (DTA) shows that the incorporation of  $\text{Li}_2\text{O}$  increased the stability of the tellurite glass. FTIR spectra showed a large absorption peak between  $650 - 680 \text{ cm}^{-1}$  which corresponds to the  $\text{TeO}_4$  stretching vibration mode. However, the peak shifted towards a higher wave number as the  $\text{Li}_2\text{O}$  was increased. The peak between  $730 - 770 \text{ cm}^{-1}$  which corresponds to the  $\text{TeO}_3$  stretching vibration mode. However, the peaks at  $3400 \text{ cm}^{-1}$  and between  $1620 - 1650 \text{ cm}^{-1}$  correspond to H-OH and M-OH stretching vibration respectively. It was also observed that the glass with high  $\text{Li}_2\text{O}$  content has a high transmission intensity.

### **INTRODUCTION**

Tellurite glass is one of the candidate for new optical materials because of its superior properties, such as wide band infrared transmittance from  $0.33$  to  $6.5 \mu\text{m}$ , high refraction index [1] and elastic constants which results in an extremely low shear sound velocity. Tellurite glass is suitable as laser host due to its physical properties such as low melting temperature, high dielectric constant and large third order non-linear susceptibility [2,3]. It is capable of incorporating large concentrations of rare-earth ion into the matrix [4]. In this study, the effects of  $\text{Li}_2\text{O}$  content on the properties and structures are investigated using DTA and FTIR.

### **EXPERIMENTAL DETAILS**

The  $\text{TeO}_2$ - $\text{ZnO}$ - $\text{ZnCl}_2$ - $\text{Li}_2\text{O}$  glass was prepared by mixing appropriate quantities of reagent grade  $\text{TeO}_2$  (purity 99.995%, Aldrich),  $\text{ZnO}$  (purity 99.9%, Fluka),  $\text{ZnCl}_2$  (purity 99.999%, Merck),  $\text{Li}_2\text{CO}_3$  (purity 99.997%, Aldrich) and  $\text{Eu}_2\text{O}_3$  (purity 99.9%, Aldrich) in a batch 10 g of glass. The powders were well mixed for 90 min. by mechanical mixing. The mixed powder was melted in air at  $850^\circ\text{C}$  for 30 min in a platinum crucible. The melt was then quenched between two stainless steel plates and annealed for 5 h at  $300^\circ\text{C}$ ,  $10^\circ\text{C}$  above glass transition temperature,  $T_g$ , which is determined by DTA [5]. The samples were kept in a desiccator to prevent possible reactions with moisture. Powder X-ray diffraction (XRD) was used to examine all the as-quenched melts to confirm the amorphous state of the samples. XRD diffraction measurements were undertaken using a Bruker D5005 diffractometer, at  $40 \text{ kV}$ - $30 \text{ mA}$

power. Scans were taken between  $10^\circ - 80^\circ$  ( $2\theta$  degree) at  $0.02^\circ$  increments, 6 seconds/increment or 16 seconds/ increment with a 3 mm divergence slit.

DTA was used to study the glass transition temperature,  $T_g$ , crystallization temperature,  $T_c$  and melting temperature,  $T_m$  of the glasses [6]. All measurements were carried out in air using Perkin Elmer DTA. About 10 mg sample placed in a platinum crucible. The sample was heated from  $27^\circ\text{C}$  to  $1000^\circ\text{C}$  with at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . The reference sample used was  $\text{Al}_2\text{O}_3$ .

FTIR absorption spectra were recorded between frequency range  $400 - 4000 \text{ cm}^{-1}$  using Perkin Elmer GXFT-IR spectroscopy at room temperature. The spectral resolution was  $2 \text{ cm}^{-1}$ . 1.0 mg of glass sample powder was mixed with 100 mg of spectroscopic grade dried KBr in mortar and then compressed mixtures into pellet of 10 mm diameter. The FTIR spectra for each sample represents an average of 64 scans, which have been elaborated by mean of a FTIR spectroscopy software.

## RESULTS AND DISCUSSION

The samples were all transparent. Compositions, glass transition temperature,  $T_g$ , crystallization temperature,  $T_c$ , melting temperature,  $T_m$  and temperature difference,  $\Delta T = T_c - T_g$  are shown in Table 1.

Table1: Characteristic temperatures of glasses in the  $(74.5 - y)\text{TeO}_2 - 15\text{ZnO} - 10\text{ZnCl}_2 - y\text{Li}_2\text{O} - 0.5\text{Eu}_2\text{O}_3$ , ( $y=1, 3, 5, 7, 9 \text{ mol } \%$ ) system.

Sample No.	Mol % $\text{Li}_2\text{O}$	$T_g$ ( $\pm 1^\circ\text{C}$ )	$T_c$ ( $\pm 1^\circ\text{C}$ )	$T_m$ ( $\pm 1^\circ\text{C}$ )	$\Delta T = T_c - T_g$ ( $\pm 1^\circ\text{C}$ )
SL1	1.0	322	420	563	98
SL3	3.0	313	423	543	109
SL5	5.0	307	430	512	123
SL7	7.0	301	434	504	133
SL9	9.0	289	440	520	151

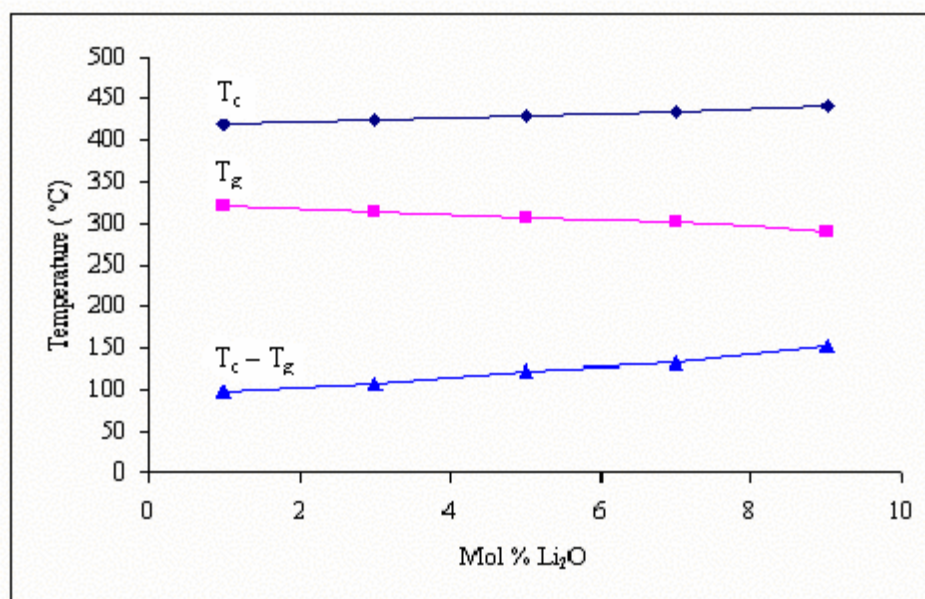


Figure 1: Graph of transition temperature,  $T_g$ , crystallization temperature,  $T_c$  and temperature difference,  $\Delta T = T_c - T_g$  against mol %  $\text{Li}_2\text{O}$ .

Figure 1 shows a plot of  $T_g$ ,  $T_c$  and  $\Delta T$  versus mol%  $\text{Li}_2\text{O}$ , for samples with 1, 3, 5, 7 and 9 mol%  $\text{Li}_2\text{O}$ . The addition of  $\text{Li}_2\text{O}$  to vitreous  $\text{TeO}_2$  between 1 and 9 mol % results in a decrease of  $T_g$  from 322°C to 289°C. Tatsumisago et al. [7] reported that the  $T_g$  decreased with  $\text{Li}_2\text{O}$  in the same glass system due to the cleavage of the networks formed by  $\text{TeO}_4$  trigonal bipyramid units and the increase of NBO atoms. The decrease in the  $T_g$  depicts a more open network and imply a decrease in the rigidity of the network. The result obtained suggests that  $\text{Li}_2\text{O}$  acts as a network modifier and  $\text{TeO}_2$  acts as the network former in the network structure. The trends of  $T_c$  and  $\Delta T$  increase gradually with  $\text{Li}_2\text{O}$  content. The glass crystallization temperature,  $T_c$  increase slightly from 420°C to 440°C, which results in a wide glass-forming range ( $T_c - T_g$ ). Glass stability or glass formation ability can be determined qualitatively by the difference  $\Delta T = T_c - T_g$ .  $\text{Li}_2\text{O}$  has long been recognized as a good glass modifier. Addition of  $\text{Li}_2\text{O}$  to the glass increase the thermal stability and increase the resistance for crystallization. The sample with 9 mol %  $\text{Li}_2\text{O}$  in the glass matrix is the most thermally stable with  $\Delta T = 151^\circ\text{C}$ .

The room temperature FTIR absorption spectra of the sample shown in Figure. 2 and IR bands are tabulated in Table 2. Measurements were carried out on identical KBr pellets containing the same weight of the glass powder to enable us to roughly compare the relative intensities of the bands. This bands shifted from 640 to 650  $\text{cm}^{-1}$  on adding  $\text{Li}_2\text{O}$  to the glass system. All spectra exhibit six broad absorption bands between 400 – 4000  $\text{cm}^{-1}$ . The most intense absorption bands lie between 650 – 680  $\text{cm}^{-1}$  region. It becomes less intense between 730 – 770  $\text{cm}^{-1}$  and least intense between 1620 – 1650  $\text{cm}^{-1}$ . It was reported earlier [8,9] that pure tellurite glasses have an IR absorption band at 640  $\text{cm}^{-1}$  with attributed to  $\text{TeO}_4$  tetragonal pyramids.

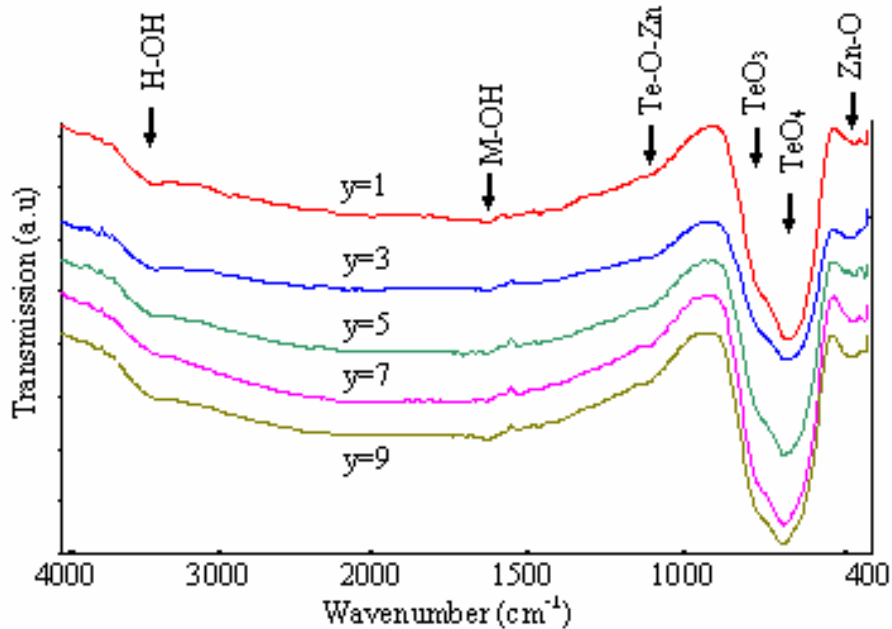


Figure 2: FTIR transmission spectra of  $(74.5 - y)\text{TeO}_2 - 15\text{ZnO} - 10\text{ZnCl}_2 - y\text{Li}_2\text{O} - 0.5\text{Eu}_2\text{O}_3$  ( $1 \leq y \leq 9$  mol %) glasses.

Table 2: The FTIR peaks position for  $(74.5 - y)\text{TeO}_2 - 15\text{ZnO} - 10\text{ZnCl}_2 - y\text{Li}_2\text{O} - 0.5\text{Eu}_2\text{O}_3$  glasses where  $1 \leq y \leq 9$  mol % glasses.

Sample No.	mol % Li <sub>2</sub> O	IR bands (cm <sup>-1</sup> )					
		Zn-O	TeO <sub>4</sub>	TeO <sub>3</sub>	Te-O-Zn	M-OH	H-OH
SL1	1	451	661	746	1126	1635	3402
SL3	3	477	665	739	1111	1627	3402
SL5	5	451	676	746	1122	1635	3402
SL7	7	458	680	735	1120	1650	3402
SL9	9	455	683	746	1118	1631	3402

The peaks around  $460 \text{ cm}^{-1}$  is due to Zn-O tetrahedral band. The broad bands between  $650 - 680 \text{ cm}^{-1}$  and  $730 - 770 \text{ cm}^{-1}$  region are assigned to the stretching vibration of equatorial and axial Te-O bonds in the TeO<sub>4</sub> trigonal bipyramids unit and TeO<sub>3</sub> trigonal pyramids respectively [10]. In these bands are mixed structures of TeO<sub>3</sub> groups, symmetric TeO<sub>4</sub> groups and deformed TeO<sub>4</sub> groups [13]. Sekiya et al [11,12] reported that the glass structure change from trigonal bipyramids to TeO<sub>3+1</sub> polyhedral and then to TeO<sub>3</sub> trigonal pyramids units with NBO atoms formed in glass with addition of the alkali oxides. The bands at  $3400 \text{ cm}^{-1}$  and between  $1620 - 1650 \text{ cm}^{-1}$  correspond to

stretching vibration of the hydroxyl group in hydrogen bonding (H–OH) and strong metal bonding (M–OH) respectively.

The sharp absorption peaks between 650 – 680  $\text{cm}^{-1}$  mode shift towards higher frequency from 661  $\text{cm}^{-1}$  to 683  $\text{cm}^{-1}$  with  $\text{Li}_2\text{O}$  content increase. The relative intensity of the band around 658  $\text{cm}^{-1}$  rises with increasing the  $\text{Li}_2\text{O}$ .

### CONCLUSION

The thermal stability and FTIR spectra in the glass system change significantly with the replacement of  $\text{TeO}_2$  by  $\text{Li}_2\text{O}$  content from 1 to 9 mol %. These glasses show good thermal stability as the stability increases with  $\text{Li}_2\text{O}$  concentration. FTIR spectra clearly indicate the presence of the Zn–O,  $\text{TeO}_4$ ,  $\text{TeO}_3$ , Te–O–Zn, H–OH and M–OH bands. With an increase in the  $\text{Li}_2\text{O}$ , the  $\text{TeO}_4$  transform into  $\text{TeO}_3$  trigonal pyramids at 746  $\text{cm}^{-1}$ .

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