

## **DTA AND IR ABSORPTION SPECTRA OF (80-x)TeO<sub>2</sub> – 20ZnO – (x)Er<sub>2</sub>O<sub>3</sub> GLASS SYSTEM**

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### **ABSTRACT**

Er<sup>3+</sup>-doped tellurite glasses of (80-x)TeO<sub>2</sub>-20ZnO-(x)Er<sub>2</sub>O<sub>3</sub> system (0.5mol% ≤ x ≤ 2.5mol%) has successfully been made by melt quenching technique. The thermal stability and structure of glass has been investigated by means of DTA and FTIR spectroscopy. The thermal parameters, such as the glass transition temperature (T<sub>g</sub>) and crystallization temperature (T<sub>c</sub>) were determined. It is found that this system provides a wide and stable glass formation in which the glass stability around 99°C–140°C was obtained and increases with the Er<sub>2</sub>O<sub>3</sub> content. The spectral shift in FTIR spectra is related to the change in the coordination of the erbium ions. The changes observed were consistent with the stretching vibration mode of TeO<sub>4</sub> trigonal bipyramids and TeO<sub>3</sub> trigonal pyramids, and bending vibration mode of Te–O–Zn in the linkages. It is also found that the sharp absorption peaks shifted from 650cm<sup>-1</sup> to 672cm<sup>-1</sup> and consistent with the increases of the Er<sub>2</sub>O<sub>3</sub> content. The small absorption peaks around 770cm<sup>-1</sup>, 1115cm<sup>-1</sup> and 3420cm<sup>-1</sup> are found in all samples.

### **INTRODUCTION**

The TeO<sub>2</sub>–ZnO glass system is expected to have a unique optoelectronic property (Nukui et al. 2001), put to good use in laser light modulators (Mallawany et al. 2002) and thermally stable for fiber drowing (Neindre et al. 1999). Zinc tellurite glasses are reported to be suitable host for optically active rare earth ions (Sidebottom et al. 1997). It has also been reported elsewhere (Marjanovic et al. 2003) that emission results of newly fabricated double-clad Er<sup>3+</sup>-doped tellurite single mode fibers, showing their potential use for fiber lasers and optical amplifier. Er<sup>3+</sup>-doped tellurite glasses have been attractive research subjects for up-conversion emission due to their low phonon energy (Neindre et al. 1999). To produce a better laser glass, it is necessary to know the thermal behavior, structural changes and phase existence, which might occur during the glass formation. Almost all studies of the TeO<sub>2</sub>–ZnO glass system are concerned with glass formation and structural property (Burger et al. 1992, Nukui et al. 2001). From FTIR spectral, a linear evolution of the glass network with composition may be seen. To develop such glass, a study on their structural properties is very important. Structural measurements in tellurite glasses are very essential to interpret their physical and

chemical properties. The stability of tellurite glasses lends itself to the need for reliable structural measurements (Mallawany et al. 2002). This paper will report the latest development of structural properties on the glass. All the results will be discussed with respect to their composition.

## EXPERIMENT

The erbium-doped tellurite glasses of the  $(80-x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$  system ( $0.5\text{mol}\% \leq x \leq 2.5\text{mol}\%$ ) were prepared by melt quenching technique. Batches of 20 g were prepared from commercial powders of  $\text{TeO}_2$  (purity 99%),  $\text{ZnO}$  (purity 99%) and  $\text{Er}_2\text{O}_3$  (purity 99.9%). A well mixed mixture was preheated to  $400^\circ\text{C}$  and melted in a silica crucible at  $900^\circ\text{C}$ . The crucible was then removed from the furnace and the melts was then quenched between two brass plates followed by annealing at  $200^\circ\text{C}$  for 3h and then allowed to cool to the room temperature.

DTA (Differential Thermal Analyzer) was used to determine the thermal characteristics of the glasses. 10 mg glass samples were heated in the DTA furnace with a heating rate of  $10^\circ\text{C}/\text{min}$  from  $100^\circ\text{C}$  to  $1100^\circ\text{C}$ . Typically about 2 mg of a finely ground sample is mixed with 200 mg of KBr before being pressed in to a pellet. The IR spectra recorded in the range of  $400-4000\text{ cm}^{-1}$ . The Parkin Elmer GX FT-IR spectroscopy has been used to get the IR spectra.

## RESULTS AND DISCUSSION

Series of  $(80-x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$  glasses in the ( $0.5\text{mol}\% \leq x \leq 2.5\text{mol}\%$ ) have successfully been made and their composition, are listed in the Table 1. The DTA curves from some of the samples are shown in Figure 1. As can be seen from Table 1, addition of  $\text{Er}_2\text{O}_3$  content in the tellurite glasses from 0.0 mol% to 0.5 mol% results in a regular decreases of  $T_g$  from  $325$  to  $321^\circ\text{C}$ . Further increases of  $\text{Er}_2\text{O}_3$  concentration above 0.5 mol% show an increase in the glass transition temperature and reaches  $335^\circ\text{C}$  for tellurite glasses containing 2.5 mol%  $\text{Er}_2\text{O}_3$ . The difference temperature  $\Delta T (=T_c-T_g)$  corresponding to the thermal stability of glasses is also calculated. As the  $\text{Er}_2\text{O}_3$  content is being increased,  $\Delta T$  increases from  $99^\circ\text{C}$  to  $140^\circ\text{C}$ .

**Table 1: Glass composition and thermal characteristic**

Sample No	Composition (mol%)			T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	T <sub>c</sub> -T <sub>g</sub> (°C)
	TeO <sub>2</sub>	ZnO	Er <sub>2</sub> O <sub>3</sub>				
S1	80.0	20.0	0.0	325	439	615	114
S2	79.5	20.0	0.5	321	420	611	99
S3	79.0	20.0	1.0	322	442	607	120
S4	78.0	20.0	2.0	323	460	609	137
S5	77.5	20.0	2.5	335	475	610	140

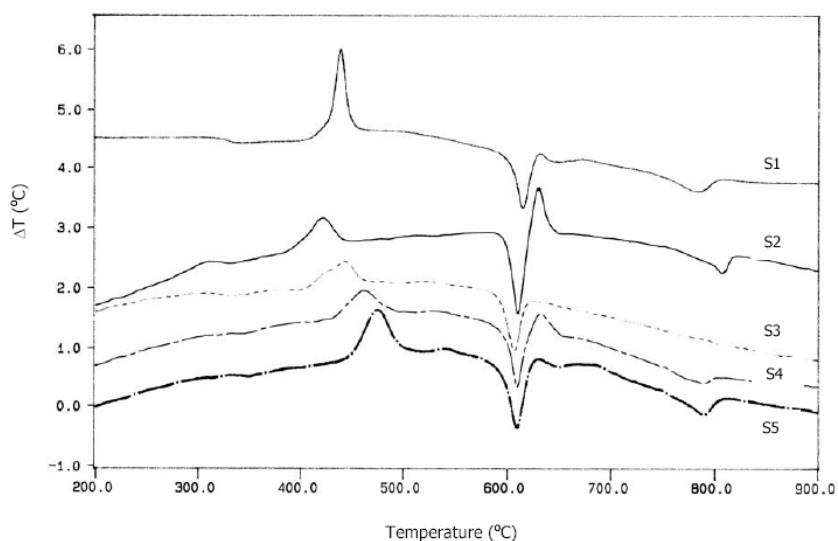


Figure 1: DTA curve of (80-x)TeO<sub>2</sub>-20ZnO-(x)Er<sub>2</sub>O<sub>3</sub> glasses with various compositions.

The FTIR spectra of glasses are given in Figure 2 and the results are summarized in the Table 2. From Figure 2, it can clearly be seen that a sharp absorption peaks around 650cm<sup>-1</sup> has steadily been shifted to 672cm<sup>-1</sup> as the Er<sub>2</sub>O<sub>3</sub> content gradually increased. The small absorption peaks around 770cm<sup>-1</sup> and 1115cm<sup>-1</sup> are found in all samples.

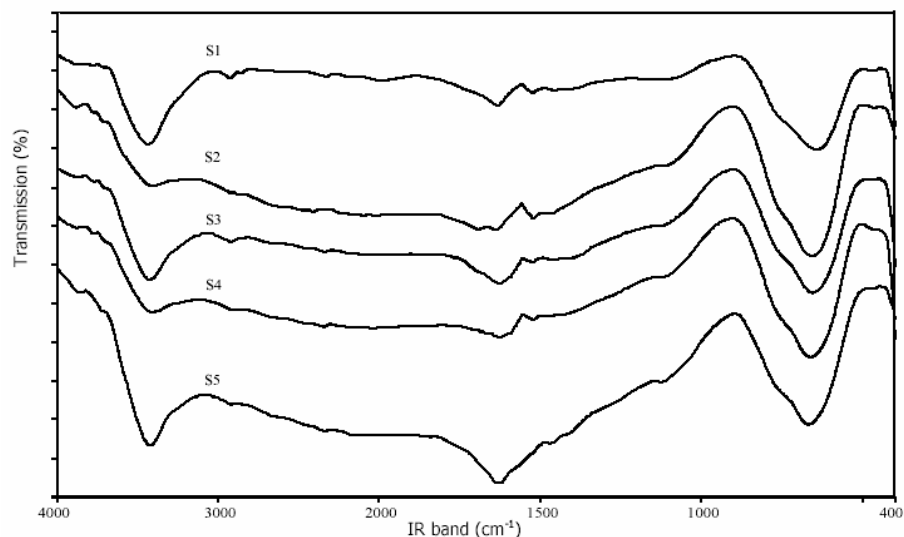


Figure 2: Infrared transmission spectra of (80-x)TeO<sub>2</sub>-20ZnO-(x) Er<sub>2</sub>O<sub>3</sub> glasses with various compositions.

Table 2: The FTIR peaks positions the (80-x)TeO<sub>2</sub>-20ZnO-(x) Er<sub>2</sub>O<sub>3</sub>, (0.0mol % ≤ x ≤ 2.5mol%)

Sample No	Composition (mol%)			IR bands (cm <sup>-1</sup> )
	TeO <sub>2</sub>	ZnO	Er <sub>2</sub> O <sub>3</sub>	
S1	80.0	20.0	0.0	462; 650; 768; 1111, 3431
S2	79.5	20.0	0.5	462; 658; 768; 1115, 3416
S3	79.0	20.0	1.0	470; 661; 772; 1118, 3416
S4	78.0	20.0	2.0	470; 665; 772; 1118, 3416
S5	77.5	20.0	2.5	470; 672; 776; 1118, 3424

The DTA curve for the glasses show broad endothermic hump corresponding to the glass transition temperature T<sub>g</sub>. This transition is followed by one exothermic peak corresponding to crystallization temperature T<sub>c</sub> and other endothermic event corresponding to the melting temperature T<sub>m</sub>. The relationship between T<sub>g</sub>, T<sub>c</sub>, T<sub>c</sub> -T<sub>g</sub> as a function of mol% Er<sub>2</sub>O<sub>3</sub> was plotted and shown in Figure 3. From Table 1 and Fig 3, as the addition of Er<sub>2</sub>O<sub>3</sub> content in the tellurite glasses from 0.0mol% to 0.5 mol% results in the decrease of T<sub>g</sub> from 325 to 321°C. This decreases in the glass transition temperature implies a decreases in the rigidity of the network. The glass has the continuous tellurite network and Te atoms are 4-coordinated (El-Moneim, 2002).

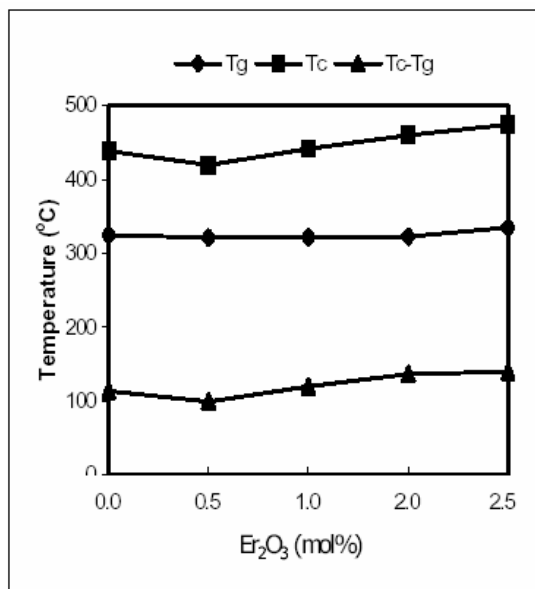


Figure 3: The relationship between T<sub>g</sub>, T<sub>c</sub>, T<sub>c</sub> -T<sub>g</sub> as a function of Er<sub>2</sub>O<sub>3</sub> content.

Further increases Er<sub>2</sub>O<sub>3</sub> concentration above 0.5 mol% show an increases in the glass transition temperature and reaches 335°C for tellurite glasses containing 2.5 mol% Er<sub>2</sub>O<sub>3</sub>. The change in T<sub>g</sub> indicates a change related to the manner in which Er<sub>2</sub>O<sub>3</sub> gets arranged in the glass (El- Moneim, 2002). This result suggests that the glass structure change at 0.5 mol% Er<sub>2</sub>O<sub>3</sub> content. This behavior already reported could be explained by an increase of the rigidity of the network strengthened by the presence of erbium, which can partially participate to the formation of the glasses network (Nazabal et. al. 2003).

The difference temperature  $\Delta T$  (=T<sub>c</sub> -T<sub>g</sub>) corresponding to the thermal stability of glasse is also calculated. From table 1, the relation between T<sub>g</sub>, T<sub>c</sub>, and T<sub>c</sub>-T<sub>g</sub> may be plotted against the Er<sub>2</sub>O<sub>3</sub> content, this is shown in Fig 3. As can be seen in Figure 3, the linear relationship between T<sub>c</sub>-T<sub>g</sub> and T<sub>c</sub> indicates that the glass is easily fabricated (Sahar et al. 1995). As the Er<sub>2</sub>O<sub>3</sub> content is being increased, .T is increases from 99°C to 140°C. The increase in glass stability might due to the structural formation of ZnTeO3 unit (Sahar et. al. 1997). These results suggest that TeO<sub>2</sub> –based glasses containing a large amount of Er<sub>2</sub>O<sub>3</sub> tend to be not crystallizing easily (Kawasaki et. al. 2003).

As shown in Figure 2, exhibits the absorption band at around 650cm<sup>-1</sup> and 770cm<sup>-1</sup>, which have been ascribed to the stretching vibration of equatorial and axial Te–O bonds in the TeO<sub>4</sub> tpb unit and TeO<sub>3</sub> tp (Sahar et al. 1995). The broad peaks around 650cm<sup>-1</sup> and 770cm<sup>-1</sup> in the 80TeO<sub>2</sub>–20ZnO glass system may be ascribed to the mixing structures of TeO<sub>3</sub> groups, symmetric TeO<sub>4</sub> groups and deformed TeO<sub>4</sub> groups (Hu et. al. 1996). However, when the Er<sub>2</sub>O<sub>3</sub> content is being increased, the sharp absorption peaks shift from 650cm<sup>-1</sup> to 672cm<sup>-1</sup>. For Er<sub>2</sub>O<sub>3</sub> content, 0.5mol%≤x≤1.0mol%, the absorption peak is slightly blue shift (Hu et al. 1996). This may be due to the mixing structure of symmetric and deformed TeO<sub>4</sub> groups in this glass. At the same time, the shoulder at 776cm<sup>-1</sup> and 768cm<sup>-1</sup> started to emerge and can be assigned to the TeO<sub>3</sub> tp

of ZnTeO<sub>3</sub> (Sahar et al. 1995). The position absorption peaks shift from 462 cm<sup>-1</sup> to 470 cm<sup>-1</sup> consistently with the increases of the Er<sub>2</sub>O<sub>3</sub> content and can be assigned to the Zn–O tetrahedral bond (Liu et al. 1997). It can also be noted that a lot of additional small intensity peaks in the spectra of the glass sample in the range 462cm<sup>-1</sup> – 470cm<sup>-1</sup> appear as Er<sub>2</sub>O<sub>3</sub> content increase. Those small peaks occur due to the deformation of the Te–O bond vibration (Burger et al. 1992, Xia et al. 2003). Meanwhile, the absorption peaks around 1115cm<sup>-1</sup>, which corresponds to the Te–O–Zn linkages (Liu et al. 1997), was not affected by vibration in composition.

The absorption peaks around 3420cm<sup>-1</sup> in all the samples may be ascribed to the O–H stretching vibration (Sahar et al. 1997). The OH group is the glasses in one kind of impurities in the hosts and can also be regarded as the ingredient of the glasses. Therefore the frequency of the fundamental vibration of free OH is affected not by the association of OH with other ions but by the association with the glass former cations. So they should be associated in the network of the glass former through hydrogen bonding (Feng et al. 2001).

## CONCLUSIONS

In the present work, DTA and FTIR spectral of the (80-x)TeO<sub>2</sub>–20ZnO–(x) Er<sub>2</sub>O<sub>3</sub> system (0.5mol % ≤ x ≤ 2.5mol%) has successfully been studied. With the increases of Er<sub>2</sub>O<sub>3</sub> concentration above 0.5 mol% glass transition temperature an increases and reaches 335°C for tellurite glasses containing 2.5 mol% Er<sub>2</sub>O<sub>3</sub>. This result suggests that the glass structure change at 0.5 mol% Er<sub>2</sub>O<sub>3</sub> content. As the Er<sub>2</sub>O<sub>3</sub> content is being increased, T<sub>g</sub> is increases from 99°C to 140°C. This fact indicates that thermal stability against crystallization is considerably high. From IR studies, the sharp absorption peaks of 650cm<sup>-1</sup> shifted consistently to 672cm<sup>-1</sup> with the increases of the Er<sub>2</sub>O<sub>3</sub> content. However, for Er<sub>2</sub>O<sub>3</sub> content in the range of (0.5mol% ≤ x ≤ 1.0mol%), the absorption peak is slightly blue shifted. This might be due to the mixing of symmetric and deformed structure of TeO<sub>4</sub> groups in the glass. At the same time, the shoulder at 776cm<sup>-1</sup> and 768cm<sup>-1</sup> started to emerge which correspond to the basic structural unit of TeO<sub>3</sub> tp.

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