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THERMAL STABILITY AND STRUCTURAL STUDIES IN THE TeO_2–ZnO–MgO–Li_2O–Er_2O_3 GLASS SYSTEM

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ABSTRACT

Series of (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3 glass system (0.5mol.% ≤ x ≤ 2.5 mol.%) has successfully been made by melt quenching technique. The thermal stability and structure of glass has been investigated by means of TG/DTA and FTIR spectroscopy. The thermal parameters, such as the glass transition temperature (T_g), crystallization temperature (T_c) and thermal stability (T_c - T_g) were determined. It is found that this system provides a wide and stable glass formation in which the glass stability around 97 °C- 117 °C may be obtained. The broad absorption peaks were observed around 657 cm^{-1} - 671 cm^{-1} and 755cm^{-1}-758cm^{-1}, which correspond to the stretching vibration mode of TeO_4 tbp and TeO_3 tp, respectively. The absorption peaks around 1600 cm^{-1} and 3400 cm^{-1} are assigned to a stretching vibration of the hydroxyl group participating in the strong metal and hydrogen bonding respectively.

INTRODUCTION

Tellurium dioxide (TeO_2) is the most stable oxide of tellurium (Te), with a melting point of 773^{o}C. The stability of tellurium oxide is one of the properties that originally attracted researchers, first to the crystalline solids and then to tellurite glasses [1]. Tellurite glasses are known to be an important amorphous system that has many potential commercial applications. The TeO_2–ZnO glass system is expected to have a unique optoelectronic properties [2] because of not only their low transition temperature but also their excellent infrared transmission [3] in the range of 0.4 – 6.0μm [4], which give them potential application in pressure sensors or a new laser host [1] and thermally stable for fiber drawing [5]. Zinc tellurite glasses are reported to be suitable host for optically active rare earth ions [6]. It has also been reported elsewhere [7] that emission results of newly fabricated double-clad Er^{3+}–doped tellurite single mode fibers, showing their potential use for fiber lasers and optical amplifier. Er^{3+}–doped tellurite glasses have been attractive research subjects for up–conversion emission due to their low phonon energy [5].

To produce the 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_2–ZnO glass system are concerned with glass formation and structural property [2,4]. 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

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tellurite glasses lends itself to the need for reliable structural measurements [1]. This paper will report the latest development of structural properties on the glass. All the results will be discussed with respect to their composition.

EXPERIMENTAL DETAILS

The Erbium doped zinc-tellurite glasses in the (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3 system (0.5mol%≤x≤2.5mol%) were prepared by melt quenching technique. Batches of 10 g were prepared from commercial powders of TeO_2, ZnO, MgO, Li_2O and Er_2O_3. A well-mixed mixture was milled for 0.5h before being melted in silica crucible at 900^oC for 0.5h. After a required viscosity is achieved, the melts is quenched between two brass plates followed by annealing at 250^oC for 5h before allowed to cool down to room temperature.
Pyris Diamond TG/DTA (Thermogravimetri / Differential Thermal Analyzer) was used to determine the thermal characteristics of the glasses. 10 mg glass samples were heated in the TG/DTA furnace with a heating rate of 10^oC/min from 25^OC to 1000^OC. The Parkin Elmer GX FT–IR spectroscopy has been used to get the IR spectra. 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 were recorded in the range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Series of (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3 glass system in the range (0.5mol%≤x≤2.5mol%) have successfully been made and their corresponding thermal parameter are summarized in the Table 1. Meanwhile, the TG/DTA curves from some sample are shown in Fig.1. The DTA curve for the glasses show broad endothermic hump corresponding to the glass transition temperature T_g. This transition is followed by one exothermic peak corresponding to crystallization temperature T_c and other endothermic event corresponding to the melting temperature T_m. The difference temperature ΔT (=T_c -T_g) corresponding to the thermal stability of glasses in also calculated. The relationship between T_g, T_c and T_c -T_g as a function of mol% Er_2O_3 was plotted and shown in Fig 2.

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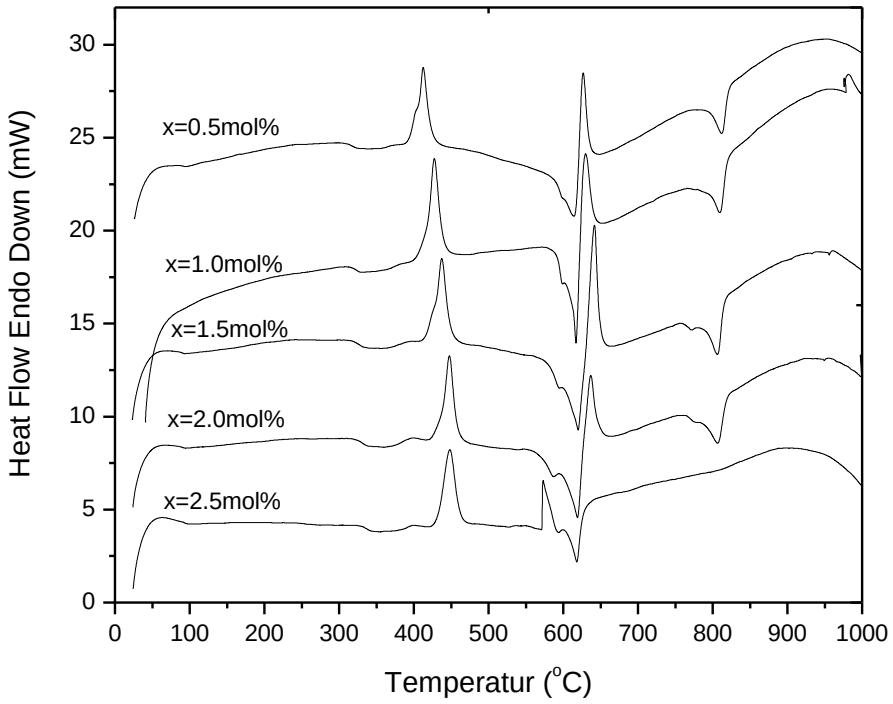

Figure 1: DTA curve of (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3

Tabel 1: Glass composition and thermal characteristics

Sample	Composition (mol %)					Temperature (°C)			
No	TeO_2	ZnO	MgO	Li_2O	Er_2O_3	T_g	T_c	T_c–T_g	T_m
C1	79.5	18.0	1.0	1.0	0.5	315	412	97	615
C2	79.0	18.0	1.0	1.0	1.0	321	427	106	617
C3	78.5	18.0	1.0	1.0	1.5	322	437	115	620
C4	78.0	18.0	1.0	1.0	2.0	330	447	117	619
C5	77.5	18.0	1.0	1.0	2.5	332	448	116	618

From Table 1 and Fig 2, as the addition doping of Er_2O_3 content in the tellurite glasses from 0.5mol% to 2.5mol% results in regular increases of T_g from 315°C to 332°C. The glass transition temperature increases with addition of Er_2O_3 in the glass system due to the cleavage of the networks implies increases in the rigidity of the network formed by TeO_3 tp units and the increase of NBO atoms in the glasses [8,9]. Thus, the increased Er_2O_3 content, the crystallization temperature from 412°C to 448°C (T_c) and increasing the thermal stability from 97°C to 117°C affect the ease of crystallization [10]. The increase in glass stability is also reported to be due to the structural formation of $ZnTeO_3$ units [11].

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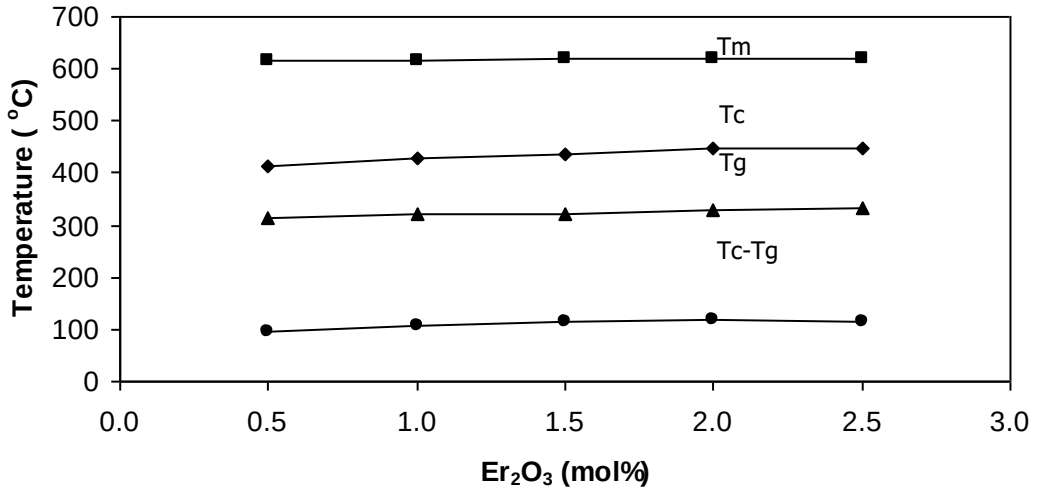

Figure 2: The relationship between T_g, T_c, T_c -T_g as a function of Er_2O_3 content.

The melting temperature T_m increases from 615 ^oC to 620^oC when Er_2O_3 dopant from 0.5mol% to 1.5mol% respectively, indicating that the rigidity of the network the glass increase [9].

The IR transmission spectra of glasses are given in Figure 3 and their corresponding absorption bands are summarized in the Table 2. As can be observed from Figure 3 and Table 2, the absorption peaks are consistently observed at 458cm^{-1} with the increase of the Er_2O_3 content and this can be assigned to the Zn–O tetrahedral bond [12]. It should however be noted that there are many small peaks occur within these ranges as the Er_2O_3 content is being increased. The occurrence of these small peaks is presumably due to the deformation of the Te–O bond vibration [4,13].

The broad peaks that were observed around 650cm^{-1} and 770cm^{-1} can be ascribed to the mixing structures of TeO_3 groups, symmetric TeO_4 groups and deformed TeO_4 groups respectively [14]. However, as the Er_2O_3 content increases, the sharp absorption peaks shift from 657cm^{-1} to 671cm^{-1}. This may be due to the mixing structure of symmetric and deformed TeO_4 groups in this glass of $Zn_2Te_3O_8$ [4]. For Er_2O_3 content, 0.5mol% ≤ x ≤ 2.5mol%, the absorption peak is slightly blue shift [14]. At the same time, the shoulder at 758cm^{-1} and 755cm^{-1} started to emerge. This can be assigned to the TeO_3 tp of $ZnTeO_3$ [3]. This might be due to the perturbation of TeO_4 tbp unit into TeO_3 tp unit via the intermediate coordination of TeO_{3+1} [15,16,17]. Sekiya et al. reported that TeO_{3+1} polyhedra and TeO_3 tp units including NBO ions were formed in glasses with addition of the alkali oxides [18].

Mean while, the absorption peaks around 1110cm^{-1}, which corresponds to the Te–O–Zn linkages [12], seem do not affected by the variation in composition.

Another well known IR absorption peaks occur around 1600cm^{-1} and 3400cm^{-1}, these are assigned to a stretching vibration of the hydroxyl group participating in the strong metal bonding as well as in the hydrogen bonding respectively [13]. The existence of these groups is very common to the oxide glass system.

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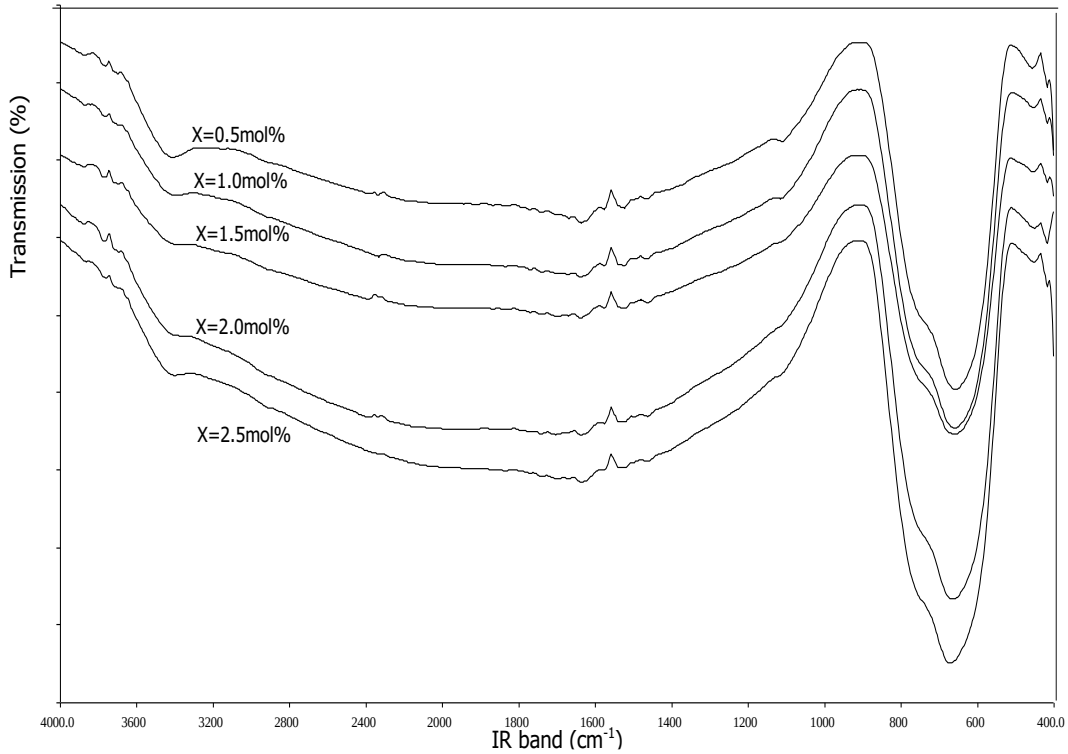

Figure 3: Infrared transmission spectra of (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3

Table 2: The FTIR peaks positions the (80-x)TeO_2-18ZnO-1MgO-1Li_2O-xEr_2O_3 (1.0mol % ≤ x ≤ 5.0mol%)

Sample No	Composition (mol%)					IR bands (cm^{-1})
	TeO_2	ZnO	MgO	Li_2O	Er_2O_3	
C1	79.5	18.0	1.0	1.0	0.5	458; 657; 755; 1110; 1636; 3417
C2	79.0	18.0	1.0	1.0	1.0	458; 660; 758; 1113; 1636; 3411
C3	78.5	18.0	1.0	1.0	1.5	458; 662; 758; 1113; 1636; 3411
C4	78.0	18.0	1.0	1.0	2.0	458; 665; 758; 1113; 1636; 3411
C5	77.5	18.0	1.0	1.0	2.5	458; 671; 758; 1113; 1636; 3411

CONCLUSION

From the above discussions, the following conclusions may be drawn:

1. The addition of Er_2O_3 content in the tellurite glasses results in the increase of T_g from 315°C to 332°C, which implies in an increases in the rigidity of the network.
2. As the addition of Er_2O_3 content is being increases from 0.5mol% to 2.5mol%, thermal stability of glass is increased from 97°C to 117°C.
3. The broad absorption band occurs around 660cm^{-1} and 760cm^{-1}, which can be ascribed to the stretching vibration of equatorial and axial Te–O bonds in the TeO_4 tbp unit and TeO_3 tp respectively.

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