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Full Length Research Article

THERMAL PROPERTIES OF TeO_2-ZnO-Na_2O GLASSES: EFFECT OF Dy_2O_3 DOPING

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ABSTRACT
Over the years there has been numerous researches on thermal stability and other thermal parameters of glasses. Among the glasses, tellurite glasses has become more interesting but challenging lately. These properties are essential in unravelling the physical properties of the glasses. But there is not much information on thermal properties of Dysprosium doped zinc sodium tellurite glass, hence the need for this study. Therefore systematic series of quaternary zinc sodium tellurite glasses doped with dysprosium ion in the form (65-x)TeO_2-25ZnO-10NaO-xDy_2O_3 (where x = 0.0, 0.4, 0.8, 1.2, 1.6, and 2.5 mol%) have been successfully prepared via conventional melt quenching technique. X-Ray Diffraction (XRD) pattern was used to confirm the amorphous nature of the glasses, while density (ρ) of the prepared glasses were obtained via Archimedes method. Differential thermal analysis (DTA) curves for the studied glass samples with different Dy_2O_3 contents have been obtained to determine the glass transition temperature (T_g), crystallization temperature (T_c), glass stability temperature (ΔT_s) Hruby's parameter (H). From the DTA profile, the glass transition temperature T_g, was in the range of 287-302 °C, crystallization temperature T_c from 408-502 °C, glass melting temperature T_m, 662-659 °C and crystallization onset temperature T_x is estimated to be between 354-389 °C. The thermal stability factor, defined as $\Delta T_s = T_c - T_g$, for all the samples are higher than 100 °C while Hruby's parameter H, is 0.47-1.33. These suggest that the prepared tellurite glass exhibits a good thermal stability and consequently might be a potential candidate for fibre drawing and other nonlinear optical devices.

Keywords: Tellurite glass, DTA, Thermal stability & Hruby's Parameter

1. INTRODUCTION

In recent years, there has been an extensive research on glass hosts with low phonon energy and high stability, which are ideal for doping lanthanide (Ln) ions as they reduce multi phonon de-excitation between Ln ion energy levels and favour the observation of some transitions between levels, which are closely spaced in addition to enhancing the quantum efficiency of luminescent transitions. Such materials have numerous applications in the field of photonics (Babu*, et al,* 2010). Among oxide glasses, tellurite glasses have the advantages of good transparency in the mid-infrared (0.35-6 nm), high dielectric constants, good glass stability and Ln ion solubility. They have lower phonon energy (700–800 cm^{-1}) and larger refractive index, compared to other oxide glasses (such as silicate, borate and phosphate), both of which are beneficial for high radiative transition rates of Ln ions (Kumar*, et al,* 2006 & Babu, *et al,* 2010). Tellurite glasses could also be used in the production of optical fibres and planar waveguides. Indebt knowledge of thermal stability, provides the possibility of using enhanced TeO_2-based glasses hosting rare earth elements, leading to non-linear optical material (El-Mallawany, *et al,* 2008). Many researches on thermal properties of tellurite glasses have been carried out among which are: Oxyhalide tellurite glasses which represent favourable compromise between the requirements of low phonon energy and a relatively high thermal stability, high chemical durability and ease of fabrication (Babu, *et al,* 2010). Properties of TeO_2-Na_2O-ZnO ternary glass system (good durability, thermally stable to crystallisation, and high rare-earth solubility) was first examined and stated by (Wang, *et al,* 1994) creating the aforementioned compositions, is ultimate for optical fibre devices. In above study the thermal properties of the glass (mol%) 75TeO_2-5Na_2O-20ZnO were observed. The viscosity-temperature behaviour (essential when considering fibre-drawing) of the soda zinc tellurite glass was intermediate in behaviour between a silicate glass (strong) and ZBLAN (fragile) (Angell, 1985 & Martin, *et al,* 1986). DTA of this glass composition gave characteristic temperatures as: T_g = 299 °C and T_x = 417 °C, which gives a T_x - T_g value of 118 °C, around three times as much as the soda tellurite composition also studied by (Wang, *et al,* 1994) showing the stability of the ternary system.

Watanabe, *et al,* 2001 studied the Vickers' hardness (Hv) of a glass of composition (mol%) 70TeO_2-15ZnO-15Na_2O (Hv = 2.6 GPa at room temperature) around its glass transition region (T_g = 264 °C). There was a sharp decrease in hardness of this glass at around T/T_g = 0.9 to 1.0. This can be attributed to the 'fragile' (Angell, 1985 & Martin, *et al,* 1986) nature of TeO_2- based glasses, so the breaking of atomic bonds and atomic rearrangement occur easily around T_g.

Aida, *et al,* 2001 studied the thermal stability of the compositions (mol%) 80TeO_2-10ZnO-10Na_2O and 70TeO_2-15ZnO-15Na_2O as well as many other ternaries. Soda zinc tellurite glasses are exceptionally stable, the composition containing 10 mol% ZnO and 10 mol% Na_2O exhibiting a weak crystallisation exotherm and the composition containing 15 mol% ZnO and 15 mol% Na2O, showing no sign of devitrification. This study related the optical basicity of the oxides (numerical expression of the average electron donor power of the oxide species) to the thermal stability (Aida, *et al,* 2001).

Apart from their applications, there is a lack of data about investigations on thermal properties of these TeO_2-ZnO-Na_2O Dysprosium doped glass systems in the literature. Therefore, the aim of this research is to study the effect of Dy_2O_3 on the thermal properties of zinc sodium tellurite glass system in order to

understand the effect of Dysprosium ion doping.

2. Experimental Method

2.1 Glass Preparation

High purity chemicals (99.9%) tellurium dioxide (TeO_2), Zinc oxide (ZnO), Sodium dioxide (Na_2O), and Dysprosium dioxide (Dy_2O_3) (all Sigma Aldrich) were used in the glass preparation of Dy_2O_3 doped zinc sodium tellurite glass using the melt quenching technique. The compositions of the prepared glass samples are as follows:

(1) $65.0TeO_2$-25ZnO-$10Na_2O$-$0.0Dy_2O_3$
(2) $64.6TeO_2$-25ZnO-$10Na_2O$-$0.4Dy_2O_3$
(3) $64.2TeO_2$-25ZnO-$10Na_2O$-$0.8Dy_2O_3$
(4) $63.8TeO_2$-25ZnO-$10Na_2O$-$1.2Dy_2O_3$
(5) $63.4TeO_2$-25ZnO-$10Na_2O$-$1.6Dy_2O_3$
(6) $62.5TeO_2$-25ZnO-$10Na_2O$-$2.5Dy_2O_3$.

About 15 g of starting materials were mixed via a milling machine and put in a porcelain crucible melt at 950 °C for 15 min in an electric furnace. The melt was poured onto a pre-heated brass plate and then annealed below the glass transition temperature for 2 hours in order to remove thermal stress. Table 1 summarizes the prepared glass samples, their codes, composition and density.

2.2 Density Measurement

The density (ρ in gcm^{-3}) of the glasses was determined by Archimedes method with toluene as an immersion liquid using equation (1).

$$\rho = \frac{W_a}{W_a - W_l}\left(\rho_l - \rho_a\right) + \rho_a \quad \text{---------- (1)}$$

where W_a and W_l are the weight of glass in air and in liquid, respectively. While ρ_a is the air density (0.001 g cm^{-3}) and ρ_l is the density of toluene (0.8669 g cm^{-3}). (Burger, *et al,* 1985, Sidek, *et al,* 2004 & Sidek, *et al,* 2009).

2.3 XRD

To check the amorphous nature, the X-ray diffraction was carried out for glass sample using a computer controlled Xpert Pro Diffractometer (PAnalytical B.V., The Netherlands) with Cu Kα radiations (λ = 1.54 Å) at 40 kV and 40 mA, scanning angle 2θ ranges between 10° − 80°, step size 0.02° with 0.01°. Fine powder of the samples is pressed in the sample holder making a plane loaded surface to record the XRD pattern.

2.4 DTA

The characteristics temperatures like T_g, T_x, T_c and the T_m are obtained via Perkin-Elmer Pyris Diamond TG/DTA 7 series system run through incorporated computer and software. The extreme temperature attained is about 1500 ºC under a heating level of 10 °C/min. About 15 mg of the sample in powdered form is loaded. The change in temperature is recorded in relation to the standard aluminium batch. The machine is operated under N_2 atmosphere per a flow rate ~200 mL/min. The thermal stability range (ΔT_s) for the glass can be estimated using the relation (Tanko, *et al,* 2016):

$$\Delta T_s = T_c - T_g \quad \text{---------- (2)}$$

where T_c and T_g have their usual meanings for a sample heated at a specified linear rate. To perform further thermal stability criterion on this particular samples the glass-forming tendency also known as the Hruby's parameter (H), which is a useful devitrification tendency measure for the glass (Tanko, *et al,* 2016), is given by:

$$H = \frac{T_c - T_g}{T_m - T_c} \quad \text{---------- (3)}$$

where T_m is the melting temperature

Table. 1. Summary of Prepared glass samples, their codes, compositions and Density

Glass sample codes	Compositions				Density ρ (gcm^{-3})
	TeO_2 (mol %)	ZnO (mol %)	Na_2O (mol %)	Dy_2O_3 (mol %)	
TZND0.0	65.0	25.0	10.0	0.0	5.334
TZND0.4	64.6	25.0	10.0	0.4	5.342
TZND0.8	64.2	25.0	10.0	0.8	5.352
TZND1.2	63.8	25.0	10.0	1.2	5.358
TZND1.6	63.4	25.0	10.0	1.6	5.361
TZND2.5	62.5	25.0	10.0	2.5	5.366

3. Result and Discussion

3.1 XRD

The XRD patterns of glass samples were found to show no discrete or continuous sharp peaks but broad halo at around 25°–35°, which reflected the characteristic of amorphous glass structure. This indicates the absence of long-range atomic arrangement and the periodicity of the three-dimensional network in the glassy materials. (Ghoshal, *et al,* 2015).

3.2 Density

The increase in the density (as depicted in Table 1) can be related to two reasons: The first reason is, density (ρ) increases as the Dy_2O_3 concentration increase because molecular mass of Dy_2O_3 (372.998 $gmol^{-1}$) been higher than TeO_2 (159.610 $gmol^{-1}$) contribute to elevated packing density which is the degree of compactness of a substance. The upsurge in density means an intensification of glass system rigidity. The increase in glass density is as a result of a creation of more Bridging Oxygen in the system as put forward by previous researches (Reddy, *et al,* 1995, McLaughlin, *et al,* 2001, & Arunkumar, *et al,* 2013). The second reason may be due to the transformation of TeO_3 to TeO_4 where the formation of TeO_{3+1} polyhedron has one non bridging oxygen atom. This increase can be attributed to the Dy^{3+} ions that occupy the interstitial position, and therefore the three dimensional structure of tellurite glass is not destroyed. These behaviours of the studied glasses are agreed with reported data elsewhere (Kozhukharov, *et al,* 1986 & Khattak, *et al,* 2002).

3.3 Thermal Analysis

The DTA curves for glass with changing Dy^{3+} concentration is presented in Figure 1. Typical thermal spectra may contain one or more exothermic peaks due to crystallization of different phases, but the lowest temperature peak is considered in discussing glass

stability. Once a significant number of crystals are formed, subsequent events at higher temperatures are not considered important in glass stability (Hirashima, *et al,* 1988). In order to look into the thermal properties, the values of temperature such as glass transition temperature (T_g), glass crystallization temperature (T_c), glass melting temperature (T_m), glass stability range (T_c - T_g) and glass forming tendency, H for all the glass compositions are obtained as summarized in Table 2.

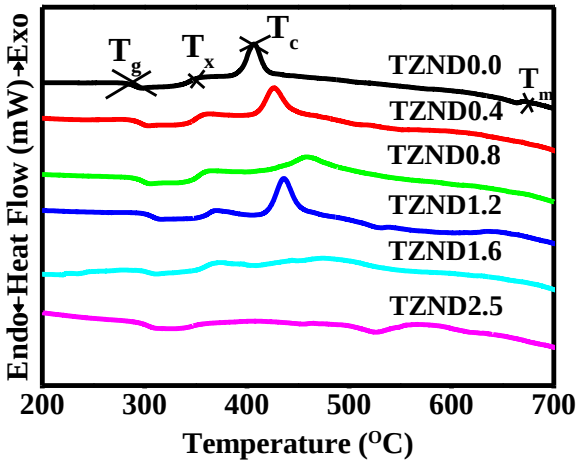

Figure 1: DTA curves of the glass samples.

3.3.1 Glass Transition Temperature T_g

Glass transition temperature, T_g, plays a vital role in understanding the physical properties of glass (El-Mallawany, 1999 & Nishara, *et al,* 2006). In the present investigation, all of the glasses have an endothermic change between 287 °C and 302 °C, which attributes to the glass transition temperature, T_g. Figure 2 depicts an increasing T_g with increasing Dy^{3+} ions concentration, this is due to the ability of Dy^{3+} ions to strongly combine with the structural unit by exerting strong columbic interaction with the surrounding oxygen of the network, even though a slight decline for TZND1.6 and TZND2.5 samples. This is attributed to an increase of average crosslink density and more number of bonds per unit volume. TZND1.2 sample is the highest and optimum because it has more number of bonds per unit volume (El-Mallawany & Ahmed, 2008).

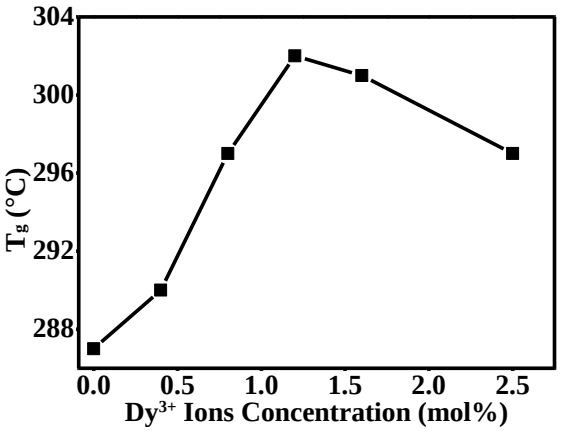

Figure 2: T_g with Varying Dy^{3+} ions Concentration.

3.3.2 Crystallisation Temperature T_c

Figure 3 illustrate the behaviour of T_c with increasing Dy^{3+} ions concentration. There is an increase of the crystallization temperature T_c, except for the sample TZND1.2, as the dopant concentration increases. Samples with low T_c is due to the nucleation processes followed by the crystalline phase having a low internal free energy while high T_c values is attributed to the formation of a more relaxed crystalline phase (Shaltout, *et al,* 1995).

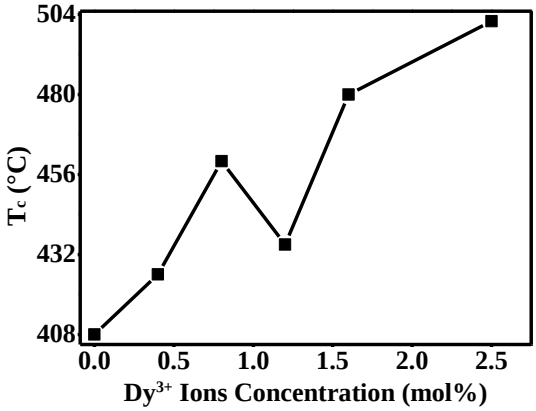

Figure 3: T_c with Varying Dy^{3+} Ions Concentration.

3.3.3 Thermal Stability ΔT_s

The glass forming ability automatically leads to glass stability (Shelby, 2005). The glass transition temperature T_g helps to reveal the close or loosely packed structure of the glass, where the higher the single-bond energy in glass network, the more stable the glass-forming system (Hirashima, *et al,* 1988). The values of ΔT_s (Table 2 and figure 4) are higher than 100 °C for all the prepared samples, which show that the prepared glasses have quite noble thermal stability (Babu, *et al,* 2010). The growing thermal stability shows the declining crystallization tendency as demonstrated in sample with 2.5 mol% Dy^{3+} ion concentration.

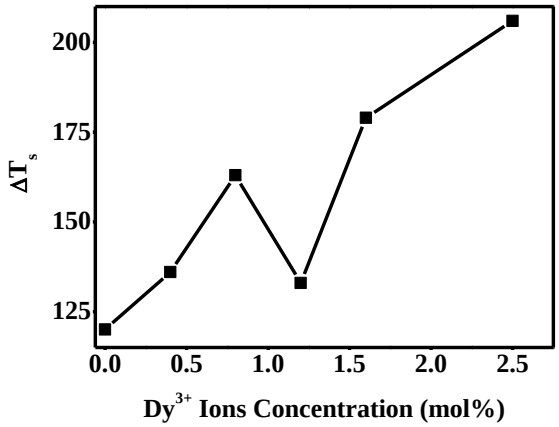

Figure 4: ΔT_s with Varying Dy^{3+} Ions Concentration.

3.3.4 Hruby's Parameter H

There is changing in the Hruby's (H) parameter a glass-forming and a useful devitrification tendency measure for the glass with changing Dy^{3+} concentration as shown in figure 5. TZND2.5 glass shows the highest value of H with 1.33 indicating the maximum

glass forming ability. The increase of *H*, implies the stronger is the inhibition to nucleation and crystallization processes, and consequently, the larger the thermal stability of the glass. These findings agree well with other works on similar glass system. (Zhang, *et al,* 2002 & El-Mallawany *et al,* 2008).

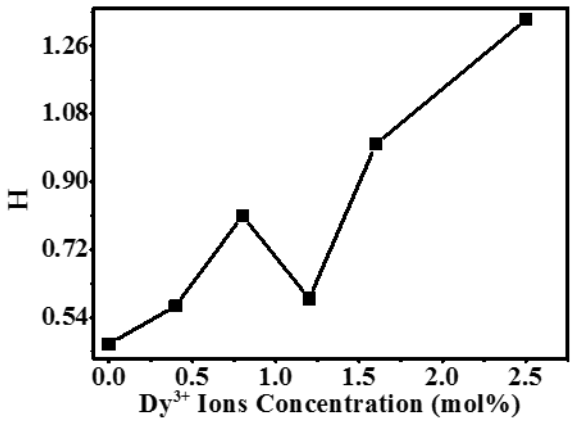

Figure 5: Variation of *H* with Dy^{3+} ions concentration

Table. 2. Prepared samples with their thermal parameters

Sample codes	Thermal Parameters					
	T_c (°C)	T_x (°C)	T_g (°C)	T_m (°C)	ΔT_s (°C)	*H*
TZND0.0	408	354	287	662	120	0.47
TZND0.4	426	389	290	664	136	0.57
TZND0.8	460	366	297	662	163	0.81
TZND1.2	435	366	302	661	133	0.59
TZND1.6	480	371	301	659	179	1.00
TZND2.5	502	362	297	657	206	1.33

4. Conclusion

Melt quenching technique have been employed where six series of dysprosium doped zinc sodium tellurite glass systems were prepared.

The increase in the density of glasses from 5.334-5.366 gcm^{-3} due to a change in crosslink between TeO_2 chains and coordination number of Te^{2+} ions.

The thermal properties of tellurite glasses such as the glass transformation temperature, T_g, crystallization temperature T_c, glass stability temperature and Hruby's parameter *H*, were studied with respect to Dy_2O_3 content.

- Glass transition temperature T_g was obtained in the range of 287-302 °C
- Crystallization temperature T_c, is between 408-502 °C
- These glass samples possess high thermal stability greater than the 100 °C required by the thermal stability criteria. Hence, all the studied samples are promising candidates for rare-earth-doped optical fibre.
- Hruby's parameter is from 0.47-1.33.

Experimental data shows that the density and thermal properties are greatly enhanced with the addition of Dy_2O_3 content. Hence these glass is a promising material for optical fibre devices due to the good thermal stability.

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