

The Crystallization Kinetic of Te-Li Glass System

Aida Faeghinia, Roghaieh Nemati, and Mandana Sheikhani

Abstract—80mol% TeO₂-20mol% LiF glass composition with 0.005 mole Gd₂O₃ and TbF₃ was prepared by conventional casting technique. DTA analyses were carried out on the glass at different heating rates and an activation energy value of 129 kJ/mol for surface crystallization was determined graphically from a Kissinger-type plot and using the method of Ozawa and Augis-Bennett the activation energy values were 142 kJ/mol and 136 kJ/mol respectively.

Index Terms—Activation energy crystallization, glass, kinetic, tellurite.

I. INTRODUCTION

In comparison with silicate and borate glasses, telluride glasses have more advantages as frequency up conversion laser hosts due to their physical properties. Such as low melting temperature, high dielectric constant [1], high refractive index [2], large third order nonlinear susceptibility [3] and better infrared transmissivity [4]. Furthermore, they present large transparency between the near ultraviolet to the middle infrared region. In addition, they are resistant to atmospheric moisture and capable of incorporating large concentrations of rare earth ions such as Tb³⁺ into the matrix. Currently there exists a substantial amount of literature which reported the thermal, optical and physical properties of TeO₂ based glasses and regarding the structure of pure TeO₂ and M₂O-TeO₂ (where M=Li, Na, K, Rb and Cs) glasses characterized by using X-ray diffraction [5]. However, no reported literature is available on the formation of crystalline phases in TeO₂±LiF glass systems and thus no detailed studies related to the crystallization kinetics have been conducted. The present study aims to full this task. The present paper focuses on the crystallization kinetics of the crystallizing phase in the TeO₂-LiF binary system. Glass doped with 0.005 mol. of Gd₂O₃, and 0.005 mol. TbF₃ were investigated using DTA techniques. Further, DTA analysis at different heating rates was used to determine the activation energy for crystallization.

Due to anomalous glass-forming behavior of tellurite glasses, tellurium oxide (TeO₂) as the main but conditional glass former, does not transform to the glassy state as a pure oxide in normal conditions. The alkali oxide addition M₂O (where M=Li, Na, K, Rb or Cs) to TeO₂ based glasses increases their glass forming tendency and produces non-bridging oxygen (NBO) sites, which decrease the average coordination number [6]. Thus resulting in glasses that require only modest cooling over a specific range of added modifier and resistant to crystallization [7]. An

understanding of the crystallization behavior is important to develop and use TeO₂-based glasses, as a laser material, or an optical switching device, which will bear high thermal loads and thus will be subjected to crystallization during laser operation [8]. The investigation of crystallization kinetics, in these glass systems, has often been limited by the elaborate nature of the experimental procedures, which are in use. The increasing use of thermo analytical techniques, such as differential thermal analysis (DTA), or differential scanning calorimetry (DSC), has offered the promise of obtaining useful data, with simple methods [9].

II. EXPERIMENTAL PROCEDURE

80mol% TeO₂-20mol% LiF glass composition with 0.05, 0.005, mole Gd₂O₃ and TbF₃ respectively, were prepared. The conventional casting technique was used. High purity powders of TeO₂ (99.99% purity, Alfa Aesar), Gd₂O₃ (99.8% purity, Alfa Aesar) and LiF (99.95% purity, Alfa Aesar) were thoroughly mixed. 7g size powder batches were melted in a platinum crucible with a closed lid at 750-800°C for 30 min in an electrical furnace. To achieve homogeneity, the cast was crushed, pulverized and re-melted at the same temperature for additional 30 min and was cast using the same procedure. Wet chemistry analyses carried out on bulk as-quenched TeO₂-LiF-Gd₂O₃ glass samples revealed that the initial elemental stoichiometry of samples did not change after quenching. The melts were cooled on stainless steel plate in annealing furnace. Each glass was annealed for 2h at 350°C and then cooled to room temperature slowly. The cooling rate was estimated about 10K/s. The samples were cut into small pieces with thickness of 2mm and well-polished. To recognize the thermal behavior of the glass samples, differential scanning calorimetric analyses were carried out in a Netzsch DSC 204 F1 (limit of detection: <0.1 W, with an error estimate of ±1°C) using a constant sample weight of 25 ± 1mg in aluminum pans, under air with a heating rate of 10 °C/min. The glass transition (T_g), first crystallization onset and peak (T_c/T_p) temperatures were determined from the DTA traces. The glass transition temperatures (T_g) were taken as the inflection point of the endothermic change of the calorimetric signal. Crystallization onset temperatures were specified as the beginning of the reaction where the crystallization first starts and peak temperatures represent the maximum value of the exotherm. Differential scanning calorimetry was performed for glasses at different heating rate of 5, 10 and 20°C/min to determine the activation energy of crystallization. Nucleation and crystallization rates can be measured from the microscopic images but DSC study is essential for the quantitative evaluation of crystallization in different glassy systems [9].

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III. RESULT AND DISCUSSION

Fig. 1, Fig. 2 and Fig. 3 show the DTA thermo gram of the as-casteless sample scanned at the heating rates of 5, 10 and 20°C/min. The T_g and T_p values for different heating rates are listed in Table I.

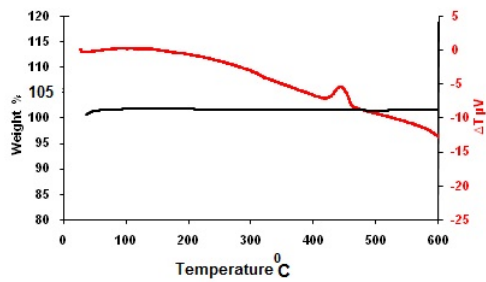


Fig. 1. The DTA thermo gram of the glass sample scanned at the heating rates of 5°C/min.

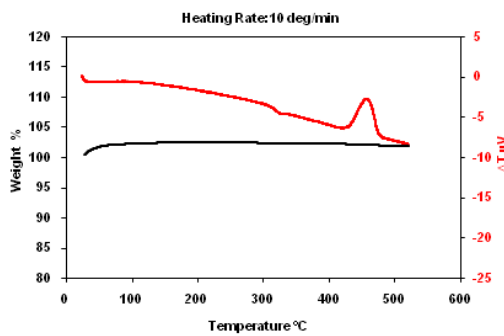


Fig. 2. The DTA thermo gram of the glass sample scanned at the heating rates of 10°C/min.

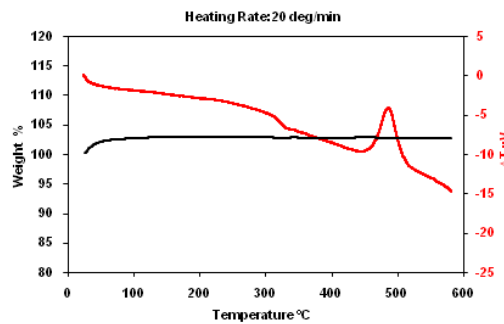


Fig. 3. The DTA thermo gram of the glass sample scanned at the heating rates of 20°C/min.

TABLE I: GLASS TRANSITION (T_g) AND PEAK TEMPERATURE (T_p) OF GLASS SAMPLE AT THE HEATING RATE OF 5, 10 AND 20 °C/

Rate of heating (°C/min)	T_g (°C)	T_p (°C)
5	313	442
10	309	457
20	303	485

As expected, both the T_g and T_p temperatures shift to higher values with increasing heating rate, such a behavior also reported in the DTA studies of other glass systems [10].

On the basis of DTA results, X-ray diffractometry scans were carried out to verify the nature of crystallizing phases in the glassy matrix at DTA peak temperature (460°C) at a rate of 10°C/min followed by quenching in air showed the evidence of devitrification. All the peaks in Fig.4, matched the d-values of the para tellurite (TeO_2) phase which, has a

tetragonal crystal structure with lattice parameters $a=0.481$ nm and $c=0.761$ nm. Three-trace crystal peaks also can be detected which corresponds to Lithium-Terbium-oxide.

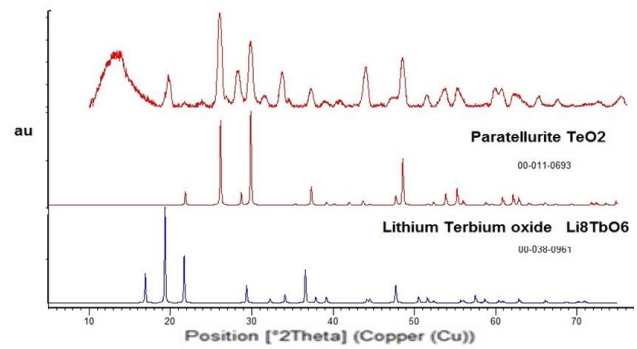


Fig. 4. XRD patterns of heat-treated glass at 460°C.

The shift of peak temperatures with heating rate in anon-isothermal DTA study was analyzed by Kissinger in the study of kinetics of chemical react ions.

As shown by Matusita and Sakka [11], if the number of crystal nuclei formed at temperatures above T_g can be assumed constant in a glass matrix, and then the rate of change of volume fraction of crystals can be denoted as:

$$\frac{dx}{dt} = KB^{-(n-1)}(1-x)^k \exp\left(\frac{-mQ}{RT}\right) \quad (1)$$

With its maximum at $T=T_p$ for any non-isothermal DTA condition. Therefore, as stated by Matusita and Sakka, Eq. (1) can be solved at $(d^2x/dt^2)=0$ and re-expressed as:

$$\ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mEc}{RT_p} + \epsilon \quad (2)$$

Assuming that the term $(1-x_c)^k$ is constant for $x=x_c$, $T=T_p$. Thus it seems that the three unknown sin Eq. (2) can be calculated using the parameters B and T_p given in Table I in three equations.

As stated previously, the para tellurite (TeO_2) crystals form because of surface crystallization [1]. Thus, $n=m=1$ for all heating rates can be assumed which leads to the Kissinger equation: [12]

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_c}{RT_p} \quad (3)$$

Fig. 5 is a graphical solution of the Eq. (3) where the T_p and α values listed in Table I are used to plot $\ln(\alpha/T_p^2)$ as a function of $(1000/T_p)$ to calculate the activation energy for crystallization.

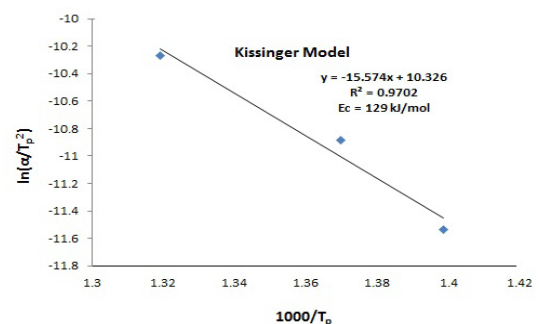


Fig. 5. A Kissinger kinetic plot of Glass constructed from DTA data.

As seen in Fig. 5, parameters measured in three different non-iso thermal DTA analyses provide a linear of data points and the slope is nothing but E_c/R (where $R=8.314$ J/K- mol, gas constant).The activation energy, E_c can then be calculated as 129 KJ/mol. Since paratellurite crystallization in TeO₂-based glasses and glass-ceramics has been not reported in the literature, this value can only be compared to the activation energies of crystal growth in SiO₂-based glasses and glass-ceramics. This value is larger than the activation energy value of 150 KJ/mol for surface crystallization of the diopsied phase in SiO₂-rich glass-ceramic [13].

Also Different equations used for calculation of activation energies of crystallization that are provided below:

Augis-bennett equation [14],

$$\ln \frac{\alpha}{T_p} = -\frac{E_c}{RT_p} + C \quad (4)$$

Ozawa equation [15],

$$\ln \alpha = \frac{-E_c}{RT_p} + C \quad (5)$$

where α is the heating rate, T_p is the temperature at which maximum of the DSC crystallization peak exo-therm is noted, R is the universal gas constant, E_c is the activation energy for crystallization, and C is a constant.

From Augis-bennett (Fig. 6) model plot of $\ln(\alpha/T_p)$ versus $1000/T_p$ slopes were measured to estimate activation energy of crystallization as 136 KJ/mol.

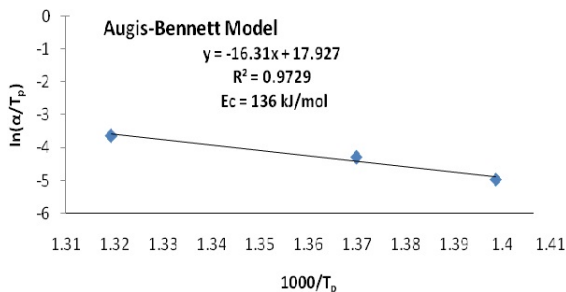


Fig. 6. Augis-bennett kinetic plot of. Glass constructed from DTA data.

In Ozawa model (Fig. 7) plot of $\ln \alpha$ versus $1000/T_p$, furnish activation energies 142 KJ/mol.

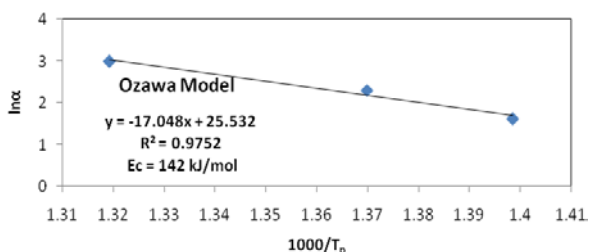


Fig. 7. An Ozawa kinetic plot of Glass constructed from DTA data.

IV. CONCLUSION

On the basis of the results reported in the present investigation, the following conclusions can be drawn:

Devitrification of the $(1 - x)TeO_2 \pm xLiCl$ (with $x=0.3 \pm 0.4$ mol) glasses dope d with 0.005 mol of Tm 2 O 3 takes place

in the vicinity of 400 C with the formation of the para tellurite (TeO₂) as the only crystallizing phase in the glassy matrix.

Using the analysis of Matusita and Sakka, the activation energy for surface crystallization in the 0.7TeO₂±0.3LiCl glass was calculated as 238 kJ / mole from the slope of the Kissinger plot.

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