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The Experimental Investigation of Kinetics of Glass Transition of ZBLAN Glass by using Differential Scanning Calorimetry

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A ZBLAN glass is a heavy metal fluoride (HMF) glass that possesses high thermal stability and excellent property as a transmitting material. The current study examines the thermal properties of ZBLAN glass utilizing Differential scanning calorimetry (DSC) at various heating rates. The temperature of glass transition, Tg, is observed to vary with heating rate, indicating its kinetic nature. Through the use of Kissinger's and Augis- Bennett's methodologies and the heating rate dependency of Tg, the activation energy (E) has been determined. These methodologies have also been used to obtain the fragility index (m), which can be used to evaluate the glass forming ability (GFA) of the system. The fragility index found is greater than 16, indicating that the ZBLAN glass is "fragile."

Keywords: Kinetics of Glass transition; ZBLAN glass; Activation energy; Fragility index

1 Introduction

The amorphous nature of glasses attracts researchers in one or another way due to their exotic properties and applications. However, the discovery of heavy metal fluoride (HMF) glasses has opened the prospects of these glasses to explore as transmitting materials in the infrared region[1]. Because of the wide transmitting window, small optical dispersion, small refractive index, simplicity of machining and polishing, and minimal heat dependency of the optical properties, HMF glasses have attracted significant interest in the fields of physics, chemistry, and materials science[2-3]. Among such fluoride glasses, ZBLAN glass is the most stable one against devitrification[4]. A ZBLAN glass is a composition of zirconium fluoride (ZrF_4), barium fluoride (BaF_2), lanthanum fluoride (LaF_3), aluminum fluoride (AlF_3) and sodium fluoride (NaF) and the specimen of the ZBLAN glass has been procured from the Institute of Photonics & Advanced Sensing (IPAS), The University of Adelaide, Australia. The NaF-containing HMF *(i.e.*, ZABLAN glass) has the drawback of having poor chemical durability[5]. In the past, many researchers have chosen ZBLAN glass to investigate its various properties like excited state absorption spectra[6], the temperature dependence of elastic properties[7], nucleation and crystal growth rate[8] and some thermodynamic properties[1,9]. But the kinetic study of glass transition is still a point of interest.

Some thermo-analytical methods, such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA), are extensively used to study the glass transition kinetics by conducting experiments under both isothermal (annealing) and non-isothermal (linear heating) conditions[10]. The study of glass transition kinetics is useful for finding the temperature at glass transition (T_g) to understand the thermal stability of glasses. Furthermore, the results of these experiments can be used to calculate kinetic parameters *e.g.*, energy of activation (E), constant of a rate of reaction (K), Avrami exponent (n), and so on, for which numerous methods have been established[11]. These methods are classified as (i) isokinetic methods, in which the transformation process is expected to be constant over the temperature/time range and the kinetic properties should be constant regarding time and temperature, and (ii) Isoconversional process for linear heating presume a constant rate of reaction which is temperature dependent[10].

The DSC has evolved into an extremely useful instrument for studying the thermal stability and

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kinetics of phase transformation in amorphous materials. In the current work, the thermal stability of the ZBLAN glass has been investigated thoroughly using DSC at varied Scanning rates. The values of T_g obtained for various heating rates have been used to calculate the energy of activation and the fragility index (m) using various approaches. X-ray diffraction (XRD) is used to investigate the amorphous nature of the ZBLAN glass.

2 Experimental Details

Samples of ZBLAN glass has been heated in DSC-25 (TA Instruments, USA) under the linear heating conditions at various linear heating rates (5, 10, 15, 20 °C/min) from room temperature to 550 °C in a nitrogen atmosphere. The obtained thermo grams have been shown in Fig. 1. X-ray Diffraction (XRD) has proven the amorphous nature of the glass samples, which does not show any prominent peak. The obtained data of DSC has been utilized to evaluate activation energy values derived from Kissinger's and Augis-Bennett's methods and the fragility index has also been evaluated using the so obtained activation energy values.

3 Results and Discussion

The glass transition phenomena define the changing behavior of metallic glasses at higher temperatures, whereas the energy of activation explains the least amount of energy required during phase transition. The glass transition temperatures at various scanning rates are determined during the heating process and shown in Fig.1 by denoting as T_g. This clearly illustrates that increasing the scanning rate (β) raises Tg. This is because the system does not have optimal time for crystallization and nucleation at higher temperatures. This means that increasing heating rate causes the decrease in the relaxation time and hence T_g increases. The obtained results of T_g have been presented in Table 1 and one can see that these values lie close to the actual value of T_g (*i.e.*, 265 °C) which is provided by the IPAS, The University of Adelaide, Australia who have supplied this sample to us.

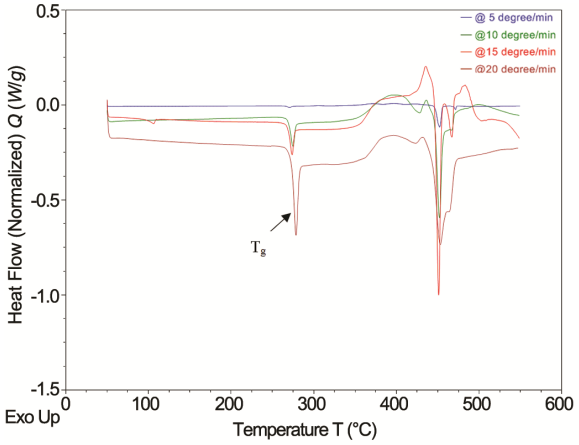

Fig. 1 — The Glass Transition Temperature for ZBLAN Glass at Four Different Heating Rates.

Employing the glass transition having kinetic nature and structural relaxation proposed by several researchers[12–14], the energy of activation (E) of the system at glass transition has been evaluated by utilizing the Kissinger[15] and the Augis-Bennett approaches[16].

One method that is frequently employed to ascertain the energy of activation at the glass transition is the Kissinger approach[17] which can be expressed as:

$$\ln\left(\frac{\beta}{T_g^2}\right) = -\frac{E}{RT_g} + \ln\left(\frac{k_0 R}{E}\right) \qquad \ldots(1)$$

Where, T_g: the peak glass transition temperature,

E: energy of activation of the system at glass transition in kJ/mol

β: heating rate or scanning rate in degree/min

R: well-known universal gas constant

k_0: pre-exponential factor (also known as frequency factor) in s^{-1}

A graph of $\ln(\beta/T_g^2)$ vs. $1000/T_g$ is linear in nature (Fig. 2) and E can be evaluated from the slope.

Table 1 — The glass transition temperature for ZBLAN glass at four different heating rates

Heating (or scanning) rate (β) (°C/min)	Glass transition temperature, T_g (°K)
5	540.53
10	541.88
15	542.18
20	544.32

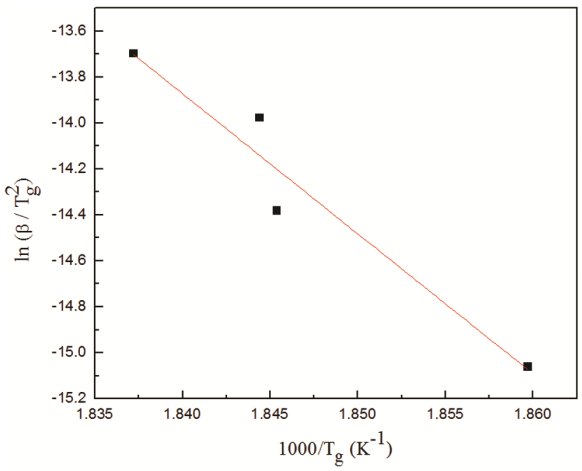

Fig. 2 — Kissinger Plot.

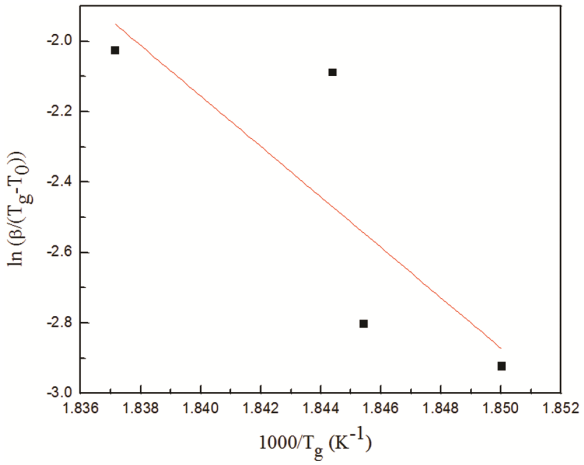

Fig. 3 — Augis-Bennett Plot.

Table 2 — The activation energy obtained for ZBLAN glass from Kissinger and Augis-Bennett methods.

Method	E (kJ/mol)
Kissinger's method	506.8 ± 10
Augis and Bennett's method	594.10 ± 35

Table 3 — The fragility parameter (m) obtained for ZBLAN glass from Kissinger, Augis-Bennett methods.

Heating rate (β) (°C/min)	Glass transition temperature, T_g (°K)	Fragility index (m) from Kissinger's method	Fragility index (m) from Augis Bennett's method
5	540.53	48.98	57.41
10	541.88	48.86	57.27
15	542.18	48.83	57.23
20	544.32	48.63	57.01

The kinetic nature of glass transition has also been applied to the Augis-Bennett method which incorporates the onset value of T_g. Hence, Eq. (1) turns to be:

$$\ln\left(\frac{\beta}{T_g - T_0}\right) = -\frac{E}{RT_g} + \ln k_0 \qquad \ldots(2)$$

Where, T_0: onset value of T_g

T_g: peak value of T_g

A graph of ln $(\beta/(T_g - T_0))$ vs. $1000/T_g$ is also linear in nature (Fig. 3) and E can be evaluated again from the slope.

These two approaches (Eqs. 1 and 2) are used in the present study to determine the energy of activation at glass transition for ZBLAN glass. The results are presented in Fig. 3, respectively along with the numeric values that are provided in Table 2. The energy required to transit from one state to another in the glassy phase, where reshuffles of the atom occur, is known as the activation energy at glass transition temperature.

The fragility is related to the viscosity which is temperature dependent. Since, there is a rise in T_g which causes a decrease in relaxation times, the nature of viscosity diverges from its Arrhenius tendency[18], and glass-forming liquids become fragile depending on their fragility index (m). It can be written as[19]:

$$m = \frac{E}{R\,T_g\,\ln 10} \qquad \ldots(3)$$

where E being the energy of activation.

If m is smaller than 16, the system is categorised as the "strong" glass-forming liquid group. If m is between 16 and 200, the system is classified as "fragile" glass-forming liquid[20]. The fragility indices m for ZBLAN glass are evaluated in this work using activation energies derived from the Kissinger and Augis-Bennett approaches and are provided in Table 3. The values of m obtained using both approaches are greater than 16, indicating that the ZBLAN glass belongs to the "fragile" group of glass-forming liquids.

4 Conclusions

The glass transition kinetics of ZBLAN glass is studied through DSC under linear heating circumstances at various scanning rates. Due to the involvement of the activation energy in molecular motion at glass transition, it helps to rearrange the atoms near T_g. As a result, the study of glass transition kinetics prompts to determine the activation energy at T_g.

The results of E at T_g are obtained by utilizing the Kissinger method and Augis-Bennett approaches. However, these approaches are frequently used to analyze data of crystallization process through DSC which gives information about the phase transition from amorphous liquid to solid crystalline phase. The results of glass transition activation energy obtained through this work have been found nearer to each other and close to the given value of T_g by suppliers and suggest that these approaches for the study of crystallization are also valid to investigate the glass transition kinetics. Moreover, the values of m for ZBLAN glass have also been evaluated from the obtained values of E and T_g from Kissinger and Augis-Bennett methods. The values of m shows that the ZBLAN glass belongs to the "fragile" group of glass-forming liquids.

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