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**KINETICS STUDY OF $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Cd}_x$ GLASSY ALLOY BY
DIFFERENTIAL THERMAL ANALYSIS USING NON-ISOTHERMAL
TECHNIQUE**

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The kinetics of crystallization in $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Cd}_x$ ($x = 0, 2, 4$ and 6) alloys at different heating rates have been studied by Differential Thermal Analysis in non-isothermal condition. A comparison of various quantitative methods to assess the level of stability of the glassy material in the above mentioned system is presented. All these methods are based on the characteristics temperature obtained by heating of the samples, such as glass transition temperature (T_g), temperature of crystallization (T_c), and the melting temperature (T_m). From the dependence of glass transition temperature on heating rate, the activation energy (E_g) has been calculated on the basis of the Kissinger and Moynihan models.

Keywords: CHALCOGENIDE GLASSES, ACTIVATION ENERGY, T_g , DTA, Se-Te-Cd.

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1. INTRODUCTION

Thermal analysis has been extensively used for studying the kinetics of chemical reaction [1-2] and crystallization of glasses [3-8]. The concepts of kinematical studies are always connected with the activation energy. In calorimetric measurements, two basic methods can be used: isothermal and non-isothermal [9-13]. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time while in the non-isothermal method, the sample is heated at a fixed rate (β) and the heat evolved is recorded as a function of temperature or time [14]. The main factor, which leads to the stability of amorphous phase of a compound near room temperature, is its glass transition temperature, if the melting temperature of the compound is high, and the glass transition temperature, T_g , of it is expected to be considerably higher than room temperature [15]. The activation energy plays a dominant role in deciding the utility of the material for the specific purpose. One of the most important aspects of the study of glasses is the composition dependence of properties. Among amorphous chalcogenide alloys, selenium based melt are characterized by high viscosity [16]. This feature favors the glass formation in bulk form by air-quenching or water-quenching as well as in evaporated thin film forms. Since tellurium based melts with the same elements generally have low viscosity, a high cooling rate is required to prevent nucleation and growth during quenching and to obtain bulk glasses. Glassy alloys of the Se-Te system have become materials of considerable commercial, scientific and technological importance as they

have greater hardness, higher crystallization temperature, higher photo-sensitivity and smaller ageing effects than pure Se [17]. The addition of a third element (Cd) expands the glass forming area and also creates compositional and configurational disorder in the system. Present paper is concentrated on kinetic studies of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Cd}_x$ ($x = 0, 2, 4, 6$) glassy alloy under non-isothermal technique by using DTA.

2. EXPERIMENTAL PROCEDURE

For preparation of Se-Te-Cd glasses, high purity (5N) elements in appropriate atomic percentages were weighted into the quartz ampoules and sealed off in a vacuum of 10^{-5} torr and then heated in furnace at around 1000°C for 12h. The ampoules were rotated frequently to ensure homogenization. The ampoules were then rapidly quenched in ice-water to obtain the glasses and samples were removed by breaking the quartz ampoule. SHIMADZU DTG-60, simultaneous TG/DTA module is used to measure the caloric manifestation of the phase transformation. The TG/DTA scans are taken at four heating rate (10, 15, 20, $25^\circ\text{C}/\text{min}$) for the four different composition in the micro alumina pans under dry nitrogen gas. The masses of the samples varied between 10 and 30 mg. The amorphous nature of the resulting glassy alloys was verified by X-ray diffraction as no prominent peak was observed.

3. RESULT AND DISCUSSION

The glass transition temperature represents the strength or rigidity of the glassy structure of the alloy. In present work glass transition region has been studied in terms of variation of glass transition temperature with the heating rate. Three approaches are used to analyze the dependence of T_g on the heating rate (β). The first is the empirical relationship, which has originally been suggested by Lasocka [18] and has the form,

$$T_g = A + B \ln\beta \quad (1)$$

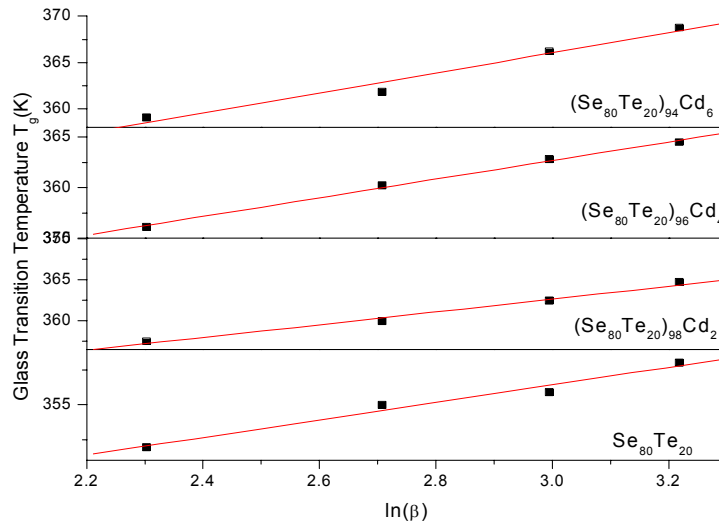


Fig. 1 – Plots of T_g versus $\ln\beta$

where A and B are constants for a given glass compositions and calculated values are given in Table 1. Plots of T_g versus $\log\beta$ indicates the validity of Eq. (1) for our compositions (Fig. 1).

The activation energy (E_g) of the glass transition process is one of the most important parameters for understanding the thermal relaxations that occur in glassy networks during the glass transition. The activation energy for glass transition (E_g), depends on T_g as a function of the heating rate (β) have been evaluated using Kissinger's equation [19-21] and is given by the following expression,

$$\ln(\beta/T_g^2) = -E_g/RT_g + \text{constant} \quad (2)$$

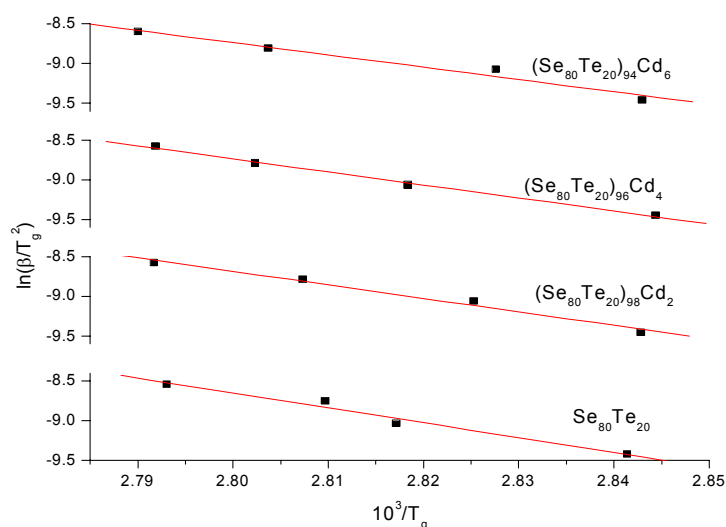


Fig. 2 – Shows the plots of $\ln(\beta/T_{g2})$ versus $10^3/T_g$

The activation energy of the glass transition (E_g) also has been evaluated using the Moynihan [22] relation derived, based on the concept of thermal relaxation.

The plot of $\ln\beta$ versus $10^3/T_g$ yields a straight line, the slope of which gives the activation energy of glass transition (Fig. 3). Table 1 lists the values of E_g obtained using the Kissinger and Moynihan models, which are in good agreement with each other with the difference within experimental error. The glass transition activation energy is the amount of energy that is absorbed by a group of atoms in the glassy region so that a jump from one metastable state to another state is possible [23]. Accordingly, the atoms in a glass having minimum activation energy have a higher probability to jump the metastable (or local minimum) state of lower internal energy and, hence, are the most stable.

Table 1 – E_g obtained from the Kissinger and Moynihan Models (kJ/mol)

Composition	Kissinger Model	Moynihan Model	A(K)	B(K)
$x = 0$	155.88	161.86	337.48	6.32
$x = 2$	131.09	137.09	339.25	7.80
$x = 4$	110.64	116.62	335.06	9.21
$x = 6$	92.67	98.72	333.51	10.83

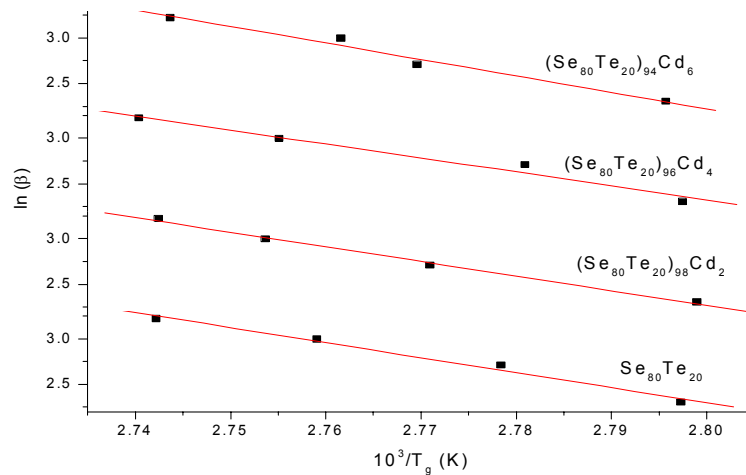


Fig. 3 – The plot of $\ln\beta$ versus $10^3/T_g$

4. CONCLUSION

The values of activation energies for glass transition were found to decrease with increase in Cd content in Se-Te glassy alloy. The values of activation energies, using two different methods, are in good agreement with each other. So it can be concluded that any of these two methods can be used to calculate glass transition activation energy.

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