

Kinetic Parameters of Glass Transition in Glassy $\text{Se}_{1-x}\text{Sb}_x$ Alloys

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Abstract

Differential Scanning Calorimetry (DSC) is performed at different heating rates under non-isothermal conditions to study the glass transition kinetics of glassy $\text{Se}_{1-x}\text{Sb}_x$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) alloys. The activation energy of glass transition E_t has been calculated using the two different non-isothermal methods. One of the two methods is based on the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers, while the other relation is well-known Kissinger's relation. The results show that the values of E_t determined from both the methods are in good agreement with one another. The variation of glass transition temperature T_g with heating rate and composition has also been studied and the results have been explained in terms of the glassy structure of Se-Sb system.

Key Words: Differential scanning calorimetry, Glass transition temperature, Activation energy of glass transition.

1. Introduction

Antimony containing non-oxide chalcogenide glasses have been extensively studied for their interesting electronic and optoelectronic properties [1–5]. The continued scientific interest in Se-Sb binary system is due to potential use of Se-Sb films in photoconductive elements [6] and as a data storage material [7–11]. Charge trapping and transport properties [12, 13] and the relation between the band gap and chemical composition [14] of Se-Sb thin films have been reported in the literature. Recently, dielectric studies on Se-Sb alloys have also been reported by our group [15]. However, there is very little information on the thermal properties of Se-Sb binary glasses. Se-Sb glasses, like many other chalcogenide glasses, are expected to show glass transition and crystallization behaviour due to structural rearrangements and relaxation processes toward equilibrium accompanied by a change in the enthalpy and heat capacity. A proper description of thermal transformations of these glasses is important for a fundamental understanding of their properties and applications.

The glass transition temperature T_g is one of the most important parameters for characterization of the glassy state as it is related to the rigidity of the glassy network. The nature of glass transition is complex and even today remains poorly understood. The glass transition is exhibited as an endothermic peak or a shift in the base line in Differential Scanning Calorimetry (DSC) due to change in specific heat. The heating

rate dependence of T_g is well known, which makes possible the study of glass transition kinetics. We have therefore used non-isothermal DSC technique for study of glass transition kinetics in the present work. The present paper reports the glass transition kinetics in glassy $\text{Se}_{1-x}\text{Sb}_x$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) system. The activation energy of glass transition is calculated using Kissinger's relation and Moynihan's relation.

2. Experimental

Glassy alloys of $\text{Se}_{1-x}\text{Sb}_x$ were prepared by quenching technique. High purity materials (99.999% pure) were weighted according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5} Torr. Each ampoule was kept inside the furnace at 800°C to be sure both constituents are melted, with the final temperature reached being raised at of $3\text{--}4^\circ\text{C}/\text{min}$. The ampoules were rocked frequently for 10 hrs at the maximum temperature to homogenize the melt. The ampoules were quenched in ice water and the glassy nature of alloys was checked by x-ray diffraction technique. The x-ray diffraction (XRD) patterns of all the five samples were taken at room temperature using a Philips, PW 1140/09 x-ray diffractometer. The x-ray source produced $\text{Cu K}\alpha_1$ $\lambda = 1.54 \text{ \AA}$ radiation. The glasses, thus prepared, were ground to make fine powder for DSC studies.

The thermal behaviour was investigated using a Rheometric DSC-plus differential scanning calorimeter (Rheometric Scientific, UK). The temperature precision of this equipment is $\pm 0.1 \text{ K}$ with an average standard error of about $\pm 1 \text{ K}$ in the measured values (glass transition and crystallization temperatures).

10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Four heating rates ($5, 10, 15$ and $20^\circ\text{C}/\text{min}$) were chosen in the present study. Measurements were made under almost identical conditions.

3. Theoretical Basis

One of the most important problems in the area of glasses is the understanding of glass transition kinetics, which can be studied in terms of glass transition temperature T_g and activation energy of thermal relaxation E_t . The evaluation of E_t under the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers [16–18] from the heating rate dependence of glass transition temperature is widely used in the literature.

Some attempts have also been made to evaluate E_t using Kissinger's relation [19–25]. Since E_t evaluated from this relation has less dependence on thermal history, this method seems to have some extra advantage. As this method is basically given for amorphous to crystalline transformation, the validity of its use for glass transition kinetics has always been questionable. The application of this relation for glass transition means that some kind of transformation is assumed in this case as well. Some authors have given the name of this transformation as the glass-to-amorphous transformation [23]. It is, therefore, interesting to see whether the Kissinger's relation can be applied in general for chalcogenide glasses for evaluating the activation energy of structural relaxation, which is normally obtained by Moynihan's relation. This motivates us to compare the values of activation energy of glass transition process by both the relations in glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys. The theoretical basis of the two non-isothermal methods is given below.

3.1. Moynihan's relation

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted by Moynihan et al. in terms of thermal relaxation phenomenon. In this kinetic interpretation, the enthalpy at a particular temperature and time $H(T, t)$ of the glassy system, after an instantaneous isobaric change in

temperature, relaxes isothermally towards a new equilibrium value $H_e(T)$. The relaxation equation can be written in the form [16]

$$(\delta H/\delta t)_T = -(H - H_e)/\iota, \quad (1)$$

where ι is a temperature dependent structural relaxation time and is given by the following relation

$$\iota = \iota_o \exp(-E_t/RT) \exp[-c(H - H_e)]. \quad (2)$$

Here, ι_o and c are constants and E_t is the activation energy of relaxation time. Using the above equations, it can be shown [17, 18] that

$$d(\ln\beta)/d(1/T_g) = -E_t/R. \quad (3)$$

Equation (3) states that $\ln \beta$ vs. $1/T_g$ plot should be a straight line and the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot.

3.2. Kissinger's relation

This method is most commonly used in analyzing crystallization data in DSC. During the isothermal transformation, the extent of crystallization α of a certain material is represented by Avrami's equation [26, 27]:

$$\alpha(t) = 1 - \exp(-Kt^n), \quad (4)$$

where K is rate constant and n is the order parameter that depends upon the mechanism of crystal growth. The rate constant K is given by Arrhenius equation:

$$K = K_o \exp[-E_c/kT] \quad (5)$$

According to Kissinger, the eq. (4) can be approximated as

$$d\alpha/dt = (1 - \alpha)nK^n t^{n-1}. \quad (6)$$

Expressing t in terms of α from eq. (4), the crystallization rate $d\alpha/dt$ becomes

$$d\alpha/dt = A'nK(1 - \alpha), \quad (7)$$

where $A' = [-\ln(1 - \alpha)]^{(n-1)/n}$. In non-isothermal crystallization, it is assumed that there is a constant heating rate in the experiment. The relation between the sample temperature T and the heating rate β can be written in the form

$$T = T_i + \beta t \quad (8)$$

where T_i is the initial temperature. The derivative of K with respect to time can be obtained from eqs. (5) and (8) as follows:

$$dK/dt = (dK/dT).(dT/dt) = (\beta E_c/RT^2)K. \quad (9)$$

Using the equations (7) and (9), Kissinger showed that

$$\ln(\beta/T_c^2) = -E_c/RT_c + \text{constant}, \quad (10)$$

where T_c is peak crystallization temperature.

Although originally derived for the crystallization process, it is suggested that this relation is valid for glass transition process [28, 29] and hence the above equation takes the following form for its use in glass transition kinetics:

$$\ln(\beta/T_g^2) = -E_t/RT_g + \text{constant}. \quad (11)$$

4. Results and Discussion

Figure 1 shows typical DSC thermograms for glassy $\text{Se}_{1-x}\text{Sb}_x$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) at heating rate 15 K/min. Similar thermograms were obtained for other heating rates also (not shown here). It is clear from Figure 1 that well defined endothermic and exothermic peaks are observed at glass transition temperature T_g and crystallization temperature T_c respectively. We have taken the peak temperature for T_g and T_c .

4.1. Composition dependence of T_g

The values of glass transition temperature T_g for all the glassy alloys at a heating rate 5 K/min are given in Table 1. From this table, it is clear that the glass transition temperature decreases with increase in the concentration of Sb. The decrease of T_g with increasing Sb impurity in the present system may be explained by considering the structural changes occurring due to further addition of Sb content. The generally accepted structural model of amorphous Se (a-Se) [30] includes two molecular species: meandering chains, which contain helical chains of trigonal Se; and Se_8 ring molecules of monoclinic Se. Due to the larger size than Se, Sb atoms are forced by the steric hindrance to end a-Se chains [31]. Around 1 at% Sb, all Se chains ends have to be saturated. For compositions greater than 1 at%, Sb starts to be incorporated into Se-chains [31]. The incorporation of Sb into Se chains at concentrations above 1 at% Sb is a process, which partially destroys long Se-chains [31].

Table 1. Values of glass transition and crystallization temperatures and their difference for glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys.

Sample	T_g (K)	T_c (K)	$T_c - T_g$ (K)
$\text{Se}_{0.98}\text{Sb}_{0.02}$	328.9	373.7	44.8
$\text{Se}_{0.96}\text{Sb}_{0.04}$	327.6	394.2	66.6
$\text{Se}_{0.94}\text{Sb}_{0.06}$	326.6	389.3	62.7
$\text{Se}_{0.92}\text{Sb}_{0.08}$	325.9	382.7	56.8
$\text{Se}_{0.90}\text{Sb}_{0.1}$	324.7	381.5	56.8

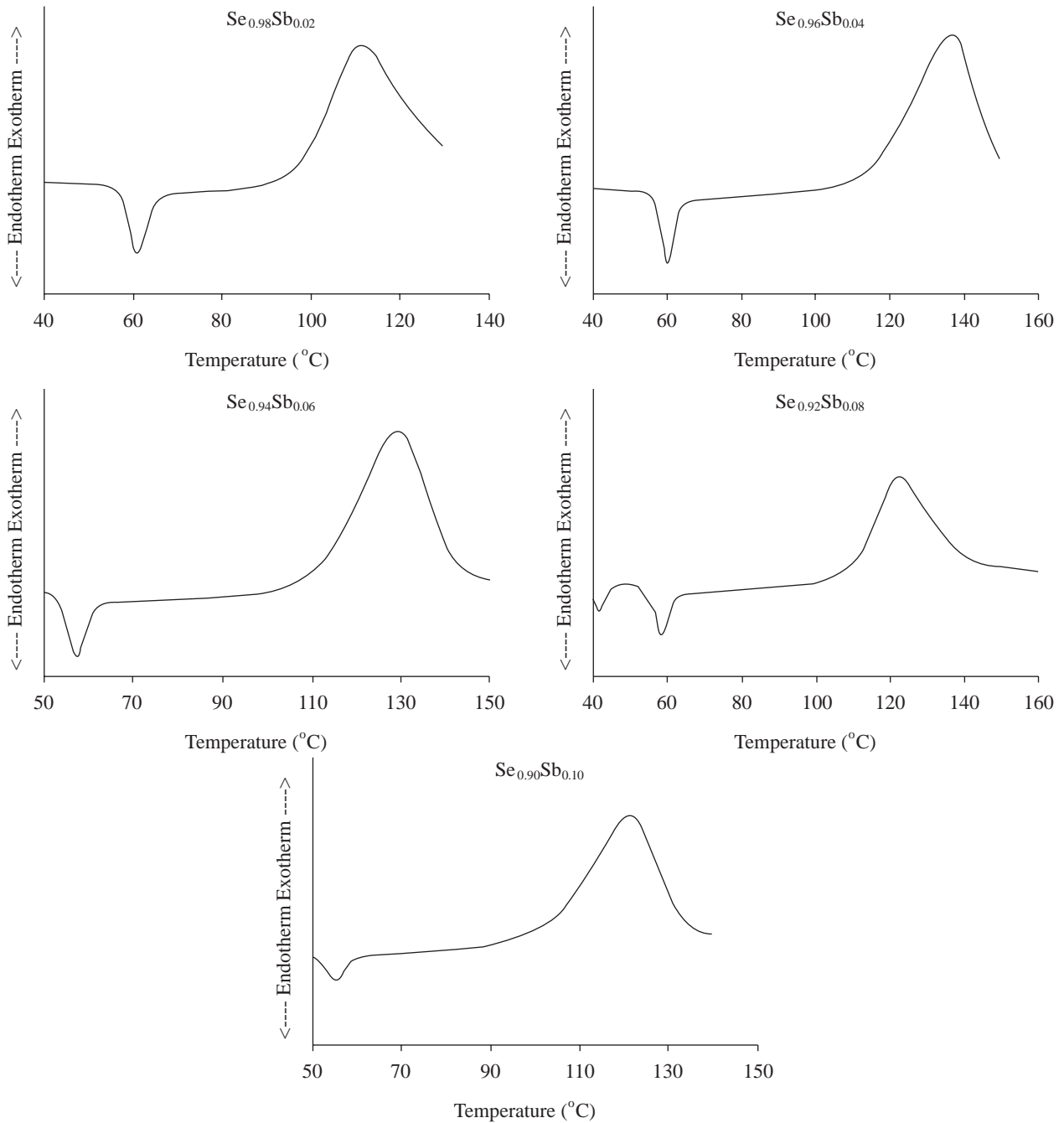


Figure 1. DSC Thermograms for glassy $\text{Se}_{1-x}\text{Sb}_x$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) alloys at heating rate of 15 K/min.

Therefore, as Sb contents are incorporated, they are probably dissolved in the Se chains, increasing relatively the number of Se_8 rings while the number of long Se-Se chains is decreased [32]. It is known that [33] the glass transition temperature T_g should increase with increasing chain length and decreases with increasing ring concentration. This is probably the reason for the decrease in T_g values with increasing Sb concentration. Al-Zaida et al. [34] also reported decrease in T_g in glassy $\text{Se}_{1-x}\text{Sb}_x$ system with the increase in Sb concentration. A similar trend is also observed in glassy $\text{Se}_{1-x}\text{In}_x$ system by Imran et al. [35]. The composition dependence of T_g is shown in Figure 2.

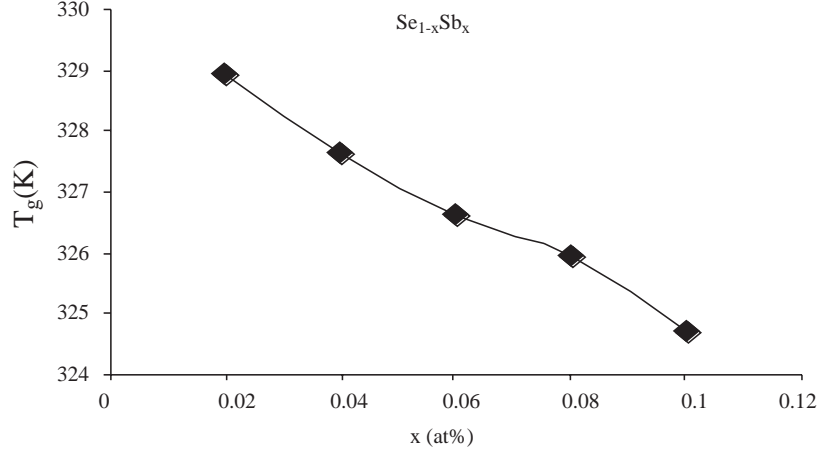


Figure 2. Composition dependence of glass transition temperature.

4.2. Thermal stability of glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys

The glass transition temperature T_g represents the strength or rigidity of the glass structure in chalcogenide glasses. Hence T_g affords valuable information on the thermal stability of the glassy state [36, 37], but T_g alone does not give any information on the glass-forming tendency (GFT) [38]. It has been found that the difference of T_c and T_g is a strong indication of both the thermal stability [39] and GFT. Higher the values of $(T_c - T_g)$, the greater is the thermal stability. The values of T_c and $(T_c - T_g)$ at all heating rates are given in Table 1 for heating rate of 5 K/min. It is interesting to note that the value of $(T_c - T_g)$ is maximum for binary $\text{Se}_{0.96}\text{Sb}_{0.04}$ alloy at all the four heating rates. This shows maximum thermal stability at 4 at% of Sb additive in $\text{Se}_{1-x}\text{Sb}_x$ glassy system.

4.3. Heating rate dependence of T_g

The glass transition temperature T_g represents the strength or rigidity of the glassy structure of the alloys. It is well known that T_g of glassy alloys varies with the heating rate β [40–44]. The empirical relation used to analyze the dependence of T_g on β is of the form

$$T_g = A + B \log \beta, \quad (12)$$

where A and B are constants. The value of A indicates the glass transition temperature for the heating rate of 1 K/min. It has been found by various workers that the slope B in eqn. (12) is related to the cooling rate of the melt: lower the cooling rate of melt, lower the value of B . The physical significance of B seems to be related with the response of the changes in configuration within the glass transformation region. A plot of T_g vs. $\log \beta$ for glassy $\text{Se}_{0.98}\text{Sb}_{0.02}$ alloys is shown in Figure 3. Similar curves are obtained for the other glassy alloys. The values of A and B for different alloys are given in Table 2. The values of B for glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys have been found to be different, indicating that these glassy alloys undergo different structural changes. The results shown in Table 2 indicate the validity of this relationship for glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys.

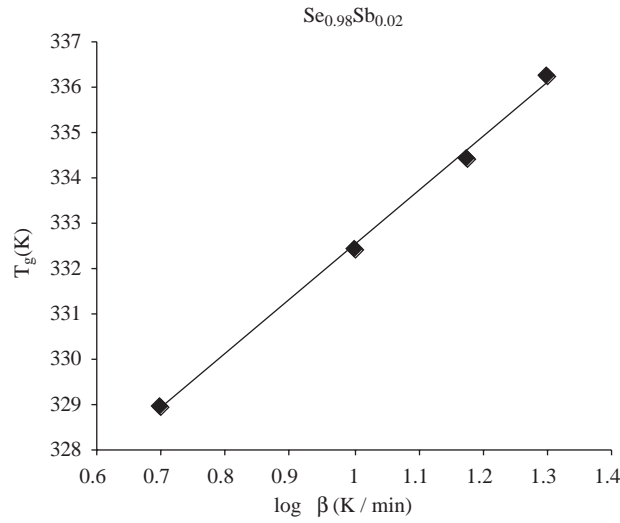


Figure 3. Plot of T_g vs $\log(\beta)$ for glassy $\text{Se}_{0.98}\text{Sb}_{0.02}$ alloy.

Table 2. Kinetic parameters of glass transition process in glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys.

Sample	A (K)	B (min)	E_t (eV)	
			eqn. (3)	eqn. (11)
$\text{Se}_{0.98}\text{Sb}_{0.02}$	320.5	11.9	1.83	1.77
$\text{Se}_{0.96}\text{Sb}_{0.04}$	318.7	12.3	1.74	1.68
$\text{Se}_{0.94}\text{Sb}_{0.06}$	320.9	8.5	2.42	2.36
$\text{Se}_{0.92}\text{Sb}_{0.08}$	318.0	11.2	1.86	1.80
$\text{Se}_{0.90}\text{Sb}_{0.1}$	319.0	8.0	2.63	2.58

4.4. Evaluation of activation energy of glass transition E_t

Using Moynihan's relation, eqn. (3), the plots of $\ln\beta$ against $10^3/T_g$ were plotted for various glassy alloys and are shown in Figure 4 for glassy $\text{Se}_{0.98}\text{Sb}_{0.02}$ alloy. Similar curves are obtained for the other glassy alloys. The slopes of these plots were used to calculate the activation energy of glass transition process. Table 2 shows the E_t values obtained from eqn. (3).

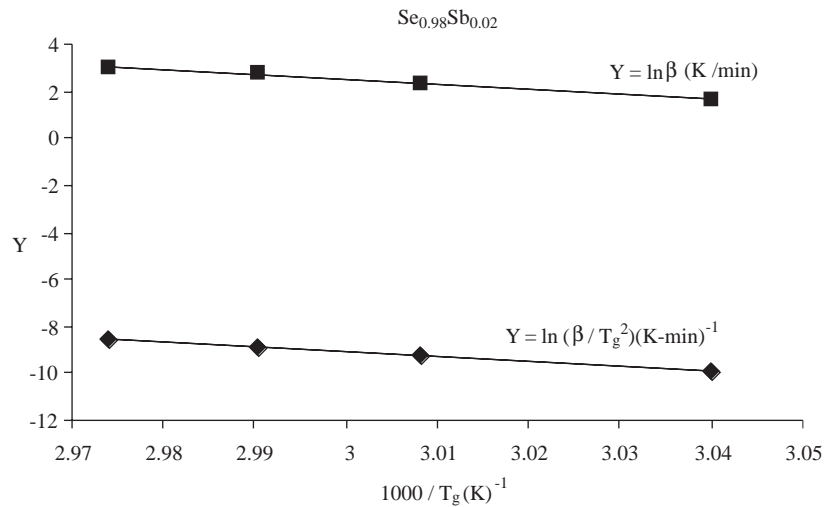


Figure 4. Plots of $\log(\beta)$ and $\ln(\beta/T_g^2)$ against $1000 / T_g$ for glassy $\text{Se}_{0.98}\text{Sb}_{0.02}$ alloy.

The values of E_t are also evaluated using Kissinger's relation [eqn. (11)] from the slopes of plots of $\ln(\beta/T_g^2)$ against $10^3/T_g$ for various glassy systems. The plots of $\ln(\beta/T_g^2)$ vs. $1000/T_g$ are also shown in Figure 4 for glassy $\text{Se}_{0.98}\text{Sb}_{0.02}$ alloy. Similar curves are obtained for the other glassy alloys. These values are given in Table 2. No systematic variation of E_t with Sb concentration has been observed in this glassy system, though there is a monotonic decrease in T_g with Sb concentration (see Tables 1 and 2).

It is also clear from Table 2 that E_t values obtained from Kissinger's relation are in good agreement with the E_t values obtained using Moynihan's relation. This means that one can use either of equations (3) and (11) to calculate the activation energy of glass transition.

5. Conclusions

Calorimetric measurements have been performed in glassy $\text{Se}_{1-x}\text{Sb}_x$ alloys. DSC scans of these alloys show the well-defined endothermic peak at glass transition temperature T_g . It has been found that the glass transition temperature decreases with increase in the concentration of Sb. This decrease in T_g of ternary alloys is explained in terms of decrease in number of Se chains in these alloys. The activation energy of glass transition process has been determined using Kissinger's relation for various glassy alloys in order to compare the E_t values obtained from this relation with the E_t values obtained using Moynihan's relation.

The results show that E_t values obtained from Kissinger's relation are in good agreement with the E_t values obtained using Moynihan's relation. It has also been found that the composition dependence of E_t values obtained using the two relations are similar in glassy $\text{Se}_{1-x}\text{Sb}_x$ system. Thus, one can use any of the two relations (Kissinger's relation and Moynihan's relation) for the evaluation of E_t values. No systematic variation of E_t with Sb concentration has been observed in this glassy system though there is a monotonic decrease in T_g with Sb concentration.

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