Chalcogenide Letters Vol. 6, No. 8, September 2009, p. 403 – 414

STUDY OF GLASS TRANSITION KINETICS IN GLASSY ALLOYS OF $Se_{100-x}Bi_x$

SPHOORTI SRIVASTAVA[a], M. ZULFEQUAR[b], A. KUMAR[a*]
[a]Department of Physics, Harcourt Butler Technological Institute, Kanpur, India
[b]Department of Physics, Jamia Millia Islamia, New Delhi, India

Differential scanning calorimetric runs have been taken for $Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6, 10) glasses under non-isothermal conditions at different heating rates for the thermal study. Well defined endothermic and exothermic peaks are obtained at glass transition (T_g) and crystallization temperature (T_c). The activation energy of glass transition (E_g) has been evaluated on the basis of Moynihan and Kissinger model. The dependence of glass transition temperature on the heating rate β has been reported. The value of (T_c-T_g) and stability parameter S have been calculated for each glassy alloy.

(Received July 6, 2009; accepted September 5, 2009)

Keywords: Chalcogenide glasses, DSC technique, Activation energy of glass transition

1. Introduction

The intensive developement of modern technology has led to the synthesis of new materials. In recent years there has been a great deal of interest in the study of chalcogenide glasses from the point of view of basic physics [1-3] as well as of device technology [4-6]. It is well known that Se rich chalcogenide glasses exhibits high resistivity values implying certain limitations in their application. It is worth then to add more than one component in to Selenium matrix in order to produce considerable changes in the properties of new complex glasses. Certain additives are used especially, Se-Te, Se-Sb, Se-Ge and Se-In [7,8] alloys which have shown great interest due to their better properties like greater hardness, higher sensitivity, higher crystallization temperature, higher conductivity and smaller aging effects as compared to pure amorphous Se [9]. In the present work binary system Se-Bi has been taken for the study of glass transition kinetics.

Structural studies of chalcogenide glasses play an important role in determining the transport mechanism, thermal stability and practical applications. Different experimental techniques such as electrical resistivity, electron microscope, X-ray diffraction and thermal analysis have been used to study these transformations. The crystallization of the $Se_{1-x}Bi_x$ alloys has already been studied by Fieury et. al. [10], who have determined the crystallization parameters by means of conductivity measurements.

Kinetic studies are always connected with the concept of activation energy. The activation energy in the glass transition phenomenon is associated with nucleation and growth process .Studies of the glass transition and crystallization of a glass upon heating can be interpreted in terms of several theoretical models [11-14]. The study of crystallization kinetics using the differential scanning calorimetry (DSC) methods has been widely discussed in the literature [15-19].Thermally activated transformations in the solid state can be investigated by isothermal or nonisothermal experiments [20-22]. Experiments performed at constant heating rate are a much more rapid way of studying a transformation, while isothermal experiments are generally time

*Corresponding author: dr_ashok_kumar@yahoo.com

consuming. Another disadvantage of isothermal analysis is the impossibility of reaching a test temperature instantaneously and during the time, which the system needs to stabilize, no measurements are possible. Constant heating rate experiments do not have this drawback

The present work concerns with the study of the glass transition kinetics in $Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6, 10) glasses under non-isothermal conditions.

2. Material preparation and experimental procedure

Glassy $Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6 and 10) alloys were prepared by quenching technique. The exact proportions of high purity (99.999%) Se and Bi elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm. The materials were then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules (length ~ 5cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 800 ^{0}C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melt was cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction.

The glasses thus prepared, were ground to make fine powder for DSC studies.10 to 20 mg of the powder was heated at constant heating rate and the changes in heat flow with respect to an empty reference pan were measured. DSC plus instrument (Rheometric Scientific Company, U. K.) was used at four different heating rates of 5, 10, 15 and 20 ^{0}C/ min. Measurement were made under almost identical conditions.

3. Results and discussion

Figs. 1 & 2 show typical DSC thermograms for glassy $Se_{100-x}Bi_x$ (x = 0.5,& 6) at a heating rate of 15 K/min. Similar thermograms were obtained for other heating rates and for other glasses (results not shown here). It is clear from these figures that well defined single endothermic and exothermic peaks are observed at glass transition temperature T_g and crystallization temperature T_c respectively, which indicates that these glasses exist in single phase.

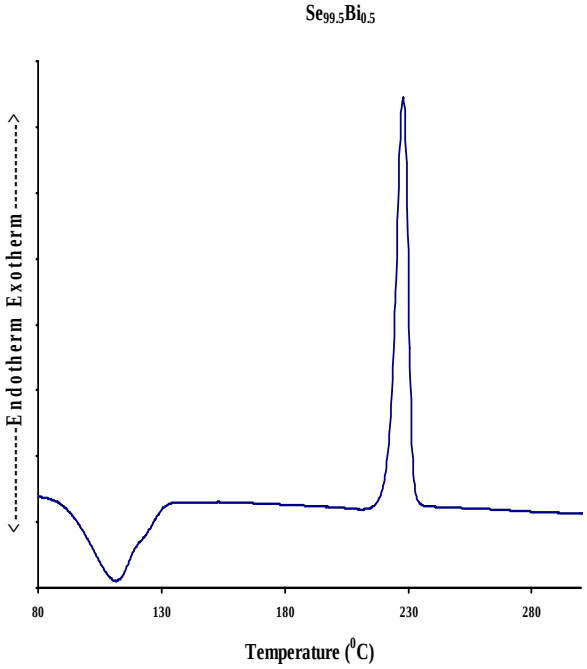

Fig1. DSC thermo gram for glassy $Se_{99.5}Bi_{0.5}$ alloys for heating rate 15 (K / Min)

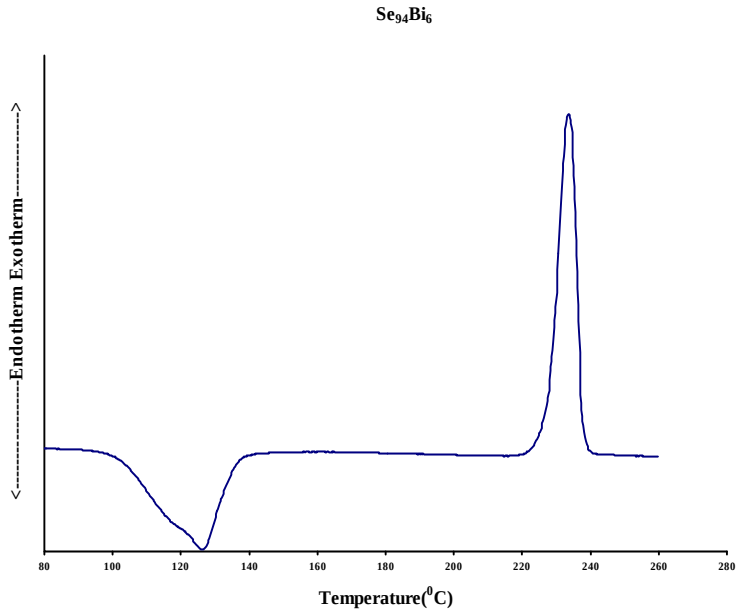

Fig2. DSC thermogram for glassy $Se_{94}Bi_6$ alloy for heating rate 15 (K / min)

3.1 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 rateβ [23-27]. The empirical relation used to analyze the dependence of T_g on β is of the form:

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

Where A and B are constants .The values 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 eq. (1) is related to the cooling rate of 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 β for glassy $Se_{94}Bi_6$ alloy is shown in Fig.3. Similar curves are obtained for the other glassy alloys. The values of A and B for different alloys are given in Table1. The values of B for glassy $Se_{100-x}Bi_x$ alloys have been found to be different for different composition, indicating that these glassy alloys undergo different structural changes. The results shown in Table 1 indicate the validity of this relationship for various alloys in glassy $Se_{100-x}Bi_x$ system.

Table 1: Kinetic parameters of glass transition process in glassy $Se_{100-x}Bi_x$

Sample	A(K)	B(min)
$Se_{99.5}Bi_{0.5}$	373.38	4.88
$Se_{97.5}Bi_{2.5}$	358.39	10.66
$Se_{96}Bi_4$	364.14	12.76
$Se_{94}Bi_6$	358.96	14.70
$Se_{90}Bi_{10}$	364.12	12.04

Table 2: Glass transition temperature T_g at different heating rates in glassy $Se_{100-x}Bi_x$

Heating rate	$Se_{99.5}Bi_{0.5}$	$Se_{97.5}Bi_{2.5}$	$Se_{96}Bi_4$	$Se_{94}Bi_6$	$Se_{90}Bi_{10}$
5 K/min	373.59	375.91	384.36	383.65	384.39
10 K/min	379.89	383.06	393.72	390.09	390.56
15 K/min	383.81	386.81	399.66	399.16	396.36
20 K/min	391.54	390.95	401.47	403.80	401.30

3.2 Composition dependence of T_g

It is clear from Table 2 that in glassy $Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6 and 10) the glass transition temperature T_g increases with increasing Bi content. The slight increase of T_g with increasing Bi in the present system may be explained by considering the structural changes occurring due to the further addition of Bi content. The generally accepted structural model of amorphous Se includes [28] two molecular species, meandering chains, which contain helical chains of trigonal Se and Se_8 ring molecules of monoclinic Se. Therefore, as Bi is incorporated in Se, they are probably dissolved in the Se chains increasing relatively the number of Se_8 rings while the numbers of chain Se-Se are decreased [29]. It is known [30] that the glass transition temperature T_g should increase with increasing chain length and decrease with increasing ring concentration. In the present case, the increase in T_g may, therefore, be related to the increase in chain length on increasing Bi concentration.

3.3 Activation energy of glass transition E_g

The evaluation of activation energy of glass transition (E_g) from the heating rate dependence of glass transition temperature is widely used in the literature. The theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers [31-33] has been used for this purpose. Some attempts have also been made to evaluate E_g using Kissinger's relation [34-40]. Since E_g 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 [38]. 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 $Se_{100-x}Bi_x$ alloys. The theoretical basis and the results obtained from them are given below:

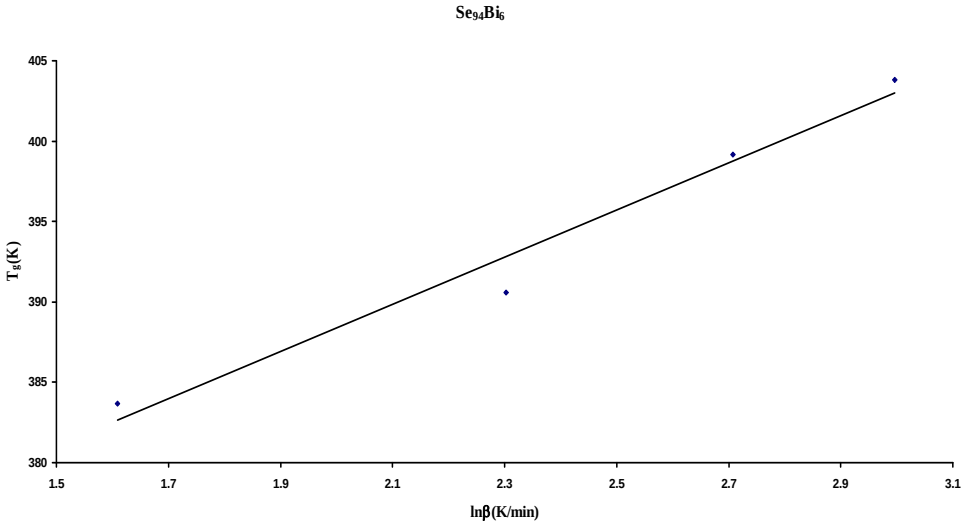

Fig.3 Variation of T_g with heating rate for $Se_{94}Bi_6$

3.3.1 Moynihan's relation

Heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted by Moynihan et. al [33].in terms of thermal relaxation phenomena. 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 $H_c(T)$. The relaxation equation can be written as: [31]

$$(\partial H / \partial t)_T = -(H - H_g) / \tau \qquad (2)$$

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

$$\tau = \tau_0 \exp(-E_g / RT) \exp[-C(H - H_c)] \qquad (3)$$

Where τ_0 and C are constants and E_g is the activation energy of the relaxation time.Using the above equations, it can be shown [11, 41] that:

$$d \ln \beta / d(1/T_g) = -E_g / R \qquad (4)$$

From equation (4), the ln β versus $1/T_g$ 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.

Using Moynihan's relation, eq.4, the plots of lnβ against $10^3/T_g$ are plotted for

various glassy alloys. These plots are shown in Figs. 4 -8 for various glassy alloys of -$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6 and 10) .The slopes of these plots are used to calculate the activation energy of glass transition process. Table 3 shows the E_g values obtained from eq.(4).

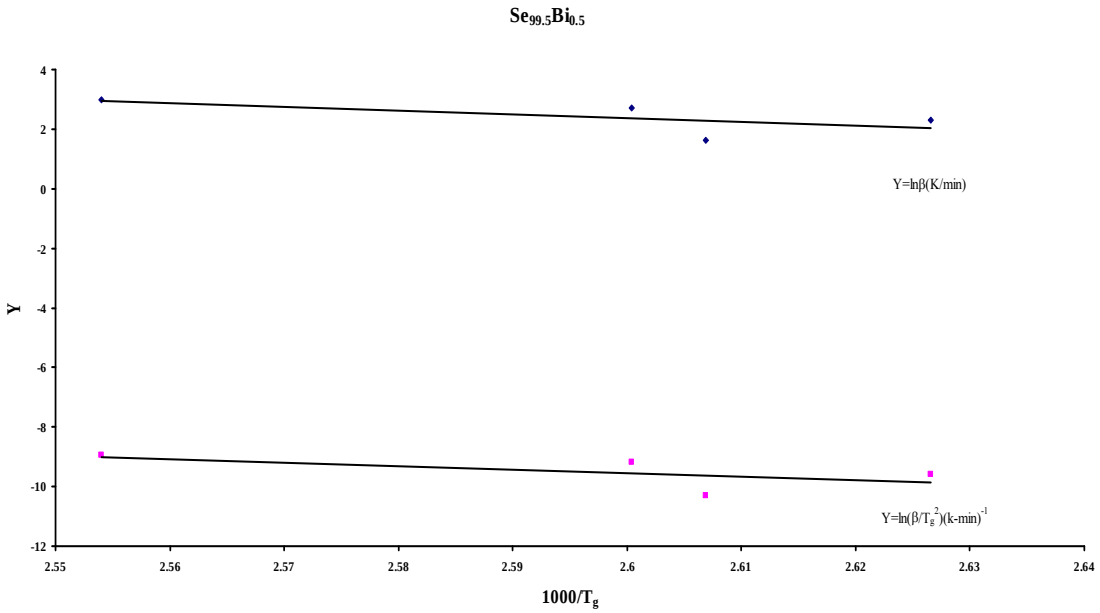

Fig 4 Plots of $ln(\beta/T_g^2)$, $ln(\beta)$ against $10^3 / T_g$ for $Se_{99.5}Bi_{0.5}$

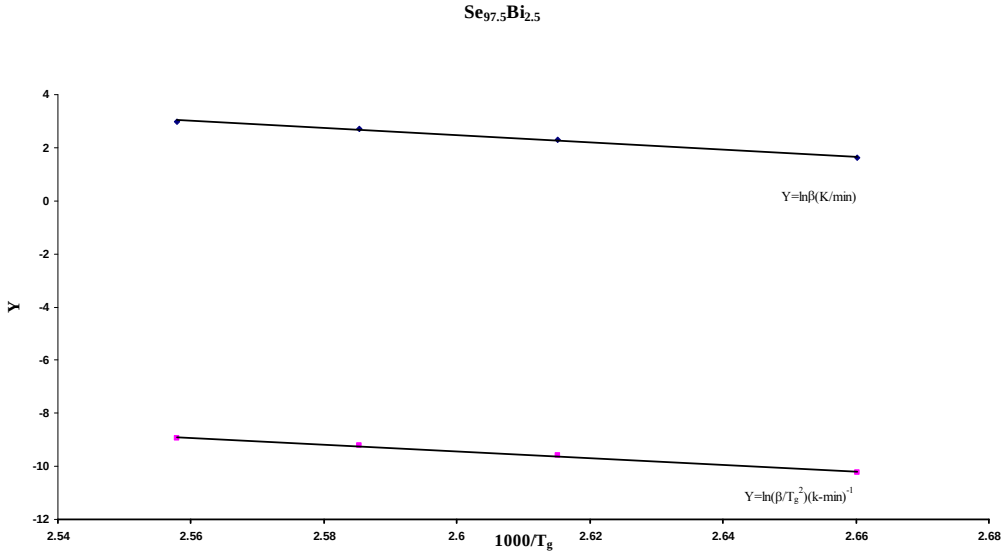

Fig 5 Plots of $ln(\beta/T_g^2)$, $ln(\beta)$ against $10^3 / T_g$ for $Se_{97.5}Bi_{2.5}$

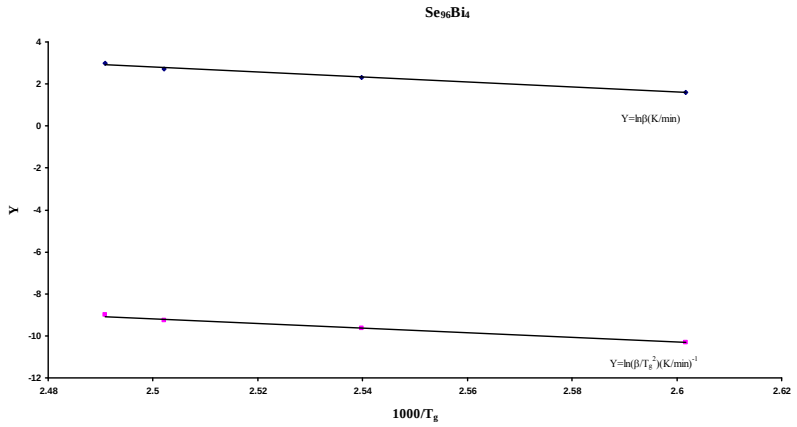

Fig 6 Plots of ln (β / T_g^2), ln (β) against $10^3/T_g$ for $Se_{96}Bi_4$

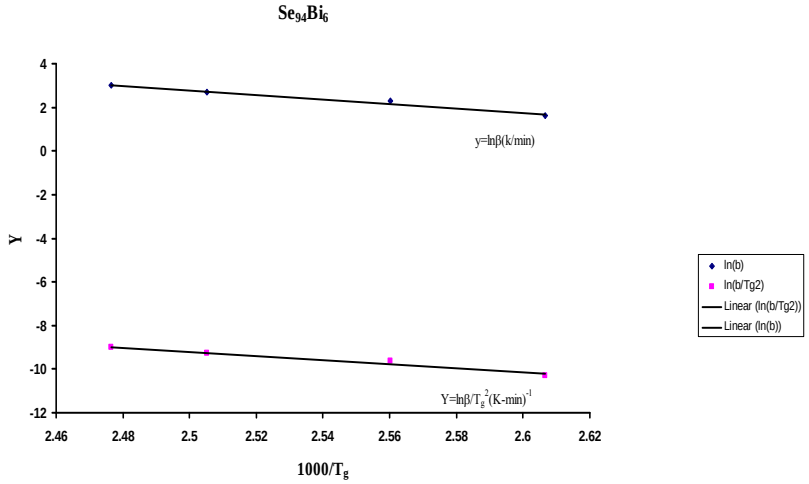

Fig 7 Plots of ln (β / T_g^2), ln (β) against $10^3 / T_g$ for $Se_{94}Bi_6$

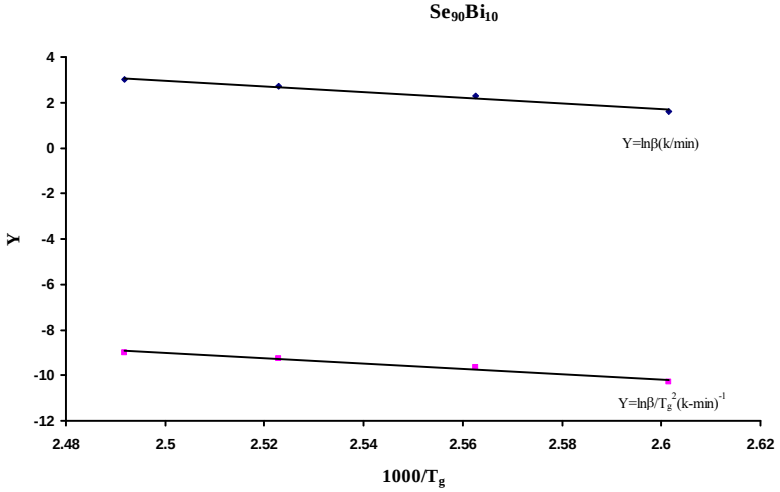

Fig 8 Plots of ln (β / T_g^2), ln(β) against $10^3 / T_g$ for $Se_{90}Bi_{10}$

3.2 Kissinger's relation

This method is most commonly used in analyzing crystallization data of DSC experiment. During the isothermal transformation, the extent of crystallization (α) of a certain material is represented by the Avrami's equation [42, 43]:

$$\alpha(t) = 1- \exp [-(Kt)^{n}] \quad (5)$$

where n is Avrami exponent (order parameter) which depends on the mechanism of growth and on the dimensionality of the crystal growth, K is defined as the reaction rate constant, which is usually assumed to have an Arrhenius temperature dependence.

$$K= K_{o} \exp (-E_c / RT) \quad (6)$$

Where E_c is the activation energy of crystallization and K_o is the frequency factor.
According to Kissinger Eq.(5) can be approximated as:

$$(d\alpha / dt) = n K^{n} t^{n-1}(1- \alpha). \quad (7)$$

Expressing t in terms of α from Eq. (5), the crystallization rate ($d\alpha/dt$) becomes

$$(d\alpha /dt) = An K (1-\alpha) \quad (8)$$

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 temperature T and the heating rate βcan be written in the form:

$$T = T_i+ \beta t \quad (9)$$

where T_i is the initial temperature
the derivative of K with respect to time can be obtained from Eq (6) and (9) as

$$\frac{dK}{dt} = \left(\frac{dK}{dT}\right).\left(\frac{dT}{dt}\right) = \left(\frac{\beta E_c}{RT^2}\right)K \quad (10)$$

Using Eq.(8)&(10), Kissinger showed that:

$$\ln (\beta/T_c^{2}) = \text{constant}- E_c /RT_c \quad (11)$$

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 [44-45] and hence the above equation takes the following form for its use in glass transition kinetics:

$$\ln (\beta/T_g^{2})= -E_g / R T_g + \text{constant} \quad (12)$$

The values of E_g are also evaluated from the slopes of plots of $\ln(\beta/T_g^{2})$ against $10^3/T_g$ for various glassy systems using Kissinger's relation eq.(12). The plots of $\ln (\beta/T_g^{2})$ vs. $1000/T_g$ are also shown in Figs. 4 - 8 for glassy alloys of $Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6 and 10) . These values of E_g are also given in Table 3.

Table 3: Activation energy of glass transition E_g (eV)

Sample	Moynihan's relation	Kissinger's relation
$Se_{99.5}Bi_{0.5}$	1.07	1.00
$Se_{97.5}Bi_{2.5}$	1.18	1.11
$Se_{96}Bi_4$	1.03	0.96
$Se_{94}Bi_6$	0.89	0.82
$Se_{90}Bi_{10}$	1.07	1.01

It is clear from Table 3 that E_g values obtained from Kissinger's relation are in good agreement with the E_g values obtained using Moynihan's relation. This means that one can use either of the equations (4) & (12) to calculate the activation energy of glass transition. It is reported that [46-50] E_g is responsible for the molecular motion and rearrangement of the atom around T_g and the glass with lower E_g is the most stable.

It is evident from the table 3 that E_g varies with Bi concentration and show discontinuities at 2.5 and 6 at. %. Fig. 9 shows composition dependence of E_g in glassy $Se_{100-x}Bi_x$. Such types of discontinuities have been observed in chalcogenide glasses in various properties and have been related to structural and chemical stability at certain average co-ordination numbers at different compositions.

4.4 Thermal stability of glassy $Se_{100-x}Bi_x$

The thermal stability and glass forming tendency (GFT) play an important role in determining the utility of chalcogenide alloys as recording materials due to the fact that phase change optical recording and erasing techniques are based on the laser induced thermal amorphyzation and crystallization of chalcogenide glasses. The origin of the thermal stability and GFT is, therefore, a subject of great interest [51-62]. Recently, some work has been done in this area [52, 63].

The glass transition temperature T_g represents the strength or rigidity of the glass structure in chalcogenide glasses. Hence, T_g offers valuable information on the thermal stability of glassy state but T_g alone does not give any information about the GFT. However, it has been found that the difference of T_c and T_g is a strong indicator of both the thermal stability and GFT. The higher the values of (T_c-T_g), the greater is the GFT, because the higher the value of this difference, the more the delay in the nucleation process [64]

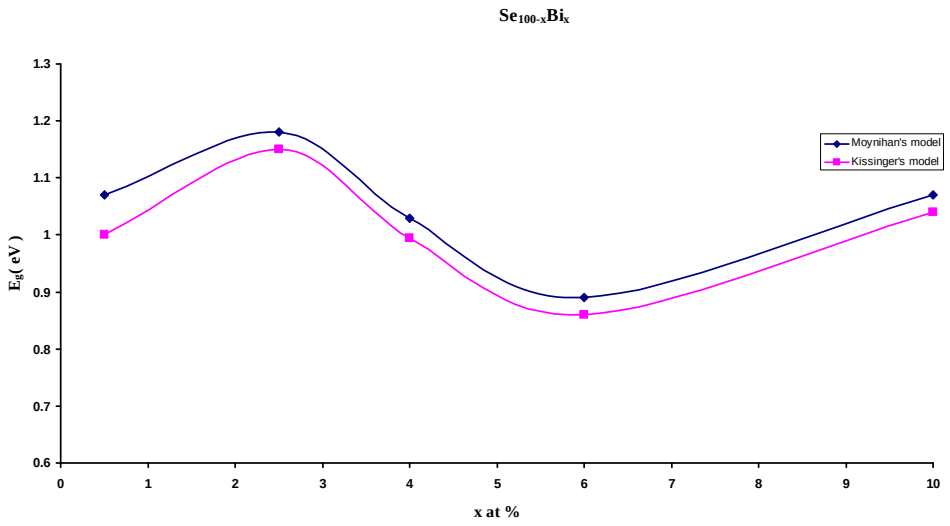

Fig. 9 E_g vs. atomic percentage of Bi in glassy $Se_{100-x}Bi_x$

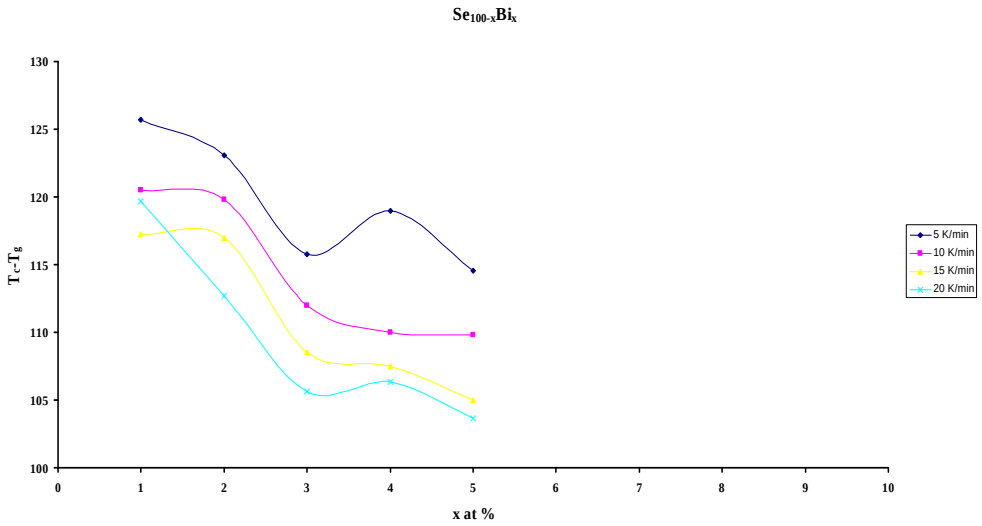

Fig. 10 $T_c - T_g$ vs. atomic percentage of bi in glassy $Se_{100-x}Bi_x$

Table 4 shows the crystallization temperature T_c (peak temperature of exothermic peak) at various heating rates for all the glasses studied. Values of difference of glass transition temperature (T_g) and crystallization temperature (T_c) for glassy alloys of $Se_{100-x}Bi_x$ are given in Table 5. Fig.10 shows the variation of (T_c- T_g) for different compositions at four heating rates. It is clear from this figure that T_c- T_g decreases with Bi concentration. This indicates that thermal stability is lower at higher concentration of Bi.

Table 4: Crystallization temperature T_c at different heating rates in glassy $Se_{100-x}Bi_x$

Heating rate	$Se_{99.5}Bi_{0.5}$	$Se_{97.5}Bi_{2.5}$	$Se_{96}Bi_4$	$Se_{94}Bi_6$	$Se_{90}Bi_{10}$
5^0c/min	499.30	498.99	500.12	502.64	498.97
10^0c/min	500.39	502.89	505.72	500.09	500.39
15^0c/min	501.06	503.06	508.16	506.66	501.36
20^0c/min	511.20	503.62	507.13	510.13	504.97

Table 5: $T_c - T_g$ for various glassy alloys of $Se_{100-x}Bi_x$

Heating Rate	$Se_{99.5}Bi_{0.5}$	$Se_{97.5}Bi_{2.5}$	$Se_{96}Bi_4$	$Se_{94}Bi_6$	$Se_{90}Bi_{10}$
5^0c/min	125.71	123.08	115.76	118.99	114.58
10^0c/min	120.50	119.83	112.00	110.00	109.83
15^0c/min	117.25	117.00	108.50	107.49	105.00
20^0c/min	119.66	112.67	105.66	106.33	103.67

The thermal stability parameter is also defined in the literature [59] by the following expression:

$$S = (T_c - T_o)(T_c - T_g) / T_g \quad (13)$$

Here T_o represents the on set crystallization temperature, i.e., the temperature where crystallization peak starts.

Thermal stability parameter reflects the resistance to divitrification after formation of the glass. In eq. (13), the term (T_c- T_o) is related to the rate of divitrification transformation of the

glassy phases. On the other hand, the higher values of the term (T_c-T_g) delay the nucleation process. The values of 'S' are given in Table 6 for various glassy alloys at all the heating rates.

Table 6. 'S' values for various glassy alloys of $Se_{100-x}Bi_x$

Heating Rate	$Se_{99.5}Bi_{0.5}$	$Se_{97.5}Bi_{2.5}$	$Se_{96}Bi_4$	$Se_{94}Bi_6$	$Se_{90}Bi_0$
5^0c/min	1.81	2.37	1.99	2.56	2.41
10^0c/min	2.01	3.34	3.14	1.52	2.38
15^0c/min	1.99	3.16	3.33	2.75	2.32
20^0c/min	3.77	3.07	3.24	3.16	3.01

5 Conclusions

Calorimetric measurements have been performed in glassy a-$Se_{100-x}Bi_x$ (x = 0.5, 2.5, 4, 6 & 10) alloys. DSC scans of these alloys show only one endothermic and one exothermic peak at glass transition temperature T_g and crystallization temperature T_c respectively, which shows that these glasses are in single phase. The activation energy of glass transition E_g has been determined by using Moynihan's relation and Kissinger's relation. On comparison of the values of E_g obtained from these two relations, a good agreement has been found. The composition dependence of E_g values are similar for both the relations (Moynihan's relation and Kissinger's relation). Thus one can use any of the two relations for evaluation of E_g which varies with Bi concentration and show discontinuities at 2.5 and 6 at %. Thermal stability is found to be lower at higher concentration of Bismuth.

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