

Kinetic parameters of glass transition in glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys

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Glass transition kinetics have been studied in glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys under non-isothermal conditions using Differential Scanning Calorimetric (DSC) technique. The activation energy of glass transition (E_t) has been evaluated using the heating rate dependence of glass transition temperature (T_g). The specific heat (ΔC_p) of these alloys is also calculated and its temperature dependence has been discussed. The composition dependence of T_g and E_t shows a reversal at 2 at %. The results are explained in terms of dependence of fragility of these glasses on the average coordination number.

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1. Introduction

The intensive development of modern technologies 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 exhibit high resistivity values implying certain limitation in their application. It is worth then to add more than one component into selenium matrix in order to produce considerable changes in the properties of new complex glasses.

The properties of the Ge-Se system have been studied in detail and it has been established that physical properties in this system are highly composition dependent [7-12]. Chalcogenide glasses in Ge-Se system are interesting materials for infrared optics too. They have a large range of transparency and good mechanical properties such as hardness, adhesion, low internal stress and water resistance. The addition of third element in tetrahedral structure of Ge-Se glass make the glass interesting material and new, promising properties of the material are expected. With this point of view, we have started a study of the Ge-Se system with some metallic additives.

In Se-Ge glasses, the conduction changes from p-type to n-type at certain compositions as a function of Bi [13, 14]. Since then, electrical and photo-electrical properties of Se-Ge-Bi glassy system have been studied by various workers [15-20] in detail but thermal properties, especially glass transition kinetics have not been studied in detail. Apart from the technical importance, the knowledge of glass transition process is very useful for a better understanding of the short-range order in these materials. The present paper reports on glass transition kinetics of glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys.

2. Experimental

Glassy alloys $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed out using an electronic balance (LIBROR, AEG-120) with a sensitivity of 10^{-4} gm. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). Each ampoule was kept inside the furnace at a temperature of 1000 °C (where the temperature was raised at a rate of 3-4 °C /min). During heating, all the ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were attached in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping rapidly into ice-cooled water. The ingots were then taken out by breaking the quartz ampoules. The size of the samples was ~ 3 cm in length and ~ 8 mm in diameter. 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.

3. Results and discussion

Fig. 1 shows the typical DSC scans for $(\text{Se}_{80}\text{Ge}_{20})_{98}\text{Bi}_2$ at different heating rates. It is clear from these figures that well defined peaks are observed at glass transition temperatures (T_g). We have taken the peak temperature of endothermic peaks as glass transition temperature for each alloy. Similar DSC scans were obtained for the other two chalcogenide glasses.

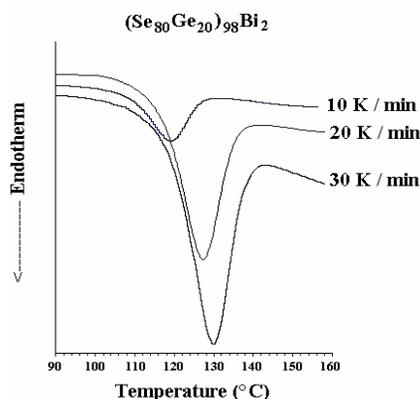


Fig. 1. DSC scans for glassy $(\text{Se}_{80}\text{Ge}_{20})_{98}\text{Bi}_2$ alloys at different heating rates.

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 rate β [21 - 25]. 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 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 the Eqn (1) is related to the cooling rate of the melt: the lower the cooling rate of melt, the lower the value of B. The physical significance of B seems to be related with the response of the configurational changes within the glass transformation region. The plot of T_g vs $\log \beta$ for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys is shown in Fig. 2. The values of A and B for different alloys are given in Table 1. The values of B for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys have been found to be different, indicating that these glassy alloys undergo different structural changes. The results shown in Table 1 indicate the validity of this relationship for the present glassy alloys.

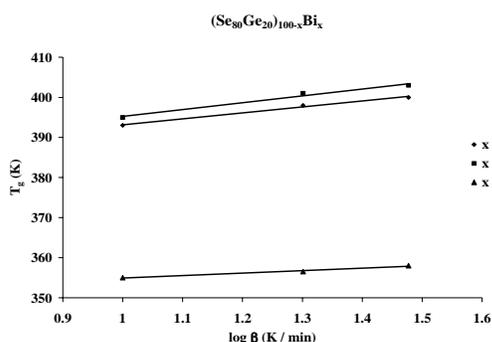


Fig. 2. Plots of T_g vs $\log(\beta)$ for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

Table 1. Kinetic parameters 'A' and 'B' for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

Sample	A (K)	B (min)
$\text{Se}_{80}\text{Ge}_{20}$	378.1	17.1
$(\text{Se}_{80}\text{Ge}_{20})_{98}\text{Bi}_2$	378.3	14.9
$(\text{Se}_{80}\text{Ge}_{20})_{96}\text{Bi}_4$	348.8	6.1

3.2 Evaluation of activation energy of glass transition (E_t)

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 activation energy of glass transition (E_t). The evaluation of E_t using the theory of structural relaxation as developed by Moynihan and other workers [26 - 28] from the heating rate dependence of glass transition temperature is widely used in the literature.

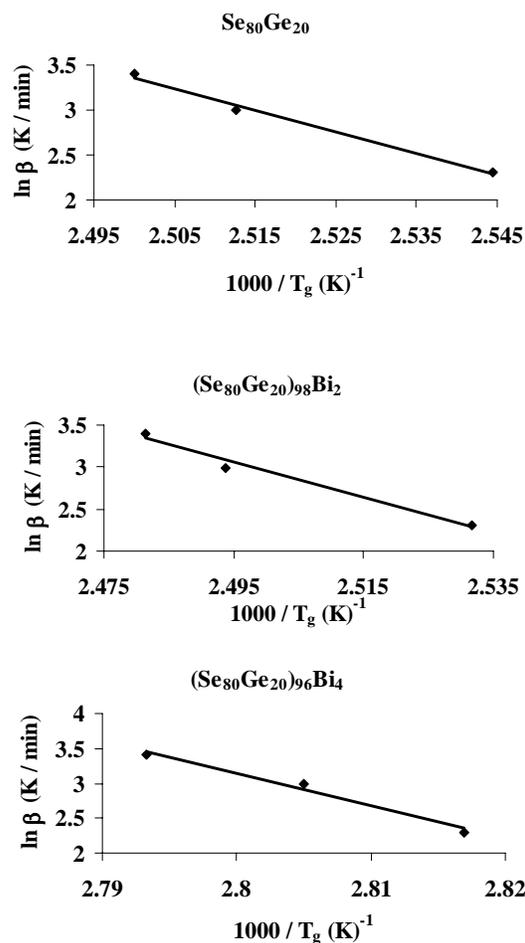


Fig. 3. Plots of $\ln(\beta)$ against $10^3/T_g$ for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

As analogous to crystallization process, the glass transition phenomenon is also a phase transformation process in chalcogenide glasses, the Kissinger's relation [29], which is originally derived for the determination of

activation energy of crystallization, can be also used for evaluation of activation energy of glass transition process in chalcogenide glasses [30].

Using Moynihan's relation [26-28]

$$(\ln \beta) = -E_t / R T_g + \text{constant}, \quad (2)$$

the plots of $\ln \beta$ against $10^3 / T_g$ were plotted for various glassy alloys. Such plots for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys are shown in Fig. 3. 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. (2).

The values of E_t are also evaluated using Kissinger's relation [29]

$$\ln(\beta / T_g^2) = -E_t / R T_g + \text{constant} \quad (3)$$

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 Fig. 4 for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ ($x = 0, 2, 4$) alloys. These values are also given in Table 2.

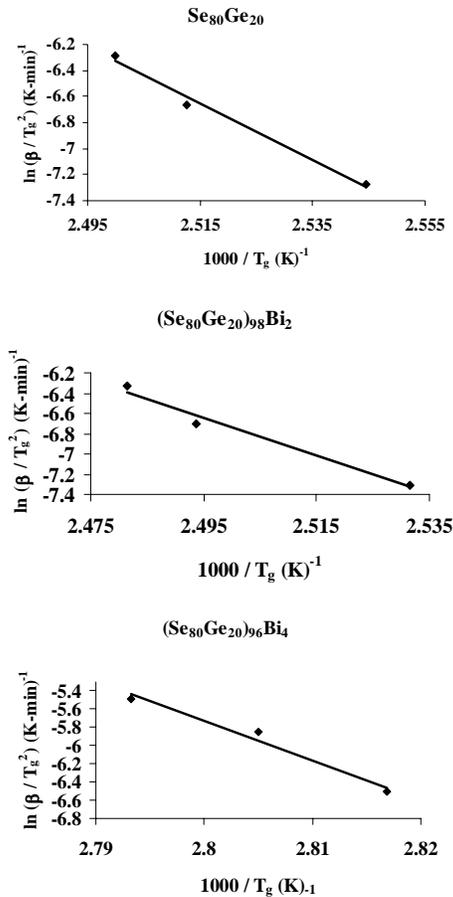


Fig. 4. Plots of $\ln(\beta / T_g^2)$ against $10^3 / T_g$ for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

It is 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 any of the two equations (2) and (3) to calculate the activation energy of glass transition [30].

Table 2. Activation energy of glass transition process in glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

Sample	E_t (eV)	
	Moynihan's method	Kissinger's method
$\text{Se}_{80}\text{Ge}_{20}$	2.077	1.857
$(\text{Se}_{80}\text{Ge}_{20})_{98}\text{Bi}_2$	1.813	1.595
$(\text{Se}_{80}\text{Ge}_{20})_{96}\text{Bi}_4$	4.015	3.753

3.3 Specific heat evaluation

Specific heat is very sensitive to the way in which atoms or molecules are dynamically bound in a solid [31]. Thus measurement of such parameters as the heat capacity is an effective way of characterizing glassy substances. An abrupt change in specific heat at the glass transition is characteristic of the all chalcogenide glasses. The parameter detects sensitively the change in the microstructure of the glass which can be seen by the jump of the specific heat close to the Dulong and the Petit value of $C_p = 3R$. Some attempts [32 - 34] have been made to measure the specific heat of chalcogenide glasses.

When a material is subjected to a linear temperature programme, the heat flow rate into the sample is proportional to its instantaneous specific heat. Since the scanning rate of the DSC analyzer is linear and the instrument measures heat flow directly, the specific heat of a sample material is easily calculated.

The variation of C_p as a function of temperature at the heating rate of 30 K/min for glassy $(\text{Se}_{80}\text{Ge}_{20})_{98}\text{Bi}_2$ alloy is shown in Fig. 5. Similar plots are obtained for the other alloys. It is clear from this figure that below glass transition temperature, C_p is weakly temperature dependent. However, near to the glass transition temperature, C_p increases drastically with the increase of temperature and shows maxima at the glass transition temperature. After glass transition temperature, C_p attains a stable value, which is slightly higher compared to C_p below the glass transition temperature. The sudden jump in C_p value for each alloy at glass transition can be attributed [35] to the anharmonic contribution to the specific heat. The overshoot in the value of C_p at the upper end of the " C_p jump" at the glass transition is due to the relaxation effects. The time scale [36] for structural relaxation is highly dependent both on temperature and on the instantaneous structure itself. The observed peak in C_p at T_g may be due to the fact that the structural relaxation times at this temperature becomes of the same order as the time scale of the experiment.

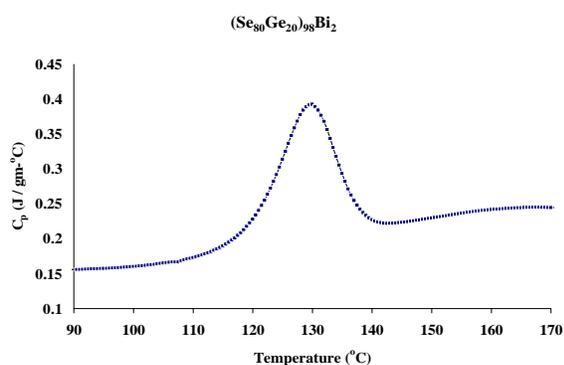


Fig. 5. Temperature dependence of C_p for glassy $(Se_{80}Ge_{20})_{98}Bi_2$ alloy.

The difference of specific heat values (ΔC_p) between C_p after glass transition (i.e., the equilibrium liquid specific heat C_{pe}) and before glass transition (i.e., glass specific heat C_{pg}) has been calculated for each glassy alloy and the values of C_{pe} , C_{pg} and ΔC_p are given in Table 3.

Table 3. Values of C_{pg} , C_{pe} and ΔC_p of glassy $(Se_{80}Ge_{20})_{100-x}Bi_x$ alloys.

Sample	C_{pg} (J/gm °C)	C_{pe} (J/gm °C)	ΔC_p (J/gm °C)
$Se_{80}Ge_{20}$	0.034	0.102	0.068
$(Se_{80}Ge_{20})_{98}Bi_2$	0.190	0.227	0.037
$(Se_{80}Ge_{20})_{96}Bi_4$	0.139	0.144	0.005

3.4 Composition dependence of glass transition temperature (T_g) and activation energy of glass transition (E_t)

The composition dependence of glass transition temperature (T_g) activation energy of glass transition (E_t) are shown in Figs. 6 and 7. From these figures, it is clear that a reversal in the trend is observed at 2 at % of Bi.

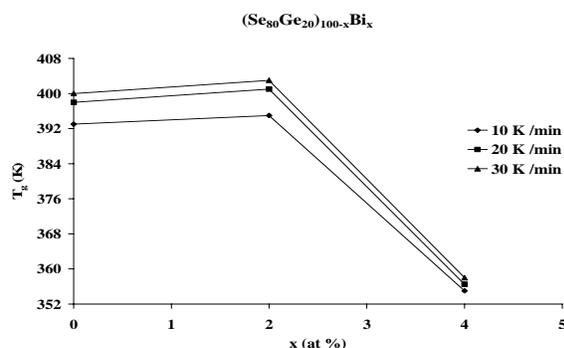


Fig. 6. Composition dependence of T_g for glassy $(Se_{80}Ge_{20})_{100-x}Bi_x$ alloys.

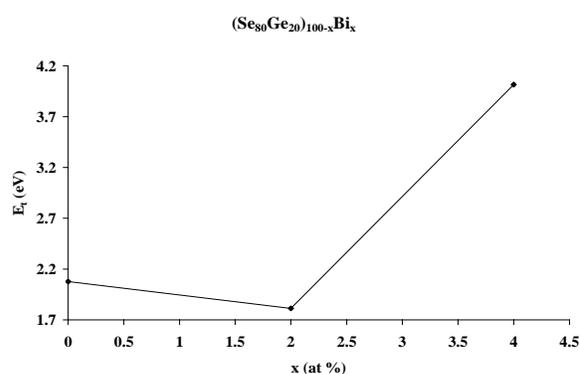


Fig. 7. Composition dependence of E_t for glassy $(Se_{80}Ge_{20})_{100-x}Bi_x$ alloys.

This peculiarity which appears at nearly $\langle z \rangle = 2.43$, can be explained in terms of a parameter, named the fragility (F), which characterizes and quantifies the anomalous non-Arrhenius transport behaviour of glassy materials as they approach the ergodicity-breaking glass transition [37, 38]. Fragile glasses are usually substances with non-directional interatomic /intermolecular bonds. Strong glasses are those which show resistance to structural degradation in the liquid state and usually associated with small specific heat changes.

The fragility is calculated using the following relation [39]:

$$F = E_t / (T_g \ln 10) \quad (4)$$

The values of F for different glassy alloys are given in Table 4. Fig. 8 shows the variation of F with $\langle z \rangle$. From this figure, it is clear that both F and E_t decrease with $\langle z \rangle$, reaching a minimum value at $\langle z \rangle = 2.43$. They then increase with $\langle z \rangle$. In fact, the minimum value of F at a particular value of $\langle z \rangle$ can be related to the fact that the two-dimensional layered structure is fully achieved at this composition. This is confirmed from the variation of T_g and E_t with $\langle z \rangle$ shown in Figs. 6 and 7. The increase of F after $\langle z \rangle = 2.43$ means that the glasses become more fragile and their tendency to structural arrangement increases with increasing non-directional interatomic bonds. This confirms that the glass structure beyond this value of $\langle z \rangle$ transform to three-dimensional cross-linked network. Similar results have been recently, reported by our group in Se-Ge-In system [40].

Table 4. Fragility index for glassy $(Se_{80}Ge_{20})_{100-x}Bi_x$ alloys.

Sample	F		
	10 K/min	20 K/min	30 K/min
$Se_{80}Ge_{20}$	221.1	218.4	217.31
$(Se_{80}Ge_{20})_{98}Bi_2$	192.1	189.2	188.3
$(Se_{80}Ge_{20})_{96}Bi_4$	473.3	471.3	469.3

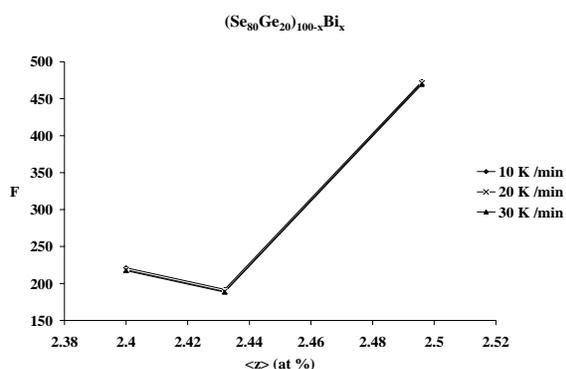


Fig. 8. Plots of fragility index F vs $\langle z \rangle$ for glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys.

4. Conclusions

Kinetic parameters (T_g and E_t) of the glass transition kinetics in glassy $(\text{Se}_{80}\text{Ge}_{20})_{100-x}\text{Bi}_x$ alloys have been determined using DSC technique. The activation energy of glass transition (E_t) has been evaluated using the Kissinger's relation and the relation suggested by Moynihan. The results show that E_t values obtained from Kissinger's relation are in good agreement with the E_t values which were obtained using Moynihan's relation. The results show that T_g and E_t have same type of composition dependence and a reversal in the trend at a particular composition (2 at % of Bi) is observed. These results can be explained on the basis of the structural phase transition of the present glasses from two-dimensional layered to three-dimensional cross-linked network, which is clear from the dependence of fragility of these glasses on average coordination number.

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