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

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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 \( \beta \) has been reported. The value of (T_c-T_g) and stability parameter S have been calculated for each glassy alloy.

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1. Introduction

The intensive development 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 exhibit 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...
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 ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5cm and internal diameter ~ 8 mm). The ampoules containing material were heated to $800^\circ$C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 $^\circ$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 $^\circ$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.
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 $\beta$ [23-27]. The empirical relation used to analyze the dependence of $T_g$ on $\beta$ is of the form:
\[ T_g = A + B \log \beta \]  

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. \( \log \beta \) 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>
<thead>
<tr>
<th>Sample</th>
<th>A(K)</th>
<th>B(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(<em>{99.5})Bi(</em>{0.5})</td>
<td>373.38</td>
<td>4.88</td>
</tr>
<tr>
<td>Se(<em>{97.5})Bi(</em>{2.5})</td>
<td>358.39</td>
<td>10.66</td>
</tr>
<tr>
<td>Se(<em>{96})Bi(</em>{4})</td>
<td>364.14</td>
<td>12.76</td>
</tr>
<tr>
<td>Se(<em>{94})Bi(</em>{6})</td>
<td>358.96</td>
<td>14.70</td>
</tr>
<tr>
<td>Se(<em>{90})Bi(</em>{10})</td>
<td>364.12</td>
<td>12.04</td>
</tr>
</tbody>
</table>

Table 2: Glass transition temperature \( T_g \) at different heating rates in glassy Se\(_{100-x}\)Bi\(_x\)

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Se(<em>{99.5})Bi(</em>{0.5})</th>
<th>Se(<em>{97.5})Bi(</em>{2.5})</th>
<th>Se(<em>{96})Bi(</em>{4})</th>
<th>Se(<em>{94})Bi(</em>{6})</th>
<th>Se(<em>{90})Bi(</em>{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 K/min</td>
<td>373.59</td>
<td>375.91</td>
<td>384.36</td>
<td>383.65</td>
<td>384.39</td>
</tr>
<tr>
<td>10 K/min</td>
<td>379.89</td>
<td>383.06</td>
<td>393.72</td>
<td>390.09</td>
<td>390.56</td>
</tr>
<tr>
<td>15 K/min</td>
<td>383.81</td>
<td>386.81</td>
<td>399.66</td>
<td>399.16</td>
<td>396.36</td>
</tr>
<tr>
<td>20 K/min</td>
<td>391.54</td>
<td>390.95</td>
<td>401.47</td>
<td>403.80</td>
<td>401.30</td>
</tr>
</tbody>
</table>

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:

![Graph showing the variation of Tg with heating rate for Se94Bi6](image)

**Fig.3 Variation of Tg with heating rate for Se94Bi6**

### 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]

$$\left( \frac{\partial H}{\partial t} \right)_T = \frac{\tau}{\tau_0} \exp \left( \frac{E_g}{R T} \right) \exp \left[ - C (H - H_c) \right]$$

(2)

where $\tau$ is a temperature dependent structural relaxation time and is given by the following relation:

$$\tau = \tau_0 \exp \left( \frac{E_g}{R T} \right) \exp \left[ - C (H - H_c) \right]$$

(3)

Where $\tau_0$ 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:

$$\frac{d \ln \beta}{d (1/T_g)} = - \frac{E_g}{R}$$

(4)

From equation (4), the ln $\beta$ 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 ln$\beta$ 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 6 Plots of $\ln\left(\frac{\beta}{T_g^2}\right)$, $\ln(\beta)$ against $10^3/T_g$ for Se$_{96}$Bi$_4$

Fig 7 Plots of $\ln\left(\frac{\beta}{T_g^2}\right)$, $\ln(\beta)$ against $10^3 / T_g$ for Se$_{94}$Bi$_6$

Fig 8 Plots of $\ln\left(\frac{\beta}{T_g^2}\right)$, $\ln(\beta)$ 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 ($\alpha$) of a certain material is represented by the Avrami’s equation [42, 43]:

$$\alpha(t) = 1 - \exp \left[-(Kt)^n\right]$$  \hspace{1cm} (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.

$$K = K_o \exp \left(-\frac{E_c}{RT}\right)$$  \hspace{1cm} (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:

$$\left(\frac{d\alpha}{dt}\right) = nK^n(1-\alpha).$$  \hspace{1cm} (7)

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

$$\left(\frac{d\alpha}{dt}\right) = A\left(1-\alpha\right)$$  \hspace{1cm} (8)

where

$$A = \left[-\ln \left(1-\alpha\right)\right]^\frac{(n-1)}{n}$$

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 $\beta$ can be written in the form:

$$T = T_i + \beta t$$  \hspace{1cm} (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

$$\frac{dK}{dt} = \left(\frac{dK}{dT}\right) \left(\frac{dT}{dt}\right) = \left(\frac{\beta E_c}{RT^2}\right)K$$  \hspace{1cm} (10)

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

$$\ln \left(\frac{\beta}{T_c^2}\right) = \text{constant} - \frac{E_c}{RT_c}$$  \hspace{1cm} (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:

$$\ln \left(\frac{\beta}{T_g^2}\right) = -\frac{E_g}{R T_g} + \text{constant}$$  \hspace{1cm} (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)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moynihan’s relation</th>
<th>Kissinger’s relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}<em>{99.5}\text{Bi}</em>{0.5}$</td>
<td>1.07</td>
<td>1.00</td>
</tr>
<tr>
<td>$\text{Se}<em>{97.5}\text{Bi}</em>{2.5}$</td>
<td>1.18</td>
<td>1.11</td>
</tr>
<tr>
<td>$\text{Se}<em>{96}\text{Bi}</em>{4}$</td>
<td>1.03</td>
<td>0.96</td>
</tr>
<tr>
<td>$\text{Se}<em>{94}\text{Bi}</em>{6}$</td>
<td>0.89</td>
<td>0.82</td>
</tr>
<tr>
<td>$\text{Se}<em>{90}\text{Bi}</em>{10}$</td>
<td>1.07</td>
<td>1.01</td>
</tr>
</tbody>
</table>

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 $\text{Se}_{100-x}\text{Bi}_x$. 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 $\text{Se}_{100-x}\text{Bi}_x$

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]

$$\text{Se}_{100-x}\text{Bi}_x$$

![Fig. 9 $E_g$ vs. atomic percentage of Bi in glassy $\text{Se}_{100-x}\text{Bi}_x$](image)
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 $\text{Se}_{100-x}\text{Bi}_x$ 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.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Heating rate & $\text{Se}_{99.5}\text{Bi}_{0.5}$ & $\text{Se}_{97.5}\text{Bi}_{2.5}$ & $\text{Se}_{96}\text{Bi}_{4}$ & $\text{Se}_{94}\text{Bi}_{6}$ & $\text{Se}_{90}\text{Bi}_{10}$ \\
\hline
5$^\circ$C/min & 499.30 & 498.99 & 500.12 & 502.64 & 498.97 \\
10$^\circ$C/min & 500.39 & 502.89 & 505.72 & 500.09 & 500.39 \\
15$^\circ$C/min & 501.06 & 503.06 & 508.16 & 506.66 & 501.36 \\
20$^\circ$C/min & 511.20 & 503.62 & 507.13 & 510.13 & 504.97 \\
\hline
\end{tabular}
\caption{Crystallization temperature $T_c$ at different heating rates in glassy $\text{Se}_{100-x}\text{Bi}_x$}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Heating Rate & $\text{Se}_{99.5}\text{Bi}_{0.5}$ & $\text{Se}_{97.5}\text{Bi}_{2.5}$ & $\text{Se}_{96}\text{Bi}_{4}$ & $\text{Se}_{94}\text{Bi}_{6}$ & $\text{Se}_{90}\text{Bi}_{10}$ \\
\hline
5$^\circ$C/min & 125.71 & 123.08 & 115.76 & 118.99 & 114.58 \\
10$^\circ$C/min & 120.50 & 119.83 & 112.00 & 110.00 & 109.83 \\
15$^\circ$C/min & 117.25 & 117.00 & 108.50 & 107.49 & 105.00 \\
20$^\circ$C/min & 119.66 & 112.67 & 105.66 & 106.33 & 103.67 \\
\hline
\end{tabular}
\caption{$T_c - T_g$ for various glassy alloys of $\text{Se}_{100-x}\text{Bi}_x$}
\end{table}

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

\[ S = \frac{(T_c - T_o) (T_c - T_g)}{T_g} \]  \hspace{1cm} (13)

Here $T_o$ represents the onset 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>
<thead>
<tr>
<th>Heating Rate</th>
<th>Se(<em>{99.5})Bi(</em>{0.5})</th>
<th>Se(<em>{97.5})Bi(</em>{2.5})</th>
<th>Se(<em>{96})Bi(</em>{4})</th>
<th>Se(<em>{94})Bi(</em>{6})</th>
<th>Se(<em>{90})Bi(</em>{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°c/min</td>
<td>1.81</td>
<td>2.37</td>
<td>1.99</td>
<td>2.56</td>
<td>2.41</td>
</tr>
<tr>
<td>10°c/min</td>
<td>2.01</td>
<td>3.34</td>
<td>3.14</td>
<td>1.52</td>
<td>2.38</td>
</tr>
<tr>
<td>15°c/min</td>
<td>1.99</td>
<td>3.16</td>
<td>3.33</td>
<td>2.75</td>
<td>2.32</td>
</tr>
<tr>
<td>20°c/min</td>
<td>3.77</td>
<td>3.07</td>
<td>3.24</td>
<td>3.16</td>
<td>3.01</td>
</tr>
</tbody>
</table>

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.

References