Kinetic Study of Non-Isothermal Crystallization in \(\text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x\) (\(x = 0, 2, 4, 6\)) Chalcogenide Glasses

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Abstract

Crystallization and glass transition kinetics of \(\text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x\) (\(x = 0, 2, 4, 6\)) chalcogenide glasses prepared by conventional melt-quenching technique were studied under non-isothermal condition using a differential scanning Calorimeter (DSC) measurement at different heating rates 5, 7, 10 and 12°C/min. The glass transition temperatures \(T_g\), the crystallization temperatures \(T_c\) and the peak temperatures of crystallization \(T_p\) were found to be dependent on the compositions and the heating rates. From the dependence on the heating rates of \(T_g\) and \(T_p\), the activation energy for glass transition, \(E_g\), and the activation energy for crystallization, \(E_c\), are calculated and their composition dependence is discussed. The activation energy of glass transition \(E_g\), Avrami index \(n\), dimensionality of growth \(m\) and activation energy of crystallization \(E_c\) have been determined from different models.

Keywords

Crystallization Kinetics, Chalcogenide Glasses, Crystallization Temperature, Activation Energy, Differential Scanning Calorimetry

1. Introduction

Chalcogenide glasses are of wide-ranging importance in a variety of technological. They are based on chalcogen elements S, Se and Te. These glasses are formed by the addition of other elements such as Ga, In, Si, Ge, Sn, As, Sb, Bi, Ag, Cd, Zn. Many researchers have studied the structure, electrical properties, photoconductivity, glass formation and crystallization kinetics of the glassy system [1]-[7]. The current interest in chalcogenide materials centers on X-ray imaging [8], xerography [9], optical recording [10], memory switching [11] and electrographic
applications such as photoreceptors in photocopying and laser printing [12]-[14]. The binary Se-Zn alloys have more advantages due to their wide band gap; they are an example of potential applications in optoelectronic devices like blue light emitting diodes and blue diode lasers [15] and white Light Emitting Diodes (LEDs) and infrared lenses [16]. The proprieties of binary SeZn can be modified by adding a third element. The work presented in this paper has been done with the purpose of studying the effect of Sb on various thermal parameters in binary Se-Zn system, the crystallization kinetics and the evaluation of the crystallization parameters of Se_{90-x}Zn_{10}Sbx (x = 0, 2, 4, 6) glassy alloy under non-isothermal conditions. Using the differential scanning calorimetry (DSC) measurement, the kinetic parameters such as activation energy of glass transition $E_g$, Avrami index $n$, dimensional growth $m$ and activation energy of crystallization $E_c$ have been determined from different models.

2. Experimental

Bulk sample of the Se_{90-x}Zn_{10}Sbx (x = 0, 2, 4, 6) were prepared by the melt quenching technique. High purity materials (99.999%) were weighted according to their atomic percentages and were sealed in quartz ampoules under the vacuum of $10^{-5}$ Torr. The sealed ampoules are kept inside the furnace where the temperature was raised to 800°C for 10 h. The ampoule was frequently rocked to ensure the homogeneity of the melt. The quenching was done in ice water to obtain the composition in the glass state.

The amorphocity of the samples was confirmed by the absence of any sharp peak in the X-ray diffraction pattern, Figure 1 shows the X-ray diffraction pattern of Se_{86}Zn_{10}Sb_{4} glass at room temperature.

3. Results and Discussions

DSC thermograms of glassy alloys Se_{90-x}Zn_{10}Sbx (x = 0, 2, 4, 6) were recorded at different heating rate 10°C/min is shown in Figure 2. The endothermic peak of glass transition, exothermic peak of crystallization and endothermic pick present the melting of sample have been clearly observed in the Figure 2. The values of the glass transition temperature $T_g$ and the crystallization temperature $T_c$ for each sample at different heating rates 5, 7, 10, 12°C/min are given in Table 1. From the Table 1 it is clear that glass transition temperature $T_g$ and crystallization temperature $T_c$ both shift towards higher temperatures as the heating rate increases from 5 to 12°C/min. is found that the glass transition temperature $T_g$ decreases as Sb concentration increases and the crystallization temperature $T_c$ increases with increasing Sb.

Glass transition region

Two approaches have been used to study the dependence of $T_g$ on the heating rate $\alpha$ the first approach is the empirical relation suggested by Lasocka [17]

$$T_g = A + B \ln \alpha$$

(1)

where $A$ and $B$ are constants for a given glass composition. The value of $A$ indicates the glass transition temperature for the heating rate of 1°C/min, while $B$ is proportional to the time taken by the system to reduce its glass transition temperature, when its heating rate is lowered from 10 to 1 K/min [18]. Figure 3 depicts the

![Figure 1. XRD pattern of Se_{86}Zn_{10}Sb_{4} glassy alloy.](image)
Figure 2. DSC thermograms of Se$_{90-x}$Zn$_{10}$Sb$_x$ (x = 0, 2, 4, 6) glassy alloys at heating rate of 10°C/min.

Table 1. The values of glass transition temperature $T_g$ and crystallization temperature $T_c$ at different heating rates 5, 7, 10, 12°C/min for Se$_{90-x}$Zn$_{10}$Sb$_x$ (x = 0, 2, 4, 6) glassy alloys.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Se$<em>{90}$Zn$</em>{10}$</th>
<th>Se$<em>{89}$Zn$</em>{10}$Sb$_2$</th>
<th>Se$<em>{88}$Zn$</em>{10}$Sb$_4$</th>
<th>Se$<em>{86}$Zn$</em>{10}$Sb$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (K)</td>
<td>$T_c$ (K)</td>
<td>$T_g$ (K)</td>
<td>$T_c$ (K)</td>
</tr>
<tr>
<td>05</td>
<td>325</td>
<td>374</td>
<td>323</td>
<td>388</td>
</tr>
<tr>
<td>07</td>
<td>328</td>
<td>377</td>
<td>324</td>
<td>397</td>
</tr>
<tr>
<td>10</td>
<td>331</td>
<td>381</td>
<td>329</td>
<td>401</td>
</tr>
<tr>
<td>12</td>
<td>332</td>
<td>385</td>
<td>331</td>
<td>405</td>
</tr>
</tbody>
</table>

variation of the glass transition temperature $T_g$ with ln$\alpha$ for the investigated Se$_{90-x}$Zn$_{10}$Sb$_x$ (x = 0, 2, 4, 6) glassy systems. From Figure 3 the value of $A$ and $B$ can be obtained from the slope of straight line of the plot $T_g$ versus ln$\alpha$.

The calculated values of $A$ and $B$ for the different compositions are listed in Table 1.

The second approach is the evaluation of the activation energy for the glass transition $E_g$ using Kissinger equation [19]

$$\ln\left(\frac{\alpha}{T_{gp}^2}\right) = -\frac{E_g}{RT_{gp}} + \text{constant}$$  \hspace{1cm} (2)

where $\alpha$ is the heating rate, $T_{gp}$ is the peak glass transition temperature, $E_g$ is the activation energy for the glass transition and $R$ is the gas constant. Figure 4 shows $\ln(\alpha/T_{gp}^2)$ versus $1000/T_{gp}$ plots for different composition
Se$_{90-x}$Zn$_{10}$Sbx (x = 0, 2, 4, 6) glassy systems.

The values of activation energy of glass transition $E_g$ calculated from the slope of the straight line of the plots between ln($\alpha/T_{gp}^2$) and 1000/$T_{gp}$ are listed in Table 2. From Table 2 the value of $E_g$ decreases with increasing Sb.

![Figure 3. Plots of $T_g$ versus ln$\alpha$ for Se$_{90-x}$Zn$_{10}$Sbx (x = 0, 2, 4, 6) glasses.](image)

![Figure 4. Plots of ln($\alpha/T_{gp}^2$) versus $T_g$ for Se$_{90-x}$Zn$_{10}$Sbx (x = 0, 2, 4, 6) glasses.](image)

<table>
<thead>
<tr>
<th>Composition</th>
<th>$A$ (K)</th>
<th>$B$ (min)</th>
<th>$E_g$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{90}$Zn$</em>{10}$</td>
<td>312.30 ± 0.79</td>
<td>8.01 ± 0.37</td>
<td>73.92 ± 0.85</td>
</tr>
<tr>
<td>Se$<em>{88}$Zn$</em>{10}$Sb$_2$</td>
<td>308.84 ± 1.67</td>
<td>9.02 ± 0.79</td>
<td>70.65 ± 1.03</td>
</tr>
<tr>
<td>Se$<em>{86}$Zn$</em>{10}$Sb$_4$</td>
<td>307.33 ± 1.90</td>
<td>8.70 ± 0.90</td>
<td>68.98 ± 0.74</td>
</tr>
<tr>
<td>Se$<em>{84}$Zn$</em>{10}$Sb$_6$</td>
<td>303.92 ± 2.94</td>
<td>9.74 ± 1.39</td>
<td>66.44 ± 0.68</td>
</tr>
</tbody>
</table>

Table 2. The values of $A$, $B$ and Activation energy of glass transition $E_g$ for Se$_{90-x}$Zn$_{10}$Sbx (x = 0, 2, 4, 6).
Crystallization region

The crystallization fraction $x$, can be expressed as a function of time according to the Johnson–Mehl–Avrami equation [20]-[22]:

$$x(t) = 1 - \exp\left[-\left(kt^+\right)^n\right]$$

(3)

where $n$ is the Avrami exponent which depends on the mechanism of the growth and dimensionality of crystal growth and $K$ is defined as the reaction rate constant and is given by:

$$K = K_0 \exp\left(-E_c/kT\right)$$

(4)

where $E_c$ is the activation on energy of crystallization, $k$ is the Boltzmann constant, $T$ is the isothermal temperature and $K_0$ is the frequency factor. The activation energy of crystallization $E_c$ for Se$_{90-x}$Zn$_{10}$Sbx ($x = 0, 2, 4, 6$) glassy system have been determined using Matusita, Kissinger and Ozawa methods.

3.1. Matusita Model

In the non-isothermal method, the crystallized fraction $x$, precipitated in a glass heated at constant rate $\alpha$, is related to the activation energy for crystallization $E_c$ through the following expression [23] [24]

$$\ln\left[-\ln(1-x)\right] = -n \ln \alpha - 1.052 \frac{mE_c}{RT} + \text{constant}$$

(5)

where $n$ is the Avrami index depending on the nucleation process, $m$ is an integer which depends on the dimensionality of the crystal. Here $n = m + 1$ is taken for a quenched glass containing no nuclei and $n = m$ for a pre-heated glass containing sufficiently large number of nuclei, the values of $n$ and $m$ for different crystallization are given in Table 3. The fraction volume $x$ crystallized at any temperature $T$ is given as $x = S/T_f$, where $S_f$ is the total area of the exotherm between $T_i$ where the crystallization just begins and the temperature $T_f$ where the crystallization is completed and $S$ is the area between $T_i$ and $T_f$ as shown by the hatched portion in Figure 5.

Figure 6 shows linear plots of $\ln\left[-\ln(1-x)\right]$ versus $\ln\alpha$ at three fixed temperatures for Se$_{90-x}$Zn$_{10}$Sbx ($x = 0,

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$n$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-dimensional growth</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Two-dimensional growth</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>One-dimensional growth</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Surface nucleation</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. The Values of $n$ and $m$ for different crystallization mechanism.

Figure 5. The DSC curve indicating the estimation of volume fraction crystallized.
2, 4, 6) glasses system. Using Equation (5), the values of \( n \) have been determined from the slopes of these curves at each temperature and are given in Table 4 for \( \text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x \) \( (x = 0, 2, 4, 6) \) glassy system, the observed values reveal the dimension growth is two dimensional for the binary \( \text{Se}_{90}\text{Zn}_{10} \) and three for the ternaries \( \text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x \) \( (x = 2, 4, 6) \).

Figure 7 shows the plot of \( \ln[-\ln(1 - x)] \) versus \( \frac{1000}{T} \) for \( \text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x \) \( (x = 0, 2, 4, 6) \) at different heating rates 5, 7, 10 and 12°C/min. The deviation from the straight line nature at higher temperature is due to saturation of nucleation sites during the latter stage in the process of crystallization [25] or to the restriction of crystal growth by the small size of the particles [26]. From Figure 7, the value of activation energy of crystallization \( E_c \) was calculated from the slope of the \( \ln[-\ln(1 - x)] \) versus \( \frac{1000}{T} \) for all heating rates, the values are given in Table 4.

Table 4. The values of Avrami index \( n \) and dimensionality of growth \( m \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{Se}<em>{90}\text{Zn}</em>{10} )</th>
<th>( \text{Se}<em>{98}\text{Zn}</em>{10}\text{Sb}_{2} )</th>
<th>( \text{Se}<em>{96}\text{Zn}</em>{10}\text{Sb}_{4} )</th>
<th>( \text{Se}<em>{94}\text{Zn}</em>{10}\text{Sb}_{6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) (K)</td>
<td>384</td>
<td>392</td>
<td>400</td>
<td>405</td>
</tr>
<tr>
<td>( n )</td>
<td>4.14 ± 0.52</td>
<td>3.21 ± 0.10</td>
<td>2.13 ± 0.18</td>
<td>4.49 ± 0.15</td>
</tr>
<tr>
<td>Average value</td>
<td>3.16 ± 0.26</td>
<td>4.12 ± 0.22</td>
<td>4.10 ± 0.30</td>
<td>4.11 ± 0.33</td>
</tr>
<tr>
<td>( m )</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 6. The plots of \( \ln[-\ln(1 - x)] \) versus \( \ln \alpha \) for different composition \( \text{Se}_{90-x}\text{Zn}_{10}\text{Sb}_x \) \( (x = 0, 2, 4, 6) \) at any fixed temperature.
Table 5. From Table 5 the value of activation energy of crystallization \( E_c \) of Se Zn Sb glassy increases with decreasing Sb.

3.2. Kissinger Method

The activation energy for crystallization \( E_c \) can be obtained from the heating-rate dependence on the peak temperature of crystallization \( T_p \), using the Kissinger equation [19].

\[
\ln \left( \frac{\alpha}{T_p^2} \right) = -\frac{E_c}{RT_p} + \text{constant} \quad (6)
\]

Figure 7. The plots of \( \ln[-\ln(1-x)] \) versus \( \ln \alpha \) at different heating rates for Se\(_{90-x}\)Zn\(_{10}\)Sb\(_x\) (\( x = 0, 2, 4, 6 \)) glasses.

Table 5. The values of activation energy of crystallisation obtained from Matusita method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( E_c ) (KJ/mol)</th>
<th>( E_c ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(<em>{90})Zn(</em>{10})</td>
<td>93.53 ± 8.42</td>
<td>0.96 ± 0.08</td>
</tr>
<tr>
<td>Se(<em>{88})Zn(</em>{10})Sb(_2)</td>
<td>104.44 ± 6.60</td>
<td>1.08 ± 0.06</td>
</tr>
<tr>
<td>Se(<em>{86})Zn(</em>{10})Sb(_4)</td>
<td>127.52 ± 4.30</td>
<td>1.32 ± 0.04</td>
</tr>
<tr>
<td>Se(<em>{84})Zn(</em>{10})Sb(_6)</td>
<td>165.33 ± 8.19</td>
<td>1.71 ± 0.08</td>
</tr>
</tbody>
</table>
A plot of ln(α/\(T_p^2\)) versus 1/\(T_p\) for compositions Se\(_{90-x}\)Zn\(_{10}\)Sbx (x = 0, 2, 4, 6) is shown in Figure 8. The slope of these straight lines gives the activation energy of crystallization \(E_c\), the values of \(E_c\) for all compositions are given in Table 6.

### 3.3. Ozawa Method

The activation energy of crystallization \(E_c\) can also be obtained from the variation of the temperature at maximum peak \(T_p\) with heating rate by using Ozawa’s [27] relation as

\[
\ln \alpha = -E_c / RT_p + \text{constant}
\]  

The plots of ln\(\alpha\) versus 1/\(T_p\) for different compositions are shown in Figure 9. The Values of the activation energy \(E_c\) for the crystallization processes are listed in Table 6.

### 4. Conclusion

The crystallization kinetics in glassy Se\(_{90-x}\)Zn\(_{10}\)Sbx (x = 0, 2, 4, 6) alloys have been studied under non-isothermal conditions using the DSC technique. The glass transition temperature \(T_g\) decreases with an increase in the Sb

![Figure 8](image_url_8.png)

**Figure 8.** The plots of ln(\(\alpha/\(T_p^2\)) versus 1/\(T_p\)) for Se\(_{90-x}\)Zn\(_{10}\)Sbx (x = 0, 2, 4, 6) glasses.

![Figure 9](image_url_9.png)

**Figure 9.** The plots of ln\(\alpha\) versus 1/\(T_p\) for Se\(_{90-x}\)Zn\(_{10}\)Sbx (x = 0, 2, 4, 6) glasses.
Table 6. The values of activation energy of crystallisation obtained from Kissinger and Ozawa methods.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_c$ (KJ/mol)</th>
<th>$E_c$ (eV)</th>
<th>$E_c$ (KJ/mol)</th>
<th>$E_c$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{90}$Zn$</em>{10}$</td>
<td>85.86 ± 7.06</td>
<td>0.89 ± 0.07</td>
<td>92.50 ± 8.39</td>
<td>0.95 ± 0.08</td>
</tr>
<tr>
<td>Se$<em>{90}$Zn$</em>{10}$Sb$_{2}$</td>
<td>89.84 ± 8.56</td>
<td>0.93 ± 0.08</td>
<td>96.74 ± 12.38</td>
<td>1.00 ± 0.12</td>
</tr>
<tr>
<td>Se$<em>{88}$Zn$</em>{10}$Sb$_{4}$</td>
<td>98.49 ± 6.17</td>
<td>1.02 ± 0.06</td>
<td>105.39 ± 3.90</td>
<td>1.09 ± 0.04</td>
</tr>
<tr>
<td>Se$<em>{84}$Zn$</em>{10}$Sb$_{6}$</td>
<td>122.34 ± 7.67</td>
<td>1.26 ± 0.07</td>
<td>129.33 ± 9.89</td>
<td>1.34 ± 0.10</td>
</tr>
</tbody>
</table>

contents and the crystallization temperature $T_c$, increase with increase in Sb. The activation energy of glass transition $E_g$ calculated from Kissinger model decreases with the increase in Sb. The calculated values of the kinetic exponent $n$ suggest two dimensional growth for the binary Se$_{90}$Zn$_{10}$ and three dimensional growth for ternaries Se$_{90-x}$Zn$_{10}$Sb$_x$ ($x = 0, 2, 4, 6$), the activation energy of crystallization $E_c$ has been calculated using Kissinger, Ozawa and Matusita models there are in good agreement with each other.

References


