CHAPTER - 4

KINETICS OF CRYSTALLIZATION IN SOME CHALCOGENIDE GLASSES USING ISOTHERMAL ANNEALING TECHNIQUE
4.1 INTRODUCTION

In non-isothermal measurements discussed in previous chapter, uniform temperature programming throughout the sample body is required for a successful investigation of kinetic parameters. A lag in temperature occurs between the furnace and the sample. Moreover, the kinetic analysis of non-isothermal data is not possible if the reaction kinetics change with the temperature range under consideration. The reaction mechanism can, therefore, not be accurately determined and hence the meaning of the activation energy of crystallization are uncertain. On the other hand the theoretical analysis of isothermal crystallization is simple and well understood. However, isothermal measurements are more difficult to perform under ideal conditions. During isothermal studies a considerable part of the sample undergoes some reaction in order to reach the desired temperature.

* The work reported in this chapter has been accepted for publication in the following Journals:

3. Journal de Physique III (to be revised).
In view of the above discussions one should make crystallization kinetic studies by both the methods and then compare the results to arrive at a conclusion regarding the activation energy of crystallization. We, therefore, made isothermal measurements on two binary glassy systems $\text{Se}_{100-x}\text{Te}_x$ and $\text{Se}_{100-x}\text{In}_x$ with varying $x$. The results have been compared with non-isothermal measurements reported in the same system in the last chapter. As isothermal measurements could not be performed using DSC technique due to experimental limitations, conductivity measurements have been made for such studies.

The present chapter also reports crystallization studies in one ternary glassy system $\text{Ge}_{20}\text{Se}_{80-x}\text{In}_x$ in which non-isothermal measurements could not be performed due to absence of sharp exothermic peaks at crystallization temperature. No comparison is therefore possible in this case.

Section 4.2 describes the theory of measurements. The results have been presented and discussed in section 4.3. The last section deals with the conclusions of the present work.

4.2 THEORY OF MEASUREMENTS

During isothermal transformation, the extent of crystallization ($\alpha$) of a certain material is represented by the Avrami's equation [25,26] as follows:

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

(4.1)
where, \( K \) is a rate constant and \( n \) is the order parameter which depends upon the mechanism of crystal growth.

\( K \) is given by the Arrhenius equation

\[
K = K_0 \exp \left( -\frac{\Delta E_C}{RT} \right)
\]  

(4.2)

here \( K_0 \) is a constant and \( \Delta E_C \) represents the activation energy of crystallization. Any physical quantity which changes measurably upon crystallization can be taken as a characteristic parameter to evaluate \( \alpha \) as a function of time. D.C. conductivity has been used [53-55] as a parameter to study the crystallization kinetics in chalcogenide glasses. Landauer [56] developed a theory for random mixtures based on the assumption that one of the phases (the dispersed phase) is surrounded by a homogeneous medium (the continuous phase) which has a different conductivity. According to this theory, the extent of crystallinity \( (\alpha) \) is given by the equation

\[
\alpha = \left( \frac{\sigma_c + 2\sigma_a}{\sigma + 2\sigma_a} \right) \left( \frac{\sigma - \sigma_a}{\sigma_c - \sigma_a} \right)
\]  

(4.3)

where \( \sigma \) is the overall conductivity of the mixture, \( \sigma_c \) is the conductivity of the crystalline phase and \( \sigma_a \) the conductivity of the amorphous phase.

However, equation 4.3 as pointed out by Landauer, is only valid for spheroid inclusions and can not be applied
to mixtures having needle or disc shaped inclusions. However, this assumption may not always be valid for complicated systems, e.g., alloys as used in the present measurements.

Odelevsky [57] has suggested a power formula to calculate the conductivity of a mixture ($\sigma$) during amorphous to crystalline transformation. According to him,

$$\sigma^l = a\sigma_c^l + (1-a)\sigma_a^l$$  \hspace{1cm} (4.4)

where $\sigma_c$ and $\sigma_a$ are the conductivities of crystalline and amorphous phases having volume fraction $a$ and $(1-a)$ respectively.

For the power $(l) = 1$ the measured conductivity ($\sigma$) at a particular time during crystallization can be written as:

$$\sigma = a\sigma_c + (1-a)\sigma_a$$  \hspace{1cm} (4.5)

On the other hand, when $\log \sigma$ is considered to represent the sensitive parameter characterizing the conductivity content dependence, an empirical power formula may be written as:

$$\log \sigma = \log \sigma_c + (1-a)\log \sigma_a$$  \hspace{1cm} (4.6)

Kotkata et al. [58] have used equations 4.5 and 4.6 to calculate the extent of crystallization in some Se based chalcogenide glasses and found that equation 4.6 is more satisfactory as $(\sigma_c - \sigma_a)$ is quite large in these
chalcogenide glasses.

In these glasses the conductivity increases by several orders of magnitude on crystallization, hence equation 4.6 should be used to calculate $\alpha$ by measuring $\sigma$ as a function of time during isothermal annealing at temperatures near the crystallization temperature. Once the values of $\alpha$ as a function of time are known at different isothermal temperatures of transformation, the kinetic parameters, activation energy ($\Delta E_c$) and Avrami exponent ($n$), can be calculated using equations 4.1 and 4.2.

4.3 RESULTS AND DISCUSSIONS

Glassy alloys of $\text{Se}_{100-x}\text{Te}_x$ ($5 \leq x \leq 30$), $\text{Se}_{100-x}\text{In}_x$ ($5 \leq x \leq 30$) and $\text{Ge}_{20}\text{Se}_{80-x}\text{In}_x$ ($0 \leq x \leq 20$) were prepared by quenching technique as described in chapter 2 of the present thesis.

For studying crystallization kinetics, samples in the pellet form were mounted inside a specially designed sample holder as shown in (Fig. 2.2, chapter 2). The samples were annealed at various annealing temperatures between glass transition and melting temperatures and the d.c. conductivity was measured with time in each case of annealing. The annealing temperature was obtained at a faster heating rate and then maintained constant till a saturation in current is reached. The current was measured by a Keithley
electrometer (model 614). The temperature was measured using a copper constantan thermocouple mounted very near to the sample.

The results of the above measurements for each glassy system are given in the following sections.

4.3.1 $\text{Se}_{100-x}\text{Te}_x$ Glassy Alloys

Figs. 4.1 - 4.4 show the time dependence of the d.c. conductivity at various annealing temperatures for glassy $\text{Se}_{95}\text{Te}_5$, $\text{Se}_{90}\text{Te}_{10}$, $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{70}\text{Te}_{30}$. It is clear from these figures that the d.c. conductivity increases with time during isothermal annealing at a certain temperature.

The transformation from the amorphous to the crystalline state occurs in three stages represented by AB, BC and CD as shown in Figs 4.1 - 4.4. The part AB of these curves is linear with time (t) and represents a gradual increase of $\sigma$ as a result of normal heating of the sample. The part BC represents a gradual but less pronounced increase in $\sigma$ which may be due to nucleation of crystalline phase. The part CD which shows a sharp rise in $\sigma$ may be attributed to rapid growth of crystalline state, a process which is accompanied by the liberation of heat energy associated with the transition from a non-equilibrium to an equilibrium thermodynamic state. CD attains a limiting value after certain time (point D).
Fig. 4.1

$\ln \sigma (\Omega^{-1} \text{cm}^{-1})$

Time of Anneal (min)

Se$_{95}$Te$_5$
- $85^\circ$C
- $75^\circ$C
- $70^\circ$C
- $65^\circ$C
Fig. 4.2

$\ln \sigma (\Omega^{-1} \text{cm}^{-1})$

Time of Anneal (min)

Se$_{90}$Te$_{10}$

- $85^\circ$C
- $80^\circ$C
- $75^\circ$C
- $70^\circ$C
Fig. 4.3

Se$_{80}$Te$_{20}$
- $\circ$ 85°C
- $\triangle$ 80°C
- $\square$ 75°C
- $\blacktriangle$ 70°C

Time of Anneal (min)

$\ln \sigma$ (Ω$^{-1}$cm$^{-1}$)
Fig. 4.4

Se$_{70}$Te$_{30}$

Time of Anneal (min)

$\ln \sigma$ (\Omega$^{-1}$cm$^{-1}$)

-9

-13

-17

-21

-25

-29

-33

-37

-41

90 °C

85 °C

80 °C

75 °C
In the present study we are interested to understand the crystallization kinetics of crystal growth, i.e., the CD part of the curves in Figs. 4.1 - 4.4.

Using the measured value of conductivity, $\alpha$ is calculated as a function of time at various annealing temperatures using eq. (4.6) where $\sigma_a$ is taken as the conductivity at point C as we are interested in the growth kinetics of crystallization. $\sigma_c$ represents the conductivity at point D in each curve of Figs. 4.1-4.4. The variation of $\alpha$ as a function of time for various glassy alloys is shown in Fig. 4.5.

Following eq. (4.1), the value of the order parameter $n$ can be calculated by plotting $\ln[-\ln(1-\alpha)]$ versus $\ln t$ at different annealing temperatures. Fig. 4.6 show such plots in case of Se$_{100-x}$Te$_x$ alloys. The values of $n$ at various temperatures are given in Table 4.1 for all the glassy alloys studied. It is clear from this table that the value of $n$ is 1.00 $\pm$ 0.15 for all the samples at all the temperatures of measurements. The value of $n = 1$ represents one dimensional growth of crystallites in the present glassy system [58].

For calculating the activation energy of crystallization ($\Delta E_C$), the values of $K$ were evaluated from the intercepts of the curves in Fig. 4.6. The $\ln K$ versus $1000/T$ curves (see Fig. 4.7) come out to be straight lines for all the glassy alloys confirming the validity of eq. (4.2) in the
Fig. 4.5
Fig. 4.6
TABLE - 4.1

Temperature dependence of the order parameter \( (n) \), in Se\( _{100-x} \)Te\( _x \) glassy alloys

<table>
<thead>
<tr>
<th></th>
<th>Se( _{95} )Te( _5 )</th>
<th>Se( _{90} )Te( _{10} )</th>
<th>Se( _{80} )Te( _{20} )</th>
<th>Se( _{70} )Te( _{30} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>65</td>
<td>1.00</td>
<td>70</td>
<td>1.03</td>
<td>70</td>
</tr>
<tr>
<td>70</td>
<td>0.95</td>
<td>75</td>
<td>1.00</td>
<td>75</td>
</tr>
<tr>
<td>75</td>
<td>1.00</td>
<td>80</td>
<td>1.03</td>
<td>80</td>
</tr>
<tr>
<td>85</td>
<td>1.03</td>
<td>85</td>
<td>1.03</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95</td>
</tr>
</tbody>
</table>
present case. The values of $\Delta E_c$ are calculated for each glassy alloy from the slopes of $\ln K$ vs $1000/T$ curves (Fig. 4.7). The values of $\Delta E_c$ thus calculated are given in Table 4.2 which also contains the value of $\Delta E_c$ obtained from the non-isothermal DSC measurements reported in the previous chapter.

Fig. 4.3 shows the variation of $\Delta E_c$ with Te concentration in $\text{Se}_{100-x}\text{Te}_x$ glassy system. It is clear from this figure that $\Delta E_c$ increases with Te concentration. The increase of $\Delta E_c$ with Te concentration indicates that the rate of crystallization is faster in Te rich alloys as compared to alloys containing small concentration of Te. This is in agreement with the non-isothermal measurements in the same glassy system reported in the previous chapter. It is, however, evident from Table 4.2 that a difference of 15 kJ/mole is observed in $\Delta E_c$ values obtained in two methods of measurements. It may be due to some kind of artifact in the data analysis in two cases as in one case non-isothermal and in other case isothermal analysis is applied. The similar composition dependence, however, suggested that both the methods can be successfully applied to arrive at the same conclusion.

4.3.2 $\text{Se}_{100-x}\text{In}_x$ Glassy Alloys

Figs. 4.9-4.13 show the time dependence of the d.c. conductivity at various annealing temperatures for glassy $\text{Se}_{95}\text{In}_5$, $\text{Se}_{90}\text{In}_{10}$, $\text{Se}_{85}\text{In}_{15}$, $\text{Se}_{80}\text{In}_{20}$ and $\text{Se}_{70}\text{In}_{30}$
Fig. 4.7
Fig. 4.8
TABLE 4.2
Composition dependence of activation energy of crystallization in Se$_{100-x}$Te$_x$ glassy alloy

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_C$ (kJ/mole) (present measurements)</th>
<th>$\Delta E_C$ (kJ/mole) DSC measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{95}$Te$_5$</td>
<td>67.9</td>
<td>69.4</td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{10}$</td>
<td>106.0</td>
<td>90.6</td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{20}$</td>
<td>116.4</td>
<td>104.1</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{30}$</td>
<td>153.1</td>
<td>139.7</td>
</tr>
</tbody>
</table>
\[\ln \sigma (\Omega^{-1} \text{cm}^{-1})\]

Time of Anneal (min)

**Fig. 4.9**

\(\text{Se}_{95}\text{In}_{5}\)

- ○ 88°C
- △ 83°C
- □ 78°C
- ▼ 73°C

---

Time of Anneal (min)
Fig. 4.10

\[ \ln \sigma (\Omega^{-1} \text{cm}^{-1}) \]

Time of Anneal (min)

- \(93^\circ C\)
- \(88^\circ C\)
- \(83^\circ C\)
- \(73^\circ C\)
Fig. 4.12

\[ \ln \sigma (\Omega^{-1}\text{cm}^{-1}) \]

Time of Anneal (min)

Se\textsubscript{80}In\textsubscript{20}

- O 93°C
- △ 88°C
- □ 83°C
- ▼ 78°C
Fig. 4.13

Time of anneal (min)

Se_{70} In_{30}

93 °C
83 °C
78 °C
73 °C
respectively. It is clear from these figures that d.c. conductivity increases with time during isothermal annealing at a certain temperature. In this system also, the transformation from amorphous to the crystalline state occurs in three stages represented by AB, BC and CD as shown in Figs. 4.9 - 4.13. As mentioned in section 4.3.1 the CD part represents the growth of the crystalline state.

Using the measured value of conductivity, \( \alpha \) is calculated as a function of time at various annealing temperatures using eq. (4.6). In this case also, \( \sigma_a \) is taken as the conductivity at point C as we are interested in the growth kinetics of crystallization. \( \sigma_c \) represents the conductivity at point D in each curve of Figs. 4.9 - 4.13. The variation of \( \alpha \) as a function of time for glassy Se\(_{100-x}\)In\(_x\) alloys is shown in Figs. 4.14 & 4.15.

The value of the order parameter \( (n) \) is calculated by plotting ln[-\( \ln(1-\alpha) \)] versus ln(t) curves at different temperatures for each glassy alloy. These curves came out to be straight lines in each case (see Figs. 4.16 & 4.17). The values of \( n \) thus calculated are given in Table 4.3 for all the glassy alloys studied. It is clear from this table that the value of \( n \) is 1.00 \( \pm \) 0.15 for all the samples at all the temperatures of measurements. The value of \( n = 1 \) represents one dimensional growth of crystallites [58] in the present glassy system.
Fig. 4.14

\[ \text{Time of Anneal (min)} \]

\[ \alpha (\%) \]

\[ \text{Se}_{95}\text{In}_{5} \]

- \(\bigcirc\) 88°C
- \(\triangle\) 83°C
- \(\square\) 78°C
- \(\blacktriangledown\) 73°C
Fig. 4.15
Fig. 4.16

Graph showing the relationship between $\ln[-\ln(1-\alpha)]$ and $\ln t$ for different temperatures:

- $88^\circ C$: Circles
- $83^\circ C$: Triangles
- $78^\circ C$: Squares
- $73^\circ C$: Triangles inverted

The graph is labeled as $\text{Se}_{95}\text{In}_{5}$. 
Fig. 4.17
**TABLE - 4.3**

Temperature dependence of the order parameter (n), in Se$_{100-x}$In$_x$ glassy alloys

<table>
<thead>
<tr>
<th></th>
<th>Se$_{95}$In$_5$</th>
<th>Se$<em>{90}$In$</em>{10}$</th>
<th>Se$<em>{85}$In$</em>{15}$</th>
<th>Se$<em>{80}$In$</em>{20}$</th>
<th>Se$<em>{70}$In$</em>{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
<td>n</td>
</tr>
<tr>
<td>73</td>
<td>0.94</td>
<td>73</td>
<td>1.20</td>
<td>73</td>
<td>1.23</td>
</tr>
<tr>
<td>78</td>
<td>0.87</td>
<td>83</td>
<td>1.11</td>
<td>78</td>
<td>1.10</td>
</tr>
<tr>
<td>83</td>
<td>0.85</td>
<td>88</td>
<td>1.10</td>
<td>83</td>
<td>1.17</td>
</tr>
<tr>
<td>88</td>
<td>0.92</td>
<td>93</td>
<td>1.06</td>
<td>103</td>
<td>1.29</td>
</tr>
</tbody>
</table>
The values of $\Delta E_c$ were calculated by plotting $\ln K$ vs $1000/T$ curves (see Fig. 4.18) for each glassy alloy in Se$_{100-x}$In$_x$ system. The values of $\Delta E_c$ thus calculated are given in Table 4.4 which also contains the value of $\Delta E_c$ obtained from the non-isothermal DSC measurements reported in the previous chapter.

It is evident from Table 4.4 that $\Delta E_c$ increases with the increase of In concentration in Se$_{100-x}$In$_x$ system. Fig. 4.19 shows the variation of $\Delta E_c$ with In concentration which indicates that $\Delta E_c$ increases monotonically with In concentration. This is in agreement with the results obtained from DSC measurements (see Table 4.4). It is evident from this table that a difference of 15 kJ/mole occurs between two methods of measurements in this system also as obtained in Se$_{100-x}$Te$_x$ system (see section 4.3.1). As mentioned earlier, this may be a consequence of data analysis approach which is different in two cases. However, as obtained in Se-Te system, in Se-In also the composition dependence of $\Delta E_c$ come out to be similar by the two methods.

4.3.3 Ge$_{20}$Se$_{80-x}$In$_x$ Glassy Alloys

Figs. 4.20-4.24 show the time dependence of the d.c. conductivity at various annealing temperatures for glassy Ge$_{20}$Se$_{80}$, Ge$_{20}$Se$_{75}$In$_5$, Ge$_{20}$Se$_{70}$In$_{10}$, Ge$_{20}$Se$_{65}$In$_{15}$ and Ge$_{20}$Se$_{60}$In$_{20}$ respectively. It is clear from these
Fig. 4.18

- Seg In5
- Seg In10
- Seg In15
- Seg In20
- Seg In30

\[ \ln K \]

\[ 10^3 / T (\text{K}^{-1}) \]
Fig 4.19
### TABLE - 4.4

Composition dependence of the activation energy of crystallization in Se\(_{100-x}\)In\(_x\) glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Delta E_c) (kJ/mole)</th>
<th>(\Delta E_c) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>present work</td>
<td>DSC measurements</td>
</tr>
<tr>
<td>Se(_{95})In(_5)</td>
<td>62.8</td>
<td>72.7</td>
</tr>
<tr>
<td>Se(<em>{90})In(</em>{10})</td>
<td>70.3</td>
<td>86.6</td>
</tr>
<tr>
<td>Se(<em>{85})In(</em>{15})</td>
<td>81.1</td>
<td>92.4</td>
</tr>
<tr>
<td>Se(<em>{80})In(</em>{20})</td>
<td>89.7</td>
<td>103.9</td>
</tr>
<tr>
<td>Se(<em>{70})In(</em>{30})</td>
<td>98.8</td>
<td>116.9</td>
</tr>
</tbody>
</table>
Fig. 4.20

\[ \ln \sigma (\Omega^{-1} \text{cm}^{-1}) \]

-14.5
-16.5
-18.5
-20.5
-22.5
-24.5

Time of Anneal (min)

Ge\textsubscript{20}Se\textsubscript{80}

○ 196°C
△ 186°C
□ 176°C

Fig. 4.20
Fig. 4.21
Fig. 4.22

$\ln \sigma$ ($\Omega^{-1} \text{cm}^{-1}$) vs. Time of Anneal (min)

Ge$_{20}$Se$_{70}$In$_{10}$

- $196^\circ \text{C}$
- $176^\circ \text{C}$
- $166^\circ \text{C}$
- $156^\circ \text{C}$
Fig. 4.23

$\ln \sigma$ (Ω$^{-1}$ cm$^{-1}$)

Time of Anneal (min)

$\text{Ge}_{20}\text{Se}_{65}\text{In}_{15}$

- $186 ^\circ C$
- $176 ^\circ C$
- $156 ^\circ C$
- $146 ^\circ C$
Fig. 4.24

**Ge<sub>20</sub>Se<sub>60</sub>In<sub>20</sub>**

- ○ 181°C
- ▲ 161°C
- ● 151°C
- □ 141°C

Time of Anneal (min)

Inσ (Ω⁻¹·cm⁻¹)
figures that d.c. conductivity increases with time during isothermal annealing at a certain temperature.

Using the measured value of conductivity, \( \alpha \) is calculated as a function of time at various annealing temperatures using eq. (4.6). As mentioned in previous sections, \( \sigma_\alpha \) is taken as the conductivity at point C as we are interested to study the growth kinetics of crystallization. \( \sigma_c \) is taken as the conductivity at point D in each curve of Figs. 4.20–4.24. The variation of \( \alpha \) as a function of time for glassy Ge\(_{20}\)Se\(_{80-x}\)In\(_x\) alloys is shown in Figs. 4.25 & 4.26.

The value of the order parameter (n) is calculated by plotting \( \ln[-\ln(1-\alpha)] \) versus \( \ln t \) curves at different temperatures for each glassy alloy. These curves were found to be straight lines for all the glassy alloys studied (see Figs. 4.27&4.28). The values of n thus calculated are given in Table 4.5 for all the glassy alloys studied. It is clear from this table that the value of n is different at different temperatures.

The values of \( \Delta E_C \) were calculated by plotting \( \ln K \) versus 1000/T curves (see Fig. 4.29) for each glassy alloy in Ge\(_{20}\)Se\(_{80-x}\)In\(_x\) system. The values of \( \Delta E_C \) thus calculated are given in Table 4.6 and plotted as a function of x in Fig. 4.30. This figure indicates that \( \Delta E_C \) decreases on In incorporation in Ge-Se system up to 15 at %. However, a further increase in In concentration increases the value of \( \Delta E_C \) again. A similar type of discontinuity at 15 at % of
Fig. 4.25

Ge$_{20}$Se$_{80}$

196 °C

186 °C

176 °C

Time of anneal (min)
Fig. 4.26
Fig. 4.27

\[ \ln (\ln (\frac{1}{x})) \]

\[ \ln t \]

Ge\textsubscript{20}Se\textsubscript{80}

-4.0
-3.0
-2.0
-1.0

196°C
186°C
176°C

Fig. 4.27
Fig. 4.28
### TABLE - 4.5

Temperature dependence of the order parameter (n), in Ge$_{20}$Se$_{80-x}$In$_x$ glassy alloys

<table>
<thead>
<tr>
<th></th>
<th>Ge$<em>{20}$Se$</em>{80}$</th>
<th>Ge$<em>{20}$Se$</em>{75}$In$_5$</th>
<th>Ge$<em>{20}$Se$</em>{70}$In$_{10}$</th>
<th>Ge$<em>{20}$Se$</em>{65}$In$_{15}$</th>
<th>Ge$<em>{20}$Se$</em>{60}$In$_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
<td>n</td>
<td>Temp (°C)</td>
<td>n</td>
</tr>
<tr>
<td>176</td>
<td>0.97</td>
<td>166</td>
<td>0.72</td>
<td>156</td>
<td>1.01</td>
</tr>
<tr>
<td>186</td>
<td>0.89</td>
<td>176</td>
<td>0.82</td>
<td>166</td>
<td>1.00</td>
</tr>
<tr>
<td>196</td>
<td>0.89</td>
<td>186</td>
<td>0.77</td>
<td>176</td>
<td>1.04</td>
</tr>
<tr>
<td>196</td>
<td>0.86</td>
<td>196</td>
<td>0.93</td>
<td>186</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.29
### TABLE - 4.6
Composition dependence of activation energy of crystallization in $\text{Ge}_{20} \text{Se}_{80-x} \text{In}_x$ glassy alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta E_c$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ge}<em>{20} \text{Se}</em>{80}$</td>
<td>59.8</td>
</tr>
<tr>
<td>$\text{Ge}<em>{20} \text{Se}</em>{75} \text{In}_5$</td>
<td>51.1</td>
</tr>
<tr>
<td>$\text{Ge}<em>{20} \text{Se}</em>{70} \text{In}_{10}$</td>
<td>43.4</td>
</tr>
<tr>
<td>$\text{Ge}<em>{20} \text{Se}</em>{65} \text{In}_{15}$</td>
<td>28.9</td>
</tr>
<tr>
<td>$\text{Ge}<em>{20} \text{Se}</em>{60} \text{In}_{20}$</td>
<td>48.2</td>
</tr>
</tbody>
</table>
Fig. 4.30

\( \Delta E_c \) (kJ/mole)

In (at %)

Ge\(_{20}\) Se\(_{80-x}\) In\(_x\)
In was also observed in our X-ray spectroscopic measurements in the same glassy system [59].

If one writes \( \text{Ge}_{20}\text{Se}_{80-x}\text{In}_x \) as \( \text{Ge}_{20}\text{Se}_{40+x}\text{In}_{40-x} \), then the largest value of \( x \) which contains \( \text{In}_2\text{Se}_3 + \text{Se} \) is \( x=16 \). For higher concentration of In (\( x>16 \)), one can therefore expect the formation of \( \text{In}_2\text{Se}_3 + \text{GeSe}_2 + \text{GeSe} \) which are the most stable phases as suggested by the phase diagrams. An increase in the activation energy of crystallization for \( (x>15) \) in the present case may, therefore, be a consequence of the formation of such stable phases in Ge-Se-In system.

4.4 CONCLUSIONS

Crystallization kinetics have been studied in some binary and ternary alloys using isothermal annealing at various temperatures (near \( T_c \)) and measuring the time dependence of d.c. conductivity. The extent of crystallization has been calculated using an empirical relation used by Kotkata et al. [58] in chalcogenide glasses. Avrami's theory of isothermal transformation is applied to calculate the activation energy of crystallization (\( \Delta E_c \)) and the order parameter (\( n \)). The results indicate that \( \Delta E_c \) increases with the increase of Te concentration in \( \text{Se}_{100-x}\text{Te}_x \) glassy system. Similar results were also obtained from non-isothermal measurements using DSC technique. In \( \text{Se}_{100-x}\text{In}_x \) glassy system, \( \Delta E_c \) increases with the increase of In concentration. These results are also in agreement with the results obtained
by non-isothermal DSC technique. A comparison of $\Delta E_c$ values in two cases (isothermal and non-isothermal) shows that the values of $\Delta E_c$ in isothermal measurements are different by about 15 kJ/mole in Se$_{100-x}$Te$_x$ and Se$_{100-x}$In$_x$ glasses as compared to non-isothermal measurements reported in the previous chapter. This consistent difference may be due to some kind of artifact in data analysis in two different methods.

Isothermal measurements were also made in one ternary system Ge$_2$OSe$_{80-x}$In$_x$ ($5 \leq x \leq 20$) where no comparison could be made with non-isothermal case due to non-existence of exothermic peaks in the measuring range of temperature in DSC technique. The results of isothermal measurements however indicate that $\Delta E_c$ decreases on In incorporation in Ge-Se system upto 15 at %. A further increase in In concentration increases the value of $\Delta E_c$ again. These results are in agreement with the conclusions drawn from X-ray spectroscopic measurements in these glasses [59]. A discontinuity at 15 at % of In is associated with the formation of stable phases (In$_2$Se$_3$+GeSe$_2$+GeSe) at higher concentration of In in Ge-Se-In system.