CHAPTER 3

KINETICS OF CRYSTALLIZATION IN SOME CHALCOGENIDE GLASSES USING NON-ISOTHERMAL DSC TECHNIQUE
3.1 INTRODUCTION

On heating a glassy substance above a certain temperature, considerable amount of heat is released as it comes to thermodynamically equilibrium state, i.e., when it crystallizes. Well defined exothermic peaks can, therefore, be observed when thermoanalytical techniques are applied to study crystallization kinetics. The present chapter deals with the crystallization studies of chalcogenide glasses using differential scanning calorimetry. The following two sections deal with an introduction to thermoanalytical techniques to study crystallization kinetics and also various theoretical analysis involved in such techniques. Next section of this chapter deals with the results obtained in various glassy alloys. The last section deals with the conclusions of the present work.

3.2 AN INTRODUCTION TO THERMOANALYTICAL TECHNIQUE

Thermoanalytical technique is such in which a physical property of a substance and the reaction products are measured as a function of temperature, whilst the

*The work reported in this chapter has been published in the following journals:
substance is subjected to a controlled temperature programme. Among various thermoanalytical techniques, thermal analysis method is used to study the different physical properties of the system which occur during the change in temperature with time, such as endothermic and exothermic enthalpic transition reactions which occur due to phase transition of the system.

In late 18th century various accurate temperature measuring techniques such as thermocouple, resistance thermometer, optical pyrometer etc. were developed. Le'Chatlier introduced heating rate change curves in 1887. Differential Thermal Analysis (DTA) was originally conceived by Robert Austen in 1889 in which the temperature of the sample was compared to that of the reference material. The technique eliminated the effect of heating rate and other disturbances that changes the temperature of the sample. Photographic recorder was developed by saladin. Burgess [24] also studied these techniques. An elaborate form of DTA instrument including Differential Scanning Calorimeter (DSC) was introduced by Watson in 1964. DSC and DTA are not synonyms, although the field of application is virtually identical. DSC is a technique for recording the energy necessary to establish a zero temperature difference between a substance and the reference material as the two specimens are subjected to identical conditions. As well defined endothermic and exothermic peaks at glass transition and crystallization occurs in DSC scans of chalcogenide glasses, such a technique can
be used to study glass transition and crystallization kinetics in these glasses.

3.3 THEORY OF CRYSTALLIZATION

Heating of an amorphous glass results into crystallization phenomena and one can regard this crystallization process to be associated with the nucleation and growth that dominate devitrification of glassy solids. The initial process of heating leads to the growth of crystal called primary nucleation known as homogeneous process, the enhanced nucleation process of growth is called heterogeneous crystallization. The basic feature of identification of crystallization is an addition of single molecule to the growing crystal. Crystallization studies can be done using several techniques. In order to study the kinetics of phase transformation during calorimetric measurements two basic methods are used. These methods are based on spontaneous nucleation of new phase either through the volume or upon the grain surfaces which is a function of time or temperature.

When the sample is brought quickly to a temperature above glass transition temperature ($T_g$) and heat evolved during the process is recorded as a function of time the method is named as 'isothermal'. For dynamic measurements (non-isothermal) a fixed heating rate is employed to heat the sample and heat evolved is recorded as a function of temperature/time. Several theoretical models have been
reported in the literature to study the kinetics of crystallization. The following section gives a brief account of these theories which are used to calculate the kinetic parameters from the experimental data using isothermal as well as non-isothermal techniques.

3.3.1 Isothermal Technique

Crystallization phenomena is an activated process of nucleation and growth which dominate the devitrification of solids.

In fact, separate activation energy must be calculated for nucleation and growth processes but Piloyan [28] has used the activation energy of overall transformation. In isothermal method the extent of crystallization ($\alpha$) is measured as a function of time ($t$) under constant temperature.

Using John-Mehl-Avrami [25, 26] equation, $\alpha$ in case of isothermal transformation is given as

$$\alpha = 1 - \exp\left(-Kt^n\right)$$  \hspace{1cm} (3.1)

where,

$\alpha$ = time dependent fraction crystallised after time $t$.

$K$ = rate constant of crystallization which is temperature dependent.

$n$ = constant responsible for nucleation and growth mechanism.
The general expression used for the temperature dependence of rate constant is considered to be Arrhenius type and is expressed as:

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

(3.2)

where

- \( K_0 \) = pre-exponential factor
- \( \Delta E \) = activation energy of crystallization
- \( R \) = gas constant
- \( T \) = absolute temperature

It is clear from eq. 3.1 that slope of \( \ln[-\ln(1-\alpha)] \) versus \( \ln t \) curve can be used to calculate the value of \( n \). The intercept of this curve will give the value of \( K \). If the values of \( K \) are determined at various temperatures, the value of the activation energy (\( \Delta E \)) can be calculated using eq. (3.2) by plotting \( \ln K \) as a function of \( 1/T \).

3.3.2 Non-Isothermal Technique

Non-isothermal crystallization process of nucleation and growth can be derived by extending the Avrami equation [25] which is used for isothermal kinetics investigation. Evans [27] theory of growth of extending circles has been modified for this purpose. According to Murray and Vaughan [29,30] the rate equation at constant temperature can be written as:

\[ \left(\frac{d\alpha}{dt}\right)_T = K_T (1-\alpha) \]  

(3.3)
where $K_T$ can be given as an Arrhenius relation

$$K_T = K_0 \exp \left(-\frac{\Delta E}{RT} \right)$$

when the temperature is changing with time the rate of reaction is given as:

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t} \right)_T + \left(\frac{\partial \alpha}{\partial T} \right)_t \frac{dT}{dt}$$

The second term $\left(\frac{\partial \alpha}{\partial T} \right)_t \rightarrow 0$ as the time coordinate is fixed or one can simply say that the number of particles and the positions of the particles is fixed in the system of interest and hence

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t} \right)_T = (K)_T (1-\alpha)$$

$$= K_0 (1-\alpha) \exp \left(-\frac{\Delta E}{RT} \right)$$

The above equation is true for any value of 'T', as the temperature is either constant or variable when 'x' and 'T' are calculated simultaneously. The maximum rate of reaction occurs at $T = T_m$ (maximum temperature), i.e., at $T_m$

$$\frac{d\alpha}{dt} \left(\frac{d\alpha}{dt} \right) = 0$$

$$\frac{d\alpha}{dt} \left[ - K_0 \exp \left(-\frac{\Delta E}{RT_m} \right) + \frac{\Delta E}{RT_m^2} \frac{dT}{dt} \right] = 0$$

or

$$\frac{\Delta E}{RT_m^2} \frac{dT}{dt} = K_0 \exp \left(-\frac{\Delta E}{RT_m} \right) \quad (3.4)$$
Replacing $\frac{dT}{dt}$ by $\beta$ (constant heating rate) the equation 3.4 can be written as:

$$\ln\left(\frac{\beta}{T^2_m}\right) + \text{const.} = -\frac{\Delta E}{RT_m}$$

(3.5)

Using eq. 3.5 the value of activation energy can be calculated by plotting $\ln(\beta/T^2_m)$ versus $1/T_m$ curves. Kissinger [31] used the above equation for his system and found 8% error in the determination of $\Delta E$ for the first order reaction.

Piloyon [28] discussed the methods of chemical kinetics given by [27,31&32] and showed that the activation energy of the system can be calculated using a single scan technique also. According to him multiscan technique used by Kissinger has following shortcomings:

1. Several heating rate scans are required, which loses the actual superiority of the dynamic method.

2. Special temperature control devices are required to maintain the temperature constant which has technical difficulties.

Piloyon [28] used a single scan at any constant heating rate and the shift in the base line ($\Delta T$) has been described as:

$$\Delta T = S \frac{d\alpha}{dt}$$

(3.6)

Here, $S$ is the area of the thermal effect, $d\alpha/dt$ is the rate of reaction. In the general form, rate of reaction can
be written as:

\[
\frac{d\alpha}{dt} = K_0 \exp \left(-\frac{AE}{RT}\right) \cdot f(\alpha)
\]

putting the value of \( \frac{d\alpha}{dt} \) in the eq. (3.6) one gets

\[
\Delta T = S \cdot K_0 \exp \left(-\frac{AE}{RT}\right) \cdot f(\alpha) \quad (3.7)
\]

taking logarithm of the eq. (3.7) equation takes the form

\[
\ln \Delta T = \ln \left(S \cdot K_0\right) - \frac{AE}{RT} + \ln f(\alpha)
\]

or,

\[
\ln \Delta T = \text{constant} - \frac{AE}{RT} + \ln f(\alpha) \quad (3.8)
\]

Under isothermal conditions '\( \alpha \)' is only variable, but, in non-isothermal measurements, temperature also varies. For 0.0 < \( \alpha \) < 0.8, change in temperature affects \( \Delta T \) largely in comparison to \( f(\alpha) \), so the equation (3.8) can take the form as given by Borchardt et al. [32]

\[
\ln \Delta T = \text{constant} - \frac{AE}{RT} \quad (3.9)
\]

Using the above eq. (3.9) the value of \( \Delta E \) can be estimated. Harnisch [33] also supported the method of single scan. However, later, single scan method was criticised by several authors as the error was found to be \( \pm 20\% \) in the data determination.

On the other hand, some authors [34-38] applied the John-Mehl-Avrami equation to the non-isothermal crystalliza-
tion. Recently, Marotta et al. [39] have also pointed out the limitations of single scan technique and showed that it is rather difficult to calculate the value of $\Delta E$ and $'n'$ from the single scan technique. They have suggested that using the theory of non-isothermal crystallization developed by Matusita and Sakka [40-42] multiple scan technique can be successfully used for calculating the activation energy of crystallization ($\Delta E_c$) and the order parameter ($n$) from the same set of measurements.

According to this theory, $\alpha$ is given by:

$$-\ln(1-\alpha) = \frac{B}{\beta^n} \exp \left(-\frac{n \Delta E_c}{RT}\right) \quad (3.10)$$

where, $\beta$ is the heating rate. $B$ is a constant, proportional to the number $N$ of nuclei per unit volume.

For evaluating $n$, different values of $'\alpha'$ have to be determined at the same temperature $T$ on the multiple DSC scans recorded at different heating rates. As evident from equation (3.10), the value of $n$ can be calculated by the straight line $[\exp (-n \frac{\Delta E_c}{RT}) = \text{const}]$ obtained by plotting $\ln (\ln (1-\alpha)^{-1})$ versus $\ln \beta$. The activation energy $\Delta E_c$ can be evaluated from the same set of curves, determining on each curve the temperature $T$ corresponding to the same crystallization degree $\alpha$. As it has been demonstrated [34-36] that, at peak temperature $T_c$, the crystallization degree $\alpha$ does not depend on the DSC heating rate, $\beta$, the value of
$\Delta E_c$ can be calculated by the straight line $(\ln(1-\alpha)^{-1} = \text{constant})$ obtained by plotting $\ln \beta$ against $1/T_c$.

It is clear from the above discussion that the value of $\Delta E_c$ and $n$ can be calculated from multiscan technique using the same set of measurements.

In the present work, the above mentioned technique has been applied and the values of $\Delta E_c$ and $n$ have been calculated by plotting $\ln \beta$ vs $1/T_c$ and $\ln[\ln(1-\alpha)^{-1}]$ vs $\ln \beta$ curves.

The values of $\alpha$ at a particular temperature have been calculated by dividing the partial area by the total area of the exothermic peak in DSC scans.

### 3.4 RESULTS AND DISCUSSIONS

As mentioned in the previous section, the values of order parameter and the activation energy of crystallization can be calculated from the multi-scan technique. DSC thermograms have been obtained at five different heating rates (5 to 25°C/min) in various glassy alloys in $\text{Se}_{100-x}\text{Te}_x$ ($5 \leq x \leq 30$), $\text{Se}_{100-x}\text{In}_x$ ($5 \leq x \leq 30$), $\text{Se}_{80-x}\text{Te}_{20}\text{In}_x$ ($0 \leq x \leq 20$) and $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x$ ($0 \leq x \leq 1$) systems.

The results of the above measurements have been presented and discussed in the following sections:

#### 3.4.1 $\text{Se}_{100-x}\text{Te}_x$ Glassy Alloys

DSC thermograms for $\text{Se}_{95}\text{Te}_5$, $\text{Se}_{90}\text{Te}_{10}$, $\text{Se}_{85}\text{Te}_{15}$,
$Se_{80}Te_{20}$, $Se_{75}Te_{25}$ and $Se_{70}Te_{30}$ glassy alloys at five different heating rates are given in Figs. 3.1-3.6. It is clear from these figures that well defined endothermic peaks are observed at glass transition temperature, 'T_g' and at higher temperatures exothermic peaks are observed which represent the crystallization temperature 'T_c'. These figures clearly show that T_g and T_c both shift to higher temperatures as the heating rate is increased from 5 to 25°C/min. Table 3.1 gives the variation of T_c with the heating rate in each glassy alloy in $Se_{100-x}Te_x$ system.

The values of α at different temperatures were calculated after dividing the partial area by the total area of the exothermic peak in a DSC curve. Such calculations were made at all the five different heating rates in each glassy alloy.

To calculate the order parameter n, $\ln[\ln(1-\alpha)^{-1}]$ versus $\ln\beta$ curves were plotted at various temperatures for $Se_{95}Te_5$, $Se_{90}Te_{10}$, $Se_{85}Te_{15}$, $Se_{80}Te_{20}$, $Se_{75}Te_{25}$, and $Se_{70}Te_{30}$ glassy alloys as shown in Figs. 3.7-3.9. These plots were found to be straight lines. As discussed in section 3.3, the values of n are calculated from the slopes of these curves. Table 3.2 shows the results of these calculations at various temperatures in $Se_{100-x}Te_x$ glassy alloys. It is evident from this table that, in each alloy the value of n decreases with increasing temperature. A similar temperature dependence has also been observed in various other glassy systems[43,44]
Fig. 3.1

Se_{95}Te_{5}

Temperature (°C)

Endothermic

Exothermic

T_g

T_c

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

Fig. 3.1
Fig. 3.2
Fig. 3.3
Fig. 3.4

Se_{80}Te_{20}

Temperatures: 25°C/min, 20°C/min, 15°C/min, 10°C/min, 5°C/min

T_g, T_c

Endothermic

Exothermic
Fig. 3.5

Se<sub>75</sub>Te<sub>25</sub>

Temperature (°C)

Exothermic

Endothermic

T<sub>c</sub>

T<sub>g</sub>

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

40 60 80 100 120 140 160 180 200
TABLE - 3.1

Heating rate dependence of crystallization temperature, $T_c (^\circ \text{C})$ in $\text{Se}_{100-x}\text{Te}_x$ glassy alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate 5°C/min</th>
<th>Heating rate 10°C/min</th>
<th>Heating rate 15°C/min</th>
<th>Heating rate 20°C/min</th>
<th>Heating rate 25°C/min</th>
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<tbody>
<tr>
<td>$\text{Se}_{95}\text{Te}_5$</td>
<td>120</td>
<td>128</td>
<td>139</td>
<td>148</td>
<td>151</td>
</tr>
<tr>
<td>$\text{Se}<em>{90}\text{Te}</em>{10}$</td>
<td>117</td>
<td>122</td>
<td>126</td>
<td>130</td>
<td>136</td>
</tr>
<tr>
<td>$\text{Se}<em>{85}\text{Te}</em>{15}$</td>
<td>124</td>
<td>132</td>
<td>135</td>
<td>138</td>
<td>144</td>
</tr>
<tr>
<td>$\text{Se}<em>{80}\text{Te}</em>{20}$</td>
<td>105</td>
<td>111</td>
<td>115</td>
<td>119</td>
<td>122</td>
</tr>
<tr>
<td>$\text{Se}<em>{75}\text{Te}</em>{25}$</td>
<td>113</td>
<td>123</td>
<td>126</td>
<td>128</td>
<td>130</td>
</tr>
<tr>
<td>$\text{Se}<em>{70}\text{Te}</em>{30}$</td>
<td>114</td>
<td>120</td>
<td>123</td>
<td>125</td>
<td>128</td>
</tr>
</tbody>
</table>
Fig. 3.7
Fig. 3.8

*Se_{85}Te_{15}*

\[ \ln[-\ln(1-\alpha)] \]

-6  -4  -2  0  2  4  6

\[ \ln(\beta) \text{ (K/min)} \]

-6  -4  -2  0  2  4  6

-6  -4  -2  0  2  4  6

\[ \ln[-\ln(1-\alpha)] \]

90°C  95°C  100°C  105°C  110°C

*Se_{80}Te_{20}*

\[ \ln[-\ln(1-\alpha)] \]

-6  -4  -2  0  2  4  6

\[ \ln(\beta) \text{ (K/min)} \]

-6  -4  -2  0  2  4  6

-6  -4  -2  0  2  4  6

\[ \ln[-\ln(1-\alpha)] \]
**TABLE - 3.2**

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

<table>
<thead>
<tr>
<th>(\text{Se}_{95}\text{Te}_5)</th>
<th>(\text{Se}<em>{90}\text{Te}</em>{10})</th>
<th>(\text{Se}<em>{85}\text{Te}</em>{15})</th>
<th>(\text{Se}<em>{80}\text{Te}</em>{20})</th>
<th>(\text{Se}<em>{75}\text{Te}</em>{25})</th>
<th>(\text{Se}<em>{70}\text{Te}</em>{30})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) (°C)</td>
<td>(n)</td>
<td>(T) (°C)</td>
<td>(n)</td>
<td>(T) (°C)</td>
<td>(n)</td>
</tr>
<tr>
<td>100</td>
<td>2.30</td>
<td>100</td>
<td>3.01</td>
<td>95</td>
<td>1.78</td>
</tr>
<tr>
<td>105</td>
<td>1.96</td>
<td>105</td>
<td>2.52</td>
<td>100</td>
<td>1.40</td>
</tr>
<tr>
<td>110</td>
<td>1.67</td>
<td>110</td>
<td>2.04</td>
<td>105</td>
<td>1.20</td>
</tr>
<tr>
<td>115</td>
<td>1.43</td>
<td>115</td>
<td>1.56</td>
<td>110</td>
<td>1.04</td>
</tr>
</tbody>
</table>
The decrease of n with temperature indicates that crystallization mechanism gradually changes from sporadic to predetermined.

In order to calculate the activation energy for crystal growth, the values of $T_c$ at various heating rates were noted from the DSC scans. The plots of $\ln \beta$ as a function of $1000/T_c$ were obtained for Se$_{95}$Te$_5$, Se$_{90}$Te$_{10}$, Se$_{85}$Te$_{15}$, Se$_{80}$Te$_{20}$, Se$_{75}$Te$_{25}$ and Se$_{70}$Te$_{30}$ glassy samples. These curves are found to be straight lines, (see Fig. 3.10). $\Delta E_c$ was calculated from the slopes of these curves and the values of activation energy are given in Table 3.3. $\Delta E_c$ versus Te concentration curve is plotted in Fig. 3.11 for Se$_{100-x}$Te$_x$ glassy system. It is clear from the Table 3.3 and Fig. 3.11 that the activation energy increases with the increase of Te concentration in amorphous Se-Te system. This increase of $\Delta E_c$ with Te addition indicates that the rate of crystallization is faster in 'Te' rich alloys as compared to that of small concentration of Te. Such studies have also been made on Se-Te films [45]. This monotonic increase of $\Delta E_c$ with the increase of Te concentration can be understood in terms of bonding. Amorphous Se consists of long polymeric chains and Se$_8$ rings. When Te is added to it Se-Te, polymeric chains and Se-Te mixed rings are formed which makes the system more rigid. As Te concentration increases in Se-Te system it becomes more and more rigid and thus a larger amount of activation energy is required.
### TABLE - 3.3

Composition dependence of activation energy of crystallization in $\text{Se}_{100-x}\text{Te}_x$ glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_C$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}_{95}\text{Te}_5$</td>
<td>67.9</td>
</tr>
<tr>
<td>$\text{Se}<em>{90}\text{Te}</em>{10}$</td>
<td>106.0</td>
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<tr>
<td>$\text{Se}<em>{85}\text{Te}</em>{15}$</td>
<td>112.2</td>
</tr>
<tr>
<td>$\text{Se}<em>{80}\text{Te}</em>{20}$</td>
<td>116.4</td>
</tr>
<tr>
<td>$\text{Se}<em>{75}\text{Te}</em>{25}$</td>
<td>124.7</td>
</tr>
<tr>
<td>$\text{Se}<em>{70}\text{Te}</em>{30}$</td>
<td>153.1</td>
</tr>
</tbody>
</table>
$\Delta E_C$ (kJ/mole) vs. at \% Te

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

Fig. 3.11
3.4.2 \( \text{Se}_{100-x}\text{In}_x \) Glassy Alloys

DSC thermograms for \( \text{Se}_{95}\text{In}_5 \), \( \text{Se}_{90}\text{In}_{10} \), \( \text{Se}_{85}\text{In}_{15} \), \( \text{Se}_{80}\text{In}_{20} \) and \( \text{Se}_{70}\text{In}_{30} \) alloys were obtained at different heating rates and the results are shown in Figs. 3.12-3.16. It is clear from these figures that well defined exothermic peaks occur at crystallization temperature. The peak temperature increases with the increase in the heating rate (see Table - 3.4).

The extent of crystallinity \( \alpha \) at different temperatures was calculated by dividing the partial area by the total area of the exothermic peak. \( \ln[\ln(1-\alpha)^{-1}] \) versus \( \ln \beta \) curves were plotted at different temperatures for \( \text{Se}_{95}\text{In}_5 \), \( \text{Se}_{90}\text{In}_{10} \), \( \text{Se}_{85}\text{In}_{15} \), \( \text{Se}_{80}\text{In}_{20} \) and \( \text{Se}_{70}\text{In}_{30} \) glassy samples (see Figs. 3.17-3.19). It is clear from these figures that such plots yield straight lines and slope of these curves give the value of \( n \). The values of 'n' at various temperatures for each \( \text{Se}_{100-x}\text{In}_x \) glassy alloy are given in Table 3.5. It is evident from this table that the value of \( n \) decreases with the increasing temperature. Similar temperature dependence has been observed in Se-Te glassy system also (see section 3.4.1). The decrease of 'n' with the increase in temperature means that the crystallization mechanism changes from sporadic to predetermined [44].

The activation energy of crystallization for the glass forming materials under non-isothermal conditions can
Fig. 3.13

Se_{90}In_{10}

Exothermic

Endothermic

Temperature (°C)

T_c

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

40 60 80 100 120 140 160 180
Fig. 3.14

Se$_{85}$ In$_{15}$

Temperature (°C)

Exothermic

Endothermic

$T_c$

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

40 60 80 100 120 140 160 180 200

Fig. 3.14
Fig. 3.15

Se$_{80}$In$_{20}$

Temperature (°C)

Exothermic

Endothermic

$T_c$

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

40 60 80 100 120 140 160 180

Temperature (°C)

Fig. 3.15
Fig. 3.16

Se$_{70}$In$_{30}$

Temperature (°C)

Exothermic

Endothermic

T$_c$

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

50 70 90 110 130 150 170 190 210
TABLE - 3.4

Heating rate dependence of crystallization temperature $T_c$ (°C) in $\text{Se}_{100-x}\text{In}_x$ glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate 5°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
<th>20°C/min</th>
<th>25°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{95}$In$_5$</td>
<td>120</td>
<td>125</td>
<td>130</td>
<td>143</td>
<td>145</td>
</tr>
<tr>
<td>Se$<em>{90}$In$</em>{10}$</td>
<td>105</td>
<td>114</td>
<td>119</td>
<td>124</td>
<td>127</td>
</tr>
<tr>
<td>Se$<em>{85}$In$</em>{15}$</td>
<td>114</td>
<td>123</td>
<td>131</td>
<td>135</td>
<td>138</td>
</tr>
<tr>
<td>Se$<em>{80}$In$</em>{20}$</td>
<td>115</td>
<td>124</td>
<td>129</td>
<td>135</td>
<td>138</td>
</tr>
<tr>
<td>Se$<em>{70}$In$</em>{30}$</td>
<td>114</td>
<td>122</td>
<td>124</td>
<td>127</td>
<td>135</td>
</tr>
</tbody>
</table>
Fig. 3.17
Fig. 3.18
Fig. 3.19
**TABLE - 3.5**

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

<table>
<thead>
<tr>
<th>(\text{Se}_{95}\text{In}_5)</th>
<th>(\text{Se}<em>{90}\text{In}</em>{10})</th>
<th>(\text{Se}<em>{85}\text{In}</em>{15})</th>
<th>(\text{Se}<em>{80}\text{In}</em>{20})</th>
<th>(\text{Se}<em>{70}\text{In}</em>{30})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_n) ((^\circ\text{C}))</td>
<td>(T_n) ((^\circ\text{C}))</td>
<td>(T_n) ((^\circ\text{C}))</td>
<td>(T_n) ((^\circ\text{C}))</td>
<td>(T_n) ((^\circ\text{C}))</td>
</tr>
<tr>
<td>100 2.61</td>
<td>100 3.38</td>
<td>100 3.09</td>
<td>100 3.02</td>
<td>95 2.81</td>
</tr>
<tr>
<td>105 2.23</td>
<td>105 2.74</td>
<td>105 2.45</td>
<td>105 2.43</td>
<td>100 2.20</td>
</tr>
<tr>
<td>110 1.84</td>
<td>110 2.45</td>
<td>110 2.01</td>
<td>110 1.92</td>
<td>105 1.84</td>
</tr>
<tr>
<td>115 1.65</td>
<td></td>
<td></td>
<td></td>
<td>115 1.50</td>
</tr>
<tr>
<td>120 1.32</td>
<td></td>
<td></td>
<td></td>
<td>110 1.47</td>
</tr>
</tbody>
</table>
be calculated using eq. 3.10. The reciprocal of $T_c$ at various heating rates were plotted against $\ln\beta$ for Se$_{95}$In$_5$, Se$_{90}$In$_{10}$, Se$_{85}$In$_{15}$, Se$_{80}$In$_{20}$ and Se$_{70}$In$_{30}$ glassy samples (see Fig. 3.20). From the slopes of these curves the value of activation energy was calculated for Se$_{100-x}$In$_x$ glassy alloys. The results of these calculations are given in Table 3.6. It is clear from this table that activation energy of crystallization increases with the increase of In content in pure Se-In system. Fig. 3.21 shows a monotonic increase of $\Delta E$ with the In at $\chi$, indicating that the rate of crystallization is faster in In rich alloys than in alloys with small In contents.

3.4.3 Se$_{80-x}$Te$_{20}$In$_x$ Glassy Alloys

Figs. (3.4, 3.22-3.25) show the typical DSC thermograms for Se$_{80}$Te$_{20}$, Se$_{75}$Te$_{20}$In$_5$, Se$_{70}$Te$_{20}$In$_{10}$, Se$_{65}$Te$_{20}$In$_{15}$ and Se$_{60}$Te$_{20}$In$_{20}$ glassy samples at different heating rates. It is evident from these figures that well defined endothermic peaks are observed at glass transition temperature. At higher temperatures an exothermic peak is also observed which represents the crystallization temperature. An increase in $T_c$ is observed as the heating rate is increased from 5°C/min to 25°C/min (see table 3.7). To calculate the order parameter, the values of $\alpha$ were calculated and $\ln[\ln(1-\alpha)^{-1}]$ versus $\ln\beta$ curves were plotted. Figs. (3.8, 3.26 & 3.27) show such plots for Se$_{80-x}$Te$_{20}$In$_x$ ($0<\chi<20$) samples at
Fig. 3.20
**TABLE - 3.6**

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>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{95}$In$_5$</td>
<td>72.7</td>
</tr>
<tr>
<td>Se$<em>{90}$In$</em>{10}$</td>
<td>86.6</td>
</tr>
<tr>
<td>Se$<em>{85}$In$</em>{15}$</td>
<td>92.4</td>
</tr>
<tr>
<td>Se$<em>{80}$In$</em>{20}$</td>
<td>103.9</td>
</tr>
<tr>
<td>Se$<em>{70}$In$</em>{30}$</td>
<td>116.9</td>
</tr>
</tbody>
</table>
$\Delta E_x^2$ (kJ/mole) vs. (at\% In)

Fig. 3.21
Fig. 3.22

Se$_{75}$Te$_{20}$In$_5$

Temperature (°C)

Exothermic

Endothermic

$T_c$

$T_g$

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

Temperature (°C)
Fig. 3.23

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

Temperature (°C)

Exothermic

Endothermic

T$_g$

T$_c$

25°C/min

20°C/min

15°C/min

10°C/min

5°C/min

40 60 80 100 120 140 160
Figure 3.24: Thermogram of Se$_{65}$Te$_{20}$In$_{15}$ showing endothermic and exothermic reactions at different heating rates (5°C/min, 10°C/min, 15°C/min, 20°C/min, 25°C/min).
### TABLE - 3.7

Heating rate dependence of crystallization temperature, $T_c$ (°C) in Se$_{80-x}$Te$_{20}$In$_x$ glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate</th>
<th>5°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
<th>20°C/min</th>
<th>25°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td></td>
<td>105</td>
<td>111</td>
<td>115</td>
<td>119</td>
<td>122</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{20}$In$_5$</td>
<td></td>
<td>130</td>
<td>137</td>
<td>144</td>
<td>148</td>
<td>150</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{20}$In$_{10}$</td>
<td></td>
<td>117</td>
<td>123</td>
<td>127</td>
<td>133</td>
<td>136</td>
</tr>
<tr>
<td>Se$<em>{65}$Te$</em>{20}$In$_{15}$</td>
<td></td>
<td>103</td>
<td>110</td>
<td>123</td>
<td>125</td>
<td>129</td>
</tr>
<tr>
<td>Se$<em>{60}$Te$</em>{20}$In$_{20}$</td>
<td></td>
<td>111</td>
<td>116</td>
<td>122</td>
<td>124</td>
<td>127</td>
</tr>
</tbody>
</table>
different heating rates. The value of $n$ was calculated from the slope of these curves (see Table 3.8). It is clear from this table that $n$ decreases with the rise in temperature in all the glassy alloys. However, no systematic composition dependence in the values of $n$ is found in these glasses.

The activation energy of crystallization of the glass forming materials was calculated using eq. 3.3. The peak temperature at different heating rates was noted and $\ln \beta$ vs $1000/T_c$ curves were plotted. These curves yield straight lines for all the glassy alloys studied (see Fig. 3.28). The values of activation energy was calculated from the slope of these curves and the values are given in Table 3.9. It is clear from this table that activation energy, $\Delta E_c$, decreases with the In concentration upto 15 at %. However, with the further increase in In concentration in the binary Se-Te system, an increase in activation energy is observed (see Fig. 3.29).

As evident from Fig. 3.29, $\Delta E_c$ decreases with the increase of In concentration in $\text{Se}_{30-x}\text{Te}_{20}\text{In}_x$ upto $x=15$. However, at higher concentration of In ($x > 15$), a reversal in the trend is observed.

In, which belongs to group III of the periodic table, when added to the Se-Te system may break the Se-Te chains or Se-Te mixed rings to satisfy its coordination number and form a cross linked structure. Due to cross linking of In within the Se-Te system, the tendency of
Fig. 3.26
Fig. 3.27

\( \ln[-\ln(1-\alpha)] \)

\( \ln \beta \) (K/min)

- Se\(_{65}\)Te\(_{20}\)In\(_{15}\)
  - 95°C
  - 100°C
  - 105°C
  - 110°C

- Se\(_{60}\)Te\(_{20}\)In\(_{20}\)
  - 1.6
  - 2.0
  - 2.4
  - 2.8
  - 3.2
TABLE - 3.8

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

<table>
<thead>
<tr>
<th></th>
<th>Se$<em>{80}$Te$</em>{20}$</th>
<th>Se$<em>{75}$Te$</em>{20}$In$_5$</th>
<th>Se$<em>{70}$Te$</em>{20}$In$_{10}$</th>
<th>Se$<em>{65}$Te$</em>{20}$In$_{15}$</th>
<th>Se$<em>{60}$Te$</em>{20}$In$_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>n</td>
<td>T (°C)</td>
<td>n</td>
<td>T (°C)</td>
<td>n</td>
</tr>
<tr>
<td>90</td>
<td>2.11</td>
<td>115</td>
<td>3.41</td>
<td>105</td>
<td>2.34</td>
</tr>
<tr>
<td>95</td>
<td>1.78</td>
<td>120</td>
<td>2.82</td>
<td>110</td>
<td>1.82</td>
</tr>
<tr>
<td>100</td>
<td>1.52</td>
<td>125</td>
<td>2.35</td>
<td>115</td>
<td>1.53</td>
</tr>
<tr>
<td>105</td>
<td>1.34</td>
<td>135</td>
<td>2.03</td>
<td>120</td>
<td>1.39</td>
</tr>
</tbody>
</table>
Fig. 3.28

\[ \ln \beta (K/min) \]

\[ 1000/T_C (K^{-1}) \]
TABLE - 3.9

Composition dependence of activation energy of crystallization in Se$_{80-x}$Te$_{20}$In$_{x}$ glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_C$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td>116</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{20}$In$_{5}$</td>
<td>108</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{20}$In$_{10}$</td>
<td>103</td>
</tr>
<tr>
<td>Se$<em>{65}$Te$</em>{20}$In$_{15}$</td>
<td>71</td>
</tr>
<tr>
<td>Se$<em>{60}$Te$</em>{20}$In$_{20}$</td>
<td>120</td>
</tr>
</tbody>
</table>
Fig. 3.29

\[ \Delta E_c \text{ (kJ/mole)} \]

\[ \text{Se}_{80-x}\text{Te}_{20}\text{In}_x \]

\[ \text{In (at \%) } \]

Se\text{ }80-x\text{ }Te\text{ }20\text{ }In\text{ }x
crystallization is retarded. A decrease in $\Delta E_c$ at low concentration of In may be understood in terms of the decrease in the rate of crystallization due to the crossed linked structure of the Se-Te-In system. At higher concentration of In ($x > 15$), an increase in $\Delta E_c$ is observed which shows some kind of bonding change at this concentration. Similar kind of discontinuity has also been observed [46] in X-ray K-absorption edge studies at $x = 15$, which is explained in terms of the change in bonding at this composition.

3.4.4 \( \text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x \) Glassy Alloys

Crystallization kinetics of $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x$ ($0 < x < 1$) glassy alloys were studied using Differential Scanning Calorimeter. Figs. 3.4, 3.30&3.31 show the DSC scans at various heating rates for $\text{Se}_{80}\text{Te}_{20}$, $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$ and $\text{Se}_{80}\text{Te}_{19}\text{Sb}_{1}$ alloys. Well defined endothermic and exothermic peaks are observed in DSC scans, which indicates the glass transition and crystallization temperatures respectively. The peaks shift towards the higher temperatures as the heating rate is increased from 5°C/min to 25°C/min. The values of crystallization temperatures at different heating rates for $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x$ ($0 < x < 1$) alloys are indicated in Table 3.10. It is evident from this table that $T_c$ increases after incorporating Sb into binary $\text{Se}_{80}\text{Te}_{20}$ alloys.

The degree of crystallization $\alpha$ is calculated after dividing the partial area by the total peak area of the exothermic peak in a DSC curve.
$\text{Se}_{80} \cdot \text{Te}_{19.5} \cdot \text{Sb}_{0.5}$

**Fig. 3.30**

- **Temperature (°C)**
  - Exothermic
  - Endothermic
  - Curves for different heating rates: 25°C/min, 20°C/min, 15°C/min, 10°C/min, 5°C/min.
### TABLE 3.10

Heating rate dependence of crystallization temperature, $T_c (^\circ C)$ in $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x$ glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate 5°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
<th>20°C/min</th>
<th>25°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}<em>{80}\text{Te}</em>{20}$</td>
<td>105</td>
<td>111</td>
<td>115</td>
<td>119</td>
<td>122</td>
</tr>
<tr>
<td>$\text{Se}<em>{80}\text{Te}</em>{19.5}\text{Sb}_{0.5}$</td>
<td>107</td>
<td>114</td>
<td>119</td>
<td>122</td>
<td>125</td>
</tr>
<tr>
<td>$\text{Se}<em>{80}\text{Te}</em>{19}\text{Sb}_1$</td>
<td>126</td>
<td>132</td>
<td>139</td>
<td>144</td>
<td>149</td>
</tr>
</tbody>
</table>
To calculate the order parameter $n$, the eq. 3.10 was used. $\ln[\ln(1-\alpha)^{-1}]$ against $\ln\beta$ curves were plotted for $\text{Se}_{80}\text{Te}_{20}$, $\text{Se}_{80}\text{Te}_{19.1}\text{Sb}_{0.5}$ and $\text{Se}_{80}\text{Te}_{19}\text{Sb}_{1}$ glassy samples at various temperatures (see Figs. 3.8 & 3.32). Such plots yield straight lines, the values of $n$ were calculated from the slopes of these curves. Table 3.11 shows the results of these calculations for $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_{x}$ $(0 < x < 1)$ glassy alloys at different temperatures. It is clear from this table that the value of $n$ varies with temperature. Similar results were also reported for Se-Te alloys by Kotakata [55] using isothermal technique, i.e., by studying the change in d.c. conductivity during isothermal annealing. To calculate the activation energy of crystallization ($\Delta E_c$), the values of $T_c$ were noted from DSC curves at various heating rates and $\ln\beta$ versus $1000/T_c$ curves were plotted. Fig. 3.33 show such plots for $\text{Se}_{80}\text{Te}_{20-x}\text{Sb}_{x}$ $(0 < x < 1)$ alloys. The values of $\Delta E_c$ were calculated from the slopes of these curves using equation 3.10 and the values are mentioned in Table 3.12.

One can see from this table and figure that the value of $\Delta E_c$ decrease systematically as Sb is incorporated into the binary $\text{Se}_{80}\text{Te}_{20}$ alloy.

Schottmiller et al. [47] have studied the effect of addition of Te and group V elements (Bi, As) on the structure of glassy Se by Infra-red and Raman spectroscopies. According to them, in glassy Se about 40% of the atoms have a ring structure and 60% of the atoms are bonded as polymeric
Fig. 3.32
TABLE - 3.11

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

<table>
<thead>
<tr>
<th></th>
<th>Se$<em>{80}$Te$</em>{20}$</th>
<th>Se$<em>{80}$Te$</em>{19.5}$Sb$_{0.5}$</th>
<th>Se$<em>{80}$Te$</em>{19}$Sb$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T(\degree C)$</td>
<td>$n$</td>
<td>$T(\degree C)$</td>
<td>$n$</td>
</tr>
<tr>
<td>90</td>
<td>2.11</td>
<td>95</td>
<td>2.4</td>
</tr>
<tr>
<td>95</td>
<td>1.78</td>
<td>100</td>
<td>2.3</td>
</tr>
<tr>
<td>100</td>
<td>1.52</td>
<td>105</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Fig. 3.33

- $\text{Se}_80\text{Te}_{20}$
- $\text{Se}_80\text{Te}_{19.5}\text{Sb}_{0.5}$
- $\text{Se}_80\text{Te}_{19.0}\text{Sb}_{1.0}$

$\ln(\beta \text{ (K/min)})$ vs. $1000/T_C (\text{K}^{-1})$
TABLE 3.12
Composition dependence of activation energy of crystallization in \( \text{Se}_{80}\text{Te}_{20-x}\text{Sb}_x \) glassy alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \Delta E_c ) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Se}<em>{80}\text{Te}</em>{20} )</td>
<td>116</td>
</tr>
<tr>
<td>( \text{Se}<em>{80}\text{Te}</em>{19.5}\text{Sb}_{0.5} )</td>
<td>108</td>
</tr>
<tr>
<td>( \text{Se}<em>{80}\text{Te}</em>{19}\text{Sb}_1 )</td>
<td>95</td>
</tr>
</tbody>
</table>
chains. An introduction of Te decreases the 'Se' ring concentration favouring Se-Te mixed rings. A slight increase in the polymeric chains of Se is also observed.

The effect of incorporation of 'Sb' on the electrical properties of these alloys has also been studied by various workers [48-52]. It was found that the activation energy for d.c. conduction and thermoelectric power decrease with the addition of Sb content and photoconductive decay becomes slower. Since 'Sb' belongs to group V of the periodic table, when added to Se-Te system may break the Se-Te chains or Se-Te mixed rings to satisfy its coordination number and thus leads to cross linked structure, which enhances the disorder in the system and hence leads to a deeper penetration of the localized states into the energy gap. Due to cross-linking of 'Sb' within Se-Te system, the tendency of crystallization is retarded. One may expect that 'Sb' might enter into 'Se' polymeric chains making Se-Sb bonds. This is probably the reason why $T_c$ increases drastically on 'Sb' incorporation into Se$_{80}$Te$_{20}$ binary system (see Table 3.10). It is quite interesting to note that activation energy of crystallization decreases on 'Sb' incorporation into the Se-Te system (see Table 3.12). Such a decrease in the $\Delta E_c$ may also be understood in terms of the decrease in the rate of crystallization due to the cross linked structure of the Se-Te-Sb system.
3.5 **CONCLUSIONS**

Crystallization kinetics have been studied in various glassy alloys in Se-Te, Se-In, Se-Te-In and Se-Te-Sb glassy systems. Differential Scanning Calorimetry technique has been used for such studies. The crystallization temperature is found to be dependent on the heating rate. The degree of crystallization under non-isothermal conditions fits well with the theory of Matusita and Sakka. Multiscan technique has been successfully applied to calculate the activation energy of crystallization ($\Delta E_c$) and order parameter (n). In general, the values of n are found to decrease with the increase of temperature.

In Se$_{100-x}$Te$_x$ glassy system, $\Delta E_c$ increases with the increase in Te concentration which indicates that the rate of crystallization becomes faster as Te concentration increases in Se-Te system.

In Se$_{100-x}$In$_x$ glassy system also, $\Delta E_c$ is found to increase with the increase of In concentration. However, in Se-Te-In glassy system, $\Delta E_c$ decreases with the increase of In concentration up to 15 at.%. However, on further increase of In concentration, $\Delta E_c$ again increases. This is explained in terms of some kind of bonding change at higher concentration of In. In Se-Te-Sb system, $\Delta E_c$ decreases with the increase of Sb. The decrease of $\Delta E_c$ in Se-Te-In as well as in Se-Te-Sb as compared to binary Se-Te alloys is explained in
terms of cross linked structure in ternary systems. The glass transition and crystallization temperatures are also found to increase due to cross linking of third element (In and Sb) in Se-Te-In and Se-Te-Sb systems. These results indicate the stability of ternary alloys as compared to binary Se-Te system.