Crystallisation kinetics in glassy Se$_{100-x}$In$_x$

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Differential scanning calorimetry was used to study the crystallisation kinetics in the glassy Se$_{100-x}$In$_x$ system, where x varied from 5 to 30 at%. Scans were obtained at five different heating rates from 5 to 25 K/min and the theory of nonisothermal crystallisation is applied to calculate the activation energy, $\Delta E$, and the order parameter, n. The results indicate that $\Delta E$ increases monotonically with In concentration and that, in each case, the value of n decreases with temperature.

Chalcogenide glasses have recently gained much importance as, unlike conventional oxide glasses, they show semiconducting properties and hence can be used in various solid state devices. Since the crystallisation in some of these glasses occurs at quite moderate temperatures, the study of crystallisation kinetics is important from the application point of view. Such studies may also be useful in predicting the switching behaviour in these glasses as the type of switching (threshold or memory) depends upon the rate of crystallisation. Those materials which have a higher tendency to crystallise, normally show memory switching. Apart from the practical applications, such studies may also be helpful in the understanding of the short range order in these materials.

Amorphous Se–In alloys show a fairly large photo-voltaic effect and attempts have already been made to utilise them in solar cells. The electrical transport and optical properties of this system have therefore been studied in detail but no crystallisation studies have so far been reported.

In the present paper we report a study of the crystallisation kinetics in glassy Se–In alloys using differential scanning calorimetry. This technique is suitable for the study of crystallisation kinetics in chalcogenide glasses as they show a well defined exothermic peak on crystallisation.

The crystallisation kinetics of glass forming materials are controlled by a nucleation and growth mechanism which can be characterised by an activa-

\begin{equation}
\Delta E = \text{activation energy},
\end{equation}

and an Avrami exponent, $n$, according to the Johnson–Mehl–Avrami kinetic law, which is represented by the following equation in the case of isothermal transformation:

\begin{equation}
-\ln(1 - a) = (Kt)^n
\end{equation}

where $K$ is the rate constant and $a$ is the extent of crystallisation. The rate constant is related to the absolute temperature, $T$, by an Arrhenius type of equation

\begin{equation}
K = A \exp \left( - \frac{\Delta E}{RT} \right)
\end{equation}

The expression for $a$ under nonisothermal conditions has been derived by various workers, some of whom have demonstrated the use of the single scan technique to study crystallisation kinetics in oxide glasses and polymers. However, Marotta et al. have recently pointed out the limitation of the single scan technique and showed that it is difficult to calculate the value of $\Delta E$ and $n$ from the same set of measurements using the theory of nonisothermal crystallisation developed by Matusita & Sakka. According to this theory, the value of $n$ can be calculated from the slope of the plot of $\ln(1 - a)^{-1}$ against $\ln \beta$ and $\Delta E$ from the slope of $\ln \beta$ against $1/T_F$, where $\beta$ is the heating rate and $T_F$ is the temperature at which a maximum in exothermic peak is observed. The extent of crystallisation, $a$, at a particular temperature is calculated by dividing the partial area by the total area of the exothermic peak.

In the present study we used the multiple scanning technique and calculated the values of $\Delta E$ and $n$ for each alloy using the method described above. The scans were obtained at five heating rates, from 5 to 25 K/min, and the values of $n$ were calculated at various temperatures. The results indicate that $n$ depends on temperature in these materials and $\Delta E$ is strongly dependent upon composition.

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Experimental

Glassy Se$_{100-x}$In$_x$ alloys were prepared by rapid cooling from the melt. High purity (5N) materials were sealed in quartz ampoules with a vacuum $10^{-5}$ torr and kept inside a furnace where they were rocked for about 10 h at 600°C to make the melt homogeneous. Quenching was done in ice water and the glassy nature of the alloys was verified by x-ray diffraction.

The glassy alloys were ground to a fine powder for the differential scanning calorimetry studies and samples weighing 5–10 mg were placed in closed aluminium pans and heated at a constant rate from 50 to 200°C in a DuPont model 910 differential scanning calorimeter. Heating rates of 5, 10, 15, 20, and 25 K/min were chosen for the study of the crystallisation kinetics using the multiscan technique. Well defined exothermic peaks were obtained during crystallisation of the glassy alloys but no exothermic peak was observed if the crystallised sample was heated again, indicating that complete crystallisation had taken place in the first cycle. Almost identical conditions were maintained for the scans for different samples so that a comparison of the crystallisation parameters could be made in order to determine the effect of In concentration.

Results and discussion

Figure 1 shows the thermograms for the Se$_{95}$In$_5$ alloy; similar results were obtained with Se$_{90}$In$_{10}$, Se$_{85}$In$_{15}$, Se$_{80}$In$_{20}$, and Se$_{75}$In$_{30}$ alloys. It is clear from Figure 1 that well defined exothermic peaks were obtained at all heating rates and that the peak temperature, $T_p$, increases as the heating rate is increased.

The degree of crystallinity, $\alpha$, at different temperatures is calculated by dividing the partial area by the total area of the exothermic peak and this was done at all the heating rates for each alloy. To calculate the order parameter, $n$, curve of $\ln(1-\alpha)^{-1}$ against ln $\beta$ were plotted at various temperatures for each sample and Figure 2 shows such plots for the Se$_{95}$In$_5$ alloy; it is clear from this Figure that such plots yield straight lines. Similar results (not shown here) were also obtained for the other alloys. As has been pointed out, the value of $n$ is calculated from the slopes of the curves shown in Figure 2 and Table 1 gives the results of these calculations at various temperatures for all the alloys used in the present study. It is evident from this Table that, in each alloy, the value of $n$ decreases with increasing temperature, and a similar temperature dependence has been observed in various other glassy systems. Such a decrease in $n$ means that the crystallisation mechanism gradually changes from sporadic to predetermined.

To calculate the activation energy of crystallisation, $\Delta E$, the reciprocal of $T_p$ at various heating rates was plotted against ln $\beta$. Figure 3 shows such a plot for the Se$_{95}$In$_5$ alloy and it is clear from this Figure that it
yields a straight line. Similar results were obtained with all the other alloys used in the present study and the value of $\Delta E$ may be calculated from this slope; the results are given in Table 2. Figure 4 shows a plot of $\Delta E$ against In content and it is clear that $\Delta E$ increases almost linearly with increasing In, indicating that the rate of crystallisation is faster in In rich alloys than in alloys with small In contents.

**Conclusions**

Nonisothermal crystallisation in glassy $\text{Se}_{100-x}\text{In}_x$ was studied by differential scanning calorimetry. The results indicate that the degree of crystallisation, $\alpha$, fits well with the theory of Matusita & Sakka. A multiple scanning technique was used to calculate $\Delta E$ and $n$ according to the above theory and it was found that $n$ decreases with temperature in all the glassy samples studied while $\Delta E$ increases with the increasing In content. However, no systematic variation of $n$ with In content was observed.

**References**

Short Notes

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Crystallization Kinetics in Glassy Se$_{80}$Te$_{20-x}$Sb$_{x}$

By

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Se-Te alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller aging effects as compared to pure Se glass. The effect of incorporation of Sb on the electrical properties of these alloys has been studied by various workers /1 to 5/. In general, it is observed that the dc conductivity increases, the activation energy for dc conduction decreases, the thermoelectric power decreases, and the photoconductive decay becomes slower on incorporation of Sb to the binary Se$_{80}$Te$_{20}$ alloy. To explain the above results it is generally assumed that the addition of Sb in the Se-Te system leads to a cross-linking of the Se-Te chains which enhances the disorder in the system and hence leads to a deeper penetration of the localized states into the energy gap. The present note reports crystallization kinetics studies in glassy Se$_{80}$Te$_{20-x}$Sb$_{x}$ alloys, where $x = 0, 0.5,$ and 1, with a view to study the effect of Sb incorporation on the crystallization behaviour of the Se$_{80}$Te$_{20}$ binary alloy. Calorimetric measurements have been made under non-isothermal conditions and a multi-scan technique is used for the crystallization studies.

Glassy alloys of Se$_{80}$Te$_{20-x}$Sb$_{x}$ with $x = 0, 0.05,$ and 1 were prepared by the quenching technique. 5N pure materials were sealed in quartz ampoules under a vacuum of $\approx 10^{-5}$ Torr. The ampoules were kept inside a furnace where the temperature was raised slowly (3 to 4 K/min) to 600 °C. The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous and the quenching was done in ice water. The glassy nature of the alloys was verified by X-ray diffraction.

The glassy alloys thus prepared were ground to make fine powder for the thermoanalytical studies. DSC scans were obtained by heating 6 to 15 mg of the powdered sample kept in closed aluminium pans at constant heating rates (5 to 25 K/min). A Dupont type DSC Thermal Analyser (model 910 Differential Scanning Calorimeter) was used for recording the thermograms. The temperature was varied from 50 to 200 °C and the recording was done during the heating cycle. DSC scans showed a well defined endothermic peak at the glass transition temperature

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and an exothermic peak at the crystallization temperature. If the crystallized sample was heated again, no endothermic or exothermic peak was observed in the above temperature range which ensured complete crystallization in the first cycle. Measurements were made under almost identical conditions for different samples so that a comparison of the crystallization parameters could be made in order to understand the effect of Sb incorporation upon the binary $\text{Se}_{80}\text{Te}_{20}$ glassy alloy.

Under non-isothermal conditions, the degree of crystallization ($\alpha$) at temperature $T$ is well expressed by the following equation derived by Matusita and Sakka /6, 7/ from the classical Johnson-Mehl-Avrami equation:

\[-\ln(1-\alpha) = \frac{B}{\beta^n} \exp\left(\frac{n\Delta E}{RT}\right),\]

where symbols have their usual meanings /6, 7/.

Marotta et al. /8/ have recently pointed out the limitations of the use of the single scan technique to calculate the activation energy $\Delta E$ and the order parameter $n$. They have stressed that the multiple scan technique should be used to calculate $\Delta E$ and $n$ separately. According to them, for evaluating $n$, different values of $\alpha$ have to be determined at the same temperature $T$ on the multiple DSC scan recorded at different heating rates ($\beta$). As evident from (1), the value of $n$ can be calculated by plotting $\ln \ln(1-\alpha)$ versus $\ln \beta$.

The activation energy $\Delta E$ can be evaluated /8/ by determining, on each curve, the temperature $T$ corresponding to the same crystallization degree $\alpha$. As it has been demonstrated /9/ that, at peak temperature ($T_c$), the crystallization degree $\alpha$ does not depend on the heating rate, the value of $\Delta E$ can therefore be calculated from the slope of the $\ln \beta$ versus $1/T_c$ curve as also suggested by Ozawa /10/.

Fig. 1 and 2 show the DSC scans at different heating rates for $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$ glassy alloys. The results for $\text{Se}_{80}\text{Te}_{19}\text{Sb}_{1}$ alloy were similar. It is clear from these figures that well defined endothermic and exothermic peaks are observed in DSC thermograms which indicate glass transition and crystallization temperatures, respectively. The peaks shift towards higher temperatures as the heating rate is increased from 5 to 25 K/min. To compare the glass transition temperature ($T_g$) and crystallization temperature ($T_c$), the values of these parameters, at a particular heating rate 10 K/min, are indicated in Table 1. It is evident from this table that $T_g$ and $T_c$ both increase after incorporating Sb into the binary $\text{Se}_{80}\text{Te}_{20}$ alloy.

The degree of crystallization ($\alpha$) is calculated after dividing the partial area by the total area of the exothermic peak in a DSC curve. To calculate the order parameter $n$, $\ln \ln (1-\alpha)^{-1}$ versus $\log \beta$ curves are plotted at various temperatures. Fig. 3 shows such plots for $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$ glassy
Fig. 1. DSC scans at different heating rates for glassy Se$_{80}$Te$_{20}$ alloy

Fig. 2. DSC scans at different heating rates for glassy Se$_{80}$Te$_{19.5}$Sb$_{0.5}$ alloy

Table 1

The glass transition temperature, crystallization temperature, and the activation energy of crystallization for various glassy alloys at a heating rate of 10 K/min

<table>
<thead>
<tr>
<th>no.</th>
<th>sample</th>
<th>$T_g$ (K)</th>
<th>$T_c$ (K)</th>
<th>$\Delta E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td>337</td>
<td>384</td>
<td>116</td>
</tr>
<tr>
<td>2</td>
<td>Se$<em>{80}$Te$</em>{19.5}$Sb$_{0.5}$</td>
<td>339</td>
<td>387</td>
<td>108</td>
</tr>
<tr>
<td>3</td>
<td>Se$<em>{80}$Te$</em>{19}$Sb$_{1}$</td>
<td>342</td>
<td>405</td>
<td>95</td>
</tr>
</tbody>
</table>
Fig. 3. ln ln(1-α) versus ln β curves for glassy a) Se$_{80}$Te$_{20}$ and b) Se$_{80}$Te$_{19.5}$Sb$_{0.5}$ alloys. The solid lines represent the least-squares fit, T = ○ 363 K, ● 368 K, × 373 K, □ 378 K.

alloys. The results for the Se$_{80}$Te$_{19}$Sb$_{1}$ alloy were similar. The values of n were calculated from the slopes of these curves. Table 2 shows the results of these calculations for various glassy alloys at different temperatures. It is clear from this table that the value of n varies with temperature. Similar results are also reported for Se-Te alloys by Kotkata and El-Mously /11/ using the isothermal technique, i.e., by studying the change in dc conductivity during isothermal annealing.

To calculate the activation energy of crystallization (ΔE), the values of Tc are noted from the DSC curves at various heating rates and ln β versus 10$^3$/Tc curves are plotted. Fig. 4 shows such plots for various glassy alloys used in the present study. The values of ΔE can be calculated from the slopes of these curves. Such values of ΔE are mentioned in Table 1 for various glassy alloys. It is clear from this table that the value of ΔE decreases systematically as Sb is incorporated into the binary Se$_{80}$Te$_{20}$ alloy.

**Table 2**

Temperature dependence of the order parameter (n) in various glassy alloys

<table>
<thead>
<tr>
<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(K)</td>
<td>n</td>
<td>T(K)</td>
</tr>
<tr>
<td>363</td>
<td>2.1</td>
<td>368</td>
</tr>
<tr>
<td>368</td>
<td>1.8</td>
<td>373</td>
</tr>
<tr>
<td>373</td>
<td>1.5</td>
<td>378</td>
</tr>
</tbody>
</table>
Fig. 4. In $\beta$ versus $10^3/T_c$ curves for various glassy alloys. The solid lines represent the least-squares fit:

- $\text{Se}_80\text{Te}_{20}$
- $\text{Se}_80\text{Te}_{19.5}\text{Sb}_{0.5}$
- $\text{Se}_80\text{Te}_{19}\text{Sb}_1$

Schottmiller et al. /12/ 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 chains. An introduction of Te decreases the Se ring concentration favouring Se-Te mixed rings. A slight increase in the polymeric chain of Se is also observed.

Sb, which belongs to group V 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 Sb within the Se-Te system, the tendency of crystallization is retarded. This is probably the reason why $T_c$ increases drastically on Sb incorporation into the Se-Te system (see Table 1). It is interesting to note that the activation energy of crystallization decreases on Sb incorporation into the Se$_{80}$Te$_{20}$ binary system (see Table 1). Such a decrease in $\Delta E$ 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.

References
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Kinematic studies by differential scanning calorimetry of the glass transition and crystallisation in Se\textsubscript{100-x}Te\textsubscript{x}

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From the heating rate dependence of the glass transition and crystallisation temperatures, the activation energy for structural relaxation (\(\Delta E_\text{s}\)) and the activation energy of crystallisation (\(\Delta E_\text{c}\)) are calculated and their composition dependence is discussed in terms of the structure of the Se–Te glassy system.

Among chalcogenide glasses, Se–Te glassy alloys have gained much importance because of their superiority over amorphous Se. Alloying of Se with Te reduces its electronic band gap and thus results in a photo-receptor having a more desirable spectral response for xerographic purposes. Apart from this, these alloys have higher photosensitivity, greater hardness, higher crystallisation temperature, and smaller ageing effects than Se glass and hence can be used in various other devices.

The electrical, dielectric, and x-ray spectroscopic studies of this system have already been reported by us\textsuperscript{(1–3)} and the present paper reports kinematic studies of glass transition and crystallisation in Se\textsubscript{100-x}Te\textsubscript{x} alloys using differential scanning calorimetry. The activation energies for structural relaxation and crystallisation have been calculated from the dependence of glass transition and crystallisation temperatures upon heating rate, and their composition dependence is discussed in terms of the structure of the Se–Te glassy system.

Experimental

Se\textsubscript{100-x}Te\textsubscript{x} glassy alloys, where \(x = 5, 10, 15, 20, 25,\) or 30, are prepared by quenching. Materials (99-999\% pure) were weighed according to their atomic percentages and were sealed in quartz ampoules (length \(\sim 5\) cm, internal diameter \(\sim 8\) mm) in a vacuum of \(\sim 10^{-5}\) Torr. The ampoules were placed inside a furnace where the temperature was raised to 600°C at a rate of 3–4 deg C/min and frequently rocked for 10 h at the maximum temperature to make the melt homogeneous. The melts were quenched in ice water and the glassy nature of the alloys was ascertained by x-ray diffraction. To attain thermodynamic equilibrium, the samples were kept in the dark at room temperature for about a month before calorimetric measurements\textsuperscript{(4)}.

The alloys were ground to a fine powder for the differential scanning calorimetry studies, 5–10 mg of the powdered sample being placed in closed aluminium pans and heated at a constant rate using a Dupont series 99 thermal analyser (model 910 differential scanning calorimeter): heating rates of 5, 10, 15, 20, and 25 deg C/min were used.

Results

Glass transition kinetics

Figure 1 shows typical differential scanning calorimetry thermograms at different heating rates for the Se\textsubscript{90}Te\textsubscript{10} glassy alloy.
imetry thermograms at different heating rates for the Se₉₀Te₁₀ alloy, and it is evident from this Figure that well defined endothermic peaks are observed at the glass transition temperature ($T_g$) rather than a shift in the base line. Above the glass transition temperature there is an exothermic peak which represents the crystallisation temperature ($T_c$). It is clear that both $T_g$ and $T_c$ shift to higher temperatures as the heating rate is increased from 5 to 25 deg C/min and similar results (not shown here) were obtained with the other alloys used in the present study.

Figure 2 presents plots of the variation of $T_g$ with Te content at a heating rate of 10 deg C/min and it is clear from this that $T_g$ increases with increasing Te; similar results were obtained at other heating rates. This increase in $T_g$ with Te content in the Se–Te system has also been reported by other workers$^{(5–7)}$ and it may be associated with an increase in the number of long polymeric chains or with an increase in the effective molecular weight as the Te content increases as suggested by Das et al.$^{(5)}$

A shift in the base line or an endothermic peak is normally observed in differential scanning calorimetry due to a change in specific heat at the glass transition temperature. However, such an endothermic peak may also be expected in chalcogenide glasses when the glassy system relaxes quickly at the glass transition temperature due to a decrease in the viscosity; this peak is caused by a rapid increase in enthalpy due to structural relaxation. The heating rate ($\beta$) dependence of the glass transition in these glasses may therefore be interpreted in terms of thermal relaxation phenomena and it has been shown by Moynihan et al.$^{(9)}$ that the activation energy for structural relaxation ($\Delta E_s$) can be related to $T_g$ and $\beta$ by

$$\frac{d\ln \beta}{d\left(\frac{1}{T_g}\right)} = -\Delta E_s/R.$$  \hspace{1cm} (1)

It is evident from Equation (1) that a plot of ln$\beta$ against $1/T_g$ should yield a straight line and that the activation energy involved in the molecular motions and rearrangements around $T_g$ can be calculated from the slope of this plot.

Figure 3 shows plots of ln$\beta$ against 1000/$T_g$ for various glassy alloys in Se₁₀₀–Teₓ systems and, in the present work, such plots are found to be straight lines. The values of $\Delta E_s$ calculated from the slopes shown in Figure 3 are plotted in Figure 4 as a function of Te content and it is clear from this Figure that $\Delta E_s$ increases with Te content up to $x = 15$ and then decreases with further increases in Te content. The reasons for such a behaviour are discussed later in this paper.

![Figure 2](image1.png)

**Figure 2.** Composition dependence of the glass transition temperature at a heating rate of 10 deg C/min

![Figure 3](image2.png)

**Figure 3.** Heating rate dependence of the glass transition temperature

![Figure 4](image3.png)

**Figure 4.** Composition dependence of the activation energy for thermal relaxation
Crystalisation kinetics

The crystalisation kinetics of glass forming materials are controlled by nucleation and growth mechanism which can be characterised by an activation energy ($\Delta E_c$) and an Avrami exponent ($n$) according to the Johnson–Mehl–Avrami kinetic law.(9–11)

An expression for the extent of crystalisation ($\alpha$) has been derived under nonisothermal conditions by various workers,(12–15) some of whom have demonstrated the use of a single scan technique to study the crystalisation kinetics in oxide glasses and polymers. Recently, however, Marotta et al.(17) have pointed out the limitations of this technique and have shown that it is rather difficult to calculate the value of $\Delta E_c$ and $n$ using only a single scan. They have suggested that a multiple scan technique can be used successfully for the determination of $\Delta E_c$ and $n$ from the same set of measurements using the theory of nonisothermal crystallisation developed by Matusita & Sakka.(16) According to this theory, the value of $n$ can be calculated from the slope of the plot of $\ln \ln (1 - \alpha)^{-1}$ against $\ln \beta$ and $\Delta E_c$ from the slope of the plot of $\ln \beta$ against $1/T_c$, where $T_c$ is the temperature at which the maximum in the exothermic peak is observed.

We have used the above technique to determine the values of $\Delta E_c$ and $n$ for various glassy alloys in the present work. The degree of crystallinity was calculated at all heating rates for each of the alloys by dividing the partial area by the total area of the exothermic peak in a differential scanning calorimetry curve. To calculate the order parameter, $n$, curves for $\ln \ln (1 - \alpha)^{-1}$ against $\ln \beta$ were plotted at various temperatures for all samples, and from Figure 5, which shows plots for the Se$_{90}$Te$_{10}$ alloy, it is clear that such plots yield straight lines; similar results were obtained for the other alloys. The values of $n$ calculated from the slopes of the curves shown in Figure 5 are given in Table 1 at various temperatures for all the alloys used in the present study. It is evident from this Table that, for every alloy, the value of $n$ decreases with increasing temperature.

**Table 1. Temperature dependence of the order parameter in various alloys**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>368</th>
<th>373</th>
<th>378</th>
<th>383</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{90}$Te$</em>{10}$</td>
<td>373</td>
<td>2.33</td>
<td>2.00</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{15}$</td>
<td>301</td>
<td>2.14</td>
<td>1.79</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{20}$</td>
<td>206</td>
<td>1.53</td>
<td>1.27</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{25}$</td>
<td>149</td>
<td>1.30</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{30}$</td>
<td>149</td>
<td>1.30</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{35}$</td>
<td>149</td>
<td>1.30</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 5. $\ln \ln (1 - \alpha)^{-1}$ as a function of $\ln \beta$ at different temperatures for the Se$_{90}$Te$_{10}$ glassy alloy: the solid lines represent the least squares fit*

*Figure 6. $1/T_c$ as a function of $1000/T_\alpha$ for the Se$_{90}$Te$_{10}$ glassy alloy: the solid line represents the least squares fit*

*Figure 7. Composition dependence of $\Delta E_c$ in glassy Se$_{100-x}$Te$_x$ alloys*
To calculate the activation energy for crystallisation, the values of the peak temperature were noted at each heating rate. Plots of ln$\beta$ against 1000/$T_p$ were made for all samples and from Figure 6, which shows such a plot for the Se$_{90}$Te$_{10}$ alloy, it is clear that the plots yield straight lines. Similar results were obtained for the other alloys in the system. The value of $\Delta E_c$ was calculated from the slope of these plots as described by Marotta et al.\(^{(17)}\) and Figure 7 presents plots of $\Delta E_c$ against Te content: it is clear from this Figure that $\Delta E_c$ increases monotonically as the content increases.

Discussion

Tellurium glass contains short chains, while selenium glass consists of a mixture of long chains and Se$_2$ rings. The introduction of Te decreases the number of Se rings and increases the number of long Se–Te polymeric chains and Se–Te mixed rings; this makes the system more rigid, so that a higher activation energy is needed for molecular motions and re-arrangements near the glass transition temperature. As the Te content increases further, the possibility of Te–Te bonding arises and, as Te chains are shorter, molecular motion and rearrangements may take place at lower activation energies near the glass transition temperature.

In the present study, $\Delta E_c$ increases up to 15 at% Te and then decreases as the Te content increases further, and this may be understood in terms of the above concepts. However, the activation energy for crystallisation ($\Delta E_c$) increases monotonically with increasing Te, indicating that the rate of crystallisation is faster in Te rich alloys than in alloys with small Te contents.

The order parameter ($n$) decreases with the increasing temperature in all the alloys in the Se–Te system. A similar temperature dependence has also been observed by Elmously & El-Zaida\(^{(18)}\) and such a decrease in $n$ means that the crystallisation mechanism gradually changes from sporadic to predetermined.

Conclusions

Kinematic studies made on various glassy alloys in Se–Te system make it clear that the glass transition and crystallisation temperatures depend on the heating rate. Such studies can be used to determine the activation energies for molecular motions and rearrangements around the glass transition temperature which, in turn, are useful in the understanding of thermal relaxation phenomena in these glasses.

The studies the crystallisation kinetics indicate that the extent of crystallisation under nonisothermal conditions fits well with the theory of Matusita & Sakka. A multiple scanning technique can be successfully used to calculate the activation energy for crystallisation and the order parameter, the results indicating that the activation energy for crystallisation increases monotonically as the Te content increases.

References

Amorphous to crystalline transition in glassy Se\textsubscript{100-x}In\textsubscript{x}

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The crystallization kinetics in glassy Se\textsubscript{100-x}In\textsubscript{x} is studied using isothermal annealing near the crystallization temperature and measuring the DC conductivity as a function of time. The kinetic parameters are calculated using Avrami's theory of isothermal transformation and the results are found to be in agreement with those obtained using non-isothermal measurements by thermo-analytical methods in Se\textsubscript{100-x}In\textsubscript{x} glassy systems.

1. Introduction

Glassy Se-In alloys have drawn great attention because of their potential use in solar cells [1, 2]. As the crystallization temperature of these alloys is not too far from ambient temperature, crystallization studies of this system are important from an application point of view. In our earlier communication [3] we studied the crystallization kinetics of glassy Se\textsubscript{100-x}In\textsubscript{x} systems by differential scanning calorimetry, hence using non-isothermal measurements. The results indicated that the activation energy of crystallization was highly composition dependent in this system.

In the present paper we report the crystallization studies in glassy Se\textsubscript{100-x}In\textsubscript{x} where 0 ≤ x ≤ 30 using an isothermal technique, i.e. by isothermal annealing near the crystallization temperature and measuring the DC conductivity as a function of time. The kinetic parameters are calculated by fitting the extent of crystallization to Avrami's theory of isothermal transformation. The results indicate that the activation energy of crystallization increases monotonically with the In concentration as also found in the non-isothermal DSC measurements [3].

2. Theory of measurement

During isothermal transformation, the extent of crystallization (α) of a certain material is represented by the Avrami equation [4] as follows

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

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

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

where \( K_0 \) is a constant and \( \Delta E \) 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. DC conductivity has been used [5-7] as a parameter to study the crystallization kinetics in chalcogenide glasses. Landauer [8] 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

\[ \alpha = \left( \frac{\sigma_\alpha + 2\sigma_d}{\sigma + 2\sigma_d} \right) \left( \frac{\sigma - \sigma_\alpha}{\sigma - \sigma_d} \right) \]
where \( \sigma \) is the overall conductivity of the mixture, \( \sigma_t \) the conductivity of the crystalline phase and \( \sigma_a \) the conductivity of the amorphous phase.

Equation (3), as pointed out by Landauer, is only valid for spheroid inclusions and cannot 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 case.

Odelevsky [9] has suggested a power formula to calculate the conductivity of a mixture \( (\sigma) \) during amorphous to crystalline transformation. According to ref. [9],

\[
\sigma' = a \sigma_c + (1 - a) \sigma_a
\]  

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

\[
\sigma = a \sigma_c + (1 - a) \sigma_a
\]  

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

\[
\log \sigma = a \log \sigma_c + (1 - a) \log \sigma_a
\]  

Kotkata et al. [10] have used (5) and (6) to calculate the extent of crystallization in some Se based chalcogenide glasses and found that eq. (6) is more satisfactory as \((\sigma_c - \sigma_a)\) is quite large in these glasses.

In the present case the conductivity increases by several orders of magnitude on crystallization hence eq. (6) should be used to calculate \( a \) by measuring \( \sigma \) as a function of time during isothermal annealing at temperatures near the crystallization temperature. Once the values of \( a \) as a function of time are known at different isothermal temperatures of transformation, the kinetic parameters \((\Delta E \text{ and } \eta)\) can be calculated using eqs. (1) and (2).

3. Experimental

Glassy alloys of \( \text{Se}_{x} \text{In}_{1-x} \), with \( x = 5, 10, 15, 20 \) and 30 were prepared by a quenching technique. High purity (5N) materials were sealed in quartz ampoules with a vacuum \( \sim 10^{-3} \text{Torr} \). The ampoules were kept inside a furnace where the temperature was raised slowly \((3-4 \degree C/\text{min})\) to \( 600 \degree C \). The ampoules were rocked frequently for \( 10 \) h at maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was verified by X-ray diffraction.

The glassy alloys were ground to a very fine powder and pellets (diameter \( \sim 6 \text{mm} \) and thickness \( \sim 0.5 \text{mm} \)) were obtained after compressing the powder in a die at a base pressure of \( 3-4 \) tons.

The amorphous to crystalline transformation \((\text{a-c})\) was studied by measuring the DC conductivity \( (\sigma) \) as a function of time \((\frac{1}{2} \text{min intervals})\) at various temperature between the glass transition \( (T_g) \) and melting \( (T_m) \) temperatures.

The conductivity measurements were taken in vacuum \( \sim 10^{-3} \text{Torr} \) by mounting the samples in a specially designed metallic sample holder. The current was measured using a Keithley Electrometer (model 614). The temperature was measured using a calibrated copper constantan thermocouple. Different pellets were taken for each temperature of annealing. The annealing temperature was obtained at a fast heating rate and then maintained constant till saturation in the current was reached.

4. Results and discussions

Figure 1 shows the time dependence of the DC conductivity at various annealing temperatures for glassy \( \text{Se}_{70} \text{In}_{30} \). The results for other glassy alloys, i.e., \( \text{Se}_{x} \text{In}_{3}, \text{Se}_{x} \text{In}_{10}, \text{Se}_{x} \text{In}_{15}, \text{Se}_{x} \text{In}_{20} \) were also of the same nature. It is clear from fig. 1 that the DC 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 fig.
Fig. 1. Annealing time dependence on the DC conductivity for the Se$_{70}$In$_{30}$ sample during isothermal amorphous-crystalline phase transformation.

1. 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 the crystalline phase. The part CD which shows a sharp rise in $\sigma$ may be attributed to rapid growth of the 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 a certain time (point D).

In the present study we are interested to understand the crystallization kinetics of crystal growth, i.e. the CD part of the curve in fig. 1. Using the measured value of conductivity, $\sigma$ is calculated as a function of time at various annealing temperatures using eq. (6) where $\sigma_g$ is taken as the conductivity at point C as we are interested in the growth kinetics of crystallization. $\sigma_g$ represents the conductivity at point D in each curve of fig. 1. The variation of $\sigma$ as a function of time for glassy Se$_{70}$In$_{30}$ is shown in fig. 2. For the other glassy alloys similar results were obtained.
Following eq. (1), the value of the order parameter \( n \) can be calculated by plotting \( \ln \left[ \ln \left( 1 - \alpha \right) \right] \) versus \( \ln t \) at different annealing temperatures. Figure 3 shows such plots in the case of glassy Se\textsubscript{a},In\textsubscript{b}. For other glassy alloys similar results were obtained. The values of \( n \) at various temperatures are given in Table 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 [10] in the present glassy system.

For calculating the activation energy of crystallization (\( \Delta E \)), the values of \( K \) were evaluated from the intercept of the curves in fig. 3. The ln \( K \) versus 1000/\( T \) curves (see fig. 4) come out to be straight lines for all the glassy alloys confirming the validity of eq. (2) in the present case. The values of \( \Delta E \) are calculated for each glassy alloy from the slope of ln \( K \) versus 1000/\( T \) curve (fig. 4). The values of \( \Delta E \) thus calculated are given in Table 2 which also contains the values of \( \Delta E \) obtained from the non-isothermal DSC measurements [3].

It is evident from Table 2 that \( \Delta E \) increases with the increase of the In concentration in Se\textsubscript{1-x},In\textsubscript{x} system. Figure 5 shows the variation of \( \Delta E \) with the In concentration which indicates that \( \Delta E \) increases monotonically with the In concentration.

This is in agreement with our DSC measure-
Fig. 3. Avrami plots of the crystallization of Se$_{100-x}$In$_x$ for different isotherms.

Fig. 4. Arrhenius plots of crystallization of Se$_{100-x}$In$_x$.

Fig. 5. Composition dependence of the activation energy of crystallization in the Se$_{100-x}$In$_x$ system.

Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>$n$</th>
<th>$T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{95}$In$_5$</td>
<td>7.0</td>
<td>73</td>
</tr>
<tr>
<td>Se$<em>{90}$In$</em>{10}$</td>
<td>0.94</td>
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</tr>
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<td>Se$<em>{85}$In$</em>{15}$</td>
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<td>83</td>
</tr>
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<td>Se$<em>{80}$In$</em>{20}$</td>
<td>0.85</td>
<td>88</td>
</tr>
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<td>Se$<em>{75}$In$</em>{25}$</td>
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<td>93</td>
</tr>
<tr>
<td>Se$<em>{70}$In$</em>{30}$</td>
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<td>103</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta E$ (kJ/mol)</th>
<th>$\Delta E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{95}$In$_5$</td>
<td>62.8</td>
<td>72.7</td>
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<tr>
<td>Se$<em>{90}$In$</em>{10}$</td>
<td>70.3</td>
<td>86.6</td>
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<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$<em>{75}$In$</em>{25}$</td>
<td>100.3</td>
<td>116.9</td>
</tr>
</tbody>
</table>

Table 1: Values of $n$ at various annealing temperatures.

Table 2: Composition dependence of $\Delta E$. 
ment,[3] in the same glassy system. A difference of 15 kJ/mol is, however, observed (see table 2) in the ΔE values obtained from the present measurements as compared to the DSC measurements. It might be due to some kind of artifact in the data analysis as in the case of DSC we have used the non-isothermal technique while in the present case the isothermal technique.

5. Conclusions

Using the electrical conductivity as a characteristic quantity to follow the growth of crystalline phases in the amorphous matrix, the crystallization kinetics have been studied in glassy Se_{100-x}In_x, where x = 5, 10, 15, 20 and 30. The kinetic parameters have been calculated by fitting the extent of crystallization to Avrami's theory of isothermal crystallization. The results indicate that the activation energy of crystallization increases with the In concentration. This is in agreement with our earlier results obtained in non-isothermal crystallization studies using a thermo-analytical technique [3].

Acknowledgement

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References

Crystallization kinetics in glassy Ge\textsubscript{20}Se\textsubscript{80-\(x\)}In\textsubscript{x} alloys

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Crystallization kinetics is studied in glassy Ge\textsubscript{20}Se\textsubscript{80-\(x\)}In\textsubscript{x} (0 \(\leq\) \(x\) \(\leq\) 20) using isothermal annealing at temperatures between the glass transition and melting. D.c. conductivity is taken as a parameter to estimate the extent of crystallization (\(\alpha\)). The activation energy of crystallization (\(\Delta E\)) and the order parameter (\(n\)) are calculated by fitting the values of \(\alpha\) in the Avrami equations of isothermal crystallization. The results indicate that \(\Delta E\) is highly composition-dependent, which is explained in terms of the stable phases in the Ge–Se–In system.

1. Introduction

The properties of the Ge–Se system have been studied in detail and it has been established that physical properties in this system are highly composition-dependent [1–5]. The addition of impurities as a third element has been quite useful in the understanding of the structure and transport properties in chalcogenide glasses. With this point of view, we have started a study of the Ge–Se system with some metallic additives. X-ray spectroscopic studies, photoconductivity and dielectric behaviour of Ge–Se–M (where M is a metal) have already been reported [6–9] from our laboratory. The present paper reports a study of crystallization kinetics in the Ge–Se–In system with varying In concentration. Such studies are quite important for a better understanding of the short-range order in these materials.

The extent of crystallization (\(\alpha\)) of a certain material is represented by the Avrami equation [10] as follows:

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

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

The temperature dependence of \(K\) can be given by the Arrhenius equation

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

where \(K_0\) is a constant, \(\Delta E\) represents the activation energy of crystallization and \(k\) is the Boltzmann constant.

Any physical quantity which changes drastically upon crystallization can be used to monitor the extent of crystallization (\(\alpha\)) and hence the kinetic parameters (\(\Delta E\) and \(n\)) can be calculated using the above equations. Kottakota and co-workers [11–13] have used d.c. conductivity as a parameter to study the crystallization kinetics and have suggested an empirical relation to calculate \(\alpha\) which is given by

\[
\ln\sigma_m = \ln\sigma_c + (1 - \alpha)\ln\sigma_a
\]

\(\sigma_c\) and \(\sigma_a\) are the conductivities of the crystalline and amorphous phases having volume fractions \(\alpha\) and \(1 - \alpha\), respectively, and \(\sigma_m\) is the conductivity of a mixture during the amorphous to crystalline (a–c) transformation. This equation is found to be most suitable when \((\sigma_c - \sigma_a)\) has quite a large value, as also found in the present case. We have, therefore, used the same equation to study the crystallization kinetics in glassy Ge\textsubscript{20}Se\textsubscript{80-\(x\)}In\textsubscript{x} where \(x = 0, 5, 10, 15\) and 20. The results indicate that the kinetic parameters are composition-dependent, which is explained in terms of the stable phases in the Ge–Se–In system.

2. Experimental procedure

Glassy alloys of Ge\textsubscript{20}Se\textsubscript{80-\(x\)}In\textsubscript{x} with \(x = 0, 5, 10, 15\) and 20 were prepared by quenching technique. 5N pure materials were sealed in quartz ampoules (internal dia ~ 8 mm) in a vacuum of \(~10^{-3}\) Torr. The ampoules were kept in a furnace where the temperature was raised slowly (3–4°C min\(^{-1}\)) to 1000°C. The ampoules were rocked for about 10 h at the maximum temperature to make the melt homogeneous and the quenching was done in air by an air blower.

The solidified substances were ground to a very fine powder and pellets (diameter ~ 6 mm and thickness ~ 0.5 mm) were obtained after compressing the powder in a die at a pressure of 3–4t.

The (a–c) transformation was studied by measuring the d.c. conductivity (\(\sigma\)) as a function of time (0.5 min intervals) at various temperatures above the glass transition temperature (\(T_g\)).

The conductivity measurements were taken in a vacuum of \(~10^{-3}\) Torr by mounting the samples in a specially designed metallic sample holder. The current was measured using a Keithley electrometer model 614. The temperature was measured using a calibrated copper–constantan thermocouple.
Figure 1: Annealing time dependence of d.c. conductivity for Ge_{20}Se_{80} sample during different isothermal amorphous-crystalline phase transformations: (a) 176 °C, (b) 186 °C, (c) 196 °C.

### TABLE 1 Values of $n$ at various annealing temperatures

<table>
<thead>
<tr>
<th>Ge_{20}Se_{80}</th>
<th>Ge_{20}Se_{10}In_{10}</th>
<th>Ge_{20}Se_{15}In_{15}</th>
<th>Ge_{20}Se_{40}In_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td>$n$</td>
<td>Temp. (°C)</td>
<td>$n$</td>
</tr>
<tr>
<td>176</td>
<td>0.97</td>
<td>186</td>
<td>0.89</td>
</tr>
<tr>
<td>186</td>
<td>0.89</td>
<td>176</td>
<td>0.72</td>
</tr>
<tr>
<td>196</td>
<td></td>
<td>156</td>
<td>1.01</td>
</tr>
</tbody>
</table>

3. Results and discussion

During isothermal annealing at temperatures between glass transition and melting, the electrical conductivity ($\sigma$) is found to vary with time ($t$). Figs 1 and 2 show the time dependence of $\sigma$ at various annealing temperatures for glassy Ge_{20}Se_{80} and Ge_{20}Se_{80}In_{20}, respectively. The results for other glassy alloys, i.e. Ge_{20}Se_{10}In_{10}, Ge_{20}Se_{15}In_{15}, and Ge_{20}Se_{40}In_{20}, were also of the same nature.

The transformation from amorphous to crystalline state occurs in three stages represented by AB, BC and CD in Figs 1 and 2. The part AB of these curves is
Figure 2 Annealing time dependence of d.c. conductivity for Ge$_{10}$Se$_{80}$ sample during different isothermal amorphous-crystalline phase transformations: (▲) 141 °C, (●) 151 °C, (▲) 161 °C, (○) 181 °C.

Figure 3 Crystallinity percentage versus annealing time for Ge$_{10}$Se$_{80}$ crystallized for different isotherms: (●) 176 °C, (▲) 186 °C, (○) 196 °C.
linear and represents a gradual increase of $\sigma$ as a result of normal heating of the sample. The part BC shows a sharp rise of $\sigma$ which may be due to the liberation of heat energy associated with the transition from a non-equilibrium to an equilibrium thermodynamic state. The third part represents the release of thermal energy, during the growth of the crystalline phase, which is being lost asymptotically from the sample and acquires a constant limiting value after a certain time. In the present study we are interested in understanding the crystallization kinetics during the growth process, i.e. the part CD of the curves in Figs 1 and 2.

As mentioned earlier, the extent of crystallization ($x$) can be calculated using Equation 1 where $\sigma_2$ represents the conductivity at point C and $\sigma_1$ that at point D in each curve in Figs 1 and 2. Using the measured value of conductivity ($\sigma_m$) at a given time, $\sigma$ is calculated as a function of time at various annealing temperatures for all the glassy samples studied. The results of these calculations are plotted in Figs 3 and 4 for Ge$_{20}$Se$_{80}$ and Ge$_{20}$Se$_{60}$In$_{20}$, respectively. The results for other glassy alloys were also of the same nature (results not shown here). Figs 5 and 6 show plots of $\ln[\ln(1 - x)^{-1}]$ versus $\ln t$ at various temperatures for Ge$_{20}$Se$_{80}$ and Ge$_{20}$Se$_{60}$In$_{20}$, respectively. Using Equation 1, the value of $n$ can be determined at various temperatures from the slope of these curves. Table I shows the values of $n$ at various temperatures for different glassy alloys.

From the intercepts of Figs 5 and 6, the values of $K$ can be calculated at various temperatures for each glassy alloy. Fig. 7 shows that $\ln K$ versus $1000/T$ curves come out to be straight lines for all the glassy alloys, confirming the validity of Equation 2. From the slope of these curves, the values of $\Delta E$ are calculated for each glassy alloy; the results are given in Table II and plotted in Fig. 8. This figure indicates that $\Delta E$
Figure 6. Arrhenius plots of the crystallization of Ge$_2$O$_2$Se$_6$ for different isotherms: (A) 14°C, (B) 25°C, (C) 35°C.

Figure 7. Arrhenius plots of the crystallization of Ge$_2$O$_2$Se$_6$ for different isotherms: (A) 175°C, (B) 186°C.
A similar type of discontinuity at 15 at% In was also observed in our X-ray spectroscopic measurements in the same glassy system [6]. If one writes $\text{Ge}_{10}\text{Se}_{30-\text{In}}$ as $\text{Ge}_{10}\text{Se}_{30} + \text{Se}_{40-\text{In}}$, 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 the Ge-Se-In system.

### Table 11 Composition dependence of $\Delta E$

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta E$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>$\text{Ge}<em>{10}\text{Se}</em>{30}$</td>
<td>0.62</td>
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<tr>
<td>$\text{Ge}<em>{10}\text{Se}</em>{15}\text{In}_5$</td>
<td>0.53</td>
</tr>
<tr>
<td>$\text{Ge}<em>{10}\text{Se}</em>{10}\text{In}_{10}$</td>
<td>0.45</td>
</tr>
<tr>
<td>$\text{Ge}<em>{10}\text{Se}</em>{5}\text{In}_{15}$</td>
<td>0.30</td>
</tr>
<tr>
<td>$\text{Ge}<em>{10}\text{Se}</em>{0}\text{In}_{20}$</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### 4. Conclusions

The crystallization kinetics of glassy $\text{Ge}_{20}\text{Se}_{60-\text{In}}$ has been studied by the isothermal technique, i.e. by annealing the sample at certain fixed temperatures above the glass transition and measuring the d.c. conductivity with time during crystallization. The results...
fit well with the Avrami equation of isothermal transformation. The kinetic parameters $\Delta E$ and $n$ have been calculated for all the glassy alloys studied. A discontinuity in $\Delta E$ versus In concentration curve is observed for $x > 15$, which can be understood in terms of the formation of stable phases $\text{In}_x\text{Se}_3 + \text{GeSe}_2 + \text{GeSe}$ at higher concentration of $\text{In}(x > 15)$.

References


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