PHOTOCRYSTALLIZATION IN AMORPHOUS THIN FILMS OF Se\textsubscript{100-x}In\textsubscript{x}

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The present paper reports a study of photocristallization in a-Se\textsubscript{100-x}In\textsubscript{x} films (5 ≤ x ≤ 30). The photocristallization is achieved by shining white light at room temperature for different exposure times. The results indicate that the photocristallization is suppressed on addition of In (up to 15 at%) in Se–In system. However, at higher concentration of In (x > 15), photocristallization again increases. This is explained in terms of mechanically stabilized structure at this composition.

1. INTRODUCTION

CHALCOGENIDE glasses have recently drawn great attention from scientists due to their technological importance in various solid state devices. Among these glasses, Se–Te and Se–In alloys have recently gained much importance as these alloys are found to be more photosensitive and harder than amorphous Se. They have higher glass transition and crystallization temperatures and a smaller ageing effect than amorphous Se. The electrical transport, optical and structural properties of these systems have therefore been studied in detail [1–8].

Photocrystallization in amorphous solids was first observed in amorphous selenium by Dresner and Stringfellow [9] and then by de Neufville [10], Clement et al. [11] and Kim and Turnbull [12]. These authors showed that photocrystallization effects result from the production of hole electron pairs in the vitreous phase. Kotkata et al. [13] have studied the effect of light on crystallization kinetics in amorphous selenium that was doped with sulphur and showed that the effect of shining light is to destroy the Se–Se bonds, reducing the length of the selenium chain and opposing the crystal growth. The photocrystallization in amorphous Ge\textsubscript{1–x}Se\textsubscript{x} (0 ≤ x ≤ 0.2) has been investigated by Matsushita et al. [14] and they have shown that for Ge\textsubscript{0.85}Se\textsubscript{0.15} films only, the crystallization effect is enhanced over thermal effects. However, for other compositions, the crystallization effect is suppressed. In the case of Se\textsubscript{1−x}Te\textsubscript{x} films, Okuda et al. [15] have shown that photocrystallization is suppressed for Se\textsubscript{0.96}Te\textsubscript{0.04} films more than pure Se films, whereas for the compositions x > 0.1 the photocrystallization was certainly enhanced over the case of pure Se film. In our earlier communication [16] we have reported that the photocrystallization effects are suppressed on addition of 5 at% of Te in a-Se. However, at higher concentration of Te, photocrystallization increases as compared to pure a-Se.

The present paper reports the photocrystallization studies in Se\textsubscript{100-x}In\textsubscript{x} glassy system to understand the effect of In on the photocrystallization of a-Se. As the d.c. conductivity increases by several orders of magnitude on crystallization in chalcogenide glasses, it has been widely used [17–19] to study crystallization kinetics in chalcogenide glasses. In the present study also, we have measured dark conductivity and photoconductivity after each cycle of exposure to white light.

To ascertain crystallization of the amorphous films, X-ray diffraction studies were made on the films before and after light exposure. The logarithmic difference between the conductivity in amorphous and crystallized state, has been taken as a measure of the extent of crystallization for understanding the composition dependence of photocrystallization in a-Se\textsubscript{100-x}In\textsubscript{x}. The results indicate that the photocrystallization is highly composition dependent in Se\textsubscript{100-x}In\textsubscript{x} system where x is varied from 5 to 30.

2. EXPERIMENTAL

Glassy alloys of a-Se\textsubscript{100-x}In\textsubscript{x} (x = 5, 10, 15, 20, 30) were prepared by quenching technique. Thin films of these alloys were prepared by a vacuum evaporation technique keeping substrates at room temperature and at a base pressure of ~ 10\textsuperscript{-3} torr. The thickness of the amorphous films was ~ 5000 Å. Predeposited

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thick indium electrodes on well degassed glass substrates were used for the electrical contact. The amorphous films were kept in the deposition chamber for about 24 h to attain thermodynamic equilibrium as pointed out by Abkowitz [20] in chalcogenide glasses.

All the measurements were made in a vacuum \( \sim 10^{-3} \text{torr} \) by mounting the films in a metallic sample holder which has a quartz window to shine light for exposing the films as well as for the photoconductivity measurements. White light from a 200 W tungsten lamp (intensity 3000 LX) was used for light exposure. The temperature dependence of dark and photoconductivity were made after each cycle of exposure, using the planar geometry of the film (length \( \sim 1.2 \text{ cm} \), electrode gap \( \sim 0.5 \text{ mm} \)). The digital electrometer (Keithley model 614) was used to measure the current.

The sample was allowed to relax for 24 h after each cycle of exposure to avoid the presence of any residual photocurrent while measuring the temperature dependence of dark conductivity. The temperature of the sample was not allowed to increase to more than 327 K to avoid thermally induced crystallization. The d.c. conductivity at room temperature returned back to its original value after each cycle of heating. This ensured the absence of thermally induced crystallization during each set of measurements.

3. RESULTS AND DISCUSSIONS

Temperature dependence of d.c. conductivity \((\sigma)\) is studied before and after exposing the films to a white light for different exposure times. The results for a particular glassy alloy \(Se_{95}In_{15}\) are shown in Fig. 1. The results for other glassy alloys used in the present study were also of the same nature. It is clear from Fig. 1 that \(\ln \sigma\) vs \(1000/T\) curves are straight lines before and after light exposure which indicates that the conductivity is thermally activated with a single activation energy \((\Delta E)\) in the temperature range of measurements \((300-327 \text{ K})\). The values of \(\Delta E\) are calculated from the slopes of the \(\ln \sigma\) vs \(1000/T\) curves.

It is clear from Fig. 1 that no appreciable effect on \(\sigma\) and \(\Delta E\) occurs after an exposure of \(a-Se_{95}In_{15}\) to a white light for 90 min. However, when the films are exposed to higher exposure times \(\sigma\) increases drastically with a decrease in \(\Delta E\). Similar results were also obtained in other glassy alloys used in the present study.

The inset of Fig. 1 plots the variation of room temperature conductivity as a function of total exposure time for \(a-Se_{95}In_{15}\). It is evident from this figure that \(\sigma\) increases drastically after a certain exposure time. Similar type of change in dark conductivity is observed for other glassy alloys used in the present study (see Fig. 2).

While exposing the sample to white light, photoconductivity \((\sigma_{ph})\) is also measured. Figure 3 plots the values of \(\sigma_{ph}\) at 300 K and at an intensity of 3000 LX, as a function of exposure time for \(a-Se_{100-x}In_x\). It is clear from this figure that at higher exposure times \(\sigma_{ph}\) increases drastically similar to dark conductivity \((\sigma)\).

The X-ray diffraction patterns obtained on films do not show any sharp diffraction peak except a broad halo in case of films exposed to white light up to 90 min indicating the absence of crystallization.

However, for higher exposure times, the crystallization peaks appear in the diffraction pattern indicating crystallization of the films after certain exposure time. This is probably the reason why conductivity changes by orders of magnitude on exposure to white light.

As the present measurements were done below the crystallization temperature, the possibility of thermally induced crystallization can be ruled out. Moreover, we have verified experimentally, that on annealing the films for 2 h at 327 K (the maximum temperature used in the present study), no change in
Fig. 2. D.C. conductivity ($\sigma$) as a function of exposure time in $a$-Se$_{100-x}$In$_x$ films. $\sigma_a$ represents the conductivity in amorphous state and $\sigma_c$ in crystalline state.

Fig. 3. Photoconductivity ($\sigma_{ph}$) as a function of exposure time in $a$-Se$_{100-x}$In$_x$ films.
the dark or photoconductivity occurred in any of glassy alloy used in the present study. The increase in \( \sigma \) on light exposure at room temperature, in the present case, may therefore be due to photocrystallization and not due to thermal crystallization.

The increase in photoconductivity on crystallization may be related to the change in band gap, optical absorption coefficient on crystallization. In the absence of these measurements exact reason cannot be predicted.

As mentioned earlier in this paper, the logarithmic increase in d.c. conductivity has been widely used [17–19] to calculate the crystallization kinetics in chalcogenide glasses, we have taken \( \ln \sigma_c - \ln \sigma_a \) as a measure of the extent of photocrystallization to compare the results in various glassy alloys used in the present study. Here \( \sigma_a \) represents the conductivity without light exposure and \( \sigma_c \) represents the conductivity when the films are exposed to white light for an exposure time 17 h (see Fig. 2).

The values of \( \ln \sigma_c - \ln \sigma_a \) for an exposure time of 17 h, as a function of \( x \) in \( \text{Se}_{100-x}\text{In}_x \) glassy system are plotted in Fig. 4. It is clear from this figure that \( \ln \sigma_c - \ln \sigma_a \) first decreases (upto \( x = 15 \)) and then increases at 20 at\% of In. This indicates that photocrystallization effect is minimum at 15 at\% of In. Similar kind of discontinuity at 15 at\% of In in composition dependence of X-ray K absorption edge of Se in \( \text{Se}_{100-x}\text{In}_x \) system has already been reported by us in X-ray spectroscopic measurements [5].

In chalcogenide glasses a discontinuity in various physical properties has been observed [21–28] at a particular composition when the average co-ordination number reaches 2.4 which is explained by Phillips and Thorpe [29] in terms of a mechanically optimised structure at critical glass composition. According to this model, the composition at which this mechanically stabilized glass occurs is defined on the basis of the average co-ordination number \( \langle r \rangle \) which is given by

\[
\langle r \rangle = \left[ Z_A(x) + Z_B(100 - x) \right]/100, \tag{1}
\]

where \( Z_A \) and \( Z_B \) are the co-ordination numbers of elements \( A \) and \( B \) respectively.

In the present case, co-ordination number of Se is 2 and of In is 3. Hence at a composition \( \text{Se}_{65}\text{In}_{15} \), \( \langle r \rangle \) comes out to be 2.15 which is less than 2.4 as observed in IV–VI binary glasses. Phillips [30–32] has considered the interaction between atoms to be purely covalent while arriving at the balance condition. Such assumption may be valid for Ge–Se glasses but may not be equally applicable for the present system In–Se. This is probably the reason why the physical properties in this system show a discontinuity at \( \langle r \rangle = 2.15 \) instead of 2.4 as observed in Ge–Se glasses.

**4. CONCLUSIONS**

Photocrystallization in \( a\text{-Se}_{100-x}\text{In}_x \) films is studied by a shining white light (intensity 3000 LX) at room temperature for different exposure times. Dark conductivity is taken a characteristic quantity to measure the extent of photocrystallization. The present results indicate that photocrystallization effects are decreased on addition of In up to 15 at\% in \( \text{Se}_{100-x}\text{In}_x \) system. However, at higher concentration of In, photocrystallization increases. This is explained in terms of mechanically optimised structure at 15 at\% of In.

**REFERENCES**


X-Ray Spectroscopic Studies of Photo-Structural Changes in Glassy Se\textsubscript{100-x}Te\textsubscript{x}

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Recently it has been reported that reversible and irreversible photo-structural changes occur in amorphous chalcogenide glasses. The present paper reports an X-ray spectroscopic study of Se\textsubscript{100-x}Te\textsubscript{x} (x = 5 to 30) alloys before and after the light exposure. The results indicate that no change in Se K-edge occurs up to x = 5 at%. However, at higher concentration of Te (x > 5 at%), Se K-edge shifts towards higher energy side with respect to Se K-edge in unexposed sample. A high energy shift of the K-absorption edge of Se in the present case may, therefore, be related to photocrystallization due to light exposure. The results also indicate that the photocrystallization is highly composition dependent in Se\textsubscript{100-x}Te\textsubscript{x} glassy system.

KEYWORDS: X-ray spectroscopy, glassy semiconductors, photostructural changes, photocrystallization

Chalcogenide glasses have drawn great attention due to their potential use in various solid state devices. Amorphous Se-Te alloys have recently been found more useful for photograft applications due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects as compared to pure amorphous Se. We have therefore started a systematic study of various electrical and structural properties of Se-Te glassy system in our laboratory. The results indicate that the properties are highly composition dependent in the glassy system.

The photocrystallization in chalcogenide glasses has been studied by various workers who showed that in some cases light exposure enhances thermal crystallization while in some cases it suppresses the crystallization. It has been also reported that the long exposure to white light produces the photo crystallization in Se\textsubscript{85}Te\textsubscript{15} alloy even at room temperature where possibility of thermal crystallization can be neglected. In our recent communication, we have reported the effect of photo crystallization on the electrical properties such as dark conductivity and photoconductivity in amorphous Se\textsubscript{100-x}Te\textsubscript{x}.

The present paper reports the effect of photocrystallization on the X-ray absorption spectra in Se\textsubscript{100-x}Te\textsubscript{x} glassy system where x is varied from 5 to 30. In the present study, we have measured X-ray K-absorption edge of selenium before and after the exposure to white light. The difference in chemical shift before and after light exposure has been taken as the extent of crystallization for understanding the composition dependence of photocrystallization in Se\textsubscript{100-x}Te\textsubscript{x} amorphous system. The results indicate that the photocrystallization is highly composition dependent in this system.

Glasses of Se\textsubscript{100-x}Te\textsubscript{x} (x = 5 to 30) were prepared by quenching technique from the melt. The materials (99.999% pure) were weighed in proportion to their atomic percentages and sealed in quartz ampoules evacuated to 10\textsuperscript{-5} Torr and kept in a furnace where the temperature was raised up to 700°C at a rate of 3-4°C/min. After that, ampoules were rocked frequently for 10 hours at the maximum temperature to make the melt homogeneous. Quenching was done in the ice water.

The solidified substance was crushed to a fine powder and spread uniformly over a cellophane adhesive tape to form an absorption screen. The theoretically calculated thickness of absorption screens was slightly less than the actual thickness used to give the best spectra. They contained 15-20 mg of sample per cm\textsuperscript{2}.

A bent crystal transmission spectrograph, employing a well tested high quality mica sheet oriented to reflect from (100) planes and bent to a radius of 30 cm, was used to record the K-edge of selenium. A chiraiina sealed X-ray tube with a copper target was used as a source of continuous radiation. The tube was operated at 30 kV, 10 mA with a Radon House Power supply.

The WL lines were emitted besides the Cu K-lines by the tube which served as reference lines for the absorption edges. The WL\textsubscript{N} lines and the Br K-absorption edges served as reference lines to measure the Se K-edge. The spectra were recorded on a IILford FP4 single coated films and developed using Kodak D-76 developer.

The spectra were made on a Carl-Zeiss microphotometer at a magnification of 100. The records give a dispersion of 0.789 mA/mm\textsuperscript{-1}. The measurements were carried out by a glass reticule graduated in 0.1 mm divisions. The shifts are thus correct up to 0.1 mA. The maximum shift in the K-edge was 1.78 mA and the minimum shift was 0.88 mA. The dispersion therefore was good enough to resolve out these shifts. The lowest value of the difference in the edge shift before and after light exposure is 0.83 mA which is reliable enough with an error of ±0.1 mA. The position of K-absorption edge of selenium is measured at the inflexion point of the edge.

First, the measurements were made on the K-edge of the single element Se in crystalline as well as in glassy form and checked whether the reference lines used by us yielded the values of edge wavelength matching well with the standard results tabulated by Bearden. This was found true. Thereafter, the glassy samples were subjected to a similar recording. These glassy materials of Se\textsubscript{100-x}Te\textsubscript{x} (x = 5 to 30) were exposed for 17 hours with the 200 W lamp to make them crystallized.

Table I collects the data on the shift of the selenium
Table I. K-absorption edge of the Selenium in Se$_{100-x}$Te$_x$ binary alloys without light exposure.

<table>
<thead>
<tr>
<th>Substances</th>
<th>$\lambda_K$ (mÅ)</th>
<th>$\left(\frac{\nu}{R_K}\right)$</th>
<th>$\left(\frac{\Delta\nu}{R_K}\right)$</th>
<th>$\Delta E_K$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se (pure)</td>
<td>976.16</td>
<td>933.53</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Se$<em>{95}$Te$</em>{5}$</td>
<td>977.94</td>
<td>931.83</td>
<td>-1.70</td>
<td>-23.1</td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{10}$</td>
<td>977.30</td>
<td>932.44</td>
<td>-1.09</td>
<td>-14.8</td>
</tr>
<tr>
<td>Se$<em>{85}$Te$</em>{15}$</td>
<td>977.75</td>
<td>932.01</td>
<td>-1.52</td>
<td>-20.6</td>
</tr>
<tr>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td>977.24</td>
<td>932.50</td>
<td>-1.03</td>
<td>-14.0</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{25}$</td>
<td>977.18</td>
<td>932.55</td>
<td>-0.98</td>
<td>-13.3</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{30}$</td>
<td>977.04</td>
<td>932.69</td>
<td>-0.84</td>
<td>-11.4</td>
</tr>
</tbody>
</table>

K-absorption edge in Se$_{100-x}$Te$_x$ binary alloys with respect to the Se K-absorption edge in glassy Se. The symbols $\lambda$, $\nu$, $R$, $\Delta E$ represent the wavelength of the edge, the wave number of the edge, the Rydberg constant and the difference in energy respectively. This table shows that the glassy Se K-absorption edge shifts towards the lower energy side by $-23.1$ eV when 5 at% of Te is incorporated in glassy Se. A further increase in Te concentration decreases the edge shift (see Table I).

According to the Pauling, the electronegativity of an atom is its power to attract electrons to itself in a molecule. When two atoms which differ in electronegativity value combine to form alloys, the element of higher electronegativity attracts an electron pair more than the other element and behaves as an anion. The other element will behave as a cation. Sapre and Mande have shown that the absorption discontinuity in a compound shifts towards the higher or lower energy side with respect to the corresponding discontinuity in a pure element depending upon whether the absorbing atom is a cation or an anion. The electronegativity of Se is 2.4 and that of tellurium is 2.1. Therefore, Se should behave as anion in Se–Te alloys and hence the K-absorption edge of Se in these alloys should shift towards the lower energy side.

In the present case, the Se K-edge shifts towards the lower energy side after incorporation of the Te into the Se (see Fig. 1). Table I shows that the maximum chemical shift is observed at $x = 5$ at% of the tellurium, then the shift decreases as the concentration of Te increases in Se–Te alloys. Our results indicate that the behaviour of the Se–Te glassy alloys is different at low concentration of Te as compared to high concentration. Parthasarathy and Gopal have also found a different behaviour in Se$_{100-x}$Te$_x$ glasses for $0 \leq x \leq 6$ and $8 \leq x \leq 30$ in their pressure dependent conductivity results.

Schottmiller et al. have studied the effect of addition of Te on the structure of glassy Se by infrared 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 concentrations forming Se–Te mixed rings. At very low concentration, the Te atoms may be distributed randomly over the Se chains leading to a shift of the K-absorption edge towards the negative side. Se–Te bonds may cause such a negative shift as expected by the

![Fig. 1. Chemical shift of Se K-absorption edge in Se$_{100-x}$Te$_x$ glassy system before and after light exposure with respect to pure Se. The inset shows the composition dependence of the difference in chemical shift before and after light exposure.](image)

Pauling's electronegativity concept. A decrease in the K-edge shift on increasing the Te concentration indicates that mixed Se–Te rings appear which may also allow Te–Te bonding at higher concentration of Te.

Table II collects the data on the shifts of the selenium K-absorption edge in Se$_{100-x}$Te$_x$ binary alloys after the light exposure of 17 hours with respect to the pure Se K-absorption edge. It is clear from the Table II that the Se K-absorption edge still shifts towards the lower energy side with respect to pure Se K-edge but this shift is smaller in comparison to the Se K-edge shift before light exposure (see Fig. 1).

Table II. K-absorption edge of the Selenium in Se$_{100-x}$Te$_x$ binary glassy system after light exposure.

<table>
<thead>
<tr>
<th>Substances</th>
<th>$\lambda_K$ (mÅ)</th>
<th>$\left(\frac{\nu}{R}_{KL}\right)$</th>
<th>$\left(\frac{\Delta\nu}{R}_{KL}\right)$</th>
<th>$\Delta E_{KL}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se (pure)</td>
<td>976.16</td>
<td>933.53</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Se$<em>{95}$Te$</em>{5}$</td>
<td>977.94</td>
<td>931.83</td>
<td>-1.70</td>
<td>-23.1</td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{10}$</td>
<td>977.30</td>
<td>932.44</td>
<td>-1.09</td>
<td>-14.8</td>
</tr>
<tr>
<td>Se$<em>{85}$Te$</em>{15}$</td>
<td>977.75</td>
<td>932.01</td>
<td>-1.52</td>
<td>-20.6</td>
</tr>
<tr>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td>977.24</td>
<td>932.50</td>
<td>-1.03</td>
<td>-14.0</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{25}$</td>
<td>977.18</td>
<td>932.55</td>
<td>-0.98</td>
<td>-13.3</td>
</tr>
<tr>
<td>Se$<em>{70}$Te$</em>{30}$</td>
<td>977.04</td>
<td>932.69</td>
<td>-0.84</td>
<td>-11.4</td>
</tr>
</tbody>
</table>
Table III. Chemical shift before and after light exposure in binary Se_{100-x}Te_x glassy system.

<table>
<thead>
<tr>
<th>Substances</th>
<th>ΔE_K (eV)</th>
<th>ΔE_KL (eV)</th>
<th>(ΔE_KL−ΔE_K) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se_{93}Te_7</td>
<td>-23.1</td>
<td>-23.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Se_{95}Te_10</td>
<td>-14.8</td>
<td>-7.5</td>
<td>7.3</td>
</tr>
<tr>
<td>Se_{95}Te_15</td>
<td>-20.6</td>
<td>-12.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Se_{95}Te_20</td>
<td>-14.0</td>
<td>-3.7</td>
<td>10.3</td>
</tr>
<tr>
<td>Se_{95}Te_25</td>
<td>-13.3</td>
<td>-3.1</td>
<td>10.2</td>
</tr>
<tr>
<td>Se_{95}Te_30</td>
<td>-11.4</td>
<td>-0.7</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Table III collects the data on the chemical shift of the Se K-absorption edge (ΔE_K) before exposure and the chemical shift (ΔE_KL) after light exposure as a function of composition in glassy Se_{100-x}Te_x. It is clear from this table that no change in K-absorption edge occurs at 5 at% of Te. However, at higher concentration, ΔE_KL is more than ΔE_K. The difference ΔE_KL−ΔE_K increases with the increase of Te concentration.

Soules and Shaw have also shown that K-absorption edge shifts towards higher energy side as one goes from gaseous to solid argon. Our earlier results on Se and Ge also showed higher energy shift in polycrystalline samples as compared to amorphous films. A high energy shift of the Se K-edge in the present case may, therefore, be related to photocristallization due to light exposure.

The inset of Fig. 1 shows the composition dependence of ΔE_KL−ΔE_K due to photocristallization. Our results indicate that ΔE_KL−ΔE_K is zero at 5 at% of Te indicating no photocristallization at this composition. However, at higher concentration of Te, photocristallization effect becomes more and more pronounced as ΔE_KL−ΔE_K increases with the increase of Te concentration. The similar behaviour has also been found in our earlier work on photocristallization in a-Se_{100-x}Te_x in which we measured the dark conductivity and photoconductivity before and after light exposure of 17 hours. These observations were in accordance with the photocristallization studies of Okuda et al. who used electron microscopy to calculate the crystallization velocity of the nuclei formed during crystallization. From their studies they also concluded that the crystallization velocity increases sharply as Te concentration increases more than 4 at% of Te. The present results are therefore in agreement with our earlier published results on photocristallization using electrical methods in the same glassy system as well as with the results of Okuda et al. using electron microscopy.

Acknowledgements

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Photocrystallization in amorphous thin films of Se$_{80-x}$Te$_{20}$In$_x$

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Photocrystallization in chalcogenide glasses has been studied by various workers [1-6] and it has been shown that in some cases light exposure enhances thermal crystallization whereas in other cases it suppresses the crystallization. We have reported [7, 8] that long exposure to white light produces crystallization in vacuum-evaporated amorphous thin films of Se-Te, even at room temperature where the possibility of purely thermal crystallization can be neglected. The results indicate that photocrystallization effects are suppressed by addition of 5 at% Te in a-Se. However, at a higher concentration of Te photocrystallization increases compared with pure a-Se.

The effect of incorporation of a third element into binary chalcogenide alloys has been studied by various workers in order to obtain stable glassy alloys as well as to understand the basic physics of these materials. Such studies have already been reported from our laboratory [9-11]. The aim of the present study was to investigate the effect of In as a third element on photocrystallization in the Se-Te-In system.

Photocrystallization was achieved by shining white light (3000 lx) for different exposure times. The dark and photocconductivities were measured after each exposure. The logarithmic difference between the conductivity in the amorphous and crystalline states was taken as a measure of the extent of photocrystallization. The results indicate that the photocrystallization is highly dependent on the composition in the Se$_{80-x}$Te$_{20}$In$_x$ system, where $x$ is varied from 0 to 20. The results are explained in terms of the structure of the Se-Te-In system.

Glassy alloys of a-Se$_{80-x}$Te$_{20}$In$_x$ ($x = 0, 5, 15$ and 20) were prepared by the quenching technique. Thin films of these alloys were prepared by vacuum-evaporation, keeping substrates at room temperature at a base pressure of about 1.3 mPa. Predeposited thick In electrodes on well-degassed glass substrates were used for electrical contact. The amorphous films were kept in the deposition chamber for about 24 h to attain thermodynamic equilibrium, as stressed by Akkowitz et al. [12] for chalcogenide glasses. All measurements were made in a vacuum of about 0.13 Pa by mounting the films in a metallic sample holder which had a quartz window through which to shine light for exposing the films as well as for the photocconductivity measurements.

White light from a 200 W tungsten lamp (intensity 3000 lx) was used for light exposure, which was done in a vacuum of about 0.13 Pa, for different exposure times (30 min to 17 h). The measurements of dark and photocconductivities were made after each cycle of exposure, using the planar geometry of the film (length approximately 1.3 cm, electrode gap 0.5 mm and thickness 500 nm). A digital electrometer (Keithley model 614) was used to measure the current.

The sample was allowed to relax for 24 h after each cycle of exposure to avoid the presence of any residual photocurrent while measuring the temperature dependence of the dark conductivity. The temperature of the sample was not allowed to increase to more than 340 K during these measurements, to avoid thermally induced crystallization. The d.c. conductivity at room temperature returned to its original value after each cycle of heating, and this ensured the absence of thermally induced crystallization during each set of measurements.

Fig. 1 shows the temperature dependence of dark conductivity ($\sigma$) before and after exposing the sample to white light for different exposure times in amorphous thin films of Se$_{80}$Te$_{20}$In$_{15}$. The results for other glassy alloys used in the study were also of the same nature. It is clear from Fig. 1 that the ln $\sigma$ versus 1000/T curves are straight lines after each cycle of exposure, which indicates a thermally activated process for d.c. conduction with a single activation energy ($\Delta E$) in the temperature range of measurements (300-340 K).

![Graph](image-url)
The values of $\Delta E$ were calculated from the slopes of the $\ln \sigma$ versus $1000/T$ curves. It is clear from Fig. 1 that $\sigma$ decreased for light exposure up to 180 min. and $\Delta E$ increased. However, when the films were exposed to higher exposure times, $\sigma$ increased drastically with a decrease in $\Delta E$. Similar results were also obtained in other glassy alloys used in the study.

Fig. 2 is a plot of the variation in room-temperature conductivity as a function of total exposure time for various glassy alloys in the $\text{Se}_{80-x} \text{Te}_{20} \text{In}_x$ system. It is evident from this figure that $\sigma$ increased drastically after a certain exposure time. A slight decrease in $\sigma$ was also observed in the beginning in some cases (see Fig. 2). The reasons for such a decrease are not clear from the present measurements.

While exposing the sample to white light, the photoconductivity ($\sigma_{\text{ph}}$) was also measured. Fig. 3 shows the values of $\sigma_{\text{ph}}$, at 300 K and at an intensity of 3000 lx, as a function of the exposure time for various glassy alloys in the a-$\text{Se}_{80-x} \text{Te}_{20} \text{In}_x$ system. It is clear from this figure that there was initially a slight decrease in the values of $\sigma_{\text{ph}}$. However, at higher exposure times $\sigma_{\text{ph}}$ increased drastically, similarly to the dark conductivity ($\sigma$). A decrease in $\sigma_{\text{ph}}$ may be due to the increase in the defect states on light exposure, as observed in chalcogenide glasses by Biegelsen and Street [13].

As the present measurements were done below the crystallization temperature, the possibility of thermally induced crystallization can be ruled out. Moreover, we verified experimentally that, upon annealing the films for 2 h at 340 K (the maximum temperature used in the study), no change in the dark or photoconductivities occurred in any of the glassy alloys used in the study. The increase in $\sigma$ upon light exposure at room temperature, in the present case, may be due to photocristallization and not due only to thermal crystallization.

An increase in $\sigma_{\text{ph}}$ upon light exposure may be a consequence of photocristallization. However, the bandgap and optical absorption coefficient may change during crystallization, which may influence the photoconductivity. In the absence of these measurements the exact reason for the increase in photoconductivity upon crystallization cannot be predicted.

The logarithmic increase in the d.c. conductivity has been widely used to calculate the crystallization kinetics in chalcogenide glasses. We have taken $\ln \sigma_{\text{c}} - \ln \sigma_{\text{a}}$ as a measure of the extent of photocristallization in order to compare the results in various glassy alloys used in the present study. Here $\sigma_{\text{a}}$ represents the conductivity without light exposure and $\sigma_{\text{c}}$ represents the conductivity when the films are exposed to white light for an exposure time of 17 h (see Fig. 2).

In Fig. 4 the values of $\ln \sigma_{\text{c}} - \ln \sigma_{\text{a}}$ for an exposure time of 17 h are plotted as a function of $x$ in the $\text{Se}_{80-x} \text{Te}_{20} \text{In}_x$ glassy system. It is clear from this figure that $\ln \sigma_{\text{c}} - \ln \sigma_{\text{a}}$ first decreased (up to $x = 15$) and then increased at 20 at % In. This indicates that the photocristallization effect is minimum at 15 at % In. A similar kind of discontinuity at 15 at % In for the $\text{Se}_{80-x} \text{Te}_{20} \text{In}_x$ system has already been reported by us in X-ray spectroscopic measurements. This can be understood in terms of the structure of Se–Te glasses.

In elemental Se each atom must have two neighbours to satisfy the valence requirements. This is achieved either by the formation of small molecules (Se$_2$) or linear polymeric chains (Se$_n$). These structural groupings do not alter with the isoelectronic
addition of Te or Se. However, the addition of Te favours the formation of mixed eight-membered rings, i.e. Se₈₋ₓTeₓ.

When In is incorporated in the binary Se₈₀Te₂₀ system, the In atoms may interact with Se in the polymeric chains of Se, but also with Se in the mixed Se–Te chains. A crosslinked structure may thus be formed, which stabilizes the structure of the Se–Te–In system. This is probably why photocrystallization is decreased upon addition of In to binary Se₈₀Te₂₀ alloys. However, at higher concentrations of In, due to In–Te bonding, photocrystallization is again increased.

In conclusion, photocrystallization in a-SeₓSe₈₀–ₓTe₂₀In, was studied by shining white light (intensity 3000 lx) at room temperature for different exposure times. The dark conductivity was taken as a characteristic quantity to measure the extent of photocrystallization. The results indicate that photocrystallization effects are minimum at 15 at% In in SeₓSe₈₀–ₓTe₂₀In. However, at higher concentrations of In the photocrystallization increases. This is explained in terms of the structure of the Se–Te–In system.

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An additive property of Slater’s screening constants with reference to X-ray $K$-emission lines

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Abstract: The Mosley plots for X-ray $K$-satellite lines show an interesting feature. The screening for the $K\alpha_1$ satellites is lower than that for the parent line $K\alpha_1$. The case for the satellites of $K\beta_1$ is just the reverse. It is shown that this can be accounted for by suitably adding the Slater screening values for the initial and final configurations arising out of the double ionisation.

Keywords: Screening constants, X-ray satellite lines, double ionisation.

PACS No.: 32.30. Rj

Our objective behind putting this note is to point out that Slater’s screening constants can be used additively to obtain the screening shown by the X-ray $K$-lines. Table 1 below shows this property.

<table>
<thead>
<tr>
<th>Line and transition</th>
<th>Screening obtained from Mosley plots</th>
<th>Screening obtained by adding Slater’s screening constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\alpha_1$</td>
<td>$KL_{III}$</td>
<td>$\sigma_{1s} + \sigma_{2p} = 0.3 + 0.85 = 1.15$</td>
</tr>
<tr>
<td>$K\alpha_2$</td>
<td>$KL_{II}$</td>
<td>$\sigma_{1s} + \sigma_{2p} = 0.3 + 0.85 = 1.15$</td>
</tr>
<tr>
<td>$K\beta_{1,3}$</td>
<td>$KM_{III,II}$</td>
<td>$\sigma_{1s} + \sigma_{3p} = 1 + 0.85 = 1.85$</td>
</tr>
<tr>
<td>$K\beta_{2,5}$</td>
<td>$KM_{IV,V}$</td>
<td>$\sigma_{1s} + \sigma_{3p} = 1 + 1 = 2$</td>
</tr>
</tbody>
</table>

The $K\beta_{2,5}$ line is a faint and a broad line. It is not purely an atomic transition because its features are greatly influenced by the solid state effects. Hence, there is a discrepancy in observed and estimated values of $\sigma$. Here the following values of $\sigma$ have been used for different subshells (Slater 1930, 1955, 1960; Agarwal 1979)

\[
\begin{align*}
\sigma_{1s} &= 0.3 & \sigma_{3s} &= 0.35 \\
\sigma_{2s} &= 0.35 & \sigma_{3p} &= 0.85 \\
\sigma_{2p} &= 0.85 & \sigma_{3d} &= 1
\end{align*}
\]

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For \( n = 1 \), the above values hold good but for \( n > 2 \), \( \sigma_{1v} \) is taken as \( 1 \). These are Slater’s rules.

As such there is no theory to predict the screenings obtained for X-ray lines, only the Mosley plots yield the screening values. It is seen that the screening of an X-ray \( K \)-line is obtained by adding Slater’s screening* for the missing electron. The authors have no theoretical explanation for this result at present. The advantage of this empirical result is that if accepted it can account for certain features of the \( K \) X-ray satellites which are otherwise not explicable.

The X-ray satellites arise out of double ionisation in the inner shells. Therefore, the screening shown by the Mosley plot of these satellites should be less than that of the parent line. This holds true for the \( K\alpha \) satellites but not for the satellites of \( K\beta \). The present method of adding Slater’s screening for the missing electrons accounts for this fact as will be shown below. We first justify the use of Mosley law for X-ray satellites.

**Justification for using Mosley law for X-ray satellites:**

An atom, doubly-ionised in the inner shells is a He-like atom, in which one electron is in the ground state which the other one is in the excited. The initial states for \( K\alpha \) satellites have configuration \((1s, 2p), (1s, 2s)\) etc. Such He-like levels can be approximated according to Bethe and Salpeter (1957) by

\[
E_{n, l, j} = -\frac{Z^2}{2} - \frac{(Z - 1)^2}{n^2}
\]

and will, therefore, obey the Mosley law. The final states have both the electrons in the excited levels. Analytical expressions for such states in \( L-S \) coupling are not to be found but in \( j-j \) coupling. Candlin (1955) writes for a level,

\[
\text{Energy value} = \text{a term proportional to } Z^2 - \sigma^2 + \text{a relativistic term + a minor term in } Z
\]

Replacing \( Z^2 - \sigma^2 \) by \((Z - \sigma)^2\) has a small error (about 10-15% in \( Z = 20 - 30 \) range). Thus the Mosley law holds for both initial and final states.

**\( K\alpha \) satellites:**

Data on \( v/R \) values for various \( K\alpha \) satellites were taken from the paper by Deodhar and Padalia (1963) and also from Deodhar (1931), Wetterbald (1927), Randall and Parratt (1940), Shaw and Parratt (1936). The Mosley graph fitting was done using a computer programme. Table 2 collects the data indicating the transitions assigned by Kenard and Ramberg (1934). These authors do not regard \( K\sigma^*3 \) as an emission between to doubly ionised states. This line

\* Sommerfeld’s \( \sigma_{1} \) are not additive:

\[
(\sigma_{1})_{K\alpha_{1, 2}} \neq (\sigma_{1})_{\text{edge}} + (\sigma_{1})_{L, \text{III edge}}
\]
Table 2. Calculation of the screening constants for $K\alpha$ satellites as described in the text.

<table>
<thead>
<tr>
<th>Line</th>
<th>Initial state</th>
<th>$\sigma_1$</th>
<th>Final state</th>
<th>$\sigma_2$</th>
<th>$\sigma = \sigma_1 + \sigma_2$</th>
<th>Observed $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\alpha_4$</td>
<td>$1s\ 2p$</td>
<td>$^3p$</td>
<td>$2p\ 2p$</td>
<td>$^1D$</td>
<td>$(2\sigma_{2p} - 2\sigma_{2s} - 2\sigma_{2}^2)$</td>
<td>0.85</td>
</tr>
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<td></td>
</tr>
<tr>
<td>$K\alpha_3$</td>
<td>$1s\ 2s$</td>
<td>$^3S$</td>
<td>$2s\ 2p$</td>
<td>$^3p$</td>
<td>$(\sigma_{2s} + \sigma_{2p} - 2\sigma_{2}^2)$</td>
<td>0.80</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$K\alpha_3$</td>
<td>$1s\ 2p$</td>
<td>$^3p$</td>
<td>$2p\ 2p$</td>
<td>$^3p$</td>
<td>0.4</td>
<td>0.85</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K\alpha'$</td>
<td>$1s\ 2p$</td>
<td>$^1p$</td>
<td>$2p\ 2p$</td>
<td>$^1p$</td>
<td>0.4</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K\alpha''$</td>
<td>$1s\ 2s$</td>
<td>$^1S$</td>
<td>$2s\ 2p$</td>
<td>$^1p$</td>
<td>0.5</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Table 3. Estimation of $\sigma$ for $K\beta$ satellites.

<table>
<thead>
<tr>
<th>Line</th>
<th>Initial state</th>
<th>$\alpha$</th>
<th>Final state</th>
<th>$\beta$</th>
<th>$\sigma = \alpha + \beta$</th>
<th>Observed $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\beta_7$</td>
<td>$KM_{II, III}$</td>
<td>((\alpha_{1s} + \alpha_{3s} - 2\alpha_{3d}))</td>
<td>$M_{III}^{2}$</td>
<td>$2\alpha_{3p} - 2\alpha_{3d}$</td>
<td>(1 + 0.85 - 0.7 = 1.15)</td>
<td>2.15</td>
</tr>
<tr>
<td>$K\beta_6$</td>
<td>$KL_4$</td>
<td>$\alpha_{1s} + \alpha_{2s}$</td>
<td>$L_4 M_0$</td>
<td>$\alpha_{3p} + \alpha_{3p} - 2\alpha_{3d}$</td>
<td>(1 + 0.35 = 1.35)</td>
<td>0.35 + 0.85 - 2 x 0.35 = 0.5</td>
</tr>
<tr>
<td>$K\beta_5$</td>
<td>$KL_{II, III}$</td>
<td>$\alpha_{1s} + \alpha_{2s} - 2\alpha_{3s}$</td>
<td>$L_{III} M_{III}$</td>
<td>$\alpha_{3p} + \alpha_{3p} - 2\alpha_{3d}$</td>
<td>(1 + 0.85 - 0.7 = 1.15)</td>
<td>0.85 + 0.85 - 0.7 = 1.0</td>
</tr>
<tr>
<td>$K\beta_3$</td>
<td>$KL_4$</td>
<td>1.35</td>
<td>$L_4 M_{III}$</td>
<td>(\alpha_{3s} + \alpha_{3p})</td>
<td>(1 + 0.35 = 1.35)</td>
<td>0.35 + 0.85 = 1.2</td>
</tr>
</tbody>
</table>

Data from Deodhar and Padalia (1962)

<table>
<thead>
<tr>
<th>Line</th>
<th>Initial state</th>
<th>$\alpha$</th>
<th>Final state</th>
<th>$\beta$</th>
<th>$\sigma = \alpha + \beta$</th>
<th>Observed $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\beta_6$</td>
<td>$KM_1$</td>
<td>$\alpha_{1s} + \alpha_{3s}$</td>
<td>$M_1 M_{II, III}$</td>
<td>$\alpha_{3s} + \alpha_{3p}$</td>
<td>(1 + 0.35 = 1.35)</td>
<td>0.35 + 0.85 = 1.2</td>
</tr>
<tr>
<td>$K\beta_7$</td>
<td>$KM_{II, III}$</td>
<td>$\alpha_{1s} + \alpha_{2s} - 2\alpha_{3s}$</td>
<td>$M_1 M_{IV, V}$</td>
<td>$\alpha_{3s} + \alpha_{3d}$</td>
<td>(1 + 0.85 - 2 \times 0.35 = 1.15)</td>
<td>0.35 + 0.85 = 1.2</td>
</tr>
<tr>
<td>$K\beta_6$</td>
<td>$KL_{II, III}$</td>
<td>1.15</td>
<td>$L_{III, III} M_{II, III}$</td>
<td>(\alpha_{3s} + \alpha_{3p})</td>
<td>(1 + 0.35 = 1.35)</td>
<td>0.35 + 0.85 = 1.2</td>
</tr>
<tr>
<td>$K\beta_6$</td>
<td>The same as above</td>
<td>1.15</td>
<td>$L_{III, III} M_{II, III}$</td>
<td>(\alpha_{3s} + \alpha_{3p})</td>
<td>(1 + 0.35 = 1.35)</td>
<td>0.35 + 0.85 = 1.2</td>
</tr>
</tbody>
</table>

Data from Cauchois and Senecaud (1978)
has not been included in the present calculation. Also included in this table are calculations for $\sigma$ using the above method. These $\sigma$ values are compared with the observed values obtained by Mosley law after a computer fitting of the data was made.

It may be remarked that $1s\, 2s$ has states $^1S, ^1P$ and $^3S$. The wave function of these states will be different but the present empirical method does not take into account this difference. This is a limitation of this method. For better results two-electron wave functions should be used in eq. (3).

*The $K\beta$ satellites:

Data on $K\beta$ satellites were collected from two sources: Deodhar and Padalia (1962) and wavelength tables of Cauchois and Senemaud (1978). The later authors quote a reference due to Sawada (1932) who assigned transitions to some of the satellites using a different nomenclature but the lines could be identified from their $\nu / R$ values. Table 3 collects data for $K\beta$ satellites and its arrangement is similar to that of Table 2.

*A possible interpretation of the empirical method:

In the case of double ionisation satellites it is customary to consider the atom with atomic number $Z + 1$ which is regarded as the effective nuclear charge, created by the absence of $1s^1$ electron or better called as the $K$-hole. If the screening due to $1s$ electron is 0.3 in Slater’s scheme, its absence should raise the nuclear charge by 0.3 instead of 1. For a vacancy in $1s\, 2s$ the nuclear charge should be raised by $\sigma_{1s} + \sigma_{2s} = 0.3 + 0.35 = 0.65$. For vacancies in $1s\, 3p$ we have $n = 2$ and $\sigma_{1s} = 1$, the increase in charge should be 1.85. Then come the effects due to the shielding of electrons present in the subshells. It is seen that the $s$-electrons due to their most spread out wave function have the largest effect because they offer that largest overlap. In a $1s\, 3p$ vacancy the shielding due to $3s$ need be subtracted as $2s$ wave function offers comparatively lesser overlap with $3p$.

Another question that deserves attention is that why the net screenings due to both the states, initial and final have to be added? This is perhaps because the emission of a line occurs during the time when vacancies exist in both the states: before the emission only the initial state has a vacancy, after the emission only the final state has the vacancy, but during the transition both the states have vacancies. The above attempt is merely a speculation rather than reasoning based on exact quantum mechanical calculations.

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