Investigation of Kinetics of crystallization Processes of S\textsubscript{15}-Se\textsubscript{85}, S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} Chalcogenide glasses

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Abstract. In the present work, S\textsubscript{15}-Se\textsubscript{85}, S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} chalcogenide glasses are prepared by using conventional melt quenching technique. The as-prepared samples are studied by experimental techniques like X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC). XRD studies have confirmed that the as-prepared samples are amorphous in nature. It is clear from DSC studies that the as-prepared samples are glassy in nature. Kinetic analysis of the crystallization process of as-prepared glasses is carried using DSC curves. Activation energy for glass transition and Activation energy for crystallization are determined using Kissinger method. Activation energy for glass transition of S\textsubscript{15}-Se\textsubscript{85} and S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} glasses is found to be 84.5076 and 275.801 KJ/Mole respectively. Activation energy for crystallization of S\textsubscript{15}-Se\textsubscript{85} glass is found to be 106.2622 KJ/Mole for 1st peak while Activation energy for crystallization of S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} glasses is found to be 97.93 KJ/Mole for 1st peak and 84.20 KJ/Mole for 2nd peak. Kauzmann temperature (T\textsubscript{k}) is determined from the heating rate dependent glass transition and crystallization temperatures. T\textsubscript{k} value for S\textsubscript{15}-Se\textsubscript{85} glass sample is 236.68 K (1st peak) and for S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} is 283.53 K (1st peak) and 286.33 K (2nd peak). Avrami Index (n) is also determined for as-prepared glasses. Avrami Index (n) value for S\textsubscript{15}-Se\textsubscript{85} glass sample is 1.8 (1st peak) and for S\textsubscript{15}-Se\textsubscript{81}-Cu\textsubscript{4} is 2.9 (1st peak) and 1.4 (2nd peak). The crystalline phases by thermal treatment of as-prepared glasses are identified using XRD patterns.

Keywords. Chalcogenide glasses, XRD, DSC, Crystallization kinetics.

1. Introduction

Chalcogenide glasses are the known inorganic glassy materials and these are of great interest due to their wide range of applications such as electrical switches, memories, image storage and photo resistors etc. Chalcogenide glasses consisting of Se based metals are the useful materials in optical memory devices due to the unique reversible transformation property of Selenium (Se). Short life time and low sensitivity are the main problems concerned to the Se based chalcogenide glasses. But these problems can be rectified easily by adding suitable additives. The presence of Se in Chalcogenide glasses makes it powerful as Selenium (Se) in alloy form exhibits exclusive properties like greater hardness and sensitivity, higher crystallization temperature and conductivity and low aging affects. The studies of glass transformation and crystallization process in the amorphous glasses are interesting not only from the fundamental aspect of establishing the reaction mechanism of crystal nucleation and growth, but also from a technological point of view [1-4]. Chalcogenide glasses are attracting many scientists attention due to their studies of glass transition and crystallization behavior which are the key concepts for their various applications [5-6].

The detailed information of chalcogenide glasses about their durability in working conditions is obtained using crystallization kinetics. Crystallization kinetics on glassy material is done using differential scanning calorimetry which in turn can be performed in two distinct modes, namely isothermal and non –
isothermal. The former one involves measurement of drastic change in physical quantities as a function of time when specimen is brought near to crystallization temperature. The latter one i.e. non isothermal mode involves heating the specimen at fixed rate and measuring the change in physical parameters as a function of temperature. The studies of glass transition and crystallization behavior can well be described by using thermal analysis which uses the exothermic and endothermic peaks of Differential Scanning Calorimetry (DSC) curves under non-isothermal and isothermal conditions [7-10]. The studies on preparation and characterization of various chalcogenide glasses are available in literature. Chalcogenide glasses are also being called as lone-pair semiconductors, because, the lone pair electrons have an important role in the glass formation. [11-14]

In the present work, crystallization kinetics of S_{15}-Se_{85} and S_{15}-Se_{81}-Cu_{4} has been investigated under non-isothermal conditions. The nucleation and growth morphology have been determined through the JMA model. Also other kinetic parameters like activation energy of crystallization and activation energy for glass transition have been determined. Identification of the phases at which the alloy crystallize after thermal process has been proposed using X-ray diffraction.

2. Experimental

In the present work S_{15}-Se_{85} and S_{15}-Se_{81}-Cu_{4} glasses were prepared using melt quenching technique. Sulphur, Selenium and Copper elements of high purity (99.999%) were weighed in appropriate atomic weight proportions using electronic balance and introduced into quartz ampoules (10cm length, 18mm inner diameter and 20mm outer diameter). These ampoules were sealed under a vacuum of 10^{-5} torr to remove the possibility of any reaction of alloys with oxygen at high temperature and then heated in a rocking furnace at the rate of 3°C/min up to 950°C for 24 hours. During the melt process, the ampoule was frequently rocked to ensure homogeneity and isotropic nature of the sample. Finally the melt was quenched rapidly in ice water to obtain the glass alloy. The sample was collected by breaking the ampoule.

The amorphous nature of as prepared samples was verified by XRD patterns, recorded using Philips X-ray diffractometers with CU-K\(\alpha\) radiation (\(\lambda=1.54056\text{Å}\)). The thermal behavior of the as-prepared samples were investigated using DSC Q20 (TA Instrument) with 10mg powder with different heating rates.

3. Results and Discussion

The XRD patterns of as-prepared glass samples are shown in Figure 1. These patterns indicate the similar amorphous trends in both samples.

![Figure 1. XRD patterns of the S-Se and S-Se-Cu Chalcogenide glasses.](image-url)
The DSC curves of as-prepared glass samples at different heating rates (5, 10, 15, 20 °C/min) are shown in Figure 2. Figure 2(a) show the DSC curves of S-Se glass that indicate an endothermic peak followed by exothermic peak whereas Figure 2(b) show the DSC curves of S-Se-Cu glass that indicate an endothermic peak followed by two exothermic overlapped peaks ($T_{p1}$ & $T_{p2}$). The two exothermic overlapped peaks of S-Se-Cu glass are separately indexed and shown in Figure 3. It clearly understood from Figure 2 that the glass transition ($T_g$) and crystallization ($T_p$) temperatures shift towards higher temperatures with increasing heating rate indicating the kinetic nature of the glass transition and crystallization. The studies of heating rate dependent glass transition and crystallization would further explain the thermal behavior of S$_{15}$Se$_{85}$ and S$_{15}$Se$_{81}$Cu$_4$ glasses.

![Figure 2. DSC curves of (a) S-Se (b) S-Se-Cu Chalcogenide glasses measured at different heating rates.](image1)

![Figure 3. Separation of the two overlapped crystallized peaks of S$_{15}$Se$_{81}$Cu$_4$.](image2)
The effect of heating rate (β) on \( T_g \) and \( T_p \) has been evaluated using the Lasocka’s relation as shown below [15].

\[
T_g = A_g + B_g \log \beta \tag{1}
\]

and

\[
T_p = A_p + B_p \log \beta \tag{2}
\]

where \( A_g \) and \( A_p \) are the glass transition and crystallization temperatures for the heating rate of 1k/min and \( B_g \) and \( B_p \) are the constants. The Lasocka equations are used to evaluate Kauzmann temperature (\( T_k \)) which is an important parameter to characterize glassy materials from thermodynamic point of view. For some heating rate one can assume \( T_g = T_p = T_k \) with reference to equations (1) and (2). Now after solving equations (1) and (2) for \( T_k \), the following relation is obtained [16]

\[
T_k = \frac{B_p A_g - A_p B_g}{B_p - B_g} \tag{3}
\]

The plots of \( T_g \) and \( T_p \) versus \( \log \beta \) for \( S_{155}\)-Se85, \( S_{155}\)-Se81-Cu4 glasses are shown in Figure 4 and 5. The values of \( A_g, A_p, B_g \) and \( B_p \) estimated from Fig 4 and 5 are given in Table 1. \( T_k \) value is measured using equation 3 and given in Table 1.

| Table 1. \( T_g, T_p, B_g, A_g, B_p, A_p \) values |
| Sample       | \( A_g \) | \( B_g \) | \( A_p \) | \( B_p \) | \( T_k \) |
|--------------|----------|----------|----------|----------|--------|
| S-Se         | 283.81   | 8.74     | 334.24   | 18.09    | 236.68 |
| S-Se-Cu 4-1\textsuperscript{st} peak | 304.36   | 6.38     | 339.53   | 17.15    | 283.53 |
| S-Se-Cu 4-2\textsuperscript{nd} peak | 304.36   | 6.38     | 345.25   | 20.86    | 286.33 |

\( T_k \) value is measured using equation 3 and given in Table 1.

![Figure 4. \( T_g \) versus \( \log \beta \) for \( S_{155}\)-Se85, \( S_{155}\)-Se81-Cu4](image-url)
The activation energy \( E_g \) associated with glass transition is involved in the molecular motion and rearrangement of atoms in a system at around critical transition temperature. The activation energy \( E_g \) for the glass transition for the as-prepared glass is evaluated using Kissinger’s method [17] that uses the following relation.

\[
\ln \left( \frac{\beta}{T_g^2} \right) = \frac{-E_g}{RT_g} + \text{constant}
\]  

(4)

where \( R \) is the universal gas constant. A plot of \( \ln \left( \frac{\beta}{T_g^2} \right) \) versus \( \frac{1}{1000/T_g} \) is shown in Figure 6. The estimated activation energy for glass transition \( E_g \) for both the samples are given in Table 2.

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Crystallization process constitutes of three types of activation energy, an activation energy for nucleation, an activation energy for growth and an activation energy \( E_c \) for the whole crystallization process. The activation energy \( E_c \) for the crystallization for both of the glasses is evaluated using Kissinger’s method that uses the following relation.

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

(5)

A plot of \( \ln \left( \frac{\beta}{T_p^2} \right) \) versus \( \frac{1}{1000/T_p} \) is shown in Figure 7. The estimated activation energy for crystallization \( E_c \) for both samples are presented in Table 2.
The theory of transformation kinetics was developed by Jhonson and Mehl [18] and Avrami [19]. The crystallized fraction $\chi$ at a temperature $T$ is given by $\chi = A_{T}/A$, where $A$ is the total area of the exothermic peak between $T_i$ (the initial temperature of crystallization) and $T_f$ (the temperature at which the crystallization is completed), $A_T$ is the area between $T_i$ and $T$. The $\chi$ value is determined using the values obtained from Figure 8 for the S-Se-Cu (1st peak) composition.

The table below shows the values of $E_a$ and $E_c$ for different compositions:

| Sample       | $E_a$ (KJ/mole) | $E_c$ (KJ/mole) |
|--------------|-----------------|-----------------|
| S-Se         | 84.5076         | 102.2622        |
| S-Se-Cu      | 275.801         | 97.93           |

Table 2. $E_a$ and $E_c$ values

Figure 7. In($\beta/T_p^2$) vs 1000/T_p for S13-Se25, S13-Se34-Cu_i

Figure 8. DSC graph of S-Se-Cu at heating rate $\beta=5^\circ$C/min
Figure 9 (a-c) signify the volume crystallization fraction of S$_{15}$-Se$_{85}$, S$_{15}$-Se$_{81}$-Cu$_4$ glasses at different heating rates that indicate typical sigmoid curves as a function of temperature in crystallization processes.

The Avrami Index ($n$) is calculated by using the following equation.

$$\ln(-\ln(1-\chi)) = - n \ln(\beta) - \frac{1.052mE_c}{RT} + \text{Constant}$$

A plot of $\ln(-\ln(1-\chi))$ versus $\ln(\beta)$ is shown in Figure 10. The estimated $n$ values are given in Table 3.
The resultant values of ‘n’ for the as-prepared glasses calculated are summarized in Table 3. These results are comparable to the model proposed by Mahadevan et al [20]. It is clear from the evaluated Avrami Index (n) values for the as-prepared glass samples that n=1.8 (≈2) for the first peak of S-Se sample means volume nucleation and one dimensional growth for the S-Se composition. Similarly, n=2.9 (≈3) for the first peak of S-Se-Cu sample means volume nucleation and two dimensional growth for the S-Se-Cu sample and n=1.4 (≈1) for the second peak of S-Se-Cu sample means surface nucleation and one dimensional growth form surface to inside. The non-integer values of n for the as-prepared glass samples means the two and three dimensional growth working in the same time during the amorphous crystalline transformation. It is understood that addition of copper in small quantity leads to cross-linking of the chains to some extent, creating a two dimensional network. Three dimensional growth responsible for crystallization of the S-Se-Cu sample may be due to the formation of ternary crystalline phase.

| Sample   | Avrami Index (n) |   |
|----------|------------------|--|
|          | First peak | Second peak |
| S-Se     | 1.8          | -           |
| S-Se-Cu  | 2.9          | 1.4         |

**3.1. Identification of crystalline phases**

The X-ray diffraction patterns of S$_{15}$Se$_{85}$ and S$_{15}$Se$_{81}$Cu$_4$ alloys that are annealed at 85°C and 95°C respectively at 10°C/min heating rate for 5 hours are shown in Figure 11. The XRD patterns of the transformed material after the crystallization processes suggest the presence of nanocrystallites of Se (JCPDS Card No.: 73-0465), Se$_x$S$_{3.3}$ (JCPDS Card No.: 71-0248), S (JCPDS Card No.: 78-1889) in S$_{15}$Se$_{85}$ and nanocrystallites of Cu$_2$Se (JCPDS Card No.: 65-7737), Se (JCPDS Card No.: 73-0465),
Se$_{4.7}$S$_{3.3}$ (JCPDS Card No.: 71-0248), S (JCPDS Card No.: 78-1889) in S$_{15}$Se$_{85}$Cu$_4$ samples. The estimated grain sizes using Scherer method for these phases for S-Se are 54.9, 18.4 and 16.5 nm whereas for S-Se-Cu are 19.54, 24.20, 19.69 and 8.28 nm respectively.

**Conclusions**

Se based chalcogenide glasses such as S$_{15}$Se$_{85}$ and S$_{15}$Se$_{81}$Cu$_4$ are successfully prepared using conventional melt quenching technique. The as-prepared samples are amorphous and glassy in nature. The glass transition and crystallization kinetics of the glass samples, which are of scientific relevance, have been studied. Kauzman temperature is found to be 236.68K (1$^{\text{st}}$ peak) for the S$_{15}$Se$_{85}$ glass sample and 283.53K, 286.33K for the S$_{15}$Se$_{81}$Cu$_4$ (1$^{\text{st}}$ peak and 2$^{\text{nd}}$ peak) respectively. Activation energy for glass transition of S$_{15}$Se$_{85}$ and S$_{15}$Se$_{81}$-Cu$_4$ glasses is found to be 84.5076 and 275.801 KJ/Mole respectively. Activation energy for crystallization of S$_{15}$Se$_{85}$ glass is found to be 106.2622 KJ/Mole for 1$^{\text{st}}$ peak while Activation energy for crystallization of S$_{15}$Se$_{81}$-Cu$_4$ glasses is found to be 97.93 KJ/Mole for 1$^{\text{st}}$ peak and 84.20 KJ/Mole for 2$^{\text{nd}}$ peak. The value of Avrami index (n) is found to be 1.8 for the S$_{15}$Se$_{85}$ (1$^{\text{st}}$ peak) glass sample and 2.9 and 1.4 for the S$_{15}$Se$_{81}$Cu$_4$ (1$^{\text{st}}$ peak and 2$^{\text{nd}}$ peak) respectively. The thermal parameters that are obtained in the present study are crucial for controlling the crystallization in bulk samples.

**Acknowledgements**

The authors thank Dr.P.S.R. Prasad, Scientist-EII, NGRI, Hyderabad for providing characterization facilities. The authors thank UGC providing BSR-RFSMS fellowship for research student for carrying the research.

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