Iso-conversional study of crystallization activation energy of amorphous-crystallization transformation for Se$_{79}$Te$_{20}$Pb$_{1}$ glass using non-isothermal differential scanning calorimetry technique

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The ternary Se$_{79}$Te$_{20}$Pb$_{1}$ chalcogenide glass is prepared using melt quenching technique. Differential scanning calorimetry technique (DSC) is used to investigate the kinetics of crystallization of amorphous-crystallization (a-c) phase transformation under non-isothermal conditions at three different heating rates; 5, 10 and 15°C min$^{-1}$. The variation of crystallized activation energy ($E_c$) with crystallized fraction ($\chi$) and hence, with temperature ($T$) is investigated using five iso-conversional methods namely KAS, OFW, Friedman, Tang and Chen and Starink. It is found that $E_c$ is not constant but vary with $\chi$ as well as $T$. Thus, the iso-conversional analysis of investigated glass indicates that the assumption of constant $E_c$ is not appropriate.

Keywords: Chalcogenide glass, Differential scanning calorimetry, Non-isothermal methods, Iso-conversional analysis

1 Introduction

Chalcogenide glasses have received attention of researchers because of their important properties like wide transmission range, high refractive index, good chemical durability, optical switching, and amorphous to crystalline phase transition$^{1-3}$. Thermal analysis is an important quantitative analysis that provides an insight into the structural arrangement, thermal stability, phase transitions, phase separations and their effect on the various transport mechanism, thermo-mechanical, optical and electrical properties. Therefore, the study of thermodynamical properties of chalcogenide glasses is an important area of materials science which gives a deeper understanding of the elementary process of transformation of amorphous system to stable crystalline system. Out of all the standard thermal analysis techniques, differential scanning calorimetry (DSC) is the most widely used technique because it is easy to carry out, very sensitive, non-destructive and requires small amount of sample. The kinetics of glass transformation can be studied by isothermal$^7$ and non-isothermal measurements$^{5-13}$. The thermal stability of glasses against crystallization is a critical issue for potential technological applications and it enables us to determine the range of operating temperatures.

Se based chalcogenide glasses have wide range of properties such as high transparency in broad middle and far infrared regions, reversible transformations and have strong non-linear properties$^{14}$. The doping of tellurium helps to overcome the problems like short lifetime and low sensitivity of amorphous Se. The addition of third element to Se-Te glassy system creates compositional and configurational disorder with respect to the binary system$^{15}$. Addition of metallic impurity like Pb not only increases conductivity and thermal stability of the system but also leads to transition in conduction from p type to n type$^{16-19}$ which makes them ideal materials for replacing the conventional p-n junction. Pb additive chalcogenide materials are being considered to be used for high resolution spectroscopy, optical fiber analysis, optical communication, detecting atmospheric pollutants such as hydrocarbons and fast automotive exhaust analysis which makes them an attractive area for further research$^{20,21}$.

The dielectric study$^{22}$ of Se$_{60-x}$Te$_x$Pb$_x$ (0 ≤ $x$ ≤ 2) has been done in our lab. The dielectric parameters

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viz dielectric constant, dielectric loss and AC conductivity in frequency range 10 Hz to 500 kHz and temperature 300-320 K have been evaluated. It is found that for dielectric constant, dielectric loss and AC conductivity the glassy system show unique trends at x=1 at % for same temperature and frequency. Hence, it has been concluded that \( \text{Se}_{79}\text{Te}_{20}\text{Pb}_1 \) is critical composition and thus, it is further investigated for various studies. Further, in our previous work\textsuperscript{23}, various kinetic parameters including glass transition activation energy, activation energy for crystallization and Avrami exponent have been deduced using different empirical approaches. From the values of the kinetic parameters, it has been revealed that crystallization mechanism has one dimensional growth. It was also concluded that \( \text{Se}_{79}\text{Te}_{20}\text{Pb}_1 \) is made from good glass forming liquids.

According to JMA model, the Avrami exponent \((n)\) and the activation energy of crystallization \((E_c)\) should be constant during the transformation process\textsuperscript{5}. However, recently researchers have shown that \( n \) and \( E_c \) values are not necessarily constant but vary during the amorphous-crystallization (a-c) transformation\textsuperscript{5,7}. Therefore in continuation of our previous work\textsuperscript{23}, the present study aims to substantiate the variation of \( E_c \) for amorphous to crystallization transformation in \( \text{Se}_{79}\text{Te}_{20}\text{Pb}_1 \) glass. This variation with degree of crystallization and temperature has been reported and discussed in detail by employing different five different iso-conversional methods.

2 Experimental Details
The investigated \( \text{Se}_{79}\text{Te}_{20}\text{Pb}_1 \) chalcogenide alloy was prepared by melt quenching technique. 5N high purity (99.999 %) Se, Te and Pb, procured from Sigma Aldrich, were weighed in appropriate atomic weight percentage with accuracy of \( 10^{-4} \) g and sealed in a quartz ampoule (length ~ 8 cm, diameter ~ 10 mm) under high vacuum of \( \sim 2 \times 10^5 \) mbar. The sealed ampoule was heated in a muffle furnace for 10 h with the rate of 3 °C/min up to 900 °C. The ampoule was rocked frequently to maintain homogeneity. The heated ampoule was quenched rapidly in ice cooled water. The ingot of the sample was taken out by breaking the quartz ampoule and then it was crushed into a fine powder using mortar and pestle. The structural characterization was carried out using PANalyticalX’Pert Pro x-ray diffractometer in the range 5°<2θ<90° at the scanning rate of 1°/min equipped with a Ni filter using Cu \( K_\alpha \) (\( \lambda = 1.5406 \) Å) radiation as x-ray. No prominent peak was observed in the x-ray diffraction pattern of the investigated glass which confirms the amorphous nature of the material\textsuperscript{22}.

The glassy nature of the material was confirmed through DSC technique (NETZSCHSTA 4491 DSC). The temperature precision of this instrument is ±0.1 K in the measured values. 3-5 mg of sample was sealed in standard aluminum pan and heated under non-isothermal conditions in dry nitrogen atmosphere at the flow rate of 40 mL min\textsuperscript{-1} at three different heating rates 5, 10 and 15 °C min\textsuperscript{-1} in the range 300-575 K to investigate thermal transformation region. The DSC thermograms at 5, 10 and 15 °C min\textsuperscript{-1} are shown in our previous work\textsuperscript{23}.

3 Results and Discussion
In the present study, the non-isothermal a-c transformation data obtained from DSC has been analyzed using different iso-conversional methods of kinetic analysis. The degree of crystallization \( \chi \) has been determined using partial area technique. The crystallized fraction \( \chi \) at any temperature \( T \); \( \chi = A_T/A \). Here \( A \) is the total area of the exothermic peak between temperature \( T_i \) (on which the crystallization just begins) and \( T_f \) (at which the material is completely crystallized) and \( A_T \) is the area of the peak between temperatures \( T_i \) and \( T \). The temperature dependence of crystallized fraction \( \chi \) is observed to be a sigmoid curve as shown in Fig. 1. The experimental data of the plot displayed in Fig. 1 has been used to calculate activation energy of crystallization using five iso-conversional methods. The iso-conversional methods namely KAS, OFW, Tang and Chen and Starink, use approximations for the evaluation of the integral appearing in the rate equation whereas

![Fig. 1 — Variation of crystallized fraction as a function of temperature for ternary Se\textsubscript{79}Te\textsubscript{20}Pb\textsubscript{1} glass.](image)

Friedman method uses a differential form of the rate equation which leads to the simple linear equations for evaluating the activation energy.

3.1 Iso-conversional analysis

The crystallized fraction $\chi$ can be expressed in terms of time $(t)$, is provided by Johnson-Mehl-Avrami (JMA)\textsuperscript{23-26}, in which the volume crystallized $\chi(t) = 1 - \exp[-(Kt)^n]$ where $\chi(t)$ is the crystallized fraction or the fraction of the first phase which has transformed into the second phase in time $t$, $n$ is Avrami exponent that depends upon the growth mechanism and the dimensionality of the glassy alloy, $K$ is defined as the effective overall reaction rate constant and it usually has an Arrhenian temperature dependence as $K = K_0 \exp(-E_c/R)T)$ where $K_0$ is the pre-exponential frequency factor, $E_c$ is the activation energy for crystallization and $R$ is universal gas constant.

The isothermal a-c transformation rate can be given as:

$$\frac{d\chi}{dt} = nK(1-\chi)\left[-\ln(1-\chi)\right]^{(n-1)/n} \quad \ldots(1)$$

Using the assumptions of isothermal condition, the isothermal transformation rate can be written as:

$$\frac{d\chi}{dt} = K(T)f(\chi) \quad \ldots(2)$$

Where, $f(\chi)$ is the reaction model, $\chi$ is the conversion fraction that represents the volume of the crystallized fraction.

Substituting expression for $K$, the transformation rate can be rewritten as:

$$\frac{d\chi}{dt} = K_0 \exp\left(-\frac{E_c}{RT}\right)f(\chi) \quad \ldots(3)$$

Under non-isothermal conditions with a constant heating rate of $\alpha = dT/dt$, Eq. (3) can be modified as:

$$\frac{d\chi}{dT} = \frac{d\chi}{dt} \frac{dt}{dT} = \frac{K_0 \alpha}{R} \exp\left(-\frac{E_c}{RT}\right)f(\chi) \quad \ldots(4)$$

The integral form of the reaction model can be obtained by integrating Eq. (4) using the method of separation of variables as follows:

$$g(\chi) = \int_0^{\chi} \frac{dx}{f(x)} = \frac{K_0 \alpha}{R} \int_{\chi_o}^{T_o} \exp\left(-\frac{E_c}{RT}\right)dT \quad \ldots(5)$$

In the present work, the variation of activation energy for amorphous-crystallization transformation in Se$_{79}$Te$_{20}$Pb$_1$ chalcogenide glass using five iso-conversional methods is deduced and discussed. These methods are as follows:

3.2 Kissinger-akahira-sunose (KAS) method

The KAS method\textsuperscript{27-29} or generalized Kissinger method may be obtained applying logarithm and rearranging Eq. (5) as:

$$\ln \left(\frac{\alpha_i}{T_i^{2}}\right) = \ln \left[\frac{d(\chi)}{d\chi} \left(\frac{K_oR}{E_c}\right) \frac{E_{ci}}{RT_i}\right] \quad \ldots(6)$$

The subscript $i$ denotes different heating rates. For each degree of conversion $\chi$ (0.1 - 0.9), a corresponding temperature $T_i$, and heating rate $\alpha_i$ are used to plot $\ln(\alpha_i/T_i^2)$. As shown in Fig. 2, the plot obtained is straight lines which were desired from Eq. (6) and the slopes of these lines are used to calculate the activation energy $E_{ci}$ as listed in Table 1. It is observed that $E_{ci}$ decrease with crystallized fraction $\chi$.

3.3 Ozawa-Flynn-Wall (OFW) method

In OFW method\textsuperscript{30,31}, the temperature $T_\chi$ corresponding to a fixed value of fraction crystallized $\chi$ is measured from the experiments at different heating rates $\alpha$. The OFW method is based on the following equation:

$$\ln \left(\frac{\alpha_i}{T_i^2}\right) = \ln \left[\frac{d(\chi)}{d\chi} \left(\frac{K_oR}{E_c}\right) \frac{E_{ci}}{RT_i}\right] \quad \ldots(6)$$

![Fig. 2 — Plot of $\ln(\alpha_i/T_i^2)$ versus $1000/T_i$ for Se$_{79}$Te$_{20}$Pb$_1$ glassy alloy obtained using KAS method.](image)

<table>
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<th>Friedman</th>
<th>Tang &amp; Chen</th>
<th>Starink method</th>
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\[
\ln(\alpha) = -\frac{1.0516 E_x}{RT_x} + \text{constant} \quad \ldots(7)
\]

The plot of \(\ln(\alpha)\) versus \(1000/T_x\) (Fig. 3) gives the slope \(-0.0516 E_x/R\) from which the activation energy is calculated and deduced values of \(E_x\) are reported in Table 1.

### 3.4 Friedman method

The differential iso-conversional method suggested by Friedman\(^32\) can be used directly from the Eq. (5) for the various heating rates \(\alpha_i\) at a specific crystallization fraction \(\chi\) as:

\[
\ln \left( \frac{dx}{dt} \right)_{\chi_i} = \ln \left( K_x f(\chi) \right) - \frac{E_{\chi_i}}{RT_{\chi_i}} \quad \ldots(8)
\]

The activation energy \(E_{\chi_i}\) at the specific value of \(\chi\) is estimated from the plot of \(\ln(\text{d}\chi/\text{d}t)_{\chi_i}\) versus \(1/ T_{\chi_i}\) for different heating rates and repeated for all values of \(\chi\) giving continuous function of \(\chi\) for \(E\) as shown in Fig. 4. The values of \(E\) calculated from Friedman method are different from those obtained by other methods (Table 1) as unlike others this method involves differentiation of crystallized fraction \(\chi\).

### 3.5 Tang and Chen method

In Tang and Chen method\(^33\), the relation between the temperature \(T_{\chi_i}\) and heating rate \(\alpha_i\) is given by:

\[
\ln \left( \frac{\alpha_i}{T_{\chi_i}^{1.895}} \right) = -\frac{1.0008 E_x}{RT_{\chi_i}} + \text{constant} \quad \ldots(9)
\]

The graphs of \(\ln(\alpha_i/T_{\chi_i}^{1.895})\) versus \(1000/ T_{\chi_i}\) for Se\(_{79}\)Te\(_{20}\)Pb\(_1\) chalcogenide glass is plotted as displayed in Fig. 5. From the slope of straight lines obtained in the graph, \(E_x\) is evaluated and tabulated in Table 1.

### 3.6 Starink method

In Starink method\(^34\), the relation between the temperatures \(T_{\chi_i}\) and heating rate \(\alpha_i\) is given by:

\[
\ln \left( \frac{\alpha_i}{T_{\chi_i}^{1.895}} \right) = -\frac{1.0008 E_x}{RT_{\chi_i}} + \text{constant} \quad \ldots(10)
\]

The graphs of \(\ln(\alpha_i/T_{\chi_i}^{1.895})\) versus \(1000/ T_{\chi_i}\) for Se\(_{79}\)Te\(_{20}\)Pb\(_1\) are drawn as presented in Fig. 6. The values of activation energy \(E\) are calculated from the slopes of the straight lines thus obtained and recorded in Table 1.

The estimation of activation energy at degree of conversion \(\chi = 0.5\) using the five iso-conversional methods for the crystallization peak of Se\(_{79}\)Te\(_{20}\)Pb\(_1\) alloy is given in Fig. 7. Figure 8 displays the dependence of activation energy with both the extent of crystallization and temperature for investigated...
glass. The purpose of applying these various iso-
conversional methods is to check their validity. It is
observed that all the iso-conversional methods show
decrease in $E_c$ with increase in temperature which
implies that the amorphous-crystallization
transformation rate increases with the increase in
temperature. It is also worth to note that the values
obtained from KAS, OFW, Tang and Chen and
Starink methods, are in good agreement except those
of Friedman method. A similar observation was also
reported for Ge$_{22.5}$Te$_{77.5}$ using KAS, Tang,
Starink and OFW methods. The values of activation
energy evaluated by KAS and OFW methods are
different from those obtained by the Friedman
method. Friedman method employs instantaneous
heating rate values due to which it is sensitive to
experimental noise and tends to be numerically
unstable especially when rate is estimated by
numerical differentiation of experimental data.

It is evident from the temperature dependence of
the activation energy observed in the present
investigated system that a-c transformation must be
described by complex multi-step reactions involving
several processes of growth with different activation
energies and mechanisms rather than a single-step
mechanism. The observed decrease of activation
energy with temperature validates the fact that the two
processes of nucleation and growth determines the
rate constant of crystallization. These two
mechanisms tend to have different activation energies
as a consequence the effective activation energy of
a-c transformation will vary with temperature. This
interpretation is based on the nucleation theory
suggested by Fisher and Turnbull. According to this
theory, the temperature dependence of the
crystallization rate $r$ as $r = r_0 \exp \left( \frac{-E_D}{k_BT} \right) \exp \left( \frac{-\Delta F}{k_BT} \right)$
where $r_0$ is the pre-exponential factor, $k_B$ is the
Boltzmann constant, $E_D$ is the activation energy for
diffusion and $\Delta F$ is the maximum free energy
necessary for the nucleus formation.

4 Conclusions
In the present work, investigated Se$_{79}$Te$_{20}$Pb$_1$
chalcogenide glass is prepared using melt quenching
technique. The thermal behaviour of the glass is
investigated using differential scanning calorimetry
(DSC) under non-isothermal conditions. Amorphous
to crystallization transformation has been analyzed
using five iso-conversional methods viz. KAS, OFW,
Friedman, Tang and Chen and Starink. There is
agreement in the values of activation energy of crystallization $E_c$ and similar variation of $E_c$ is observed with degree of conversion $\chi$ and temperature in all iso-conversional methods. When the amorphous material is reheated, a new complex phase is obtained as the nuclei come together, i.e., nucleation takes place. Simultaneously, growth of the new phase takes place. Because the two processes, nucleation and growth are likely to have different activation energies of a-c transformation, the effective crystallized activation energy will vary with temperature according to the theory of Turnbull and Fisher. Hence, it is concluded by iso-conversional analysis that the assumption of constant $E_c$ is not appropriate.

The values of crystallization activation energy $E_c$ as calculated by the five iso-conversional methods are not constant but vary with crystallized fraction and hence, with temperature.

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