

Kinetics of phase transition and thermal stability in $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glasses

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Abstract $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glasses have been prepared using conventional melt quenching technique. The kinetics of phase transformations (glass transition and crystallization) have been studied using differential scanning calorimetry (DSC) under non-isothermal condition at five different heating rates in these glasses. The activation energy of glass transition (E_t), activation energy of crystallization (E_c), Avrami exponent (n), dimensionality of growth (m), and frequency factor (K_0) have been investigated for the better understanding of growth mechanism using different theoretical models. The activation energy is found to be highly dependent on Zn concentration. The rate of crystallization is found to be lowest for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy alloy. The thermal stability of these glasses has been investigated using various stability parameters. The values of these parameters were obtained using characteristic temperatures, such as glass transition temperature T_g , onset crystallization temperature T_c , and peak crystallization temperature T_p . In addition to this, enthalpy-released during crystallization has also been determined. The values of stability parameters show that the thermal stability increases with the increase in Zn concentration in the investigated glassy samples.

Keywords Amorphous materials · Differential scanning calorimetry (DSC) · Kinetics · Thermal stability

Introduction

The considerable interest of research workers in chalcogenide glasses is due to the possibility of their various applications in different fields of electronics due to the fact that they combine the characteristic features of disordered system and some properties of the crystalline semiconducting materials. The rapidly increasing use of amorphous Se motivated several authors to improve its physical properties, like low sensitivity and thermal instability, by alloying it with other elements [1–4]. It has recently been pointed out that the addition of Se to Te improves its corrosion resistance [5]. Moreover, Se–Te alloys are preferred because of their high sensitivity, greater hardness, higher crystallization temperature, and small aging effects as compared to pure Se [6]. Substitution of Te for Se partly breaks up the Se_8 ring structure and increases the chain fraction but reduces the chain length of the Te structure. Moreover, addition of third element such as Zn to the binary chalcogenide Se–Te system produces stable glassy alloys. It is observed that the addition of the third element helps in getting cross linked structure thus increasing the glass transition and crystallization temperature of the binary alloy. Enhance working performance of ternary chalcogenides makes them suitable for a broad range of applications in civil, medical, and military areas, especially in the fields of infrared optics, optoelectronics, photonics, etc.

In the present study, Zn has been added as a third element in binary Se–Te system to see the effect of Zn incorporation not only on the phase transformations, but also on thermal stability. The reason for the selection of Zn as chemical modifier in Se–Te system is based on the fact that, like silver, Zn can also be used for photo doping of chalcogenide glassy semiconductors [7–9] and the

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development of light emitting diodes and lasers. Furthermore, the addition of third elements like Zn to Se–Te alloys will also expand the glass-forming region and create compositional and configurational disorders, which offer ample possibilities for controlling the desired thermal properties by means of changing the chemical composition.

The amorphous state is essentially a metastable one; therefore, it inherently possesses the possibility of transforming into a more stable crystalline state. The most promising properties of chalcogenide glasses have been found to deteriorate drastically during crystallization. Understanding the micromechanism of crystallization is, therefore a prerequisite for most of the applications, as stability against crystallization determines their effective working limits.

In view of the above, in the present article crystallization kinetics and thermal stability of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems have been investigated using differential scanning calorimetry (DSC) at five different heating rates, i.e., 10, 20, 30, 40, and 50 K/min. Accordingly the article has been divided into two parts. The first part of the article deals with experimental study of the effect of Zn impurity on the glass transition and crystallization temperatures of the resulting ternary Se–Te–Zn glasses. The glass transition and crystallization temperatures as a function of composition and heating rate have been studied to aid our understanding of glass transition and crystallization process. The crystallization process is a heterogeneous reaction, which occurs at the phase boundary and consists of two consecutive events: Atomic or molecular diffusion to the phase boundary and the crystallization reaction at the boundary [10]. Therefore, knowledge of the glass transition activation energy E_g , activation energy of crystallization E_c , Avrami exponent (n), frequency factor (K_0), and dimensionality of growth (m) of both the phase transformations (glass transition and crystallization) has been acquired by employing various theoretical models [5, 6] reported in literature for kinetics of phase transformations.

The second part of the article deals with the thermal stability and glass forming ability (GFA) of these glasses. Different quantitative methods have been developed in order to determine the GFA and thermal stability of the glasses. Most of these methods are based on characteristic temperatures, such as the glass transition temperature, T_g , the onset crystallization temperature, T_c , and the peak crystallization temperature, T_p . The first thorough study on the thermal stability of various compounds was done by Sakka and Mackenzie [11], using the ratio T_g/T_m . Dietzel [12] formulated another parameter, $T_c - T_g$, which is commonly employed to obtain the glass-forming ability and thermal stability of alloy systems. Saad and Poulain [13, 14] introduced two other parameters, the weighted

thermal stability H' and the S -parameter. In addition to this, enthalpy-released (ΔH_c) during crystallization can also be used to evaluate the glass forming ability (GFA) and stability of glasses.

Experimental details

$\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems have been prepared by melt quenching technique. The materials of high purity (99.999%) were weighed according to their atomic weight percentages into a quartz ampoule. The content of the ampoule was sealed in the vacuum of 10^{-6} Torr and heated in a furnace. The temperature of the furnace was raised at a rate of 3–4 °C min^{-1} up to 925 °C and kept around that temperature for 12 h.

The ampoule was frequently rocked to ensure the homogeneity of the sample. The molten sample was then rapidly quenched in the ice-cooled water to get glassy state. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using Bragg-Brentano geometry on PANalytical X'pert Pro diffractometer in 2θ range of 15°–60° with CuK_α radiation source ($\lambda = 1.5406 \text{ \AA}$). The X-ray tube was operated at 45 kV and 40 mA. The thermal behavior of the samples has been investigated using Rigaku 8230 differential scanning calorimetry (DSC). The accuracy of heat flow measurement is $\pm 0.01 \text{ mW}$, and the temperature precision as determined by the microprocessor of the thermal analyzer is $\pm 0.1 \text{ K}$. DSC runs have been taken at five different heating rates, i.e., 10, 20, 30, 40, and 50 K/min on accurately weighed (10–15 mg) samples taken in aluminum (Al) pans under non-isothermal conditions. The temperature range covered in DSC was from room temperature (294 K) to 450 K.

Results and discussion

Structural and thermal analysis

Figure 1 shows the X-ray diffraction pattern of as-prepared $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy system at room temperature (294 K). The absence of any sharp peak confirms the amorphous nature of these alloys.

The phase transformations of the samples have been studied through DSC at five different heating rates, i.e., 10, 20, 30, 40, and 50 K/min under non-isothermal conditions. Figure 2 shows the DSC curves of all the as-prepared samples at a heating rate of 10 K/min as a representative case.

When the sample is heated at a constant heating rate in a differential scanning calorimetry experiment, the glass undergoes structural changes and eventually crystallizes. In

Fig. 1 XRD patterns of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy system

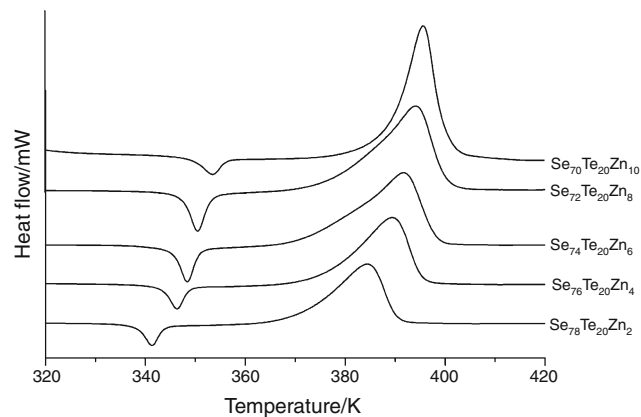


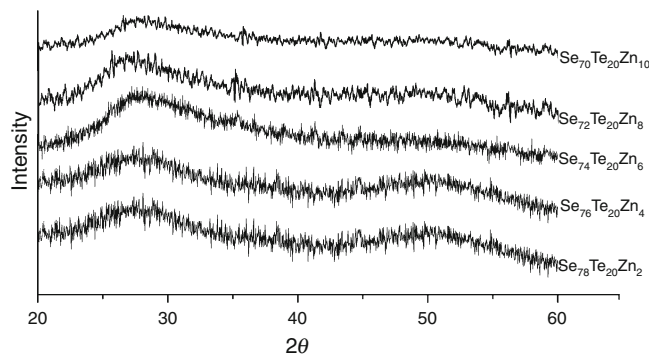
Fig. 2 DSC thermograms of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy system at a heating rate of 10 K/min

addition to the large exothermal crystallization peak, the DSC trace shows an endothermic peak before crystallization occurs and is denoted as glass transition peak. This calorimetric glass transition is generally considered to occur due to the changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased. The DSC thermogram of all the samples show single glass transition and crystallization, which confirms the homogeneity of the samples. Table 1 lists the characteristic temperatures of all the samples at a heating rate of 10 K/min.

It is observed from Table 1 and Fig. 2 that the glass transition temperature of these samples increases with the increasing concentration of Zn. A similar trend has been observed for these samples at other heating rates. This

Table 1 Characteristic temperatures of all the samples at heating rate of 10 K/min

Sample	T_g/K	T_c/K	T_p/K
$\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$	337.9	370.2	382.0
$\text{Se}_{76}\text{Te}_{20}\text{Zn}_4$	341.6	374.9	386.5
$\text{Se}_{74}\text{Te}_{20}\text{Zn}_6$	342.9	377.5	389.5
$\text{Se}_{72}\text{Te}_{20}\text{Zn}_8$	345.1	381.6	394.6
$\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$	346.2	385.3	395.8



increase in T_g can be explained on the basis of the structural change that occurs due to the introduction of Zn atoms in the Se–Te system. In Se–Te–Zn system, various bonds involved are Se–Se, Se–Te, Se–Zn, Zn–Zn, Zn–Te, etc. The strength of Se–Se bond is greater than that of Te–Te bond and the electro-negativity of Se is also greater than that of Te. Since Zn–Se bonds are stronger [15, 16] than Zn–Te bonds, therefore the metallic additive Zn is expected to combine preferably with Se. It is expected that the metallic Zn dissolved in Se-chains which results in the reduction of Se–Se bonds (104 kJ/mol) [17, 18]. The formation of Zn–Se bonds takes place along with the Zn–Zn bonds, having bond energy equal to 161 and 204 kJ/mol in Se–Zn glassy matrix [17, 18]. With the increase of Zn content, the glassy matrix becomes heavily cross-linked and steric-hindrance increases. Further addition of Zn favors the formation of Zn–Zn bonds thus reducing the Se–Zn bond concentration. This in turn results in an increase of bond energy of the system. As more and more Zn–Zn bonds are formed, the cohesive energy of the system increases, which in turn increases the glass transition temperature (T_g). Hence, T_g increases with the increase in Zn content.

The variation of crystallization temperature with Zn concentration has also been shown in Table 1 and can be determined from the thermogram given in Fig. 2. T_c is maximum for 10 at.wt% of Zn in the Se–Te–Zn system. It is found that the presence of cross-linked chains and increase in the cohesive energy of the system increases the crystallization temperature T_c [19].

Kinetics of phase transformations

Glass transition region

The glass transition region consists of various metastable states separated by energy barriers. The atoms in these metastable states tend to attain more stable state by overcoming this energy barrier. The activation energy needed to cross this energy barrier is known as activation energy of

glass transition, E_t . The glass transition region has been studied in terms of variation of glass transition temperature with the composition and heating rate. In addition to this, activation energy of glass transition (E_t) has been evaluated and composition dependence of E_t has also investigated.

The dependence of T_g on heating rate (α) can be discussed on the basis of two approaches. The first approach is the empirical relation suggested by Lasocka [20], which has the form.

$$T_g = A + B \ln \alpha \quad (1)$$

where A and B are constants for a given glass composition. The value of A depicts the value of the glass transition temperature (T_g) at a heating rate of 1 K/min, while B is proportional to the time taken by the system to reduce its glass transition temperature (T_g), when its heating rate is lowered from 10 to 1 K/min. The variation of T_g with $\ln(\alpha)$ for the investigated $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems has been depicted in Fig. 3.

From Fig. 3, it is found that this equation holds good for our samples. The values of A and B for all samples are listed in Table 2.

The second approach that shows the dependence of T_g on heating rate is known as the Kissinger formulation [21]. This equation is used for the evaluation of the activation energy for the amorphous glass-transition (E_t). In spite of the fact that this equation is used for the evaluation of the activation energy of the crystallization, it has been frequently used for the determination of the activation energy of glass transition using the peak glass transition temperatures. The Kissinger model is based on peak shift method and if the shift in the glass transition peak with heating rate is similar to peak shifts in the crystallization region, then this equation can be used for the determination of the

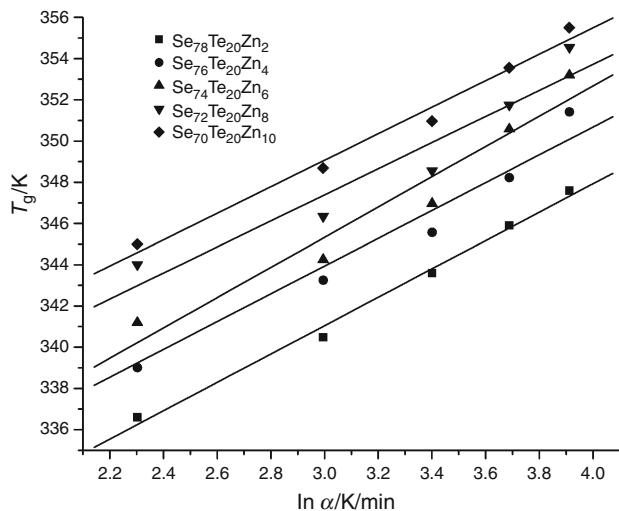


Fig. 3 Variation of T_g with $\ln(\alpha)$ of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy system

Table 2 The values of A , B and Activation energy of glass transition (E_t) for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy alloys

Composition	A/K	B/min	$E_t/\text{kJ/mol}$
$\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$	322.5	6.26 ± 0.97	135.35 ± 0.13
$\text{Se}_{76}\text{Te}_{20}\text{Zn}_4$	326.1	5.81 ± 1.20	126.37 ± 0.25
$\text{Se}_{74}\text{Te}_{20}\text{Zn}_6$	327.9	5.99 ± 0.21	115.64 ± 0.17
$\text{Se}_{72}\text{Te}_{20}\text{Zn}_8$	330.8	5.66 ± 1.32	103.51 ± 0.18
$\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$	332.3	5.34 ± 0.68	100.52 ± 0.58

activation energy of glass transition [22]. This condition is satisfied in the measurements mentioned in this study.

The Kissinger equation relating, the peak temperature with heating rate (α) is written as:

$$\ln \alpha / T_{gp}^2 = - (E_t / RT_{gp}) + \text{Const} \quad (2)$$

where E_t is the activation energy of the glass transition, T_{gp} is the peak glass transition temperature, α is the heating rate, and R is the universal gas constant. Figure 4 shows the plot of $\ln(\alpha/T_{gp}^2)$ versus $1000/T_{gp}$ for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy alloys.

The slope of the resulting straight line gives the activation energy E_t . The values of E_t for all the compositions are also listed in Table 2. It is observed that the glass transition activation energy decreases with increasing Zn content. This decrease in E_t is due to the increase in internal energy. This is due to the fact that Se–Te both are twofold coordinated, whereas Zn is sixfold coordinated. When Zn is introduced into Se–Te system, it tries to satisfy its coordination and bond energy requirements by making bonds with Se atoms. This gives rise to bond disorder with some degrees of topological disorder, which increases the entropy of the system [23]. Therefore, the internal energy,

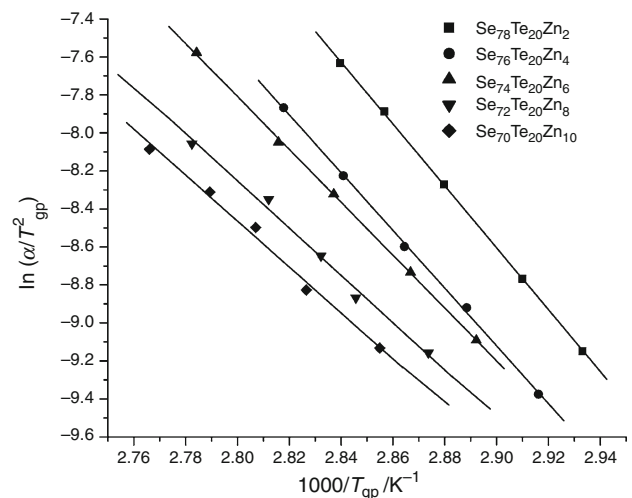


Fig. 4 Plot of $\ln(\alpha/T_{gp}^2)$ against $1000/T_{gp}$ of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems

which arises from the motion of the atoms, increases, i.e., the barrier height between two metastable states decreases. The decrease in the barrier height between two adjacent metastable states in the glassy region means that activation energy decreases and a jump to more stable metastable state in this region are preferable. It is reported [24] that the atoms in the glass having minimum activation energy have higher probability to jump to the metastable state of lower internal energy and hence the glasses with minimum activation energy of the glass transition are the most stable. It is observed that $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy alloy has the minimum value of the glass transition activation energy, which indicates that this particular glass has a greater probability to jump to a state of lower configurational energy and higher stability in the glassy region.

Crystallization region

When the sample is heated at a constant heating rate in a differential scanning calorimetry experiment, the glass undergoes structural changes and eventually crystallizes and is observed as a large exothermal crystallization peak. This calorimetric transition is generally considered to be due to changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased. The crystallization kinetics of the glassy samples has been studied under non-isothermal conditions using three theoretical models. These models have been used for extracting kinetics parameters like activation energy of crystallization (E_c), Avrami exponent (n), dimensionality of growth (m), frequency factor (K_0), crystallization rate factor (K).

It has been pointed out [25] that in a crystallization process, three types of activation energies have to be considered: activation energy of nucleation, activation energy of growth, and the activation energy E_c for the whole crystallization process. Further, it has been shown through various studies [26, 27] that the activation energy for growth may be taken equal to the activation energy for the whole crystallization process E_c , provided it is evaluated using thermal analysis of the sample. Since it is well known that activation energy of crystallization (E_c) is the energy required by the atoms in the glassy region to go to crystalline region; therefore, one may infer that the sample with the highest value of E_c , will be the most stable sample.

The activation energies of crystallization (E_c) for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems have been estimated using the following methods.

Kissinger model

The activation energy for crystallization E_c can be obtained from the heating-rate dependence on the peak temperature

of crystallization, T_p , using the equation derived by Kissinger [19].

$$\ln\left(\alpha/T_p^2\right) = -E_c/RT_p + \text{Const.} \quad (3)$$

Figure 5 shows the variation of $\ln(\alpha/T_p^2)$ with $1000/T_p$ for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glasses.

The variations are given by the straight lines for different compositions the slope of these straight lines gives the activation energy of crystallization, E_c . The values of E_c for all composition are listed in Table 3.

Matusita and Sakka model

Crystallization kinetics has also been studied using a method suggested specially for non-isothermal experiments by Matusita et al. [26]. The value of fraction crystallized (x), in glass heated at constant heating rate (α) is related to the effective activation energy of amorphous-crystalline transformation (E_c), through the following expression:

$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.502mE_c/RT + \text{Const} \quad (4)$$

where x is the volume of the fraction crystallized at any temperature, m and n are constants related to the crystallization mechanism. The plot of $\ln[-\ln(1-x)]$ against $1000/T$ at five different heating rates, i.e., 10, 20, 30, 40, and 50 K/min for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy alloy is shown in Fig. 6 as a representative case.

In higher temperature range, a break in linearity is seen at all heating rates and for different compositions of Se–Te–Zn glasses. The break in linearity may be due to the saturation of nucleation sites in the final stages of crystallization [28] or to the restriction of crystal growth by small size of the particle [29]. The value of mE_c was calculated

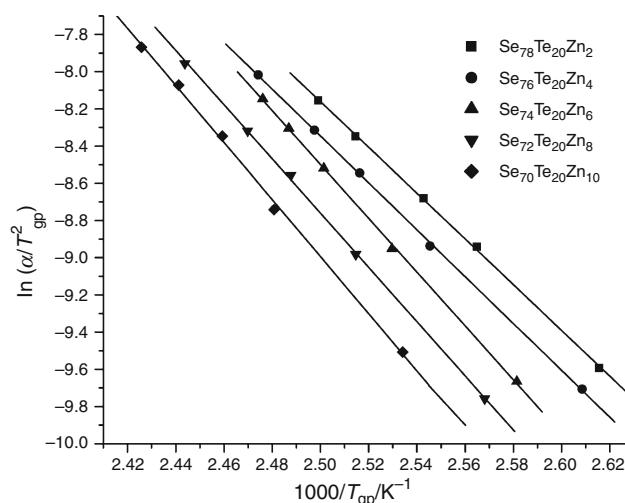
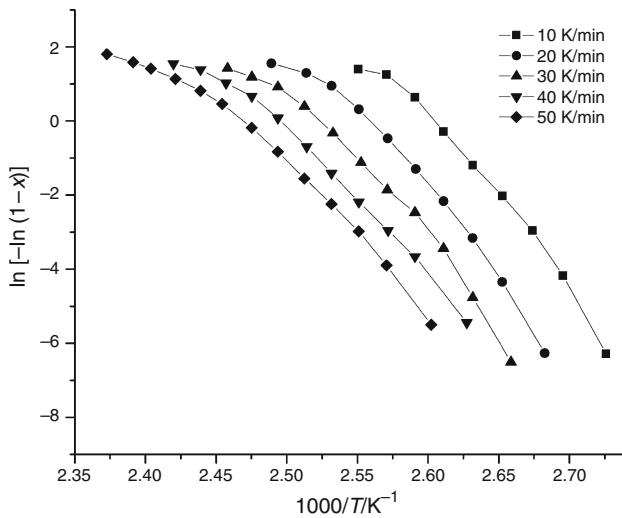


Fig. 5 Plot of $\ln(\alpha/T_p^2)$ against $1000/T_p$ of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems

Table 3 Activation energy of crystallization (E_c) of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy systems using different theoretical models

Composition	Activation energy of crystallization/ E_c /kJ/mol		
	Kissinger model	Matusita model	Augis and Bennet model
$\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$	99.85 ± 0.13	174.17 ± 2.63	116.56 ± 1.45
$\text{Se}_{76}\text{Te}_{20}\text{Zn}_4$	104.76 ± 0.12	188.92 ± 2.17	129.86 ± 1.83
$\text{Se}_{74}\text{Te}_{20}\text{Zn}_6$	120.22 ± 0.19	191.21 ± 2.16	137.14 ± 0.78
$\text{Se}_{72}\text{Te}_{20}\text{Zn}_8$	124.63 ± 0.18	196.93 ± 1.71	141.25 ± 1.49
$\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$	130.45 ± 0.67	208.85 ± 2.75	148.32 ± 1.33

**Fig. 6** Variation of $\ln[-\ln(1-x)]$ with $1000/T$ at different heating rates for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glass

from the linear portion of $\ln[-\ln(1-x)]$ versus $1000/T$ curves for all heating rates.

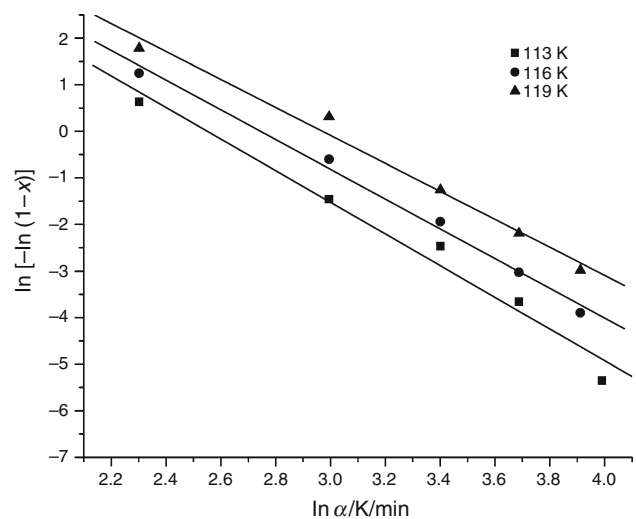
In addition to the evaluation of activation energy, the dimensionality of growth and Avrami exponent has also been calculated from the Matusita equation. When the liquid is cooled in the glass transition region, the relaxation times for the molecules movements become comparable to the experimental time scale. Therefore, the diffusive motion of the liquid is trapped and the system falls out of thermal equilibrium [29]. At this moment, the size of the nuclei does not reach the critical size required to initiate the nucleation process and hence the glass is assumed to have no nuclei (of critical size). According to Matusita et al. [26], when the glass is heated in the DSC furnace, the rate of crystal nucleation in the glass reaches the maximum at a temperature somewhat higher than the glass transition temperature and then decreases rapidly with the increasing temperature, while the crystal growth reaches the maximum at a temperature much higher than the temperature at

which the nucleation rate is highest. When the glass is heated at a constant rate, crystal nuclei are formed only at lower temperatures and crystal grow in size at higher temperatures without any increase in number. Here, $n = m + 1$ is taken for a quenched glass containing no nuclei, and $n = m$ for a preheated glass containing sufficiently large number of nuclei, where m is an integer which represents the dimensionality of growth.

At constant temperature, Eq. 4 can be written as

$$\ln[-\ln(1-x)] = -n \ln \alpha + \text{Const} \quad (5)$$

Figure 7 shows linear plots of $\ln[-\ln(1-x)]$ versus $\ln \alpha$ at three fixed temperatures for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glass. Using Eq. 4, the values of n have been determined from the slopes of these curves at each temperature and are given in Table 4 for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy system. As no heat treatment was given to nucleate the sample before DSC scans, therefore, n is considered to be equal to $(m + 1)$. The average value of n is nearly equal to 2. The value of the corresponding m is equal to 1. The result indicates that the crystallization process is carried out by surface nucleation with one-dimensional growth.

**Fig. 7** Variation of $\ln[-\ln(1-x)]$ with $\ln \alpha$ of $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy alloy**Table 4** Values of Avrami exponent and Frequency factor for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy alloys

Sample	Avrami exponent/ n	Frequency factor/ K_0
$\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$	2.03	6.70×10^{18}
$\text{Se}_{76}\text{Te}_{20}\text{Zn}_4$	2.22	9.73×10^{17}
$\text{Se}_{74}\text{Te}_{20}\text{Zn}_6$	2.06	8.71×10^{17}
$\text{Se}_{72}\text{Te}_{20}\text{Zn}_8$	2.49	1.12×10^{17}
$\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$	2.11	2.78×10^{15}

From the value of n and the average mE_c , the activation energy of crystallization of the $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy alloys can be calculated.

Augis and Bennet model

The activation energy (E_c) of crystallization as well as frequency factor can also be determined by an approximation method developed by Augis and Bennet [30], which is given as follows:

$$\ln(\alpha/T_c) = -E_c/RT_c + \ln K_0 \quad (6)$$

where T_c is the temperature at which the crystallization just begins and K_0 is the frequency factor (s^{-1}). The plots between $\ln(\alpha/T_c)$ and $1000/T_c$ for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy system are shown in Fig. 8.

The value of K_0 , which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier, can be calculated from the knowledge of $\ln K_0$ from the Eq. 6. The values of K_0 for all the samples are given in Table 4. These values are indicative of the fact that the barrier to crystallization increases with the increase in Zinc (Zn) content, which in turn decreases the attempts made by the nuclei's to overcome the crystallization barrier. The decrease in number of attempts to cross crystallization barrier also decreases the tendency of crystallization and hence makes the sample more stable against crystallization. The number of attempts made by the nuclei's to cross the barrier and the rate of crystallization is lowest for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glass, which indicates the higher stability of this glassy composition. The values of activation energy of crystallization obtained from above discussed theoretical models have been listed in Table 3.

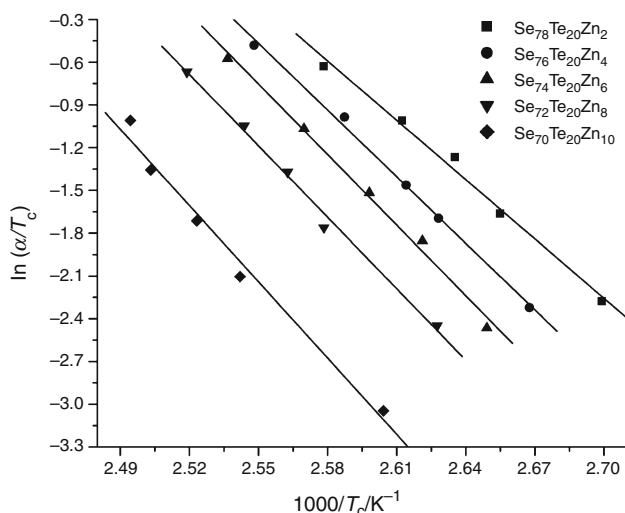


Fig. 8 Variation of $\ln(\alpha/T_c)$ with $1000/T_c$ $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8,$ and 10) glassy system

It is observed from Table 3 that values of activation energy of crystallization (E_c) obtained from all three models Kissinger model, Matusita model, and Augis and Bennett model increases with the increase in Zinc (Zn) content in the investigated glassy samples. This suggests that energy barrier to crystallization increases with the increase in Zinc content in the samples and hence making the sample more stable at higher Zn composition. The activation energy of glass transition, E_v , also gives the same conclusion. Therefore, $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ is the most stable glass among the series. The difference in the activation energy as calculated with the different models, even for the same sample, may be attributed to the different approximations used in the models. Besides, one of the factors influencing the activation energy may be the temperature gradient, which may not be the same for all heating rates, when the sample is placed in the DSC furnace. This arises due to the error in placing the pan in the DSC furnace with respect to the position of thermocouple. Another factor influencing the activation energy is that the models like Kissinger equation were developed for clays but have been frequently used in literatures [31, 32] for determining the activation energy of the glasses.

The Kissinger equation was basically developed for studying the variation of the onset crystallization temperature and the peak crystallization temperature with heating rate. In Kissinger's formulation, the transformation under non-isothermal condition is represented by a first-order (i.e., $n = 1$) reaction and the concept of nucleation and growth has not been included. Matusita et al. have developed a method on the basis of the fact that crystallization does not advance by an n th-order reaction but by a nucleation and growth process. They emphasized that crystallization mechanisms such as bulk crystallization (bulk nucleation followed by two- or three-dimensional growth) or surface crystallization (surface nucleation followed by linear growth) should be taken into account for obtaining E_c . In addition to activation energy, Matusita's method provides information about the Avrami exponent and dimensionality of growth. Augis-Bennett methods is helpful in obtaining kinetic parameters, such as frequency factor (K_0), rate constant (K) along with activation energy of crystallization and therefore preferred for the calculation of the kinetics over the other models.

Thermal stability

The thermal stability and glass forming ability (GFA) play an important role in determining the utility of chalcogenide alloys as recording material due to the fact that phase change in optical recording and erasing techniques are based on the laser-induced thermal amorphization and crystallization of chalcogenide glasses. The origin of

thermal stability and GFA is, therefore, a subject of great interest [33, 34]. The glass transition temperature T_g represents the strength and rigidity of the glass structure in chalcogenide glasses. Hence, T_g offers valuable information on the thermal stability of the glassy state, but T_g alone does not give any information about the GFA. However, it has been found that the difference of T_c and T_g is a strong indicator of both thermal stability and GFA, the higher value of $(T_c - T_g)$, the greater is the glass-forming tendency and thermal stability. Figure 9 shows a plot of $T_c - T_g$ against the Zn content of the samples at all five heating rates (10, 20, 30, 40, and 50 K/min).

It is clear from the Fig. 9 that the values of $T_c - T_g$ are highest at $x = 10$ in $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glassy systems. This indicates that GFA is highest for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glass among all studied glasses in the series.

Saad and Poulain [13, 14] proposed two parameters viz weighted thermal stability, H^1 and S -parameter to determine the stability of the glasses. S -parameter is defined as:

$$S = (T_c - T_g) (T_p - T_c) / T_g \quad (7)$$

The S -parameter reflects the resistance to devitrification after the formation of the glass. Higher value of $(T_c - T_g)$ delays nucleation and $(T_p - T_c)$ is related to the rate of devitrification transformations of the glassy phases [30].

Weighted thermal stability, H^1 has the form:

$$H^1 = (T_c - T_g) / T_g \quad (8)$$

The values of H^1 and S obtained for all the samples at a heating rate of 10 K/min are listed in Table 5. The value of H^1 increases with the increasing Zn concentration and is

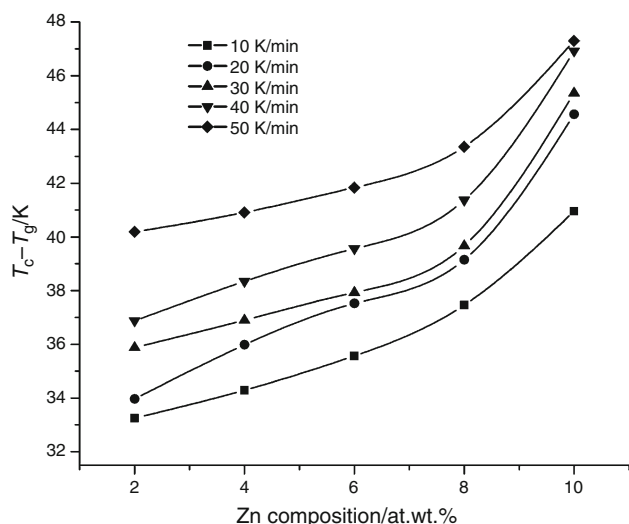


Fig. 9 Plot of $T_c - T_g$ against Zn composition at five different heating rates (10, 20, 30, 40, and 50 K/min)

Table 5 Values of different stability parameters for $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) samples

Sample	$\Delta T = T_c - T_g / \text{K}$	H^1 / K	S -parameter / K	$\Delta H_c / \text{J/g}$
$\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$	32.3	0.096	1.12	214.54
$\text{Se}_{76}\text{Te}_{20}\text{Zn}_4$	33.3	0.098	1.13	188.39
$\text{Se}_{74}\text{Te}_{20}\text{Zn}_6$	34.6	0.101	1.21	175.17
$\text{Se}_{72}\text{Te}_{20}\text{Zn}_8$	36.5	0.106	1.37	162.18
$\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$	38.1	0.110	1.38	138.76

highest for $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy sample, which confirms the highest stability of $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glass.

It has been reported that [35] the enthalpy-released ΔH_c during crystallization is associated with stability of glasses, i.e., glasses with the lowest value of $T_c - T_g$ will have a maximum value of ΔH_c . The experimental determination of enthalpy-released (ΔH_c) during crystallization process has been done by measuring the area under the exothermic peak

$$\Delta H_c = KA/M \quad (9)$$

where K is the instrumental constant, A is the area under the crystallization peak, and M is the mass of the sample. The value of K was deduced by measuring the total area of the complete melting endotherm of high purity Tin, Indium, and Lead and used the well known enthalpy of melting of these standard materials. Values of ΔH_c for all samples at a heating rate of 10 K/min are given in Table 5. The enthalpy release is related to the meta-stability of these glasses. It can be observed from this parameter that the minimum heat is released for the composition with 10% of Zn in Se-Te system, which confirms the maximum stability of the glass.

It is well known that the above-discussed criteria allow a prediction of glass-forming ability (GFA) and thermal stability of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glasses. The stability of the samples increases with the increase in Zn content. Thus, $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$ glassy alloy is found to be the most stable over the other samples of the series.

Conclusions

A systematic study of kinetics and thermal stability of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ ($x = 2, 4, 6, 8, \text{ and } 10$) glasses have been carried out using several theoretical models and following conclusions could be made.

1. The glassy alloys under investigation shows single glass transition and crystallization region, confirming the homogeneity of the samples. The activation energy of glass transition, E_t decreases with the increase in

Zinc (Zn) content. This is due to the increase in internal energy of the system.

- Maximum values of the temperature difference ($T_c - T_g$), the stability factors H^1 and S and the minimum values of enthalpy-released ΔH_c during crystallization occur at the composition, $\text{Se}_{70}\text{Te}_{20}\text{Zn}_{10}$, demonstrating that this glass is more stable than the other glasses in this series.
- A correlation has been found between the activation energy of crystallization E_c and stability parameters. Both confirm the increase in stability of the glassy samples on the increase of Zinc content in the investigated samples.

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