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On the crystallization kinetics of In additive Se–Te chalcogenide glasses

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ABSTRACT

The calorimetric parameters of glassy $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) alloys have been investigated using Differential Scanning Calorimetry (DSC) in non-isothermal conditions at different heating rates of 5, 10, 15 and 20 °C/min. It is observed that in these glasses, the glass transition temperature, the onset crystallization temperature and the peak temperature of crystallization are found to be dependent on the composition and heating rates. The glass transition activation energy and crystallization activation energy have been determined using different empirical approaches. The kinetic analysis of the crystallization peak has been performed using Matusita's model. The values of Avrami exponent (n) and activation energy of crystallization (E_c) are evaluated. The validity of Matusita's model is ascertained by comparison with the results obtained by Kissinger model and Augis and Banett method as well as their approximations. The activation energy of crystallization is determined by analyzing the data using the isoconversional methods. The present study shows that the activation energy of crystallization varies with the degree of conversion and hence with temperature. Thermal stability and glass forming tendency have also been studied for different heating rates.

1. Introduction

Chalcogenide materials are becoming progressively popular due to their wide range of applications in solid state devices [1,2]. The rapidly increasing use of amorphous Se motivated several authors to improve its physical quantities, of low sensitivity and thermal instability, by alloying with other elements [3–5]. It has recently been pointed out that the addition of Se to Te improves its corrosion resistance [6]. Moreover, Se–Te alloys are preferred because of their high sensitivity, greater hardness, higher crystallization temperature and small ageing effects as compare to pure Se [7]. 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 In to the binary chalcogenide Se–Te system produces stable gassy alloys. The insertion of the third element expands the glass forming area and also creates compositional and configurational disorder in the system. 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. In the present study, we have chosen In as a third element in binary Se–Te system to see the effect of In incorporation on crystallization kinetics. The reason for the selection of In as an impurity in Se–Te system is based on its attractive, interesting and important applications in chalcogenide glasses [8–11].

In technological applications, the thermal stability of the chalcogenide glasses is a problem of fundamental interest, because the useful operating temperature range will be determined by the structural changes and eventual crystallization occurring at the operating temperature. In addition, crystallization studies are of interest in fundamental studies of the mechanisms of crystal nucleation and growth. The crystallization kinetics of chalcogenide glasses has been discussed extensively in literature [12–15]. DSC or DTA is a very useful tool for studying the kinetics of crystallization of glass as it is a rapid and convenient means. In the calorimetric measurements, two basic methods can be used, isothermal and non-isothermal conditions [16–18]. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (T_g) and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time (t). In the non-isothermal method, the sample is heated from room temperature generally at a fixed heating rate (α) and heat evolved in this case is again recorded as a function of temperature or time. A disadvantage of the isothermal method is the impossibility of reaching a test temperature instantaneously and during the time, which system needs to stabilize, no measurements are possible. However, the non-isothermal method does not have this drawback [19].

Due to above-mentioned reason, in the present work also, this technique has been used for a crystallization study of amorphous

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$Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) glassy alloys. From the heating rate dependence of glass transition temperature (T_g) and peak crystallization temperature (T_p), the apparent activation energies for glass transition and crystallization have been calculated using different methods. In the light of present data, the nucleation and growth mechanisms have been suggested. The DSC data is analyzed with the help of isoconversional methods to investigate the growth process involved in the transformation process. The dependence of the activation energy of crystallization with the extent of conversion and hence with temperature is discussed.

2. Experimental detail

Glassy alloys of $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) have been prepared using the melt quenching technique. 5N pure materials are weighed according to their atomic percentages and sealed in a quartz ampoule (length ∼ 5 cm, diameter ∼ 12 mm) under a vacuum of $\sim 2 \times 10^{-5}$ mbar. The sealed ampoules have been kept inside a furnace where the temperature is raised to 900 °C at a rate of 3–4 °C/min. The ampoules are rocked frequently for 10 h at maximum temperature to make the melt homogenous. The quenching is done in the ice cooled water very rapidly. The amorphous nature of the glassy alloys has been verified by X-ray diffraction.

The thermal behaviour of the glasses is investigated using Mettler Toledo Star^e DSC system. The temperature accuracy of this equipment is ±0.1 °C. Approximately, 3–5 mg of sample in powder form is encapsulated in standard aluminum pan in an atmosphere of dry nitrogen at a flow of 40 mL min^{-1} and heated at different heating rates from 5 to 20 °C/min in the range 30–500 °C. The temperature and enthalpy calibrations are checked with indium ($T_m = 156.6$ °C, $\Delta H_m = 28.55$ J/g) as the standard material. The values of glass transition temperature (T_g), the onset temperature of crystallization (T_c), the peak temperature of crystallization (T_p) and the melting temperature (T_m) are determined by using the microprocessor of the thermal analyzer. The crystallized fraction (χ) at a given temperature is given as $\chi = (A_T/A)$, where A is the total area of the exothermic peak between the onset temperature (T_i) where crystallization just begins and the temperature (T_f) where the crystallization is completed. A_T is the area between T_i and T. A best fit for the results is calculated by the least square fitting method for the activation energies and other kinetic parameters.

3. Results and discussion

DSC thermograms are recorded at different heating rates for $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) chalcogenide glasses. Fig. 1 shows the DSC traces of all investigated samples at heating rate 5 °C min^{-1}. Similar trends are also observed for all samples at other heating rates (10, 15 and 20 °C/min). It is clear from Fig. 1 that well defined single endothermic and exothermic peaks are obtained at glass transition temperature T_g and crystallization temperature T_p respectively, which indicates that these glasses exist in single phase. It is found that T_g and T_p of the samples shift to higher temperature with the increase in the heating rate. The increase in T_g with heating rate may be attributed to the relaxation dynamics in the glass transition period. Theoretically, T_g is defined as the temperature at which the relaxation time becomes equal to the relaxation time of observation. At the same time, T_g varies inversely as the relaxation time [20]. With increasing heating rate, the relaxation time of observation decreases and hence the glass transition temperature increases. The shift of T_p to the higher temperatures with heating rate can be attributed to the fact that when heating rate is high, the system does not get sufficient time for nucleation and crystallization. By the time crystallization starts taking place, the temperature goes up owing to the higher heating rates.

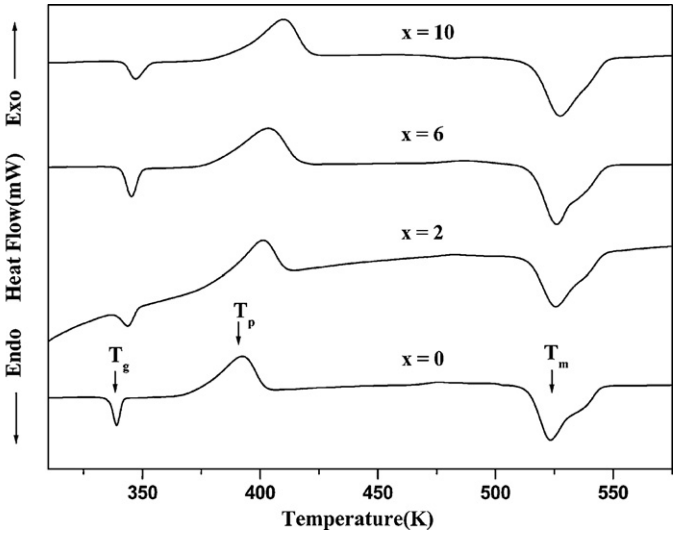

Fig. 1. DSC plot for $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) glasses at the heating rate of 5 °C/min.

The variation in the glass transition temperature (T_g) with composition for $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) system at all heating rates is shown in Fig. 2. The increasing trend of T_g with increasing In content can be explained by considering the structural changes due to introduction of In impurities. The generally accepted model of amorphous Se includes two molecular species [21], meandering chains, which contain helical chains of trigonal Se and Se_8 ring molecules of monoclinic Se. The structure of the Se–Te system prepared by the melt quenching is regarded [21–24] as a mixture of Se_8 rings, Se_6Te_2 rings and Se–Te copolymer chains. Therefore, as In content is incorporated at the cost of Se, they are probably increasing relatively the number of long chain Se–Se while the numbers of Se_8 ring are decreased [25]. It is known that [26] the glass transition temperature T_g should increase with increasing chain length and decreases with increasing ring concentration. In the present case, the increase in T_g may, therefore, be related to the increase in chain length on increasing In content. A similar trend is also reported by Agarwal et al. [8]. However, Imran et al. [10] shows that the glass transition temperature T_g goes on decreasing with increasing In impurities. An introduction of In in their case is at the cost of Te. The

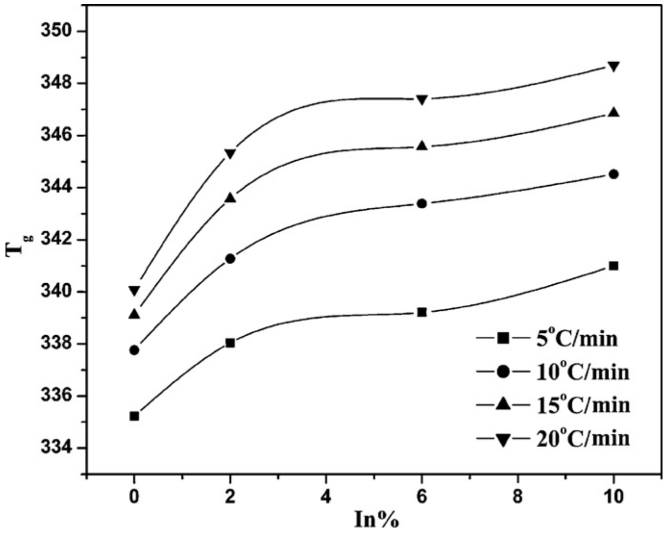

Fig. 2. Variation of T_g with composition for bulk amorphous $Se_{85-x}Te_{15}In_x$ at different heating rates.

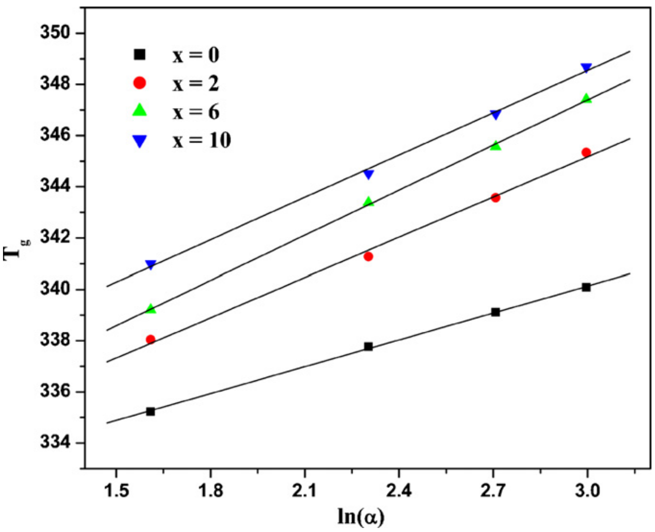

Fig. 3. Plot between T_g and $\ln(\alpha)$ for $Se_{85-x}Te_{15}In_x$ system.

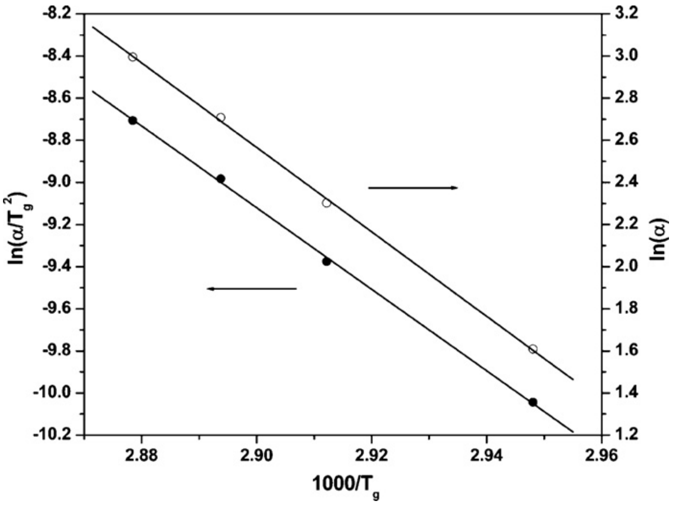

Fig. 4. Plots of $\ln(\alpha/T_g^2)$ and $\ln(\alpha)$ against $1000/T_g$ for $Se_{79}Te_{15}In_6$ chalcogenide glass.

number of Se_8 rings increases while the number of Se–Te polymeric chains and Se–Te mixed rings decreases. As mentioned earlier, T_g decreases with increasing ring concentration and increases with the decrease of ring concentration. Therefore, T_g in case of their samples decreases.

3.1. Glass transition activation energy

The glass transition region has been studied in terms of activation energy of glass transition and variation of glass transition temperature with composition and heating rate. The glass transition temperature represents the strength or rigidity of the glass structure of the investigated glassy alloy. Three approaches have been used to analyze the dependence of the T_g on the heating rate and estimation of the glass transition activation energy of $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6, 10) glasses. The first one corresponds to the empirical relation given by Lasocka [27]:

$$T_g = A + B\ln(\alpha) \tag{1}$$

where A and B are constants depending upon the glass composition and α is the heating rate used in DSC scans. It is evident from this equation that a plot of $\ln(\alpha)$ against T_g should be a straight line. It is found that this equation holds good for all samples. Fig. 3 shows the plot for all investigated samples at all heating rates for glass transition region. The value of A and B are calculated from the intercept and slope of T_g versus $\ln(\alpha)$ plot. The obtained values of A and B of the investigated samples are listed in Table 1. The change in the value of B with increasing indium content indicates that the system undergoes structural changes with incorporation of In.

In the other approach, the apparent activation energy of the glass transition E_g of the investigated glassy alloys has been determined using Kissinger's formula [28,29]. In spite of the fact that the Kissinger's equation is basically meant for the determination of activation energy for crystallization process, the similar equation can be used for the evaluation of glass transition activation energy [30–32] and may be written as:

$$\ln\left(\frac{\alpha}{T_g^2}\right) = -\frac{E_g}{RT_g} + \text{constant} \tag{2}$$

Table 1
Constants A (K), B (min) and activation energy of the glass transition E_g for different compositions of In.

Composition	A (K)	B (min)	E_g (kJ/mol)	
			Kissinger equation	Moynihan approximation
$Se_{85}Te_{15}$	329.64	3.50	265	271
$Se_{83}Te_{15}In_2$	329.47	5.23	179	185
$Se_{79}Te_{15}In_6$	329.79	5.87	161	167
$Se_{75}Te_{15}In_{10}$	332.02	5.51	173	179

A plot of $\ln(\alpha/T_g^2)$ against $1/T_g$ should be straight line and that the activation energy involved in the molecular motions and rearrangements around glass transition temperature T_g can be calculated from the slope of this plot. Fig. 4 shows the variation of $\ln(\alpha/T_g^2)$ against $1000/T_g$ for $Se_{79}Te_{15}In_6$ and found to be a straight line for all investigated samples. The calculated values of E_g for all alloys are shown in Table 1 which decreases with insertion of In content in Se–Te system and is found minimum for 6 at.% among the studied samples.

When the variation of $1/T_g^2$ with $\ln(\alpha)$ is much slower than that of $1/T_g$ with $\ln(\alpha)$, the glass transition activation energy, E_g, can be simplified and deduced from the Moynihan et al. [33] relation:

$$\ln(\alpha) = -\frac{E_g}{RT_g} + \text{constant} \tag{3}$$

The slope of the variation of $\ln(\alpha)$ versus $1/T_g$ plot gives the value of effective activation energy, E_g. Fig. 4 shows the plots of $\ln(\alpha)$ versus $1000/T_g$ for $Se_{79}Te_{15}In_6$ glasses displaying the linearity of the equations used.

Glass transition activation energy E_g is found to vary with composition indicating a structural change due to the addition of indium and the glass with lower E_g is the most stable [34]. The calculated values of E_g for glass transition region are listed in Table 1 and decreases with the incorporation of indium and have the minimum value at $x = 6$ at.%. A similar remark was also given for other In additive Se–Te glassy alloys [8–10]. This decrease in E_g is due to the increase in internal energy [10]. As mentioned earlier, when In content is incorporated to the binary Se–Te system, it is dissolved in Se and satisfies the coordination requirement for making bonds with Se atoms by breaking Se–Te chain or Se–Te mixed rings. As more and more such bonds are formed, the internal energy of the glasses increases and in turn glass transition activation energy decreases. Moreover, the glass transition activation energy is the amount of energy which is absorbed by a group of atoms in the glassy region, so that a jump from one metastable state to another is possible [35]. In other words, the activation energy is involved in the molecular motions and rearrangements of the atoms around the glass

Table 2
Values of n, m and effective crystallization activation energy, E_c (kJ/mol), by Matusita's method.

Composition	mE_c	n	m	E_c
$Se_{85}Te_{15}$	171	1.28	1	171
$Se_{83}Te_{15}In_2$	172	1.82	1	172
$Se_{79}Te_{15}In_6$	243	2.74	2	122
$Se_{75}Te_{15}In_{10}$	242	2.31	1	242

transition temperature [8]. Accordingly, the atom in a glass having minimum activation energy have a higher probability to jump to the metastable state of lower internal energy and hence is the most stable [35]. It is observed that the activation energy calculated using the two models [28,29,33] is in good agreement with each other for all investigated glasses indicating that one can use either Eq. (2) or (3) to calculate the activation energy of glass transition.

3.2. Crystallization reaction order (n)

The theoretical basis for interpreting the DSC of thermograms is provided by the formal theory developed by Johnson and Mehl [36] and Avrami [37–39] in which the crystallized fraction (χ) can be expressed as the function of time (t) according to the following relation:

$$\chi(t) = 1 - \exp[-(Kt)^n] \tag{4}$$

where n is the Avrami exponent that depends upon the growth mechanism and the dimensionality of the glassy alloy. K is defined as the reaction rate constant assumed to have Arrhenian temperature dependence:

$$K = K_o \exp\left(-\frac{E_c}{RT}\right) \tag{5}$$

where E_c is the activation energy for the crystallization and K_o is the frequency factor.

The most widely used model, the JMA-model [36–39], is derived for isothermal crystallization. Attempt has been made to apply the JMA-model for non-isothermal conditions. In the non-isothermal method, the crystallized fraction in a glass heated at a constant rate α, is related to the activation energy of crystallization, E_c, is given by Matusita's [40] relation:

$$\ln[-\ln(1-\chi)] = -n\ln(\alpha) + 1.052\frac{mE_c}{RT} + \text{constant} \tag{6}$$

where χ is the crystallized fraction and m and n are integer or half integer numbers that depend upon the growth mechanism and the dimensionality of the glassy alloy. For as-quenched glass containing no nuclei m is equal to $(n-1)$ and for glass containing a sufficiently large number of nuclei, which might occur due to the annealing of the as-quenched glass m is taken equal to n. Since the as-quenched samples are studied, the value of m is taken as $m = (n-1)$.

According to Eq. (6), a plot of $\ln[-\ln(1-\chi)]$ against $\ln(\alpha)$ at a specific temperature yields a straight line with slope equal to Avrami exponent (n). Fig. 5 shows the plot for $Se_{83}Te_{15}In_2$ at three specific temperatures. The average value of n is evaluated from the slope of the plots is listed in Table 2 for all investigated samples. It can be seen from the values of m and n in Table 2 that the mechanism of crystal growth changes with the addition of indium content to Se–Te system. For $Se_{85}Te_{15}$, $n = 1.28$ which gives $m = 1$ suggesting one-dimensional growth. The average values of the kinetic exponent n show predominantly one-dimensional growth for $Se_{83}Te_{15}In_2$ and $Se_{75}Te_{15}In_{10}$ while two-dimensional growth for $Se_{79}Te_{15}In_6$.

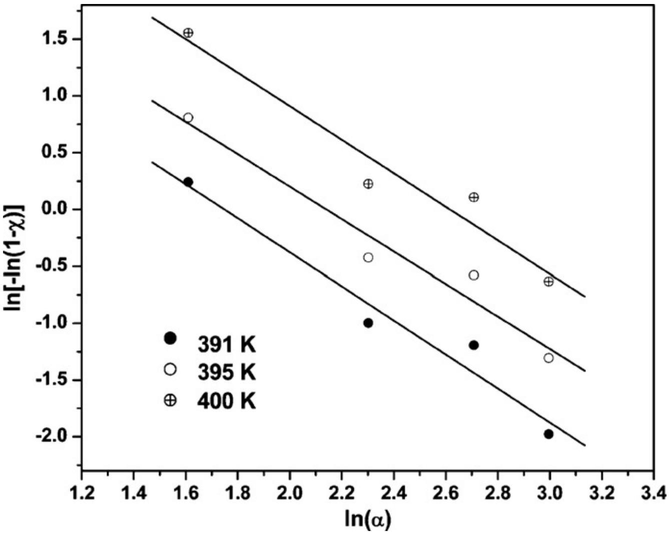

Fig. 5. Plots of $\ln[-\ln(1-\chi)]$ versus $\ln(\alpha)$ at fixed temperatures for the chalcogenide glass $Se_{83}Te_{15}In_2$.

3.3. Crystallization activation energy

Once the value of n is obtained, the effective activation energy E_c can be calculated at different heating rates following the method suggested specifically for non-isothermal data [40]. A plot between $\ln[-\ln(1-\chi)]$ and $1/T$ at a constant heating rate should give a straight line. The value of mE_c can be calculated from the slope of $\ln[-\ln(1-\chi)]$ and $1/T$ plot using Eq. (6). The plots are found to be linear over most of the temperature range but show deviations from the linear behaviour at higher temperature (not shown here). This deviation from linearity may be attributed to the saturation of nucleation sites in the final stage of crystallization [32] or to a restriction of the crystal growth by the small size of the particles [41]. For the calculation of activation energy we restricted ourselves to the linear portions of these plots. From the m value and the average value of mE_c, the activation energy for crystallization of chalcogenide $Se_{85-x}Te_{15}In_x$ ($x = 0$, 2, 6 and 10) glasses are obtained and found to vary between 122 and 242 kJ/mol given in Table 2. Fig. 6 shows the variation of $\ln[-\ln(1-\chi)]$ and $1/T$ for $Se_{83}Te_{15}In_2$.

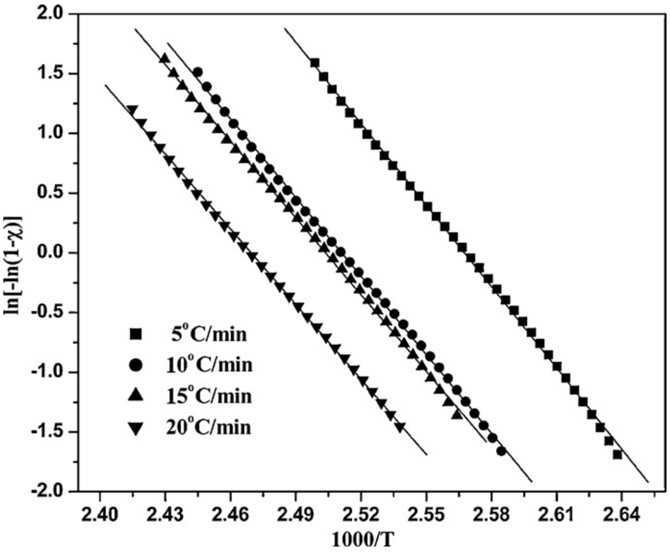

Fig. 6. $\ln[-\ln(1-\chi)]$ versus $1/T$ plots at different heating rates for the chalcogenide glass $Se_{79}Te_{15}In_2$.

Table 3
Values of activation energies of $Se_{85-x}Te_{15}In_x$ (x = 0, 2, 6 and 10).

Composition	E_c (kJ/mol)			
	Kissinger's relation	Mahadevan's approximation	Augis and Bennett method	Augis and Bennett approximation.
$Se_{85}Te_{15}$	157	161	146	161
$Se_{83}Te_{15}In_2$	104	111	94	107
$Se_{79}Te_{15}In_6$	101	108	100	105
$Se_{75}Te_{15}In_{10}$	121	127	109	124

According to the well known Kissinger's model, assumes that the reaction rate is maximum at the peak temperature, the effective crystallization activation energy (E_c) can be determined from the variation of peak crystallization temperature (T_p) with heating rate (α) by using the following relation [28,29]:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_c}{RT_p} + \text{constant} \tag{7}$$

The graph between $\ln(\alpha/T_p^2)$ versus $1/T_p$ should be a straight line and the effective activation energy can be calculated from the slope of the graph. The calculated values of effective crystallization energy are listed in Table 3. When the variation of $1/T_p^2$ with $\ln(\alpha)$ is much slower than that of $1/T_p$ with $\ln(\alpha)$, Mahadevan et al. [42] has approximated the above equation to the following form:

$$\ln(\alpha) = -\frac{E_c}{RT_p} + \text{constant} \tag{8}$$

Plots of $\ln(\alpha)$ as a function of $1000/T_p$ have been made for all the glasses studied and E_c has been derived from the slopes of these plots and results are given in Table 3. The last method used is based on the method of Augis and Bennett [43] to determine the crystallization activation energy, E_c, according to the following relation:

$$\ln\left(\frac{\alpha}{T_p - T_o}\right) = -\frac{E_c}{RT_p} + \ln K_o \tag{9}$$

where T_o is the onset temperature of crystallization. $\ln[\alpha/(T_p - T_o)]$ is plotted against $1/T_p$, a straight line is obtained whose slope gives the value of E_c/R and calculated values are given in Table 3 for all compositions. In case of $T_p \gg T_o$, the above said equation can be approximated to the following form [44]:

$$\ln\left(\frac{\alpha}{T_p}\right) = -\frac{E_c}{RT_p} + \text{constant} \tag{10}$$

The slope of this approximated formula gives the value of the crystallization activation energy (E_c) and reported in Table 3. Fig. 7 shows the variation of $\ln(\alpha/T_p^2)$, $\ln(\alpha/T_p)$, $\ln(\alpha/(T_p - T_o))$ and $\ln(\alpha)$ against $1000/T_p$ for $Se_{79}Te_{15}In_6$. Similar plots are also observed for all other investigated $Se_{85-x}Te_{15}In_x$ glasses.

Our results show that the activation energy of crystallization, E_c, decreases with addition of In content. The decrease in E_c can be explained on the basis of modification of the chemical bonds present in the Se–Te system by the introduction of In content. When the In content is incorporated in the Se–Te system, indium is expected to combine preferably with Se. As mention earlier, when In added to the Se–Te system, may break the Se–Te chains or Se–Te mixed rings to satisfy its coordination number and forms a cross-linked structure. Due to cross-linking of indium within the Se–Te system, the tendency of the crystallization is retarded and hence a decrease in crystallization activation energy is observed which agrees with the conclusion reached by others [8–10,45].

We noted that the activation energy of the binary composition determined by Matusita's method is in agreement with the values those obtained from Kissinger's model, Mahadevan's approximation, Augis and Bennett method and Augis and Bennett approximation. A similar observation was also reported for other binary alloys [5,46,47]. However, for the ternaries, we note that the values obtained from Matusita's method are different from Kissinger's model and Augis and Bennett's method as well as their approximations. This difference can also be attributed to the fact that these models are based on approximations involved in obtaining the final equation of different formalisms. The activation energy is found to be minimum at 6 at.% of In additive Se–Te system (Tables 2 and 3). We can also insist that Matusita model propounds a general model more appropriate for kinetic study of glassy alloys.

The activation energy being an important parameter since it indicates the thermal stability of the glass and its magnitude reflects the nature of transformation. The JMA model implies that the Avrami exponent and the effective activation energy should be constant during the transformation process. Recent development in this field has shown that they are not necessarily constants but show variations in different stages of the transformation [48–51]. The suggestion that the effective activation energy in solid-state transformation should be variable has been addressed by Vyazovkin [52–55]. The variation of the activation energy with the degree of crystallization and hence with temperature can provide useful information about the different mechanisms involved in the transformation process [53]. As pointed out by the Vyazovkin [53], this variation of the activation energy with the degree of crystallization and hence with temperature can provide useful information about the different mechanisms involved in the transformation process. In order to reveal this variation, the isoconversional methods are widely used to determine the activation energy of the crystallization process.

The kinetics of crystallization in amorphous materials can be described by the following rate equation [52]:

$$\frac{d\chi}{dt} = K(T)f(\chi) \tag{11}$$

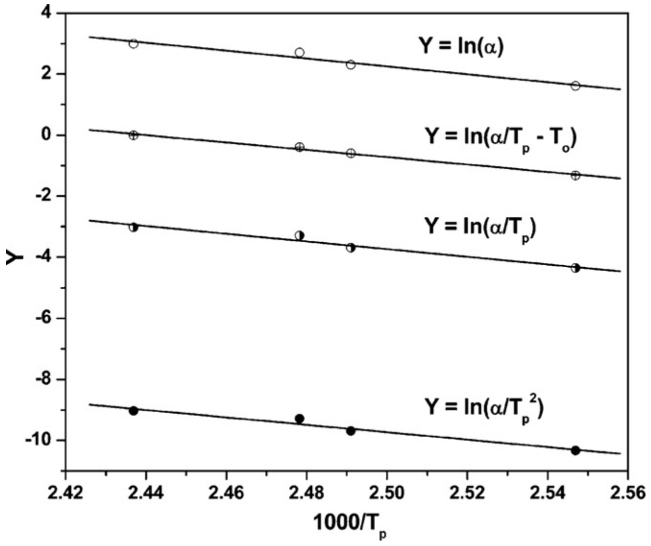

Fig. 7. Plots of $\ln(\alpha/T_p^2)$, $\ln(\alpha/T_p)$, $\ln(\alpha/(T_p - T_o))$ and $\ln(\alpha)$ against $1000/T_p$ for $Se_{79}Te_{15}In_6$.

Table 4
Local activation energy at different extent of conversion using different isoconversional methods.

χ	E_c (kJ/mol)											
	$Se_{85}Te_{15}$			$Se_{83}Te_{15}In_2$			$Se_{79}Te_{15}In_6$			$Se_{75}Te_{15}In_{10}$		
	KAS	OFW	Friedman	KAS	OFW	Friedman	KAS	OFW	Friedman	KAS	OFW	Friedman
0.1	144	143	121	124	124	119	96	97	96	135	135	120
0.2	135	134	112	117	117	112	98	99	97	130	130	116
0.3	127	127	105	109	110	108	99	100	99	127	127	114
0.4	121	121	95	104	105	105	99	101	100	124	124	111
0.5	113	114	81	97	98	103	100	101	100	122	123	109
0.6	104	105	67	91	93	103	101	102	100	121	121	107
0.7	95	97	55	85	87	104	101	102	99	119	119	106
0.8	86	88	53	79	81	107	101	103	98	117	118	104
0.9	81	83	67	71	74	113	101	102	96	115	116	103

where K is the reaction constant, $f(\chi)$ is the reaction model, χ is the conversion fraction that represents the volume of the crystallized fraction. The rate constant, K, usually has Arrhenian temperature dependence. The isothermal transformation rate can be written from Eq. (11) as:

$$\frac{d\chi}{dt} = K_o \exp\left(-\frac{E}{RT}\right) f(\chi) \tag{12}$$

Under non-isothermal conditions with a constant heating rate of $\alpha = dT/dt$, Eq. (12) may be rewritten as:

$$\frac{d\chi}{dT} = \frac{d\chi}{dt}\left(\frac{1}{\alpha}\right) = \left(\frac{K_o}{\alpha}\right) \exp\left(-\frac{E}{RT}\right) f(\chi) \tag{13}$$

There is a variety of theoretical models and mathematical treatments to explain the estimation of crystallization kinetics. The three isoconversional methods have been used in the present study to analyze the crystallization kinetics of the $Se_{85-x}Te_{15}In_x$ glasses.

The Kissinger–Akahira–Sunose (KAS) method [28,29,56] or generalized Kissinger method may be obtained through derivation of Eq. (13). Subsequent logarithm application and rearrangement yields:

$$\ln\left(\frac{\alpha_i}{T_{\chi i}^2}\right) = \ln\left[\left|\frac{df(\chi)}{d\chi}\right|\left(\frac{K_o R}{E_\chi}\right)\right] - \frac{E_{\chi i}}{RT_{\chi i}} \tag{14}$$

The subscript i denotes different heating rates. For each degree of the conversion, χ, a corresponding $T_{\chi i}$ and heating rate are used to plot $\ln(\alpha_i/T_{\chi i}^2)$. The plot should be a straight line whose slope can be used to calculate the activation energy, $E_{\chi i}$. Using Eq. (14) one gets the local activation energy E_c at particular χ value (Table 4). The temperature dependence of E_c is readily obtained by replacing χ with the temperature which is estimated as an average of the temperatures corresponding to this χ value at different heating rates [57–59].

The Ozawa–Flynn–Wall (OFW) method [60,61] involves the measurement of the temperature T_χ, corresponding to a fixed value of fraction crystallization, χ, from the experiments at different heating rates, α. The OFW method is based on the following equation:

$$\ln(\alpha) = -\frac{1.0516 E_\chi}{RT_\chi} + \text{constant} \tag{15}$$

The plot of $\ln(\alpha)$ versus $1000/T_\chi$ gives the slope $-1.0516\ E_\chi/R$ from which the activation energy has been evaluated (Table 4).

The differential isoconversional method suggested by Friedman [62] is based on Eq. (12). For various heating rates, α_i, this method can be used directly from Eq. (12) at a specific crystallization fraction χ as:

$$\ln\left(\frac{d\chi}{dt}\right)_{\chi i} = \ln(K_\chi f(\chi)) - \frac{E_{\chi i}}{RT_{\chi i}} \tag{16}$$

The parameter $E_{\chi i}$ at the specific value of χ is then estimated from a plot of $\ln(d\chi/dt)_{\chi i}$ versus $1/T_{\chi i}$ across different heating rates. The procedure is repeated for many values of χ, yielding continuous functions of χ for E_c (Table 4). The dependence of the activation energy with the extent of crystallization, χ, is shown in Fig. 8 for $Se_{75}Te_{15}In_{10}$. It is clear from the Fig. 8 and Table 4 that the activation energy of crystallization shows a variation as a function of the degree conversion χ in these three methods. A similar observation was also reported for other glasses [50,51]. However, the activation energy is particularly independent of the value of χ for $Se_{79}Te_{15}In_6$; with somewhat lower values in the terminal stage of crystallization. It is also worth to note that there is good agreement among KAS and OFW method except Friedman method. Pratap et al. [63] also reported that the activation energies evaluated by KAS and OFW methods are different than those obtained by Friedman method. It is possible that this disagreement is due to fact that the systematic errors which arise from the numerical differentiation of the experimental data involved in Friedman method [64]. Fig. 9 displays the resulting E_c dependence on temperature as obtained from Eqs. (14)–(16) for $Se_{75}Te_{15}In_{10}$. All the three isoconversional methods show that the activation energy E_c decreases with temperature indicates that the crystallization rate increases with increasing temperature. The variation of the activation energy with temperature demonstrates that the rate constant of crystallization is in fact determined by the rates of two processes, nucleation and diffusion. Because these two mechanisms are likely to have different activation energies, the effective activation energy of the transformation will vary with temperature [59]. This inter-

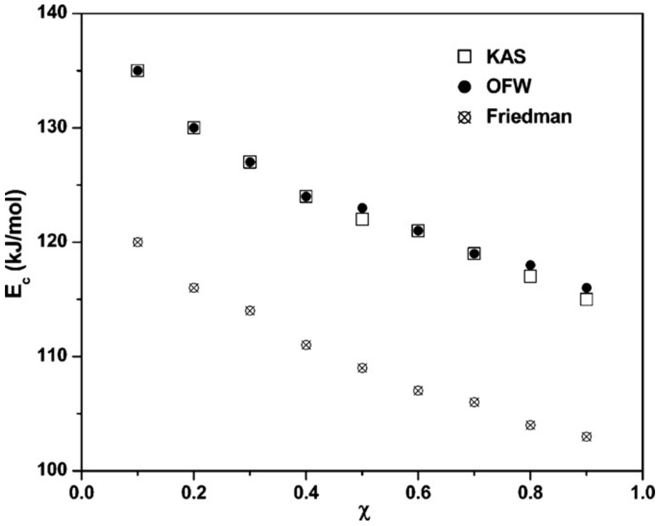

Fig. 8. The effective activation energy as a function of χ as determined using different isoconversional methods for $Se_{75}Te_{15}In_{10}$.

Table 5
Values of T_g, T_p-T_g, K_{gl} for $Se_{85-x}Te_{15}In_x$ (x = 0, 2, 6 and 10) chalcogenide glasses.

Composition	5 °C/min			10 °C/min			15 °C/min			20 °C/min		
	T_g (K)	T_p-T_g (K)	K_{gl}	T_g(K)	T_p-T_g (K)	K_{gl}	T_g(K)	T_p-T_g (K)	K_{gl}	T_g(K)	T_p-T_g (K)	K_{gl}
$Se_{85}Te_{15}$	335.23	36.79	0.20	337.77	38.10	0.21	339.11	41.88	0.23	340.08	40.49	0.23
$Se_{83}Te_{15}In_2$	338.04	50.56	0.28	341.27	56.63	0.31	343.57	54.72	0.30	345.34	59.97	0.34
$Se_{79}Te_{15}In_6$	339.21	53.42	0.29	343.39	58.05	0.32	345.57	57.94	0.32	347.41	62.94	0.35
$Se_{75}Te_{15}In_{10}$	341.00	51.66	0.28	344.52	55.29	0.30	346.85	56.95	0.31	348.69	58.58	0.32

pretation is based on the nucleation theory proposed by Fisher and Turnbull [65].

3.4. Thermal stability and the ease of glass formation

From the point of view of technological applications, the glass should be thermally stable. One of the best known relationships is the “two-*third*” rule proposed by Kauzmann, stating that T_g scales with the melting temperature as $T_g = 2/3T_m$ [66]. The ease in glass forming tendency is determined by calculating the reduced glass transition temperature:

$$T_{rg} = \frac{T_g}{T_m} \tag{17}$$

Two-third rule holds good for all compositions. The value of reduced glass transition temperature, T_{rg}, is found to be the order of 2/3 for all the samples indicating good glass forming ability for all the compositions of the material. However, in non-isothermal study, the thermal stability of the glass is usually investigated in terms of separation between T_g and T_p because higher the value of this difference, more the delay in the nucleation process [67]. Thus, the difference between T_p and T_g is an indication of the thermal stability and the glass forming tendency (GFT) of the glass against crystallization. The higher the value of (T_p-T_g), greater is the GFT. It is found that the values of (T_p-T_g) are the highest at x = 6 at.% in $Se_{85-x}Te_{15}In_x$ at all the heating rates. This indicates that thermal stability and GFT is highest in this case among all the compositions studied. Hruby has introduced a parameter K_{gl}, as an indicator of the GFT and is given by [68]:

$$K_{gl} = \frac{T_p - T_g}{T_m - T_p} \tag{18}$$

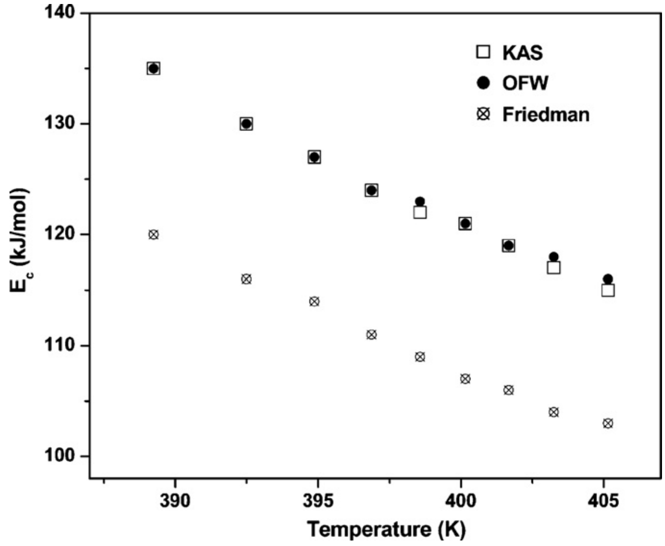

Fig. 9. The temperature dependence of the effective activation energy for $Se_{75}Te_{15}In_{10}$.

where T_m is the melting temperature. All values of T_g, (T_p-T_g) and Hruby’s parameter at all heating rates for all investigated samples are listed in Table 5.

4. Conclusions

Kinematics studies made on various glassy alloys in $Se_{85-x}Te_{15}In_x$ (x = 0, 2, 6 and 10) system indicate that the glass transition and crystallization temperatures depend on the heating rate as well as on the composition. From the heating rate dependence, the kinetic parameters, activation energy of the glass transition, activation energy for the crystallization process, kinetic exponent, n, have been deduced and found to be composition dependent. The average value of Avrami index $n \approx 1$ for binary alloy indicates one-dimensional growth; while for x = 2 and 10, the Avrami index $n \approx 2$ indicates the existence of volume nucleation with one-dimensional growth and for x = 6, the Avrami index $n \approx 3$, indicate the two-dimensional growth with volume nucleation. Thus, the introduction of indium to the Se–Te system brings about a change in crystallization mechanisms and dimension of growth. Using isoconversional methods, the activation energy of crystallization is found to vary with extent of conversion and hence with temperature. The temperature difference (T_p-T_g) is highest for the samples with 6 at.% of In. Moreover, Hruby’s parameter is the highest in this case confirms the maximum stability. Hence the glass with 6 at.% of In is the most stable among investigated glassy alloys.

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