

# Kinetics study of $\text{Se}_{88}\text{Te}_{12}$ and $\text{Se}_{88}\text{Te}_8\text{Zn}_4$ glassy compositions; phase change memory material

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## **Abstract**

Kinetics studies of  $\text{Se}_{88}\text{Te}_{12-x}\text{Zn}_x$  glassy compositions have been performed at different heating rates using differential thermal analysis technique under non-isothermal condition. An amorphous nature of considered samples has been checked by x-ray diffraction patterns. In accordance with different methods, the glass transition  $E_g$  and crystallization  $E_c$  activation energies are identified and discussed. The observed decrease of  $E_g$  with Zn addition can be explained in terms of atomic weight and heat of atomization which reflects the higher thermal stability of composition with Z content. This outcome is confirmed by investigating the thermal stability parameters such as several widely used and more recently thermal stability criteria, the rate of crystallization, the fragility index, critical heating rate, kouzmann temperature, and the relative change parameters of thermal stability criteria as well. The more suitable and sensitive thermal stability criterion and the less one for the studied chalcogenide compositions are also identified. The fragility index has been performed by Angll's equation categorized the two compositions under test as a strong glasses. In light of Losacka's empirical relation reveals that the glass transition process is found less sensitive to  $\beta$  than that of crystallization process. The present kinetics study illustrates that the compositions under review are suitable for phase change memory device .

**Keywords;** Zn addition, Thermal stability criteria, Phase change memory device, Critical heating rate, Activation energy, Strong glasses

## **1 – Introduction**

There are two distinctive calorimetric techniques include differential thermal analysis or differential scanning calorimetric have been used to investigate the kinetics

study. There are two conditions can be performed either non-isothermal or isothermal condition. The kinetics of glass transition is considered a great important study for technologic application before the inevitable crystallization takes place. The kinetics of crystallization plays an important role to determine the transport mechanism, activation energy and practical application. The addition of a third element to binary chalcogenide glasses further increases the possibility of wide variation of properties by change the composition. The binary Se-Te alloys are preferred among the various chalcogenide materials because of their higher photo sensitivity, greater hardness, high crystallization temperature comparing to pure Se. In our early published works [1, 2] the non-isothermal kinetics for Pb and Bi addition as third element in Se-Te system have been proposed and discussed. Now in our present study we added Zn in the Se-Te system as a third element of  $\text{Se}_{88}\text{Te}_{12}\text{Zn}_x$  with  $x = 0$  and  $4$ . The reason for choosing of Zn as a chemical modifier in binary Se-Te alloy is due to its attractive and important application as it can be used for a photo doping of chalcogenide glasses, development of light emitted diodes and lasers and also expand the glass forming region increasing the thermal stability. Many authors [3-7] give attention to this ternary composition. Srivastava et. al. [3] proposed that the incorporation Zn up to 4% enhance the crystallization activation energy for  $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$  ( $x=2, 4, 6, 8$ ). In another work [4] They also studied the glass transition kinetics for the same composition. The increase of thermal stability with Zn content of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  has been observed by Naqvi et. al. [5]. Moreover, The role of additive Zn in corporation on the glass/crystal thermodynamic of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x=2, 4, 6, 8, 10$ ) has been investigated in anther Naqvi et.al. research [6]. The kinetics of ternary  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  has been also discussed by Ahmed et. al. [7] with ( $x = 0.5, 1, 1.5, 2, 2.5$ ).

As mentioned above, up to now there are no research studied the kinetics and thermal stability criteria for the Zn addition to binary SeTe system in cost of Te atoms with applied more recent studies for this purpose as done in the present work. The main objective of the present work is studying the glass transition and crystallization kinetics for  $\text{Se}_{88}\text{Te}_{12-x}\text{Zn}_x$  ( $x = 0, 4$ ) using the different thermal analysis technique under no-isothermal condition at constant heating rate  $\beta$  in the range,  $50 \geq \beta \geq 20$ . The composition dependence of the glass transition activation energy and crystallization mechanism has been reported and discussion. The thermal stability has been investigated with Zn addition by determining of the fragility index, crystallization rate, the widely used and more recently thermal stability criteria.

## **2- Experimental study:**

Bulk sample have been synthesized by a well-known melt quenching technique from the pure (5N) elementary constituents of each composition. Total 5 gm of the elements were weighted in quartz ampoule according to their atomic percentage for each composition. These tubes are step wisely heated in an oscillatory furnace (after sealing under high vacuum) with constant heating rate 3-4 deg./min up to 1073K. This temperature was maintained constant for 13-15 h. A continual rocking was done to set homogeneous samples by rotating the ceramic rod of furnace. After that each tube was

then quenched in an ice water to have a glassy forms. The bulk samples were taken out by breaking the silica ampoules.

The obtained material was grinded by mortar and preserved for structure characterization. Amorphously of the prepared films is investigated by x-ray diffraction technique (XRD) using Philips x-ray unit (model x\pert) at 40 kV and 25 mA with a copper target and Ni filter. Fig. 1 shows the XRD patterns for binary and ternary considered samples. The obtained patterns are characterized by the absence of any diffraction lines, revealing the amorphous nature of the studied samples.

A quantitative chemical composition analysis were investigated and check by Energy Dispersive x-ray spectroscopy (EDX) measurements using Scanning Electron microscope (Joel-JSM-5400) magnification x2000. Elemental analysis measurements were compared with the starting compositions which was found almost identical with average deviation  $\leq 0.4\%$  in atomic fraction for each element for all the compositions under investigation .

The study of glass transition and crystallization behaviors of the considered samples were performed using Differential Thermal Analysis (DTA) measurements under non-isothermal condition , using a Shimadzu DTA-50 device. Typically, 10 mg of sample in fine powder form was sealed in standard aluminum sample pans and heated at different rates (20, 30, 40 and 50 deg/min). The characteristic temperatures (glass transition, crystallization and melting temperatures) were extracted from DTA curves.

### **3-Result and Discussion**

#### **3.1 DTA traces**

The DTA curves at various heating rates  $50 \geq \beta \geq 20$  deg/min for  $\text{Se}_{88}\text{Te}_{12}$  and  $\text{Se}_{88}\text{Te}_8\text{Zn}_4$  chalcogenide glasses are shown in Fig. (2 a%b) which can be aided to evaluate the thermal properties of these glasses. As seen, the single endothermic peak represented a glass transition temperature  $T_g$ , followed by single exothermic peak refers to a crystallization of the sample which characteristic with the onset ( $T_c$ ), peak ( $T_p$ ) and finish ( $T_F$ ) crystallization temperatures. At higher temperature, an endothermic peak has been appear characteristic the melting temperature ( $T_m$ ). Such glasses have single endothermic and exothermic peaks refer more stable glasses than those have two or multi endothermic and exothermic peak.

All the above values of the characteristic temperatures shifted toward higher temperature with heating rate as shown in Table (1&2). The increase of  $T_g$  with  $\beta$  can be attributed to relaxation dynamics in glass transition period. On the other hand the shift of  $T_p$  to high values with  $\beta$  can be discussed according to the fact that, the system does not get sufficient time for nucleation and crystallization with increasing heating rate [8].

#### **3.2. Glass transition kinetics aspects:-**

##### **3.2.1. Composition dependence of $T_g$**

The composition dependence of  $T_g$  can be observed from Table (1&2) whereas, the glass transition temperatures decrease with Zn addition to SeTe system. This outcome can be understood according to the structure change with Zn addition where Zn incorporated in Se-Te matrix. They are probably dissolved in the Se chain increasing relatively the number of  $Se_8$  rings while the number of chain Se-Se are decreased, since the  $T_g$  temperature decreases with increasing ring consentent. In other words,  $T_g$  decreases with decrease in effective molecular weight (concentration of long polymeric chain of Se-Te ) with Zn addition [7].

### **3.2.2. Determination of the Kauzmann temperature $T_k$ and critical heating rate $\beta_c$**

As observable from Tables (1&2), that, the  $T_g$  values shifted to higher values with  $\beta$  due to an increase in structural relaxation and decrease in relaxation time with raising in  $\beta$ . The heating rate reliance of  $T_g$  can be seen by fitting these data to a linear relation according to Lasocka formula [9].

$$T_g = A_g + B_g \log \beta \quad \longrightarrow \quad (1)$$

Where  $A_g$  and  $B_g$  are empirical constants related to the response of the nature of the configuration changes within the region of glass transition. Lasocka relation for glass transition has been found to be valid for heating rate dependence of the peak as well as onset crystallization temperatures.

Implementing Eq. (1) on the peak crystallization temperature  $T_p$  as

$$T_p = A_c + B_c \log \beta \quad \longrightarrow \quad (2)$$

The plots of  $T_g$  and  $T_p$  vs.  $\log \beta$  have been depicted in Fig. (3 a&b) respectively for the glassy alloys under test. Values of the constants  $A_g, A_c, B_g$  and  $B_c$  can be derived from the slopes and intercepts of those lines in the last figure and listed in Table (3). As clear, the ranges of  $A_g$  and  $B_g$  values are in a good agreement with that obtained for  $Se_{70}Te_{30-x}Zn_x$  composition [10]. Moreover the  $B_g$  has lower value than  $B_c$ , which is attributed to that the crystallization procedure is more sensitive to the heating rate than glass transition process for the investigated compositions.

The correlation proposed by Lasocka between  $T_p$  and  $T_g$  temperatures can be proposed as [11,12]

$$T_p = \frac{A_c B_g - B_c A_g}{B_g} + \frac{B_c}{B_g} T_g \quad \longrightarrow \quad (3)$$

Kauzmann temperature  $T_k$  is considered the temperature with the entropy of liquid becomes similarly to that of crystal [13]. So, the knowing the  $T_k$  value is important for a thermodynamic view point.  $T_k$  temperature can be estimated from the above Lasocka's relation for  $T_p$  and  $T_g$  correlation and defined as the most minimal the orital boundary for the glass transition. Therefor, we can say that the liquid cannot be super cooled below  $T_k$  even the slowest cooling rate. Kauzmann temperature values can be expressed as a temperature where  $T_c = T_g = T_k$  at critical heating rate  $\beta_c$ . According to Eqs. (1)&(3) we can deduced the following relations [14,15]

$$\beta_c = 10^{(A_g - A_c)/(B_c - B_g)} \longrightarrow (4)$$

and 
$$T_k = \frac{B_c A_g - A_c B_g}{B_c - B_g} \longrightarrow (5)$$

The estimated critical heating rate  $\beta_c$  and Kauzmann temperature  $T_K$  values for the compositions under test are given in Table (3) for the studied compositions. As seen the little value of  $\beta_c$  was found for the investigated glasses composition with Zn addition than that for SeTe composition, that reflects the increase of the thermal stability with Zn addition to SeTe system.

### 3.2.3. Activation energy of glass transition $E_g$

The important of glass transition activation energy raises from where it involved in the molecular motions and rearrangements around  $T_g$ . The shifting of  $T_g$  with heating rate can be used to determine the glass transition activation energy  $E_g$  as suggested early and adopted by many researchers[16-19]. Moynihan et.al [16] proposed a glass transition kinetic interpretation in terms of thermal relaxation phenomena. They provided the variation of  $T_g$  with  $\beta$  satisfied the following relation-

$$\ln \beta \propto \frac{-E_g}{R T_g} \longrightarrow (6)$$

Where R the gas constant. Kissinger [17] proposed a model to evaluate the values of  $E_g$  dependent on the follow relation

$$\ln(\beta/T_g^2) \propto -E_g/R T_g \longrightarrow (7)$$

Augis-Bennett [18] introduced a relation to determine the crystallization activation energy  $E_c$ . Saraswatet.al [19] proved the invariance of Augis - Bennett's relation from glass transition phenomenon to crystallization phenomenon and applied this relation to determine the glass transition activation energy. Since  $E_g$  evaluated from this relation has less dependence on the thermal history on the contrary the  $E_g$  value derived by Moynihan et.al which dependence substantially on the thermal history because of dependence of relaxation time on temperature and structure as well. Considering this discussion the  $E_g$  value can be determined according to Augis-Bennett [18] as follows:

$$\ln(\beta/T_g) \propto -E_g/R T_g \longrightarrow (8)$$

Fig. (4 a&b) shows the variation of  $\ln \beta$ ,  $\ln(\beta/T_g)$  and  $\ln(\beta/T_g^2)$  against  $(1000/T_g)$  satisfying Eqs. (6-8) for the studied glassy compositions. The calculated  $E_g$  values are listed in Table (4). It has been found that the obtained  $E_g$  according to mentioned above methods values are in a good agreement with each other, Thus one can use any of the above three methods to derived  $E_g$ . The observed decrease in  $E_g$  value with Zn addition can be explained in terms of atomic weight of Te (127.6 gm/mol) and Zn (65.39 gm/mol) atoms where Zn atoms added in a cost of Te atoms. The obvious difference between the atomic weight of Zn and Te atoms decrease the mean atomic weight of the studied ternary alloy. Which gives a reason for that the glass transition

occur at somewhat lower activation energy. Moreover the decrease of  $E_g$  with Zn addition can be explained in terms of average heat of atomization ( $H_s$ ) for the studied compositions. The  $H_s$  values of Se, Te and Zn atoms are 227,197 and 131 kJ/ mol respectively. Therefore the  $H_s$  calculated values for the investigated composition are listed in Table (3). As clear  $H_s$  of  $(Se_{88}Te_{12}) > H_s$  of  $(Se_{88}Te_8Zn_4)$ , that explain the higher value of  $E_g$  for the binary composition than that of ternary with Zn addition. The lower values of  $E_g$  for  $Se_{88}Te_8Zn_4$  glassy system indicate also that this particular glass has a large probability to jump to state of lower configurationally energy and higher stability in glass region. The similar  $E_g$  dependence was observed in another research for Zn addition to  $Se_{70}Te_{30}$  glasses [10]. Whereas the  $E_g$  is responsible for the molecular motion and rearrangement of the atoms around  $T_g$  and the glass with lower  $E_g$  is exhibit most stable [20] as seen in section (3-4).

### **3.2.4. Fragility index**

According to Angell's suggestion[21-23]. The fragility concept was proposed to determine the fragility index  $F_i$ , which a measure the rate at which the relaxation time decrease with the increase of temperature around  $T_g$  and given as:

$$F_i = \frac{E_g}{R T_g \ln(\beta)} \longrightarrow (8)$$

The  $F_i$  index is used to evaluate the thermal stability and glass formation ability for amorphous composition. Moreover, it is considered an important thermal stability criterion. Depending on fragility index values, the glass-forming liquid has been classified into two groups, for the first, the glasses are called "Strong" glasses with ( $F_i < 30$ ). These glasses show resistance to structural degradation and usually with a small enthalpy of the structural relaxation kinetics [2]. Second group is called "Fragile" material with ( $F_i > 100$ ). For the intermediate  $F_i$  values ( $30 > F_i > 70$ ) the glass are considered "intermediate" material [24]. Values of fragility indexes have been estimated and plotted as a function of heating rate using the  $E_g$  average value. As shown in Fig.(5), one can observed that the obtained  $F_i$  values for the studied composition of below 16 with values decrease with raising  $\beta$ , which confirmed the present glasses are classified as "Strong" glasses forming liquids. The "Strong" glasses feature is observed in other chalcogenide glass [2,25]. As clear from Fig.(5) the fragility index change with Zn addition as  $F_i(Se_{88}Te_{12}) > F_i(Se_{88}Te_8Zn_4)$  at different heating rates. This outcome shows that the studied glassy alloys with Zn addition is better thermodynamic stability and glasses formation ability than the host composition without Zn addition [12,26].

## **3.3 Crystallization kinetics aspects-**

### **3.3.1 Activation energy of crystallization $E_c$**



The acquired DTA traces can be analyzed to have different important crystallization kinetics parameters like Avrami exponent (n), the order of Dimensionality of growth (m), crystallization rate factor K and the crystallization activation energy  $E_c$  as well.

Crystallization in glass system occurs as a result of the nucleation and growth processes and it has been controlled by them. Firstly the process happens at low temperature whereas the second occurs at higher temperatures that give a reason for the increase at  $T_p$  with raising  $\beta$ . Where, if  $\beta$  has a large value, the sample has not a sufficient time for nucleation and crystallization. Therefore, by starting a time of crystallization, the increase of temperature occurs because of the higher heating rates. The activation energies of all crystallization processes is called the activation energy of crystallization  $E_c$ . Thus the  $E_c$  can be considered both of the activation energy for nucleation  $E_n$  and the activation energy for growth  $E_h$ . Different method were introduced various models to determine the  $E_c$  values using a different approximation based on the shifting occurs of peak crystallization temperature  $T_p$  with heating rate. Early, Kissinger in 1957 [27] derived a model for calculation of  $E_c$ , This model generalized by Elder [28] at the maximum reaction rate condition ( $d^2\alpha/dT^2 \approx 0$ ) as follow:

$$\ln(\beta/T_p^2) = -E/R T_p + \ln\delta_p + \ln(D R/E) \longrightarrow (10)$$

Where  $\delta_p$  is correction term that depends on the kinetics model. Then Eq.(10) can be rewritten as-

$$E_c = 1 / \left\{ 1 - \left[ \frac{d(\ln \delta_p)}{d\left(\frac{E}{RT_p}\right)} \right] \right\} - R \left\{ \frac{d\left[\ln\left(\frac{\beta}{T_p^2}\right)\right]}{d\left(\frac{1}{T_p}\right)} \right\} \longrightarrow (11)$$

The correction section in Eq.(10) has a condition of [2]  $\frac{1}{\left\{ 1 - \left[ \frac{d(\ln \delta_p)}{d\left(\frac{E}{RT_p}\right)} \right] \right\}} \approx 1$ . Now the approximate activation value according to Kissinger's model can be expressed as

$$E_c = -R \left[ \frac{d(\ln \beta/T_p^2)}{d\left(\frac{1}{T_p}\right)} \right] \longrightarrow (12)$$

The activation energy of crystallization  $E_c$  values can be also estimated by the variation of  $T_p$  with  $\beta$  using the approximate method introduced by Mahadevan et. al. [29]. They applied the condition where the variation of  $\ln(1/T_p^2)$  with  $\ln\beta$  is much slower than with  $\ln(1/T_p)$  using the following relation -

$$\ln(\beta) = \text{constant} - \frac{E_c}{R T_p} \longrightarrow (13)$$

Evaluation of  $E_c$  can be happened using another method which was proposed by Augis and Bennett [18] according the following relation-

$$\ln\left[\frac{\beta}{T_p - T_c}\right] = \ln k_0 - \frac{E_c}{R T_p} \longrightarrow (14)$$

The last equation can be approximated in the case of  $T_p \gg T_c$  as [30]

$$\ln\left[\frac{\beta}{T_p}\right] = \ln k_o - \frac{E_c}{R T_p} \longrightarrow \quad (15)$$

Where  $K_0$  is the frequency factor, that defined as the number of attempts made by nuclei per second to overcome the energy barrier. The minimum values of  $K_0$  confirm that the glass is most stable, whereas the number of attempts made by nuclei are lowest for glass. Fig. (6 a&b) depicted the variation of  $\ln(\beta)$ ,  $\ln(\beta/T_p^2)$ ,  $\ln[\beta/(T_p-T_c)]$  and  $\ln(\beta/T_p)$  versus  $(1/T_p)$  according to Eqs. (12-15) for the investigated compositions. The  $E_c$  values can be evaluated from the slopes of the fitting straight lines of Fig.(5 a&b) and reported in Table (5).

The volume fraction of crystalline phases during the process of crystallization can be determined from DTA thermo graph curves as  $\chi=A/A_o$ , where  $A_o$  is the exothermal peak total area in the range between  $T_c$  and  $T_f$  where the crystallization just start and finished and  $A$  is the area between  $T_c$  and any fixed temperature  $T$  in the range ( $T_f \geq T \geq T_c$ ). Fig. (7 a&b) shows the plot of the crystallized volume fraction ( $\chi$ ) as a function of temperature at various heating rates.

As seen all curves show a sigmoid type with temperature .A slightly increase in  $\chi$  at both of starting and at the end of the crystallization process suggests that the reaction proceeds slowly at ( $0.1 > \chi > 0.9$ ). According to Fig.(.), the crystallization reaction are divided into three region. First, the nucleation slowly and the bulk crystallization is dominant. Second, the crystallization reaction occurs stably. Third, the surface between crystallization phase and amorphous matrix decrease as a result of grain coalesce [31]. For isothermal condition  $\chi$  can be described by Johnson-Mehl-Avrami (JMA) [32] transformation equation-

$$\chi = 1 - \exp[-(kt)^n] \longrightarrow \quad (16)$$

Where  $n$  is the dimensionless Avrami exponent related to nucleation and growth process. The validity of Eq. (16) can be extended to non-isothermal kinetics with the condition of the crystallization rate doesn't depended on the previous thermal history. Matusita et al.[33] have suggested a method when the value of crystallized fraction  $\chi$  in a glass heated at uniform heating rate  $\beta$  was related to the crystallization activation energy under non-isothermal condition according to the following double-logarithmic equation

$$\ln \{-\ln(1 - \chi)\} = -n \ln \beta - \frac{1.052 m E_c}{R T} + constant \longrightarrow \quad (17)$$

Where  $m$  is a constant dependence on the dimensionality of the crystal. Fig.(8 a&b) shows the plots of  $\ln \{-\ln(1 - \chi)\}$  vs.  $(1000/T)$  at various  $\beta$  for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy composition respectively. Values of  $E_c$  have been extracted from the last figure are listed in Table (5) by known the values of  $m$  parameters.

### 3.3.2 Determination of Avrami exponent and the order of dimensional growth



In accordance to equation (17) a plot of  $\ln \{-\ln(1-\chi)\}$  vs.  $\ln\beta$  at fixed temperature can be available as seen in Fig.(8 c&d). The values of Avrami exponent  $n$  can be obtained as well as the dimensionality of crystal growth ( $m$ ). Where for the quench glass samples containing no nuclei ( $m=n-1$ )[34] values of  $m$  and  $n$  parameters at different temperature as example as well as average values have been given in Table (7). A change in the mechanism of crystal growth with Zn addition to the host binary system  $\text{Se}_{88}\text{Te}_{12}$  will be observed as a change from the bulk nucleation with 2 dimensional growth where ( $n\approx 3$  and  $m\approx 2$ ) to the bulk nucleation with three dimensional growth, where ( $n\approx 4$  and  $m\approx 3$ ). The highest value of both  $m$  and  $n$  has been observed on another chalcogenide glasses composition [1,35]. As seen in Table (5) the  $E_c$  values for the glassy studied composition corresponding to different models are in a good agreement with each other except its value obtained according to Matusita method. This observed difference may be attributed to the different approximation used in this method. Moreover, the  $E_c$  values for the host binary system have a lower value than that for  $\text{Se}_{88}\text{Te}_8\text{Zn}_4$  composition. Which indicating the increase of  $E_c$  value with Zn addition and confirmed the possibility of utility of  $\text{Se}_{82}\text{Te}_{18}$  composition with Zn addition as a recording layer material [3]. The similar behavior of  $E_c$  with Zn addition was observed in other workers for  $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$  [3] and  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ [5] glassy composition. The observed behavior of  $E_c$  with Zn addition which confirmed by that's can be explaining according to that the addition of Zn atom with high coordination number of 4 at the expense of Te atom 2 results in a progressive increase in network connectivity and rigidity. That plays an important role in explaining the increase of the memory switching field and switching voltage with Zn addition in  $\text{Se}_{88}\text{Te}_8\text{Zn}_4$  glassy alloy.

### **3-4 Thermal Stability aspects**

The resistance to devitrification of glasses alloys through the nucleation and growth processes represent the glass stability GS concept. There are many GS criteria included the widely used criteria such as Hurby  $K_r$  [37], Saad and Poulain  $K_s$  [38] and Weinberg  $K_w$  [39] criterion. In the recent years, since the late 2000s, various GS criteria have been proposed according to several researches depend on many different theories [40-47]. The advantages of these criteria that they are fast and easy estimation based upon the characteristic temperatures  $T_g$ ,  $T_c$ ,  $T_p$  and  $T_m$  values and their relationship with each other. Moreover these GS criteria are very important in terms of characterize the basic thermal behavior of glasses materials. In the present work, several widely used and recently criteria have been used as seen in Table (7). All criteria are calculated for the studied composition as a function of heating rate and listed in Table (1&2) for the commonly used criteria [37-39]. In Tables (8&9) the more recently criteria [40-47] like  $K_f$ ,  $K_{GS}$ ,  $K_{yl}$ ,  $K_{DH}$ ,  $K_{ZW}$ ,  $K_{GL}$ ,  $K_{ix}$  and  $K_{il}$  have been reported for the considered composition at different heating rate. As seen, all used GS criteria have

a larger values for the  $Se_{88}Te_8Zn_4$  glassy alloy than that for binary  $Se_{88}Te_{12}$  glassy alloy and decrease with raising heating rate except two new criteria, Zhang et. al.  $K_{ZW}$  [46] and Long et al.  $K_{lx}$  [47] exhibited an opposite behavior with heating rate and Zn addition. It is important to distinguish the most suitable and sensitive GS criterion for considered compositions for this purpose the relative change parameter  $P_{RG}$  is a parameter required estimating the largest relative changes of GS criterion with respect to the relative change parameters of the other GS criteria.  $P_{RG}$  parameter for different criteria is given as follow [48]

$$P_{RG} = (K_{max} - K_{min}) / K_{min} \longrightarrow (18)$$

Where  $K_{max}$  and  $K_{min}$  the GS criterion value at maximum and minimum  $\beta$ . The values of  $P_{RG}$  have been represented in Tables (1,2,8 and 9) for each criterion which reflect that the most suitable and sensitive criterion for our composition is Saad and Poulain  $K_S$  criterion and the less one is Fan et. al.  $K_f$  [40] criterion dependent to its gets  $P_{RG}$  value. Furthermore there are two other GS criteria  $K$  and  $K_R$  based on the rate of crystallization. These criteria proposed by Vazquez et al. [49] as follows.

$$K = K_0 \exp\left[\frac{-E_c}{R T_p}\right] \longrightarrow (19)$$

$$K_R = K_0 \exp\left[\frac{-C_r E_c}{R T_p}\right] \longrightarrow (20)$$

The values of  $K$  and  $K_R$  criteria are tabulated in Table (10) as well as the  $K_0$  factor according to equations (14,15) values for the present samples. It is clear that  $K$  and  $K_R$  values are higher for ternary composition with Zn addition composition as comparing to binary alloy. These results are consistent and confirmed the G.S criteria mentioned above expect  $K_{ZW}$  and  $k_{lx}$  criteria.

## Conclusion

Calorimetric differential thermal analysis of SeTe and SeTeZn glasses composition at different heating rate  $\beta$  (in range  $20 \leq \beta \leq 50$  deg/min) have been performed. The glass transition activation energy  $E_g$  has been estimated and discussed by Kissinger, Moynihan and Augis-Bennet approximation method and Matusita methods have been used to estimate the crystallization activation energy. It has been found that the  $E_c$  values are in good agreement with each other reflect the possibility to use any of these method, to derive the  $E_c$  values. The lowest value of  $E_g$  while the highest value of  $E_c$  were found for the studied composition with Zn addition which indicated that the ternary composition is more stable than SeTe composition, this outcome can be confirmed by investigation and evaluation of the widely used and more recently thermal stability, crystallization rate, fragility index, critical heating rate and relative change parameters of thermal stability criteria. The fitting curves according to Losacka's empirical relation reveals that the crystallization process was found more sensitive to  $\beta$  than that of glass transition process. Moreover these relation help to

determine the Kouzmann temperature and critical heating rate. Fragility index proposed that the investigated composition are categorized as strong glasses

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**Table (1) The characteristic transition temperatures and widely used thermal stability criteria for the glassy  $Se_{88}Te_{12}$  composition at different heating rate.**

Heating rate $\beta$ , deg/min	$T_g$ , K	$T_c$ ,K	$T_p$ , K	$T_f$ ,K	$T_m$ ,K	$\Delta T$ ,K ( $T_c - T_g$ )	Kr	Ks	$K_w$
<b>20</b>	342.3	373.1	401.9	407.05	532.9	30.8	0.235115	2.591411	0.057797
<b>30</b>	345.4	377.3	409.4	414.5	540.4	31.9	0.243511	2.96465	0.05903
<b>40</b>	352.9	380.7	415.8	424.3	543.5	27.8	0.217698	2.765033	0.05115
<b>50</b>	354.1	383.3	424.6	439.8	545.2	29.2	0.242123	3.405705	0.053558
<b><math>P_{RG}</math></b>	----	-----	-----	-----	-----	-----	0.0298	0.3142	0.0733

**Table (2) The characteristic transition temperatures and widely used thermal stability criteria for the glassy  $Se_{88}Te_8Zn$  composition at different heating rate.**

Heating rate $\beta$ , deg/min	$T_g$ , K	$T_c$ ,K	$T_p$ , K	$T_f$ ,K	$T_m$ ,K	$\Delta T$ ,K ( $T_c - T_g$ )	Kr	Ks	$K_w$
<b>20</b>	333.5	367.3	393.3	405.6	508.3	33.8	0.293913	2.635082	0.066496
<b>30</b>	335.3	374.5	403.7	412.5	510.5	39.2	0.367041	3.413779	0.076787
<b>40</b>	341.1	377.4	411.9	417.2	513.3	36.3	0.357988	3.671504	0.070719
<b>50</b>	348.2	379.8	419.5	432.8	517.9	31.6	0.321138	3.602872	0.061016
<b><math>P_{RG}</math></b>	----	-----	-----	-----	-----	-----	0.0926	0.367	0.0824

**Table (3) Values of Kinetic constants, critical heating rate, Kauzmann temperature and the heat of atomization for the glassy  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  compositions.**

parameters	$A_g$ , K	$B_g$	$A_p$ , K	$B_p$	$\beta_c$ , K/min	$T_k$ , K	Hs, kJ/mol
$Se_{88}Te_{12}$	302	11.4	321	25.2	$4.01 \times 10^{-2}$	522.1	221.6
$Se_{88}Te_8Zn_4$	288	15.8	305	33.4	$1.19 \times 10^{-3}$	274.1	205.06

**Table (4) Values of activation energy of glass transition  $E_g$  (kJ/mol) for the studied glassy  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  compositions according to different methods and the average values as well.**

Method	Kissinger	Moynihan approximation	Augis-Bennett	Average value
$Se_{88}Te_{12}$	59.285	57.739	61.136	59.387
$Se_{88}Te_8Zn_4$	45.186	45.843	46.603	45.878

**Table (5) Evaluation Values of crystallization activation energy  $E_c$  (kJ/mol) for the glassy  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  compositions according to different methods.**

Composition	$Se_{88}Te_{12}$	$Se_{88}Te_8Zn_4$
<i>Kissinger method</i>	48.339	69.288
<i>Augis and Bennet method</i>	49.139	70.461
<i>Augis and Bennet approximated method</i>	47.192	67.956
<i>Mahadevan method</i>	48.294	68.151
<i>Matusita method</i>	60.484	76.173



**Table (6) Values of the Avrami index (n) and the order of dimensional growth (m) for glassy  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  compositions at different fixed temperatures**

composition	$Se_{88}Te_{12}$			$Se_{88}Te_8Zn_4$		
Temperature	T=390 K	T= 395 K	T=400 K	T= 383K	T=386K	T=390 K
<b>n</b>	2.834	2.920	2.687	4.13	3.95	4.20
<b>m</b>	1.834	1.920	1.687	3.13	2.95	3.204
Average n	2.814 $\approx$ 3			4.09 $\approx$ 4		
Average m	1.814 $\approx$ 2			3.09 $\approx$ 3		

**Table(7) Some of widely used and more recently GS criteria based on different researchers.**

Envisaged by	GS parameter
Hurby[37]	$K_H=(T_c-T_g)/(T_m-T_p)$
Saad and Poulain[38]	$K_S=[(T_p-T_c)(T_c-T_g)]/T_g$
Weinberg [39]	$K_W=T_p-T_g/T_m$
Fan et al.[40]	$K_F=(T_g/T_m)(\Delta T_{xg}/T_g)^\alpha$ , $\alpha =0.143$
Lu and Liu[41]	$K_{LL}=T_p/(T_g+T_m)$
Du et.al.[42]	$K_{DH}=(2T_p-T_g)/T_m$
Chen et. al.[43]	$K_{CS}=T_p/(T_m-T_g)$
Yuan et. al.[44]	$K_{YI}=T_p T_g/(T_m-T_c)^2$
Guo et. al.[45]	$K_{GL}=(3T_p-2T_g)/T_m$
Zhang et. al. [46]	$K_{ZW}=T_g/(2T_p-T_g)-(T_g/T_m)$
Long et. al. [47]	$K_{LX}=(T_g/T_p)-[2T_g/(T_g+T_m)]$

**Table (8) The recent thermal stability criteria at different heating rate and the relative change parameters of them for the glassy  $Se_{88}Te_{12}$  composition.**

Heating rate $\beta$ , deg /min	Kf	KII	Kcs	Kyl	KDH	KGL	Kzw	K lx
20	0.455202	0.459209	2.108604	8.016454	0.866016	0.977857	0.742746	0.069483
30	0.454641	0.462181	2.099487	8.240007	0.876018	0.994449	0.730602	0.063814
40	0.451478	0.463855	2.181532	8.998173	0.880773	0.996504	0.738206	0.061354
50	0.454564	0.472145	2.221873	10.3374	0.908107	1.037417	0.716149	0.04646
<b>P<sub>RG</sub></b>	<b>-0.0014</b>	<b>0.028169</b>	<b>0.053718</b>	<b>0.289523</b>	<b>0.048603</b>	<b>0.060909</b>	<b>-0.03581</b>	<b>-0.33135</b>

**Table (8) The recent thermal stability criteria at different heating rate and the relative change parameters of them for the glassy  $Se_{88}Te_8Zn_4$  composition.**

Heating rate $\beta$ , deg/min	Kf	KII	Kcs	Kyl	KDH	KGL	Kzw	K lx
20	0.472942	0.467213	2.25	9.918	0.891403	1.00905	0.737108	0.055603
30	0.483215	0.4773	2.304224	11.86724	0.92478	1.058766	0.71122	0.037708
40	0.482364	0.482093	2.391986	13.66462	0.940386	1.078317	0.707624	0.029659
50	0.477042	0.484355	2.472009	15.08588	0.947673	1.085345	0.710427	0.025972
<b>P<sub>RG</sub></b>	<b>0.008669</b>	<b>0.03669</b>	<b>0.098671</b>	<b>0.52106</b>	<b>0.063126</b>	<b>0.075611</b>	<b>-0.0362</b>	<b>-0.53291</b>

**Table (10) The average values of frequency factor ( $K_0$ ) and crystallization rate factors ( $K$ ) and ( $K_R$ ) for the glassy  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  compositions.**

composition	$K_0/\text{min}^{-1}$		$K/\text{min}^{-1}$	$K_R/\text{min}^{-1}$
	according to Eq. ( 14)	according to Eq. ( 15)		
$Se_{88}Te_{12}$	$8.01 \times 10^6$	$5.25 \times 10^5$	$2.10 \times 10^6$	$4.263 \times 10^6$
$Se_{88}Te_8Zn_4$	$9.85 \times 10^5$	$8.93 \times 10^4$	$5.28 \times 10^5$	$5.349 \times 10^5$

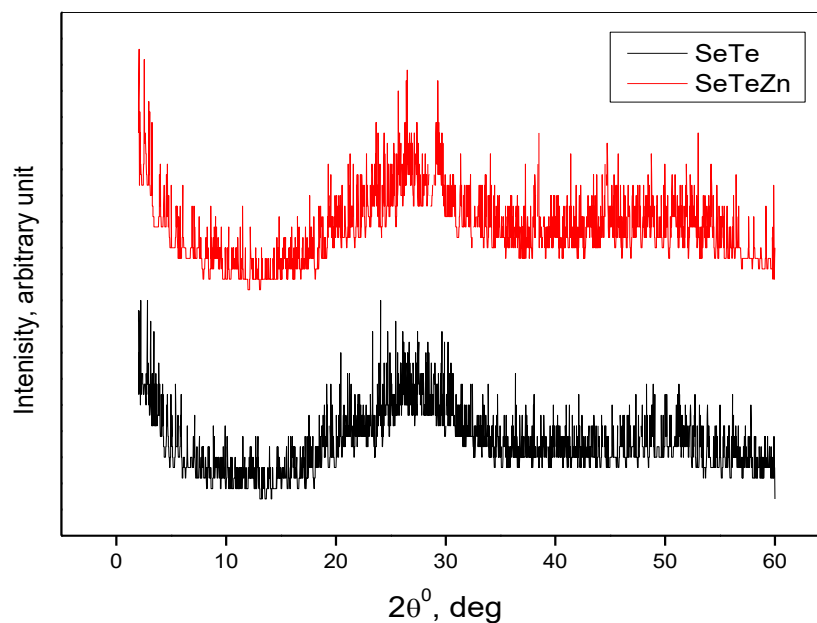


Fig.1 X- ray diffraction patterns of  $\text{Se}_{88}\text{Te}_{12}$  and  $\text{Se}_{88}\text{Te}_8\text{Zn}_4$  compositions.

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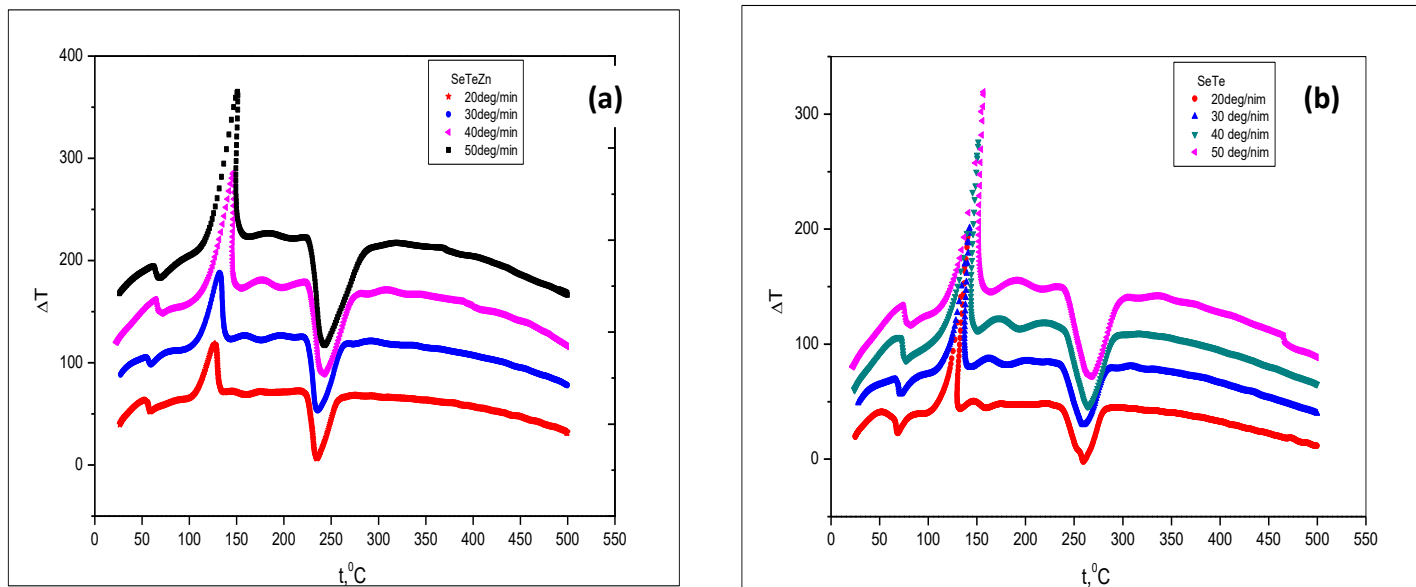


Fig.2 Differential thermal analysis curves of (a)  $Se_{88}Te_{12}$  and (b)  $Se_{88}Te_8Zn_4$  glassy compositions at different heating rates.

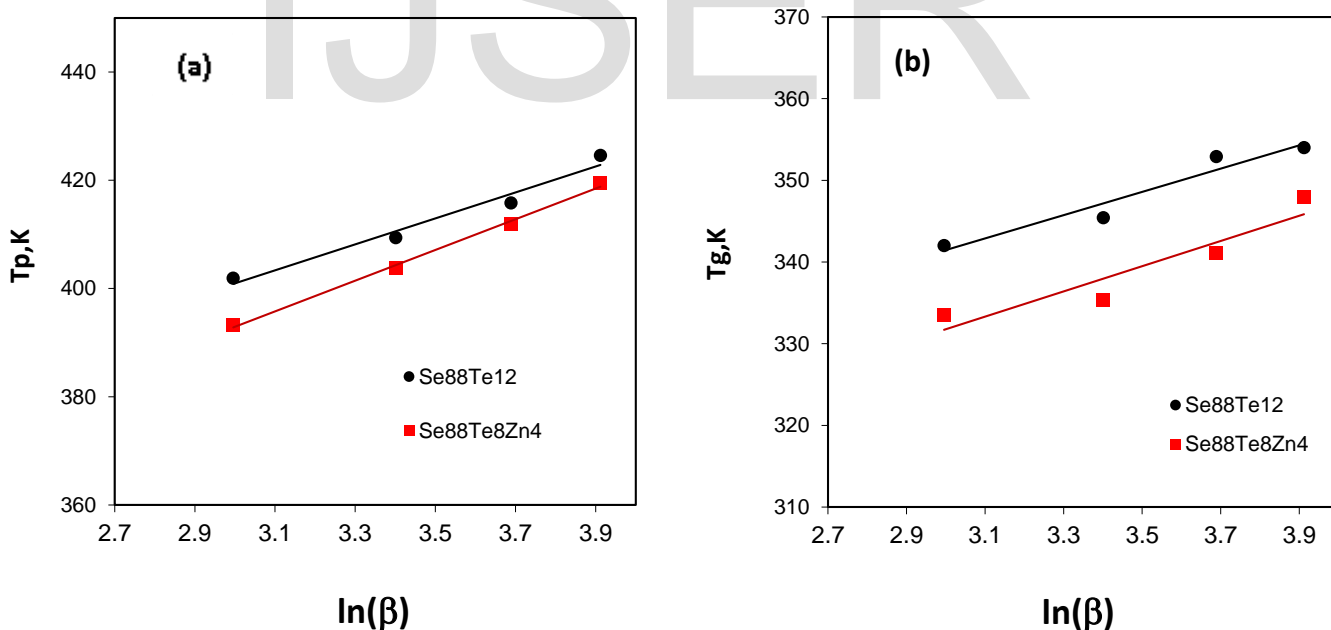


Fig.3 Heating rate dependence of (a) the crystallization and (b) glass transition temperatures for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.

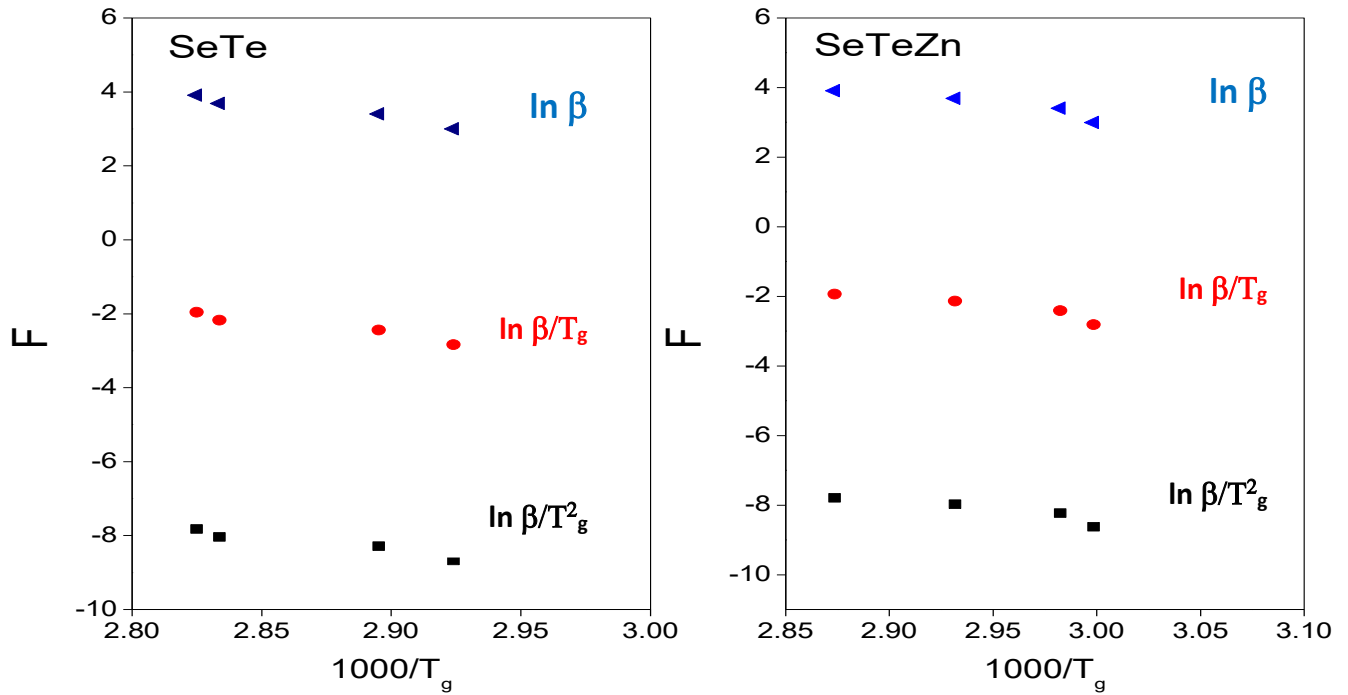


Fig.4 Plots of a function F, ( $F = \ln(\beta/T_p)$ ,  $\ln(\beta/T_p^2)$  and  $\ln(\beta)$ ) versus  $1000/T_g$  for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.

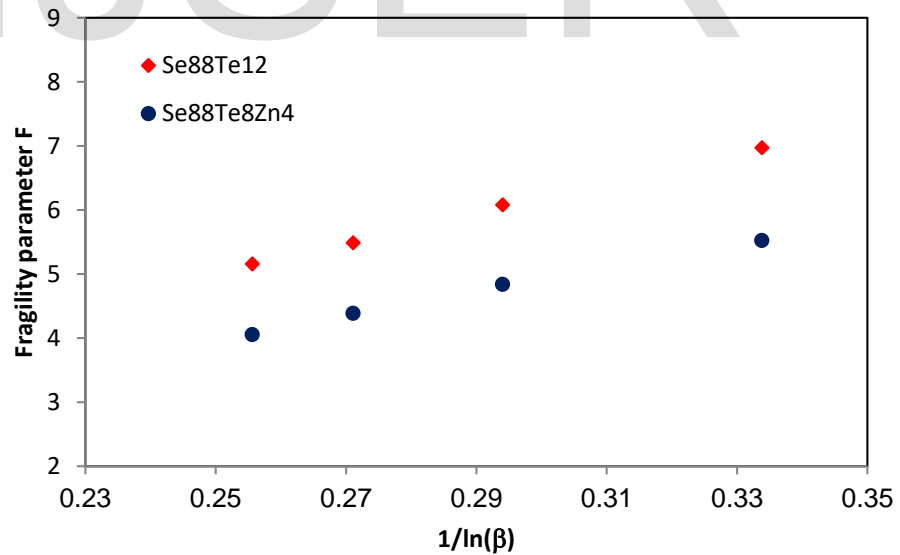


Fig.5 Heating rate dependence of the fragility index  $F_i$  for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.

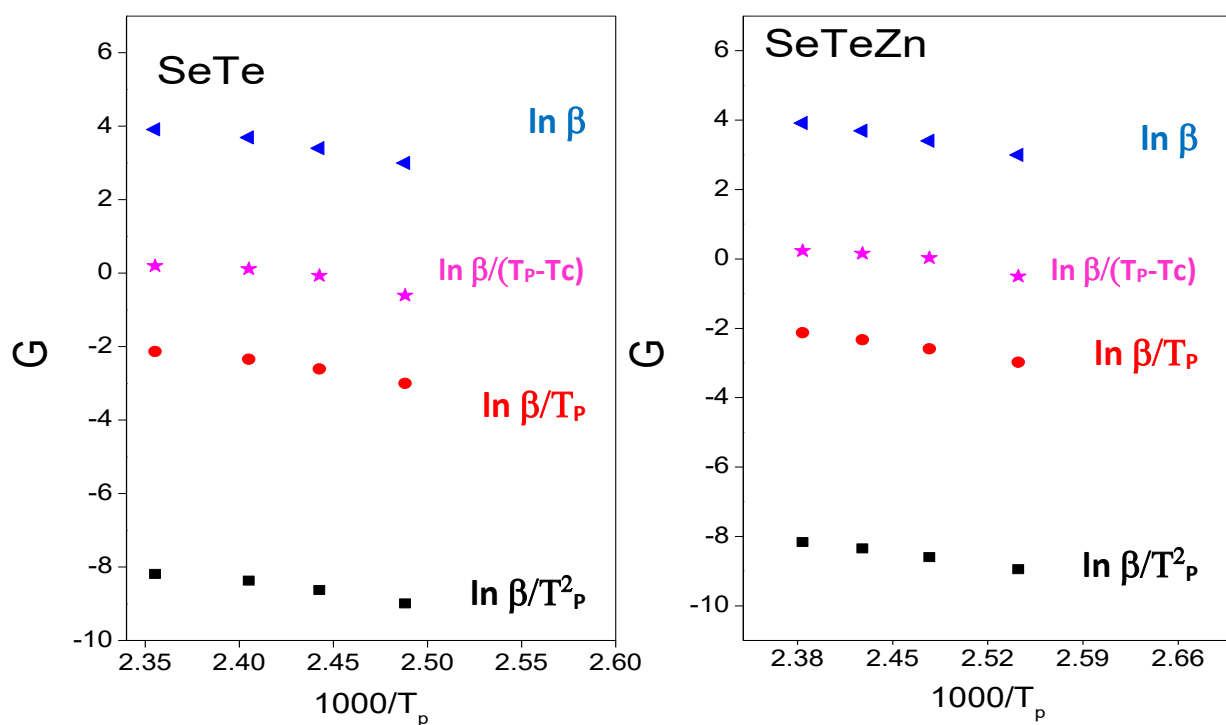


Fig.6 Plots of a function  $G$ , ( $G = \ln(\beta/T_p)$ ,  $\ln(\beta/T_p^2)$ ,  $\ln(\beta/T_p - T_c)$ , and  $\ln(\beta)$ ) versus  $1000/T_p$  for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.

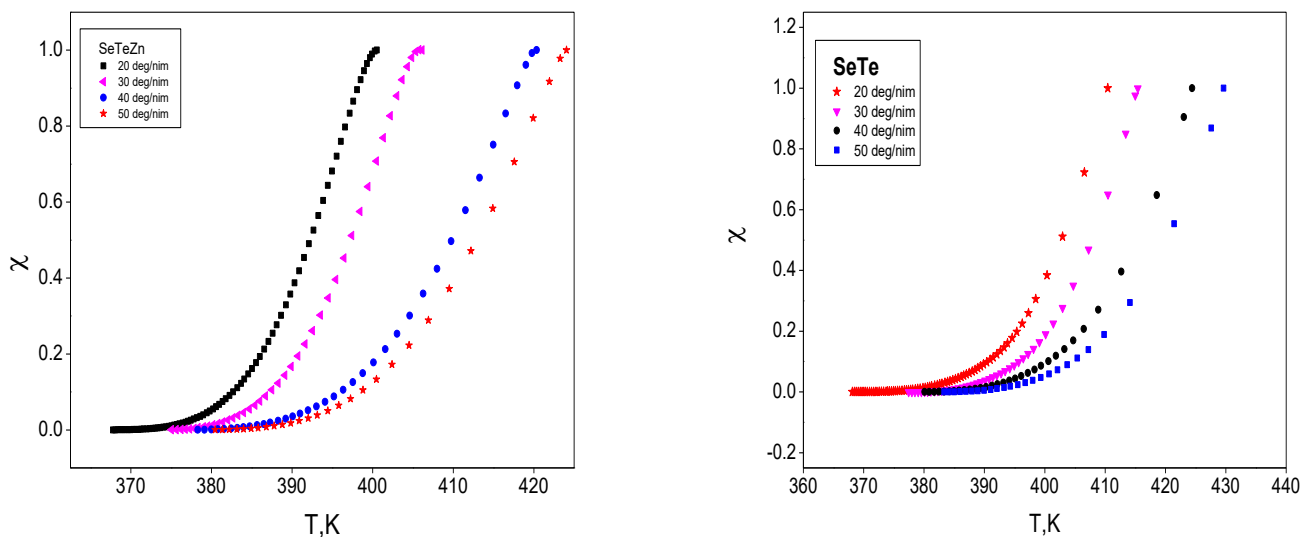


Fig.7 Extent of crystallized volume fraction  $\chi$  as a function of temperature at different heating rates for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.



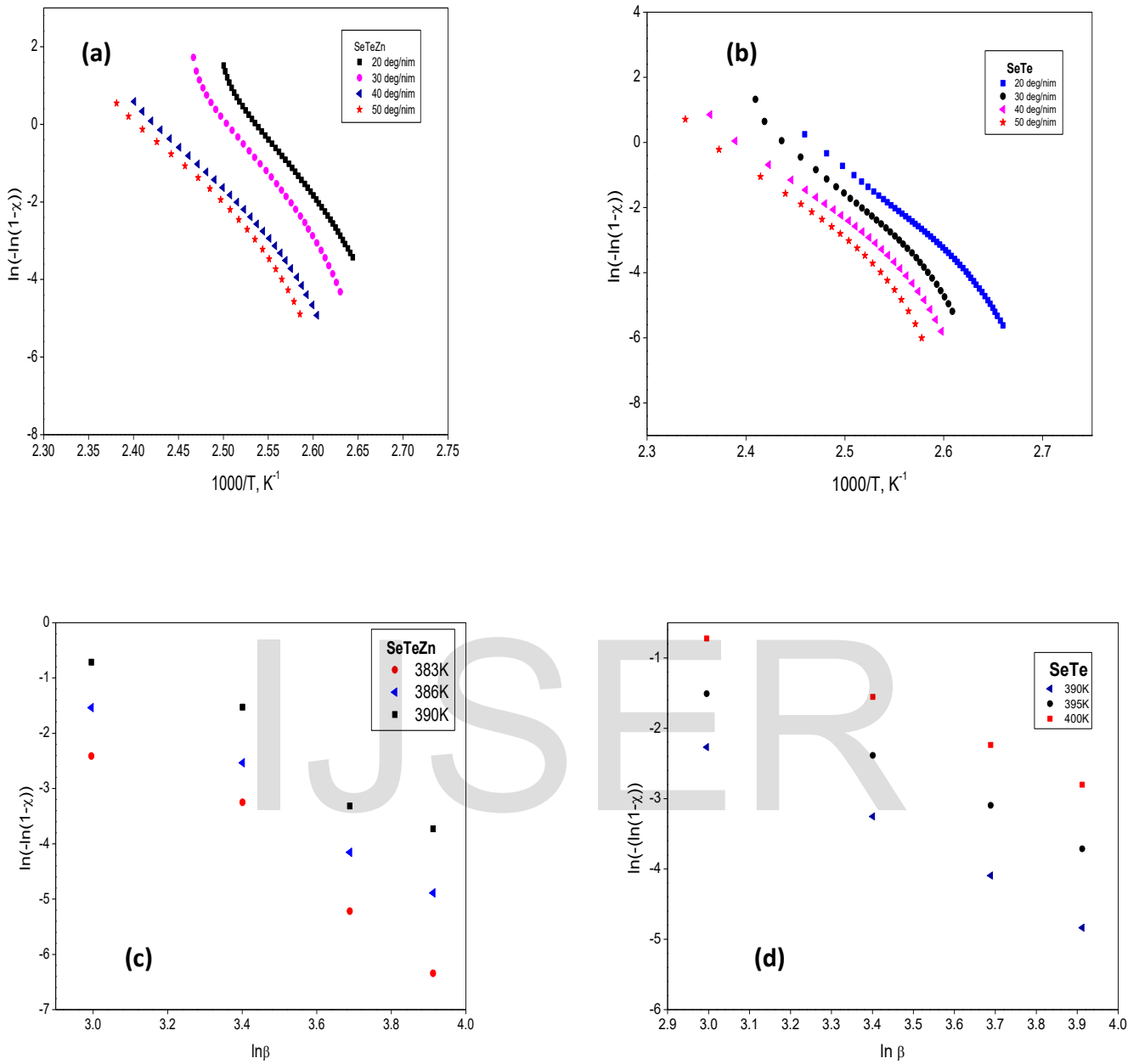


Fig.8 Plots of a  $\ln[-\ln(1-\chi)]$  versus (a&b)  $1000/T$  at different heating rate and (c&d) versus  $\ln \beta$  at different fixed temperature within exothermic peak at DTA traces for  $Se_{88}Te_{12}$  and  $Se_{88}Te_8Zn_4$  glassy compositions.