

# Thermal Analysis of $\text{In}_x\text{Te}_{10}\text{Se}_{90-x}$ Glasses

S.R. Alharbi, E. S. Al-Zahrani, M. Y. Alharbi, W. Alharbi, K.A. Aly

**Abstract:** measurements of differentially scanning calorimeter (DSC)  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$   $0 \leq x \leq 9$  under non isothermal technique (at heating rates ( $\alpha$ ) ranging from 2 to 32 K/min.) have been carried out. The ( $\alpha$ ) value is found to affect the characteristic temperatures (the temperature of glass transition ( $T_g$ ), the onset temperature of crystallization ( $T_c$ ) and the temperature of crystallized peak ( $T_p$ )) that helping us to investigate the Avrami's exponent ( $n$ ) and the activation energy for glass transition ( $E_g$ ) and crystallization ( $E_c$ ). The investigated results are discussed in terms of the chemical bond approach, the cohesive energy (CE) and the average heats of atomization ( $H_s$ ). The X-ray diffractograms confirmed the amorphous state of the as-prepared glasses.

**Keywords:** Chalcogenides; DSC; XRD.

## I. INTRODUCTION

Chalcogenide type of glasses has a lot of attention due to their wide range of technologically applications. Binary as Se-Te and In-Se glasses have many advantages in comparison with a-Se [1-3]. The In-Se system is attractive because of their uses in solar cell [4, 5]. On the other hand, Se-Te system is characterized by their large crystallization temperature, high hardness, good photosensitive as well as small ageing effects than a-Se [1]. Whereas these glasses are characterized by low thermos-mechanical properties, thus their applications can be enlarged through improving their soften temperature and mechanically strength. The Addition of third element to binary glass system (In in our case) not only enlarge their region of glass formation but, also makes compositional and configuration disorder in the glass system, the structure modification and improving the electrical as well as thermal characterization of the Se-Te glasses [6-9].

In the literature, many research papers [8, 10-12] deals with the study of electrical, photoelectrical and thermally properties of In-Se-Te glasses. From an application point of view, it is necessity to study the thermal properties of like glasses. The current study deals with the effect of In amount on the thermal analysis of different compositions of  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$   $0 \leq x \leq 9$  halcogenides.

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**S.R. Alharbi**, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia. E-mail: [srfalharbi@kau.edu.sa](mailto:srfalharbi@kau.edu.sa)

**E. S. Al-Zahrani**, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia.

**M. Y. Alharbi**, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia

**W. Alharbi**, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia.

**K.A. Aly**, Physics Department, Faculty of Science and Arts Khulais, University of Jeddah, Saudi Arabia, Physics Department, Faculty of Science, Al - Azhar University, P.O. 71452, Assiut, Egypt.

## II. THEORETICAL BASES:

Explanation of the DTA and/or DSC results is retired through the formal kinetic transformations theory in terms of the crystallized fraction (volume) ( $\chi$ ) in the time interval ( $t$ ) by using the Johnson, Mehl and Avrami's experssion [13]

$$\chi = 1 - e^{-(k.t)^n} \quad (1)$$

where  $n$  is the Avrami's exponent (is an integer or half integer depending on the mechanisms of growth and the crystal dimension),  $k$  is the effective reaction rate,

$$k = k_0 \cdot e^{-E_c/RT} \quad (2)$$

where  $E_c$  is the crystallization activation energy.

### 2.1. Afify's Method

Using Afify condition [14, 15] at  $\chi = 0.63205$  the term  $\ln(1 - \chi) = -1$  and the eq. 1 rewritten as:

$$\ln(1 - \chi) = -1 = -(k_{0.63} t_{0.63})^n \quad (3)$$

i.e

$$k_{0.63} = t_{0.63}^{-1/n} \quad (4)$$

Using equation (4) the  $k_{0.63}$  at  $\chi = 0.63205$  can be estimated at every heating rate. Then the reaction rate  $k_{0.63}$  in the logarithmic form is given by:

$$\ln(k_{0.63}) = \ln(k_0) - E_c/RT_{0.63} \quad (5)$$

The values  $E_c$  and  $k_0$  can be estimated without any dependence on the Avrami's exponent ( $n$ ) from the slope and intersect of the relationship between  $\ln(k_{0.63})$  and  $1000/T_{0.63}$ . Furthermore, eq.5 satisfied for isothermal and non-isothermal technique [13]. rewriting Eq. 3 in the logarithmic form as

$$\ln(\ln(1 - \chi)) = n \cdot \ln(k) + n \cdot \ln(t) \quad (6)$$

where  $k$  is constant at constant temperature, plotting  $\ln(\ln(1 - \chi))$  versus  $\ln(t)$  a straight line with slope equal to the  $n$  value. In iso-thermal technique, Eq. 6 is carried out for only one DSC curve whereas, in non-isothermal technique, Eq. 6 is carried out, at constant temperature for different DSC curves.

### 2.2. Bansal's Method

Bansal's method detail is quoted approximation which may cause an 3% error in the value of  $E_c/R$  in the worst cases [16] and the final relationship can be written as:

$$\ln(T_p^2 / \alpha) = -E_c / RT_p - \ln(K_0 R / E_c) \quad (7)$$

Depending on Bansal's analysis the kinetic exponent can be estimated by the use of the following relation:

$$\chi_p = n(0.37\alpha E_c) / (RT_p^2) \quad (8)$$

and exponent that based on the crystal growth dimensionality (m) also may be estimated by :

$$\left[ \frac{d\chi}{dt} \right]_p = mE\alpha(1-\chi_p) / RT_p^2 \quad (25)$$

At study the kinetics of crystallization in the glass,  $n = m$  if the nuclei are formed through any previous heat treatment prior to DSC or DTA scan. Whereas, in the case of the nuclei are formed through the heating at constant rate  $\alpha$  are dominant and  $n = m+1$  [6, 17].

### III. EXPERIMENTAL

$\text{In}_x\text{Te}_8\text{Se}_{92-x}$  ( $0 \leq x \leq 9$ ) glasses were prepared starting with highly purity In, Te and Se (99.999 %) using the well-known melt quench technique. The amorphous state of the as-prepared samples was checked using a Philips (1710) X-ray diffract meter. The elemental composition was investigated using energy dispersive X-ray spectroscopy (Link analytical EDS). The as-prepared samples as well as that starting calculation based on their ratios and atomic percentage with small error only  $\pm 0.4$  at %.

10 mg in powder form for each sample was sealed in Al boat and scanned through the temperature range 300-450 K at different heating rates ( $\alpha = 2, 4, 8, 16$  and  $32 \text{ K min}^{-1}$ ) using Shimadzu 50 DSC. The characteristic temperatures  $T_g$ ,  $T_c$ , and  $T_p$  (the temperature of glass transition, the onset of the crystallization peak, and the temperature of the crystallized peak, respectively) were estimated using the microprocessor of the thermal analyser with accuracy ( $\pm 1 \text{ K}$ ).  $T_g$ ,  $T_c$ , and  $T_p$ , are

### IV. RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  different compositions of the (where  $x = 0, 2.5, 5, 7.5$  and  $9$  at.%) glasses measured at heating rate  $10 \text{ K.min}^{-1}$ . The characteristic temperatures,  $T_g$ ,  $T_c$  and  $T_p$  are increases with the increase of In content.

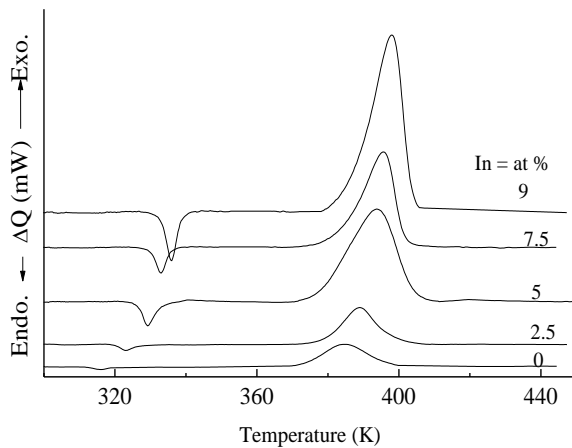


Figure 1. DSC curves for powdered  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  chalcogenides scanned at  $\alpha = 8 \text{ K/min}$ .

### 4.1. Glass Transition

The glass transition temperature dependence on the heating rate ( $\alpha$ ) obey the following relationship [18]:

$$T_g = A + B \ln(\alpha) \quad (26)$$

where A and B with the same meaning written here [19]. The A and B values were estimated by plotting  $T_g$  values versus  $\ln(\alpha)$  as shown in Fig.2. The deduced values of A and B for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  glasses in excellent agreement with eq. (26) and are listed in Table 1.

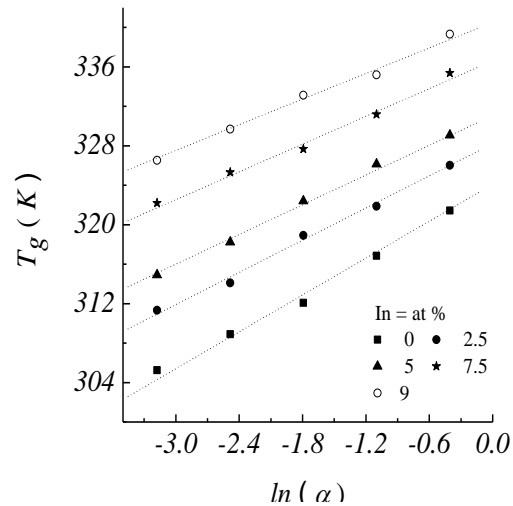


Figure.2 the  $T_g$  vs.  $\ln(\alpha)$  for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  ( $0 \leq x \leq 9$ ) chalcogenides.

On the other side, Eq.7 can be rewritten for the glass transition temperature,  $T_g$  as [20]:

$$\ln(T_g^2 / \alpha) = E_g / RT_g + \text{const.} \quad (27)$$

By plotting  $\ln(T_g^2 / \alpha)$  versus  $1000/T_g$ , the slope can be used to determine the  $E_g$  value as well as demonstrated in Figure 3.

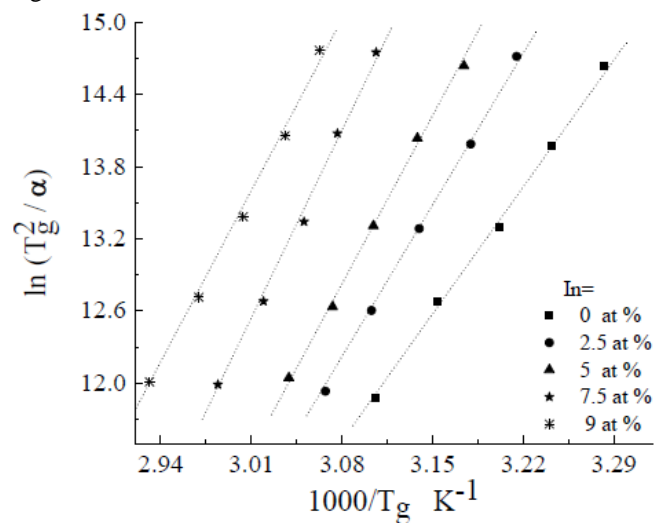


Figure 3: the values of  $\ln(T_g^2 / \alpha)$  against  $1000/T_g$  for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  ( $0 \leq x \leq 9$ ) chalcogenides.

The estimated values of  $E_g$  are agree with that was observed for chalcogenide glasses [21-23]. The  $E_g$  values increases with the increase of In content which can be considered as a result of increasing the  $T_g$  values consequentially the glass rigidity also are increased.

The glass transition temperature is strongly affected by many independent parameters for example the effective molecular weight, the optical, bonding energy, the fraction and type for different structural units formed, the average heats of atomization, cohesive energy, the mean coordination number [24, 25]. For heteronuclear bonds the bonding energy between to different atoms  $D(C-E)$  can be estimated using Pauling's relationship [26]:

$$D(C-E)=[D(C-C).D(E-E)]^{1/2} + 30(\chi_C-\chi_E)^2 \quad (28)$$

**Table 1: The Glass Transition Parameters for  $In_xTe_8Se_{92-x}$  ( $0 \leq x \leq 9$ ) Chalcogenides.**

In at. %.	A	B	$E_g$	(Eq.6)	(Eq.14)	CE	$H_s$
			kcal mol <sup>-1</sup>		Kcal.mol <sup>-1</sup>	(kcal atom <sup>-1</sup> )	(kcal g atom <sup>-1</sup> )
0	322	5.88	28.04	21	21.55	36.99	49.59
2.5	330	5.24	33.76	24.12	25.87	37.07	49.75
5	338	4.71	42.65	27.83	26.97	37.16	49.99
7.5	340	4.34	46.43	29.21	28.55	37.23	50.16
9	343	4.19	50.66	30.76	31.22	37.31	50.32

Extending Pauling's idea to the ternary glasses (In-Se-Te in the present study) according to Sadagopan et al. [30] and neglecting the heat of formation. Thus, the average heats of atomization may be calculating by using the  $H_s$  values for In, Se, and Te into the following relationship [31].

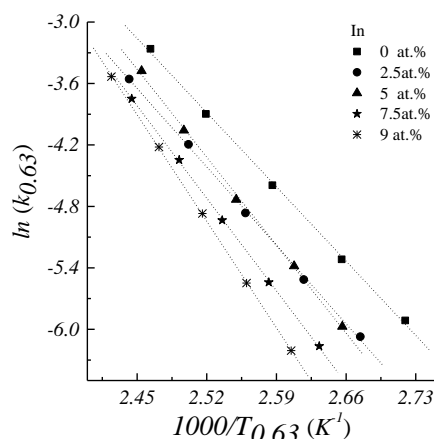
$H_s(In-Se-Te)$  is given by:

$$H_S(In-Se-Te) = \frac{1}{2} (H_S^{In} + H_S^{Se} + H_S^{Te}) \quad (31)$$

The deduced values of  $H_s$  for  $In_xTe_8Se_{92-x}$  glasses were shown in Table 1,

#### 4.2. Crystallization

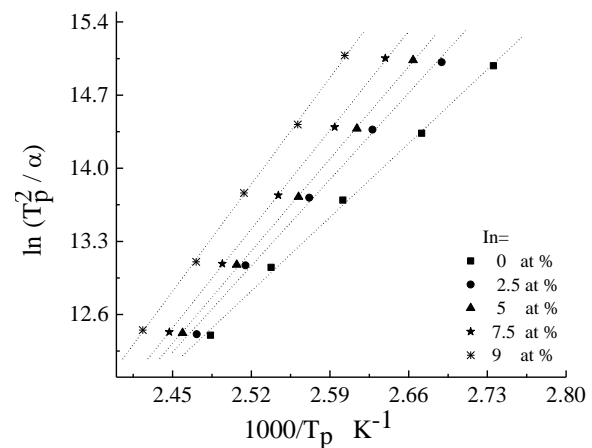
Based on Eq.6 the crystallization activation energy ( $E_c$ ) can be estimated by plotting the values of  $\ln(k_{0.63})$  as a function of  $10^3/T_{0.63}$  for  $In_xTe_8Se_{92-x}$  ( $0 \leq x \leq 9$ ) chalcogenide glasses as shown in Fig. 4. The deduced values of  $E_c$  were listed in Table 2.



**Figure 4: The  $\ln(k_{0.63})$  vs.  $1000/T_{0.63}$  for  $In_xTe_8Se_{92-x}$  ( $0 \leq x \leq 9$ ) chalcogenides.**

where  $D(C-C)$  and  $D(E-E)$  are the homonuclear bond energies in units kcal mol<sup>-1</sup> [27],  $\chi_C$  and  $\chi_E$  are the electronegativity values for C and E atoms [28]. Bond formation take place in sequence of decreasing bond energy up to the available atom valences are satisfied [29]. For In-Se-Te glasses, bonds of In-Se are expected to occur firstly because of their highly possible energy (54.321 kcal mol<sup>-1</sup>) then, Se-Te bonds (44.19 kcal mol<sup>-1</sup>) in try to saturate all available Se valences but, the Te atoms isn't enough to do this. Therefore, Se-Se defect homopolar bonds are formed. In accordance with approach of chemical bond, the bond energies are assumed to be additive. Therefore, the summation of bond energies over all the bonds expected in glass gives cohesive energy (CE). The calculated values of CE for the glasses under study are listed in Table 1 and it were increases with the increase of indium content.

On the other hand, according to Bansal's equation using the slope and intercept of the linear relation between  $\ln[T_p^2/\alpha]$  and  $10^3/T_p$ , both the  $K_0$  and  $E_c$  values can be deduced. Figure 5 shows this plot for  $In_xTe_8Se_{92-x}$  glasses.



**Figure5:  $\ln[T_p^2/\alpha]$  vs.  $1/T_p$  for  $In_xTe_8Se_{92-x}$  ( $0 \leq x \leq 9$ ) chalcogenides.**

The total amount of the alloy crystallized is directly proportional to area under DSC curve. The corresponding crystallization rates  $(d\chi/dt)_p$  is the ratio between the ordinates and the total area of the peak. In accordance the preceding theory, the sample was reheated up to a temperature slight larger than  $T_g$  for 1 hour to forming a large number of nuclei. Based on the experimentally results, It was shown that,

The correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which is the most suitable to calculate the  $n$  using Eq.(21). The value of  $n$  for the as-prepared glass isn't equal to that for the treated glass. This confirms that, the as prepared glass is free from any nuclei thus,  $n = m+1$  for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$  glasses. The kinetic parameters  $n$  and  $m$  are calculated depending on the crystallization mechanism. The  $n$  value decreases from 3 to 2 with increasing the content of indium. The value of  $n = 2$  for the as prepared glass corresponding to the mechanism of volume nucleation with one dimensional growth and  $n = 3$  corresponding to volume nucleation mechanism with two dimensional growth. At the final it was worth mentioned that, Eq. 25 gives  $m$  values which confirm the rule of  $n=m+1$  for  $\text{In}_x\text{Te}_8\text{Se}_{92-x}$ .

## V. CONCLUSIONS

Adding the In content into  $\text{Se}_{92}\text{Te}_8$  glass results in: Increasing the  $T_g$ ,  $T_c$ , and  $T_p$  with the increasing the content of In consequently both the activation energy of glass transition,  $E_g$ , and crystallization,  $E_c$  are increase. The observed results well explained in terms of the approach of chemical bonds, the mean heat of atomizations and cohesive energies (CE). Successful applied of Afify's method gives accurate values of  $E_c$ , and  $n$ .

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