International Journal of New Horizon sin Physics

http://dx.doi.org/10.18576/ijnhp/040204

Controlling the Crystallization Kinetics of Amorphous $Se_{82}In_{18}$ Chalcogenide Glass

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Received: 13 May 2017, Revised: 19 Jun. 2017, Accepted: 22 Jun. 2017.
Published online: 1 Jul. 2017.

Abstract: The present work deals with the accurately determination of the activation energy of crystallization (E_c), the frequency factor (K_o), the reaction order (n) without any approximation for amorphous $Se_{82}In_{18}$glass. Both the E_c and K_o values were determined using Afify, Augis and Bennett and Kissinger methods. In comparison between the three methods one can note that, Kissinger's method isn't suitable to determine k0. This is because that, the K_o(Kissinger) is too small compared with that determined by Afify or Augis and Bennett's method. Using theE_c and $K_o$values the overall reaction rate (K)has been calculated as a function of temperature. Where k and t is already known then Avrami's equation can be solved for the unknown quantity which is the reaction order (n) as well as recently published. Unlike other methods such as Afify, Augis and Bennett's and others, this method helps one to determine n value without any approximations. The calculated values of the crystallization fraction ,X_{th}, are in excellent agreement with that determined using the partial area techniqueeie experimentally determined, X_{exp}.

Keywords: Chalcogenide glasses; Melt quenching; Non- Ithothermal technique; Thermal analysis ;Reaction order.

1 Introduction

It is necessary to understand the kinetics of the crystallization in glasses to prevent glass devitrification. Sometimes, both the rate of crystallization and nucleation were microscopically measured. Unfortunately, this method isn't applicable in the glass because of the time interval required to nucleation and crystallization is less than one hour[1]. Studying the glass crystallization using Differential Scanning Calorimetry (DSC) has many characteristics such as, easiest carrying out, it needs a small amount of the glass (some milligrams), good sensitivity and it has no dependence on the glass shape [2]. The choice of Se because of its largecommercially applications viz. xerographic, switching and, memory [3-5].While pure Se has some defects such astoo small lifetime, poor sensitivity and thermal instability.

These problems can be solved by adding some impurities such as Ge, Te, Bi, Sb and In etc. Selenium-based glasses were characterized by reversible phase transformations which make them utilized in memory devices [6-10]. Adding Indium to Se was modifying the material properties and make it more suitable for reversible optical recording with an eraser time less than 1 microsecond [11]. It was noted that the glass structure is considerable modify by the addition of Sb[12].The present work deals with the crystallization kinetics for amorphous $Se_{82}In_{18}$ glass.

2 Experimental

$Se_{82}In_{18}$glass was prepared using the melt quenching technique. Se and In (99.999 %)) were weighed according to their atomic percentage proportions and introduced into the silica tube ofwidth 1 mm and length 12cm . The tube content (5 g) was sealed and evacuated up to 10^{-5} Torethen, putted into an electric furnace whereas the temperature was gradually increased from room temperature to 700 K using rate of 4 K. min^{-1} and kept constant for 24 hours. In order to ensure the homogeneity of the melt, the tube was frequently agitated then quenched into ice-cold water. The bulk ingots of the prepared glass were grinding lightly in a mortar to observe the powder form. The non-crystallinity of $Se_{82}In_{18}$glass was confirmed through the pattern of X-ray diffraction using a differactometer with CuKα-radiation source (λ= 1.540 Å). Figure 1 shows the XRD pattern of $Se_{82}In_{18}$glass which is free from any sharp lines confirms the non-crystallinity state of the prepared glass. The chemical composition of the prepared glass found to be $Se_{81.47}In_{18.53}$ on the basis of electron microprobe X-ray analysis, using a (Link Analytical Edx) scanning electron microscope. The calorimetric measurements have been achieved using Shimadzu50-Differential Scanning Calorimetry (DSC) under non-isothermal condition.

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Accurately weighed samples (10 milligrams powder form) introduced into aluminum pans and scanned at different heating rates (δ=1, 2.5, 5.0, 10, 20 and 40 K. min.$^{-1}$) in the temperature range300- 400 C^o.00. Fig.2 shows the DSC curves for $Se_{82}In_{18}$glass at different heating rates. The fraction (*X*) crystallized at any temperature (*T*) was determined as well as described here [13].

3 Results and Discussion

The non-crystalline nature and the homogeneity of the $Se_{82}In_{18}$glass were checked by the XRD pattern (Fig.1) and DSC curves (Fig.2). The non-crystalline nature was ascertained by the absence of any sharp lines or peaks in figure 1. An identical of glass-crystalline transformation which represented in figure 2 whereas the DSC curves at different heating rates under non-isothermal conditions of the as-prepared $Se_{82}In_{18}$ glass were represented .The DSC curves (Fig.2) of $Se_{82}In_{18}$glass shows two characteristic phenomena. The first phenomenon is corresponding to the onset glass transition temperature (T_{1g}) and the second is corresponding to the peak of crystallization that characteristic by extrapolated onset crystallization temperature, (T_{1c}), and the peak temperature of crystallization (T_{1p}).

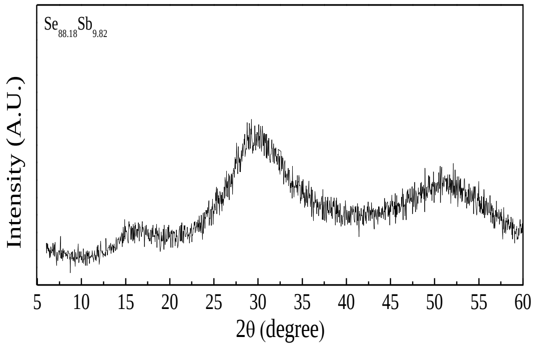

Fig.1 XRD pattern for the as-prepared $Se_{82}In_{18}$glass.

3.1 The Activation Energy of Crystallization (Ec)

The theoretical main to understand the results of DSC and DTA is introduced by chemically reaction as the crystallized volume fraction (*X*) in time (*t*) based on Avrami's relationship[15, 16]:

$$X = 1-\exp\left(-(k,t)^n\right) \qquad (1)$$

where *n* is an integer or half-integer which depends on the mechanism of growth and the dimensionality of the crystal and *k* is over all reaction rate that can be written as a function of the activation energy of crystallization (E_c), temperature (*T*) and the frequency factor (k_o)in the form of:

$$K = k_o \exp\left(-E_c \big/ (R,T)\right) \qquad (2)$$

R is the gas constant ($R=8.3415\ j.\ mol.\ K^{-1}$) According to Afify's method both the activation energy of crystallization (E_c) and the frequency factor (k_o) are easily determined without dependence on the Avrami's exponent (*n*) by substituting $X= 0.63205$into Eq.1 and rewrite it in the logarithmic form as:

$$\ln(1-0.63205) = (k_{0.63}t_{0.63}) \qquad (3)$$

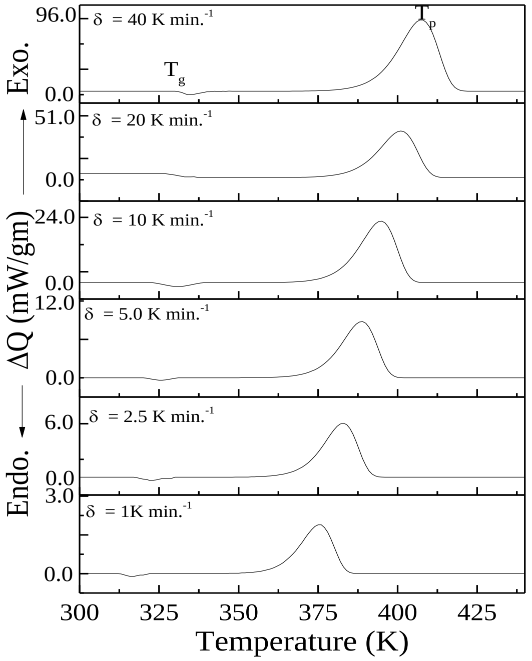

Fig.2 DSC curves for $Se_{82}In_{18}$glass recorded at different heating rates (δ).

The glass transition peak has only one onset temperature confirmed the homogeneity of the prepared $Se_{82}In_{18}$glass[14].

But, the lift hand side of Eq.3 is equal to (-1) therefore, Eq. 3 take the form of [15]:

$$1 = (k_{0.63}t_{0.63})_n \qquad (4)$$

Based on Eq. 4 the k value at$X=0.63205$, ($k_{0.63}$), can be investigated at each heating rate, i.e. the time reciprocal of ($1/t_{0.63}$)at ($1000/T_{0.63}$). The $t_{.63}$values were observed using thepartial area technique [6]. According to this technique the overall reaction rate can be rewritten in the following form:

$$[\ln(k_{0.63})] = [\ln(k_o)] - \left(E_c \big/ (RT_{0.63})^{-1}\right) \qquad (5)$$

Where$T_{0.63}$is the temperature at $\chi = 0.63205$. By plotting $[\ln(k_{0.63})]$ values versus ($1000/T_{0.63}$).values, both the (E_c)

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and $k_o$values can be determined without dependence on the value of Avrami's exponent as shown in Fig.3(a). On the other hand one can determine both the (E_c) and k_o values based on the changes in the crystallization peak of temperature (T_p)with the heating rate(δ) usingKissinger's method in the form of [17]:

$$\ln\left(\frac{T_p^2}{\delta}\right)=\frac{E_c}{(R,T)}-\ln\left(\frac{k_o R}{(E_c)}\right) \qquad (6)$$

where the quoted approximation might introduce a 3% error in the value ofE_c/Rin the worst cases. Figure 3(b)represent the $\ln\left(\frac{T_p^2}{\delta}\right)$values as a function of ($1000/T_p$) for $Se_{82}In_{18}$ glass. Also, Augis and Bennett's method has the following form[18]:

$$\ln\left(\frac{\delta}{(T_p-T_o)}\right)=\frac{-E_c}{(R,T_p)}+\ln(k_o) \qquad (7)$$

Fig.4 shows the plot of $\ln\left(\frac{\delta}{(T_p-T_o)}\right)$versus ($1000/T_p$) for $Se_{82}In_{18}$glass. The deduced values of (E_c) and $k_o$based on equations 5-7 were listed in table 1.Substituting (E_c) and $k_o$values into Eq.2 to calculate reaction rate (k_1, k_2 and k_3 corresponding to Eqs. 5, 6 and 7, respectively) at any temperature (T) lies within the temperature range of the crystallization peak (T_{in}-T_{if}). Fig. 5 represents the calculated values of (k) as a function of temperature (T). The k_o value corresponding to Kissinger's method is too small (~1/10) than that corresponding to Afify or Augis and Bennett method.As result one can note in Fig.5 that the k_2 values is too small compared with k_1 and k_3 values.Therefore, Kissinger's method isn't suitable to calculate k_0 or k value in the present case. On the other side, the E_c value deduced by Afify's is approximately equal to that deduced by Augis and Bennett's and the difference lie within the experimental error (1.2 %) while the E_c value deduced by Kissinger's is higher than that deduced by Afify's method with difference lie in the experimental error 3%.

Table 1. The deduced values ofthe activation energy of crystallization (E_{1c}) and the frequency factor (k_{1o}) for $Se_{82}In_{18}$ glass.

Method/value	E_c(kJ/mol)	k_o (s^{-1})
Afify(Eq.5)	133.50± 2.27	$8.60\text{x}10^{14}$
Kissinger(Eq.6)	139.566± 2.93	$5.598\text{x}10^{13}$
Augis and Bennett(Eq.7)	131.93± 3.177	$5.368\text{x} 10^{14}$

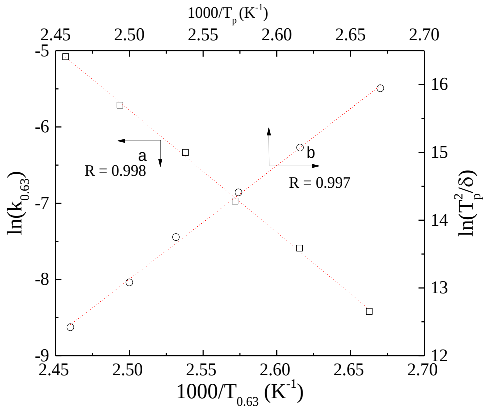

Fig.3(a)The plot of$(\ln(k_{0.63}))$ vs.$\frac{1000}{T_{0.63}}$ and (b) the values of the $\frac{(\ln[T_p]^2)}{\delta}$ vs.$\frac{1000}{T_p}$ for $Se_{82}In_{18}$ glass.

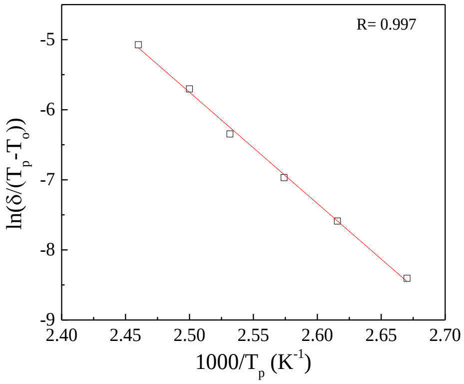

Fig. 4 The plot of$\ln\left[\frac{\delta}{(T_p-T_o)}\right]$vs.$\frac{1000}{T_p}$ for$Se_{82}In_{18}$glass.

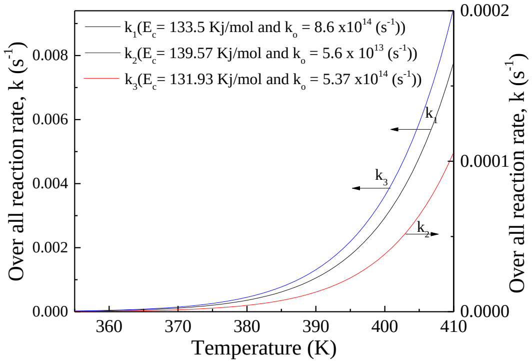

Fig.5 The calculated values of the overall reaction rate(k)corresponding to(δ=10K. min.$^{-1}$)using the deduced values of E_c and k_o for $Se_{82}In_{18}$ glass.

3.2 Reaction Order (n)

The time (*t*) at any temperature (*T*) between T_{in} *and* T_{if} is given by:

$$t = \frac{T - T_o}{\delta} \qquad (8)$$

Where T_o is the room temperature or starting measuring temperature (300 K). Hence Eq.1 become contain only one unknown (*n*). Eq. 1 can be solved for *n* as reported by Aly [19] :

$$n = \frac{\ln\left[-\ln\left(1 - X\right)\right]}{\ln\left(k, t\right)} \qquad (9)$$

According to Eq.9 when $\ln\left[-\ln\left(1 - X\right)\right]$ were plotted versus $\ln\left(k, t\right)$ a straight line passes through the origin with positive slope equals *n* value as shown in fig.6. The advantage of this method is the determination of *n* value without any approximation either in iso- or noniso-thermal technique. Furthermore, under the noniso-thermal conditions, one heating rate only is enough to determine (*n*). In the literature there are many methods used to determine (*n*) such as Afify's [15], John–Mehl–Avrami's [20] and Bansal's [21] methods which can be written as:

$$\ln\left[-\ln\left(1 - X\right)\right] = n\ln\left(k\right) + n\ln\left(t\right) \qquad (10)$$

$$\frac{dX}{dt} = \left(\frac{n^{0.37\delta E_c}}{RT_p^2}\right) \qquad (11)$$

Eq. 10 used for iso- and noniso-thermal technique but under iso-thermal condition where the temperature is constant the term $\ln\left[-\ln\left(1 - X\right)\right]$ was plotted agains $\ln\left(t\right)$ with slope equals the n value. Under noniso-thermal conditions also, the term $\ln\left[-\ln\left(1 - X\right)\right]$ was plotted agains $\ln\left(t\right)$ but at constant temperature for each heating rate (382 K) i.e at least four heating rates is required to determine n value otherwise equation 9 all the results of different heating rates are identical (see fig.6). Both the Eq.11 used only for noniso-thermal technique.

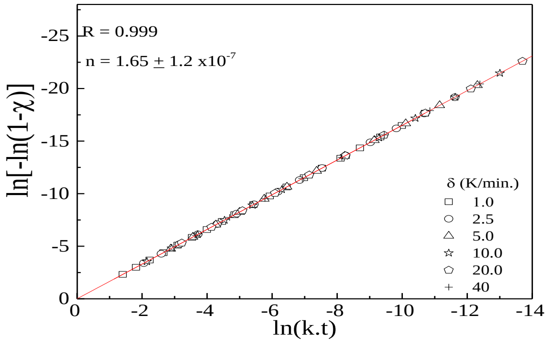

Fig.6 The plots of $\ln\left[-\ln\left(1 - X_{\exp}\right)\right]$ vs. $\ln\left(kt\right)$ at different heating rates (δ) for $Se_{82}In_{18}$ glass.

Fig.7 a and b shows The plots of $\ln\left[-\ln\left(1 - X\right)\right]$ vs. $\ln\left(\delta\right)$ and $\ln\left(t\right)$ at *T=382 C^o^*, respectively. Fig.8 represents the plot of crystallization rate dX/dt value at $T=T_p$ versus the quantity $\left(n^{0.37\delta E_c}/RT_p^2\right)$.

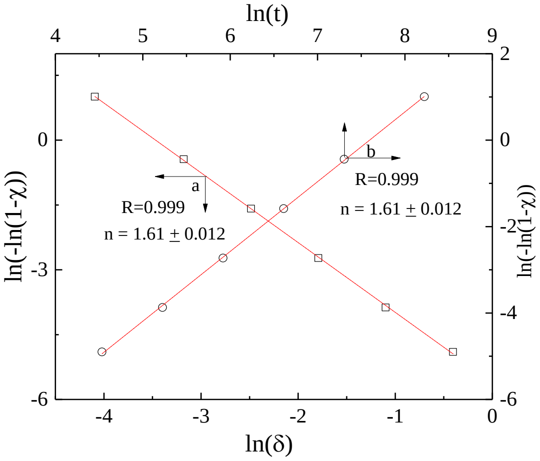

Fig.7 The plots $\ln\left[-\ln\left(1 - X_{\exp}\right)\right]$ vs. $\ln\left(\delta\right)\left(a\right)$ and $\ln\left(t\right)\left(b\right)$ at 382 K for $Se_{82}In_{18}$ glass.

As shown in Fig.8 the best fitting gives a straight line pass through the origin with positive slope equals to n value. In order to determine the best method for calculating the reaction order (*n*) one can use the values of k_o (Afify's method), k_o (Augis and Bennett's method) and n values into equation 1 at heating rate 10K. min.$^{-1}$ Fig.9 show the *X* values as a function of temperature for $Se_{82}In_{18}$ glass. From this figure one can conclude that, the X_{th} values calculated using :

$$k_1 = 8.6 \times 10^{14}\exp\left(-133.5/(R.T)\right), n = 1.65$$

(deduced by Eq. 9 or Fig. 6) and $t = \frac{T - 300}{\delta}$ are identical with the experimental values. According to the above results Afify's method is the best methods for determining both the E_c and k_o values. With respect to the reaction order, it can be determined with high accuracy based on Eq.9.The n values determined by Afify (Eq.10) is the same as that determined by John–Mehl–Avrami's and equals to 1.61 which is very close to that determined Eq.9 while Eq.11 gives *n=1.783* which is higher than that determined by Eq.9.The three *n* values 1.61, 1.65 and 1.783 are

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acceptable and the difference between them in the range of experimental error but, the n value determined by Eq.9 when used in Eq.1 makes the theoretical value of X_{th} ($X_{th}=X_3$) is the same as that experimentally determined (X).This is due to that Eqs . 5 and 9 are free from any approximation otherwise the other methods. Finally, Fig.10 shows a comparison between X (experimentally determined) and X_{th}(theoretically calculated using the deduced values E_c, k_o and n based on Eqs.5 and 9).

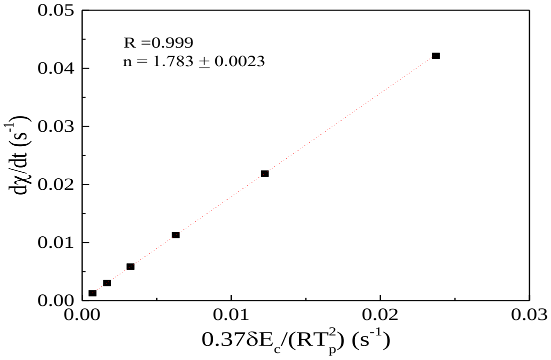

Fig.8. The plot of the crystallization rate $\frac{dx}{dt}$ vs. the quantity $0.37\delta E_c \big/ \left[RT^{Z}\!/_{p}\right]$ at ($\delta=1$, 2.5, 5.0, 10, 20 and 40 K. min.$^{-1}$) for $Se_{88}In_{18}$ glass.

As one can see an excellent agreement between X_{exp} and X_{th} as well as shown in figure 10 where the calculated values (using Eq.1 and the values of and $n=1.65$of the crystallized fraction at each heating rate and that experimentally determined. The solid lines refer to the theoretically calculated values of the crystallized fraction X_{th} using $n=1.65$ and$k_1$values that calculated using the values of $E_c=133.5$kJ/mol and $k_o=8.6\times10^{14}s^{-1}$.

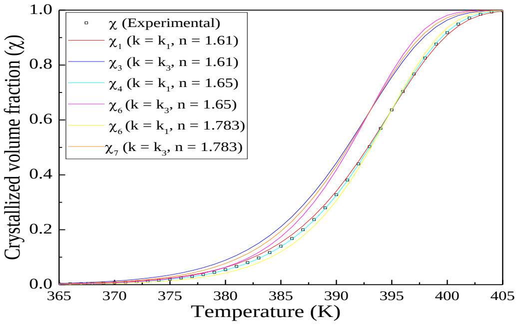

Fig.9 The experimental values of crystalized volume fraction(X_{exp}) and that theoretically calculatedX_{th}(X_1-X_6)as a function of temperature (T) where ($T_{in} \leq T \leq T_{if}$) at (δ=10K. min.$^{-1}$) for $Se_{88}In_{18}$ glass.

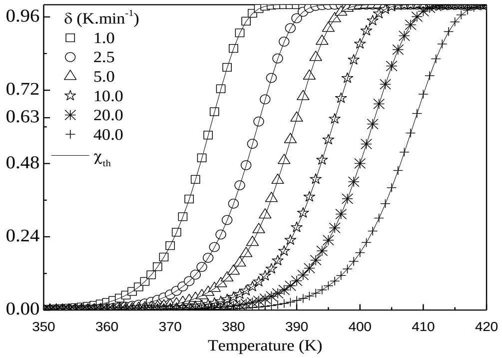

Fig.10 The temperature dependence of the crystalized volume fractionX_{exp}(experimentally determined) at different heating rates (δ) for $Se_{88}In_{18}$glass.

4 Conclusions

Glass of $Se_{88}In_{18}$ were prepared by the melt quenching technique. The non-crystalline state was confirmed by XRD. DSC measurements have been carried out under non-isothermal technique at different heating rates. The deduced values of the activation energy of crystallization (E_c) based on Afify, Kissinger and Augis and Bennett's methods within the experimental error. On the other side, the obtained value of the frequency factor (k_o) based on Kissinger's method (5.598 x$10^{13}s^{-1}$) is too small compared with the obtained by Afify's method (8.60 x 10^{14} s^{-1}) and/or Augis and Bennett's (5.368 x $10^{14}s^{-1}$) method. According to the present study the reaction order (n) was found to be equal to 1.65. In comparison with other methods it was found that n equals 1.61 and 1.783 (using eqs.10-11). Based on different values ofE_c,k_o and n the crystallized volume fraction has been calculated (X_1 –X_6). It was found that X_3that calculated using ($n=1.65$, $E_c=133.5$ kJ/mol and $k_o=8.6\times10^{14}s^{-1}$)isin excellent agreement with the experimentally determined. Therefore, Afify's method is the best one to determine both the $E_c$and$k_o$value. While both Afify and Aly arethe best to determine the value of reaction order$n=1.65$. Eq. 9 in the present study was derived from Eq.1 without any approximation therefore, it gives more accurate and highly precision value of$X=0.63205$ and it can be used for iso and non-isothermal methods as well as reported by Aly. Furthermore, in case of non-isothermal method only one heating rate is enough to determine the n value. Also, in the thermal.

References

[1] J. Vázquez, D. García, G. Barreda, P.L. López-Alemany, P. Villares, R. Jiménez-Garay, Crystallization of Ge0.08Sb0.15Se0.77 glass studied by DSC, Journal of Non-Crystalline Solids, 345-346 (2004) 142-147.

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[2] N. Mehta, P. Agarwal, A. Kumar, A study of the crystallization kinetics in Se68Ge22Pb10 chalcogenide glass, Indian Journal of Engineering and Materials Sciences, 11 (2004) 511-515.

[3] M. Fadel, K. Sedeek, N.A. Hegab, Effect of Sn content on the electrical and optical properties of Ge1-xSnxSe3 glasses, Vacuum, 57 (2000) 307-317.

[4] A. Thakur, V. Sharma, G.S.S. Saini, N. Goyal, S.K. Tripathi, Effect of light intensity and temperature on the recombination mechanism in a-(Ge20Se80)99.5Cu0.5 thin film, Journal of Physics D: Applied Physics, 38 (2005) 1959-1965.

[5] S.K. Tripathi, V. Sharma, A. Thakur, J. Sharma, G.S.S. Saini, N. Goyal, Effect of Sb additive on the electrical properties of Se-Te alloy, Journal of Non-Crystalline Solids, 351 (2005) 2468-2473.

[6] N. Suri, K.S. Bindra, R. Thangaraj, Electrical conduction and photoconduction in Se80-xTe20Bix thin films, Journal of Physics Condensed Matter, 18 (2006) 9129-9134.

[7] H.T. El-Shair, M.M. El-Nahass, S.S. Fouad, Electrical properties of thin GexSe1-x amorphous films, Vacuum, 42 (1991) 201-202.

[8] E.R. Shaaban, M.T. Dessouky, A.M. Abousehly, The effect of Bi content on the thermal stability and crystallization of Se-Te chalcogenide glass, Philosophical Magazine, 88 (2008) 1099-1112.

[9] N. Choudhary, A. Kumar, Dielectric relaxation in glassy Se100-xSbx, Turkish Journal of Physics, 29 (2005) 119-125.

[10] A. Dahshan, K.A. Aly, Determination of the thickness and optical constants of amorphous Ge-Se-Bi thin films, Philosophical Magazine, 89 (2009) 1005-1016.

[11] S. Shukla, S.P. Singh, S. Kumar, Effect of Sb incorporation on the density of defect states in a-Se 90In10 glassy alloy, Indian Journal of Pure and Applied Physics, 49 (2011) 545-549.

[12] N.B. Maharjan, D. Bhandari, N.S. Saxena, D.D. Paudyal, M. Husain, Kinetic studies of bulk Se85-xTe15Sbx glasses with x = 0, 2, 4, 6, 8 and 10, Physica Status Solidi (A) Applied Research, 178 (2000) 663-670.

[13] K.A. Aly, M.Y. Hassaan, Y.B. Saddeek, Thermal features and physical properties of sulfur modified barium vanadate glasses, Phase Transitions, 86 (2013) 477-489.

[14] K.A. Aly, F.M. Abdel Rahim, A. Dahshan, Thermal analysis and physical properties of Bi-Se-Te chalcogenide glasses, Journal of Alloys and Compounds, 593 (2014) 283-289.

[15] N. Afify, A new method to study the crystallization or chemical reaction kinetics using thermal analysis technique, Journal of Physics and Chemistry of Solids, 69 (2008) 1691-1697.

[16] M. Avrami, Kinetics of phase change. I: General theory, The Journal of Chemical Physics, 7 (1939) 1103-1112.

[17] H.E. Kissinger, Variation of peak temperature with heating rate in differential thermal analysis, J. Res. Nat. Bur. Stand., 57 (1956) 4.

[18] J.A. Augis, J.E. Bennett, Calculation of the Avrami parameters for heterogeneous solid state reactions using a modification of the Kissinger method, Journal of Thermal Analysis, 13 (1978) 283-292.

[19] K.A. Aly, crystallization study of Se86Sb14 glass; A new method to determine the kinetic exponent (n) with high accuracy, J Therm Anal Calorim, (2017).

[20] W.A. Johnson, R.F. Mehl, Reaction kinetics in processes of nucleation and growth, Transactions of the American Institute of Mining and Metallurgical Engineers, 135 (1939) 416-458.

[21] N.P. Bansal, R.H. Doremus, Surface crystallization of a fluoride glass, Journal of the American Ceramic Society, 66 (1983) c132-c133.