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KINETIC STUDY OF NON-ISOTHERMAL CRYSTALLIZATION IN SeGeX {X=0, Bi, In and Sb} CHALCOGENIDE GLASSES

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The crystallization kinetics of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) glassy alloys at different heating rates (10, 15, 20, 25 and 30°C/min) have been studied by using differential thermal analysis. The glass transition temperature at different heating rates have been determined from an emperical relation. The glass transition temperature (T_g), the crystallization temperature (T_c), the order parameter (n), the activation energy of crystallization (E_c) and activation energy of glass transition (E_g) have been calculated. The results of crystallization have been discussed on the basis of different models such as Kissinger's approach and modification for non-isothermal crystallization in addition to Johnson, Mehl and Avrami.

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1. Introduction

Chalcogenide glasses have attracted the attention because of their potential application in various solid state devices. Impurity effects in chalcogenide glasses have importance in the fabrication of glassy semiconductors.

Several workers [1-5] have reports the impurity effects in various chalcogenide glasses. Morevere, they are interesting as core materials for optical fibers used for transimission espetially when short length and flexibility are required [6-8]. Since the advent of electrophotography, amorphous selenium became a material of commerical importance. Selenium exhibit the unique properity of reversible phase transformation[9]. Its various device applications like rectifiers, photocells, vidicons, xerography, switching and memory etc. have made it attractive, but pure selenium has disadvintages like short life time and low photosensitivity. This problem can be over come by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, Sb, As etc) which gives higher photosensitivity, higher crystallization temperature and smaller ageing effects[10-12]. We have chosen Bi, Sb and In as an additives because it readily alloys with most of the chalcogenide alloy and modify their physical properities.

The increasing use of thermoanalytical technique such as differintial thermal analysis (DTA) or differintial scanning calorimetry (DSC) has offered the promise of obtaining useful data with simple methods[13] the utilization of thermoanalytical techniques depends in turn on the development of methods for analyzing the experimental data. with this objective a large number of mathematical treatments are based on the formal theory of transformation kinetics.

According to the kinetic view point, when glass transform into the crystalline state it must overcome some potential barrier. It is the activation energy of crstallization which the rearranged particles have to overcome. If the potential barrier is higher , i.e. the activation energy of crstallization is large, the nuclation and crystallization of the glass are more difficult and the

particles have not enouph time to rearrange when the glass melt is rapidly quenched. This is favourable for glass formation[13].

The crystallization of a glass upon heating can be berformed in several ways. In caloimetric measurements , two basic methods can be used, isothermal and non-isothermal. However, the results of crystallization process can be interpreted in terms of several theoritical models [14,15] .

The present work is focused on the derivation and application of three different theoritical models used to study the crystallization kinetics of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) chalcogenide glasses prepared for the first time by the melt qunching technique.

In the present work, the thermal properties of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ glassy alloys (where X=Bi, In and Sb) have been studied. Our aim is to throw light on glass transition region, crystallization and thermal stability in the given system.

2. Experimental

Glassy alloys of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) were prepared by quenching technique. Highly pure materials (99.999%) having the desired compositional ratio of elements were sealed in quartz ampoules (lenth ~10 cm , internal diameter ~0.8 cm) in a vacumm of 10-5 torr. The sealed ampouls were kept inside a programble furnace where the temperature was raised to 1223 K for 14 hours with frequent rocking to ensure the homogenization of the melt. The quenching was done in ice water. Amorphous nature of the samples has been confirmed by X-ray difractograms.

For thermal studies , we have taken 5 mg of each sample of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) glassy alloys in powder form in separate aluminium pans. Each of these samples were heated at different rates, that remain constant for every heating process (5, 10, 15, 20, 25 and 30 degree/min) and their thermograms were recorded by differential scanning calorimetry (DSC plus, Rhemetric Scientific, Uk). The measurements were made under the same experimental conditions for all the samples.

3. Results and discussion

The typical DTA trace of $Se_{0.62}Ge_{0.38}$ chalcogenide glass obtained at heating rate 25^o/min and plotted in fig (1). shows two characteristic phenomena which one resolved in the temperature region studied, the first coressponds to the glass transition temperature (T_g), and the second is the maximum peak temperature of the crystallization (T_p).

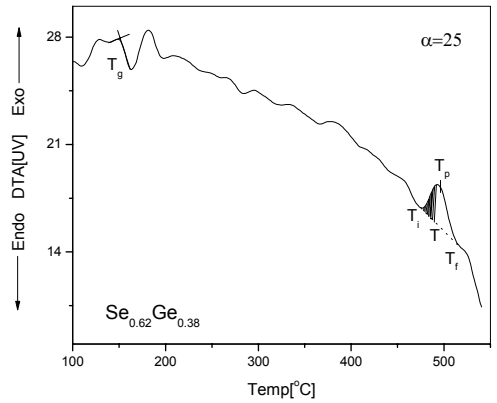

Fig.1. Typical DTA trace of $Se_{0.62}Ge_{0.38}$ at a heating rate 25^oC/min.

The values of (T_g) and (T_p) for $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) glasses are listed in table 1(a&b). Generally, the characteristic temperature (T_p) increse with the increase of heating rate on the other hand (T_g) decreases by increasing the heating rate. Moreover we can notice that $Se_{0.62}Ge_{0.35}Bi_{0.03}$ and $Se_{0.62}Ge_{0.35}In_{0.03}$ exhibit two crystallization peaks indicate that two phases are formed as in figs(2,3).

Table 1(a). Values of glass transition temperatures (T_g) as a function of heating rate for $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ glasses with X=Bi, In and Sb.

Composition	α 10 T_g , ^oC	α 15 T_g , ^oC	α 20 T_g , ^oC	α 25 T_g , ^oC	α 30 T_g , ^oC
$Se_{0.62}Ge_{0.38}$	254.68	221.72	184.35	151.88	141.52
$Se_{0.62}Ge_{0.35}Bi_{0.03}$	262.7	221.264	166.157	127.019	125.299
$Se_{0.62}Ge_{0.35}In_{0.03}$	300.69	232.1	194.2	175	107.07
$Se_{0.62}Ge_{0.35}Sb_{0.03}$	240.54	225.5	159.8	154.9	146.06

Table 1(b). Values of maximum crystalline temperature (T_p) as a function of heating rate for $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ glasses with X=Bi, In and Sb.

Composition	α 10 T_p , ^oC	α 15 T_p , ^oC	α 20 T_p , ^oC	α 25 T_p , ^oC	α 30 T_p , ^oC
$Se_{0.62}Ge_{0.38}$	476.51	484.06	490.2	494.93	495.759
$Se_{0.62}Ge_{0.35}Bi_{0.03}$ T_{p1}	348.72	353.828	350.3	357.31	369.87
$Se_{0.62}Ge_{0.35}Bi_{0.03}$ T_{p2}	414.72	424.378	428.167	432.75	435.22
$Se_{0.62}Ge_{0.35}In_{0.03}$ T_{p1}	371.33	382.527	382.924	392.9	402.59
$Se_{0.62}Ge_{0.35}In_{0.03}$ T_{p2}	460.86	466.854	469.27	475.83	480.963
$Se_{0.62}Ge_{0.35}Sb_{0.03}$	456.85	467.24	477.5	482.9	482.02

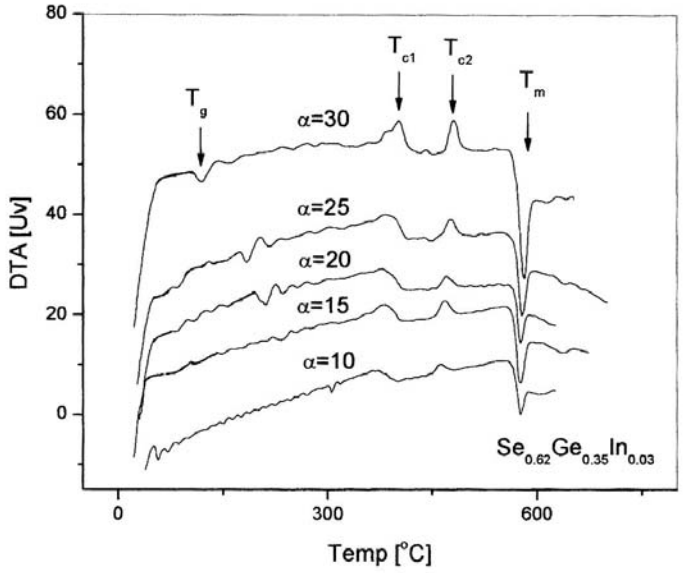

Fig.(2) Typical DTA trace of $Se_{0.62}Ge_{0.35}In_{0.03}$ at different heating rates.

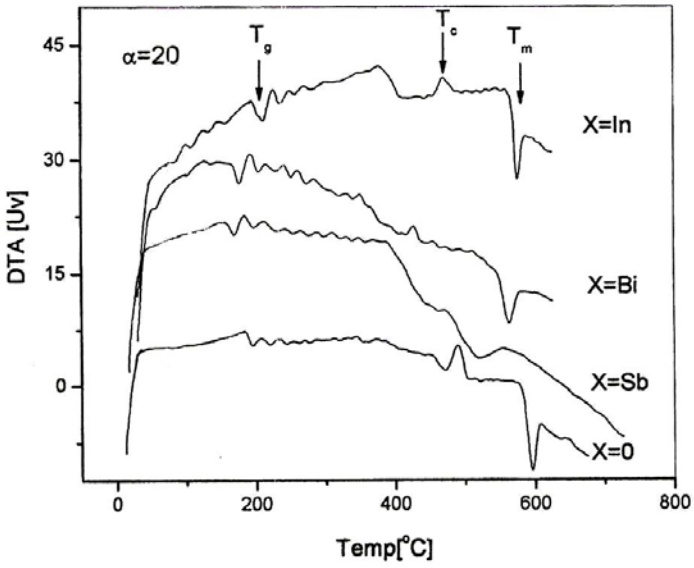

Fig.(3) Typical DTA trace of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) at a heating rate 20°C/min.

On the other hand, the crystallization process is generally understood when the four following kinetic parameters are determined, the activation energy for the glass transition (E_g), the order of the crystallization mechanism, (n), the activation energy for crystallization (E_c), the morphology of the growth (m).

The dependence of the glass transition temperature on the heating rate α , was found to obey kissinger's formula[16-18]

$$\ln(\alpha / T_g^{\,2}) = -E_g / RT_g + Cons\tan t \qquad (1)$$

where E_g is the activation energy for the glass transition.

Plots of $\ln(\alpha/T_g^{\,2})$ against $1/T_g$ for the $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) chalcogenide glass give a linear behaviour up to a heating rate of 30°C/min as shown in Fig. 4(a-d).

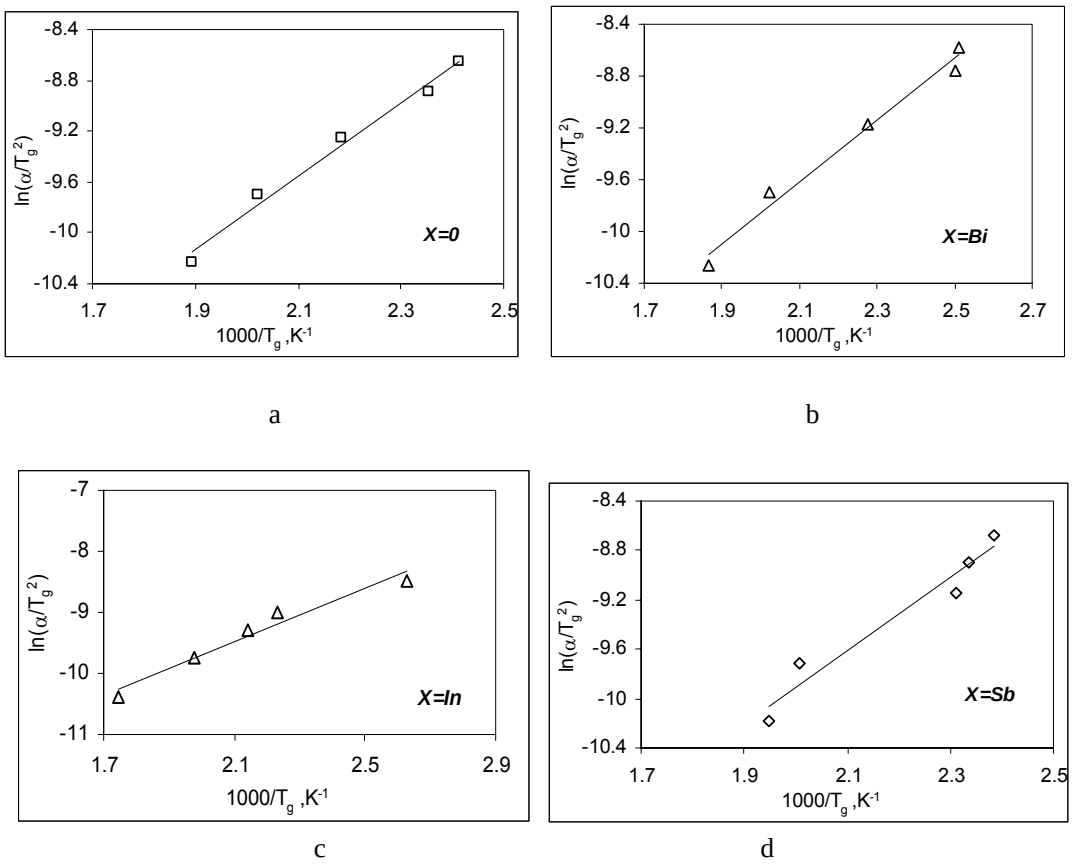

Fig. 4(a-d) Plots of $\ln(\alpha/T_g^{\,2})$ *aginst* $1/T_g$ *according to Kissinger formula for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb).*

The values of E_g dedueced using relation (1) is listed in Table (2). The approximation of mahadevan et al.[19] was used, where the variation in $\ln(1/T_g^{\,2})$ with $\ln\alpha$ is much slower than that of $\ln(1/T_g)$ with $\ln\alpha$. so, the kissinger equation can be simplified to

$$\ln(\alpha) = -E_g / RT_g + Cons\tan t \qquad (2)$$

Table 2. Values of $E_g(KJ/mol.)$ *for for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb) according to Kissinger, Mahadevan, Augis and bennett moreover lasocka formula.*

Method	***E_g (K j .mol^{-1})***			
	$Se_{0.62}Ge_{0.38}$	$Se_{0.62}Ge_{0.35}Bi_{0.03}$	$Se_{0.62}Ge_{0.35}In_{0.03}$	$Se_{0.62}Ge_{0.35}Sb_{0.03}$
Kissinger	24.067	19.927	18.091	24.433
Mahadevan	16.332	12.336	10.4288	16.721
Augis and bennett	20.2	16.131	14.26	20.577
lasocka	A= 781.89 B=-108.73	A= 853.93 B=-136.89	A= 947.65 B=-161.64	A= 740.27 B=-96.369

The variations of $\ln\alpha$ against $1/T_g$ shown in fig.5(a-d) for all investigated compositions.

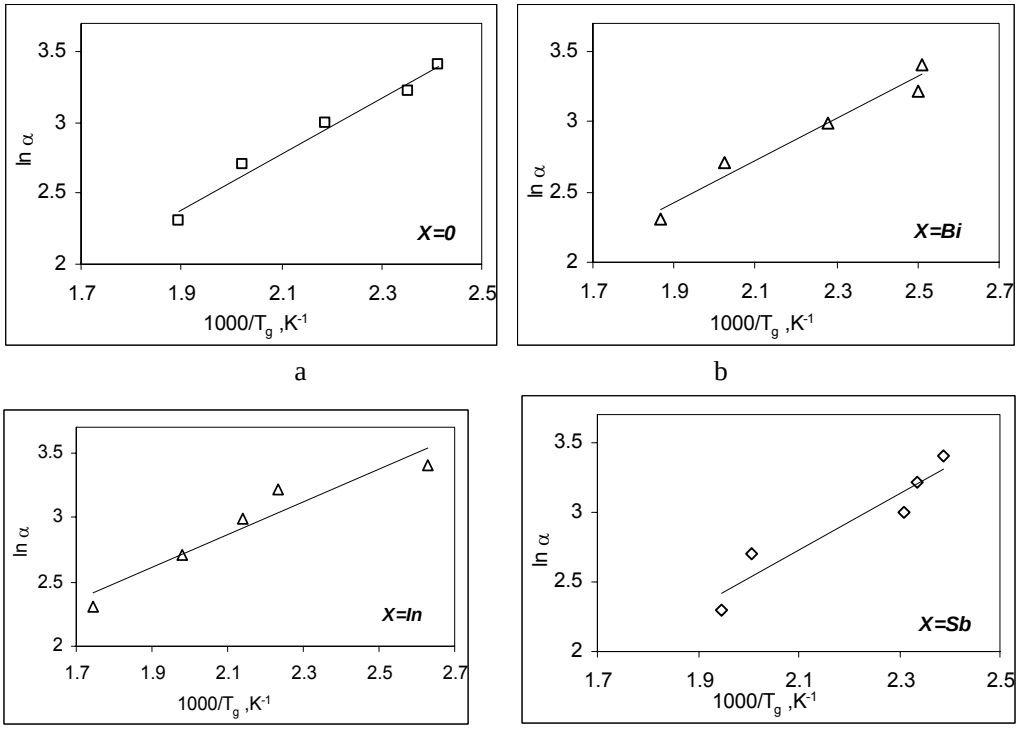

Fig.5(a-d) Plots of $\ln(\alpha)$ *aginst* $1/T_g$ *according to Mahadevan formula for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb).*

The value of E_g calculated using eq (2) and listed in Table (2). Augis and Bennett[20] suggested method to determine the activation energy of the glass E_g, according to the following equation

$$\ln[\alpha/(T_g - T_o)\ ] = -E_g / RT_g + \ln k_o \qquad (3)$$

Where k_0 is the frequency factor and T_0 is the initial temperature.

In the case of $T_g \succ\succ T_o$, the above relation can be approximated as follows [14].

$$\ln[\alpha / T_g] = -E_g / RT_g + Cons\tan t \tag{4}$$

Fig.6(a-d) show aplot of $\ln(\alpha / T_g)$ against $1/T_g$. From the slope of this approximated formula equation 4 the average value of the activation energy of glass transition calculated and listed in Table 2.

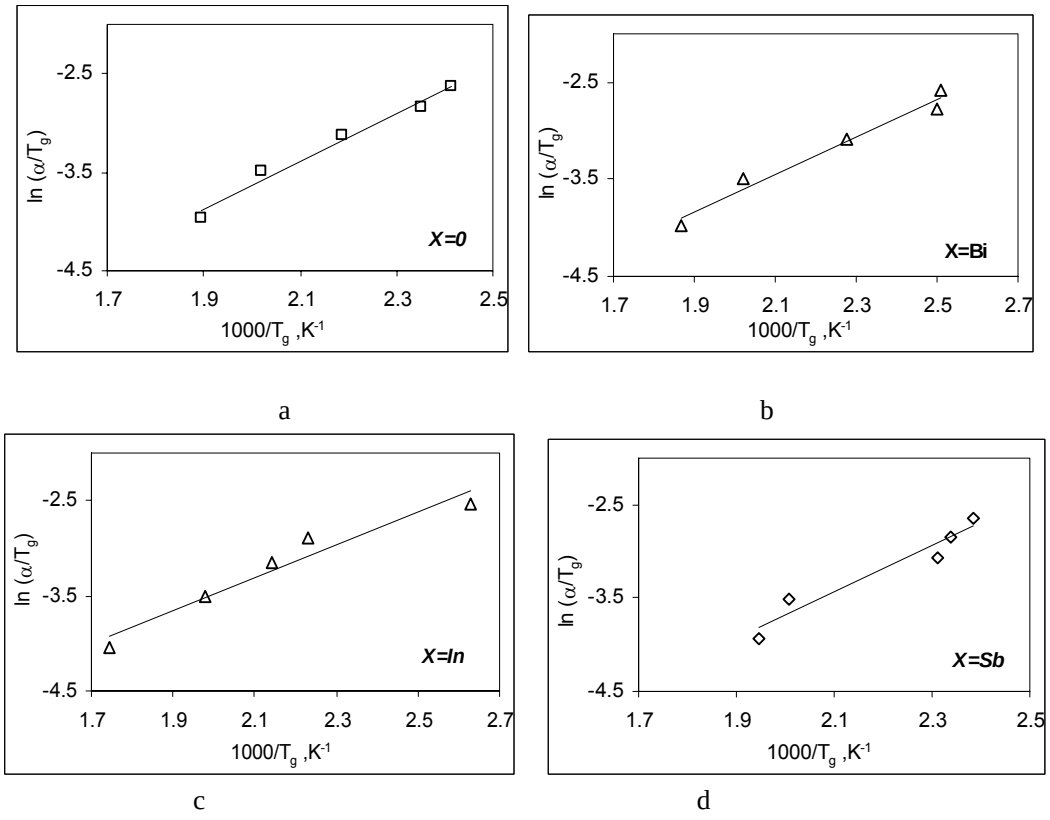

Fig.6(a-d) Plots of $\ln(\alpha / T_g)$ *versus* $1/T_g$ *according toAugis and Bennett formula for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb) glasses.*

The dependence of T_g on the heating rate, α could be discused using the empirical relation ship

$$T_g = A + B\ln\alpha \tag{5}$$

Where A and B were constants suggested by lasocka [21]. Plots of T_g versus $\ln\alpha$ for glass is shown in Fig.7(a-d) which confirms the validity of this relation. The calculated values of A and B are listed in Table (2) for $Se_{0.62}Ge_{0.38}$,$Se_{0.62}Ge_{0.35}Bi_{0.03}$,$Se_{0.62}Ge_{0.35}In_{0.03}$ and $Se_{0.62}Ge_{0.35}Sb_{0.03}$ respectively.

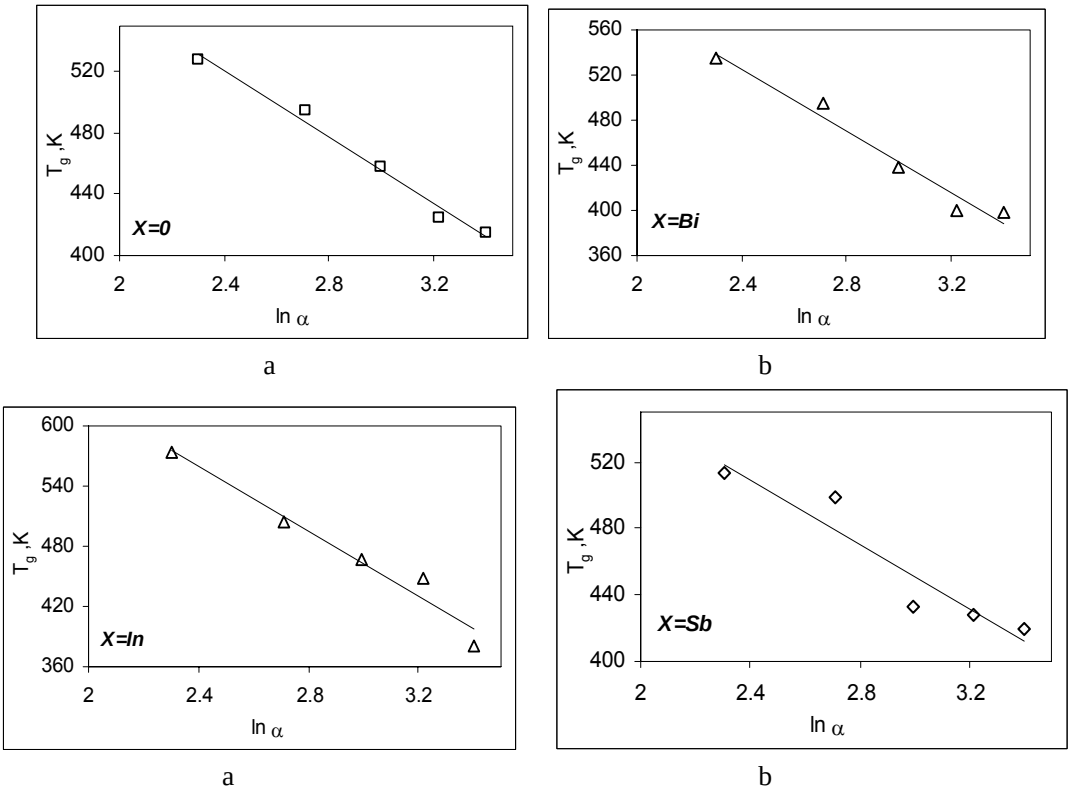

Fig.7(a-d) Plots of T_g versus $\ln\alpha$ according to Lasocka empirical relation for $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) glasses.

Kissinger [22,16] developed the method that commonly used in analyzing crystallization data in DSC and DTA experiments. The value of E_c can be obtained from the slope of

$$\ln(\alpha / T_p^{\,2}) = -E_c / RT_p + Cons\tan t \qquad (6)$$

A plot of $\ln(\alpha / T_p^{\,2})$ against $1/T_p$ is shown in Fig.8(a-d). Also, the value of the activation energy of crystalization can be calculated using the approximation of Mahadevan et al. [19] and Augis&Bennett as mentioned before eq.(2) and eq.(4).

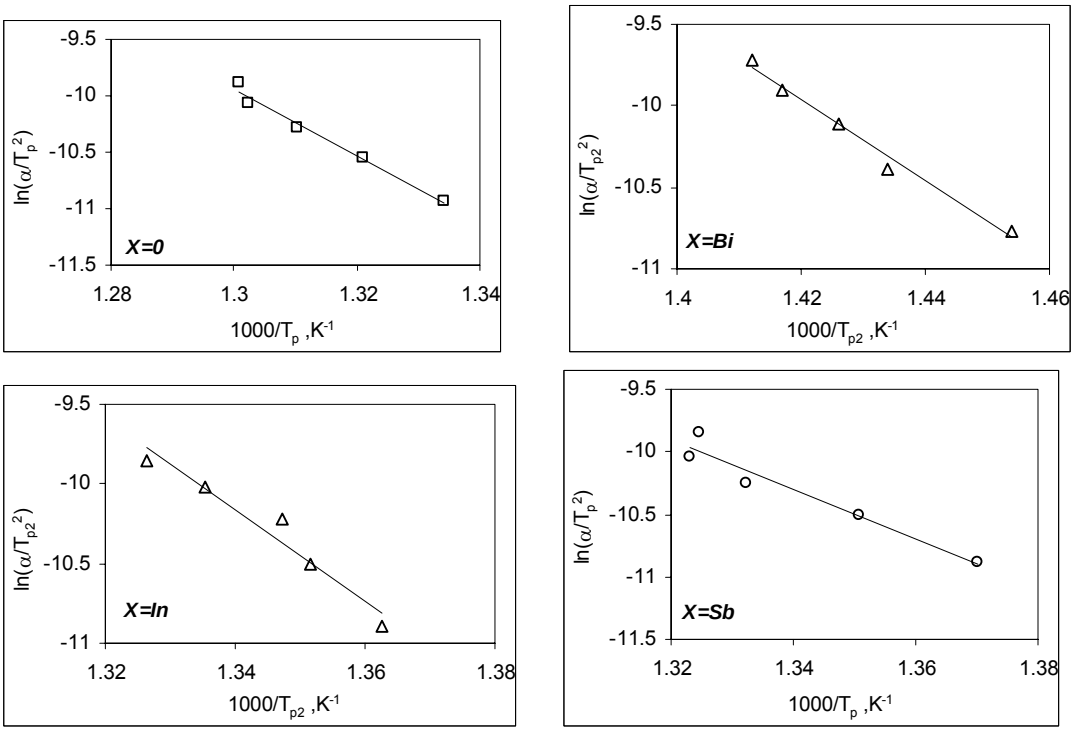

Fig.8(a-d) Plots of $\ln(\alpha / T_p^{\,2})$ *aginst* $1/T_p$ *according to Kissinger formula for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb).*

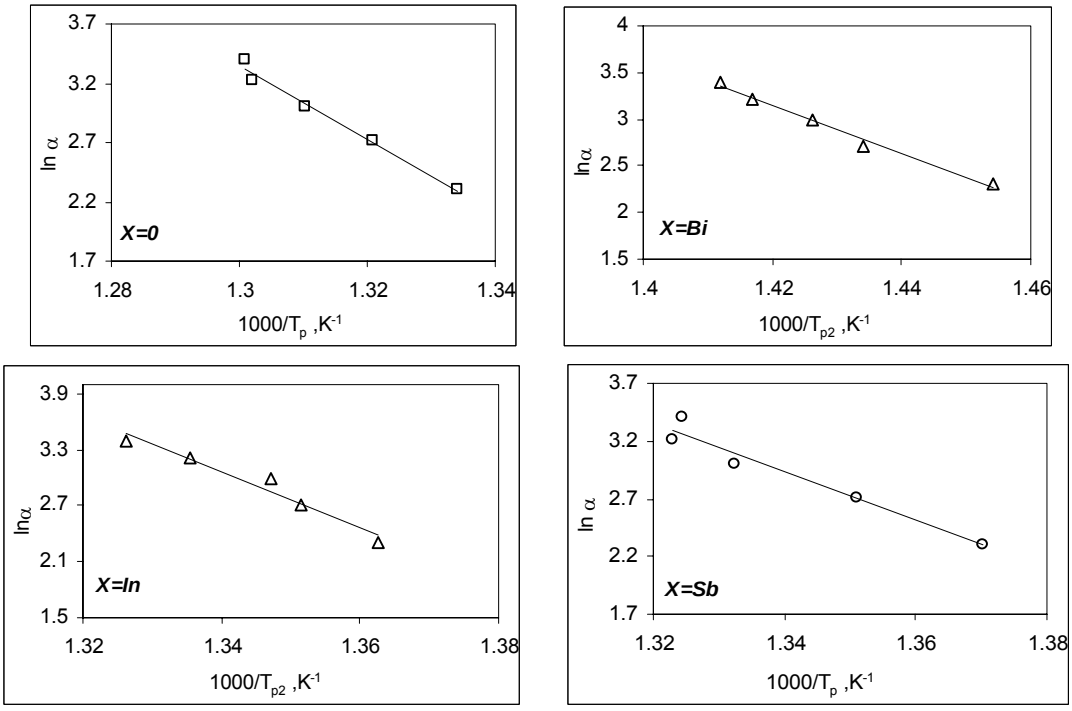

Fig.9(a-d) Plots of $\ln(\alpha)$ *versus* $1/T_p$ *according to Mahadevan approximation for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb) glasses.*

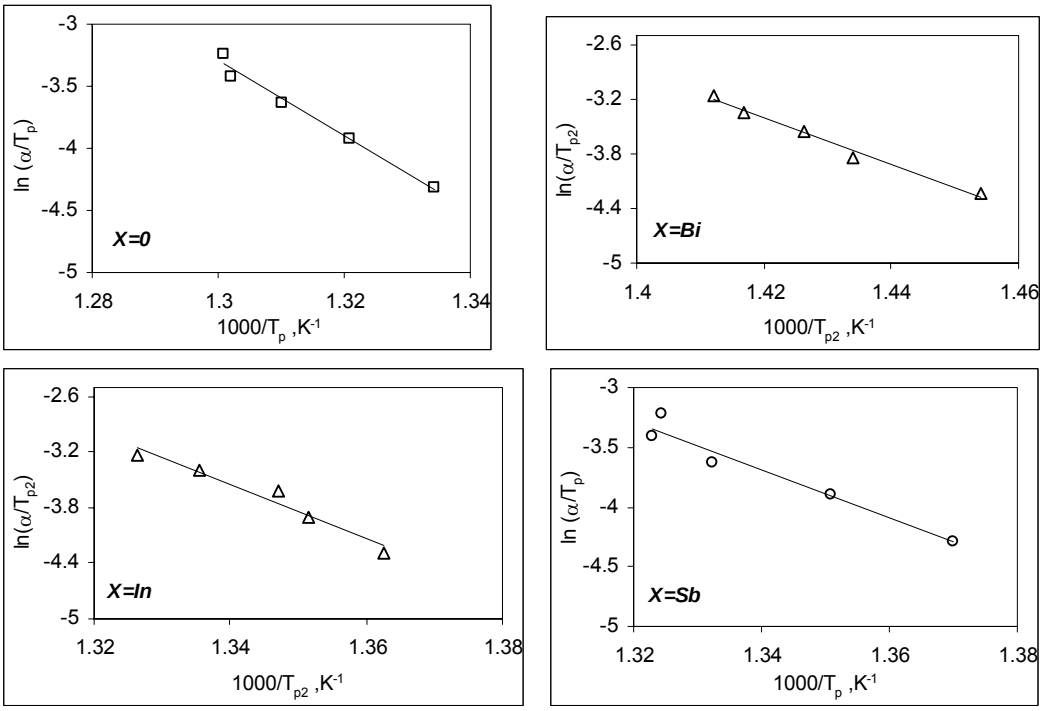

Fig.10(a-d) Plots of $\ln(\alpha/T_p)$ *versus* $1/T_p$ *according toAugis and Bennett for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb) glasses.*

Values of the activation energy of crystallization calculated using the three different methods are listed in Table (3).

Table (3)Values of $E_c(KJ/mol.)$ *for* $Se_{0.62}Ge_{0.38}$, $Se_{0.62}Ge_{0.35}In_{0.03}$, $Se_{0.62}Ge_{0.35}Sb_{0.03}$ *and* $Se_{0.62}Ge_{0.35}Bi_{0.03}$ *according to Kissinger, Mahadevan and Augis & bennett.*

Method	E_c **(Kj .mol^{-1})**					
	$Se_{0.62}Ge_{0.38}$	$Se_{0.62}Ge_{0.35}In_{0.03}$		$Se_{0.62}Ge_{0.35}Sb_{0.03}$	$Se_{0.62}Ge_{0.35}Bi_{0.03}$	
Kissinger	243.273	116.49	236.68	162.822	125.56	204.89
Mahadevan	255.902	127.46	249.05	175.177	136.08	216.49
Augis and Bennett	249.592	121.97	242.87	168.999	130.82	210.69

It is clear from this table that, the obtained values of E_c, by the three different methods are in good agreement with each other for all investigated compositions. It is well known that the

activation energy of crystallization is associated with nucleation and growth process that dominates the devitrification of most glassy solids [30-33]. In the present glassy system, In, Sb and Bi are added at the cost of Ge in Se-Ge system. The decreasing sequence of E_c is found to be in the order $(Ec)_{SeGe} \succ (E_c)_{In} \succ (Ec)_{Sb} \succ (E_c)_{Bi}$. In the present work this decreasing sequence may, therefore associated with the nucleation and growth process which requires less energy due to the decrease in the cohesive energy of the glassy network on addition of third element (In, Sb and Bi) in Se-Ge system[37], so the decreasing sequence of E_c can be explained by the decrease in the bond energy between Se the host element and the additives (In, Sb and Bi) as shown in Table (4)

Table (4) Values of bond energy of Se-Ge, , Se-In, Se-Sb and Se-Bi.

Molecule	***Bond energy, Kcal.Mol^{-1}***
Se-Ge	59.9 [34]
Se-In	59.1 [35]
Se-Sb	51.15 [34]
Se-Bi	40.7 [36]

Non-isothermal measurments of crystallization are easier to conduct than isothermal one, which are based on Avrami's equation. In a non-isothermal DSC expiriment, the temperature changed linearly with time at a known scan rate $\alpha = (dT/dt)$. We may write $T = T_o + \alpha t$

Were T_o is starting temperature and T is temperature after time t.

As temperature changes linearly with time , the reaction rate constant k is no longer a constant but varies with time as

$$\alpha(t) = 1 - \exp\{-[k(T - T_o)/\beta]^n\} \quad (7)$$

Where α is the degree of crystallization and n is the order parameter.
After rearranging and taking double logarithms of equation (7), Ozawa[23] obtained

$$\ln[-\ln(1-\chi)] = n\ln k(T - T_o) - n\ln\alpha \quad (8)$$

According to equation 8 a plot of $\ln[-\ln(1-\chi)]$ versus $\ln\alpha$ yield a straight line having slope equal to n. Fig.(11) shows the variation of $\ln[-\ln(1-\chi)]$ aginst $\ln\alpha$ at a different temperatures for $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) glassy alloys. The values of n are calculated from the slope of these curves and are given in Table 5.

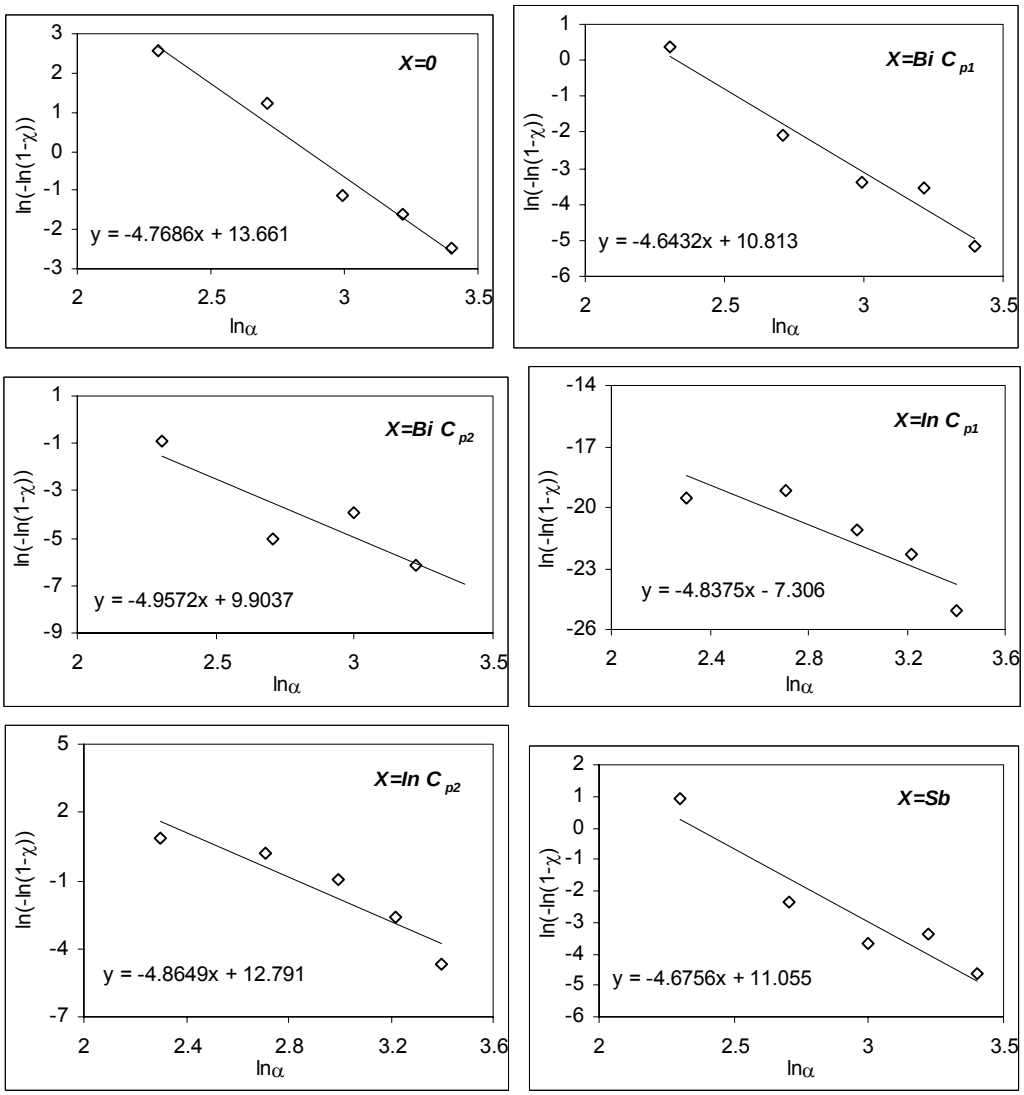

Fig.(11) Plots of $\ln\{-\ln(1-\chi)\}$ *versus* $\ln\alpha$ *according toAvrami for* $Se_{0.62}Ge_{0.38}$ *and* $Se_{0.62}Ge_{0.35}X_{0.03}$ *(X= Bi, In and Sb) glasses.*

Table(5). Values of E_c *(K j.mol*$^{-1}$*), m and n for* $Se_{0.62}Ge_{0.38}$, $Se_{0.62}Ge_{0.35}In_{0.03}$, $Se_{0.62}Ge_{0.35}Sb_{0.03}$ *and* $Se_{0.62}Ge_{0.35}Bi_{0.03}$ *glasses according to Avrami formula.*

Composition	***E_c (K j . mol^{-1})***	***n***	***m***
$Se_{0.62}Ge_{0.38}$	634.9	4.77	3.77
$Se_{0.62}Ge_{0.35}In_{0.03}$	488.1	4.838	3.838
$Se_{0.62}Ge_{0.35}In_{0.03}$	727.75	4.865	3.865
$Se_{0.62}Ge_{0.35}Sb_{0.03}$	297.7	4.67	3.67
$Se_{0.62}Ge_{0.35}Bi_{0.03}$	277.05	4.64	3.64
$Se_{0.62}Ge_{0.35}Bi_{0.03}$	349.1	4.957	3.957

The value of (n) is an integer or half integer number that depend on the growth mechanism and the dimentionality of the crystal [14], on the other hand the value of (n) in Table 5 increases on increasing the atomic weight of additives. Such an increase in order parameter n means that the crystalization is faster in Bi than others . On the other hand the theoritical basis for interpreting these results is provided by the formal theory of transformation kinetics as developed by Johnson and Mehl[24] and Avrami [25-27]. In the non-isothermal method, the crystallized fraction, χ , precipitated in a glass heated at constant rate α, is related to the activation energy for crystallization, E_c through the following expression[28,29]

$$\ln\{-\ln(1-\chi)\} = -n\ln\alpha - 1.052mE_c / RT + Cons\tan t \qquad (9)$$

Fig.(12) shows a plot of $\ln\{-\ln(1-\chi)\}$ against $1/T$ for all heating rates α =10, 15, 20, 25 and $30\,^{O}C/\min$. In this figure, all obtained lines have nearly the same slope. According to eq.(9), the average value of mE_c is determined and listed in Table 5.

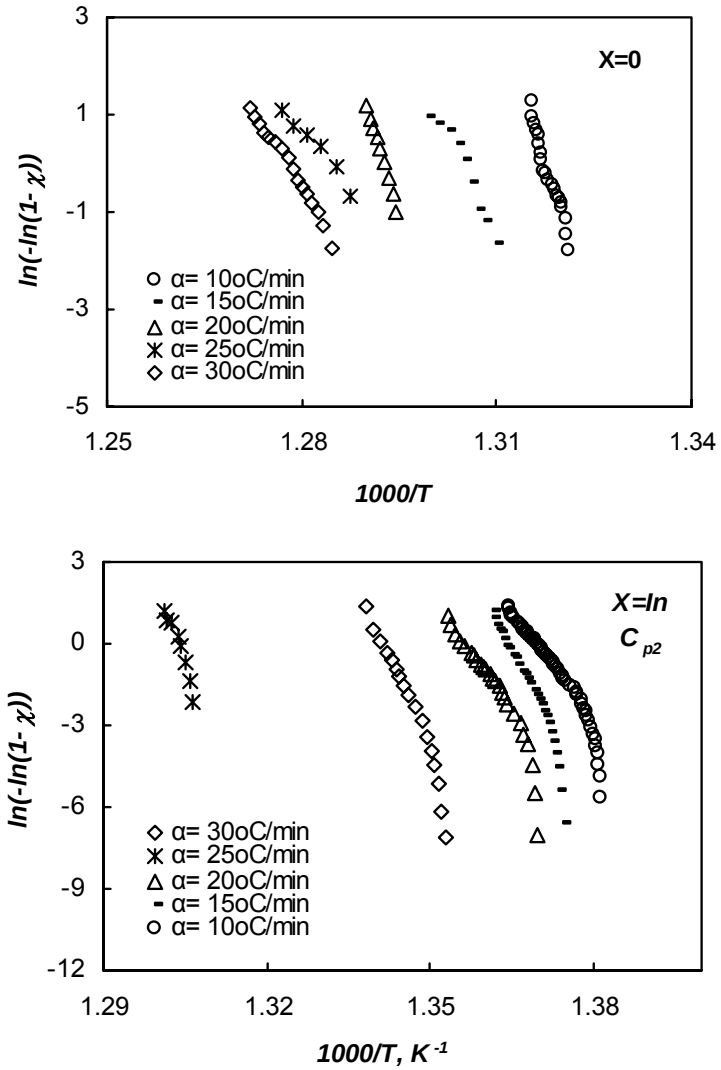

Fig.(12) A plot of $\ln\{-\ln(1-\chi)\}$ *against* $1/T$ *for all the heating rates* α *= 10, 15, 20, 25 and* $30\,^{O}C/\min$ *for all compositions.*

4 Conclusion

The crystallization behaviour of $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) chalcogenide glass was studied by using non-isothermal analysis method. The DTA results indicate that the glass transition temperature of the investigated glasses decreases by increasing the heating rate, the crystallization reactions begin to occur from 476.51 to 495.76 , 348.72 to 369.87, 371.33 to 402.59 and 456.85 to 482.02 ^{o}C for $Se_{0.62}Ge_{0.38}$, $Se_{0.62}Ge_{0.35}Bi_{0.03}$ $Se_{0.62}Ge_{0.35}In_{0.03}$ and $Se_{0.62}Ge_{0.35}Sb_{0.03}$ compositions respectively. The crystallization kinetic parameters were investigated using mathematical treatment methods. According to the above we can conclude from thermal studies that glass transition and crystallization temperatures depend on heating rate as well as on composition. T_g and T_c both increases with the increase in heating rate. The activation energies for crystallization are useful in understanding of thermal relaxation phenomena in these glasses. According to avrami index, the crystallization mechanism of the $Se_{0.62}Ge_{0.38}$ and $Se_{0.62}Ge_{0.35}X_{0.03}$ (X= Bi, In and Sb) chalcogenide glasses may be interbreted as a three-dimentional growth.

The average values of n, E_g, E_c and m at high temperatures (or in the regions of large crystallization fractions), a deviation from linearity is noticed. Generally, the deviation is attributed to the saturation of nucleation sites in the final stage of crystal growth by the small size of the particles.

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