

Determination of Crystallization Kinetics Parameters of $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ Chalcogenide Glass using Differential Scanning Calorimetry

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Abstract Amorphous semiconductor consists of one or more chalcogen (Se,Te) is called chalcogenide glass. Chalcogenide glasses have several applications in semiconductor memory devices. The present work reported the variation in kinetics parameters of chalcogenide glass $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ with five different heating rates ($5^\circ\text{C}/\text{min}$, $10^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$ and $25^\circ\text{C}/\text{min}$). Measurements of the heat flow as a function of temperature at different heating rates were carried out using Differential Scanning Calorimetry (DSC) under non-isothermal condition. Heating rate dependence of glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were measured using DSC thermograms. Johnson-Mehl-Avrami (JMA) model was used to calculate order parameter (n). Activation energy of crystallization (ΔE_c) was calculated using Kissinger and Ozawa's equations. Activation energy for structural relaxation (ΔE_r) was determined using C.T.Moynihan et al relation. Energy Dispersive X-ray Scattering (EDS) shows the presence of compositional elements in glass alloy. Scattering Electron Microscope (SEM) image depicts surface topology and nuclei growth. X-ray Diffraction (XRD) of alloy was carried out to analyze the amorphous behavior of the alloy. Based on kinetics parameters of the glass studied, it is found that difference in crystallization temperature and glass transition temperature is maximum and enthalpy of crystallization (ΔH_c) is minimum for $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ glass at heating rate $20^\circ\text{C}/\text{min}$. Therefore, this glass is more stable at heating rate $20^\circ\text{C}/\text{min}$ and hence can be used in photolithography, xerography, switching and optical memory devices.

Key words: Chalcogenide, DSC, Crystallization, Activation Energy, Enthalpy

1. Introduction

Chalcogenide glasses are inorganic glassy materials of Group IV of the periodic table which contain one or more chalcogen elements such as Se, Te, S. Se-based chalcogenide glasses have been promising materials for its applications in electronics, opto-electronic, xerography and other solid state devices [1-3]. Since pure selenium has many shortcomings such as short lifetime, low thermal stability, therefore certain additives are used to overcome these shortcomings. Se-Te, Se-In, Se-Bi alloys are of great interest owing to their properties of high sensitivity, greater hardness. These materials have the properties of changing phase from amorphous also called non-crystalline phase to crystalline phase on instantly cooling and heating. They have unique properties of reversible transformation. Because of its phase change properties, they have wide applications in solid state and optical storage devices [4]. In amorphous phase atoms are not arranged in regular fashion. They lack long range order. The process of reorganization of the atomic structure is called structural relaxation and is classified according to the property that is being observed such as enthalpy relaxation [5].

In this present work, the author aims to study the crystallization kinetics by determining kinetics parameters using DSC under non-isothermal condition. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) have been determined by DSC thermograms. The activation energies for crystallization (ΔE_c) have been determined using Kissinger and Ozawa's relations [6-8]. Activation energy for structural relaxation (ΔE_l) was determined using C.T.Moynihan et al relation [9]. Avrami exponent was obtained from JMA model [10-12]. The phases crystallized were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

Glassy alloy of $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ was prepared from high purity constituent elements (99.999%) in stoichiometric ratio by using melt quench technique. The constituent elements were sealed in quartz ampoules under a vacuum of 10^{-6} torr. The ampoule was kept inside a furnace at 900°C for 10 hrs so that all elements were melted. The temperature was raised at the rate of $3^\circ\text{C}/\text{min}$. During the heating process, the ampoule was shaken continuously so as to make it homogeneous. Quenching was done in ice water and the ingots were taken out by breaking the ampoule. Amorphous nature of as-prepared glass alloy was confirmed by XRD. Glassy alloy's Surface topography and composition have been studied by SEM image and EDS respectively.

DSC technique was used to determine the kinetic parameters of the glassy alloy at five different heating rates i.e. $5^\circ\text{C}/\text{min}$, $10^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$ and $25^\circ\text{C}/\text{min}$. DSC was done using TA instruments Q-200 Differential Scanning Calorimetry (Temp precision $\pm 0.5^\circ\text{C}$, Sensitivity $-0.2 \mu\text{W}$).

3. Results and discussion

XRD analysis of bulk glass alloy was carried out by A Regaku Ultima IV X-ray Diffractometer. The radiation source $\text{Cu K}\alpha_1$ with $\lambda = 1.54 \text{ \AA}$, diffraction angle in the range of 5° to 90° with scan speed of $2^\circ/\text{min}$ and a chart speed of $1 \text{ cm}/\text{min}$ were maintained. The pattern of graph is shown in Fig 1. In this pattern of XRD, since there is no sharp peak, therefore it confirms the amorphous nature of bulk alloy. Surface morphology of the thin film was analysed by Scanning Electron Micrograph (SEM) apparatus JEOL (Model JSM 6380). SEM image of bulk alloy is shown in Fig 2. SEM image shows the growth of nuclei. The dissociation energy for Se-In, Se-Se, Se-Bi, Te-Te are $257.5 \text{ KJ}/\text{mol}$, $239.3 \text{ KJ}/\text{mol}$, $332.6 \text{ KJ}/\text{mol}$ and $259.8 \text{ KJ}/\text{mol}$ respectively [13]. This shows that Se-Bi bonds require more energy to be dissociated which makes it robust.

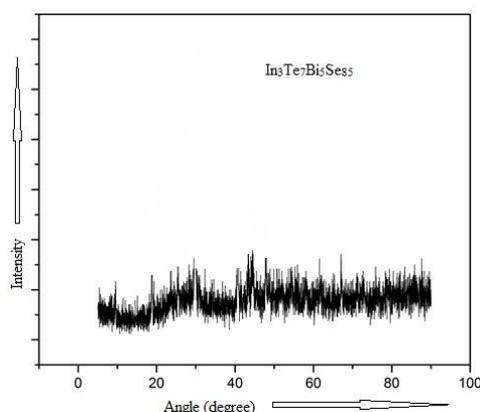


Figure 1 X-ray Diffraction Pattern of bulk alloy

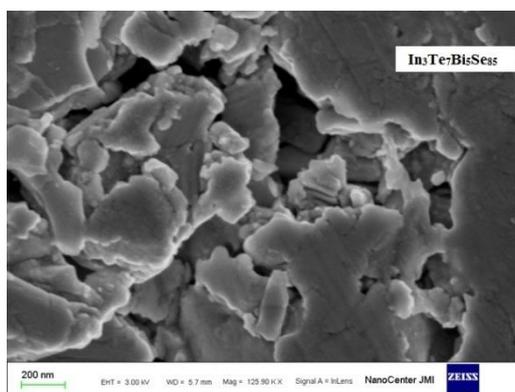


Figure 2 SEM image of bulk alloy

The elemental composition of bulk alloy was checked by using the Energy Dispersive X-ray (EDX) spectroscopy as shown in Fig 3. This image confirms the presence of constituent's elements In, Te, Bi and Se.

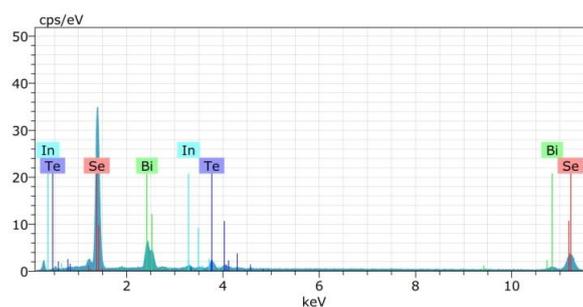
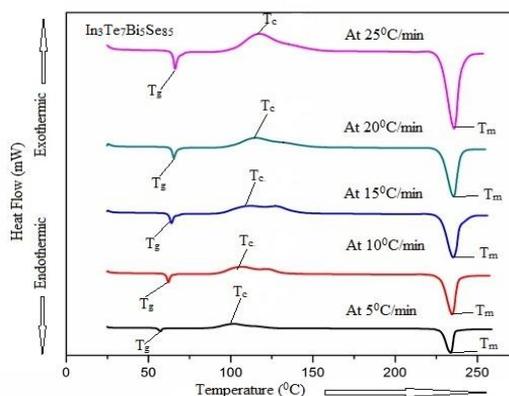


Figure 3 Energy Dispersive X-ray (EDX) of bulk alloy

The thermal behaviour of bulk alloy $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ was carried out by using DSC in the temperature range from 25°C to 250°C and at five different heating rates i.e. $5^\circ\text{C}/\text{min}$, $10^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$ and $25^\circ\text{C}/\text{min}$. The amount of 8-10 milligrams of sample is heated at a constant heating rate and changes in heat flow with respect to empty aluminium pan were measured. DSC thermograms for bulk alloy $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ at five heating rates i.e. $5^\circ\text{C}/\text{min}$, $10^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$ and $25^\circ\text{C}/\text{min}$ are shown in Fig.4 .It is cleared from the characteristics of graph that glass transition temperature (T_g) and crystallization temperature (T_c) vary with heating rates. Glass transition temperature (T_g) increases with increasing heating rates.

Figure 4 DSC thermogram of $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ bulk alloy

As shown in the above Table 1 glass transition temperature T_g is heating rate dependent. T_g increases with increasing heating rates. It leads to increasing of lattice rigidity. T_g represents the strength of the rigidity of the glass structure [14]. On the basis of short range order

concept, the decrease in T_g can be attributed to the decrease in the dimensionality of the structural units. T_g is heating rate dependent as observed and shown in Table 1. The results are in tune with those obtained by J.P. Larmagnac et al. [15] and A.H. Khafagy et al. [16]. The supercooled region of an amorphous alloy $T_c - T_g$ is widely used to characterize the thermal stability of these materials. The results present in the table shows that $T_c - T_g$ are heating rate dependants. The higher value of $T_c - T_g$ is obtained for bulk alloy $In_3Te_7Bi_5Se_{85}$ at $20^\circ C/min$, which shows the good thermal stable alloy.

Table-1

Heating rate dependence of glass transition temperature and crystallization temperature for $In_3Te_7Bi_5Se_{85}$

S.No.	Heating Rate (β) ($^\circ C/min$)	T_g ($^\circ K$)	T_c ($^\circ K$)	$T_c - T_g$ ($^\circ K$)
1	5	330.41	375.25	44.84
2	10	335.29	380.73	45.44
3	15	337.15	385.51	48.36
4	20	338.54	388.31	49.77
5	25	341.33	390.60	49.27

Crystallization kinetics of amorphous semiconductor has been studied using Johnson-Mehl-Arvami (JMA) model [17-18] in terms of crystallization fraction (α) as a function of time is expressed as

$$\ln[-\ln(1-\alpha)] = n \ln k (T - T_0) - n \ln \beta \quad (1)$$

According to Eq. (1), a plot of $\ln[-\ln(1-\alpha)]$ versus $\ln \beta$ yield a straight line with slope equal to n (order parameter). Fig.5 (a) shows the variation of $\ln[-\ln(1-\alpha)]$ against $\ln \beta$. The value of n is given in Table 2. Since as-quenched sample is studied, the value of m is taken as $m = n - 1$ [19]. The value of m is unity for binary sample while it is two in case of ternary and quaternary samples, indicating a two-dimensional growth of ternary samples [20]

The activation energy of crystallization ΔE_c can be obtained from the variation of the onset crystallization temperature T_c with heating rate by using Ozawa Equation [21-22] as

$$\ln \beta = -\Delta E_c / RT_c + C \quad (2)$$

Where C is a constant and R is a gas constant.

Fig.5 (b) shows $\log \beta$ versus $1000/T_c$ curves, which come to be linear for the entire heating rate. The value of ΔE_c calculated from the slope of straight line is given in Table 2.

The interpretation of the experimental crystallization data is given on the basis Kissinger's, Matusia's [23] and modified Ozawa's equations for the non-isothermal crystallization. The activation energy (ΔE_c) of crystallization can also be calculated by using Kissinger's equation

$$\ln(\beta/T_c^2) = -\Delta E_c / RT_c + D \quad (3)$$

The plot of $\ln(\beta/T_c^2)$ versus $1000/T_c$ is shown Fig.5(c) which appears to be straight lines. The slope of the straight line gives the value of ΔE_c and it is shown in Table 2.

The value of ΔE_c obtained by the above two theories are in good agreement to each other

The heating rate (β) dependence up on the glass transition T_g in chalcogenide glasses may be interpreted in terms of thermal relaxation phenomena and it has been shown by Moynihan et al [24] that the activation energy for structural relaxation (ΔE_t) can be related to T_g and β by

$$d \ln \beta / d(1/T_g) = -\Delta E_t / R \tag{4}$$

From the above equation we can conclude that plot of $\ln \beta$ vs $1000/T_g$ should be straight line and the slope gives activation energy for structural relaxation. Fig 5(d) shows the graph between $\ln \beta$ vs $1000/T_g$ which comes out to be a straight line. The value of activation energy for structural relaxation (ΔE_t) is determined from the slope of these straight lines which is given in Table 2.

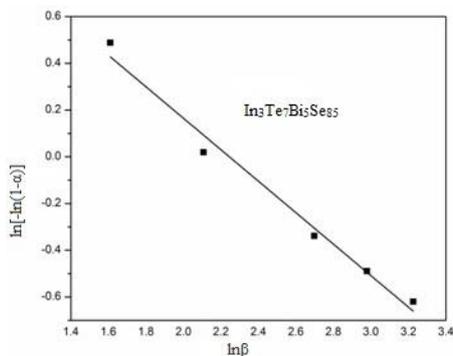


Figure 5(a) plot of $\ln[-\ln(1-\alpha)]$ vs $\ln \beta$

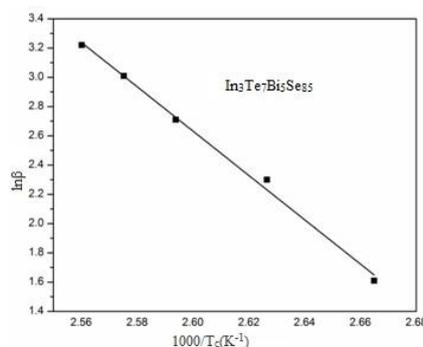


Figure 5 (b) plot of $\ln \beta$ vs $1000/T_c$ (K^{-1})

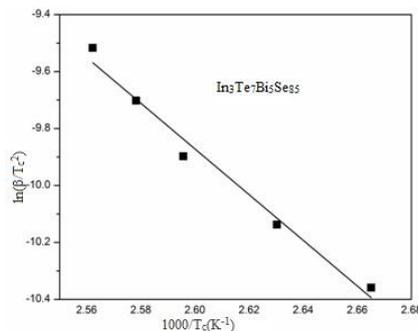


Figure 5 (c) plot of $\ln(\beta/T_c^2)$ vs $1000/T_c$ (K^{-1})

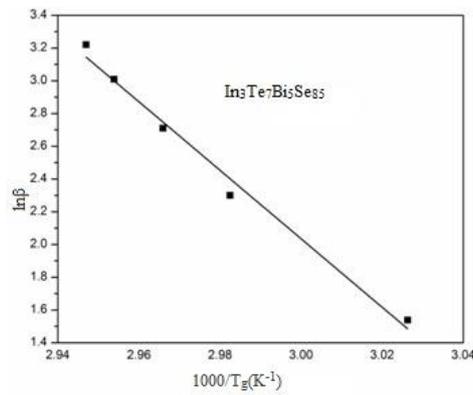
Figure 5 (d) plot of $\ln\beta$ vs $1000/T_g$ (K⁻¹)

Table 2

Activation Energy for structural relaxation and activation energy of crystallization

ΔE_t (kJ/mol)	20.23
ΔE_c (kJ/mol)	14.67
From Ozawa's relation ($\ln\beta$ vs $1000/T_c$)	
ΔE_c (kJ/mol)	13.93
From Kissinger's equation ($\ln\beta/T_c^2$ vs $1000/T_c$)	
Avrami Exponent (n)	2.87
m (=n-1)	2

Crystallisation enthalpy of the bulk alloy $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ at five heating rates ie 5^oC/min, 10^oC/min, 15^oC/min, 20^oC/min and 25^oC/min have been determined from DSC thermograms and are given in Table 3 .It is found that Crystallization enthalpy is minimum at heating rate 20^oC/min.

Table 3

Crystallization enthalpy of the alloys at different heating rates

S.No.	Heating rate (β) (^o C/min)	Enthalpy ΔH_c (J/g)
1.	5	36.77
2.	10	36.41
3.	15	35.07
4.	20	27.16
5.	25	39.03

4. Conclusion

Crystallisation kinetics of chalcogenide glass $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ at five heating rates ie 5^oC/min, 10^oC/min, 15^oC/min, 20^oC/min and 25^oC/min under non-isothermal conditions have been studied using DSC. XRD pattern confirms the amorphous nature of alloy. EDX spectroscopy of the alloy confirms the presence of constituent elements in bulk alloy. Ozawa and Kissinger equations have been used to determine Activation Energy of

crystallization (ΔE_c). It is found that they are in good agreement with each other. Activation energy for structural relaxation has been determined by Moynihan et al method. The temperature difference $T_c - T_g$ is maximum at heating rate $20^\circ\text{C}/\text{min}$ and crystallization enthalpy (ΔH_c) is minimum at the same heating rate. Therefore, chalcogenide glass $\text{In}_3\text{Te}_7\text{Bi}_5\text{Se}_{85}$ is thermally stable at $20^\circ\text{C}/\text{min}$ and it can be used in opto-electronic devices, memory and switching.

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