

Fabrication of Ternary Chalcogenide Glassy Alloys and its Calorimetric Studies

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Abstract: A ternary chalcogenide semi-conducting materials Selenium-Tellurium-Gallium has been fabricated in which a systematic investigation has been conducted to study the effect of Gallium in Selenium-Tellurium binary components. The system $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ ($0 < x < 10$) has been studied in detail with emphasis on bulk glasses of Se-Te-Ga systems and thin films are prepared by the conventional melt quenching technique and by thermal evaporation technique, respectively. X-ray diffraction and differential scanning calorimetric methods have been used to characterize the materials.

Keywords: chalcogenide glasses, thin films, quenching technique, differential scanning calorimetry.

1. Introduction

Amorphous solids, like crystalline solids can be insulators, semi-conductors, or metals, and in some cases at exceptionally low temperature they can even be semi-conductors. The quantum theory of solids as it originally developed is based completely on the presence of long-range order. The existence of semi-conductors is intimately connected with this theory because the long-range order in these materials is absent. It is believed therefore that amorphous solids could not be semi-conductors. It was Ioffe¹ who first pointed out that the basic electronic properties of a solid are determined primarily by the character of bonds between nearest neighbours rather than by the long-range order. Goryunova and Kolomiets², while working on glasses containing one or more chalcogen elements (S, Se, Te) observed that these glasses behave like intrinsic crystalline semi-

conductors. However, they lost their interest in these materials as the electrical conductivity could not be varied by the addition conventional III and V group elements. The chemical bond approach enabled Mooser and Pearson^{3,4} to predict many of the semi-conducting properties of the amorphous materials. Amorphous semi-conductors on the basis of difference in chemical bonding can be broadly classified into three major categories:

- (a) Covalent non-crystalline solids which includes Tetrahedral semi-conductors & Chalcogenide glasses
- (b) Semi-conducting oxide glasses
- (c) Dielectric films

Amorphous Silicon, Germanium, Silicon Carbide, Gallium Phosphide etc. can be obtained by vacuum evaporation of gaseous compounds as thin films. These are tetrahedrally bonded amorphous solids. They can be doped with chemically impurities and they possess some unpaired electron spins that yield magnetic effects. Tetrahedral semi-conductors are pnictide glasses (whose primary component is an element in group V of the periodic table). Chalcogenide glasses⁵ are made with compositions which include one of the chalcogen elements i.e. S, Se or Te. These are largely insensitive to impurities and do not have any unpaired spins except under the most extreme non-equilibrium conditions and generally show symmetrical current voltage characteristics. The name of this class of materials come from the fact that their properties are primarily influenced by the two non-bonding orbitals of the group VI chalcogen elements in two folds co-ordination. This group of solids which is also called lone-pair semiconductors is not well defined, but includes one or more of the elements S, Se, or Te combined with Si, Ge, As, Sb, Pb etc. These glasses form a large class of semi-conducting materials. Semi-conducting oxide glasses have strong ionic bonds and are usually insulators which can be made semi-conducting by the addition of transition metal ions in different valence states. The conduction process then proceeds via a charge exchange among the mixed transition metal ions. The conduction band of the host glass plays no role in the charge transport, the glass merely acts as the host medium and effects the tunneling conduction through the phonon and polarization interaction. these materials have been reviewed by researchers as revealed in literature⁶⁻⁹. Dielectric films are insensitive to disorder as their electronic conduction relies on deviation from stoichiometry and the presence of the defect centre which act as donors and acceptors. Selenium-Tellurium alloys have gained much importance because of their higher photosensitivity, greater hardness, higher

crystallization temperature as compared to pure Selenium glass¹⁰⁻¹³. Onozuka et.al.¹⁴ have attempted to reduce the residual potential while maintaining the resistivity at a sufficiently high level. Chalcogenide glasses find wide applications in various technology due to their peculiar properties, such as materials of television cameras, microwave devices and diodes¹⁵⁻¹⁷. This is most likely due to their high optical transparency in the IR region, strong optical nonlinearity, high photo sensitivity, ease of fabrication and processing, and good chemical durability. Chalcogenide glasses based on the chalcogen elements Sulphur, Selenium, Tellurium are used widely in ultra-fast optical switches, frequency converters, optical amplifiers, optical recording devices, an optical integrated circuit for IR operations and infrared transmitting optical fibers¹⁸⁻²¹.

In the present work, multicomponent chalcogenide $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ ($x=0, 0.5, 5, 10$) amorphous semiconductors have been developed with varying composition in the system. Detailed investigations viz. x-ray diffraction and differential scanning calorimetric methods have been used to characterize the materials. The heat of crystallization and Avrami exponent in various composition have been evaluated. Single scan technique is used in the work.

2. Experimental Procedure

Synthesis of chalcogenide glassy alloys: Glasses of different composition have different region of glass formation dictated by the type of bonds between the constituent's elements. An increased tendency to glass formation is processed by chalcogenide compounds and alloys with predominantly covalent chemical bonds. However, the specific composition up to which glass formation in binary and ternary systems is possible, cannot be predicted in prior and has to be determined experimentally, for example in the Ge-Se system, glass with composition from $\text{Ge}_{40}\text{Se}_{40}$ to elemental Selenium have been reported²²⁻²⁴ whereas in Se-Te system glass formation is possible up to a Tellurium content 30%. Thin film chalcogenide glass were prepared by conventional melt quenching technique. High purity (99.99%) materials of Ga, Se, and Te were weighed according to their atomic percentage using a electronic balance. Table-1 shows the actual amount of constituent elements taken. The materials were then sealed in evacuated (10^{-5} torr) quartz ampoules containing $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ ($0 \leq x \leq 10$) were heated to 600°C and was held at that temperature for 8-10 hours. The temperature of the furnace was raised at a rate of $3-4^\circ\text{C}/\text{min}$ for up to 1000°C for 15 hours. During heating process all the ampoules were

constantly rocked by rotating a ceramic rod to which the ampoules were took away in the furnace. This was done to obtain homogeneous glassy alloys. Thereafter, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice cold water in case of $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ ($x=0, 0.5, 5, 10$). Quenching allowed the glass to retain, as much as possible, a definite structure corresponding approximately to the structure of the melt at the synthesis temperature. The quenched samples of $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ were taken out by breaking the ampoules.

Table 1 Data for preparation of Glassy Alloys

Alloy	Element	%	Atomic Weight	Atomic Weight x %	Actual weight taken (gm)
$\text{Se}_{70}\text{Te}_{30}$	Se	70	78.96	55.2720	2.9541
	Te	30	127.60	38.2800	2.0459
$\text{Se}_{69.5}\text{Te}_{30}\text{Ga}_{0.5}$	Se	69.5	78.96	54.8772	2.9345
	Te	30	127.60	38.2800	2.0469
	Ga	0.5	69.72	0.3486	0.0186
$\text{Se}_{65}\text{Te}_{30}\text{Ga}_5$	Se	65	78.96	51.3240	2.7567
	Te	30	127.60	38.2800	2.0561
	Ga	5	69.72	3.4860	0.1872
$\text{Se}_{60}\text{Te}_{30}\text{Ga}_{10}$	Se	60	78.96	47.3760	2.5573
	Te	30	127.60	38.2800	2.0663
	Ga	10	69.72	6.9720	0.3764

Upon cooling a liquid below its melting points, it will either crystallize or form a glass. The crystallization of an amorphous material proceeds by the processes of nucleation and growth and glass formation becomes a question of preventing crystallization. Glass formation becomes more probable, the greater the cooling rate, the smaller the sample volume and the slower the crystallization rate. Liquid with small crystallization kinetic constant can thus form glasses directly from the melt. This is the basic reason why selenium is a good glass former in contrast to pure tellurium.

Characterization of the glassy alloys by x-ray diffraction analysis: Amorphous materials are defined by their diffraction patterns which consists of a few broad halos rather than sharp bragg reflections. Keeping in view, x-ray diffraction pattern were obtained by using powder techniques on x-ray diffractometer. The diffraction curves of the prepared alloys did not show any peak which confirmed that the material was in the disordered state.

Thermal characterization of the glassy alloys by DSC method: Differential scanning calorimetry (DSC) can be defined as a differential thermal analytical method in which the coordinate value at any given temperature (or time) is directly proportional to the direct heat flow between the sample and reference material and in which the integrated area under the measured curve is directly proportional to the total differential caloric input²⁵. When subjected to sufficiently high temperatures, virtually all substances will undergo physical and chemical changes ranging from simple changes in state to complete decomposition that can be studied by various methods of thermal analysis. During these physico-chemical reactions or phenomena these will be concomitant sequential or overlapping changes in the enthalpy that tend themselves to direct measurement by the technique of differential scanning calorimetry. As a thermo-analytical method, DSC may be used to characterize and experimentally evaluate a system by continuously measuring the changes in thermal properties due to physical and chemical as they occurred at elevated temperature as a function of increasing temperature. The sample under investigation by DSC is heated to elevated temperature at a predetermined rate of temperature rise. In addition, the temperature of prime interest is not sample temperature per second, but the difference between enthalpy change which occurs in a sample and that is some inert reference material, when they are both heated under same conditions. This measurement is made by means of a pair of thermocouples, one of which is placed in the sample and the other in the reference material. Both substances are provided with individual heaters. This makes it possible to use a null-balance principle. Commercially available DSC units offer a great deal of flexibility in the varying temperature, heating rate, atmospheric composition, pressure and thermal history imparted to a sample in order to obtain a complete thermal energy profile under varying experimental conditions. The DSC kinetic program permits the calculation of activation energy (E), the pre-exponential factor (Z), heat of reaction (H) and order of reaction (n) from a single DSC scan of a reaction exotherm. The DSC exotherm is used to measure two basic parameters required to solve these two equations

- (1) The reaction rate $d\alpha/dt$, by dividing the peak height at temperature T by the total peak area and
- (2) The fractional unreacted ($1-\alpha$), obtained by measuring the ratio of the partial area at temperature T to the total peak area to obtain α and the subtracting this value from unity.

3. Results and Discussions

The systematic variation of the composition in a glassy semiconductor provides means of preparing the material with the desired range of optical and electronic properties. Chalcogenides can exist over a wide range of compositions, not all of which exist in a glassy form, it is often possible to find materials with which these non-glass forming compositions can be alloyed to form a glass. Ternary glasses allow a larger variety of atoms to be incorporated into the glass structure, thus giving even greater engineering capacity. There is a growing interest in the family of special glasses The involving fluoride, chalcogenide and Heavy metal oxide glasses due to their promising properties such transmission in middle and far infrared regions of spectra, lower values of phonon energies and higher values of refractive indices as compared to SiO_2 . Chalcogenide glasses also have been identified as semi-conductors²⁶. It has been realized that the band gap depends on the existence of short-range order rather than on the long range order of the lattice and suggested that the first coordination number of the corresponding crystal (if it exists) is preserved in the amorphous structure²⁷.

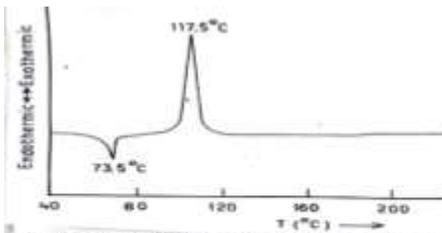


Fig.3 DSC thermogram of a-Se₇₀Te₃₀ at a heating rate 5°K / min.

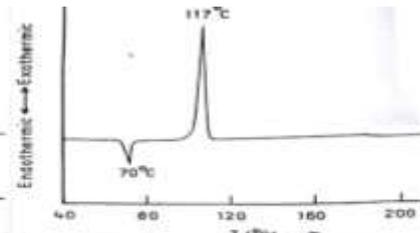


Fig.4 DSC thermogram of a-Se_{69.5}Te₃₀Ga_{0.5} at a heating rate of 5°K / min.

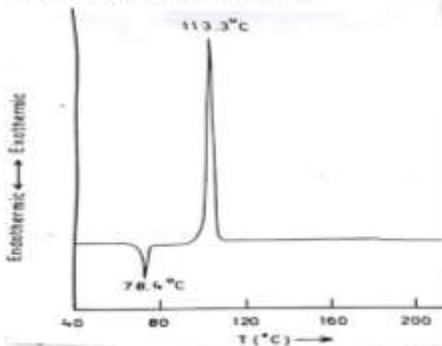


Fig.3 DSC Thermogram of a-Se₆₅Te₃₀Ga₅ at heating rate of 5°K / min.

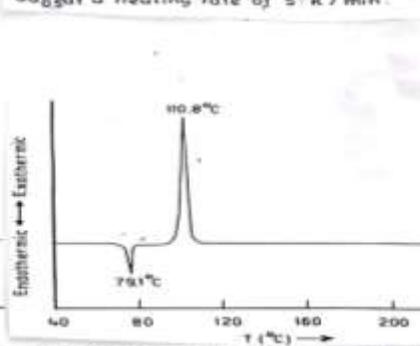


Fig.4 DSC thermogram of a-Se₆₀Te₃₀Ga₁₀ at a heating rate of 5°K / min.

The differential scanning calorimetry curves of $Se_{70}Te_{30}$, $Se_{69.5}Te_{30}Ga_{0.5}$, $Se_{65}Te_{30}Ga_5$, $Se_{60}Te_{30}Ga_{10}$, glassy alloys are shown in figures 1-4 where the parameter α (fractional area) is calculated from the differential scanning calorimetric curves for each sample. The heating rate of above DSC measurements is $5^{\circ} K /min$. Table 2 shows the data calculated from the figure 1-4 for α (fractional area) for the $Se_{70}Te_{30}$, $Se_{69.5}Te_{30}Ga_{0.5}$, $Se_{65}Te_{30}Ga_5$, $Se_{60}Te_{30}Ga_{10}$ alloys. Similarly, table 3 contains data calculated from the same figure 1-4 for α ($d\alpha/dt$) for the sample $Se_{70}Te_{30}$, $Se_{69.5}Te_{30}Ga_{0.5}$, $Se_{65}Te_{30}Ga_5$, $Se_{60}Te_{30}Ga_{10}$ glassy alloys.

Table 2 Data for calculation of α (fractional area) with temperature for Glassy Alloys

Glassy Alloy	Distance from endothermic peak x (cm)	$\Delta t = \text{change in temp. from endothermic peak}$	Temperature in $^{\circ}K$	Area upto point x A (mm ²)	Fractional area $\alpha = \frac{\Delta A}{A}$	Value derived from DSC thermograms				
						$t_{end}^{\circ}C$	$t_{exo}^{\circ}C$	$d = t_{exo} - t_{end}^{\circ}C$	D C m	A mm ²
$Se_{70}Te_{30}$	1.18	26.6	373.1	2.0	0.0147	73.5	117.5	44	1.95	135.6
	1.38	31.1	377.6	2.5	0.0184					
	1.58	35.7	382.2	7.5	0.0553					
	1.78	40.2	386.7	32.9	0.2425					
	1.98	44.7	391.2	60.9	0.4491					
$Se_{69.5}Te_{30}Ga_{0.5}$	1.46	39.21	382.2	00.04	0.0495	70	117	47	1.75	80.83
	1.66	44.58	387.6	10.30	0.1274					
	1.86	49.96	393.0	59.01	0.7300					
$Se_{65}Te_{30}Ga_5$	1.18	27.83	379.2	2.00	0.0155	78.4	113.3	34.9	1.48	129.3
	1.38	32.54	383.9	21.00	0.1623					
	1.58	37.26	388.7	96.38	0.7449					
$Se_{60}Te_{30}Ga_{10}$	1.00	23.14	375.2	1.00	0.0102	79.1	110.8	31.3	1.37	98.1
	1.20	27.77	379.9	9.00	0.0917					
	1.40	32.39	384.5	66.80	0.6809					

where, t_{end} = Temperature of endothermic peaks; t_{exo} = Temperature of exothermic peaks; d = Distance between endothermic and exothermic peak; A = Total area of the exothermic peak

Table 3 Data for calculation of α (da/dt) with temperature for Glassy Alloys

Glassy Alloy	Distance from endothermic peak x (cm)	$\Delta t =$ temperature change from endothermic peak ($^{\circ}\text{C}$)	Temp at x in $^{\circ}\text{k T}^{\circ}$	α (da/dt)	Value derived from DSC thermograms			
					t_{end} $^{\circ}\text{C}$	t_{exo} $^{\circ}\text{C}$	$\Delta t = t_{\text{en}}$ d. t_{exo}	D Cm
$\text{Se}_{70}\text{Te}_{30}$	0.80	18.05	364.05	0.00	73.5	117	44	1.95
	1.20	27.08	373.08	0.10				
	1.40	31.59	377.60	0.20				
	1.60	36.10	382.10	0.60				
	1.80	40.62	386.60	2.36				
	1.98	44.68	390.70	4.00				
$\text{Se}_{69.5}\text{Te}_{30}\text{Ga}_{0.5}$	1.10	29.54	302.5	0.00	70	117	47	1.75
	1.46	39.21	382.2	0.15				
	1.66	44.58	387.6	1.23				
	1.80	48.34	391.3	4.50				
$\text{Se}_{65}\text{Te}_{30}\text{Ga}_5$	0.60	14.25	365.7	0.00	78.4	113.3	34.9	1.48
	1.00	23.74	375.1	1.00				
	1.20	28.49	379.9	0.26				
	1.40	33.24	384.6	3.21				
	1.50	35.61	387.0	8.40				
$\text{Se}_{60}\text{Te}_{30}\text{Ga}_{10}$	0.80	18.51	370.6	0.00	79.1	110.8	31.7	1.37
	1.00	23.14	375.2	0.10				
	1.20	27.77	379.9	0.90				
	1.40	32.40	384.5	5.20				

Table 4 Data for calculation of $\ln \ln (1 - \alpha)^{-1}$ with temperature for Glassy Alloys

Glassy Alloy	T	A	$10^3/T$	$\ln \ln (1 - \alpha)^{-1}$
$\text{Se}_{70}\text{Te}_{30}$	373.1	0.0147	2.68	-4.21
	377.6	0.0184	2.65	-3.98
	382.2	0.5531	2.62	-2.87
	386.7	0.2426	2.59	-1.28
	391.2	0.4491	2.56	-0.52
$\text{Se}_{69.5}\text{Te}_{30}\text{Ga}_{0.5}$	382.2	0.0495	2.62	-2.98
	387.6	0.1274	2.58	-1.99
	393.0	0.7300	2.55	+0.27
$\text{Se}_{65}\text{Te}_{30}\text{Ga}_5$	379.2	0.0154	2.64	-4.16
	383.9	0.1623	2.61	-1.73
	388.7	0.7449	2.57	+0.31
$\text{Se}_{60}\text{Te}_{30}\text{Ga}_{10}$	375.2	0.0102	2.67	-4.58
	379.9	0.0917	2.63	-2.34
	374.5	0.6809	2.60	+0.13

Table 5 Data for calculation of $\ln \alpha$ with temperature for Glassy Alloys

Glassy Alloy	T	α	$10^3/T$	$\ln \alpha$
Se ₇₀ Te ₃₀	364.05	0.00	-	-
	373.08	0.10	2.58	-2.30
	377.60	0.20	2.65	-1.61
	382.10	0.60	2.52	-0.51
	386.60	2.36	2.59	+0.86
	390.70	4.00	2.56	+1.39
Se _{69.5} Te ₃₀ Ga _{0.5}	372.5	0.00	-	-
	382.2	0.15	2.62	-1.90
	387.6	1.23	2.55	+0.21
	391.3	4.50	2.56	+1.51
Se ₆₅ Te ₃₀ Ga ₅	365.7	0.00	-	-
	375.1	0.10	2.67	-2.30
	379.9	0.26	2.63	-1.35
	374.6	3.21	2.60	+1.17
	387.0	8.40	2.58	+2.13
Se ₆₀ Te ₃₀ Ga ₁₀	370.6	0.00	-	-
	375.2	0.10	2.67	-2.30
	379.9	0.90	2.63	+0.11
	384.5	5.20	2.60	+1.65

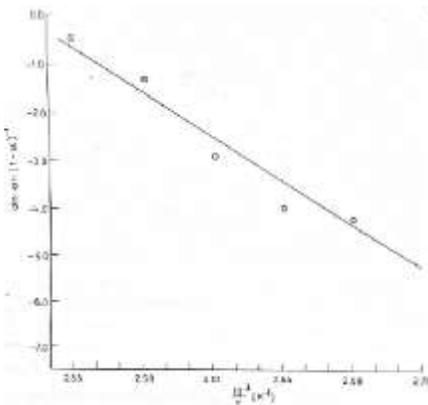


Fig. 5. $\ln(1-\alpha)$ vs. $1000/T$ curve for α -Se₇₀Te₃₀

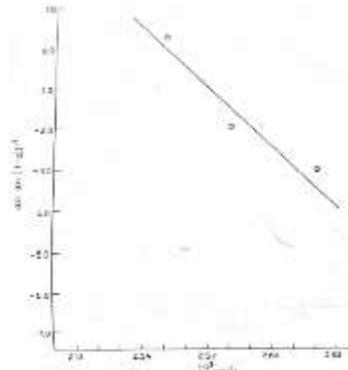


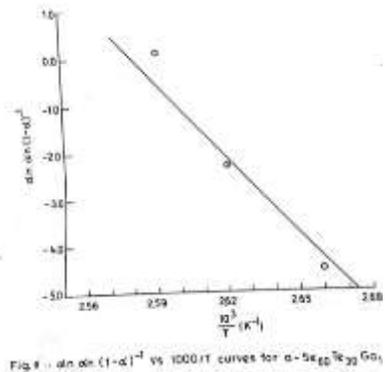
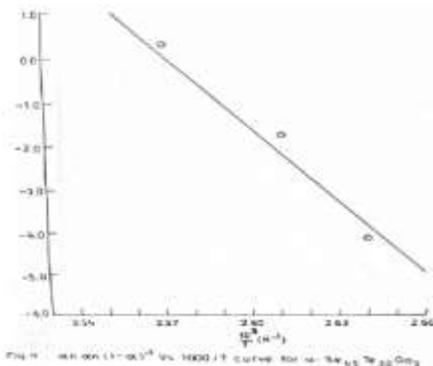
Fig. 6. $\ln(1-\alpha)$ vs. $1000/T$ curve for α -Se_{69.5}Te₃₀Ga_{0.5}

The graph between $\ln \ln (1 - \alpha)^{-1}$ with $10^3/T$ for the sample alloys Se₇₀Te₃₀, Se_{69.5}Te₃₀ Ga_{0.5}, Se₆₅Te₃₀ Ga₅, Se₆₀Te₃₀ Ga₁₀ have been plotted from figure 5-8. The graph between $\ln \alpha$ with $10^3/T$ for the above samples have been plotted. The slopes of the graphs between $\ln \ln (1 - \alpha)^{-1}$ vs $10^3/T$ have been calculated from from figure 5-8 and the values are given in table 6 for the sample Se₇₀Te₃₀, Se_{69.5}Te₃₀ Ga_{0.5}, Se₆₅Te₃₀ Ga₅ and Se₆₀Te₃₀ Ga₁₀ glassy

alloys. The slopes of the graphs (figure 9-12) between $\ln \alpha$ with $10^3/T$ from the graphs plotted above for the same samples of glassy alloys have also been summarized in table 6. The slope (figure 6) of the $\ln \ln (1 - \alpha)^{-1}$ vs $10^3/T$ will give the value of $(-\Delta E_C/K_B)$ where K_B is Boltzmann constant. After substituting the value of K_B the value of $-\Delta E_C$, activation energy of crystallization have been calculated for all the samples of glassy alloy and the value E_C is given in table 6. Similarly the slope of $\ln \alpha$ vs $10^3/T$ will give the value of $(-\Delta E_C/nK_B)$ where n is Avarani's exponent parameter. After substitution the value of $(-\Delta E_C/K_B)$ from table 6 Avarani exponent, n , is calculated from the graph for each sample which is depicted in table 6.

Table 6 Data for calculation of slope of glassy alloys from graph between $\ln \ln (1 - \alpha)^{-1}$ vs temp, $\ln \ln (1 - \alpha)^{-1}$ vs temp, activation energy of Crystallization, avarami exponent (n) of Glassy Alloys

Glassy Alloy	Data for slope of glassy alloys from graph between $\ln \ln (1 - \alpha)^{-1}$ vs $10^3/T$	Data for slope of glassy alloys from graph between $\ln \ln (1 - \alpha)^{-1}$ vs $10^3/T$	Data for the activation energy of crystallization for glassy alloy $(-\Delta E_C)$ KJ/mol	Avarami exponent (n)
Se ₇₀ Te ₃₀	30.13	45.46	256.34	0.68
Se _{69.5} Te ₃₀ Ga _{0.5}	49.18	57.14	408.60	0.86
Se ₆₅ Te ₃₀ Ga ₅	55.56	45.46	460.99	1.22
Se ₆₀ Te ₃₀ Ga ₁₀	53.57	57.69	444.49	0.93



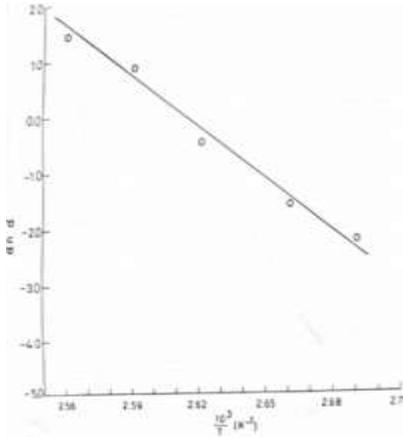


Fig.1. $\ln(1 - \alpha)$ Vs $1000/T$ curve for $a\text{-Se}_{20}\text{Te}_{30}\text{O}_{50}$ Glass

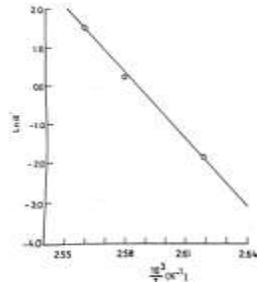


Fig.2. $\ln \alpha$ Vs $1000/T$ curves for $a\text{-Se}_{49.5}\text{Te}_{30}\text{O}_{20.5}$

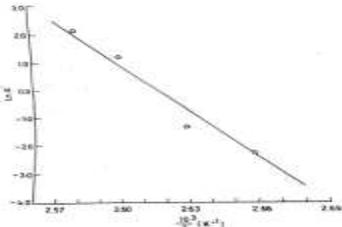


Fig.3. $\ln \alpha$ Vs $1000/T$ curves for $a\text{-Se}_{45}\text{Te}_{30}\text{O}_{25}$

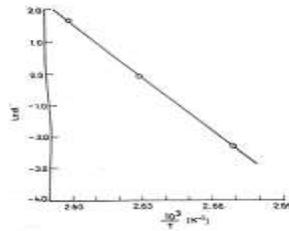


Fig.4. $\ln \alpha$ Vs $1000/T$ curves for $a\text{-Se}_{40}\text{Te}_{30}\text{O}_{30}$

The crystallization mechanism of the amorphous materials are controlled by nucleation and growth process which can be characterized by an activation energy ΔE_C , and Avrami exponent n. According to John-Mehl Avrami law the degree of crystallization is given by the following equation:

$$(3.1) \quad \alpha = 1 - \exp(-kt^n),$$

where, α – is the extent of crystallization and is calculated by dividing partial area by the total area of exothermic peak, k – is the function of temperature and in general depends on the nucleation and growth rate both. n – is a parameter which reflects the growth morphology.

The generalized temperature dependence of k can be given as

$$(3.2) \quad k = k_0 \exp\left(\frac{\Delta E_C}{kT}\right),$$

where, ΔE_c is the activation energy of crystallization and k is Boltzmann constant. According to D.W. Henderson theory the extent of crystallization is related to the activation energy of crystallization by the following equation:

$$(3.3) \quad d \left[\ln \ln(1-\alpha)^{-1} / d(T^{-1}) \right] = -(\Delta E_c / K).$$

So it is clear that the $\ln \ln(1-\alpha)^{-1}$ vs T^{-1} plot should be a straight line and the activation energy involved in the molecular motion and rearrangements around T_c can be calculated from the slope of this plot.

The plots of the glassy sample $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{69.5}\text{Te}_{30}\text{Ga}_{0.5}$, $\text{Se}_{65}\text{Te}_{30}\text{Ga}_5$ and $\text{Se}_{60}\text{Te}_{30}\text{Ga}_{10}$ are straight lines. Therefore, these plots are according to D.W. Henderson. $\Delta E_c/n$ can be determined by the same theory proposed by D.W. Henderson, according to which

$$(3.4) \quad \ln \left(\frac{d\alpha}{dt} \right) = -\frac{\Delta E_c}{nKT}.$$

The deviation of the above equations is

$$(3.5) \quad \ln \left(\frac{\ln \alpha'}{dT^{-1}} \right) = -\left(\frac{\Delta E_c}{nK} \right)$$

It is clear from the above equation that plot between $\ln \alpha'$ vs T^{-1} must be a straight line. The figures 9-12 showed a straight line for the glossy alloys $\text{Se}_{70}\text{Te}_{30}$, $\text{Se}_{69.5}\text{Te}_{30}\text{Ga}_{0.5}$, $\text{Se}_{65}\text{Te}_{30}\text{Ga}_5$ and $\text{Se}_{60}\text{Te}_{30}\text{Ga}_{10}$. The introduction of the third element in the amorphous semiconductor drastically effects. An increase in the activation energy of crystallization on addition of the Ga suggests the formation of stable structures in ternary Se-Te-Ga system as compared to binary Se-Te systems.

4. Conclusion

Calorimetric studies have been made in glassy alloy of $\text{Se}_{70-x}\text{Te}_{30}\text{Ga}_x$ ($0 < x < 10$). Single scan technique has been used to calculate the activation (ΔE_c) and the order parameter (n). The result indicates that (ΔE_c) increases on addition of Ga. However, the order parameter is found to be

almost same for all the glasses studied indicating no change in crystallization mechanism on addition of Ga to binary system Se₇₀-Te₃₀ glass. An increase in E_c on Ga addition suggests that stability of Se-Te-Ga structure as compared to binary Se-Te system.

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