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Glass Formation and Properties of Chalcogenide Systems

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Abstract

Glass-forming regions of ternary Ge-Te-Cu and Ge-Te-In chalcogenide glasses are examined by differential scanning calorimetry and by X-ray diffraction. Glass transition and crystallization temperatures are about 120 ^{0}C To 260 ^{0}C, relatively higher than those of binary Ge-Te glass [1].

Only a small range of compositions after quenching the melting alloy is characterized by disorder state, but this range of composition is widened when using a vapor deposition technique. These compositions have two glass transition temperatures, showing the existence of different phases in the sample. Both Kissinger equation and modified Kissinger Kinetic analysis were adopted to estimate the activation energy and the reaction order of the process. Ge-Te-Cu and Ge-Te-In crystallized in two stages, nucleation and crystal growth. These two processes can be distinguished by exothermal crystallization patterns.

An atomic radial distribution analysis has been made on bulk $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ with x=0.1 by X-ray diffraction techniques. The radial distribution function (RDF) is discussed in terms of the structure factor F(s). Thin films of Ge-Te-Cu and Ge-Te-In are deposited on silicate glass and silicon wafer substrates by vacuum evaporation. The optical energies E_{opt} are determined from the transmission and reflection data of deposited films. The value of E_{opt} decreased by increasing metal additive such as Cu or In and discussed as a function of the conditions of their preparation such as substrate type.

I: Introduction

Infrared optical fibers operating at 2-12 μm in wavelength are required for infrared sensing applications such as radiometric thermometer, and Co_2 laser power applications such as laser surgery [1]. The Te- based chalcogenide glasses are can fidates for such applications because their infrared absorption edges are located in a wave length region above 12 μm [2]. However, only a few compositions such as Ge-Te and As-Te based glasses have been investigated as memory switching glasses [3-7]. In this manuscribt, ternary Ge-Te-Cu and Ge-Te-In compositions are studied for use as infrared optical fiber material.

The study of glassy material is currently being strongly impulsed by the application of calorimetric techniques; through differential scanning calorimetery (DSC), it is possible to penetrate the glass-forming mechanisms, determining kinetic parameters which describe the phenomena of nucleation and subsequent crystalline growth, from amorphous materials. The knowledge of the factors which influence the glass-crystal reactions leads to a better control of the inverse reactions and, therefore, of the properties and obtention of amorphous materials. Studies Kinetics are always connected with the concept of activation energy. The value of this energy in glasses is associated with nucleation and growth mechanisms that dominate the devitrifications of most glassy solids. Studies of the crystallization of a glasses upon heating can be performed in several different ways, isothermal and non-isothermal.

The atomic structure of these solids is not completely random, as happens with gases, as the cohesion due to their chemical bonds must be present among their atoms [8]. The atoms must be in contact with each other, and there is short -range order. The structural units formed by an atom and its nearest neighbors corresponds, in away, to the unit cell of a crystal. The atomic distances and bond angles in each of these structural units are not, however, singly determined, but take a certain distribution of values and unlike in a crystalline network, the repetition of structural units is not periodical, and the orientation and structural characteristics of the clusters is different in each direction. An amorphous solid, therefore,

exhibits more variety than a crystal, infinitely increasing the technological possibilities of glasses. The energy of an amorphous material is located in a relative minimum, which is why the obtention processes are based on saving the energetic excess they posses in relation to the same crystalline alloy [9]. Although it was thought that the property of turning into glass was restricted to substances with a very wide band gap. We can now state that this property is common to condensable material in general, if subjected to suitable treatment [10]. Analysis of the optical absorption spectra is one of the most productive tools for understanding and developing the energy band diagram of both crystalline and amorphous materials.

An important step will be taken when a definite relationship is found between the structural characteristics and calorimetric magnitudes of glasses; some hypotheses have already been formulated in this sense [11,12] and verified on chalcogenide materials.

II:Manufacturing The Alloy and Preparing The samples for measurement

The glass samples investigated in the present work belong to the system $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ with (x=0.05 and 0.1 at.%). Alloys were prepared by heating the high-purity constituents at 850^0C mixed together in desired proportions in silica ampoules sealed off at 10^{-5} torr, for 8 h with continuous shaking to ensure good homogeneity. The melt was then quenched in saturated a queues solution of NaCl at around -15^0C and the alloy was solidified to the glass S.C.

The alloys were ground to a fine powder for the differential scanning calorimetry studies and samples weighing 25 mg were placed in closed aluminum pans and heated at 500^0C in a Shimadzue model (DT-50) differential scanning calorimetry. Heating rates of 5, 10, 15, 20 and 30^0C /min were chosen for the study of the crystallization Kinetics using the multiscanning technique. Standard WAXS experiments were performed on X-ray diffraction equipped with a graphite monochromatic scintillation counter and standard associated electronic equipment. Two sets of four series of intensities collected with Bragg-Brentano geometry in the angle interval $4^0 \leq 2\theta \leq 140^0$ for Cu $K\alpha_1$ (λ= 15.4056 nm) radiation with step size of $(\Delta 2\theta)=0.2^0$, were used from 4^0 to 70^0, and $(\Delta 2\theta)=0.5^0$ from 70^0 to 140^0. Counts were measured by keeping a fixed time interval for purposes of automatic data registration by means of Shimadzue systems. The intensity assigned to each observation point was the mean value of those series measured at that point. Detailed analysis of the atomic arrangement in ternary alloys requires the determination of the radial distribution function. Samples in the form of thin films were prepared by evaporating the synthesized material at a base pressure of 2×10^{-5} torr onto cleaned silicate glass and N- type silicon wafer were used as a substarate using Edward coating unit model 306. A source substrate distance of 12 cm was adjusted during deposition. No international control of the substrate temperature was preformed. The deposition parameter were kept constant so that a comparison of result could be made under identical conditions. The film thickness (d) was controlled at 200 nm with a quartz crystal monitor and confirmed by the interferometric method [13].

X-ray diffraction has been used to investigate and characterize the structure of the prepared bulk and films using machine model XD-D series Shimadzu with Cu anode.

The microstructure developed interfacially, were followed using high resolution scanning electron microscope (Jeol, JSM-T20,Japan). Transversely were mounted on silicate glass and Si wafer by silver paste adhesive and were gold sputtered.

The transmittance and reffectance of the films were measured using double beam Shimadzu UV-VIS spectrophotometer in the spectral range 200-1100 nm. wavelength.

III- Results

III.1 X-Ray Diffraction Patterns of $Ge_1Te_4Cu_x$ and $Ge_1Te_4In_x$

The pattern reveal partially crystalline for bulk sample except $In_{0.05}$. Diffuse haloes characterising the amorphous nature of the films deposited on silicate glass and some diffraction pattern for films deposited on Si wafer as shown in fig.(1) as an example.

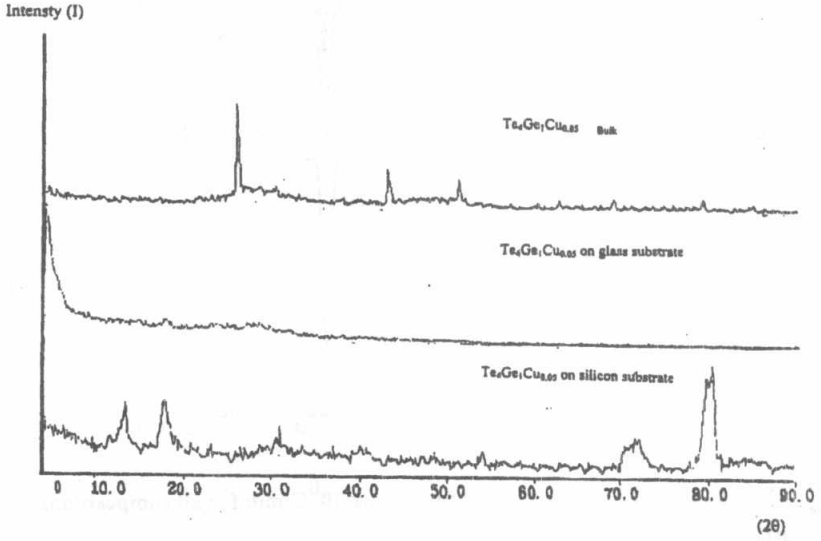

Figure (1) X-ray diffraction patterns of $Ge_1Te_4Cu_{0.05}$ as bulk and thin film

III.2: Effect of composition and heating Rate on Thermal Transition

DSC traces at rate of 10 ^{0}C/ min. of freshly prepared $Ge_1Te_4(Cu_X, In_X)$ where x=0.05 and 0.1 are shown in fig. (2). The traces follow the known common behavior, where the three characteristic temperatures T_g , T_C and T_m are observed and given in table (1). For Ge-Te doped by metal such as (Cu, In), two glass transition temp. (T_{g1},T_{g2}) and one crystallization temperatures (T_{C1}) are almostly observed in the sequence[$T_{g1}<T_{C1}<T_{g2}$ 14]. The effect of heating rate on the characteristic temperatures was investigated at five different rates for $In_{0.05}$ and $Cu_{0.05}$ and the data listed in table (1). The observed T_g is decreased by increasing the heating rate, inspection of obtained data. For an ideal glass there is lower limit to this change. But for this system the wide range of changes in T_g indicate that this system behaves as a normal glass. It is worthy mention that for x=0.05,0.1 at %, the DSC Scan for $\varphi = 2^0$C /min. shows that a small amount of the sample material has been crystallized. The crystallization of amorphous material proceeds by the proceeds by processes of nucleation and growth. Moreover, the crystallization rate is suppressed by reducing the rate of nucleation or the rate of growth. Since growth follows nucleation, in some cases if the nucleation is prevented, there will be no crystallization. However, even if nucleation occurs, the crystallization rate can still be suppressed by reducing the rate of growth. Turnbull[10] indicates that the growth rate in liquids with high viscosity is limited.

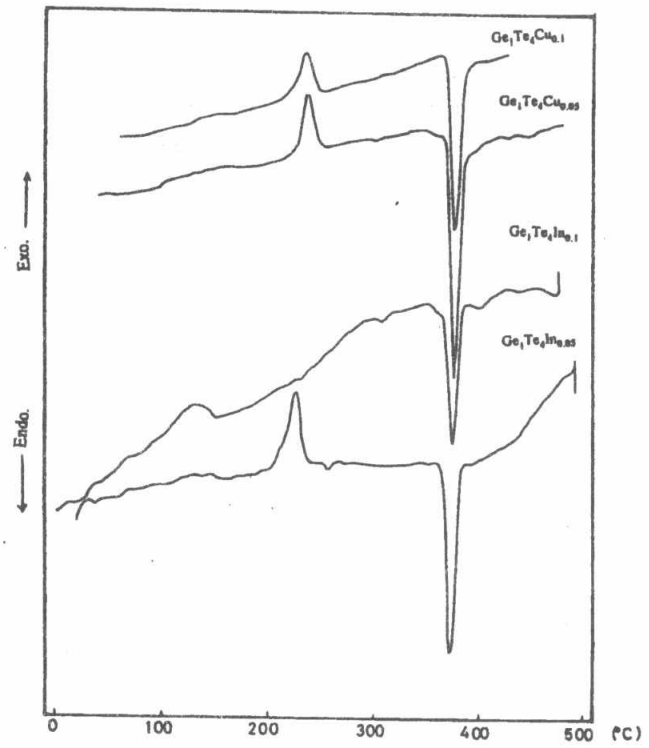

Figure (2) DTA thermograms for at rate 10^0C/min for all compositions.

III. 3 Crystallization Kinetics:

Studies of Kinetics are always connected with the concept of activation energy . The values of this activation energy in glass crystallization phenomena are associated with nucleation and growth processes that dominate the devitrification of most glassy solids [15-18]. Two basic methods can be used for knowing the crystallization of a glass upon heating, isothermal and non-isothermal.

The evaluation of non-isothermal activation energy for crystal growth has been estimated by a large number of mathematical treatment based on the formal theories of transformation kinetics. Used theories differ greatly in their assumption and in some cases, they lead to contradictory results, partial area analysis and peak shift analysis are the basic method for all mathematical treatments. However, Marbtta et al [19] have recently pointed out the limitation of the single scan technique and showed that it is difficult to calculate the value of E and n by this method. They have suggested that multiple scanning can be used successfully for calculating E and n from the same set of measurements using the theory shape index.

The Kissinger formula was used for homogenous crystallization [16] or in other words surface nucleation is dominate that n=1.

$$Ln(\varphi / T_P^2) = \{(-E / R T_P) + cons.\} \quad \text{----------(1)}$$

The plot of $Ln(\varphi / T_P^2)$ vs. $(1/ T_P)$ which are shown in fig (3) are well fitted by straight lines. From the slopes of these lines, the activation of crystallization E can be estimated, and then listed in table (2).

The Mohadeven et al approximation [15] was used, where the variation in Ln $(1/ T_P^2)$ with Ln φ is much less than that in $(1/T_P)$ with Ln φ. Therefore equation (1) can be written in the form

$$Ln(\varphi) = (-E / R T_P) + const. \quad \text{----------(2)}$$

Aplot of $Ln(\varphi)$ vs. $(1/ T_P)$ for $Ge_1Te_4(Cu_x, In_x)$ with x=0.05 and 0.1 at % give a straight line , as shown in fig. (3) . The value of E obtained from the above method is listed in table [2].

The modified Kissinger-method: In this method the relation between the rate φ and crystallization temperature T_P is assumed to have the following form.

$$Ln(\varphi^n / T_P^2) = (-mE / R\,T_P) + const. \quad \text{----------(3)}$$

If the crystallization mechanism is known precisely and does not change with the heating rate, the plot of ln (φ^n/T_P^2)vs. $(1/T_P)$ for x=0.1 gives the value of mE. Dividing mE by m, the activation energy for crystal growth can be obtained and listed in table (2). When m and n are integers have values between one and four. Where nuclei are formed on heating at constant rate, n is equal to (m+1) [3]. The order (n) of crystallization can be calculated from the DSC curve by measuring the shape index according to Kissinger [20].

$$n = 1.26(a/b)^{1/2} \quad \text{----------(4)}$$

Therefore, from table (2), the corresponding values of m are equal to 1 which means that the crystallization mechanisms of glass are surface and one-dimensional crystallization processes.

Table 1: Coordination number R, glass-forming tendency K_{gl} and characterisitic transition temperature at different rates of the different compositions.

Compositions	R	K_{gl}	T_g ^0C			T_C ^0C		T_m ^0C	
			Rate ^0C/min	T_g T_{g1}	T_{g2}	Min	T_P	Min	Mid
$Ge_1Te_4Cu_{0.05}$	2.43	1.22	2			187.8	200.0	344.4	350.7
			10	95	280	194.0	216.0	346.0	352.8
			15			205.2	220.0	341.4	354.2
			20			199.3	222.9	338.0	356.0
			30			193.0	228.6	319.9	359.0
$Ge_1Te_4Cu_{0.1}$	2.48	1.15	2			193.1	202.4	343.0	350.5
			5			190.5	209.0	345.7	352.0
			10	141	-	177.0	214.2	337.1	354.0
			15			191.0	217.0	337.0	354.8
			20			183.6	219.0	339,3	355.5
			30			192.4	222.9	329.0	358.5
$Ge_1Te_4In_{0.05}$	2.42	1.90	2			189.3	208.5	360.0	370.0
			5			183.3	217.4	363.6	370.6
			10	146	257	196.9	220.9	363.5	371.7
			20			218.0	230.0	362.9	363.6
			30			189.0	236.0	352.0	376.1
$Ge_1Te_4In_{0.1}$	2.427	-	2			-	-	-	371.7
			5			-	-	-	389.8
			10	86	243	-	-	-	385.5
			20			-	-	-	392.5
			30			-	-	-	392..7

Table 2: The thermal parameters of the ternary glassy $Ge_1Te_4Cu_x$ and $Ge_1Te_4In_x$ where x=0.05 and x=0.1 systems for the crystallization peak, E values are give in eV/atom.

Compositions	Kissinger method	Mahadevan approx.	Modified Kissinger method		
	E, when n=1	E, when n=m=1	E	n	m
$Ge_1Te_4Cu_{0.05}$	3.857	4.084	3.857	1	1
$Ge_1Te_4Cu_{0.1}$	4.991	5.128	5.748	2	1
$Ge_1Te_4In_{0.05}$	4.511	4.899	6.464	2	1

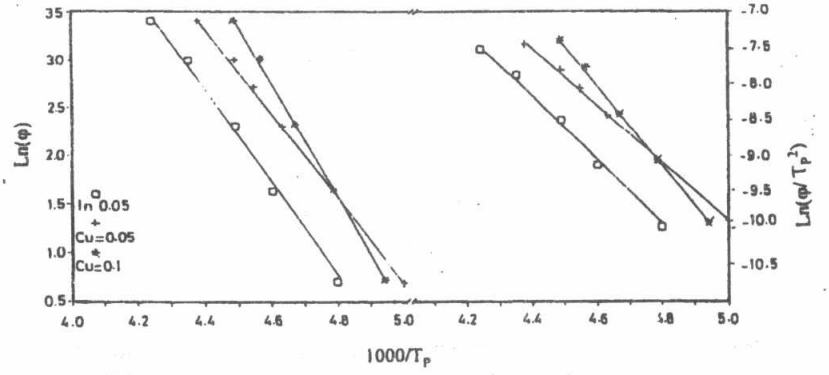

Figure (3) The relation between $[\ln(\varphi/T_p^2)]$ against $10^3/T_p$ (Kissinger method) and $[\ln(\varphi)]$ against $10^3/T_p$ (Mahadevan appro. Method) for different compositions

III. 4 Effect of Composition and Substrate on the Optical energy gap

In order to determine the absorption coefficient (α) from measured the reflectance R and the transmittance T knowing the film tkickness d, the following equation has to used [21].

$$\alpha = (1/d)\ \ln[(1-R)^2/T] \quad \text{----------(5)}$$

The absorption coefficient $\alpha(\omega)$ was calculated as a function of wavelength using (5). The absorption cofficient $\alpha(\omega)$ less than $10^{-4}cm^{-1}$ many amorphous semiconductors show an exponential dependence on photon energy $h\omega$ and obey by Tauc et al [22], and discussed in more general terms by Davis and Mott [23] whose equation was of the form

$$\alpha(\omega) = \beta\ (h\omega - E_{opt})^{\gamma}/\ h\omega \quad \text{----------(6)}$$

where β^{-1} is band edge parameter , γ is number that characterize the transition process and E_{opt} is the optical gap.

In non-crystalline systems the non-direct transitions most likely to occurred due to the absence of translation symmetry and γ=2 or 3 for allowed or forbidden non-direct transition. The present result were found to obey [24] with γ=2. Optical energy gap have been estimated from linear plots of $(\alpha h\omega)^{1/2}$ against $h\omega$ as shown in fig (4). The obtained data shows that the variation of E_{opt} and E_e with Cu or In additive and kind of substrate as shown in table (3).

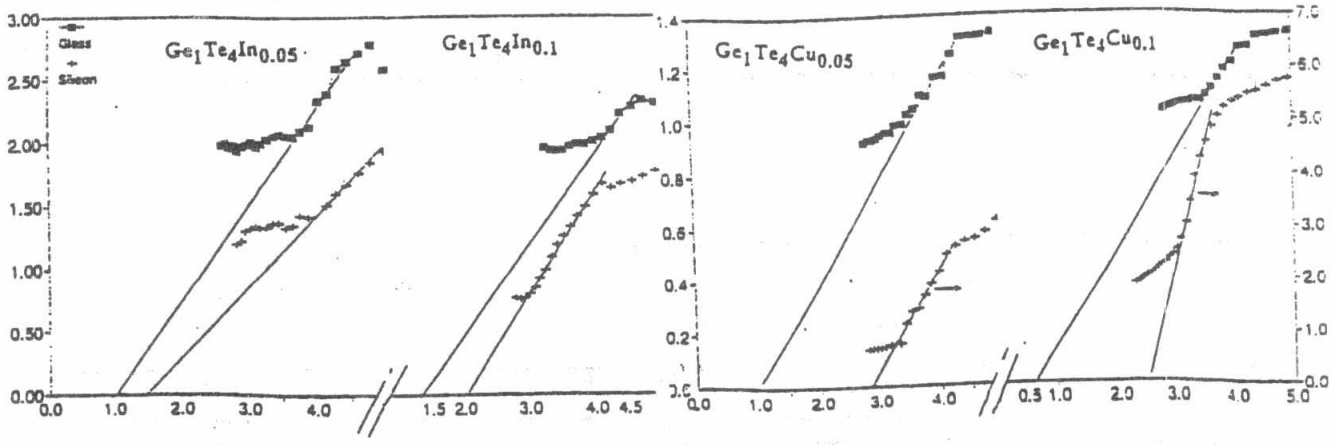

Figure (4) Dependence of $(\alpha h\omega)^{1/2}$ on the photon energy $h\omega$(eV) for $Ge_1Te_4(In\ or\ Cu)_x$ films where x=0.05 and x=0.1.

III. 5 Radial Distribution Function (RDF)

The observed intensities were corrected for back-ground, polarization, and multiple scatering and were normalized into units (e.u.) by the high-angle method [25] and, subsequently, the incoherent scatering was subtracted. The RDF is calculated as follows:

$$4\Pi r^2 \rho(r) = 4\Pi r^2 \rho_0(r) + rG(r) \quad \text{----------(7)}$$

where $\rho_0(r)$ and $\rho(r)$ represented the mean atomic distribution and the local atomic density, respectively, and G(r) stands for the fourier transformation of a function of experimental intensities, being

$$G(r) = \int_0^{SMAX} F(s)\sin(sr)ds \quad \text{----------(8)}$$

with s being equal to the scattering vector modulus, and F(s) being the interference function given by

$$F(s) = Si(s) \quad \text{----------(9)}$$

with i(s) being a function given by

$$i(s) = [I_{e.u} - \Sigma \chi_i f_i^2] / [\Sigma \chi_i f_i]^2 \quad \text{----------(10)}$$

where χ_i is the atomic fraction of the I element and f_i the atomic scattering factor with i=Cu,Ge,Te or In, Cie,Te and $I_{e.u}$ represent the resulting intensity values in electronic units after correction. The RDF after the above- mentioned procedure have been plotted for both samples as shown in fig.(5).

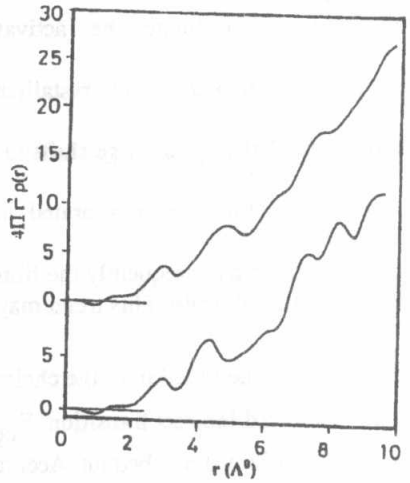

Figure (5) Reduced RDF from scattering experiments for bulk glassy compositions $Ge_1Te_4Cu_{0.1}$ and $Ge_1Te_4In_{0.1}$.

Table 3: The optical properties of thin film glasses compositions and peak position of the RDF for bulk compositions

compositions	E_{opt} Glass	E_{opt} Silicon	Frist peak (A^0)	Area (atoms)	Frist peak (A^0)	Area (atoms)
$Ge_1Te_4Cu_{0.05}$	1.055	2.832	----	----	----	----
$Ge_1Te_4Cu_{0.1}$	0.722	2.500	2.880	2.113	4.280	5.893
$Ge_1Te_4In_{0.05}$	1.351	2.000	----	----	----	----
$Ge_1Te_4In_{0.1}$	1.000	1.500	2.880	2.113	4.640	5.185

Discussion

1- The obtained results of X-ray diffraction patterns of the investigated bulk samples and thin film are show in figure (1). These figures reveals that for bulk samples are shown in partially crystalline except for In=0.05 but for thin film has no diffraction peak. In addition the diffraction peaks for silicon wafer represented a layer of SiO_2 upon silicon. We can conclude that the d values for films evaporated on Si substrate agree ASTM card of SiO_2. According to the above we can be sure that films on the two different substrate characterized by short range order.

2- By increasing the heating rate the crystallization temperature increases due the reduction in a crystal growth.

3- For $Ge_1Te_4In_x$ or $Ge_1Te_4Cu_x$ $0.05 \le x \le 0.1$ glass transition temperature T_{g1}, T_{g2} are generally observed in the sequence $T_{g1} < T_{C1} < T_{g2}$[14]. This is explained by the rejection of germanium atoms into the surrounding glass during the primary crystallization; the composition of the alloy therefore changes during heating, and the glass transition temperature shifts from T_{g1} to T_{g2} except for high speed such as 20C/min, 30C/min. T_{g2} canceled indicate more homogeneity than low speed.

4- It can be seen that In additive in the Ge-Te glasses decreases T_g than the Cu additive. Therefore, it is clear that Ge-Te-Cu glasses are more stable than Ge-Te-In glasses.

5- The glass stability of ternary Ge-Te-Cu glasses indicates the possibility of these glasses beings used in infrared optical fiber material applications.

6- Multiscan techniques, were applied to evaluate the activation energy (E), the order (n) of crystallization and the order of crystal growth .The activation energy of crystallization is increased by increasing the metal additive (In or Cu).

7- It is seen that the position of fundamental absorption edge shifts to the higher wave length by additive Cu or In.

8- We can noticed that the transmition for films evaporated upon glass substrate represented a negligibley amount comparing with films on Si substrate consequently the films Si wafer having higher absorption coefficient than films on glass substrate. This trend may be due to variety in grain size and layer of SiO_2[26].

9- Obtained results allow to conclude that the conduction in the chalcogenide glasses $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ with $0.05 \le x \le 0.1$ due to allowed indirect transition. E_{opt} for In addive more effective than Cu additive that in both silicate glass and Si wafer substrate. According to the result we excepect that evaporation upon on Si wafer reduced the defect states than in glass substrate.

10- RDF in fig (5) show small peaks at r = 0.06nm. The peak is spurious as no legitimate peak can occur at an r smaller than the sum of the smallest pair of atomic radii involved. The area under the first peak in the RDF is a measure of the number of nearest neighbours about an atom. In the present work the area has been calculated by considering the right hand side of the first peak to the symmetrical to the left-hand side. This method minimises the contribution from atoms in other coordination shells [27]. The results are given in table(4). RDF of $Ge_1Te_4In_{0.1}$ and $Ge_1Te_4Cu_{0.1}$ for powder exhibit a prominent peak and a few other sharp peaks. The sharpness of the peak may be attributed to the fact that accretion extent to crystalline states and there by a long -range periodic rearrangement of atoms is achieved. The positions(r_1) of the maxim of the peaks in RDFs are give in table (3). The position and area of the first proper peaks of RDF correspond to the Ge-Te [29,30] that is to say that Strong cprrelation between Ge -Te atoms, The interatomic distance form the first peak are 2.88 nm for Ge-Te. Structure representation has demonstrated that there are Te-Cu, Te-In and Te-Tee bonds but not Ge-Ge bonds which is a result from the smaller binding energy of Ge-Ge [31] compared with Ge-Te , Te-Cu, Te-In and Te-Te. Strong correlation between Ge -Te atoms, The interatomic distance form the first peak are 2.88 nm for Ge-Te.

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