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Effect of Metal Additive on the Electrical Properties of Glassy Ge-Te

S.A.Fayek, S.M.El Sayed, El-Sayed. A. Mehana*, A. M. Hamza*.

Department of Physics, National Center for Radiation Research and Technology,
Nasr City, Cairo, Egypt
* Department of Physics, Military Technical College, Cairo, Egypt

ABSTRACT

Ternary compositions Ge_1Te_4 (In_x or Cu_x) with x= 0.05 and 0.1 were prepared by conventional melt-quenching. Thin films of these compositions were deposited by thermal evaporation with thickness 300 nm. Dependence of d.c conductivity on compositions has been reported. It was found that the activation energy decreases with increasing additive (In or Cu). The obtained results have been interpreted in the frame of the model proposed by Mott and Davis (1979).

The ac electrical properties of adding Cu or In to amorphous GeTe system have been measured in the frequency range from 100 Hz to 100KHz and temperature range (303-208)K. It is found that, in Ge_1Te_4 (In_x or Cu_x) compositions where x is limited to x=0.05 and x=0.1, the change of conductivityσ_{ac}depends linearly on the frequency and temperature. The value of the exponent (S) in all this system is reasonably interpreted by the correlated barrier-hopping model (CBH). The analysis of the results reveals that electronic conduction of Ge_1Te_4 (In_x or Cu_x) takes place via bipolaron hopping. The dielectric investigation provides a fundamental method for studying the rotational and hopping electron processes involved in conduction. Conductivity values, which depend on the glass microstructure, are observed as a term of cohesive energy, expressed by the force of binding ions. An attempt has been made to evaluate this correlation. The experimental results support to some extent the above criterion in the case of Ge_1Te_4 (In_x or Cu_x) ternary alloy.

Introduction

Chalcogenide glassy semiconductors have a number of superior properties that can be applied to devices. They show a continuous change of various properties with change in chemical compositions. They are easily prepared in large size as homogenous glasses and are not attacked by moisture, organic solvents, some strong acids. In addition they can be well wetted by various metals (1). On the other hand, chalcogenide glass fibers are advantageous because of the flexibility and chemical durability (2). It has been reported that glass systems are suitable for the infrared fiber because of low toxicity, good thermal and chemical stability and prominent infrared transmitting characteristics. The Te based chalcogenide glasses are candidates for such applications because their infrared absorption edges are located in a wavelength region above 12μm(3). However, only a few compositions such as Ge-Te and As-Te based glasses have been investigated as memory switching glasses (4).

In the present work a glass films were prepared by thermal evaporation to study the electrical (especially ac conductivity) of films and to study its dielectric relaxation in the frequency range 100 Hz to 100KHz and in the temperature range (208K–303K).

Experimental Detail

Glassy Ge_1Te_4 (In_x or Cu_x) with x= 0.05 and 0.1 were prepared by melt quenching method. The constituent elements were mixed together and sealed in an evacuated tube at 800°c for 10hrs in a rotating furnace. Quenched in ice-water mixed with (NaOH), so as to prevent crystallization of the ingots. Samples in the form of thin films were prepared by the thermal evaporation technique. The synthesized material was deposited onto cleaned silicate glass at a vacuum of 10^{-5} torr using an Edward coating unit model E 306. A source–substrate distance of 10 cm was adjusted during deposition. No international control of the substrate temperature was performed and the deposition parameters were kept constant so that comparison of results could be made under identical condition. The film thickens (d) was controlled at 300nm using a quartz crystal monitor that was confirmed by an interferometric method (5).

X-ray diffraction technique was used to investigate and characterize the structure of the prepared films using a Shimadzu X D-D1 series model with Cu anode. For electrical measurements, thin films deposited onto glass substrates previously equipped with coplanar silver electrodes separated by a gap of width of about 0.2cm were prepared. The dc conductivity measurements in the temperature range from room temperature to 111K were carried out by keithly 616 digital electrometer for resistance measurements and by Philips PM 2441 digital voltammeter for measuring millivolts a cross the thermocouple for temperature measurements.

The a.c conductivity was measured in the temperature range (208K–303K) and frequencies from 100Hz to 100KHZ by a bridge method using a dielectric loss meter.

RESULTS AND DISCUSSION

X-ray diffraction patterns of GeTeCu and GeTeIn thin films.

Fig. (1) shows the X-ray diffraction (XRD) patterns of Ge_1Te_4(Cu or In) with x = 0.05, 0.1 respectively. Diffused haloes characterize amorphous nature of these films deposited on silicate glass.

Effect of Composition on the Activation Energy:

In chalcogenide glasses there are different conduction mechanisms that can be involved. Generally the conductivity (σ) in the chalcogenide can be written as follows (6)

$$\sigma(T) = \sigma_0 \exp(-\Delta E_{\sigma 0}/KT) + \sigma_1 \exp(-\Delta E_{\sigma 1}/KT) + \sigma_2 \exp(-\Delta E_{\sigma 2}/KT) \qquad (1)$$

The three terms arise from three different conduction processes. The first term describes the high temperature region, in which the dominant mechanism is the band conduction through the extended states. The pre-exponential factor (σ_0) depends on compositions, $\Delta E_{\sigma 0}$ is the electrical activation energy of conduction, K is the Boltzman constant, and T is the absolute temperature.

The second term is due to hopping conduction via localized states. The third term is due to hopping conduction mechanism near the Fermi level. The value of $\sigma 2 < \sigma 1 < \sigma_0$.

TABLE 1. The d.c. Dielectric parameters of the glassy Ge Te systems with different compositions

Compositions	$\Delta E_{\sigma o}$ (eV)	$\Delta E_{\sigma 1}$ (eV)	$\Delta E_{\sigma 2}$ (eV)	σ_{Rt} $(\Omega cm)^{-1}$	σ_o $(\Omega cm)^{-1}$	σ_1 $(\Omega cm)^{-1}$	σ_2 $(\Omega cm)^{-1}$
$Ge_1Te_4In_{0.05}$	0.087	0.024	0.0063	1.319	1.455	0.057	0.1068
$Ge_1Te_4In_{0.1}$	0.072	0.010	0.005	0.251	0.241	$0.887*10^{-2}$	$0.577*10^{-2}$
$Ge_1Te_4Cu_{0.05}$	0.172	0.029	0.010	$0.199*10^{2}$	$0.624*10^{2}$	$2.750*10^{-2}$	$0.696*10^{-2}$
$Ge_1Te_4Cu_{0.1}$	0.134	0.014	0.005	$0.056*10^{2}$	$0.044*10^{2}$	$0.583*10^{-2}$	$0.281*10^{-2}$

The dc conductivity σ of the investigated glasses has been measured in the temperature range from (111 - 303)K, which is well below T_g, down to about liquid-nitrogen temperature. The reproductively in measurements was remarked to be satisfactory. For thickness 300 nm The dependence of ln (σ) on (1/T) is given for the four compositions (Fig. 2), where three distinct regions of conductivity are observed. These regions corresponding to three different mechanisms of conduction. The activation energies of these regions are labeled $\Delta E_{\sigma 0}$, $\Delta E_{\sigma 1}$ and $\Delta E_{\sigma 2}$. Table (1) gives dc conductivity σ_o, σ_1 and σ_2, $\Delta E_{\sigma 0}$, $\Delta E_{\sigma 1}$ and $\Delta E_{\sigma 2}$ as function of glass compositions. The energies of the various processes of the conduction were computed from the slope of least-sqares fits. The results indicate that the room-temperature conductivity (σ_{RT}) decreases with increasing (In or Cu) content. The pre-exponential factors σ_o, σ_1, σ_2, and activation energies $\Delta E_{\sigma 0}$, $\Delta E_{\sigma 1}$ and $\Delta E_{\sigma 2}$ exhibit the same behavior. It is also observed that σ_o is composition dependent where it decreases montonically by increasing (In or Cu) content as listed in table (1). According to Mott and Davis such decrease in $\sigma_o$indicates an increase in the density of localized states. However, it is worth mentioning that Mott and Davis argued that there is no definite correlation between the intercept σ_o and activation energy ΔE. Moreover we can notice that the values of ΔE decreases linearly by increasing (In or Cu) content as listed in table (1). This effect is most likely due to the reduction of the average binding energy by (In or Cu) addition. To check this argument the cohesive energy (CE) was calculated for the investigated four composition (Table 2) It is clear that CE decreases by increasing (In or Cu) content which is in good agreement with the above assumptions.

Alternating Current Electrical Behavior:

The a.c. conductivity of these glasses shows a sublinear frequency dependence. This is a general feature of hopping conduction(7-9). A feature common to all the amorphous semiconductors and disordered systems "some noncrystalline solid" (10) are a frequency-dependent conductivity $\sigma_{ac}(\omega)$ that increases approximately linearly with frequency at least in the frequency ranges $10\ s^{-1} < \omega < 10^8 s^{-1}$, i.e.

$$\sigma_{ac}(\omega) = \sigma(\omega) - \sigma_{dc}(\omega) = A\omega^s \quad (2)$$

where A is constant , s is the frequency exponent ($s \leq 1$) and $\sigma_{dc}(\omega)$ is the dc part of the total conductivity $\sigma(\omega)$. The phenomenon has variously been ascribed to relaxation caused by the motion of electrons, or atoms, hopping or tunneling between the equilibrium sites. The complex dielectric constant of a material medium is represented by two parts $\varepsilon = \varepsilon_1 + i\varepsilon_2$ where ε_1 is the real part (dielectric constant) and ε_2 is the an imaginary part (dielectric loss). The ratio between ε_2 and ε_1 defines a loss tangent.

$$\tan \delta = \varepsilon_2 / \varepsilon_1 \qquad (3)$$

The corresponding real and imaginary parts of the ac conductivity obey the following relationship.

$$\sigma_1(\omega) = \sigma_{ac}(\omega) = \varepsilon_0 \, \omega \, \varepsilon_2 (\omega) \qquad (4)$$

$$\sigma_2(\omega) = \varepsilon_0 \, \omega \, \varepsilon_1 (\omega) \qquad (5)$$

where ε_0 is the permittvity of free space. If $\varepsilon(\omega)$ is considered over a limited frequency range; $\varepsilon(\omega)$ contains in addition a frequency-independent term ε_∞, arising from all polarizing processes at higher frequencies. It may be mentioned that tan δ is independent of the sample geometry. The objective of this paper is to study the effect of Cu or In in the $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ glassy system and its dependence on the ac. conductivity and dielectric properties in the 208-273K range as a function of both temperature and frequency. For the mechanism of ac conduction, the quantum-mechanical tunneling (QMT) model was proposed(11) to interpret impurity conduction in n-type silicon. Applying the QMT model to amorphous materials; (12) which proposed phonon-assisted hopping of localized electrons. According to the QMT model, the exponent s is almost equal to 0.8 and increases slightly with increasing temperature. In most chalcogenide glasses; values of s range from 0.7 to 1.0 at room temperature and have a tendency to decrease with increasing temperature. Therefore, QMT is considered not applicable to chalcogenide glasses. The correlated barrier hopping (CBH) model proposed (13) has been applied to the chacogenide glassy semi-conductors.

In the CBH model electrons in charged defect states hop over the coulombic barrier. In this model correlated barrier hopping of bipolaron (i.e. two electrons hopping between charged defects D^+ and D^-) has been proposed to interpret the frequency dependence of conductivity in chacogenide glasses as given in eq (2). The theory has explained the low temperature features, particularly temperature dependent values of the parameters A and s. However, it does not explain the high-temperature behavior so well, particularly in the low frequency range. The D states are produced by thermal excitation of $D^+$and /or D^- states. According to this model(14), ε_2 is given by the following equation

$$\varepsilon_2 (\omega) = (\varepsilon_0 - \varepsilon_\infty) \, 2\Pi^2 \, N(ne^2 / \varepsilon_0)^3 \, KT \, \tau_0{}^m \, W_M{}^{-4} \, \omega^m \qquad (6)$$

and $m = -(4KT / W_M)$

Where n is the number of electrons that hop, N is the concentration of localized sites, ε_0 and ε_∞ are the static and optical dielectric constants respectively, and W_M is the energy required to move the electron from a site to infinity. τ_0 is a constant characteristic relaxation time. Moreover the results are discussed in terms of cohesive energy (C.E). The cohesive energy

(C.E) values were calculated(15) in the form $C.E = {}_{i}\Sigma^{n} C_iD_i/100$ where C_i and D_i are the number of expected bonds and the energy of each corresponding bond respectively. The mole fraction of the i^{th} constituent and n is the total number of the elements in composition.

Fig. (3) as example shows the dependence of $\ln\sigma_{Ac}(\omega)$ on $\ln(\omega)$, in the frequency range (0.1-100) KHz for each compositions at (x=0.05 and 0.1) using equation (3) at room temperatures. It is clear from the investigated range that all compositions exhibit the same trend, with two linear regions. The values of (s) reveal that (s) decreases by increasing temperature which is consistent with the behavior(16). Elliot's model is appropriate for explaining the obtained frequency and temperature dependence of the a.c. conductivity and frequency exponent (s). The conductivity has composition dependence but it increases by increasing Cu, In. The bipolaron hopping conduction process gives a good fit with the experimental data. It can be placed due to the hopping of two electrons between the two charged states D^+, D^-, of the defects present in GeTeCu or GeTeIn glasses. On the basis of the correlated barrier hopping (CBH) model(17) that each pair of sites ($D^+$and D^-) is assumed to form a dipole which has a relaxation time depending on its activation energy, which can be attributed to the existence of potential barrier over which the carriers hop.

The dielectric constant ε_1 was calculated from the measured values of capacitance C(16). The frequency and temperature dependence of ε_1 for thc compositions is presented in Fig. (4) as example for x=0.05. These curves show that ε_1 has high values at low frequencies and decreases rapidly as the frequency increases to reach constant values at high frequencies. This may be due to the fact that at lower frequencies, the dielectric constant ε_1 is originated due to the contribution of electronic, ionic orientation and interfacial polarizability (18). When the frequency is increased the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. As the frequency is further raised the permanent dipoles will be completely unable to follow the field and the contribution to the static permittivity from this molecular process is negligible and the orientational polarization ceases. Also at higher frequencies the relatively heavy positive and negative ions can not follow the field variations so that the permittivity and, hence the dielectric constant becomes invariant. This behavior was observed for many other glasses. The above figures show that, at the same temperature the value of ε_1 is increased by increasing of the Cu or In content. This may be explained due to the number of homopolar Ge-Ge bonds, where increasing of Ge-Ge bonds leads to increase the dielectric constant. These weak bonds show more response to the electric field than the other bonds. These values of the dielectric constant ε_1 could be explained qualitatively by assuming a decrease in bond energies. The dielectric loss ε_2 decreases with increasing frequency, as shown in figure (5) for x=0.1. This can be attributed to migration of ions in addition to the electron polarization loss in glass, which is the main source of the dielectric loss ε_2 at low frequency. Accordingly the dielectric loss at low moderate frequency is characterized by high values according to the combination of ion jump and conduction loss of ion migration. On other hand, at high frequency values the electron polarization loss due to the ion vibrations may be only source of dielectric loss. The dependence of dielectric loss ε_2 at various frequencies on the calculated cohesive energy (C.E) is given in table (2). From this table it is clear that the dielectric loss ε_2 decreases as the cohesive energy (C.E) increases.

TABLE 2. The values of the energy W_M of the diferent compositions of $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ glassy systems.

Compositions	**CE(eV/atom)**	**Excess of bond Te-Te**	**W_M (eV)**		
			T=208K	**T=228K**	**T=273K**
$Ge_1Te_4In_{0.05}$	2.19	38	0.112	0.120	0.148
$Ge_1Te_4In_{0.1}$	2.18	38	0.072	0.080	0.104
$Ge_1Te_4Cu_{0.05}$	2.16	40	0.088	0.104	0.120
$Ge_1Te_4Cu_{0.1}$	2.14	40	0.80	0.088	0.108

These results indicate that the cohesive energy plays an important role in the variation of dielectric loss ε_2 along with presence of homopolar bonds. This may be attributed to the decrease of C.E. of composition which means that it has lower energy barriers which facilitate the ionic jumping and migration, whereas on the other hand the response of charge carriers to the dielectrical filed become large. According to the above mention it has been shown that the optical gap and a.c conductivity closely correlated with the character of the chemical order in amorphous semiconductors. In the investigated system it is found that ε_2 follows an exponential relation with frequency, i.e $\varepsilon_2 = A\,\omega^m$. Fig.(5) shows this behavior where ln ε_2 versus ln(ω) curves are found to be straight lines at various temperatures. It is clear that the values of (m) increases with the increase of temperature in all the samples as in table (3). However, the peaks in the dielectric loss ε_2 versus ln(ω) have not been observed in the present samples as expected in case of dipolar type relaxation. Such peaks may be absent because of the wide distribution of relaxation times. The calculated values of W_M are given in table (3), which decreases by decreasing C.E.

TABLE 3. The values of the parameters m at various temperatures of $Ge_1Te_4In_x$ and $Ge_1Te_4Cu_x$ glassy systems.

Compositions	T=208K	T=228K	T=273K
	m	m	m
$Ge_1Te_4In_{0.05}$	-0.637	-0.642	-0.689
$Ge_1Te_4In_{0.1}$	-0.95	-0.975	-0.990
$Ge_1Te_4Cu_{0.05}$	-0.718	-0.735	-0.750
$Ge_1Te_4Cu_{0.1}$	-0.880	-0.885	-0.960

The cohesive energy (C.E), reflects the average bond strength for a given composition and reflects the force of binding ions according to the equation (6).

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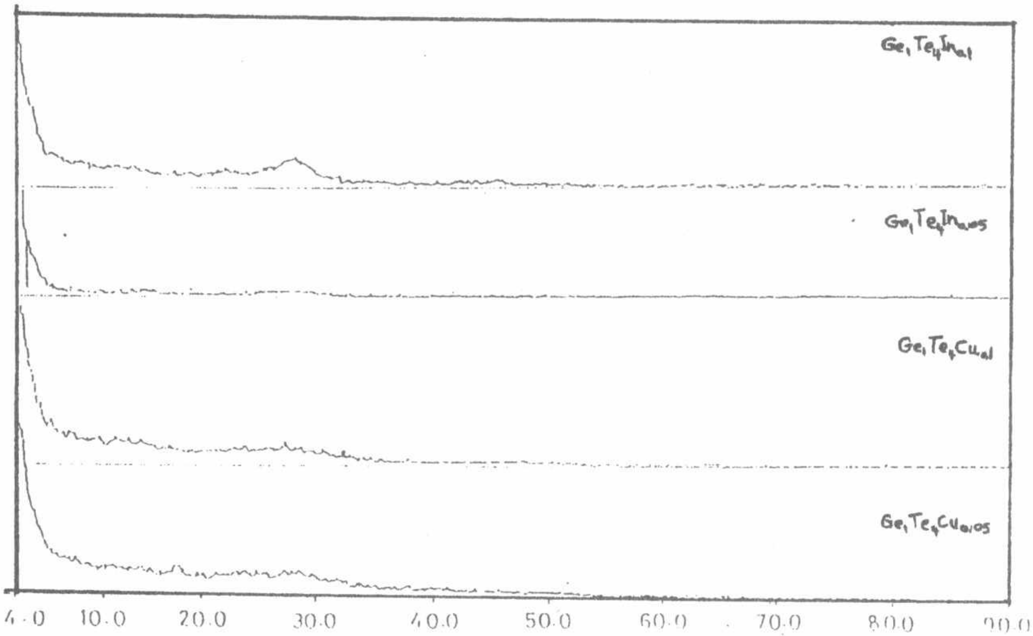

Fig.1 X-ray diffraction patterns for $Ge_1Te_4(In \text{ and } Cu)_x$ with x=0.05 and 0.1 films glassy system

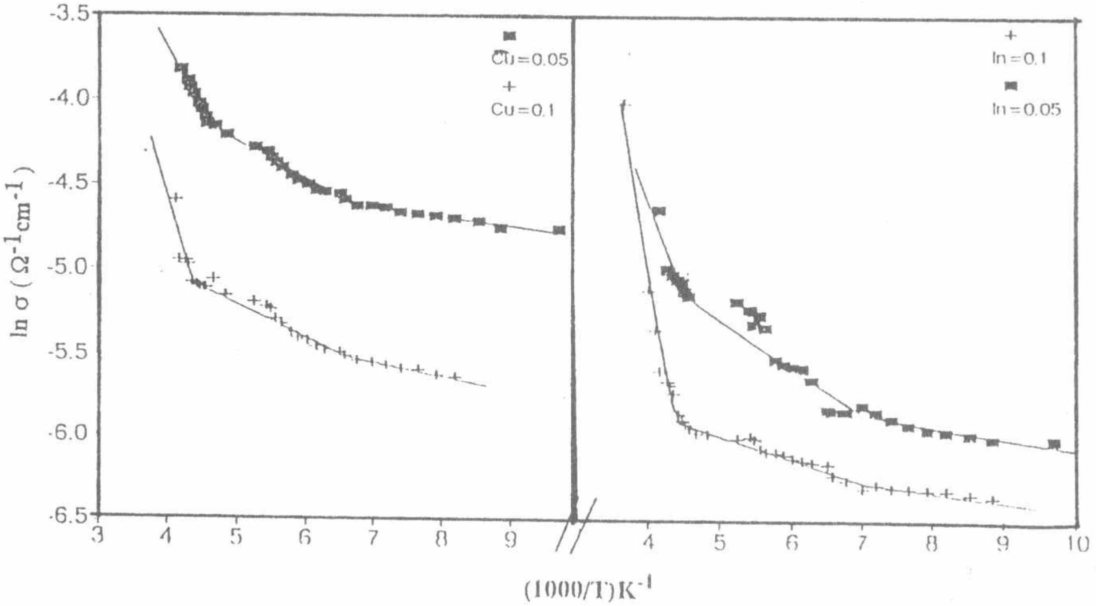

Fig.2 Variation of $\ln(\sigma)$ vs reciprocal absolute temperature $(1000/T)K^{-1}$ for films of $Ge_1Te_4(In \text{ and } Cu)_x$ with x=0.05 and 0.1 films glassy system

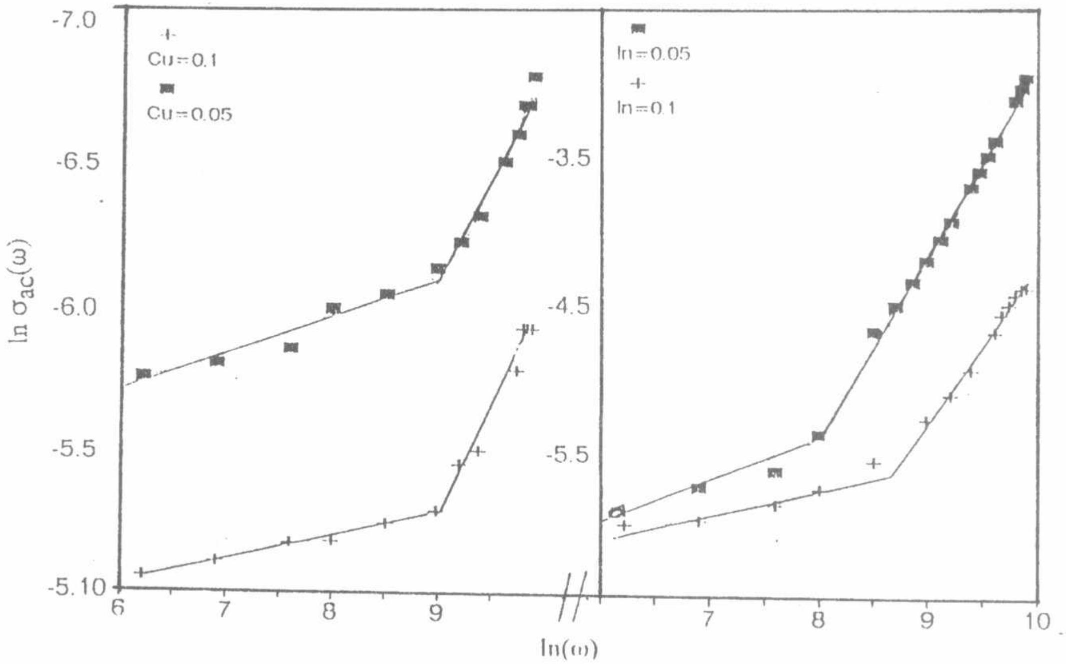

Fig. 3 The relation betweeen $\ln \sigma_{ac}(\omega)$ and $\ln(\omega)$ in $Ge_1Te_4(In\ and\ Cu)_x$ With x=0.05 and 0.1 glassy systems at room temperature.

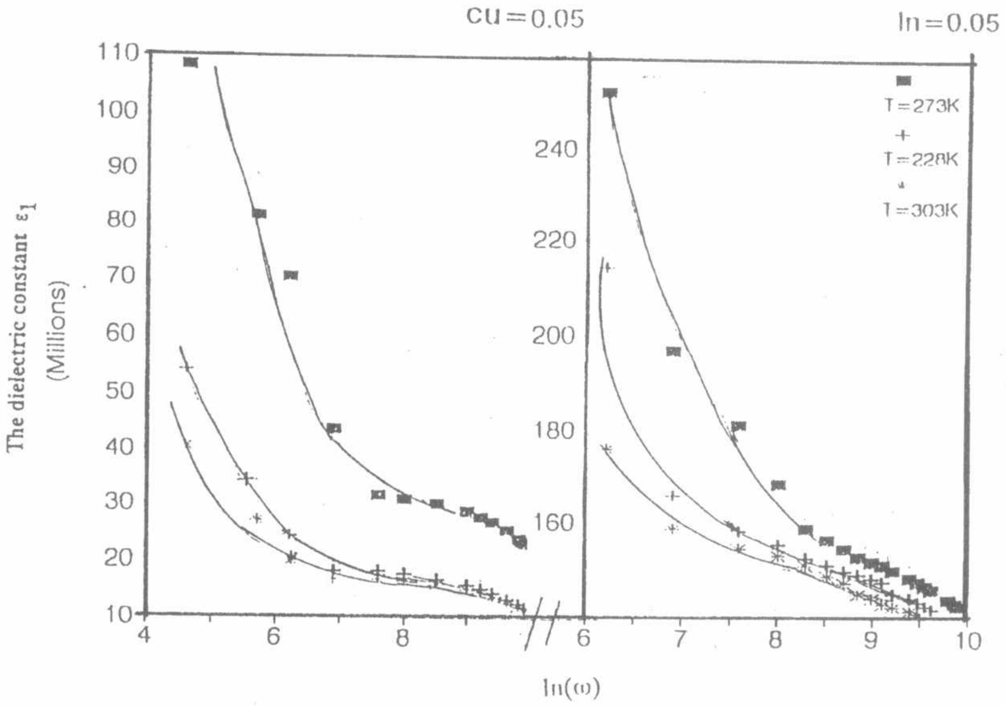

Fig.4 The relation betweeen dielectric constant ε_1 and $\ln(\omega)$ at different temperature for $Ge_1Te_4In_{0.05}$ and $Ge_1Te_4Cu_{0.05}$ glassy systems.

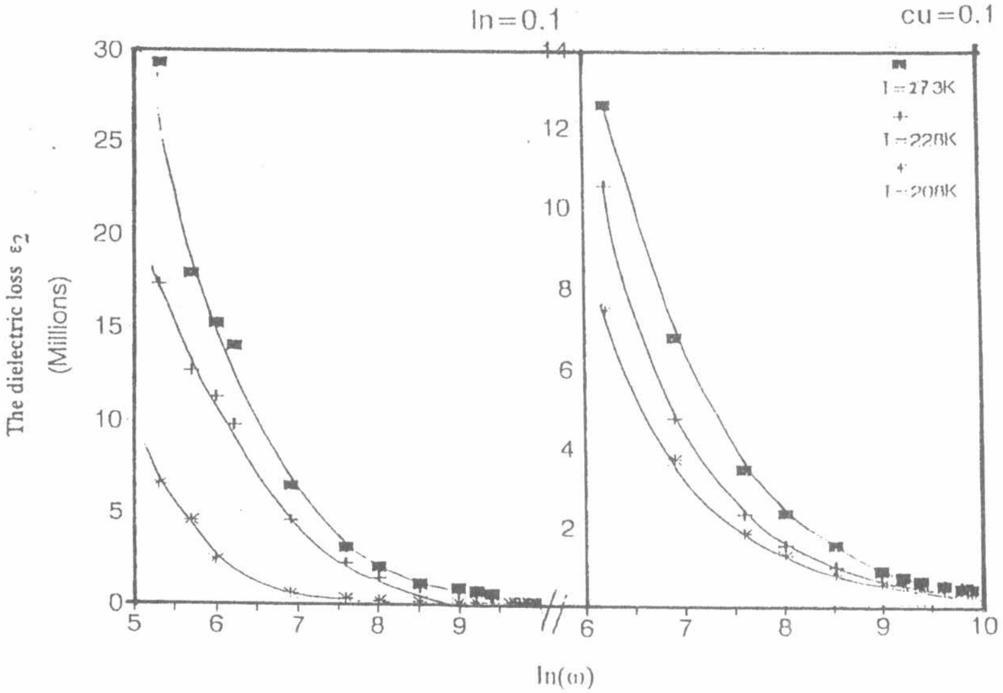

Fig.5 The relation between dielectric loss ε_2 and ln (ω) at different temperature for $Ge_1Te_4In_{0.1}$ and $Ge_1Te_4Cu_{0.1}$ glassy systems.

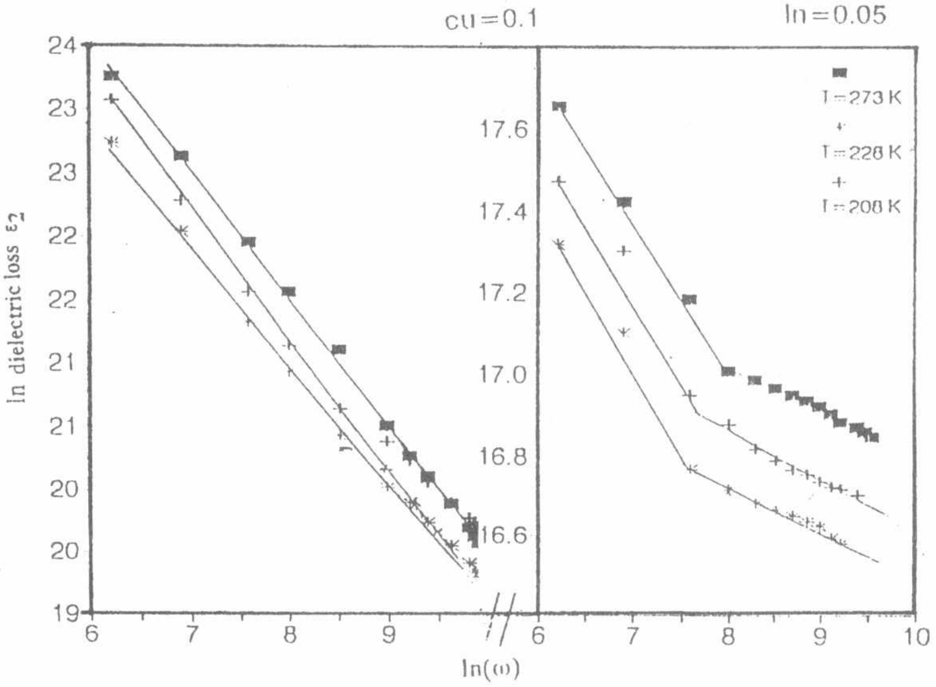

Fig. 6 The linear relationship between [ln(ε_2)] and [ln(ω)] at different temperature of the compositions $Ge_1Te_4In_{0.05}$ and $Ge_1Te_4Cu_{0.1}$ glassy systems.