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DIELECTRIC PROPERTIES OF THERMALLY EVAPORATED $CuGa_xIn_{25-x}Te_{74}$ THIN FILMS

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The dielectric parameters of the glassy system of $CuGa_xIn_{25-x}Te_{74}$ (x =0, 12.5, and 25) have been investigated. The frequency and temperature dependence of the dielectric constant *($\varepsilon^{/}$)* and dielectric loss *($\varepsilon^{//}$)* are studied in the frequency range *50 Hz –5 MHz* and in the temperature range *50-150^o C*. Dielectric dispersion is observed when Ga is incorporated in the $CuGa_xIn_{25-x}Te_{74}$ system. The results are explained on the basis of dipolar type dielectric dispersion. It is also observed that the activation energy increases upon increasing the Ga content in this system.

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Keywords: Dielectric properties, thermal evaporation, CuGaxIn25-xTe74 thin films

1. Introduction

Chalcogenide glasses have received a great deal of attention for the last two decades due to their technological applications, namely electronic, optoelectronic, optical and memory switching devices [1]. Most of the dielectric measurements for chalcogenide glasses have been reported at audio and/or radio frequencies [2]. Literature survey of the dielectric measurements shows that relatively very few measurements have been reported on these glasses as compared to electrical properties [2]. The study of dielectric behavior of chalcogenide glasses is expected to reveal structural information, which in effect can be useful for the understanding of the conduction mechanism as well. In addition, a study of temperature dependence of dielectric permittivity particularly in the range of frequencies where dielectric dispersion occurs can be of great importance for the understanding of the nature and origin of losses occurring in these materials. The dielectric relaxations are important to understand the nature and origin of the dielectric losses, which in turn may be useful to determine the nature of defects in solids [2]. Measurements of the dielectric properties of different substances have been the subject of many researches and various models have been proposed to interpret the experimental results [2–10].The aim of this work is to investigate the dielectric properties of CuGaxIn25-xTe74 thin film in a wide range of temperatures and frequencies with the objective of judging if any of the existing theories could consistently explain the dielectric data obtained, and to clarify the mechanisms of dielectric relaxation.

2. Experimental

The compound was prepared in bulk form by the melt quenching method. A mixture of highly pure components Cu, Ga, In and Te (99.999%) in their stoichiometric ratio were weighted and placed in evacuated silica tube under vacuum 10-6 Torr. The ampoule was heated in a rotating furnace and raised gradually up to 1200 C0 and then kept at this temperature for 24 hrs to ensure a high degree of homogeneity. The melt was quenched in ice water to obtain the film in the bulk

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form. CuGaxIn25-xTe74 thin films with thickness ~1.5 μm have been obtained by thermal evaporation onto ultrasonically treated glass substrate by using Edward E306 coating unit under vacuum 10-6 Torr with low deposition rate. The thickness has been controlled by crystal oscillator monitor. The composition of the film was analyzed by EDAX technique, X-ray diffraction investigations were carried out to identify the structure of the obtained materials in both bulk and thin film form by using Xpert ProPan analytical diffractometer instrument with copper CuKα radiation (λ=1.54 Å). The X-ray diffraction pattern was obtained in the range 10°–90° (2θ, 0.02°/step increments). . In this study, the dielectric properties were obtained by using the ordinary capacitive technique. The films were electroded with silver paste to form a parallel plate capacitor. The capacitance Cp and the dissipation factor D of the capacitor were directly measured in the frequency range of 50 Hz – 5 MHz and the temperature range of 50–150o C with the four-terminal coaxial cables connected to an Hioki 3532 LCR meter. Supposing the sample's thickness and the area of the electrodes are d and A, respectively, the relative dielectric constant ε/ can be obtained from

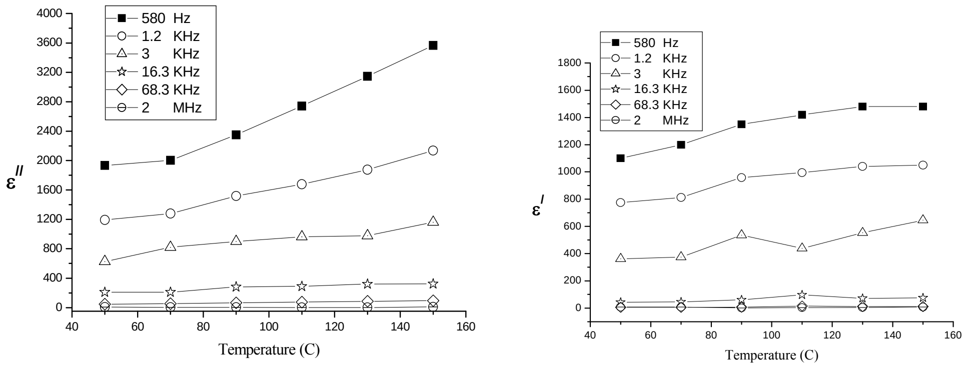
$$\varepsilon' = \frac{d}{\varepsilon_0 A} C_P$$

where ε0 is the dielectric constant of vacuum, and ε// obtained from ε// =D ε/

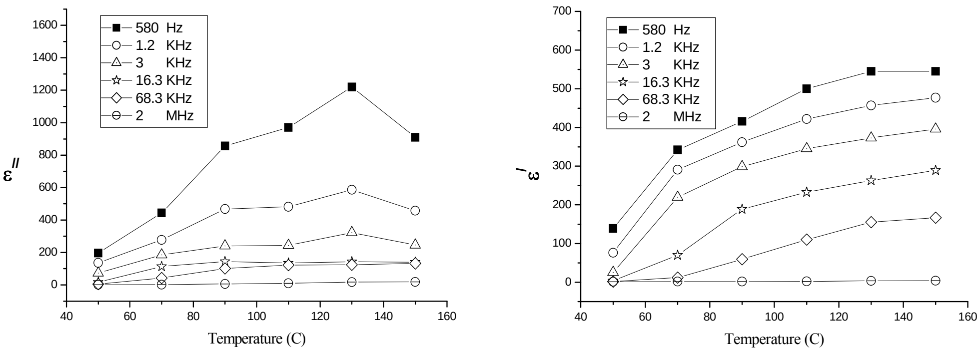
3. Results and discussion

The temperature dependence of the dielectric constant (ε/) and the dielectric loss (ε//) is studied at various frequencies (50 Hz–5 MHz) for the prepared glassy CuGaxIn25-xTe74 (x = 0, 12.5, and 25) thin film. The temperature range of measurement was from 50 to 150o C. The dielectric loss for CuGaxIn25-xTe74 (x = 0, 12.5 and 25) thin film increases with increasing temperature, in a different way for different frequencies as shown in Fig.1-a,b and c. Strong dielectric dispersion is observed at temperature above 90o C. The variation of the dielectric constant and the dielectric loss with temperature is large at lower frequencies. The temperature dependence of the dielectric constant (ε/) at various frequencies for the a-CuGaxIn25-xTe74 (x =0.12.5 and 25) system indicates that the dielectric constant (ε/) varies exponentially with temperature and that a strong dielectric dispersion is observed at above 90C. The dielectric loss for CuGa25Te74 increases with temperature and has a high value as compared to CuIn25Te74 sample. These results indicate that the concentration of gallium plays an important role in the variation of dielectric parameters with temperature. This type of behavior has also been reported by various workers in chalcogenide glasses [11-18]. Fig.2 shows the frequency response of the dielectric constant and the dielectric loss at different fixed temperatures for the a-CuGaxIn25-xTe74 thin films. It is observed that, each of ε/ and ε// decrease with increasing the frequency.

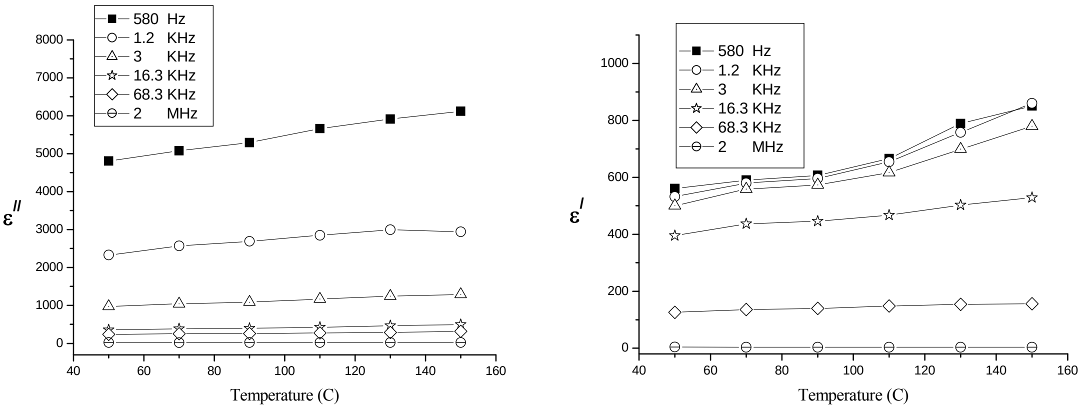
The temperature dependence of the dielectric constant (ε/) at various frequencies for CuGaxIn25-xTe74 thin film indicated that ln ε/ versus 1/T plot is a straight line for all the samples as shown in Fig.3. This type of temperature dependence is generally observed in molecular solids where the Debye theory [19] for the viscosity dependence of relaxation time holds quite well. According to this theory, the dielectric constant (ε/) should increase exponentially with temperature. The above discussion indicates that dipolar type dielectric dispersion is occurring in the present samples. However, peaks have been observed in the dielectric loss (ε//) versus frequency curves in the present samples as distribution of relaxation times [15]. Guintini et al. [20] have proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [21] of hopping of charge carriers over a potential barrier between charged defect states D+ and D-. Each pair of sites D+ and D- is assumed to form a dipole, which has a relaxation time depending on its activation energy [22,23], attributed to the existence of a potential barrier over which the carriers hop [24]. The dielectric loss in these glasses depends upon the total number of localized states. Hence, the increase of the dielectric loss with the increase of gallium content indicates that the density of defect states decreases on addition of gallium. The dielectric constant and the dielectric loss increase for all gallium concentrations. Fig.4 shows the variation of the dielectric constant and the dielectric loss with gallium concentration. The numerical values are given in Table 1.



a- $CuIn_{25}Te_{74}$ thin film



b- $CuGa_{12.5}In_{12.5}Te_{74}$ thin film



c- $CuGa_{25}Te_{74}$ thin film

Fig.1. Variation of dielectric constant and dielectric loss with temperature at different fixed frequencies for the $CuGa_xIn_{1-x}Te_{74}$(x=0, 12.5 and 25) thin film.

Guintini et al. [20] have proposed a theory of dielectric loss (ε//) in chalcogenide glasses at a particular frequency in the temperature range where dielectric dispersion occurs, leading to the relation

$$\varepsilon^{//}(\omega)= (\varepsilon_s - \varepsilon_\infty)2\pi^2 N(ne^2/\varepsilon_s)^3 kT\tau_0^m(W_m)^{-4} \omega^m \quad (1)$$

where $m = -4kT/Wm \quad (2)$

Here, n is the number of electrons that hop, N is the concentration of defect states. εs and ε∞ are the static and optical dielectric constant respectively, Wm is the energy required to move the electron from a site to infinity. From Eq. (1), (ε//) should follow a power law with frequency, i.e.

$$\varepsilon// = A\ \omega m \quad (3)$$

where m should be negative and linear with T as given by Eq. (2). In our samples we found also that (ε//) follows a power law with frequency at higher temperatures where the dielectric dispersion occurs. Fig.4 confirms this behavior when ln ε// versus ln ω curves are found to be straight lines at the fixed temperature 150o C. The power m is calculated from the slope of these curves. It is found that the values of m are negative for the present sample. From this analysis, it seems that the paired defect states behave as dipoles in a-CuGaxIn1-xTe74 thin film. The present results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliot [25] in case of chalcogenide glasses, and the dielectric dispersion is of dipolar type which is also found in the present samples.

According to the theory of Elliot[25], dielectric loss peak when predicted Wτmax = 1 and the ac conductivity is given by the formula

$$\sigma_{ac}(\omega) = \frac{\pi^2 N^2 \varepsilon'}{24}\left(\frac{8e^2}{\varepsilon' W_M}\right)^6 \frac{\omega^s}{\tau^\beta} \quad (4)$$

and the concentration of localized states N can be calculated from this equation, where β= 6kT/WM and s =1-β. According to the theory, ac conductivity has slightly sublinear frequency dependence and WM is given by

$$W_M = B - W_1 - W_2 \quad (5)$$

Where B is the band gap of the material, and W1 and W2 are approximately the distribution energies associated with the natural D0 and D+ respectively.

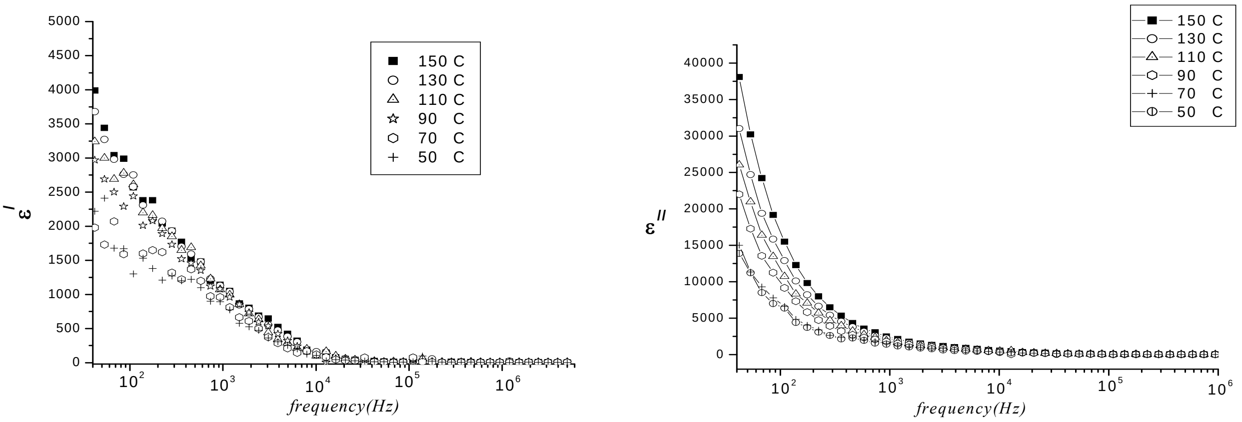
Table.1 Dielectric parameters of the a- $CuGa_xIn_{1-x}Te_{74}$ thin film at $T = 150^o$ C andf = 5300 Hz

	$\varepsilon^/$	$\varepsilon^{//}$	m
$CuIn_{25}Te_{74}$	319	628	-0.823
$CuGa_{12.5}In_{12.5}Te_{74}$	348	155	-0.954
$CuGa_{25}Te_{74}$	696	649	-0.87

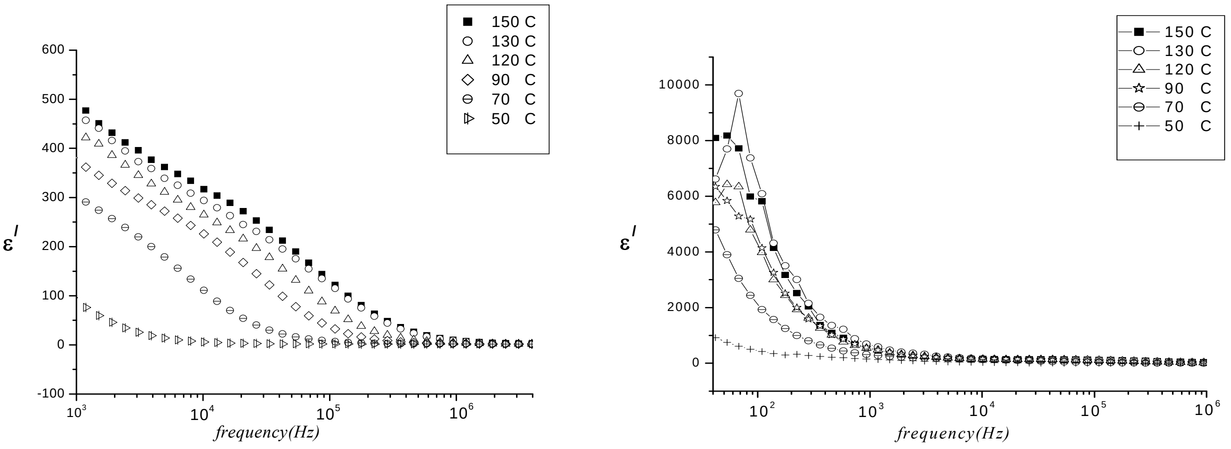
Table 2 The calculated value of N at fixed frequency(6 MHz) and different temperatures

Temperature (^{0}C)	*$CuIn_{25}Te_{74}$*	*$CuGa_{25}Te_{74}$*
50	2.10E+18	-
70	-	7.30E+23
90	-	1.00E+24
110	8.00E+24	1.60E+24
130	9.20E+24	2.30E+24
150	1.30E+25	7.00E+24

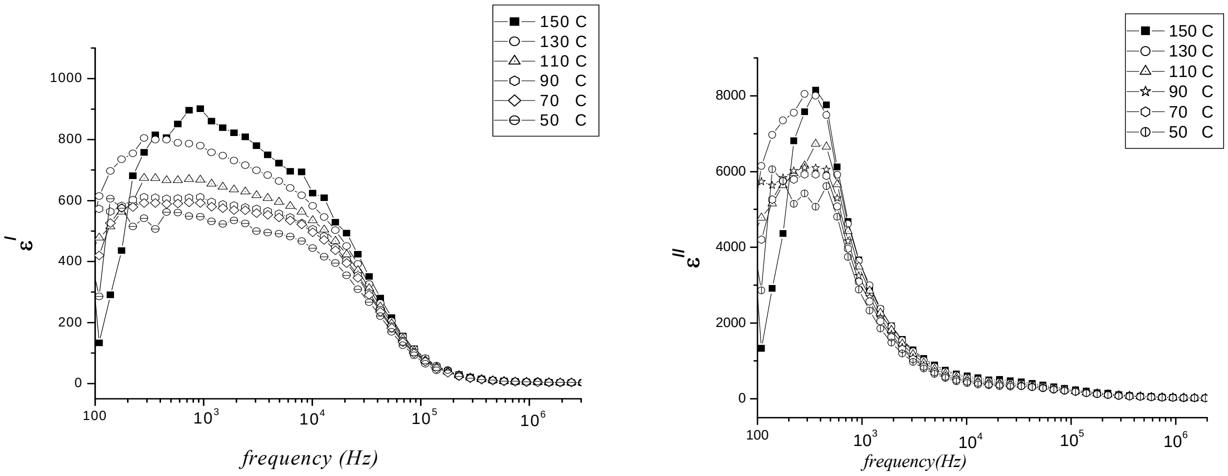
The calculated value of N at fixed frequency (6 MHz) and different temperatures are indicated in Table 2. We observe that, the number of defect states increases with increasing the temperature and decreases with increasing Ga concentration as shown in Fig.6.



a- $CuIn_{25}Te_{74}$ thin film



b- $CuGa_{12.5}In_{12.5}Te_{74}$ thin film



c- $CuGa_{25}Te_{74}$ thin film

Fig.2. Variation of dielectric constant and dielectric loss with frequency at different fixed temperatures for the CuGaxIn1-xTe74 thin film

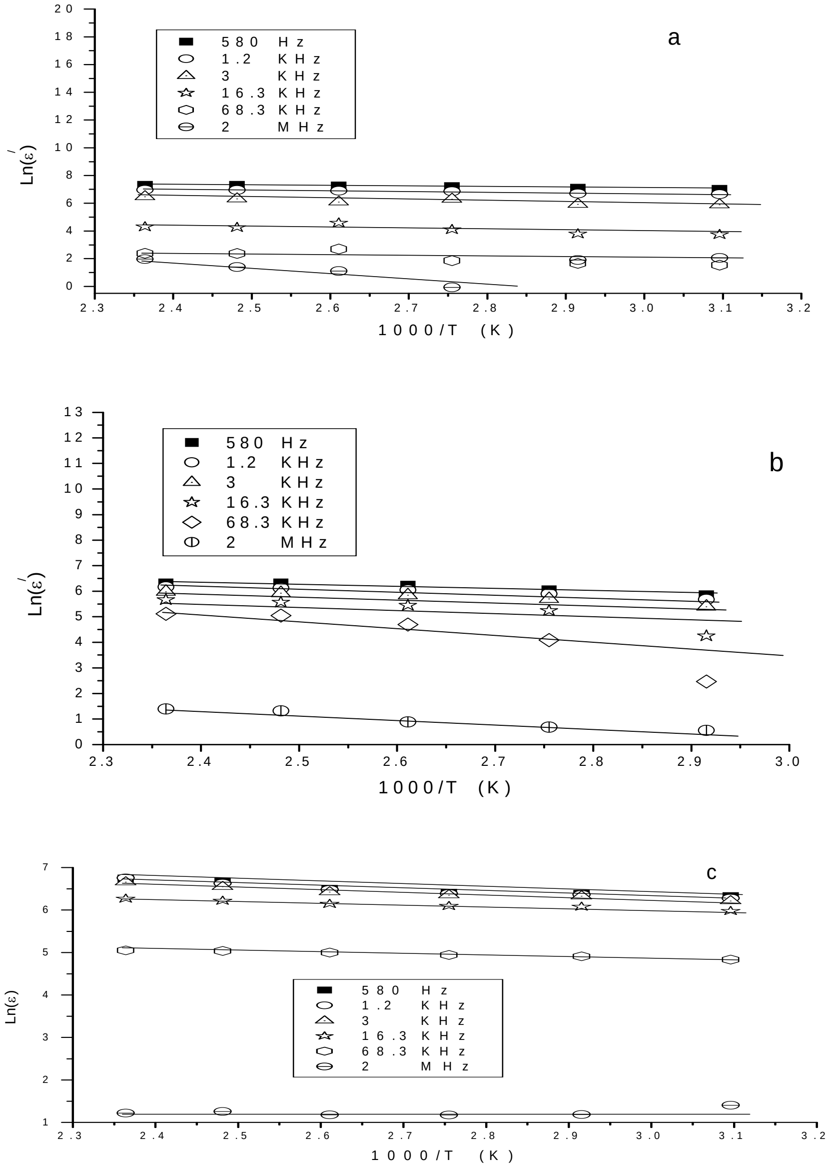


Fig.3-a,b and c The temperature dependence of the dielectric constant (ε/) at various frequencies for CuIn25Te74, CuGa12.5In12.5Te74 and CuGa25Te74 respectively.

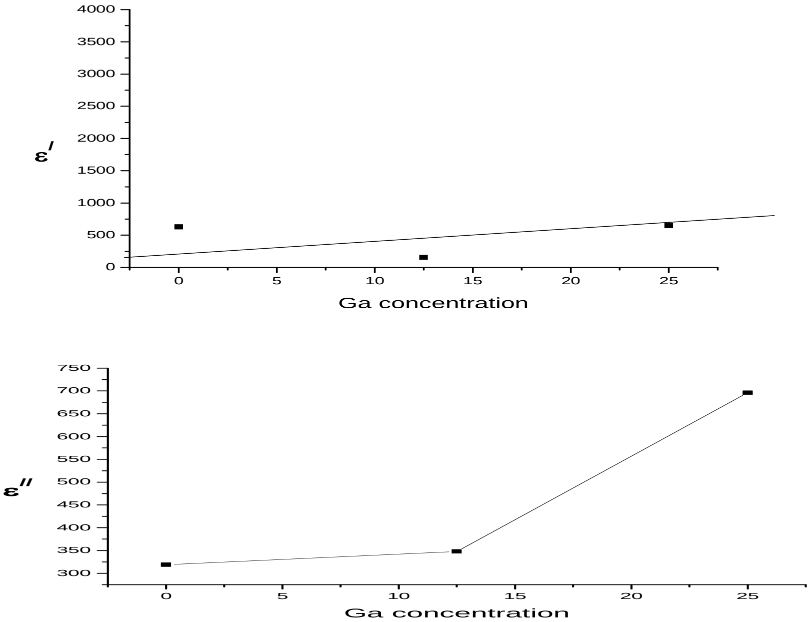


Fig.4 shows the variation of the dielectric constant and the dielectric loss with gallium concentration.

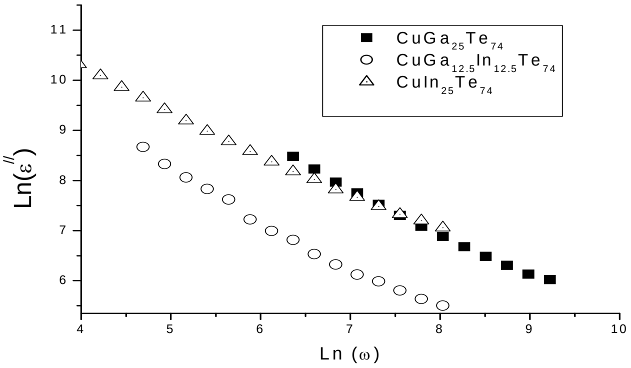


Fig.5. Variation of ln ε// with ln ω at fixed temperature (150 C) for the CuGaxIn1-xTe74 thin film

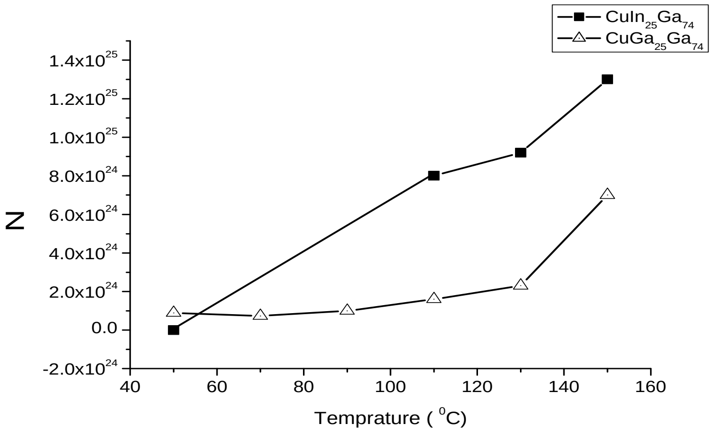


Fig.6 The number of defect states N at fixed frequency(6 MHz) and different temperatures

4. Dielectric relaxation time τ and distribution function α

Cole and Cole [26] had investigated theoretically the dielectric properties and dipole polarization of solids and showed that, for a dielectric with single relaxation time , the equation between the real ε/ and imaginary ε// parts of the dielectric constant given by Debye is the equation of a circle :

$$(\varepsilon^{/}(\omega)-\frac{\varepsilon_s+\varepsilon_\infty}{2})^2+(\varepsilon^{//}(\omega))^2=\frac{1}{4}(\varepsilon_s-\varepsilon_\infty)^2 \qquad (6)$$

Cole and Cole had generalized Debye equations for the case when the dielectric system has a distribution of relaxation times and proved that the complex plane locus obtained by plotting ε/ against ε// is generally as arc of a circle intersecting the abscissa axis at the value ε∞ and εs. The diameter drawn through the center from ε∞ makes an angle απ/2 with the axis. Tan απ/2 is determined from the plots and α is calculated. Knowing α, one can determine the macroscopic relaxation time τ0 by using the relation [26].

$$\frac{v}{u}=(\omega\tau_0)^{1-\alpha} \qquad (7)$$

Where v is the distance on the Cole-Cole diagram between εs and the experimental point, U is the distance between that point and ε∞ and ω is the angular frequency. The parameter α is equal to zero when the dielectric has only one relaxation time whereas for a distribution of relaxation times α varies between 0 and I. The larger α is, the larger is extent of the distribution of the relaxation times. Knowing τ0 one can estimate the value of the molecular relaxation time τ using the relation [27].

$$\tau=\tau_0\left(\frac{2\varepsilon_s+\varepsilon_\infty}{3\varepsilon_s}\right) \qquad (8)$$

The Cole–Cole diagram for CuIn25Te74 and CuGa25Te74 at 50o and 150o C is shown in Fig.6. The determined values of εs, ε∞, α and τ0 at different temperatures are indicated in tables 3, 4 and 5 for CuIn25Te74 ,CuGa12.5In12.5Te74 and CuGa25Te74 respectively. The Eyring theory [29] leads to the following expression [23, 29]:

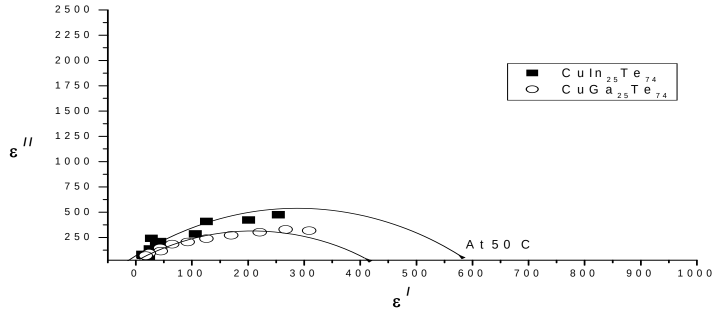
$$\tau = (h/kT)\exp(\Delta F/RT \qquad (9)$$

where ΔF is the free energy of activation for dipole relaxation, k is Boltzmann's constant, h is Planks constant, and R is the gas constant. ΔF is related to the enthalpy of activation (ΔH), and entropy of activation (ΔS) by the relation

$$\Delta F = \Delta H - T\Delta S \qquad (10)$$

Eq.(9) and (10) indicate that the plot of log (τ. T) versus 1/T should give approximately a linear relationship with slopes equal to ΔH/R from which ΔH can be calculated. Using Eq.(10), ΔF can be calculated by the relation

$$\Delta F = 2.303RT\log(kT\tau/h) \qquad (11)$$



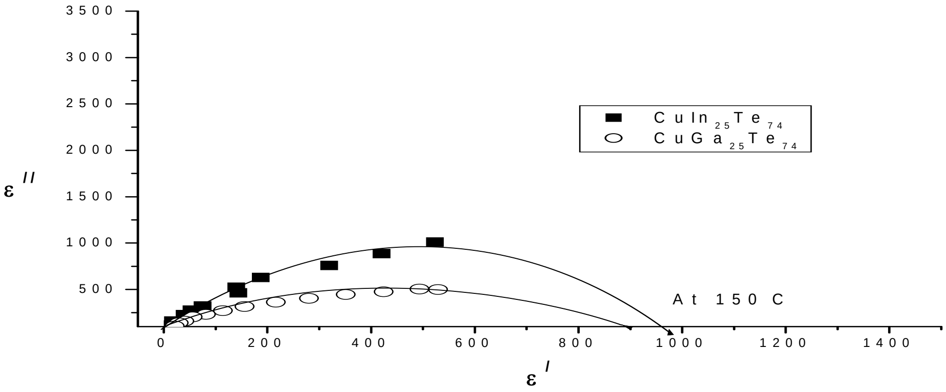


Fig.7 The Cole–Cole diagram for CuIn25Te74 and CuGa25Te74 at 50o and 150o C

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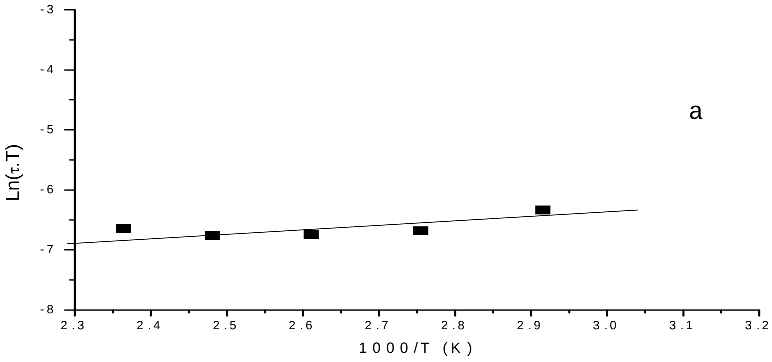

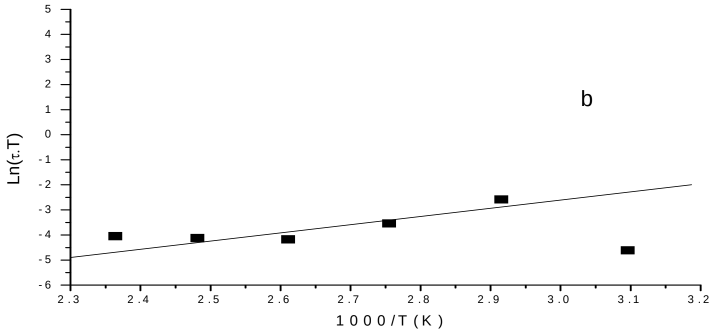

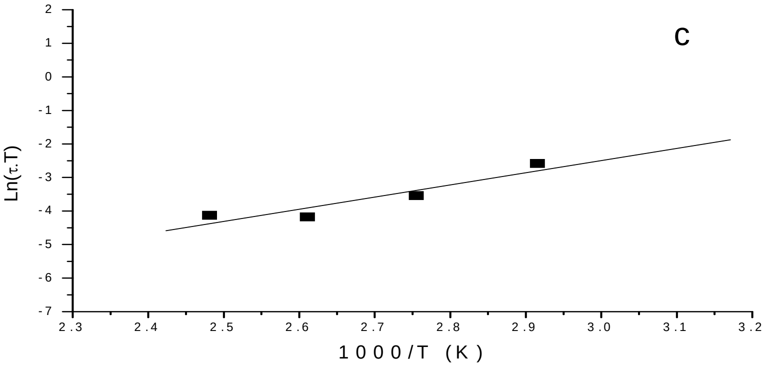

Fig.8-a,b and c. ln(τ.T) versus 1/T for CuIn25Te74, CuGa12.5In12.5Te74 and CuGa25Te74 respectively

The plots of log (τ.T) versus 1/T for CuGaxIn25-xTe74 system are shown in Fig.8 and the calculated values of ΔF are shown in Tables 3, 4 and 5. The activation free energy (ΔF) decreases as the gallium concentration increases in the present system. The existence of multi-relaxation times in chalcogenides is obtained by plotting Cole–Cole diagram. Fig.7 shows the variation of dielectric loss (ε//) versus dielectric constant (ε/) at different frequencies and fixed temperature. This figure indicates that an arc is observed at high frequency and that, due to the high DC conduction loss, the arc is not observed at lower frequency [30]. It has been observed that, for all alloys reported here, the high-frequency ε// versus ε/ curves show the arc of a circle the center of which lies below the abscissa axis. This confirms that there exists a distribution of relaxation times in the present samples. The variation of the relaxation time with temperature can be expressed as

$$\tau = \tau_o \exp(\Delta E\tau /kT) \qquad (12)$$

where τ_o is a constant and ΔEτ is the activation energy of dielectric relaxation and k is Boltzmann's constant. We calculated the activation energy of dielectric relaxation (ΔEτ). The results are given in Table 2. It is interesting to compare the values of the activation energy of dielectric relaxation with the activation energy of DC conduction (ΔE). We found that the values of the activation energy of dielectric relaxation are higher than the activation energy of DC conduction (not represented here). The larger values of the activation energy of dielectric relaxation can only be understood if the contribution to the relaxation mechanism is of dipolar type. Most of the results on the dielectric relaxation can be understood if we assume that the addition of gallium acts as a terminator of $CuGa_xIn_{25-x}Te_{74}$ system, decreasing the number of charged dangling bonds in $CuGaxIn_{25-x}Te_{74}$. This is in agreement with the decrease in the number of defect states with increasing Ga concentration.

Table.3 Dielectric relaxation parameters of the $CuIn_{25}Te_{74}$ *thin film*

T(C)	ε_s	ε_∞	α	f	u	v	τ_0	τ (Cole-Cole)	ΔF (K Cal/mol)	ΔE (K Cal/mol)
50	700	13	0.566	3075	3.8	3.6	$4.57\ 10^{-5}$	$3.08\ 10^{-5}$	12.23	2.94
70	740	9	0.611	4954	1.7	4.2	$32.9\ 10^{-5}$	$22.06\ 10^{-5}$	14.38	3.15
90	960	11	0.522	4954	2.3	4.3	$11.9\ 10^{-5}$	$7.98\ 10^{-5}$	14.53	3.33
110	760	8.8	0.455	3903	2.6	3.2	$5.9\ 10^{-5}$	$4.01\ 10^{-5}$	14.85	3.52
130	750	3	0.5	6289	2.6	4	$5.99\ 10^{-5}$	$4.00\ 10^{-5}$	15.67	3.73
150	950	9	0.544	4954	2.6	3.5	$6.17\ 10^{-5}$	$4.13\ 10^{-5}$	16.52	3.89

Table.4 Dielectric relaxation parameters of the $CuGa_{12.5}In_{12.5}Te_{74}$ *thin film*

T(C)	ε_s	ε_∞	α	f	u	v	τ_0	τ (Cole-Cole)	ΔF (K Cal/mol)	ΔE (K Cal/mol)
50	500	1.7	0.633	20720	2.3	3.5	$2.41\ 10^{-5}$	$1.88\ 10^{-5}$	11.91	1.21
70	104	2	0.544	20720	2.7	2.7	$7.68\ 10^{-6}$	$5.17\ 10^{-6}$	11.82	3.12
90	258	10	0.455	33390	2.8	2.9	$5.08\ 10^{-6}$	$3.45\ 10^{-6}$	12.26	3.22
110	328	11	0.444	42390	2.7	3	$4.54\ 10^{-6}$	$3.07\ 10^{-6}$	12.89	3.42
130	375	17	0.388	42390	2.8	3	$4.20\ 10^{-6}$	$2.86\ 10^{-6}$	13.55	3.55
150	430	20	0.455	42390	2.8	3.1	$4.52\ 10^{-6}$	$3.08\ 10^{-6}$	14.33	1.21

Table.5 Dielectric relaxation parameters of the $CuGa_{25}Te_{74}$ thin film

T(C)	ε_s	ε_∞	α	f	u	v	τ_0	τ (Cole-Cole)	ΔF (K Cal/mol)	ΔE (K Cal/mol)
50	552	1.8	0.522	29310	3	2.5	$3.70\ 10^{-6}$	$2.5\ 10^{-6}$	10.62	2.87
70	627	7	0.422	33390	2.8	3.4	$6.67\ 10^{-6}$	$4.4\ 10^{-6}$	11.72	3.15
90	610	1.3	0.477	26310	3.2	2.6	$4.06\ 10^{-6}$	$2.7\ 10^{-6}$	12.09	3.27
110	664	1.5	0.455	33390	2	2.4	$6.66\ 10^{-6}$	$4.4\ 10^{-6}$	13.18	1.92
130	805	1.9	0.53	33390	2.4	3.5	$1.07\ 10^{-5}$	$7.2\ 10^{-6}$	14.29	2.12
150	766	1.7	0.488	33390	2.1	3.7	$1.44\ 10^{-5}$	$9.7\ 10^{-6}$	15.30	2.30

5. Conclusions

The dielectric parameter $CuGa_xIn_{25-x}Te_{74}$(x=0, 12.5 and 25) are temperature and frequency dependent. Dielectric dispersion is found to occur in these alloys. Dielectric dispersion occurs due to the DC conduction loss as well as to the dipolar type of the defects in the present sample. The dielectric constant and the dielectric loss increase with addition of gallium. A possible explanation is given in terms of hopping of charge carriers over a potential barrier between charged defect states. Increasing the concentration of gallium leads to increase in the activation energy due to the decrease of the density of defect states or to the decrease of the disorder in the mobility edge. The molecular interaction energy is less than the thermal energy, therefore thermodynamic parameters increase with increasing gallium concentration in the present system. The detailed analysis of the thermodynamic parameters also supports the assumption that dipolar type dispersion also is present in the system. This is in good agreement with the system Se-Te-Ga obtained in [18]

Acknowledgements

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