Dielectric Properties of GeSeTl

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Abstract: Five amorphous samples of $Ge_{14}Se_{86-x}Tl_x$ have been prepared using melt quench technique where x = 20, 22, 23.5, 25 and 28%. The dielectric constant ε' and the loss component ε'' showed frequency, temperature and thallium content dependence. The activation energies, $E_{\varepsilon'}$ and $E_{\varepsilon''}$ belonging to the dielectric and loss components respectively found to be affected by both the applied frequency f and the thallium ratio x. The relaxation time τ and the hopping energy of the electron w_m found to be sensitive to both temperature and thallium content.

Key words: Amorphous . dielectric constant . loss . component . activation energy . relaxation time

INTRODUCTION

It is known that the conductivity of semiconducting glasses is frequency dependent that is due to conduction in localized states. Many workers [1-7] have paid special attention to measurements of ac electric conductivity of chalcogenide glasses. Accordingly [8-11], a lot of dielectric materials of practical interest have been found to posses a loss tangent, which is independent of frequency in a wide range of frequencies coupled with a relatively slight variation of the real part of the dielectric permittivity. The frequency dependent electrical conductivity is explained on terms of a distribution of relaxation times [12, 13]. On the other hand, this behavior is explained in terms of motion of free charges in dielectric and semiconducting solids, whereas, this motion is found to be hopping between well-defined localized sites within the solids. The ac conductivity at low frequency range is followed by the empirical relation: $s \propto \omega^s$, where s takes the values in the range $0.5 < s < 1$. Accordingly [1-4], the ac conductivity s (ω) is found to be temperature dependent, others have observed temperature independent of s (ω) even at frequencies f as low as 1 KHz. On the other hand, it was found that [14], the power s varies between zero for ac at high temperatures, through 0.5 at intermediate temperatures to 1 at low temperatures around 100 K or less.

In studying the dielectric properties of GeSnSe [15], it was found that both the mechanisms of polarization and loss exhibited relaxation and the estimated hopping energy of the electron was found to be small with respect to the energy gap of the considered composition. The AC conductivity of Ge_{14} Se_{66-x} Tl_x showed that, the AC conductivity measured at room temperature is attributed to the increase in Tl content, which creates charge defect centers inside the studied glassy system and the effect of Tl content on the activation energy is frequency dependent [16]. The addition of thallium to chalcogenide glasses is accompanied by marked changes in their structural and physical properties [17-21]. On the other hand, the electrical transport properties of As-Se-Tl have been investigated by many different authors [22-29].

In this work, we have measured the frequency and temperature dependent dielectric, loss component and relaxation time in $Ge_{14}Se_{86-x}Tl_x$ with a view to understand the dielectric properties in amorphous semiconductors.

Experimental technique: Samples of $Ge_{14}Se_{86-x}Tl_x$ were prepared from high purity (99.999%) Ge, Se, Tl elements by the conventional melt quench technique [3]. The contact surfaces of the circular disc form samples were painted with silver paste. Three terminal sample holder was used for measuring the different dielectric parameters. Corrections for both edge and ground capacitance were taken in consideration in order to obtain accurate values of the sample's capacitance. A circuit magnification meter-type 1245-Q-meter was used for performing all the dielectric measurements. The measurements of capacitance were carried out using parallel plate geometry in the frequency range 500 to 100 KHz and temperature range from 290 to 380 k respectively.

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RESULTS

The as-prepared samples were found to be amorphous. On the other hand, the real part ε' of the complex permittivity ε_r was measured at different ambient temperatures (T = 290, 300, 310, 320, 330, 340, 360 and 380K) and showed frequency dependence especially at the lower range of frequencies (1-10 KHz) where it decreases monotonically with increasing the frequency f as shown in Fig. 1. The decrease of ε' is larger at the higher range of the ambient temperature and becomes smaller at lower range of the ambient temperatures. Such observed behavior of ε' with f may exhibit Debye relaxation and found to agree with the behavior of different chalcogenides [16]. The variation of ε' with f found also to obey the following empirical relation;

$$\varepsilon' = C\,\omega^s \qquad (1)$$

Plotting the relations between Ln ε' and Ln ω are as shown in Fig. 2

The relation between Ln ε' vs. Ln f found to be strait lines for the x = 22 and 23.5% and kinked straight lines for x = 20, 25 and 28%, the slope of which represent the power s. The calculated values of s are recorded in Table 1 for the five compositions.

It is clear from Table 1 that, in the lower range of the applied frequency, the power s increases with increasing elevating the ambient temperature and with increasing the ratio of thallium till x = 25% and then decreases, this means that, the dielectric constant ε' is temperature and composition dependent. On the other hand, in the higher range of the applied frequency, the power s does not show clear dependence on the thallium content, but it increases with increasing the ambient temperature except for x = 20% at T = 310K.

On the other hand, the increasing of ε' with increasing the ambient temperature as shown in Fig. 1, may owed to that the dielectric constant is thermally activated and can be interpreted as due to the increase in the material's entropy, which results in an increase of the dipole disorder. Therefore, the temperature dependence of ε' can be suggested as;

$$\varepsilon' = \varepsilon_0'\, e^{-E_{\varepsilon'}/KT} \qquad (2)$$

Where $E_{\varepsilon'}$ is the activation energy, K is the Boltzmann's constant and ε_0' is the corresponding temperature independent value for the dielectric constant Fig. 3.
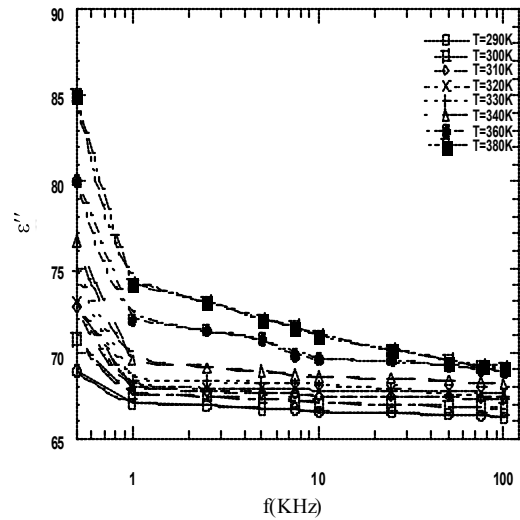

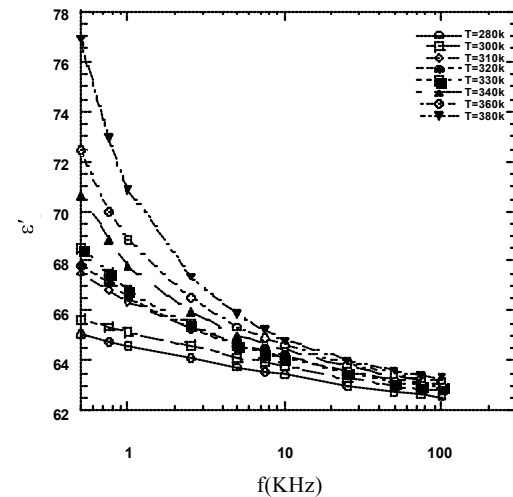Fig. 1A: Variation of the dielectric constant and the frequency at different ambient temperatures for the composition $Ge_{14}Se_{61}Tl_{25}$

Fig. 1B: Variation of the dielectric constant and the frequency at different ambient temperatures for the composition $Ge_{14}Se_{58}Th_{28}$

Shows the relations Lnε' vs. 1000/T for the composition $Ge_{14}Se_{64}Tl_{22}$ as an example. The slopes of the Lnε' vs. 1000/T of the five compositions are straight lines and used to calculate the activation energy $E_{\varepsilon'}$. The calculated values of $E_{\varepsilon'}$ at different frequencies are recorded in Table 2.

It is obvious from Table 2 that, $E_{\varepsilon'}$ decreases monotonically with increasing the applied frequency in case of thallium contents 20, 25 and 28%. Besides, the activation energy of the composition where x = 22% has a trend to decrease with increasing f and taking the approximation in consideration, the values of $E_{\varepsilon'}$ seem

Table 1: The calculated values of the power s for the five compositions at different ambient temperatures

	T = 290K	T = 300K	T = 310K	T = 320K	T = 330K	T = 340K	T = 360K	T = 380K
X = 20%	0.0047	0.0200	0.0299	0.0356	0.0822	0.0865	0.0866	0.0766
		0.0048	0.0071	0.0067	0.0100	0.0099	0.0099	0.0096
X = 22%	0.0513	0.0571	0.0576	0.0599	0.0605	0.0549	0.0652	0.0635
X = 23.5	0.0902	0.0903	0.0937	0.0943	0.0966	0.0978	0.0985	0.1068
X = 25%	0.0689	0.1144	0.1654	016740	0.2195	0.2331	0.2599	0.3418
	0.0010	0.0021	0.0028	0.0010	0.0032	0.004	0.0084	0.0136
X = 28%	0.0074	0.0100	0.0129	0.0147	0.0163	0.0184	0.0207	0.0277
	0.0066	0.0078	0.0087	0.0087	0.0101	0.0101	0.0108	0.0113

Table 2: Values of $E_{\varepsilon'}$ as a function of the ratio of thallium and frequency

f (KHz)	$E_{\varepsilon'}$ (eV)				
	x = 20%	x = 22%	x = 23.5%	x = 25%	x = 28%
50	0.01222	0.02524	0.03194	0.02103	0.01690
60	0.00604	0.02586	0.03658	0.00891	0.00485
70	0.00418	0.02445	0.03867	0.00684	0.00252
80	0.00406	0.02541	0.04022	0.00566	0.00151
90	0.00379	0.02448	0.03682	0.00469	0.00116
100	0.00308	0.02367	0.03497	0.00463	0.00115

Table 3 Values of the calculated values of m as a function of the ambient temperature and the thallium content

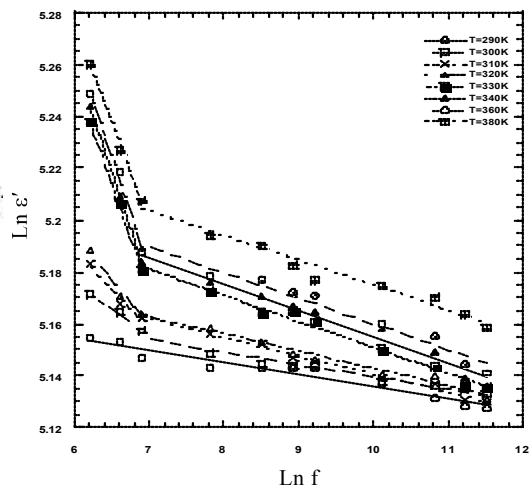| X (%)	T = 290K	T = 300K	T = 310K	T = 320K	T = 330K	T = 340K	T = 360K	T = 380K
20	0.11747	0.24440	0.40890	0.53745	0.62593	0.76593	0.82680	0.94270
22	0.31090	0.35357	0.41750	0.55160	0.64442	0.77270	0.85309	0.96880
23.5	0.62820	0.87340	0.89140	0.89340	0.96830	1.08800	1.19940	1.21240
25	0.88680	0.88680	0.93840	1.07670	1.29010	1.30210	1.35190	2.07740
28	0.07223	0.11681	0.16980	0.26962	0.34953	0.52432	0.64840	1.09760

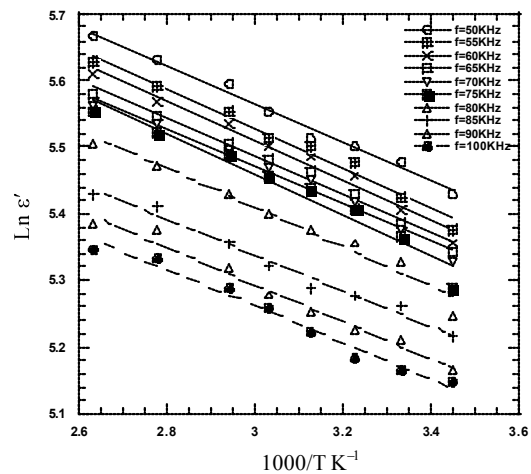Fig. 2: Variation of Ln ε' with Ln f at different ambient temperatures for the composition $Ge_{14}Se_{66}Th_{20}$

Fig. 3: Ln ε' vs. 1000/T relation at different frequencies for the composition $Ge_{14}Se_{64}Tl_{22}$

Table 4: Variation of the hopping energy w_m with respect to thallium ratio and temperature

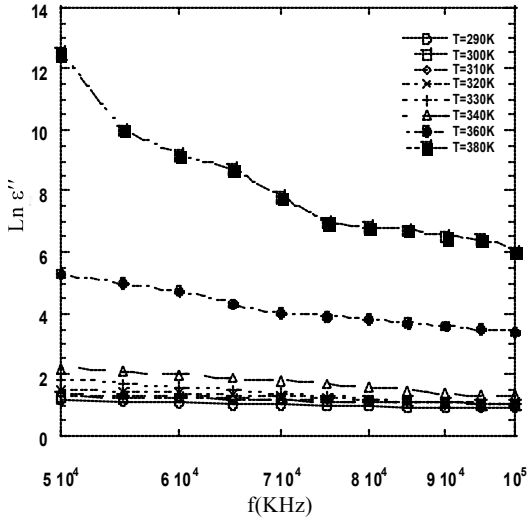| X (%)	T = 290K	T = 300K	T = 310K	T = 320K	T = 330K	T = 340K	T = 360K	T = 380K
20	0.85128	0.42367	0.26167	0.20551	0.18197	0.15321	0.15023	0.13913
22	0.32164	0.29286	0.25628	0.20023	0.17675	0.15188	0.14566	0.13538
23.5	0.15918	0.11856	0.12004	0.12363	0.11763	0.10786	0.10359	0.10818
25	0.11276	0.11676	0.11402	0.10258	0.08828	0.09012	0.09191	0.06314
28	1.38580	0.88645	0.63015	0.40966	0.32587	0.22382	0.19163	0.11949

Fig. 4: Variation of ε'' on f at different ambient temperatures for the composition $Ge_{14}Se_{64}Tl_{22}$
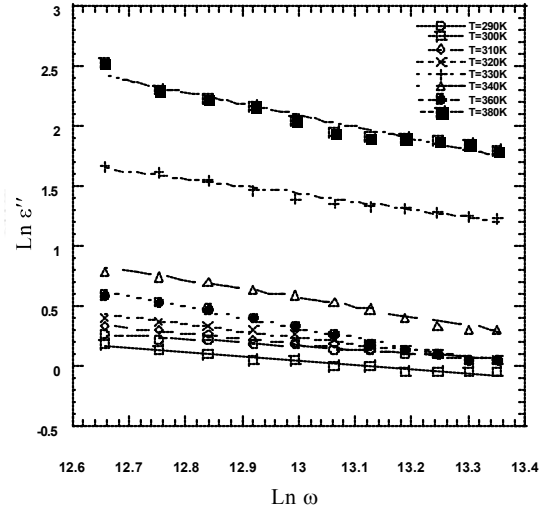

Fig. 5: $Ln\ \varepsilon''$ $Ln\ \omega$ relations at different ambient temperatures for the composition $Ge_{14}Se_{64}Tl_{22}$

to be the same ≈ 0.0248 eV. On the other hand, the activation energy related to the composition where x = 23.5% increases with increasing f in the range 50-80 KHz and then deceases with more increasing of the applied frequency.

Table 2 shows also that, the activation energy $E_{\varepsilon'}$ increases with increasing thallium contents from x = 20 to 23.5% and then decreases with more increasing of x in the all considered values of the applied frequencies.

Studying the dependence of the loss component ε'' on the frequency reveal that it decreases monotonically with increasing the applied frequency for the considered five compositions as shown in Fig. 4 as an example. It is clear that, the higher ambient temperature the more obvious decrease of ε'' with increasing the frequency and as the ambient temperature is low, the values of ε'' seem to be independent on the applied frequency.

Using the equation:

$$\varepsilon^{"} = A'\omega^{-m} \qquad (3)$$

Where the power m equals m = $-4KT/w_m$, since, K is the Boltzmann's constant.

T is the fixed temperature in Kelvin, w_m is energy required to move the electron from one site to infinity (the hopping energy of the electron) and A′ is a constant. Plotting the relations $Ln\varepsilon''$ vs. $Ln\omega$, it was found that they are straight lines as shown in Fig. 5 for the composition $Ge_{14}Se_{64}Tl_{22}$ as an example. From the slopes of the straight lines, the values of the power m have been calculated and recorded in Table 3.

It is clear from Table 3 that, the power value m increases with increasing the ambient temperature for the five compositions. Besides, the value of m increases with increasing thallium ratio till x = 25% and then decrease.

Comparing Table 1 and 3, its clear that powers s at lower range of f has the same behavior of m at higher rang of f, it means that both the dielectric constant and the dielectric loss has the same behavior with respect to the applied frequency and thallium content. On the other hand, the values of m are higher than those of s, i.e, the loss component is more depending on f and x.

From the power m in equation 3, the hopping energy has been calculated and recorded in Table 4. It is clear from Table 4 that, w_m decreases with increasing both temperature and x.

Table 5: Dependence o the calculated values of $E_{\varepsilon''}$ on both f and x

f (KHz)	$E_{\varepsilon''}$ (eV)				
	x = 20%	x = 22%	x = 23.5%	x = 25%	x = 28%
50	0.10985	0.23847	0.32330	0.33523	0.21073
60	0.07053	0.21954	0.31506	0.31731	0.21042
70	0.05246	0.20148	0.30396	0.30527	0.21007
80	0.04837	0.19837	0.28235	0.30004	0.20703
90	0.04527	0.18943	0.26228	0.27153	0.20531
100	0.04283	0.18219	0.24914	0.25376	0.20243

Table 6: Variation of τ and ε_∞ on both T and x

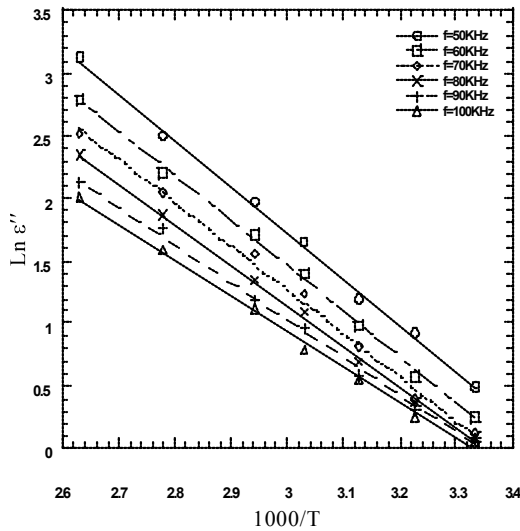| TK	X = 22%		X = 23.5%		X = 25%		X = 28%	
	$\tau_1 \times 10^{-7}$	ε_∞	$\tau_1 \times 10^{-7}$	ε_∞	$\tau_1 \times 10^{-7}$	ε_∞	$\tau_1 \times 10^{-7}$	ε_∞
290	2.66	227	2.52	227	2.24	274	0.82	205
300	2.31	224	2.24	227	2.09	270	0.72	201
310	2.29	224	2.17	229	1.83	270	0.64	205
320	1.88	226	1.78	228	1.68	270	0.57	207
330	1.87	226	1.65	229	1.46	279	0.51	208
340	1.59	227	1.43	228	1.28	269	0.43	209
360	1.38	227	1.29	228	1.13	269	0.40	206
380	1.17	227	0.98	228	0.78	272	0.34	202

Fig. 6: Ln ε'' vs. 1000/T relations at different applied frequency for the composition $Ge_{14}Se_{62.5}Th_{23.5}$

As it is seen previously that, the loss component is temperature dependent, therefore, the relations Ln ε'' vs. 1000/T have been drawn and found to be straight line as shown in Fig. 6 following the empirical relation;

$$\varepsilon'' = \varepsilon_0'' e^{-E_{\varepsilon'}/KT} \qquad (4)$$

Where ε_0'' is the pre-exponential factor and $E_{\varepsilon'}$ is the activation energy. The dependence of $E_{\varepsilon'}$ on both the applied frequency and thallium ratio is as recorded in Table 5.

As seen in Table 5 that, the activation energy $E_{\varepsilon'}$ decreases with increasing the applied frequency, further, it increases also with increasing thallium ratio till x = 25% and then decreases with more increasing of x.

Comparing Table 2 and 5, the values of $E_{\varepsilon'}$ found to be larger than those of $E_{\varepsilon'}$ revealing that the loss component is more thermally activated than the dielectric one.

To calculate the relaxation time τ and the infinite frequency dielectric ε_∞, the following relation can be used:

$$\varepsilon' = \frac{\varepsilon''}{\omega \tau} + \varepsilon_\infty \qquad (5)$$

Therefore, the relation ε' vs. ε''/ω has been plotted as shown in Fig. 7, where the slope of which is used to calculate the relaxation time and infinite frequency dielectric. Table 6 demonstrates the variation of τ and ε_∞ with T and x.
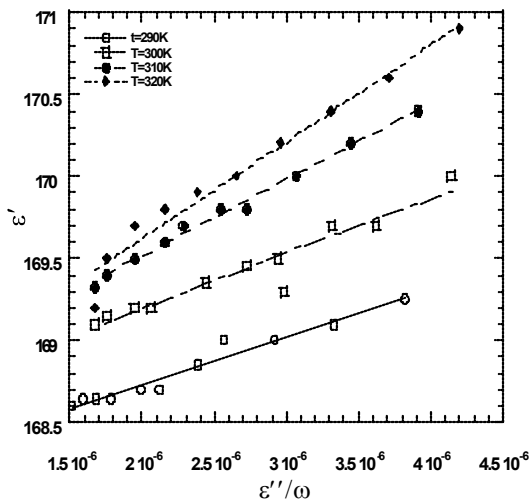
Fig. 7: ε''/ω-ε' relations at different ambient temperatures for the composition $Ge_{14}Se_{62}Tl_{22}$

It is clear that, τ decreases with increasing both T and x, whereas, ε_∞ seem to be independent on T and x. On the other hand, the calculated values of τ are very high with respect to the inverse of phonon's frequency ($\approx 10^{-13}$ sec). This might reveal that, even conduction in these compositions is due to hopping, it is not assisted by phonons.

CONCLUSION

The real as well as the imaginary components of the complex relative permittivity exhibited negative power dependence on the frequency of the applied electric field leading that, both mechanisms of polarization and loss suffer relaxation. On the other hand, the power of the frequency dependence of both the dielectric constant and the dielectric loss was smaller than unity, also, both mechanisms showed strong sensitivity to both composition and temperature. Further, the estimated hopping energy of the electron seemed small compared with the energy gap of such materials, in addition, decreasing the hopping energy with increasing thallium content may be due to, enritching with thallium enhances the density of the localized states, which results in a shortening of the average hopping length and then the hopping time, therefore, a decrease in the hopping activation energy occurred. Meanwhile, the observed increase of the dielectric constant with increasing the ambient temperatures could be due to a correspondind increase in the material's entropy. The observed increase of the thermal activation with increasing temperature proved more thermal activation of the mechanisms of polarization at higher temperatures. The activation energies belonging to the loss component always have larger values than those of the dielectric constant indicating that the loss component is more sensitive to temperature than the dielectric constant. Meanwile, the relaxation time found to decrease with increasing the temperatures and decreases with increasing thallium content.

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