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AC conductivity and dielectric properties of $GeSe_xTl_{0.3}$ amorphous thin films

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HIGHLIGHTS

- $\sigma_{ac}(\omega)$ increases with increasing temperature (T) at different frequencies.
- $\sigma_{ac}(\omega)$ proportional to ω^s, $s<1$ is the frequency exponent that decreases linearly with T.
- The dielectric constant ε' increases with T and Se content, and decreases with frequency.
- The dielectric loss ε'' increases with T and decreases with frequency.
- Values of the maximum barrier height W_M are in good agreement with the theory of hopping.

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ABSTRACT

AC conductivity and dielectric properties have been studied for amorphous thin films with different thicknesses of glassy system $GeSe_xTl_{0.3}$ with $X=3$, 4 that prepared with thermal evaporation technique. The measurements are taken at temperature range (303–403 K) and frequency range (10^2–10^5 Hz).

AC conductivity $\sigma_{ac}(\omega)$ is found to be proportional to ω^s where $s<1$. The temperature dependence of the ac conductivity and the parameter s can be discussed with the aim of the correlated barrier-hopping (CBH) model.

The dielectric constant ε' and the dielectric loss ε'' showed frequency and temperature dependence. The maximum barrier height W_M calculated from the dielectric measurements according to Giuntini equation are in good agreement with that proposed by the theory of hopping of charge carriers over a potential barrier as suggested by Elliott in the case of chalcogenide glasses.

1. Introduction

Chalcogenide glasses have received a lot of attention, because of their potential for use in various solid state devices. The common feature of these glasses is the presence of localized states in the mobility gap, as the result of the absence of long-range order as well as various inherent defects. Generally, the undoped chalcogenide glasses show low values of electrical conductivity, which could mean a serious limit to their technological application and electrical measurements. Certain additives are used to improve these properties. The electrical properties of Se-based glasses are very interesting, these materials exhibit effects such as optical memory and photo darkening [1] to which the study of their electrical behavior could light.

The investigation of electron transport in disordered systems has gradually been developed; the investigation of the gap states is of particular interest, because of their effect on the electrical properties of semiconductors [2]. The addition of thallium (Tl) to chalcogenide glasses is generally accompanied by marked changes in their structural and physical properties [3–8].

Measurements of ac conductivity of amorphous chalcogenide semiconductors have been extensively used to understand the conduction process in these materials [2,3].

In recent years, attention has been paid to the study of hopping conductivity of disordered solids. The basic characteristic of hopping conduction is a power law [9] frequency dependence of the real part of the ac conductivity.

Elliott [10] has considered a model based on the nature of defect centers in amorphous semiconductors proposed by Mott et al. [11] and Kastner et al. [12] in which spin pairing is believed to be energetically favoured, all defect centers therefore either being is positively or negatively charged. In this correlated barrier hopping CBH model, electron pair hops from doubly occupied D^+ states to a nearby D^- center over the barrier separating the two sites, the barrier height moreover being correlated with intersite separation via the coulombic interaction between the centers [13].

The study of frequency dependent electrical conductivity of amorphous compounds is important to explain the mechanism of conduction in these substances [14,15]. This leads to adapt and

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to elaborate models allowing the electronic properties of several substances to be described [16,17].

The present paper aims to study the influence of the ambient temperature, frequency and Se content on the ac conductivity and dielectric properties of $GeSe_xTl_{0.3}$ ($x = 3, 4$) amorphous thin films.

2. Experimental technique

Bulk glasses of the $GeSe_xTl_{0.3}$ ($x = 3, 4$) systems were prepared by direct mono temperature synthesis in evacuated silica tube under vacuum of 10^{-5} Torr and quenching in ice-water mixture from the melt. The starting components are extremely pure (5 N) and the temperature regime like that described in [18].

Thin films of different thicknesses of the investigated compositions (57.4–680 nm) as in [18], were deposited under vacuum of 10^{-5} Torr by thermal evaporation technique under constant conditions on dry-clean glass substrates using a high vacuum coating unit (Edward E-306A). The substrate was fixed onto a rotatable holder (up to 240 r.p.m.) to obtain homogenous deposited films. The film thickness was controlled during deposition and then determined optically after deposition by Tolansky's method of multiple beams Fizeau fringes [19].

The amorphous nature of the films was checked carefully for the investigated compositions by the absence of any diffraction lines in their X-ray patterns as in [18].

A micro DTA apparatus of a Shimadzu DT-30 model was used for the DTA investigation to determine the glass transition temperature T_g and from which the temperature range of investigation was detected.

AC measurements were carried out with sandwich structures using Al electrodes as lower and upper electrodes. A programmable automatic RLC bridge (PM 6304 Philips) was used to measure the impedance Z, the capacitance C and the loss tangent ($\tan\delta$) directly. All investigated samples are represented in the screen of the bridge by a resistance R connected in parallel with a capacitance C_x. The total conductivity was calculated from the equation $\sigma_t(\omega) = d/ZA$, where d is the thickness of the film and A is the cross sectional area. The dielectric constant was calculated from the equation $\varepsilon' = dC_x/A\cdot\varepsilon_o$, where ε_o is the permittivity of free space. The dielectric loss ε'' was calculated from the equation $\varepsilon'' = \varepsilon'\cdot\tan\delta$, where ($\delta = 90 - \varphi$) and φ is the phase angle.

3. Results and discussion

3.1. Temperature and frequency dependence of ac conductivity

Study of ac conductivity in the disordered solids gives information on the defect levels lying in the gap of these materials.

A common feature of all amorphous semiconductors is that the ac conductivity $\sigma_{ac}(\omega)$ increases with frequency according to the equation:

$$\sigma_{ac}(\omega) = \sigma_t(\omega) - \sigma_{dc} = A\omega^s \qquad (1)$$

where ω is the angular frequency, s is the frequency exponent and A is a temperature independent constant. Fig. 1a and b shows the temperature dependence of the measured total conductivity $\sigma_t(\omega)$ and dc conductivity σ_{dc} for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ thin films at different frequencies with thicknesses 155 nm and 463 nm respectively. It is clear from these figures that $\sigma_t(\omega)$ increase slightly with increasing temperature.

Fig. 2a and b represents the temperature dependence of ac conductivity $\sigma_{ac}(\omega)$ for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ thin films of thickness 333 nm and 330 nm respectively at different frequencies. Values of $\sigma_{ac}(\omega)$ obtained for films with nearly the same thickness 333 nm and 330 nm respectively at different frequencies are given in Table 1. It is obvious from the table that $\sigma_{ac}(\omega)$ increases with increasing Se content in the investigated range of frequency, and this may be due to the increase of the low bond energy (Se–Se bond) since Se–Se bond energy is lower than Ge–Se bond energy. Consequently electrical conductivity increases. Also the increase of Se content in the investigated composition decreases the non-bridging Tl atoms which increases the ionic character of the bonds, thus leading to weaker bonds in the amorphous network. This conclusion is consistent with the observed increase in the value of $\sigma_{ac}(\omega)$.

The frequency dependence of $\sigma_{ac}(\omega)$ at various temperatures in the considered ranges of temperature and thickness are shown in Fig. 3a and b for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films of thicknesses 333 nm and 330 nm respectively. It is clear from these figures that $\sigma_{ac}(\omega)$ increases linearly with increasing frequency according to Eq. (1). Values of the frequency exponent s were calculated from the slopes of linear lines of Fig. 3a and b.

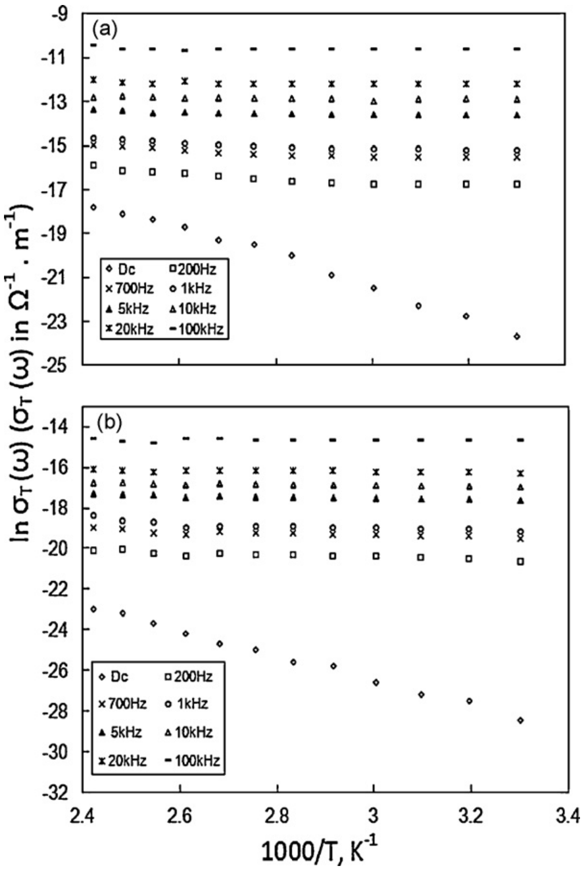

Fig. 1. Temperature dependence of the total electrical conductivity $\sigma_t(\omega)$ at different frequencies for (a) $GeSe_3Tl_{0.3}$ of thickness 155 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 463 nm.

The dependence of the frequency exponent s on the temperature for each composition for samples of different thicknesses is shown in Fig. 4. It is clear from the figure that s decreases with the increase of temperature. The calculated values of s for films of different thicknesses showed that the mean values of the obtained results lie within experimental error of approximately ±1%. Accordingly s is independent on the film thickness at any given temperature in the investigated range. It is also clear from Fig. 4 that s increases with the increase of Se content in the investigated compositions.

Table 1
Effect of Se content on ac conductivity $\sigma_{ac}(\omega)$ at different frequencies.

Composition	t (nm)	Frequency (kHz)	$\sigma_{ac}(\omega)$ $(\Omega\,m)^{-1}$
$GeSe_3Tl_{0.3}$	333	0.2	1.46×10^{-10}
		0.7	7.58×10^{-10}
		5	6.76×10^{-9}
		10	8.46×10^{-9}
		20	1.13×10^{-8}
		100	1.65×10^{-7}
$GeSe_4Tl_{0.3}$	330	0.2	3.61×10^{-9}
		0.7	3.92×10^{-9}
		5	2.33×10^{-8}
		10	3.34×10^{-8}
		20	1.289×10^{-7}
		100	1.03×10^{-6}

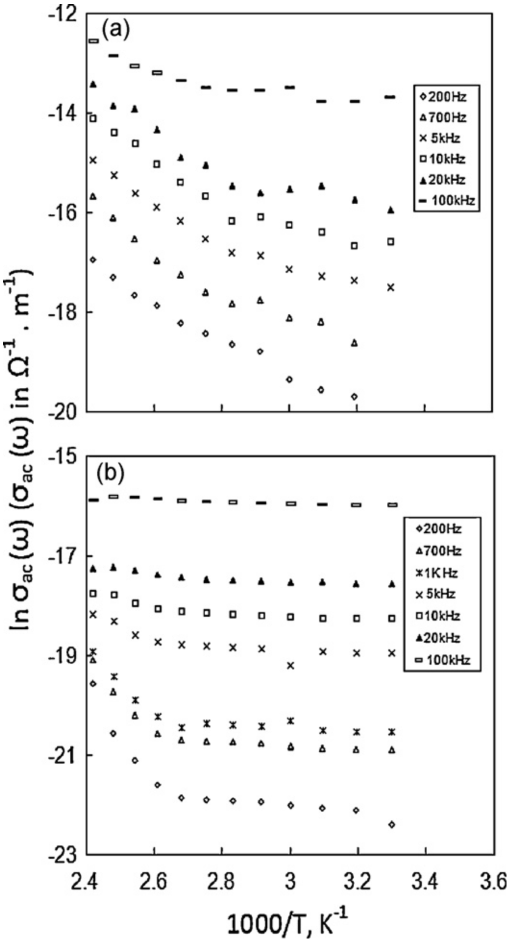

Fig. 2. Temperature dependence of ac conductivity $\sigma_{ac}(\omega)$ at different frequencies for (a) $GeSe_3Tl_{0.3}$ of thickness 333 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 330 nm.

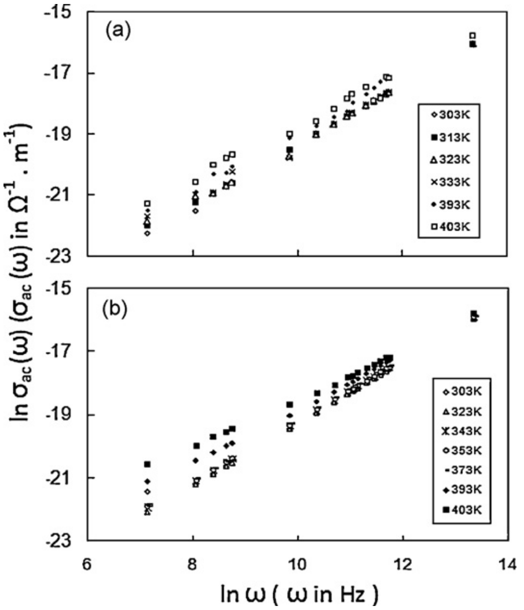

Fig. 3. Frequency dependence of ac conductivity $\sigma_{ac}(\omega)$ at different temperatures for (a) $GeSe_3Tl_{0.3}$ of thickness 333 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 330 nm.

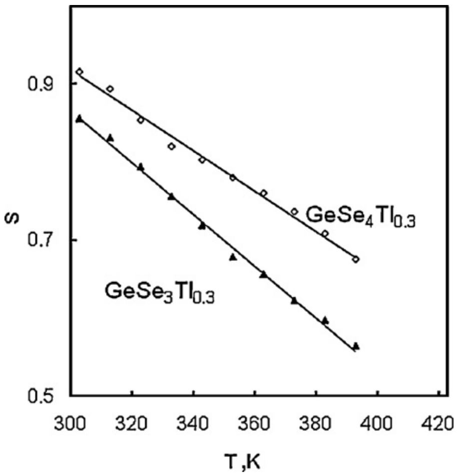

Fig. 4. Temperature dependence of the average value of the frequency exponent s for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films.

According to the correlated barrier-hopping (CBH) model, values of s are found to decrease with increasing temperature [20]. This means that the present experimental results agree well with CBH model. The critical test of CBH comes from the temperature dependence of ac conductivity and its frequency exponent s. So, the frequency dependence of $\sigma_{ac}(\omega)$ can be explained in terms of CBH model. The expression for s derived on the basis of this model is given by Elliott [10] as,

$$s = 1 - \frac{6KT}{W_m + KT\ln(\omega\tau_o)} \tag{2}$$

and this model gives the ac conductivity in the form

$$\sigma_{ac}(\omega) = \frac{\pi^3}{12} N^2 \xi_1 \xi_o \omega R_\omega^6 \tag{3}$$

The obtained data for ac conductivity given in Table 1 can be explained either by the effect of Se content on Ge–Se–Tl system bond or its effect on the concentration of the localized states N.

In view of the above discussion on the nature of the additional charged defects-induced by Tl dopant, it is quite clear that these defects are taking part in the hopping process.

3.2. Temperature and frequency dependence of the dielectric constant ε'

The variation of the dielectric constant ε' with frequency and temperature was studied for the investigated film compositions with different thicknesses in the investigated ranges of frequency and temperature.

Fig. 5a and b shows the temperature dependence of the dielectric constant ε' at different frequencies for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films with thicknesses 181.3 nm and 463 nm respectively. It is clear from these figures that ε' increases as the temperature increases over the whole investigated range of frequency.

The increase of ε' with increasing temperature can be attributed to the fact that the dipoles in polar materials cannot orient themselves at low temperatures. When the temperature is increased the orientation of dipoles is facilitated and this increases the value of the orientational polarization, which increases ε'.

Fig. 6a and b shows the frequency dependence of the dielectric constant ε' at different temperatures for $GeSe_3Tl_{0.3}$ and $GeSe_4TL_{0.3}$ with thicknesses 155 nm and 330 nm respectively. It is clear from these figures that ε' decreases with increasing frequency. The variation of ε' with frequency cannot be noticed clearly at lower values of temperature but this variation is more obvious at higher temperatures.

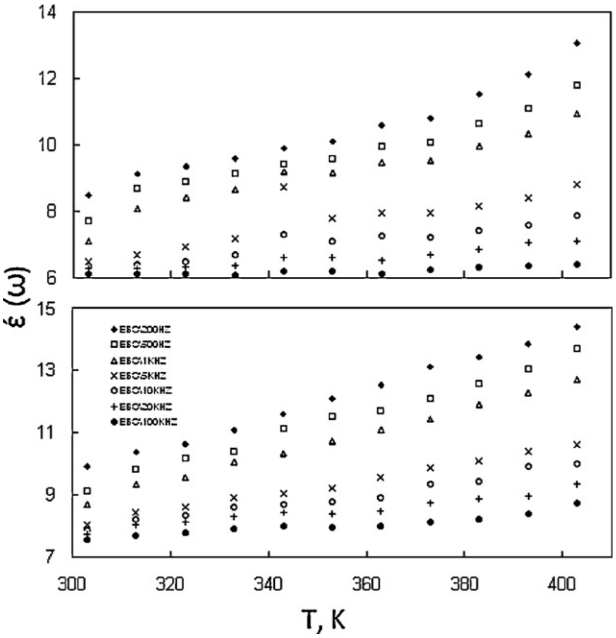

Fig. 5. Temperature dependence of the dielectric constant ε' at different frequencies for (a) $GeSe_3Tl_{0.3}$ of thickness 181.3 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 463 nm.

The decrease of ε' with frequency can be attributed to the fact that at low frequencies, the dielectric constant ε' for polar materials is due to the contribution of multicomponent of polarizability, deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization) [21]. When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is increased the dipole will be completely unable to follow the field and the orientational polarization stopped, so ε' decreases approaching a constant value at a higher frequency due to the interfacial or space charge polarization.

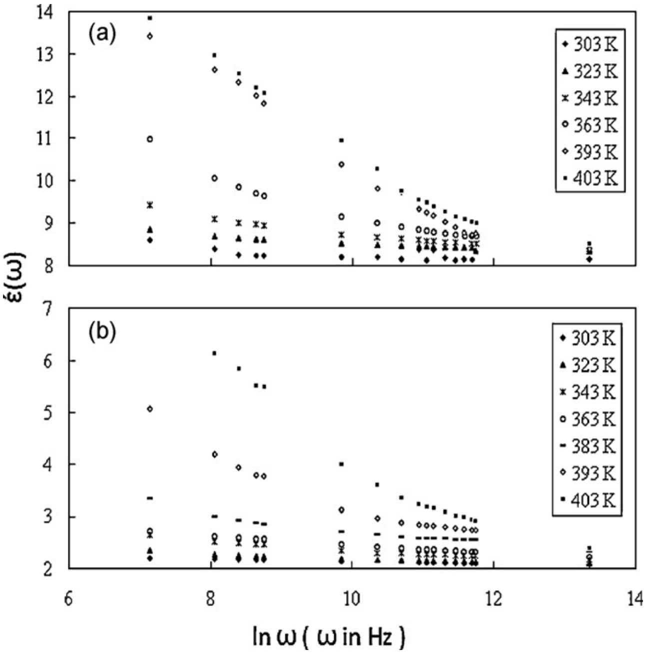

Fig. 6. Frequency dependence of the dielectric constant ε' at different temperatures for (a) $GeSe_3Tl_{0.3}$ of thickness 155 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 330 nm.

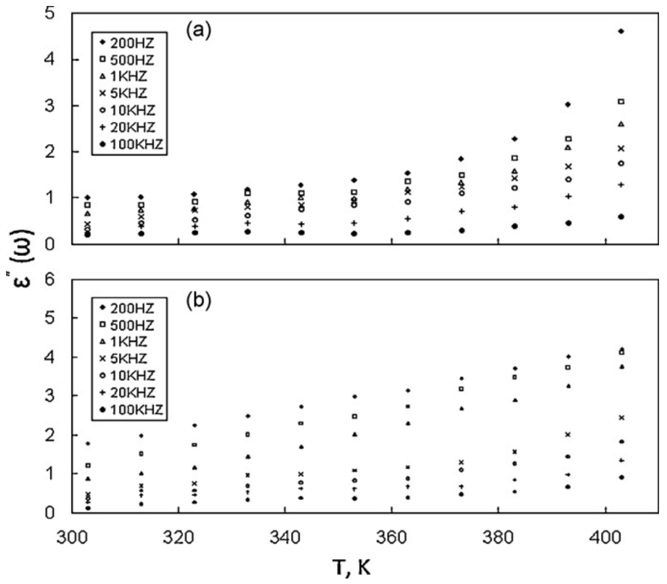

Fig. 7. Temperature dependence of the dielectric loss ε'' at different frequencies for (a) $GeSe_3Tl_{0.3}$ of thickness 181.3 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 463 nm.

Values of the relative dielectric permittivity ε' (dielectric constant) obtained from capacitance measurements are 3.015 and 2.243 respectively for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films of thicknesses 333 nm and 330 nm at 100 kHz.

3.3. *Temperature and frequency dependence of the dielectric loss ε''*

Fig. 7a and b shows the temperature dependence of the dielectric loss ε'' at different frequencies for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films of thicknesses 181.3 nm and 463 nm respectively. It is clear from these figures that ε'' increases with increasing temperature. Since the dielectric relaxation studies are important to understand the origin of dielectric losses in a material, the variation of ε'' with temperature can be explained by Stevels [22] who divided the relaxation phenomena into three parts: conduction losses, dipole losses and vibrational losses. Generally, it is obvious that at low temperature, values of conduction losses have minimum value since it is proportional to $\sigma_{ac}(\omega)$. As the temperature decreases, $\sigma_{ac}(\omega)$ decreases and so the conduction losses decreases.

The frequency dependence of the dielectric loss ε'' at different temperatures for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films of thicknesses 155 nm and 463 nm respectively can be clarified by plotting ε'' against $\ln\omega$, as given in Fig. 8a and b. It is clear from these figures that ε'' decreases with increasing frequency. The decrease of ε'' with frequency can be attributed to the fact that at low frequencies, the high value of ε'' is due to the migration of ions in the material. At moderate frequencies ε'' is due to the contribution of ion jump, conduction loss of ions migration and ion polarization loss. At high frequencies the ion vibrations may be the only source of dielectric loss, so ε'' has the minimum value.

Mott et al. [11,23] expressed that when the sample is placed in an electric field, electron hops take place between localized sites. The charge carriers that move between these sites hop from a donor to an acceptor state. In this respect each pair of sites forms a dipole. So, it can be shown that the dielectric properties of chalcogenide glasses can be interpreted, by considering a set of dipoles. As long as the temperature is high enough [24], which is experimentally verified, below a certain temperature the dielectric permittivity does not depend on temperature. It is supposed that each dipole has a relaxation time depending on its activation energy [25] which can

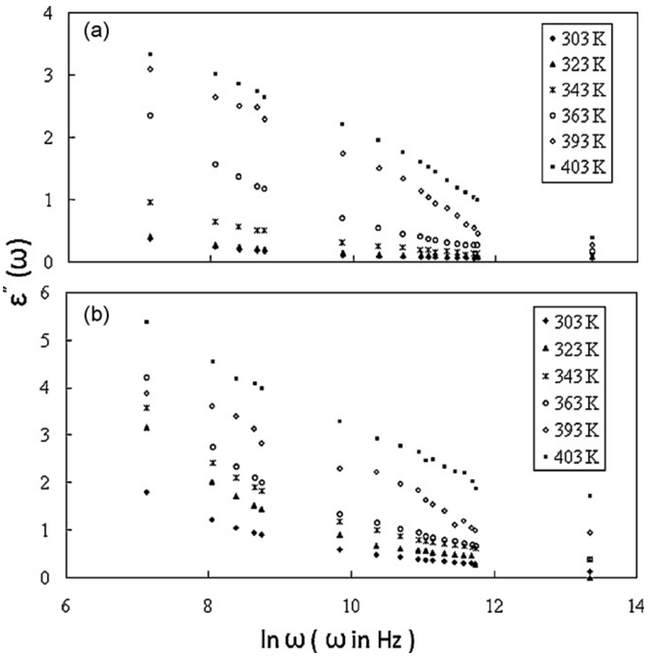

Fig. 8. Frequency dependence of the dielectric loss ε'' at different temperatures for (a) $GeSe_3Tl_{0.3}$ of thickness 155 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 463 nm.

be essentially attributed to the existence of a potential barrier W_M, over which the carriers must hop [26]. This W_M, as proposed by Elliott [10,27] is due to the Coulombic interaction between neighbouring sites forming a dipole.

At certain value of frequency ($\omega = 2\pi\nu$), the dielectric loss ε'' increases with $\sigma_{ac}(\omega)$, $\sigma_{ac}(\omega) = \omega \cdot \varepsilon''$ [28]. Since $\sigma_{ac}(\omega)$ increases with increasing Se content, so ε'' must increase with increasing Se content.

The obtained data of the frequency dependence of ε'' is represented as $\ln \varepsilon''$ versus $\ln \omega$ at different temperatures in Fig. 9a and b for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films of thicknesses 333 nm and 330 nm respectively as representative examples.

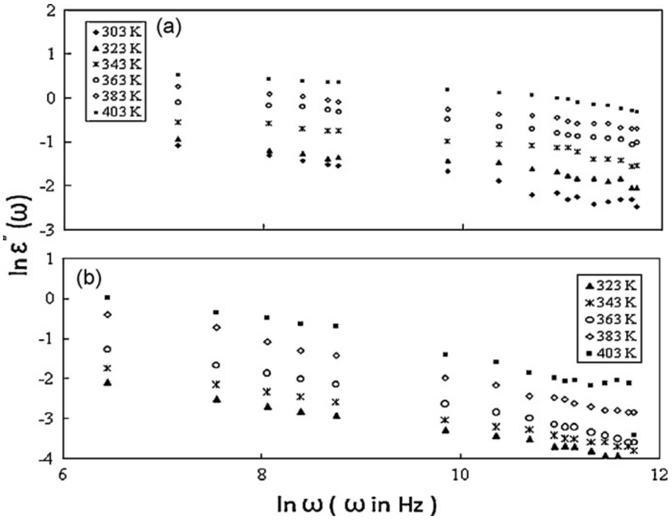

Fig. 9. Plot of $\ln \varepsilon''$ versus $\ln \omega$ at different temperatures for (a) $GeSe_3Tl_{0.3}$ of thickness 333 nm and (b) $GeSe_4Tl_{0.3}$ of thickness 330 nm.

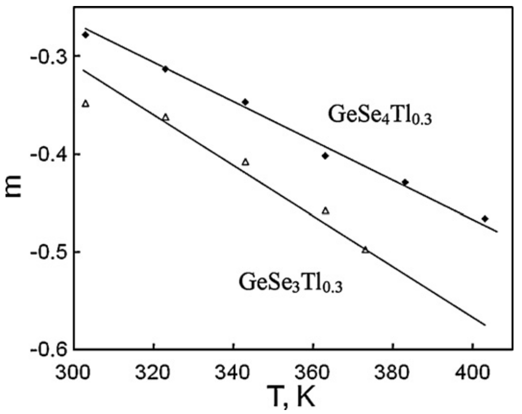

Fig. 10. Temperature dependence of the experimental mean values of m for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ films.

According to the following equation [29,30]

$$\varepsilon' = A\omega^m \tag{4}$$

where A is a constant, the power m was calculated from the negative slopes of the obtained straight lines of Fig. 9a and b at different temperatures. The obtained values of m are displayed as a function of temperature in Fig. 10. It is clear from this figure that m decreases linearly with increasing temperature for all compositions. In fact, this result is satisfied if we consider the empirical law [31,32]: $\sigma_{ac}(\omega) = \omega \cdot \varepsilon'' = A\omega^s$. It is obvious that if s is temperature dependent [10,16], m should consequently depend on T, according to Giuntini [29] equation,

$$m = \frac{-4k_BT}{W_M} \tag{5}$$

where W_M is the maximum barrier height (the energy required to move the electron from one site to infinite). From the slopes of the lines of Fig. 10, W_M was calculated according to Eq. (5). The obtained values of W_M for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ samples are 0.0563 and 0.106 eV respectively. The obtained values of W_M are in good agreement with the theory of hopping of charge carrier over potential barrier as suggested by Elliott [10] in the case of chalcogenide glasses.

4. Conclusions

Measurements of the ac conductivity $\sigma_{ac}(\omega)$ for $GeSe_3Tl_{0.3}$ and $GeSe_4Tl_{0.3}$ thin films in the temperature range (303–403 K) and frequency range (10^2–10^5 Hz) revealed the following conclusions:

(1) AC conductivity $\sigma_{ac}(\omega)$ increases with increasing temperature at different frequencies and it is proportional to ω^s, where s is the frequency exponent that decreases linearly with increasing temperature. These results were interpreted in terms of Elliott's theory, which assumes correlated barrier hopping CBH between the charged defect centers. The frequency exponent s increases also with the increase of Se content which due to the effect of Se in the ionic character of the bonds in amorphous network.

(2) The dielectric constant ε' increases with increasing temperature and decreases with increasing frequency, which can be explained in terms of the change of multicomponent of polarization: deformational polarization (electronic and ionic) and relaxation polarization (orientation and interfacial) with temperature and frequency. The obtained values of ε' at 100 kHz showed that it decreases with increasing Se content.

(3) The dielectric loss ε'' increases with increasing temperature and decreases with increasing frequency, which can be explained in terms of the change of different losses (conduction, dipole

relaxation and deformational) of the relaxation phenomenon with temperature and frequency.

(4) Values of the maximum barrier height W_M that calculated according to Giuntini equation are in good agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott in the case of chalcogenide glasses.

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