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EFFECT OF Cd ADDITION ON THE AC CONDUCTIVITY AND DIELECTRIC PROPERTIES OF $Ge_{70}Te_{30}$ FILMS

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$Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films of different thicknesses were prepared by thermal evaporation technique. X-ray diffraction patterns analysis showed that the films were in the amorphous state. The ac conductivity and dielectric properties of the obtained films in the frequency range (10^2-10^5Hz) has been investigated. The ac conductivity is found to be proportional to ω^s where $s<1$. The temperature dependence of both the ac conductivity and the parameter s is reasonably interpreted by the correlated barrier hopping CBH model. The maximum barrier height W_M ,for each composition calculated from dielectric measurements according to Guintini equation, agrees with that proposed by the theory of hopping of charge carriers over potential barrier as suggested by Elliott in case of chalcogenide glasses.

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Keywords: Ge-Te thin films; Dielectric properties; Cd addition; XRD; Conductivity

1. Introduction

Research on electrical and dielectric properties of amorphous chalcogenide materials has accelerated in recent years. This is because electronic applications have continuously provided the impetus pushing the development of new materials in a fascinating and rich variety of applications [1-3]. The common feature of this class of glasses is the presence of localized states in the mobility gap due to the absence of long-range order as well as various inherent defects [4-6]. The hopping conduction can be easily distinguished from that of the band conduction by measuring the frequency dependence of conductivity [7], which as expected, is due to conduction in localized states. Measurements of frequency dependent electrical conductivity of amorphous chalcogenides are, therefore powerful tool for obtaining information about these states. This led to adapt and to elaborate models allowing the electronic properties of these materials to be described [8-12].

The present study deals with some experimental observations of the temperature and frequency dependence of ac conductivity and dielectric properties of $Se_{70}Te_{30-x}Cd_x$ (x= 0, 10) films of different thicknesses to understand the conduction mechanism in these materials.

2. Experimental techniques

Glassy alloys of $Se_{70}Te_{30-x}Cd_x$ (x= 0, 10) were prepared by a quenching technique as mentioned before [13]. Thin films with different thicknesses of the investigated glasses (211-491 nm) were deposited under vacuum of 10^{-5} Torr, by thermal evaporation technique using molybdenum boats at constant rate on dry-clean glass substrates, using a coating unit (Edward 306 A). The substrate temperature was held at that of the room during deposition. The film thickness was measured by Tolansky's interferometric method. X-ray diffraction patterns obtained for the films reveal the amorphous nature of the structure of the films.

For ac measurements, films were sandwiched between two Al electrodes. A programmable automatic RLC bridge (PM 6304 Philips) was used to measure the sample impedance Z, the capacitance C_X and the loss tangent tan δ directly. All investigated samples are represented on 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: $\sigma_t(\omega) = d/Z A$, where d is the thickness of the film and A is the cross sectional area. The dielectric constant was calculated from the equation: $\varepsilon_1 = dC_X/A\,\varepsilon_o$, where ε_o is the permittivity of free space. The dielectric loss ε_2 was calculated from the equation: $\varepsilon_2 = \varepsilon_1 \tan\delta$, where $(\delta = 90 - \phi)$, ϕ is the phase angle. Films are annealed in air at 373 K for 2 h. The measurements were carried out through the temperature range (298-383 K) and frequency range (10^2-10^5 Hz). The temperature measurements were recorded by means of digital multimeter (Protec 81) provided by a chromel-alumel thermocouple adjacent to the sample.

3. Results and discussion

3.1 Frequency and temperature dependencies of ac conductivity

A common feature to all amorphous semiconductors is that ac electrical conductivity $\sigma_{ac}(\omega)$ increases with increasing frequency according to the equation[14].

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} = C\,\omega^s \tag{1}$$

where ω is the angular frequency (ω = 2πf), $\sigma_{tot}(\omega)$ is the measured total electrical conductivity, σ_{dc} is the dc electrical conductivity, s is the frequency exponent (s<1) and C is constant dependent on temperature. It is found that the ω^s dependence of ac conductivity $\sigma_{ac}(\omega)$ is a general characteristic for chalcogenide glasses up to a frequency of 10^6 Hz. Fig. 1 a,b shows a representative example for the relation between $\ln\sigma_{ac}(\omega)$ and $\ln\omega$ for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films of thicknesses 211 nm and 444 nm respectively at different temperatures. It is clear from the figure that $\sigma_{ac}(\omega)$ increases linearly with increasing frequency according to equation (1). The same behavior was obtained for all investigated films. Values of the frequency exponent s were calculated for all the investigated samples of different thicknesses from the slopes of the linear lines of $\ln\sigma_{ac}(\omega) = f(\omega)$ through the studied frequency and temperature ranges. It is observed that the frequency is found to have a pronounced effect on conductivity at relatively lower temperatures. The temperature dependence of the mean value of s for the investigated films is shown in Fig. 2. It is seen that $\bar{s}$ decreases as the temperature increases, independent on film thickness in the investigated range.

In most chalcogenide glasses the obtained values of s ranged from 0.7 to 1 at room temperature, and have a tendency to decrease with increasing temperature[15]. Therefore, the correlated barrier hopping model CBH [11] has been extensively applied to most chalcogenide semiconductors. The frequency exponent s is found to decrease with increasing temperature, as

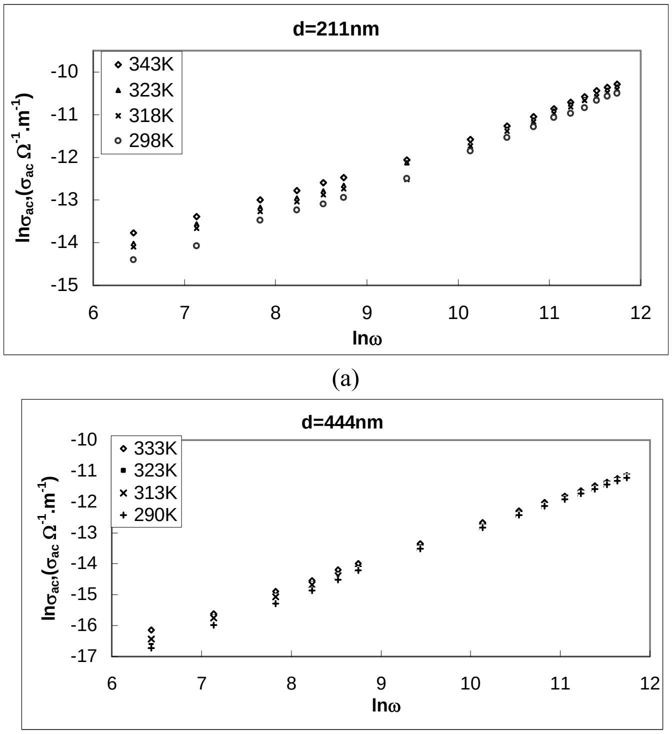
$$S = 1 - \frac{6kT}{W_M + [kT\ln(\omega\tau_o)]} \tag{2}$$

This means that the obtained experimental results agree with the correlated barrier hopping model CBH.

According to the Austin-Mott formula[16], based on CBH model, ac conductivity $\sigma_{ac}(\omega)$ can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level. $\sigma_{ac}(\omega)$ is related to the density of states $N(E_f)$ at the Fermi level by:

$$\sigma_{ac}(\omega) = (\pi/3)\,[N(E_f)]^2\,K\,T\,e^2\,\alpha^{-5}\,\omega\,[\ln(\upsilon_{ph}/\omega)]^4 \tag{3}$$

where α is the exponential decay parameter of the localized states wave function, and υ_{ph} is the phonon frequency. By assuming $\upsilon_{ph} = 10^{12}$ Hz and $\alpha^{-1} = 10$Å [17], the density of states is calculated and is given in Table (1) for the $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ at frequency 1kHz. The value of $N(E_f)$ is found to decrease with Cd addition.



(a)

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Fig. 1. Frequency dependence of the electrical conductivity (σ_{ac}) for: a- $Se_{70}Te_{30}$ film of thickness 211 nm. b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 444 nm.

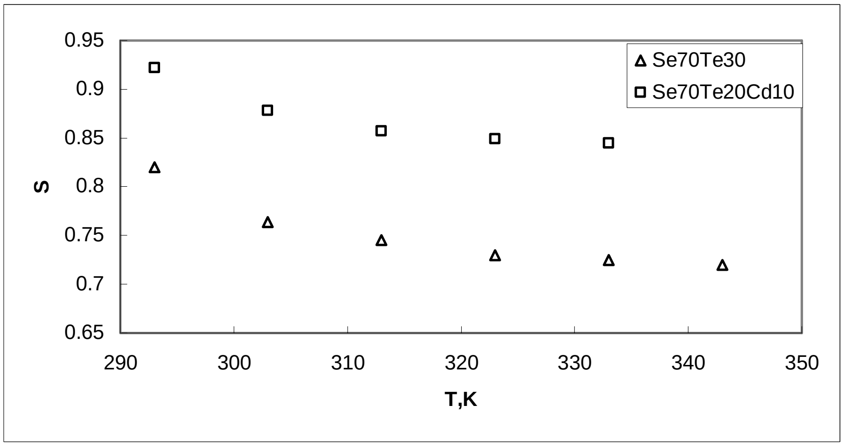
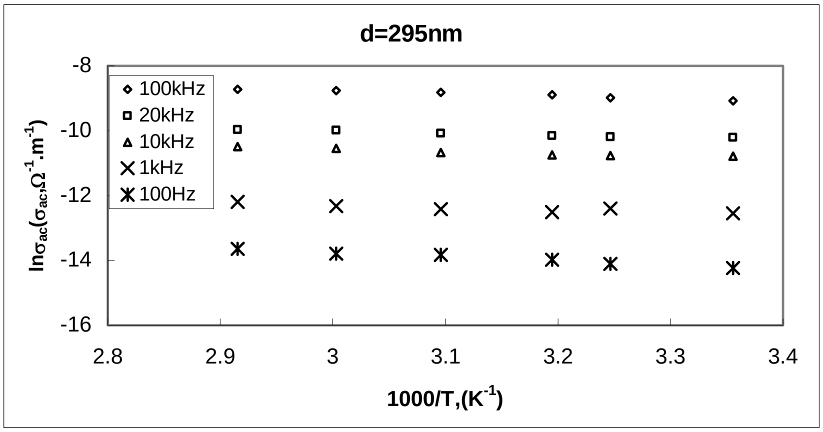


Fig. 2. Temperature dependence of the frequency exponent s for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}$ Cd_{10} films.

Temperature dependence of the ac conductivity $\sigma_{ac}(\omega)$ at different frequencies was studied for the investigated films. Fig. 3a,b shows a plot of ln $\sigma_{ac}(\omega)$ against 1000/T for the investigated film compositions of thicknesses 295 nm and 492 nm respectively as a representative example. It is clear from this figure that ln $\sigma_{ac}(\omega)$ increases linearly with the reciprocal of absolute temperature. This suggested that the ac conductivity is a thermally activated process from different localized states in the gap or its tails. The activation energy of conduction, $\Delta E_{\sigma}(\omega)$ is calculated at different frequencies from the slopes of the straight lines, obtained for all investigated thicknesses using the well known equation $\sigma=\sigma_o \exp(-\Delta E_\sigma(\omega)) / kT)$. The obtained values of $\Delta E_\sigma(\omega)$ are independent on film thickness in the investigation range. The frequency dependence of the activation energy for the investigated films is shown in Fig. 4 for all film thicknesses of both compositions. It clear that $\Delta E_\sigma(\omega)$ decreases with increase of frequency. It is also noticed that $\Delta E_\sigma(\omega)$ at any frequency is much lower than the dc activation energy obtained before (0.41 eV in case of $Se_{70}Te_{30}$ and 0.5 eV in case of $Se_{70}Te_{20}Cd_{10}$ films)[13] over the same range of temperature. This seems to be obvious since the charge carriers in the dc conduction choose the easiest paths which include some large jumps, while this is not so important in the ac conduction[18]. It can also be seen that $\Delta E_\sigma(\omega)$ tends to decrease with increasing frequency as found for other amorphous materials[19-21]. The increase of the applied field frequency enhances the electronic jumps between the localized states, consequently the activation energy $\Delta E_\sigma(\omega)$ decreases with increasing frequency. The smaller values of the ac activation energy compared with that of dc activation energy and the increase of σ_{ac} with the increase of frequency confirm the hopping conduction to be the dominant mechanism.



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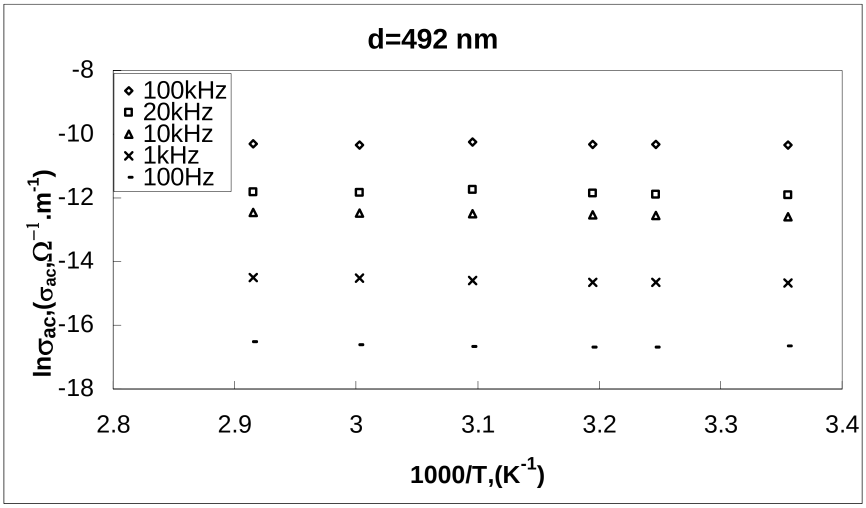

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Fig. 3. Temperature dependence of the ac electrical conductivity (σ_{ac}) fora- $Se_{70}Te_{30}$ film of thickness 295 nm. b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 492 nm.

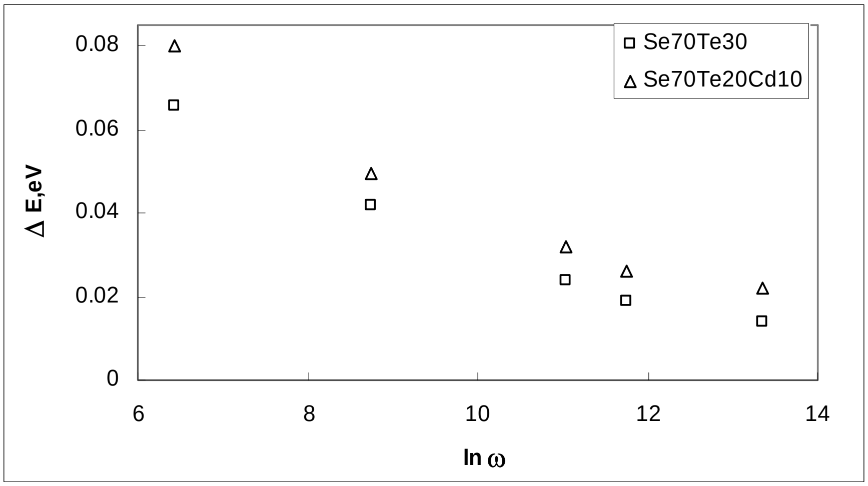


Fig. 4. Frequency dependence of the ac activation energy ($\Delta E(\omega)$) for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films.

Fig. 5 shows the relation between $\ln\sigma_{ac}(\omega)$ and $\ln\omega$ at room temperature for two films of $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ with nearly the same thickness. It is clear from this figure that at any frequency $\sigma_{ac}(\omega)$ for $Se_{70}Te_{20}Cd_{10}$ is smaller than that for $Se_{70}Te_{30}$.

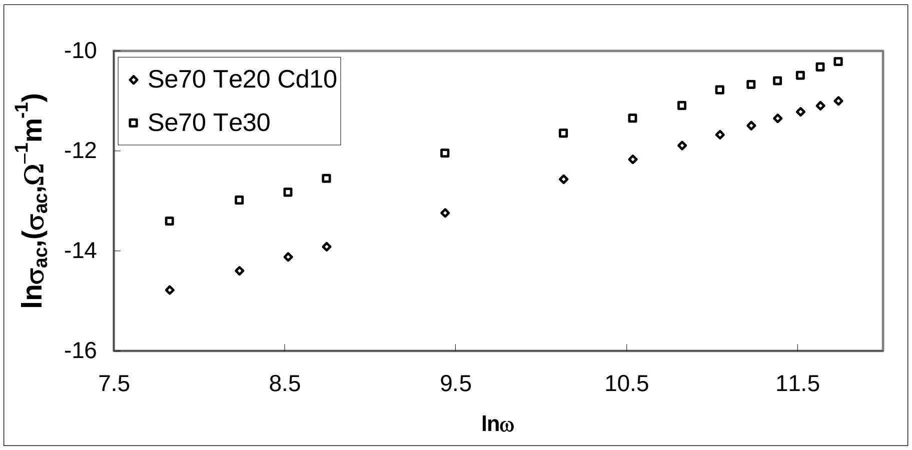
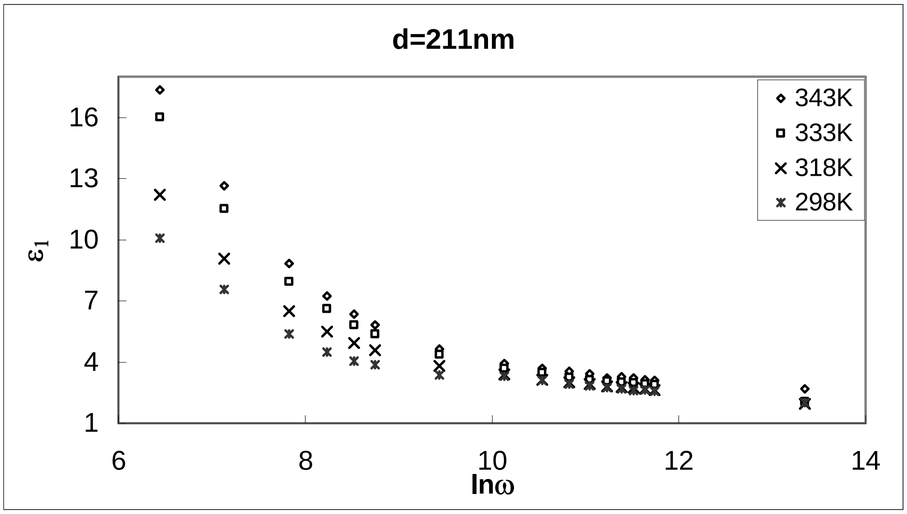


Fig. 5. Frequency dependence of the room temperature ac conductivity (σ_{ac}) for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films of nearly the same thickness.

3.2 Frequency and temperature dependencies of the dielectric constant ε_1

The variation of the dielectric constant ε_1 with frequency and temperature was studied for the investigated film compositions in the investigated ranges of frequency and temperature. The frequency dependence of the dielectric constant ε_1 at different temperatures for films of thicknesses 211 nm and 303 nm as a representative example is illustrated in Fig. 6a,b. It is clear from the figure that ε_1 decreases with increasing frequency. The same behavior was obtained for all investigated films. The obsorved decrease of ε_1 with frequency is greater at higher temperatures. The decrease of ε_1 with frequency can be attributed to the fact that at low frequencies ε_1 for polar materials is due to the contribution of multicomponent of polarization mechanisms (electronic, ionic, orientation and interfacial)[22]. When the frequency is increased the dipoles can not rotate sufficiently rapidly, so that their oscillations lag behind those of the field. As the frequency is further raised the dipole will be completely unable to follow the field and the orientation polarization ceases, so ε_1 decreases approaching a constant value at high frequencies due to the interfacial polarization only.



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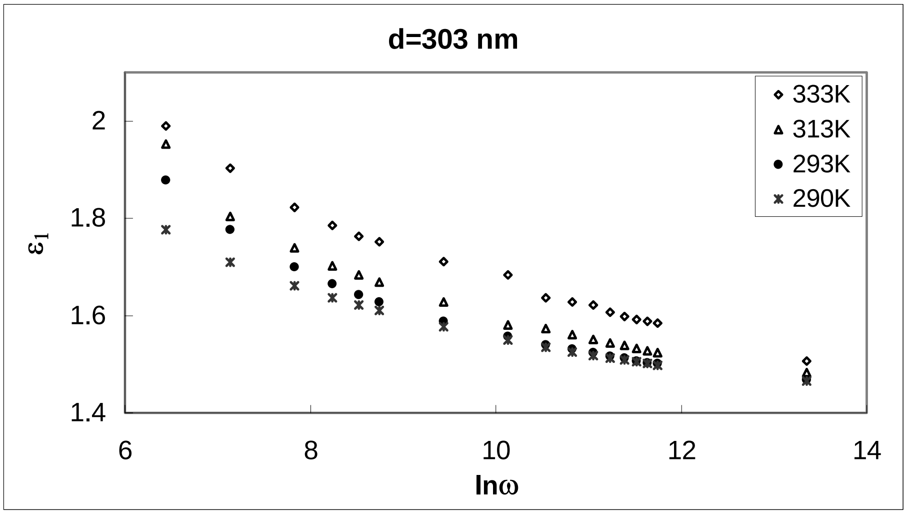
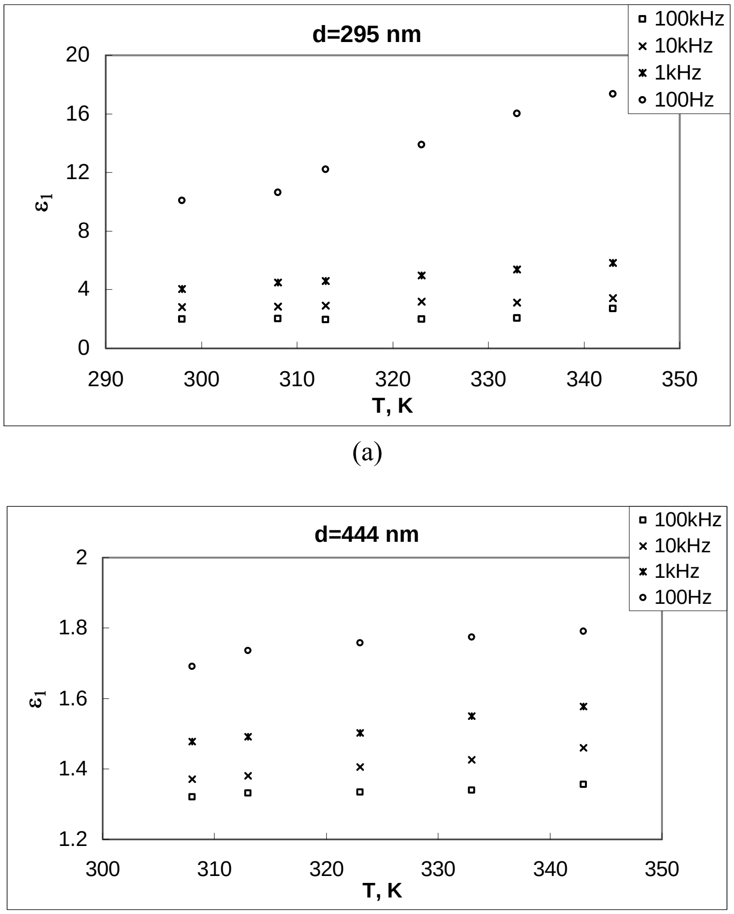


(b)

Fig. 6. Frequency dependence of the dielectric constant ε_1 for a- $Se_{70}Te_{30}$ film of thickness 211 nm. b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 303 nm.

Fig. 7a,b shows the temperature dependence of the dielectric constant ε_1 at different frequency values for the investigated films of thicknesses 295 nm and 444 nm as a representative example. It is clear from the figure that ε_1 increases as the temperature increases over the whole investigated range of frequency. The increase of ε_1 with temperature can be attributed to the fact that dipoles in polar materials can not orient themselves at low temperatures. When the temperature is raised the orientation of dipoles is facilitated and thus increases the orientational polarization, and in turn increases ε_1.



(a)

(b)

Fig. 7. Temperature dependence of the dielectric constant ε_1 for a-$Se_{70}Te_{30}$ film of thickness 295 nm.
b- $Se_{70}Te_{20}$ Cd_{10} film of thickness444 nm.

The addition of Cd (10 at%) to $Se_{70}Te_{30}$ composition leads to decrease the value of dielectric constant ε_1 for $Se_{70}Te_{20}Cd_{10}$ composition as shown in Fig. 8 for two films of nearly the same thickness. It is clear from the figure that the value of the dielectric constant ε_1, at any frequency, for $Se_{70}Te_{30}$ films is larger than that for $Se_{70}Te_{20}Cd_{10}$ films. This decrease can be understood as follows:

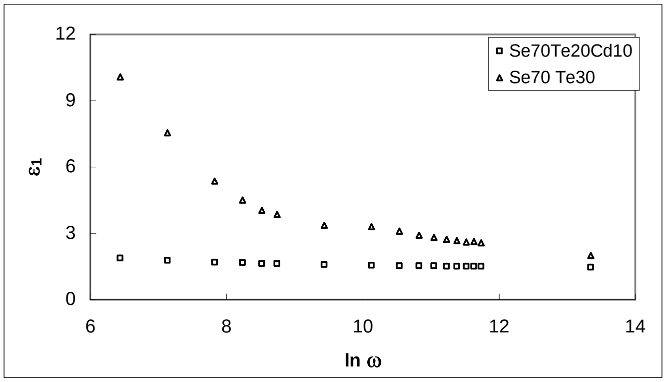
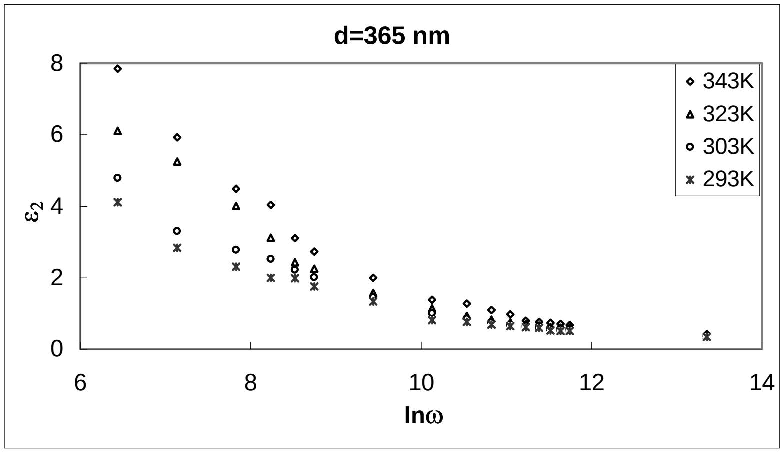


Fig. 8. Frequency dependence of the room temperature dielectric constant ε_1 for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}$ Cd_{10} films of nearly the same thickness.

Glasses containing Se are known to consist of a mixture of polymeric chains and Se_8 rings. Also Te enters as copolymer chains and tends to reduce the number of Se_8 rings [23]. Simultaneously, it increases the number of Se and Te atoms in the chain structure. The addition of Cd makes bonds with Se and Te atoms, producing Se-Cd bonds [24] of higher strength, than other bonds in the network structure. This leads to decrease the number of polymeric chains in the structure. Since the dielectric constant provides insight into the nature of bonding in the system. Thus the addition of Cd to Se-Te system leads to decrease the weaker bonds density in the investigated compositions which can responsive to ac electric field much easier than the stronger bonds (Cd-Se) and hence the dielectric constant ε_1 decreases. This conclusion is in agreement with the obtained results for the investigated compositions.

3.3 Frequency and temperature dependencies of the dielectric loss ε_2

Frequency dependence of the dielectric loss ε_2 for the investigated films of thicknesses 365 nm and 444 nm as a representative example is shown in Fig. 9a,b. It is clear from this figure that ε_2 decreases with increasing frequency in the investigated ranges of temperature and frequency . The decrease of ε_2 with frequency can be attributed to the fact that, at low frequencies, the value of ε_2 is due to the migration of ions in the material. At moderate frequencies ε_2 is due to the contribution of ions jump, conduction loss of ions migration, and ions polarization loss. At high frequencies ion vibrations may be the only source of dielectric loss and so ε_2 has the minimum value.



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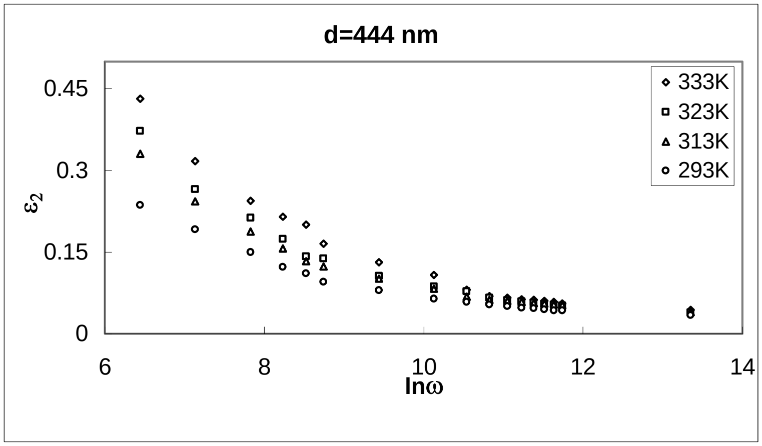


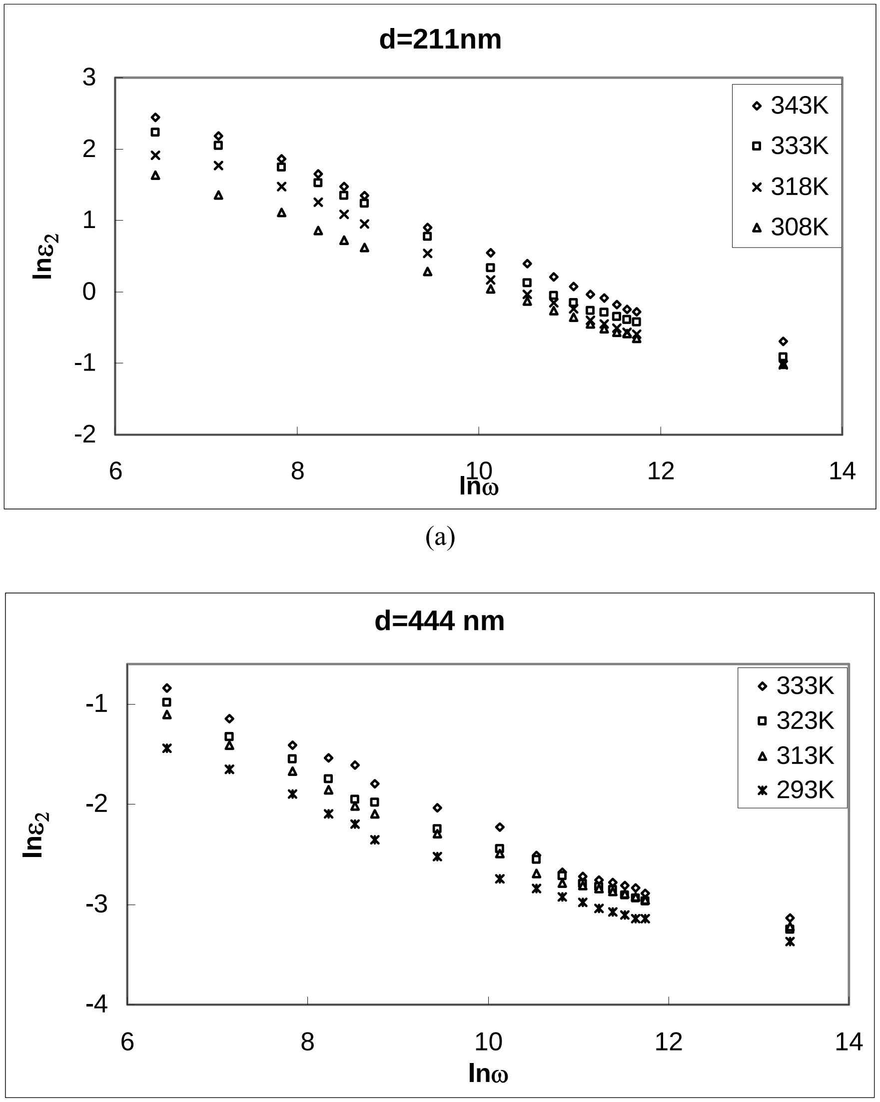
(b)

Fig. 9. Frequency dependence of the dielectric loss ε_2 for a- $Se_{70}Te_{30}$ film of thickness 365 nm. b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 444 nm.

The obtained data for the frequency dependence of ε_2 is represented as lnε_2 vs lnω at different temperatures in Fig. 10a,b satisfying the equation[25]:

$$\varepsilon_2 = A_1\, \omega^m \tag{4}$$

where A_1 is a constant, the power m was calculated from the negative slopes of the obtained straight lines of Fig. 10a,b.



(a)

(b)

Fig. 10. Plot of ln ε_2 versus ln ω at different temperatures for a- $Se_{70}Te_{30}$ film of thickness 211 nm. b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 444 nm.

This relation can be written as:

$$\varepsilon_2 = (\varepsilon_o - \varepsilon_\infty)\, 2\pi^3\, \mathrm{N}\, (\frac{n\, \mathrm{e}^2}{\varepsilon_o})^3\, \mathrm{k\, T}\, \tau_o^m\, W_{\mathrm{M}}^{-4} \tag{5}$$

Where n is the number f electrons that hop, N the concentration of localized states, ε_o the static dielectric constant, ε_∞ infinite dielectric constant arising from all polarization processes at higher frequencies[8,11],W_M the maximum barrier height and m is a constant.

Variation of m with temperature is illustrated in Fig. 11 for both film compositions. It is clear that m decreases linearly with temperature according to Guintini equation [26].

$$m = - 4k_BT / W_M \tag{6}$$

The calculated value of W_M are given also in Table 1. The values are in good agreement with the theory of single polaron hopping of charge carrier over a potential barrier as suggested by Elliott[11] and shimakawa[12] in case of chalcogenide glasses.

Table 1. AC parameters of $Se_{70}Te_{30}$ and $Se_{70}Te_{20}$ Cd_{10} thin films.

Composition	$N_{EF}X10^{22}$ eV^{-1} m^{-3}	W_M eV
$Se_{70}Te_{30}$	4.42	0.142
$Se_{70}Te_{20}Cd_{10}$	1.45	0.18

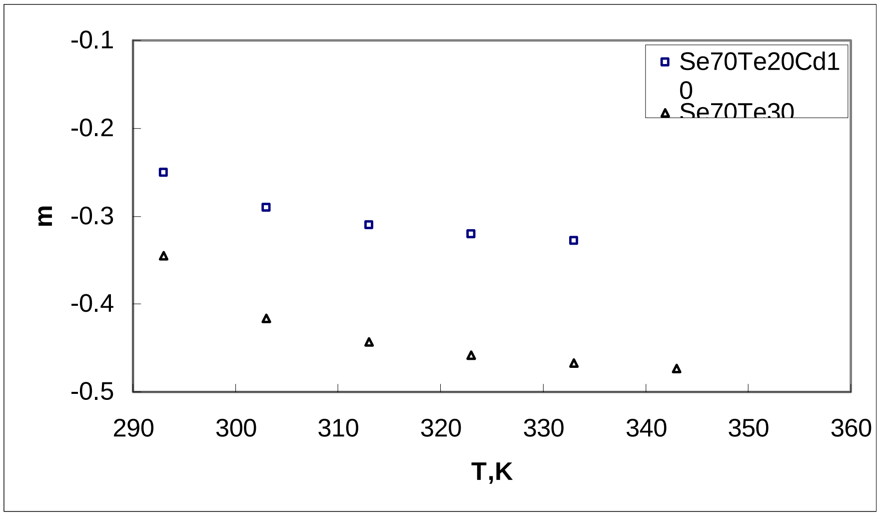
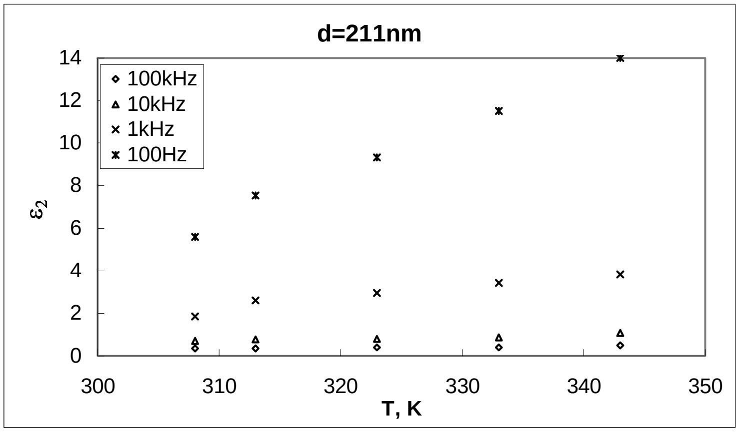


Fig. 11. Temperature dependence of the power m for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}$ Cd_{10} films.

Fig. 12 a,b shows the temperature dependence of the dielectric loss ε_2 of the investigated film compositions of thicknesses 211 nm and 444 nm respectively as a representative example at different frequency values. It is clear from the figure that ε_2 increases with increasing temperature. The loss which is attributed to conduction presumably involves the migration of ions over large distances (ions jump). This motion is the same as that occurring under direct current conditions. The ions jump over the highest barriers in the network. As the ion moves, they give some of their energy to the lattice as heat and the amount of heat lost per cycle is proportional to ($\sigma_{ac}(\omega)$) [27]. At low temperatures, conduction losses, dipole losses and vibrational losses have the minimum value. However, at higher temperatures conduction, dipole and vibrational losses all increase and contribute to the dielectric loss. This will lead to the increase in ε_2 with increasing temperature.



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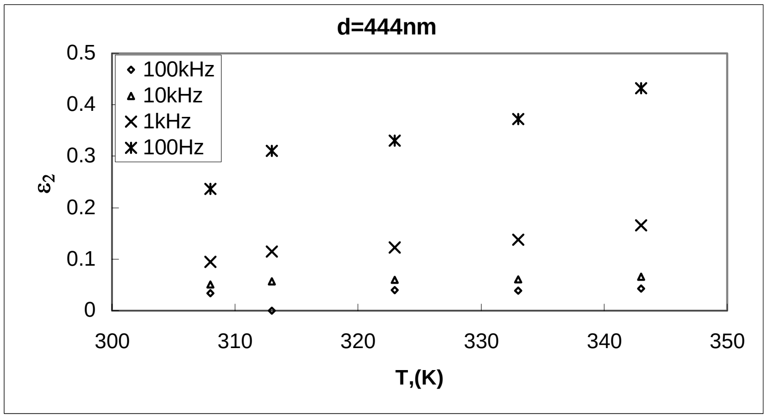

(b)

Fig. 12. Temperature dependence of the dielectric loss ε_2 for a- $Se_{70}Te_{30}$ film of thickness 211 nm.
b- $Se_{70}Te_{20}Cd_{10}$ film of thickness 444 nm.

The addition of Cd (10% at) to $Se_{70}Te_{30}$ leads to decrease the value of dielectric loss ε_2 as shown in Fig. 13 for both films of nearly the same thicknesses. The observed increase in the value of ε_2 for $Se_{70}Te_{30}$ films than that for $Se_{70}Te_{20}Cd_{10}$ films is consistent with the increase in ac conductivity for $Se_{70}Te_{30}$ films than that for $Se_{70}Te_{20}Cd_{10}$ films mentioned above in section (3.1), since ac conductivity is related to ε_2 by the following relation.

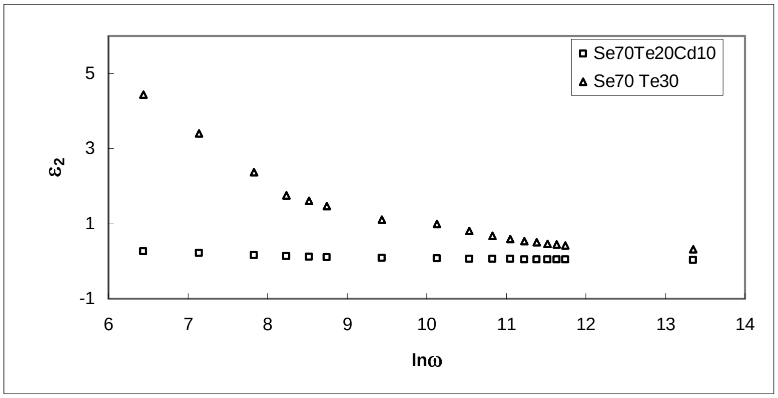

Fig. 13. Frequency dependence of the room temperature dielectric loss ε_2 for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films of nearly the same thickness.

$$\sigma_{ac}(\omega) = \varepsilon_o \, \omega \, \varepsilon_2(\omega) \tag{7}$$

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