

Dielectric properties in germanium doped chalcogenide glasses

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The temperature and frequency dependence of dc conductivity and dielectric parameters have been measured in a- $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2.5, 5$ and 15%) glasses in the temperature range (290-400K) and frequency range (120 Hz to 100 kHz). On the bases of observed results, dielectric dispersion is evidenced when Ge is incorporated in the a-Se-Te system. These results are explained on the basis of dipolar type dielectric dispersion. It is also observed that the dc conductivity decreases and the activation energy increases on incorporation of the Germanium in this system.

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1. Introduction

Chalcogenide glasses have received much attention in recent years, due to the extensive application in solid states devices. A good device is one, which has low cost and is fast, accurate and easy to use [1]. Chalcogenide, mostly Se-Te based, ternary compounds, have received particular attention [2-4], because of their high potential for application in electronics. The dc conductivity of amorphous semiconductors has been extensively studied to understand the conduction process in these materials [5]. Among these, selenium based chalcogenides glasses are more interesting, because these exhibit optical memory and photo darkening [6-7]. Thus the study of their electrical behavior is extremely important. The dielectric study of chalcogenide glasses has indicated that dielectric dispersion does exist at low frequencies even though these materials are covalently bonded. The origin and nature of dielectric losses in these materials has, therefore, become a matter of curiosity. Generally, the undoped chalcogenide glasses show low electrical conductivity values, which could mean a serious limit to their technological application. Certain additives are used to improve these properties. It was believed earlier that impurities have little effect on the properties of amorphous semiconductors as each impurity atom can satisfy its valence requirement by adjusting its nearest neighbor environment. However, Fritzsche et. al. [8] have shown that the effect of charged additives in lone-pair semiconductors depends on whether the charged additives equilibrate or not with valence alternation defects. Enormous interest has been shown to the study of a-Se-Te alloys. This is due to their great hardness, higher photosensitivity, higher crystallization temperature and smaller aging effects as compared to pure amorphous Se [9]. For many years, it was believed that foreign atoms couldn't modify the physical properties of chalcogenide glasses. However, recently, p to n transition has been reported [10-12] in binary Ge - Se, Se - Te and In-Se chalcogenide alloys, when third element is introduced in these glasses. Though the electrical and optical properties of these glasses have been studied by various scientists [13-18], only a little amount of work has been done on the dielectric properties. Since the dielectric properties of amorphous semiconductors are to a great

extent determined by the process of trapping of non-equilibrium charge carriers on localized centers of various depths, investigations into their characterization and mechanism are important to understand the energy distribution of the traps.

The purpose of this study is to report some of the electrical and dielectric features, and also the influence of germanium content on the properties of the a-Se-Te system, and to characterize its dependence on temperature and frequency. Here, germanium has been chosen as an additive material to the Se-Te system because germanium doped chalcogenide glasses have more thermal stability in wide temperature range due to its high melting points. One of the requirements for the application of these glasses in the case of high power laser radiation transport is their temperature stability. The maximum temperature up to which the fiber can be heated restricts the transmitted power of the laser radiation [19].

In the present paper, we have studied the temperature and frequency dependence of the dielectric constant and dielectric losses for bulk samples of a- $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ in the temperature range (290 to 425 K) and the frequency (120 Hz to 100 kHz) range.

2. Experimental

$(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2.5, 5$ and 15%) glasses are prepared by the melt quenching technique. Appropriate amounts of 99.999% purity elements were sealed in quartz ampoules under a vacuum of 10^{-5} Torr. The sealed ampoules were then placed in a Microprocessor-Controlled Programmable Muffle Furnace where the temperature was increased at the rate of 4 K per min. upto 1250 K. The ampoules were then kept at this temperature for 12 hours with frequent rocking to ensure the homogenization of the melt. The quenching was done in ice water. The quenched sample a- $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ was taken out by breaking the quartz ampoules. The amorphous nature of the glassy alloys was verified by X-ray diffraction. Bulk samples in the form of pellets (diameter = 1.0 cm, thickness = 0.11cm) were obtained by finally grinding the glassy alloys and compressing the powder under a pressure of 8 tons. The pellets were coated on both sides with silver paste. The coating was

done to confirm good electrical contact with the electrodes of the sample holder. The bulk sample was mounted between two steel electrodes inside a metallic sample holder for dielectric measurements. A vacuum of 10^{-3} Torr was maintained, in the sample holder, to avoid any effect of moisture absorption. The temperature was measured with a chromel alumel thermocouple mounted near the electrodes. A Keithley LCZ meter (Model 3330) was used for measuring capacitance and dissipation factor. To calculate the dielectric constant (ϵ') and dielectric loss (ϵ''), the parallel capacitance and the dissipation factor were measured simultaneously. To measure the dc conductivity of the sample, a dc voltage of 1.5 V was applied across the sample and the resulting current was measured by using a Keithley Electrometer (Model 617). These measurements were also made in the same sample holder in which dielectric measurements were taken.

3. Results and discussion

The temperature dependence of the dielectric constant (ϵ') and the dielectric loss (ϵ'') is studied at various frequencies (120 Hz to 100 kHz) for the prepared glassy a-(Se₈₀Te₂₀)_{100-x}Ge_x ($x = 0, 2.5, 5$ and 15%) alloys. The temperature range of measurement was from 290K to 425 K. The dielectric constant and the dielectric loss for a-Se₈₀Te₂₀ increase with the increasing temperature, different at different frequencies as shown in Fig. 1. Dielectric dispersion is observed even at room temperature. The variation of the dielectric constant and the dielectric loss with temperature is large at lower frequencies.

Fig. 2 shows the frequency response of the dielectric constant and the dielectric loss at different fixed temperatures for the a-Se₈₀Te₂₀ sample. It is observed that the dielectric constant and the dielectric loss decrease on increasing the frequency [20]. Fig. 3 shows the variation of the dielectric constant and the dielectric loss with temperature at different frequencies for the a-(Se₈₀Te₂₀)_{97.5}Ge_{2.5} sample. The temperature dependence of the dielectric constant (ϵ') at various frequencies for the (Se₈₀Te₂₀)_{97.5}Ge_{2.5} system indicates that the dielectric constant (ϵ') varies exponentially with temperature and that a strong dielectric dispersion is observed at above 340K temperatures. On incorporation the germanium, the dielectric constant and dielectric loss increase with temperature and have a high value as compared to pure Se-Te sample. Similar types of dispersion were also observed for other germanium concentrations in the (Se-Te)Ge system (Results not shown here). These results indicate

that the concentration of germanium 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 [21-26].

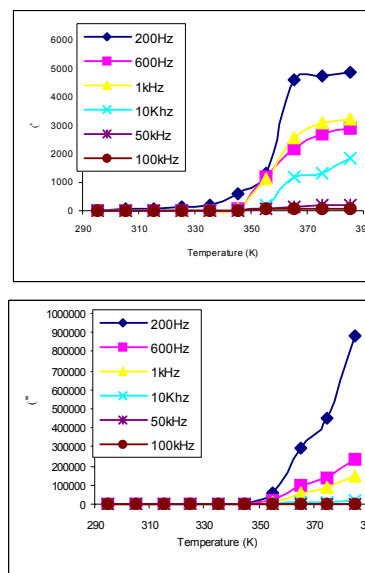


Fig. 1. Variation of dielectric constant and dielectric loss with temperature at different fixed frequency for the Se₈₀Te₂₀ system.

Fig. 4 shows that the variation of dielectric constant and dielectric loss with frequency at different fixed temperature for a-(Se₈₀Te₂₀)_{97.5}Ge_{2.5}. It is observed that the dielectric constant and the dielectric loss decrease with increase of frequency. Fig. 5 shows the variation of the dielectric constant (ϵ') and the dielectric loss (ϵ'') with temperature for different concentration of germanium at fixed frequency (200Hz). It is clear from this figure that the dielectric constant and the dielectric loss both increase with the increase of gallium concentration in a-(Se₈₀Te₂₀)_{100-x}Ge_x. The dielectric constant and the dielectric loss increase for all germanium concentrations. Fig. 6 shows the variation of the dielectric constant and the dielectric loss with germanium concentration also. The numerical values are given in Table 1. The dielectric constant and dielectric loss have a maximum at $x = 2.5\%$, and the sample with $x = 5\%$ shows the values less than undoped Se-Te glasses.

Table 1. Dielectric parameters of a-(Se₈₀Te₂₀)_{100-x}Ge_x system at 360 K and 200 Hz.

Sample Name	ϵ'	ϵ''	ϵ_{dc}''	σ_{dc} ($\Omega^{-1} \text{ cm}^{-1}$)	ΔE (eV)	σ_{dc} ($\Omega^{-1} \text{ cm}^{-1}$)	m
Se ₈₀ Te ₂₀	13.49×10^2	58.02×10^3	180.18	2.80×10^{-8}	0.55	3.27×10^{-6}	0.0028
(Se ₈₀ Te ₂₀) _{97.5} Ge _{2.5}	25.78×10^3	108.30×10^4	3.43×10^{-6}	1.36×10^{-15}	1.79	8.05×10^{-6}	0.0043
(Se ₈₀ Te ₂₀) ₉₅ Ge ₅	11.50×10^1	16.40×10^1	6.77×10^{-6}	5.20×10^{-15}	1.74	4.00×10^{-9}	0.0067
(Se ₈₀ Te ₂₀) ₈₅ Ge ₁₅	43.65×10^2	107.41×10^3	1.41×10^{-6}	1.48×10^{-18}	1.39	3.00×10^{-9}	0.0006

The temperature dependence of the dielectric constant (ϵ') at various frequencies for glassy alloys in the (Se-Te)-Ge system indicated that the $\ln \epsilon'$ versus $1/T$ plot is a straight line for all the samples (results not shown here).

This type of temperature dependence is generally observed in molecular solids where the Debye theory [27] for the viscosity dependence of relaxation time holds quite well. According to this theory, the dielectric constant (ϵ') should

increase exponentially with temperature, and such a relationship has been observed indeed for the present samples.

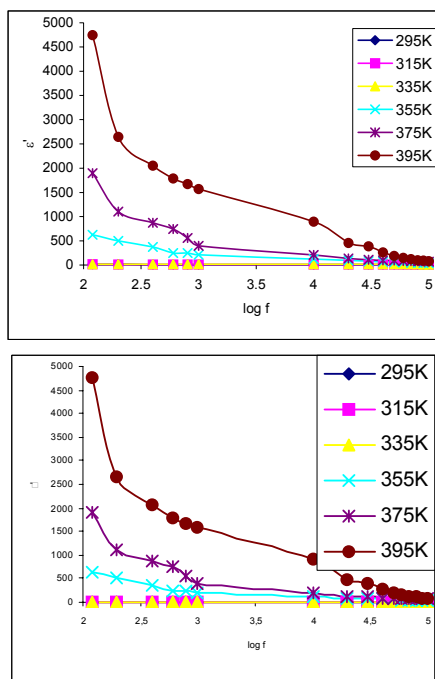


Fig. 2. Variation of dielectric constant and dielectric loss with frequency at different fixed temperature for the $\text{Se}_{96}\text{Te}_4$ system.

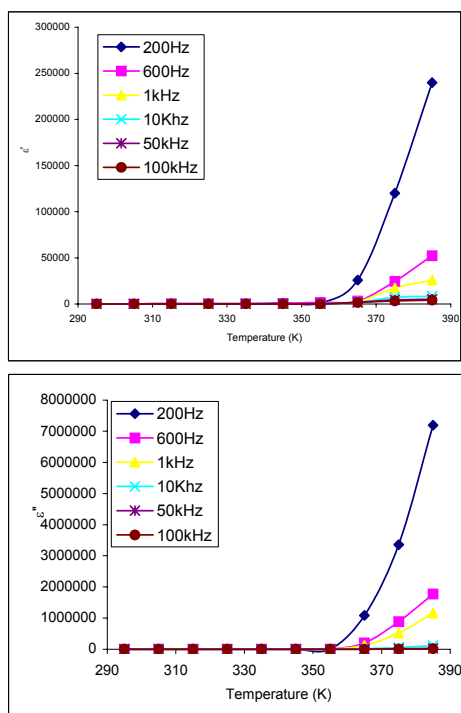


Fig. 3. Variation of dielectric constant and dielectric loss with temperature at different fixed frequency for the $(\text{Se}_{80}\text{Te}_{20})_{97.5}\text{Ge}_{2.5}$ system.

The above discussion indicates that dipolar type dielectric dispersion is occurring in the present samples. However, small peaks have been observed in the dielectric loss (ϵ'') versus $\log f$ curves in the present samples as expected in the case of dipolar-type relaxation. Such peaks may be present due to a small distribution of relaxation times [16]. Guintini et al. [28] have proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [29] 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 [30-31], attributed to the existence of a potential barrier over which the carriers hop [32]. The dielectric constant and the dielectric loss in these glasses depend upon the total number of localized states. Hence, the increase of the dielectric parameters with the increase of germanium indicates that the density of defects states decreases on addition of germanium to the $(\text{Se}_{80}\text{Te}_{20})$ binary system. Schottmiller et al. [33] studied the effect of various elements (S, Te, Bi, As and Ge) on the structure of glassy Se by infrared and Raman Spectroscopy. They reported that in glassy Se about 40% of the atoms have a ring structure and 60 % of the atoms are bonded as polymeric chains. The conducting additive in a dielectric may have a very large effect on its electrical response. The presence of additive might increase the concentration of charge carriers and there may be a shift of the Fermi level [34-36]. It is generally assumed that the addition of germanium for all the concentration to $(\text{Se}_{80}\text{Te}_{20})$ system leads to a cross linking of the Se-Te chains, reducing the disorder in the system, which in turn may decrease the density of defect states but for $x = 5\%$ of germanium, there may be reverse trend due to which the dielectric constant and the dielectric loss decreases as compared to undoped sample.

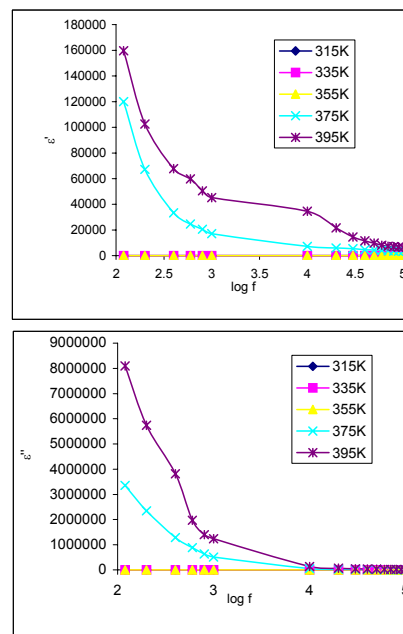


Fig. 4. Variation of dielectric constant and dielectric loss with frequency at different fixed temperature for the $(\text{Se}_{80}\text{Te}_{20})_{97.5}\text{Ge}_{2.5}$ system.

It has been shown by Goyal et. al [37] that spurious dielectric dispersion may appear in chalcogenide glasses, if there is a poor electric contact between sample and the electrodes. This is likely to occur in uncoated samples. To avoid such spurious effects, we have used silver coating pellets on both the faces of the pellets. To ensure that the measured capacitance and dissipation factor represent the values of bulk samples, we examined two silver coated pellets of $a\text{-(Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ with different thickness. Temperature and frequency dependence of capacitance and dissipation factor have been measured simultaneously. It was found that the values of capacitance and dissipation factor are thickness dependent while the corresponding dielectric constant and dielectric loss are thickness independent. These results indicate that the electrode polarization effect does not exist in the present case.

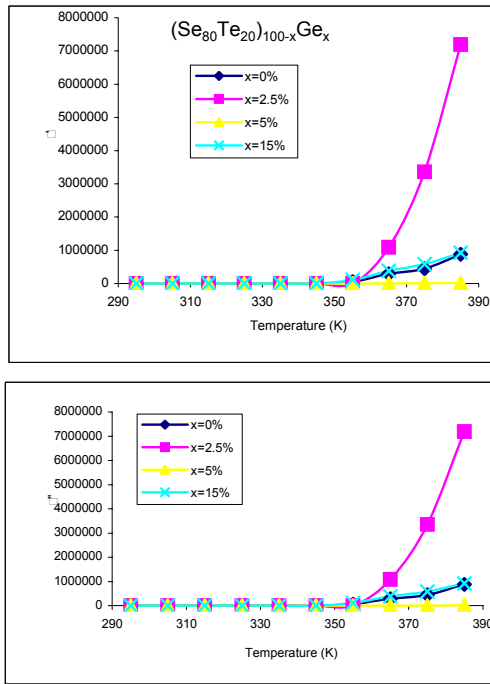


Fig. 5. Variation of dielectric constant and dielectric loss with temperature at 200 Hz for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

Guintini et al. [28] have proposed a theory of dielectric loss (ϵ'') in chalcogenides glasses at a particular frequency in the temperature range where dielectric dispersion occurs, leading to the relation

$$\epsilon''(\omega) = (\epsilon_s - \epsilon_\infty) 2\pi^2 N (ne^2/\epsilon_s)^3 k T \tau_0^m W_m^{-4} \omega^m \quad (1)$$

where

$$m = -4kT / W_m. \quad (2)$$

Here, n is the number of electrons that hop, N is the concentration of defect states, ϵ_s and ϵ_∞ are the static and optical dielectric constant respectively, W_m is the energy required to move the electron from a site to infinity.

From equation (1), ϵ'' should follow a power law with frequency, i.e.

$$\epsilon'' = A \omega^m \quad (3)$$

where m should be negative and linear with T as given by equation (2).

In our samples we found also that ϵ'' follows a power law with frequency at higher temperatures where the dielectric dispersion occurs. Fig. 7 confirms this behavior when the $\ln \epsilon''$ vs $\ln \omega$ curves are found to be straight lines at the fixed temperature 295K. 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 $a\text{-(Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$. The present results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliot [5] in case of chalcogenide glasses, and the dielectric dispersion is of dipolar type, which is also found in the present sample.

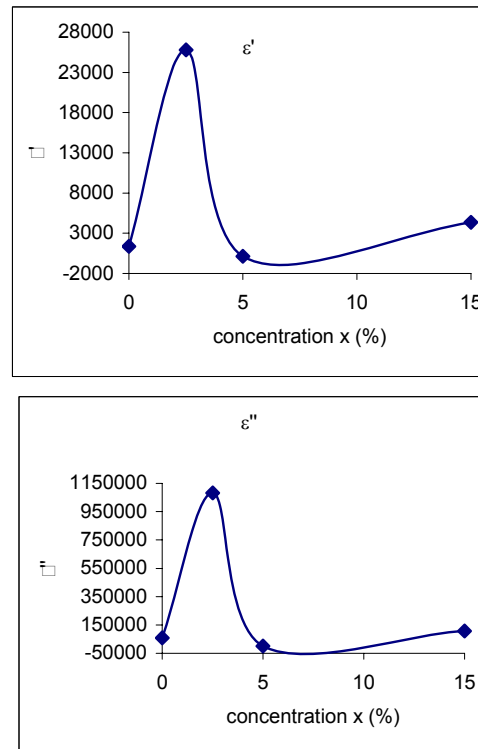


Fig. 6. Variation of dielectric constant and dielectric loss with germanium for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system at fixed 200Hz and 360 K.

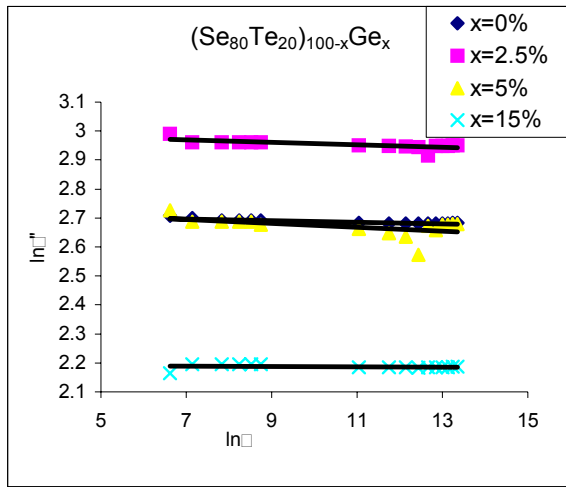


Fig. 7. Variation of $\ln \epsilon''$ with $\ln \omega$ at fixed temperature (295K) for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

The temperature dependence of the dc conductivity (σ_{dc}) is also measured for all the glassy samples. Fig. 8 shows the variation of $\ln \sigma_{dc}$ versus $1000/T$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2.5, 5$, and 15 at. %) glasses. Plots of $\ln \sigma_{dc}$ versus $1000/T$ for all samples yield straight lines, which indicate a thermally activated process for dc conduction. σ_{dc} can be expressed by the usual relation

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E / kT) \quad (4)$$

where ΔE is the activation energy for dc conduction, k is Boltzmann's constant and σ_0 is the pre-exponential factor. The activation energy (ΔE) for these alloys has been calculated using the slopes of fig. 8 and are given in Table 1, which also contains the values of σ_{dc} at 360 K. It is clear from the table that the dc conductivity decreases by eight order and the corresponding activation energy ΔE increases with increase of germanium content. An decrease of the dc conductivity with the corresponding increase in the activation energy is found to be associated with a shift of the Fermi level in impurity doped chalcogenides glasses [38]. The activation energy increase is due to a decrease of the density of localized states in the band gap near the Fermi level. Table 1 represents the variation of the dielectric loss and the dc conductivity with germanium contents. This variation may be due to the decrease of defect states.

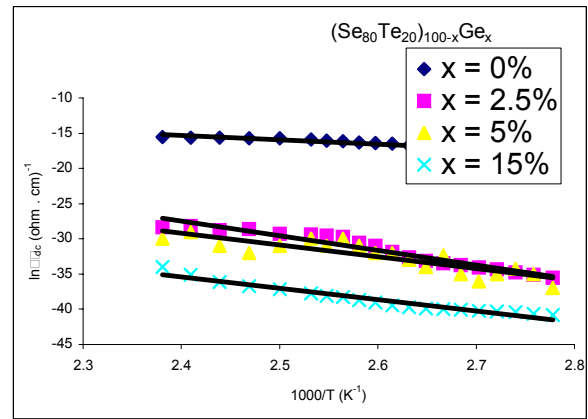


Fig. 8. Variation of $\ln \sigma_{dc}$ Vs $1000/T$ for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

The absence of sufficient studies into the behavior of ac conductivity σ_{ac} of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system with various Ge content. We have examined the dependence of conductivity on frequency and temperature. We report the frequency, temperature and germanium content dependence on the σ_{ac} of bulk $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system in the frequency range 120 Hz to 100 kHz and with germanium contents in the range Ge = 0, 2.5, 5 and 15%.

Fig. 9 shows the variation of $\ln \sigma$ (ac and dc) with $1000/T$ at various fixed frequency for the bulk $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ systems. For all the samples, σ_{ac} increase with increases the frequency. In this case, σ_{ac} is proportional to ω^s , which means that σ_{ac} dominates at all the frequency range 120Hz to 100kHz.

Fig. 10 shows the variation of $\ln \sigma_{ac}$ vs $\ln \omega$ at different fixed temperature for the given system. From the slope of fig.10, we evaluate the exponent s and we observed that the exponent have value less than unity and vary with temperature as shown in Fig. 11. Elliott [5] discussed such a case for chalcogenide glasses. The exponent fit with correlated barrier hopping (CBH) model by Elliott [29] from which ac conduction occurs between two sites over the barrier separating between them as D^+ and D^- defects center in the band gap. The decrease in the ac conductivity with germanium content may be due to the decrease of the defect states in the band gap i.e. the hopping of the charge carrier in the defect states is reduced with increase in germanium, so it may be possible to reduce the ac conductivity as well as dc conductivity.

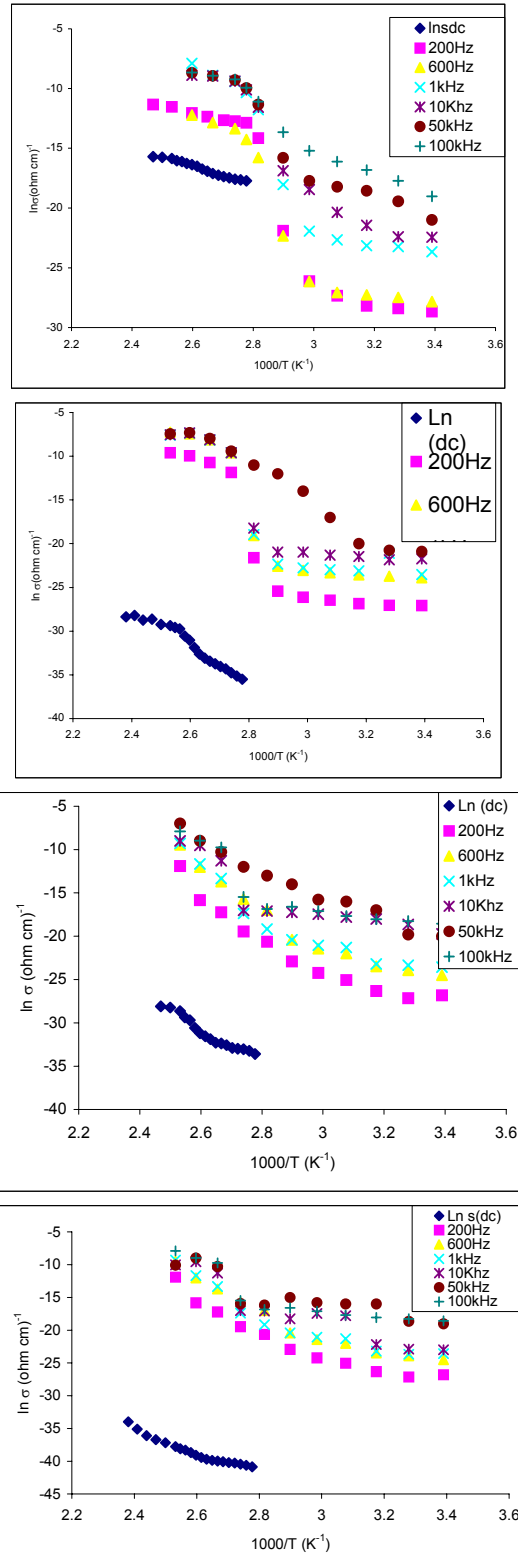


Fig. 9. Variation of $\ln \sigma$ (ac and dc) with $1000/T$ for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

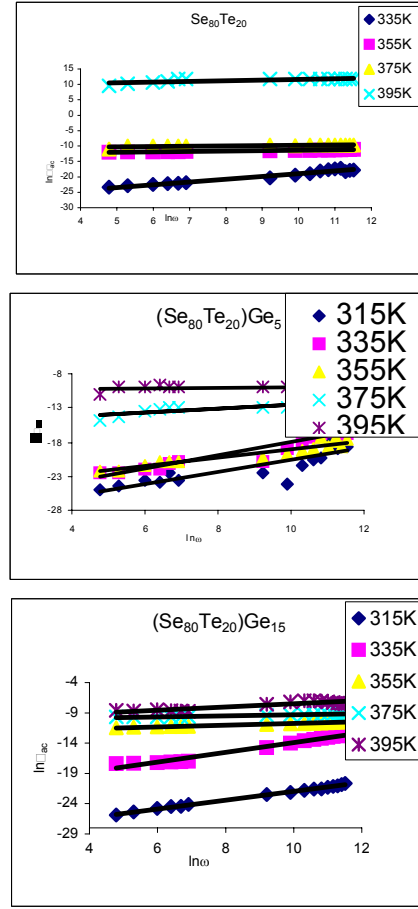


Fig. 10. Variation of $\ln \sigma_{ac}$ Vs $\ln \omega$ at different fixed temperature for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

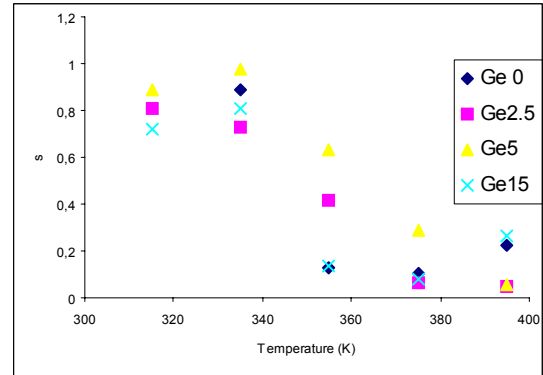


Fig. 11. Variation of S Vs temperature for the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system.

The dc conduction loss (ϵ''_{dc}) is also an important parameter to understand the dielectric dispersion in chalcogenide glasses. We also have calculated the dc conduction loss (ϵ''_{dc}) using the following relation [36, 39-40]

$$\epsilon''_{dc} = \sigma_{dc} / \omega \epsilon_0 \quad (5)$$

where σ_{dc} is the dc conductivity.

The calculated values of the dc conduction loss (ϵ''_{dc}) are shown in Table 1. The dc conduction loss is found to be smaller than the observed loss for $a-(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2.5, 5$, and 15 at. %) in the temperature range 290K to 400K , i.e. the observed loss is dominant over the dc conduction loss. The dc conduction loss decreases as the concentration of germanium increases in the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system. However, the dielectric dispersion is due to the hopping of charge carriers over a potential barrier between the charged defect states D^+ and D^- for $a-(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ sample as discussed earlier. Thus, these results indicate that the observed dielectric dispersion is attributed mainly to the dipolar type dispersion in the present system.

4. Conclusions

The dielectric parameter and electrical properties of $a-(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ are temperature and frequency dependent. Dielectric dispersion is found to occur in these alloys. Dielectric dispersion is occurring due to the dipolar type of the defects in the present sample. The dielectric constant and the dielectric loss increase on addition of germanium. A possible explanation is given in terms of hopping of charge carriers over a potential barrier between charged defect states. The increase of the dielectric parameters with germanium concentration can be understood in terms of the decreased density of defect states on to the Se-Te system. On increasing the concentration of germanium, the decrease in the dc conductivity, ac conductivity and increase in activation energy are due to the decrease of the density of defect states or to the decrease of the disorder in the mobility edge.

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