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Dielectric studies of tin based chalcogenide glasses

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Abstract The dc conductivity and dielectric parameters of glassy system of a-$Se_{70}Te_{30-x}Sn_x$ ($x = 0, 2, 4, 6, 8$ and 10) glasses have been investigated. Frequency and temperature dependence of dielectric constants (ε') and dielectric loss (ε'') are studied in the frequency range 120–100 kHz and temperature range 300–390 K. Dielectric dispersion is observed when Tin (Sn) is incorporated to a-Se–Te system in the entire temperature range. These results explain that the dc conduction loss is dominated in the present system. From dc conductivity studies it is observed that the dc conductivity and activation energy increases with increasing tin concentration in the present system.

Introduction

The measurement of dc conductivity of amorphous semiconductors has been extensively used to understand the conduction process in these materials [1]. Se-based glasses are much interesting, because these materials exhibit optical memory and photo darkening [2, 3] to which the study of their electrical behavior could shed light. The study of chalcogenide glasses has indicated that the dielectric dispersion does exist in these glasses at low frequencies even though these materials are covalently bonded. The origin and nature of dielectric losses in these material has, therefore become a matter of curiosity. Generally, the un-doped 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. 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. [4] have shown that the effect of charged additives in lone-pair semiconductors depends on whether the charged additives equilibrate or not with valence alternation defect. Enormous interest has been shown in a-Se–Te alloys due to their great hardness, higher photosensitivity, higher crystallization temperature and smaller aging effects as compared to pure amorphous Se [5]. Addition of Sn to a-Se–Te system causes structural changes in the material which in turn modify band structure, and hence the electrical properties. The purpose of this study is to report some electrical and dielectric features, and determine the influence of tin content on the properties of a-Se–Te system and characterize its dependence on temperature and frequency. That is, the Te part of the a-Se–Te content is substituted by tin, with the Se set at a fixed content. Though the electrical properties of tin doped chalcogenide glasses are being studied by various authors [6–8] in detail, a little work has been done on the dielectric properties on the present sample. In this present paper, we have studied the temperature and frequency dependence of dielectric constant and dielectric loss for the bulk sample (pellet) of a-$Se_{70}Te_{30-x}Sn_x$ alloys.

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Experimental

$Se_{70}Te_{30-x}Sn_x$ ($x = 0, 2, 4, 8$, and 10) glasses are prepared by the melt quenching technique. Appropriate mixtures of 5 N 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 up-to 1300 K and kept at that temperature for 12 h with frequent rocking to insure the homogenization of the melt. The quenching was done in ice water. The amorphous nature of the glassy alloys was verified by X-ray diffraction. Bulk samples in the form of pellets (diameter = 1.2 cm) 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 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 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 using the Keithley electrometer (model 617). These measurements were also made in the same sample holder in which dielectric measurements were taken.

Results and discussion

The temperature dependence of dielectric constant (ε') and dielectric loss (ε'') is studied at various frequencies (120–100 kHz) for glassy a-$Se_{70}Te_{30-x}Sn_x$ ($x = 0, 2, 4, 8$ and 10). The temperature range of measurement was from 300 K to 390 K. Figure 1a shows the dielectric constant (ε') increases with the temperature being different at different frequencies for a-$Se_{70}Te_{30}$. Variation of dielectric constant with increase of temperature is larger at lower frequencies. Figure 1b shows that the dielectric loss for a-$Se_{70}Te_{30}$ increases as the temperature increases being different at different frequencies. The dielectric loss is also large at low frequencies. The dielectric constant and dielectric loss decreases as the frequency increases for the $Se_{70}Te_{30}$ sample at fixed temperature (Figure not shown here). Figure 2a and b shows the variation of dielectric constant and dielectric loss with temperature at different frequencies for a-$Se_{70}Te_{28}Sn_2$. At 2% of tin concentration, a dielectric dispersion has been observed even at room temperature. Similar type of dispersion was also observed in other Tin concentrations (Results not shown here). These results indicate that the concentration of Tin 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 [9–14]. As the tin impurity is added to the a-Se–Te system, dielectric constant and dielectric loss increases. Figure 3a and b shows the variation of dielectric constant and dielectric loss with frequency at different temperature for a-$Se_{70}Te_{30}Sn_2$. The temperature dependence of dielectric constant (ε') at various frequencies for various glassy alloys in the a-$Se_{70}Te_{30-x}Sn_x$ system indicate that ε' varies exponentially with temperature. The ln ε' versus $1/T$ curve is to be a straight line. This type of temperature dependence of dielectric constant is generally observed in molecular solids where Debye theory [15–20] for the viscosity dependence of relaxation time holds quite well. In our present study, the ln ε' versus $1/T$ curves are not found to be a straight line as shown in Figure 4, so the probability of dipolar relaxation is ruled out in the a-$Se_{70}Te_{30-x}Sn_x$ sample. Figure 5a and b shows the variation of dielectric constant and dielectric loss with different concentration of Tin at fixed frequency (5 kHz) and at 320 K temperature. These figures show that the concentration of tin plays an important role in the variation of dielectric parameters with temperature. Dielectric constant (ε') and dielectric loss (ε'') increases with the addition of tin concentration; this is probably due to the increase of the defect states in the band gap near to the Fermi level i.e. the hopping of charge carrier in the defect state increases. However, the dielectric loss decreases at 4% of Tin, it may be due to the decrease of the defect states in the band tails. These values of dielectric constant and dielectric loss with increase of the Sn concentration are given in Table 1. It has been shown by Goyal et al. [21] that spurious dielectric dispersion may appear in chalcogenide glasses if there is a poor electric contact between sample and the electrodes. This is likely in uncoated sample. To avoid such spurious effects, we have used silver paste coated pellets on both the faces. To ensure that the measured values of capacitance and dissipation factor represent the values of bulk samples, we take two silver paste coated pellets of a-$Se_{70}Te_{30}$ of different thickness. Temperature and frequency dependence of capacitance and dissipation factor have been measured simultaneously. It was found that the values

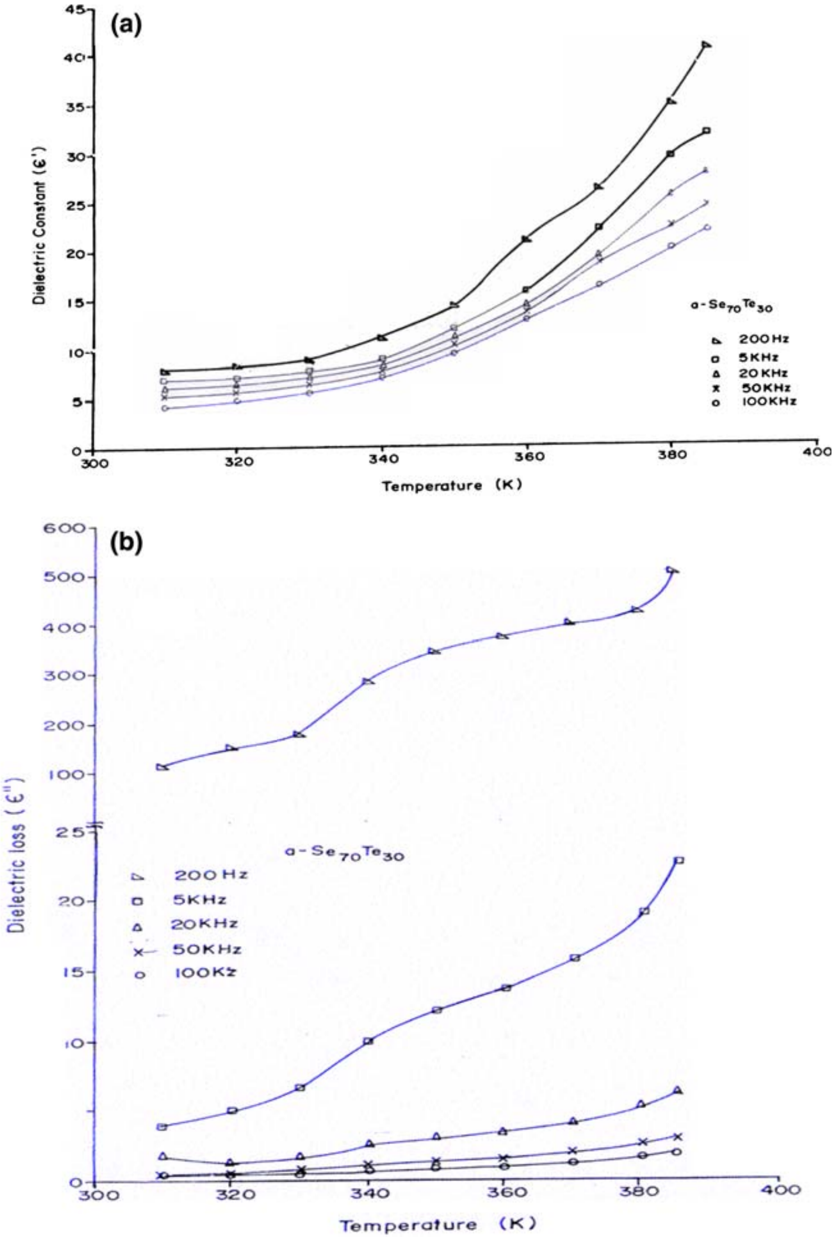

Fig. 1 (**a**) Dielectric constant (ε') versus temperature at fixed frequency for a-Se$_{70}$Te$_{30}$ sample (**b**) Dielectric loss (ε'') versus temperature at fixed frequency for a-Se$_{70}$Te$_{30}$ sample

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.

The temperature dependence of dc conductivity (σ_{dc}) was also measured for all the glassy samples. Figure 6 shows that the variation of ln σ_{dc} versus 1000/T for a-Se$_{70}$Te$_{30\text{-}x}$Sn$_x$ glasses with (x = 0, 2, 4, 6, 8 and 10 at. %). Curve of ln σ_{dc} versus 1000/T of all samples represents the straight line which indicate a thermally activated process for dc conduction. σ_{dc} can, however, be expressed by a usual relation

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E/kT) \tag{1}$$

where ΔE is the activation energy for dc conduction, k is Boltzmann constant and σ_0 is pre-exponential factor. The activation energy (ΔE) for these alloys has been calculated using the slopes of Figure 6. The calculated values of $\sigma_{dc,}$ σ_0 and ΔE given in Table 1 for these films, suggest that the conduction is due to thermally assisted tunneling of charge carriers in the localized states present in the band tails [22–23]. The activation energy (E alone does not provide any information as to whether the conduction takes place in the extended

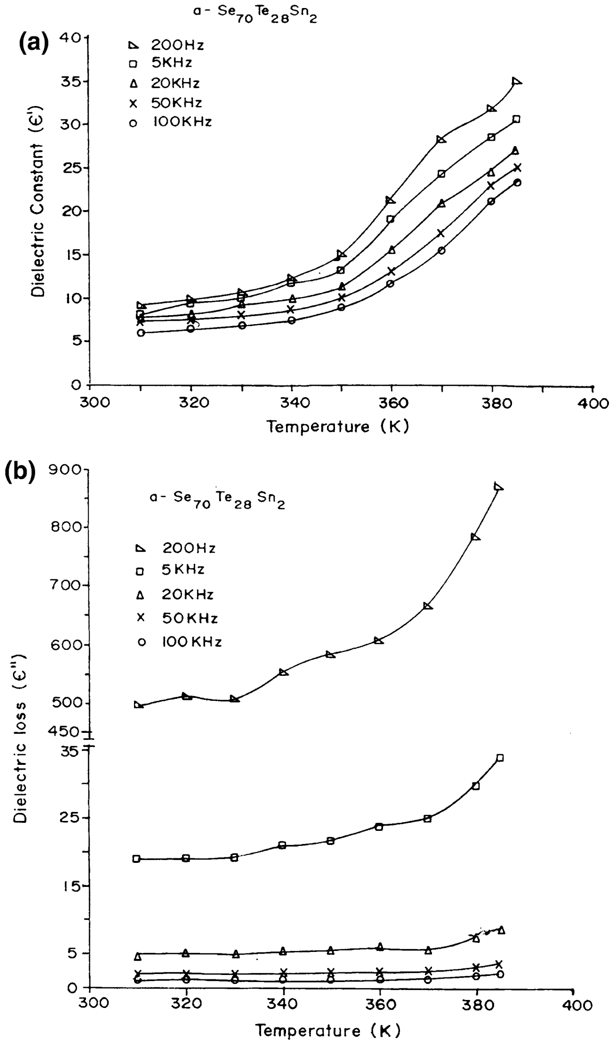

Fig. 2 (**a**) Dielectric constant (ε') versus temperature at fixed frequency for a-$Se_{70}Te_{30}$ Sn_2 sample (**b**) Dielectric loss (ε'') versus temperature at fixed frequency for a-$Se_{70}Te_{30}$ Sn_2 sample

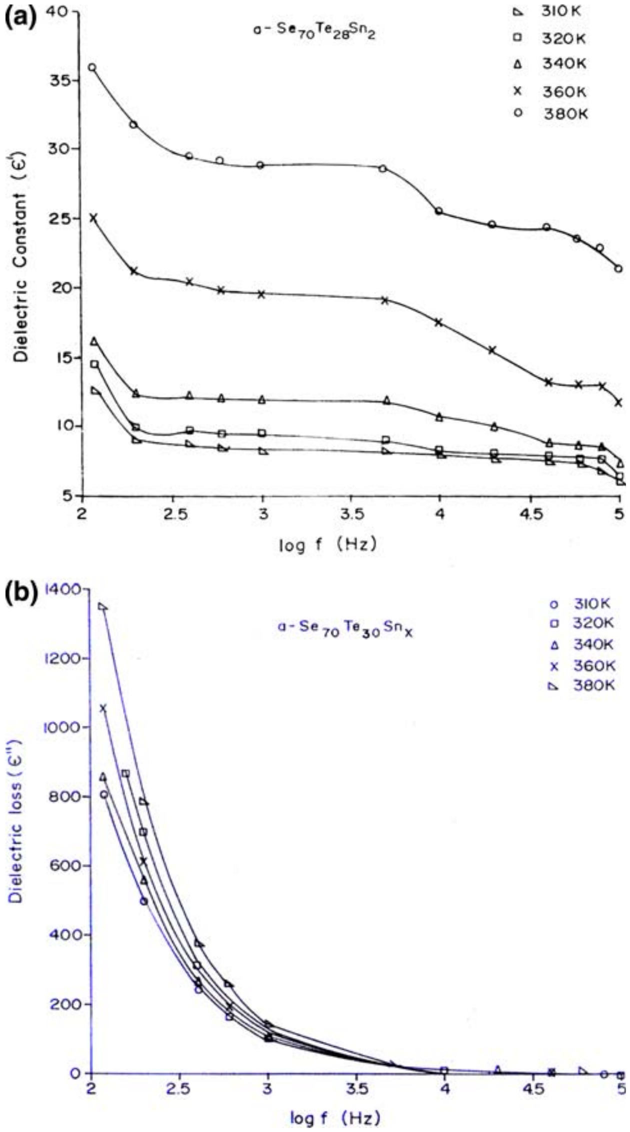

Fig. 3 (**a**) Dielectric constant (ε') versus log f at fixed temperature for a-$Se_{70}Te_{30}$ Sn_2 sample (**b**) Dielectric loss (ε'') versus log *f* at fixed temperature for a-$Se_{70}Te_{30}$ Sn_2 sample

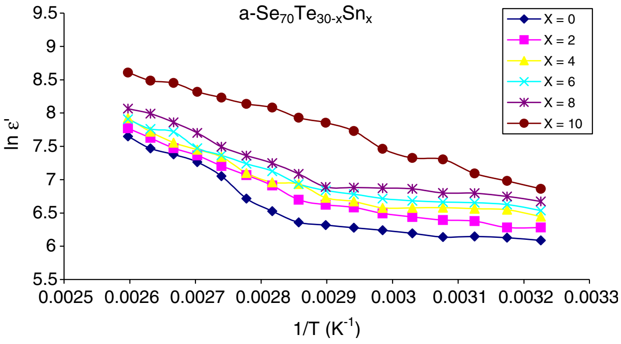

Fig. 4 ln ε' versus $1/T$ for the a-$Se_{70}Te_{30\text{-}x}$ Sn_x sample

states above the mobility edge or by hopping in the localized states. As both the conduction mechanism occur simultaneously, with the conduction via localized states dominating at low temperatures, the activation energy in the former case represents the energy difference between the mobility edge and Fermi level. In the latter case, it represents the sum of the energy separation between the occupied localized states and Fermi level, and the mobility activation energy for the hopping process between the localized states. In order to obtained a clear distinction between these two conduction mechanism, Mott [24] has suggested that the pre-exponential factor (σ_0) for conduction in the localized states should be two or three orders smaller in magnitude than for the extended states and should become still smaller for conduction in the localized states near the Fermi level. The value of the pre-exponential factor for conduction in extended states is

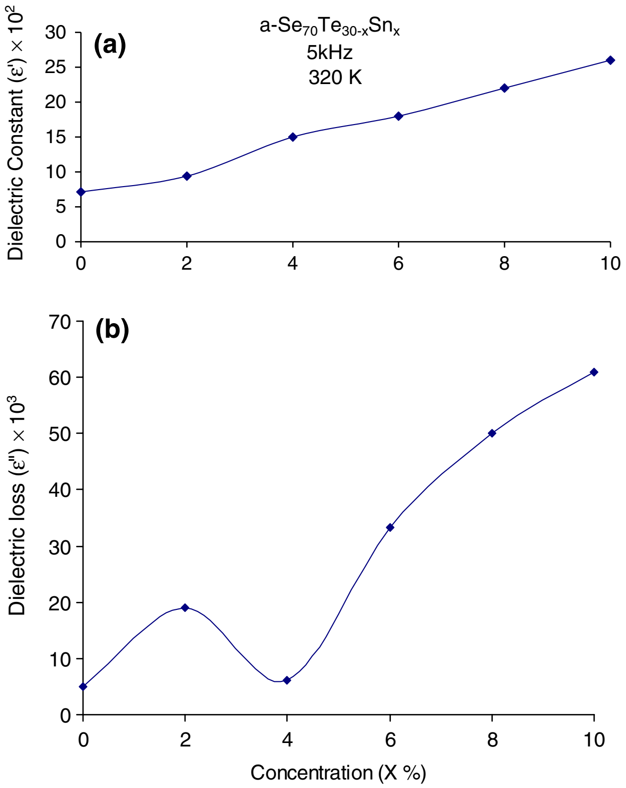

Fig. 5 (**a**) Dielectric constant (ε′) × 10^2 versus concentration of tin at fixed temperature (320 K) and frequency (5 kHz) for a-$Se_{70}Te_{30\text{-}x}$ Sn_x sample (**b**) Dielectric loss (ε″) × 10^3 versus concentration of tin at fixed temperature (320 K) and frequency (5 kHz) for a-$Se_{70}Te_{30\text{-}x}$ Sn_x sample

of the order of 10^3–10^4 Ω^{-1} cm^{-1}. In the present system, the values of pre-exponential factor increase from 10^{-3} to 10^2 Ω^{-1} cm^{-1} as the concentration of tin increases, the conduction takes place from localized states near the Fermi level to the localized states in the band. Again, the increase in the values of activation energy (ΔE) and pre-exponential factor with tin concentration shows that the mobility (hoping) of charge carriers in the trap states increases which can be attributed either to increased optical gap or due to increase the width of the localized states region and hence dc conductivity increases for each concentration of tin. An increase in dc conductivity with a corresponding increase in the activation energy is also found to be associated with the shift of the Fermi level in impurity doped chalcogenide glasses [25, 26].

Table 1 shows a correlation between σ_{dc} and dielectric loss (ε″), this represent that the dielectric loss increases as the dc conductivity increase at different concentration of tin.

The dc conduction loss (ε''_{dc}) is an important parameter to understand the dielectric dispersion in chalcogenide glasses. So we have calculate the dc conduction loss ε''_{dc} using the following relation [27–29]

$$\varepsilon''_{dc} = \sigma_{dc} / \ \omega\varepsilon_0, \qquad (2)$$

where σ_{dc} is the dc conductivity.

The calculated values of dc conduction loss (ε''_{dc}) are shown in Table 1. The dc conduction loss is dominant over the observed loss for the present system for the given temperature range. From Table 1, it is clear that the dc conduction loss increases as the concentration of tin increases to the Se–Te system. Thus, these results indicate that observed dielectric dispersion is attributed mainly due to the dc conduction loss in the present system.

Schottmiller et al. [30] studied the effect of various element (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 addition of tin, increase Se–Te–Sn polymeric chain concentration. Thus increase in the dc conductivity is due to a decrease of Se–Te ring structure i.e. decreasing the disorderness of Se–Te–Sn samples. The conducting additive in a-Se–Te system 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 change in Fermi level [29, 31–32].

Conclusion

The dielectric parameter and electrical properties of the a-$Se_{70}Te_{30\text{-}x}Sn_x$ are temperature and frequency dependent. Dielectric dispersion is found to occur in these

Table 1 Electrical and dielectric parameter in a-$Se_{70}Te_{30\text{-}x}Sn_x$ system at T = 320 K and f = 5 KHz

Samples	ε′ × 10^2	ε″ × 10^3	σ_{dc} (Ω^{-1} cm^{-1})	σ_0 (Ω^{-1} cm^{-1})	E (e V)	ε_{dc}''
$Se_{70}Te_{30}$	7	5	29.08 × 10^{-6}	90.49 × 10^{-3}	0.22	65.68 × 10^3
$Se_{70}Te_{28}Sn_2$	9	19	10.92 × 10^{-6}	80.47 × 10^{-3}	0.25	24.66 × 10^3
$Se_{70}Te_{26}Sn_4$	15	7	17.85 × 10^{-5}	22.80 × 10^{-1}	0.26	40.27 × 10^4
$Se_{70}Te_{24}Sn_6$	18	34	11.20 × 10^{-5}	25.77 × 10^1	0.40	25.29 × 10^4
$Se_{70}Te_{22}Sn_8$	22	50	13.94 × 10^{-5}	60.61 × 10^2	0.48	31.48 × 10^4
$Se_{70}Te_{20}Sn_{10}$	26	61	22.46 × 10^{-5}	23.16 × 10^2	0.45	50.73 × 10^4

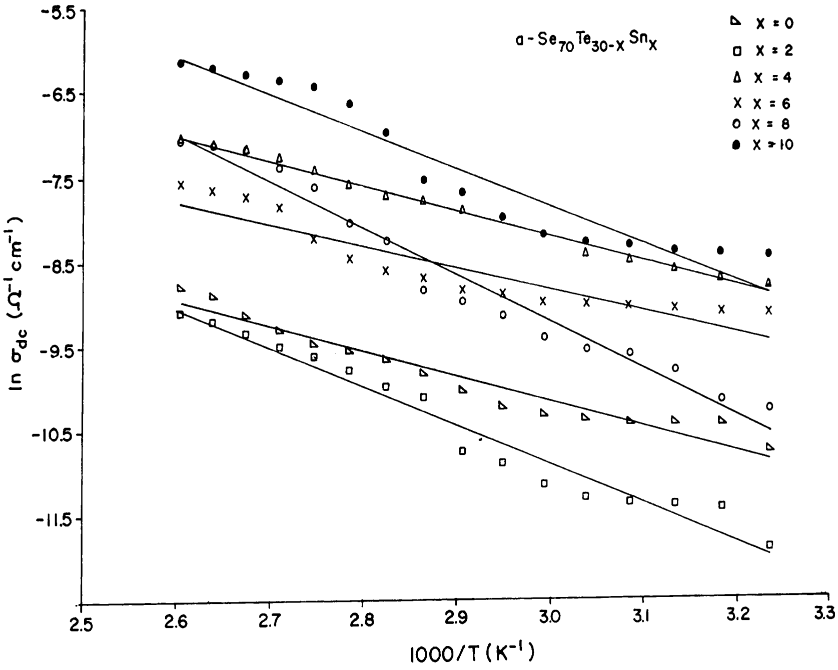

Fig. 6. ln σ_{dc} versus 1000/T for a-$Se_{70}Te_{30-x}Sn_x$ sample

alloys. Dielectric constant and dielectric loss increases with the increase of tin concentration. Detailed analyses of the result show that dielectric dispersion is mainly due to the dc conduction losses in nature. The increase of dielectric parameter with Tin concentration can be understood in terms of the increased defect states on addition of Tin to a-Se–Te system. On increasing the concentration of Tin, the increase in dc conductivity and activation energy is also due to the increase of band gap or increase of defect state in the band gap.

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