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Dielectric properties of glassy $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($\text{M} = \text{Cd}, \text{In}$ and Sb) (*)

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Résumé. — La dépendance en température et en fréquence de la constante et des pertes diélectriques dans les verres $\text{Se}_{80}\text{Te}_{20}$ et $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($\text{M} = \text{Cd}, \text{In}$ et Sb) est mesurée dans la gamme de températures de 100 à 330 K et dans la gamme de fréquence de 120 Hz à 10 kHz. La constante et les pertes diélectriques sont indépendantes de la température et de la fréquence à basse température ($T < 200$ K). Cependant, à haute température, une forte dispersion diélectrique apparaît. Les résultats sont interprétés à l'aide d'un modèle dipolaire qui considère le saut des porteurs de charge à travers la barrière de potentiel entre niveaux de défauts chargés.

Abstract. — The temperature and frequency dependence of dielectric constant and loss is measured in glassy $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($\text{M} = \text{Cd}, \text{In}$ and Sb) in the temperature range 100 K to 330 K and the frequency range 120 Hz to 10 kHz. The dielectric constant and loss are independent of temperature and frequency at low temperatures ($T < 200$ K). However, at higher temperatures, strong dielectric dispersion occurs. The results are interpreted in terms of a dipolar model which considers the hopping of charge carriers over a potential barrier between charged defect states.

Introduction.

Chalcogenide glasses have recently drawn great attention of scientists because of their technical importance in various solid states devices. It is reported that glassy Se-Te alloys have some extra advantages (higher photosensitivity, greater density, higher crystallization temperature) over glassy Se which made these alloys more important for their application in xerography and other solid state devices. Se-Te alloys are, therefore, being studied more thoroughly by various workers.

In our earlier papers [1-4] we reported the photoconducting properties and X-ray spectroscopic studies of amorphous $\text{Se}_{80}\text{Te}_{20}$ with and without metallic additives (Cd, In and Sb). A study of temperature and frequency dependence of dielectric constant (ϵ') and dielectric loss (ϵ''), particularly in the range where dielectric dispersion occurs, can be of great importance for the understanding of the

nature and origin of the losses occurring in these materials.

We report the temperature and frequency dependence of ϵ' and ϵ'' in glassy $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($\text{M} = \text{Cd}, \text{In}$ and Sb) in the temperature range 100 K to 330 K and in the frequency range 120 Hz to 10 kHz. The dc conductivity is also measured in the above temperature range to assess the dc conduction losses. Results are interpreted in terms of a theoretical model which considers hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-).

Experimental.

Glassy alloys of $\text{Se}_{80}\text{Te}_{20}$, $\text{Se}_{80}\text{Te}_{10}\text{Cd}_{10}$, $\text{Se}_{80}\text{Te}_{10}\text{In}_{10}$ and $\text{Se}_{80}\text{Te}_{10}\text{Sb}_{10}$ were prepared by melting and quenching. High purity material (5 N pure) were weighed and then sealed in quartz ampoules (length ~ 5 cm, internal dia ~ 8 mm) in a vacuum of 10^{-5} torr. The ampoules were kept inside a furnace where they were rocked frequently at 600 °C for 8 hours. Quenching was done in ice water. The

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glassy nature of the samples was verified by X-ray diffraction.

Glassy alloys thus prepared were ground to powder and pellets (dia ~ 6 mm and thickness ~ 1 -2 mm) were obtained after compressing the powder in a die under a load of 3-4 tons. The pellets were coated with indium by evaporation technique at a base pressure of 10^{-5} torr. The coating was done to ensure good electrical contact with the electrodes of the sample holder. We preferred to experiment on the pellet rather than the bulk as macroscopic effects (gas bubbles etc.) may appear in the bulk during preparation. Compressed pellets may be porous, which may affect the absolute values of the dielectric parameters. However, the conclusions of the present work will not be affected by porosity effect since the samples are compressed identically and measurements are made under the same conditions for all samples.

The coated pellets were mounted between two steel electrodes inside a metallic sample holder for dielectric measurements. A copper-constantan thermocouple mounted very near the sample measured the temperature. The sample container was maintained at $\sim 10^{-2}$ torr over the entire temperature range (100 K to 330 K). The measurements were taken during heating at a rate of 2 K/min. The frequency dependence of ϵ' and ϵ'' was also measured at constant temperatures.

The dielectric measurements were made using a GR 1620 AP capacitance measuring assembly, employing a three terminal technique. The parallel capacitance and conductance were measured simultaneously and then ϵ' and ϵ'' were calculated. The results reported in the present paper are calculated within $\pm 2\%$.

The dc conductivity of the samples was measured employing voltage of 30 V across the sample with

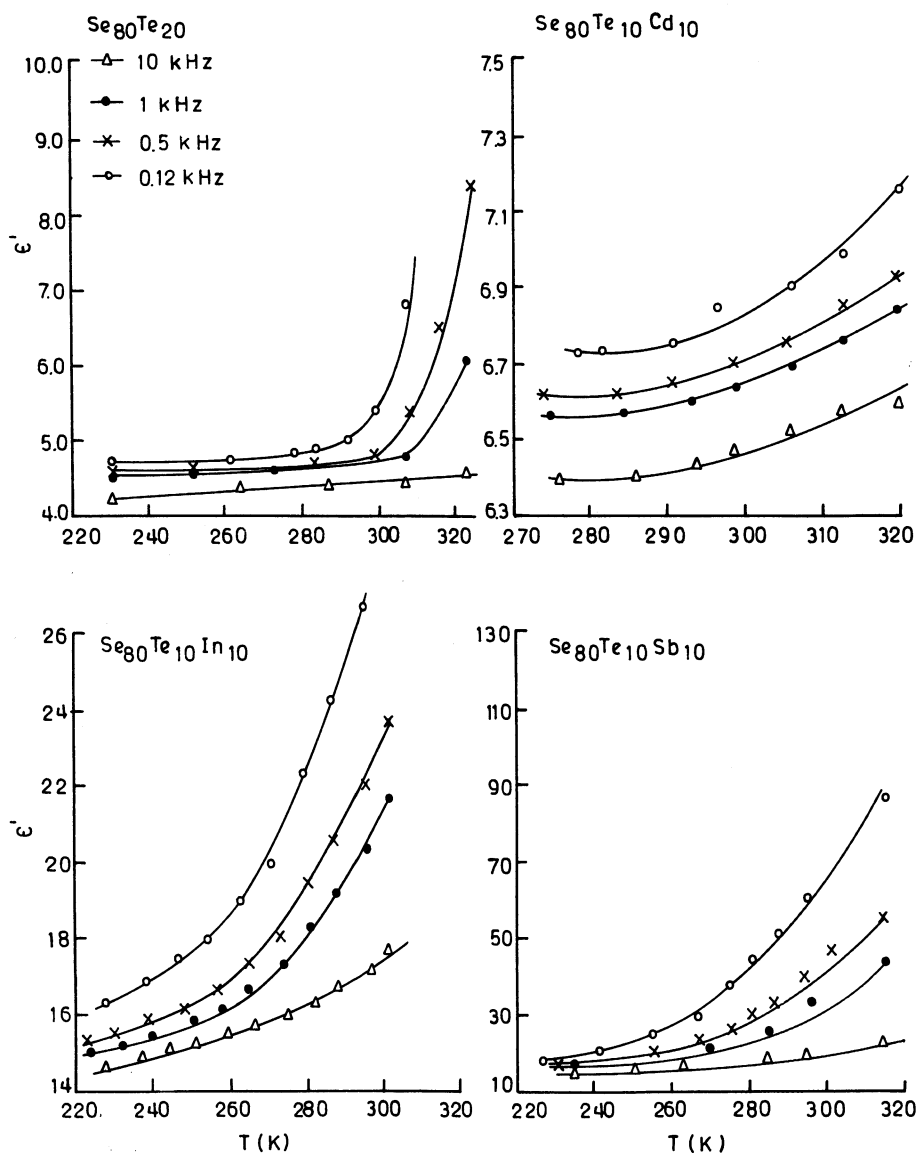


Fig. 1. — Temperature dependence of dielectric constant at certain fixed frequencies.

the current measured by a digital electrometer (Keithley model 614). These measurements were made in the same sample holder in which dielectric measurements were made.

Results.

Temperature dependence of ϵ' and ϵ'' was measured at various frequencies (0.12 to 10 kHz) for various glassy alloys. ϵ' and ϵ'' are found to be almost independent of temperature and frequency (results not shown here) at low temperatures ($T < 200$ K). However, at higher temperatures, a strong dielectric dispersion occurs in the above frequency range in all the glassy samples studied here (see Figs. 1 and 2). The solid lines in these figures pass through experimental data representing the observed variation of ϵ' and ϵ'' with temperature at certain fixed fre-

quencies. ϵ' and ϵ'' increase with the increase of temperature, the increase being different at different frequencies. This type of behaviour has been reported by various workers [5-7] in chalcogenide glasses.

Frequency dependence of ϵ' and ϵ'' is also measured at fixed temperatures in the range where dielectric dispersion occurs. At these temperatures, ϵ'' was found to follow a power law with frequency, i.e., $\epsilon'' = A\omega^m$ as $\ln \epsilon''$ varies linearly with $\ln \omega$ for all the glassy samples (see Fig. 3). The exponent m for various glassy samples was calculated from the slopes of these curves and found to increase linearly with temperature.

While studying the dielectric behaviour the temperature dependence of dc conductivity (σ_{dc}) was also measured for all glassy samples used in the present study. Figure 4 shows that $\ln \sigma_{dc}$ vs. $1000/T$

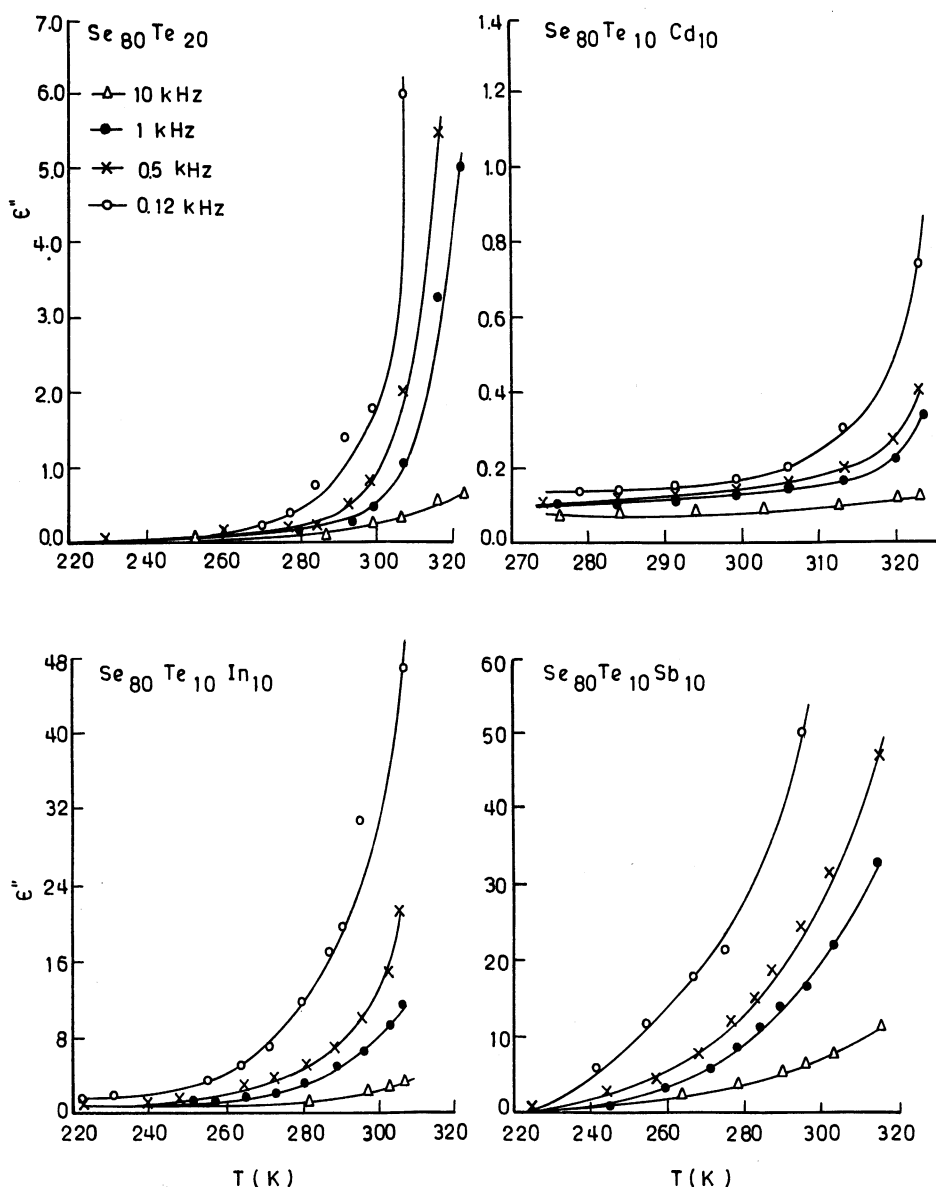


Fig. 2. — Temperature dependence of dielectric loss at certain fixed frequencies.

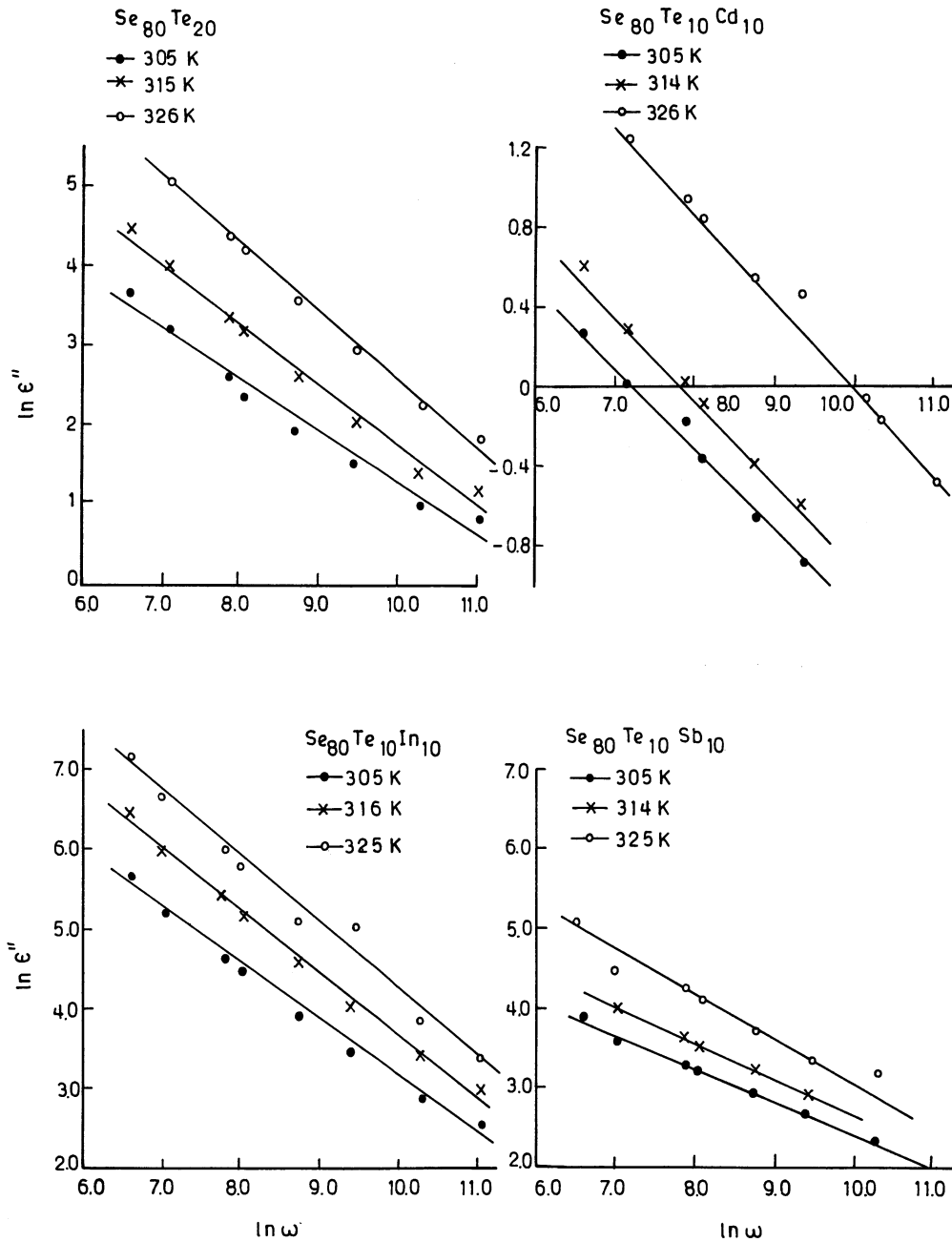


Fig. 3. — Frequency dependence of dielectric loss at certain fixed temperatures. The solid lines represent the least square fit.

curves are straight lines for various samples, which indicates that the conductivity increases with the increase of temperature, following a usual relation :

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

where ΔE is the activation energy for dc conduction and k is Boltzmann's constant.

Values of ΔE are calculated from the slopes of $\ln \sigma_{dc}$ vs. $1000/T$ curves and the results are shown in table I. The same table also contains the values of σ_{dc} at 305 K for all samples.

Table I.

Material	$\sigma_{dc} (\Omega^{-1} \text{m}^{-1})$ (305 K)	ΔE (eV)	ϵ' (305 K)	ϵ'' (305 K) 10 kHz
$\text{Se}_{80}\text{Te}_{10}\text{Cd}_{10}$	7.60×10^{-11}	1.12	5.0	0.22
$\text{Se}_{80}\text{Te}_{20}$	3.07×10^{-8}	0.77	7.5	1.22
$\text{Se}_{80}\text{Te}_{10}\text{Sb}_{10}$	2.05×10^{-7}	0.43	18.0	7.03
$\text{Se}_{80}\text{Te}_{10}\text{In}_{10}$	1.24×10^{-6}	0.47	33.5	11.02

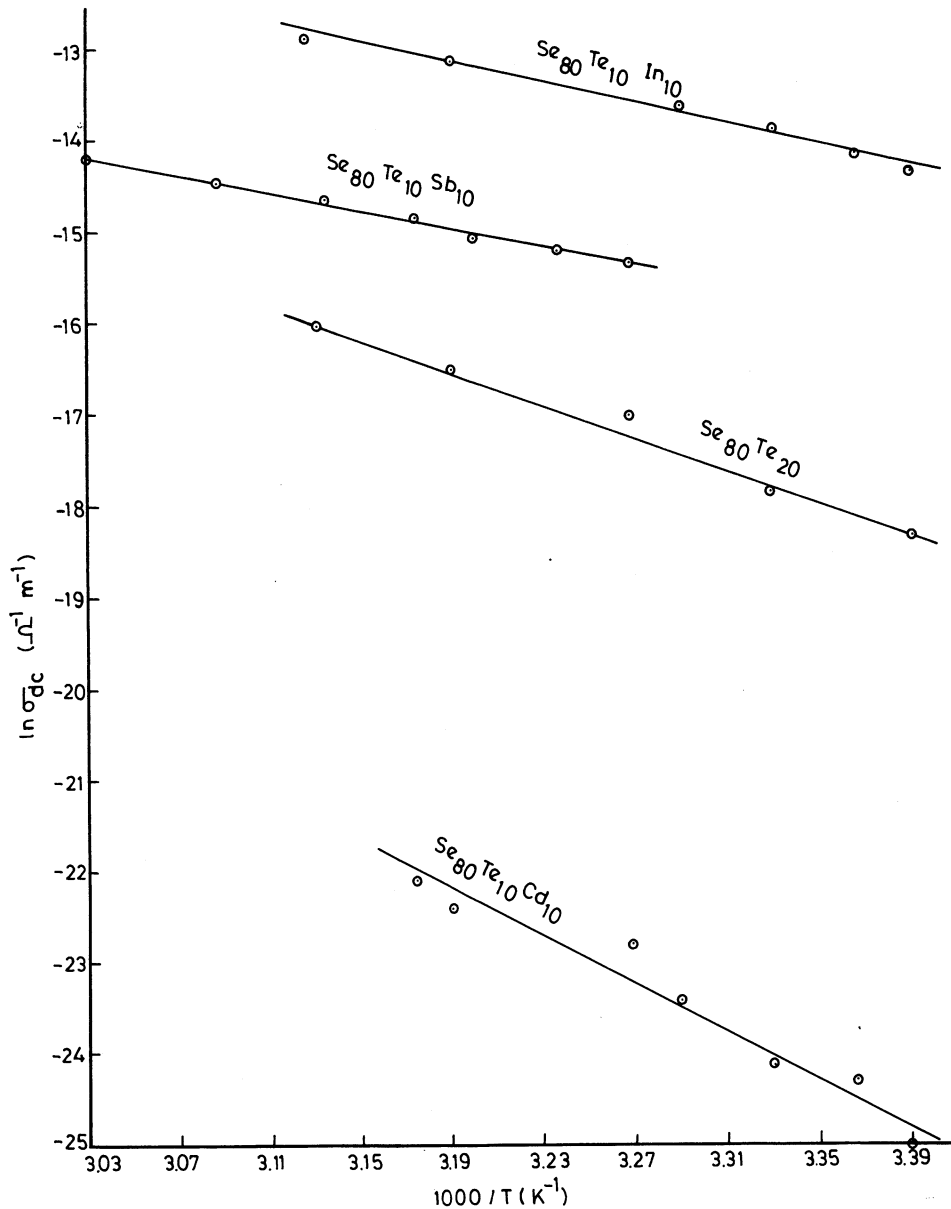


Fig. 4. — Temperature dependence of dc conductivity. The solid lines represent the least square fit.

Examination of figure 4 reveals that at all temperatures σ_{dc} decreases when 10 at % Cd is incorporated in $\text{Se}_{80}\text{Te}_{20}$ binary alloy. However, in the case of In and Sb, σ_{dc} increases and there is also a decrease in the activation energy (see Tab. I).

As mentioned earlier, $\ln \epsilon''$ vs. $\ln \omega$ curves were found to be straight lines at various temperatures (305 K to 326 K). For comparison, the frequency dependence of ϵ'' at 305 K is plotted, for all the measured samples, in figure 5. This figure indicates that, at all frequencies, ϵ'' is less for $\text{Se}_{80}\text{Te}_{10}\text{Cd}_{10}$ than for the binary alloy $\text{Se}_{80}\text{Te}_{20}$. However, in the case of $\text{Se}_{80}\text{Te}_{10}\text{In}_{10}$ and $\text{Se}_{80}\text{Te}_{10}\text{Sb}_{10}$, ϵ'' increases as compared to $\text{Se}_{80}\text{Te}_{20}$ alloy. Similar behaviour is also observed in the case of σ_{dc} as discussed earlier (see Fig. 4). In the absence of optical gap, mobility and

defect states measurements, it is difficult to point out the exact reasons for the different behaviour of Cd as compared to In and Sb. However, a correlation between σ_{dc} and ϵ'' is evident from the present measurements, i.e., ϵ'' is higher in those samples in which σ_{dc} is high (see Tab. I). Similar correlation is also reported [8] in dc and ac conductivities of some chalcogenide glasses.

Discussion.

It has been shown by Goyal *et al.* [9] that dielectric dispersion in semiconducting glasses may also appear due to poor electrical contact between the electrodes of the sample holder and the sample. This is quite likely when uncoated samples are used [9]. However,

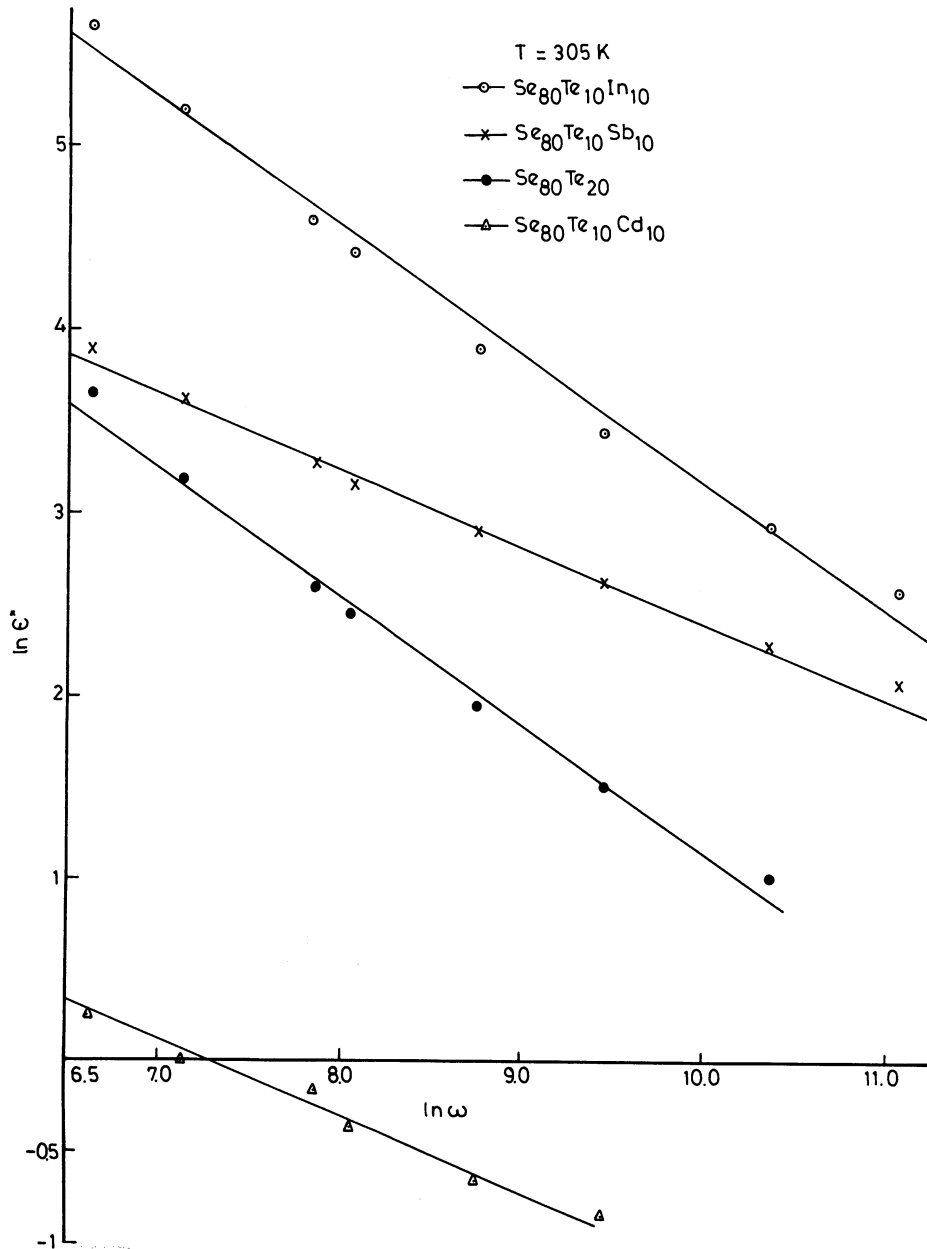


Fig. 5. — Frequency dependence of dielectric loss at 305 K. The solid lines represent the least square fit.

in the present case, the possibility of such spurious dispersion can be ruled out as we have used indium coated pellets for the dielectric measurements.

Another important parameter which may give apparent values of ϵ' in a semiconducting material, particularly at higher temperatures, is dc conduction loss. In the presence of such a loss, it is very difficult to obtain reliable values of ac loss, and the results may sometimes be misinterpreted. To avoid such discrepancies, we have calculated ϵ''_{dc} using the following relation

$$\epsilon''_{dc} = \sigma_{dc} / \omega \epsilon_0. \quad (2)$$

The calculated dc conduction loss is found to be much smaller than the observed loss at a particular

temperature for all frequencies, indicating that the observed dielectric dispersion can not be attributed to the dc conduction losses in the working temperature range for all frequencies.

In a covalently bonded solid, sharing of two electrons takes place to make a bond. However, in some structural configurations two atoms are not able to share the electrons and broken chain end containing one electron is called a neutral dangling bond (D^0). In chalcogenide glasses, transfer of an electron from one chain end to another leads to the formation of two charged defect states D^+ (no electron) and D^- (two electrons). The assumption of paired defect states is very well supported by the experimental findings in chalcogenide glasses. Elliott

[11] proposed the hopping of two electrons between paired defect states (D^+ and D^-) to explain the ac conductivity in chalcogenide glasses.

Based on the above concept, Guintini *et al.* [7] have proposed a theory of dielectric loss in chalcogenide glasses. The theory considers the hopping of charge carriers (two electron) 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 [12, 13]. The latter is related to the existence of a potential barrier over which the carriers must hop [14].

For such a system ε'' , at a particular frequency, in the temperature range where dielectric dispersion occurs, is given by

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) 2 \pi^2 N \left(\frac{ne^2}{\varepsilon_0} \right)^3 kT \tau_0^m W_M^{-4} \omega^m \quad (3)$$

where

$$m = - \frac{4 kT}{W_M} \quad (4)$$

Here, n is the number of electrons that hop, N is the concentration of localized sites, ε_0 and ε_∞ are the static and optical dielectric constant respectively, W_M is the energy required to move the electron from one site to infinity.

According to equation (3), ε'' should follow a power law with frequency, i.e., $\varepsilon'' = A\omega^m$ where m should be negative and linear with T as given by equation (4).

In our samples, we find that ε'' follows a power law with frequency at temperatures greater than 200 K. Moreover, the values of m varies linearly with temperature.

From the above discussion, it seems that our experimental results in the high temperature range ($T > 200$ K) can be explained successfully by the theory of Guintini *et al.* [7] which assumes that the paired defect states (D^+ and D^-) behave as a dipole.

Similar assumption was also made by Srivastava *et al.* [6] to explain their results qualitatively. A maximum in ε'' vs. ω curve as expected in case of dipolar type relaxation has not, however, been observed in the present samples. The absence of such a maximum may be attributed to the existence of the distribution of relaxation time which is quite likely in these materials particularly when each dipole has a relaxation time depending on its activation energy [7]. At very low temperatures ($T < 200$ K), the dipolar type behaviour is not observed in the present case which may be understood in terms of the freezing of the dipoles at low temperatures as suggested by Srivastava *et al.* [6].

Elliott [15] has shown that W_M is associated with the band gap of a material and, to a first approximation, it can be taken to be equal to the band gap (B). The correlation between observed loss and dc conductivity in the present samples (see Tab. I) can also be understood if the loss mechanism is due to hopping of charge carriers between D^+ and D^- centres. The same defects may control the dc conductivity by governing the position of the Fermi level within the gap, and they may also act as relaxation centres giving rise to dielectric loss [15].

Conclusions.

Temperature and frequency dependence of ε' and ε'' were studied in glassy $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($M = \text{Cd}, \text{In}$ and Sb), in the temperature range 100 K to 330 K and the frequency range 0.12 kHz to 10 kHz. At low temperatures ($T < 200$ K), ε' and ε'' are found to be almost independent of temperature and frequency. However, in the high temperature range ($200 \text{ K} < T < 330 \text{ K}$), a strong dielectric dispersion is observed. The frequency dependence of the dielectric loss in this temperature range could be interpreted in terms of the hopping of charge carriers, over a potential barrier, between charged defect states (D^+ and D^-). A correlation of ε'' with σ_{dc} is also observed in these materials which is also in accordance with the above model.

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