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Dielectric relaxation in glassy $Se_{90}Ge_xIn_{10-x}$

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Frequency and temperature dependence of dielectric constant (ε') and dielectric loss (ε'') are studied in glassy $Se_{90}Ge_xIn_{10-x}$, where x = 0, 2, 4, 6, 8 and 10, in the frequency range 1-10 kHz and in the temperature range 293-400 K. The experimental results indicate that no dielectric dispersion exist in glassy $Se_{90}Ge_{10}$ alloy (x = 10). However, when In concentration increases (x = 8, 6, 4, 2 and 0), dielectric dispersion starts in the above frequency and temperature range. The values of ε' and ε'' at a particular temperature and frequency increase with the increase in In concentration. An analysis of the observed dielectric loss shows that the Guintini's theory of dielectric dispersion based on two electron hopping over a potential barrier is applicable in the present case.

The properties of the Ge-Se system have been studied in detail and it has been established that physical properties in this system are highly composition dependent[1-4]. The addition of third element in binary systems has been quite useful in the understanding of the structure and transport properties in chalcogenide glasses. With this point of view, we have started a study of the Ge-Se system with some metallic additives. We have therefore chosen a glassy system $Se_{90}Ge_xIn_{10-x}$ in which it becomes binary $Se_{90}In_{10}$ for x = 0 and it becomes binary $Se_{90}Ge_{10}$ system for x = 10. The properties should show intermediate behaviour at other values of x. The composition dependence of physical parameters are therefore interesting to study in this glassy system.

The study of the dielectric behaviour of chalcogenide glasses is expected to reveal structural information which, in effect, can be useful for the understanding of the conduction mechanism as well. In addition, a study of temperature dependence of dielectric constant particularly in the range of frequencies where dielectric dispersion occurs can be of great importance for the understanding of the nature and origin of the losses occurring in these materials.

The present paper reports the frequency and temperature dependence of dielectric constant (ε') and dielectric loss (ε'') in glassy $Se_{90}Ge_xIn_{10-x}$, where x = 0, 2, 4, 6, 8 and 10, in the frequency range 1-10 kHz and in the temperature range 293-400 K. The experimental results have been analyzed in terms of the existing theory of dielectric relaxation in chalcogenide glasses.

Experimental Procedure

Preparation of glassy alloys

Glassy alloys of $Se_{90}Ge_xIn_{10-x}$ are prepared from the melt by the quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, are weighed using an electronic balance with the least count of 10^{-4} g. The materials are then sealed in quartz ampoules of about 8 mm internal diameter in vacuum (~10^{-5} Torr). The ampoules containing materials are heated upto the melting point of the constituent elements and held at that temperature for 10-12 h. The temperature of the furnace is raised slowly at a rate of 3-4°C/min.

During heating, all the ampoules are rocked, by rotating a ceramic rod to which the ampoules will be tucked away in the furnace. This is done to obtain homogenous glassy alloys. The obtained melts are cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water. The quenched samples are then taken out by breaking the quartz ampoules. The samples are characterized to be in glassy state by X-ray diffraction technique.

Dielectric measurements

Bulk samples, used for dielectric measurements, are obtained in the form of disc by compressing the powdered glassy samples in a die under a load of 3-4 tons. The diameter of the pellets is ~1 cm and thickness ~ 6 mm.

For dielectric measurements, the pellets are mounted in between the two electrodes of a metallic sample holder in which a vacuum ~ 10^{-2} Torr could be maintained. Three terminal measurements are made to avoid stray capacitance. GR 1620 A P capacitance measuring assembly is used to measure the capacitance. The instrument is used in the parallel capacitance mode where parallel conductance could be measured directly. The leads are of co-axial wire to avoid stray capacitance effect. Lead capacitance is subtracted from the measured capacitance before calculating the dielectric constant.

We preferred to experiment on the pellets rather than the bulk as macroscopic effects (like gas bubbles) may appear in the bulk during preparation. The use of the compressed pellets opens the possibility of porosity which may affect the absolute values of the dielectric parameters. However, the conclusions of the present work will not be affected by the porosity effect as all the samples were compressed almost identically and measurements were made under the same conditions for all the samples.

For the study of dielectric relaxation, pellets are coated with indium by vacuum evaporation to ensure good electrical contact between the sample and the electrodes of the sample holder. The temperature and frequency ranges of measurements are 293-400 K and 1-10 kHz, respectively. No irreversible effect is observed during heating in this temperature range excluding the possibility of electrode diffusion in the present measurements.

Results and Discussion

Temperature dependence of dielectric constant and loss is measured at different fixed frequencies of 1, 5 and 10 kHz in all the glassy alloys used in the investigation. Fig. 1 shows the temperature dependence of dielectric constant (ε') and loss (ε'') at certain fixed frequencies in case of Se_{90} Ge_{10}. It is clear from this figure that no dielectric dispersion occurs in the measurement range of temperature and frequencies. The value of the dielectric loss is zero as expected in the case of no dielectric dispersion. However, when the concentration of In increases, the dielectric dispersion starts. Figs 2 and 3 show the temperature dependence of ε' and ε'' at certain fixed frequencies in case of glassy $Se_{90}Ge_8In_2$. It is evident from these figures that ε' and ε'' increase with increase in temperature; increase being different for different frequencies.

To compare the variation of ε' and ε'', at a particular frequency, the temperature dependence of ε' and ε'' is plotted in Figs 4 and 5 for different glassy alloys at 5 kHz. It is clear from these figures that the values of ε' and ε'', at a particular temperature and frequency, are more when the In concentration is more.

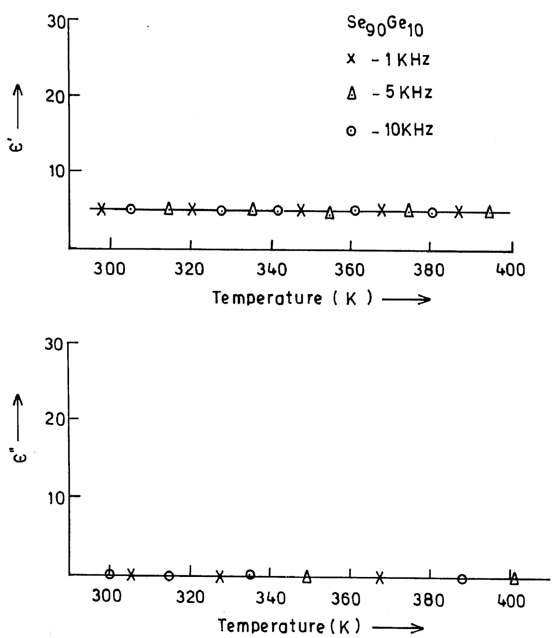

Fig. 1—Temperature dependence of dielectric constant and loss at certain fixed frequencies in glassy $Se_{90}Ge_{10}$

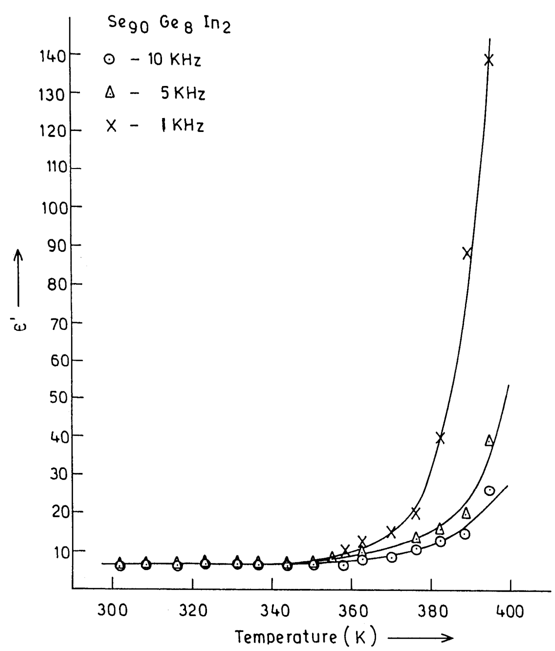

Fig. 2—Temperature dependence of dielectric constant at certain fixed frequencies in glassy $Se_{90}Ge_8In_2$

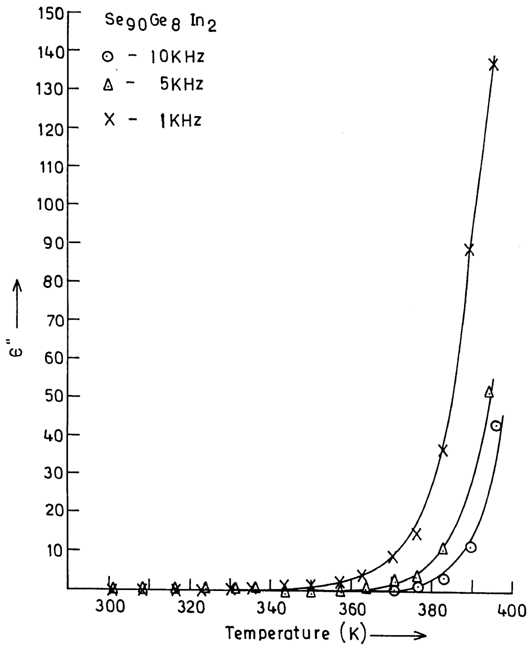

Fig. 3—Temperature dependence of dielectric loss at certain fixed frequencies in glassy $Se_{90}Ge_8In_2$

Arora and Kumar[5,6] have reported frequency and temperature dependence of dielectric constant (ε') and dielectric loss (ε'') of Se, $Se_{100-x}Te_x$ and $Se_{80}Te_{10}M_{10}$ (M = Cd, In and Sb) glassy alloys. These measurements were made in the audio frequency range 120 Hz -10 kHz and in temperature range 100 - 330 K. The results indicated that in glassy Se, ε' and ε'' are independent of temperature and frequency in the operating range of frequency and temperature. In case of $Se_{100-x}Te_x$ and $Se_{80}Te_{10}M_{10}$ (M =Cd, In and Sb) also ε' and ε'' are independent of temperature and frequency at low temperatures (T < 200 K). However, at high temperatures, they showed dielectric dispersion. The detailed analysis showed that the dielectric losses are dipolar in nature and can be understood in terms of hopping of charge carriers over a potential barrier first suggested by Elliott[7] for the case of chalcogenide glasses. Similar type of conclusions have also been drawn by Goel *et al.*[8,9] in case of Se-Te-Sb and Se-Te-Ge glasses. Some more works reported on dielectric relaxation[10-14], indicate that dielectric dispersion occurs in these materials in audio and/or radio frequency range.

Guintini *et al.*[15] have proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on the Elliott's idea[7] of hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). Each pair of site

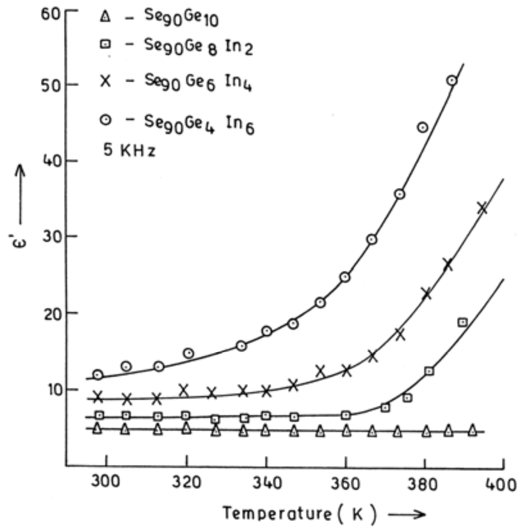

Fig. 4—Temperature dependence of dielectric constant at 5 kHz for different glassy alloys

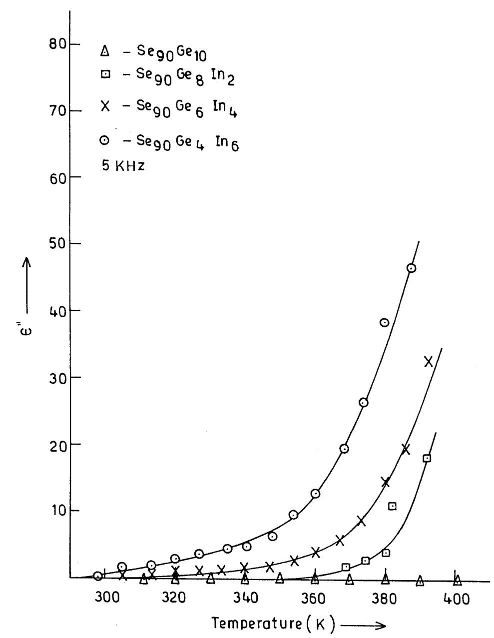

Fig. 5—Temperature dependence of dielectric loss at 5 kHz for different glassy alloys

(D^+ and D^-) is assumed to form a dipole which has a relaxation time depending on it's energy[16,17], the latter can be attributed to the existence of a potential barrier over which the carriers hop[18].

According to Guintini *et al.*[15], ε'' at a particular frequency in the temperature range, where dielectric dispersion occurs, is given by:

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\, 2\, \pi^2\, N\, (ne^2 / \varepsilon_0)^3\, k\, T\, \tau_0^{m}\, W_m^{-4}\, \omega^{m} \quad \ldots (1)$$

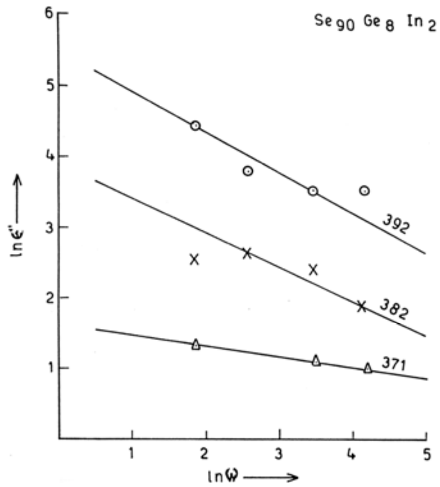

Fig. 6—ln ε" versus ln ω curves at different temperatures in glassy $Se_{90}Ge_8In_2$

where

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

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 constants, respectively, W_m is the energy required to move the electron from a site to infinity.

According to Eq. (1), 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 Eq. (2).

In our samples we found that ε" follows a power law with frequency at higher temperatures where dielectric dispersion occurs (Fig. 6). The values of m at different temperatures are negative and follow a linear relation with T (Fig. 7).

From the above discussion it seems that the paired defect states behave as dipoles in the present glasses. The present results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott in case of chalcogenide glasses[7].

In the present case, no dielectric dispersion is observed in binary $Ge_{10}Se_{90}$. However, dielectric dispersion starts occurring in ternary Ge-Se-In system. The observation of such type of losses with In incorporation indicates that the density of charged defect states increases in ternary system as compared to binary Ge-Se system.

Conclusions

The experimental results indicate that no dielectric dispersion exist in glassy $Se_{90}Ge_{10}$ alloy (x = 10). However, when In concentration increases (x = 8, 6, 4, 2 and 0), dielectric dispersion starts and the effect is more at higher concentration of In. Composition dependence of dielectric parameters show that the values of ε' and ε", at a particular temperature and frequency, increase with the increase in In concentration in glassy $Se_{90}Ge_xIn_{10-x}$.

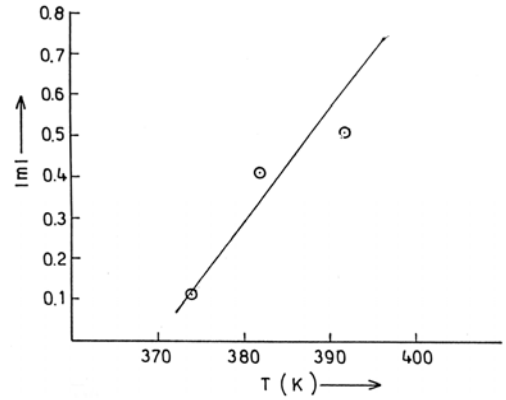

Fig. 7—m versus T curve in glassy $Se_{90}Ge_8In_2$

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