Dielectric relaxation in $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$ chalcogenide glasses

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Abstract. Temperature and frequency dependence of dielectric constant (ε') and dielectric loss (ε'') are studied in glassy $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$. The measurements have been made in the frequency range (1 to 10 kHz) and in the temperature range 300 to 395 K. No dielectric dispersion is observed in glassy $Se_{80}Ge_{20}$. However, the results indicate that the dielectric dispersion exists in $Se_{75}Ge_{20}Ag_5$ in the above frequency and temperature range. An analysis of the dielectric loss data shows that the Guintini theory of dielectric dispersion based on two electron hopping over a potential barrier is applicable in the present case.

1. Introduction

Ag-containing chalcogenide glasses have attracted widespread interest for applications in optical recording and as solid electrolytes. The importance of this combination was first established in 1967, when the effect of silver photo-diffusion in chalcogenide glasses was discovered [1]. In the following nearly 40 years, great contributions have been made to the field [2, 3] and the photo-diffusion effect has been applied in the fabrication of optical elements using relief images [4], in micro-photo-lithographic systems [5, 6] and in direct imaging by photo-induced silver surface deposition [7, 8]. The low free energy of crystallization of Ag (48 kcal/mol) was a further reason to consider the introduction of Ag in chalcogenide glasses used for phase change optical recording [9, 10]. This enabled one for the attainment of the main requirements for good optical recording-high phase transformation rate. For this reason, the crystallization kinetics of Ag-containing chalcogenide glasses have been studied by various workers [11-13] for the development of new and better phase change recording materials.

One other aspect of silver's influence in Ag-containing chalcogenide glasses is the effect on the electrical conductivity of the glasses, which can be changed by several orders of magnitude when Ag is introduced. Therefore, investigations on the influence of Ag on the physical properties of chalcogenide glasses are of relevance both from the basic science and application point of view. Our laboratory is also engaged

in this direction to study the physical properties of Ag based chalcogenide glasses [11-17].

Effect of Ag addition on crystallization kinetics in Se-Te glasses, has been studied by Sharma *et al.* [11] and Mehta *et al.* [12, 13]. X-ray spectroscopic studies of Ag doped Ge-Se glasses have been reported by Shukla *et al.* [14] to understand the nature of bonding and concluded that bonds are ion-covalent in character. High field conduction in Ag doped $Se_{80}Te_{20}$ has been studied by Kumar *et al.* [15]. Dielectric behaviour of Ge-Se and Se-Te glasses with some metallic additives has been studied by Arora *et al.* and Sharma *et al.* [16, 17], respectively.

The study of dielectric behaviour of chalcogenide glasses is expected to reveal structural information, which, in effect, can be useful to understand the conduction mechanism as well. In addition, a study of temperature dependence of dielectric permittivity particularly in the range of frequencies where dielectric dispersion occurs can be of great importance for understanding the nature and origin of the losses occurring in these materials. Though, the electrical and thermal properties of Ag-doped chalcogenide glasses have been studied by various workers, not much work has been done on the dielectric properties [16, 17]. We have, therefore, started a systematic study of dielectric relaxation in Ag doped chalcogenide glassy systems in our laboratory.

In view of the above, we have decided to work on Ag containing Se-Ge system, which shows ionic conduction, and relatively less studied as compared to other Ag doped systems, e.g., As-Se and Se-Te. In the present

paper the results of dielectric measurements in $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$ glasses are presented.

The temperature dependence of the dielectric constant (ε') and dielectric loss (ε'') has been measured in $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$ so that the effect of Ag incorporation on dielectric behaviour in $Se_{80}Ge_{20}$ could be ascertained. The measurements have been made in the temperature range 300 to 395 K, where the dielectric dispersion occurs in the audio frequency range (1 to 10 kHz in the present case). A study of temperature and frequency dependence of dielectric parameters reveals that the dielectric behaviour of chalcogenide glasses can be described with the help of the theory of dipolar relaxation.

2. Experimental details

2.1. Preparation of glassy alloys

Glassy alloys of $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$ were prepared by the quenching technique. High purity Se, Ge and Ag materials (5N) were weighed according to their atomic percentages, and were sealed in quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm), with a vacuum ~ 10^{-5} Torr. The sealed ampoules were kept inside a furnace where the temperature was raised to 1000 °C, at a rate of 3–4 °C/min. The ampoules were frequently rocked for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature was verified by X-ray diffraction.

The glassy alloys thus prepared were ground to a very fine powder and pellets (diameter ~10 mm and thickness ~ 1 mm) were obtained by compressing the powder in a die at a load of 5 Tons. The pellets were coated with vacuum evaporated indium film to ensure good electrical contact between the sample and the electrodes.

2.2. Dielectric measurements

The pellets were mounted in between two steel electrodes of a metallic sample holder for dielectric measurements. The temperature measurement was facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of ~10^{-2} Torr was maintained over the entire temperature range (300 to 395 K). The temperature dependence of ε' was studied in heating run at a heating rate of 1 K/min. Dielectric measurements were made using a GR 1620 AP capacitance measuring assembly. The parallel capacitance was measured and then ε' was calculated. Three terminal measurements were performed to avoid the stray capacitances.

We preferred to experiment on the pellet rather than the bulk as macroscopic effects (gas bubbles, *etc.*) may appear in the bulk during preparation. It has been shown by Goyal *et al.* [18], both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar dielectric behaviour in chalcogenide glasses. They find no evidence of Maxwell-Wagner losses for the suspected inhomogeneities in case of compressed pellets in these materials. The number of localized sites induced by grain boundary effects can be neglected as compared to charged defect states which are quite large (~ 10^{18} to 10^{19} eV^{-1}cm^{-3}) in these glasses. Microsoft Excel programming has been used for more accurate calculations in the present study.

3. Theoretical basis

Guintini *et al.* [19] have proposed a model for dielectric dispersion in chalcogenide glasses. This model is based on the Elliott idea [20] of hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). Each pair of site (D^+ and D^-) is assumed to form a dipole which has a relaxation time depending on it' energy [21, 22], the latter can be attributed to the existence of a potential barrier over which the carriers hop [23].

According to the above model [19], ε'' at a particular frequency, in the temperature range where dielectric dispersion occurs, is given by:

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\, 2\, \pi^2\, N\, (ne^2/\varepsilon_0)^3\, kT \times$$
$$\times \tau_0^{\,m}\, W_m^{-4}\, \omega^m \qquad (1)$$

where m is a power of angular frequency and is given by:

$$m = -4\, k\, T/\, W_m. \qquad (2)$$

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.

4. Results

It has been reported [24-29] that, in chalcogenide glasses, the temperature dependence of ε' and ε'' is appreciable only in certain temperature range. At lower temperatures, ε' is almost constant and ε'' is negligibly small. After a certain temperature, ε' and ε'' increase appreciably with temperature. Therefore, the present measurements have been made only in the high temperature region where dielectric dispersion is quite appreciable. The temperature dependence of ε' and ε'' are studied at various frequencies (1 to 10 kHz) for all the glassy alloys studied here. The temperature range of measurements is from 300 to 395 K.

4.1. Temperature dependence of dielectric constant (ε') and dielectric loss (ε'')

Fig. 1 shows the results of the dielectric constant measurements at different frequencies for $Se_{80}Ge_{20}$ glassy alloy below the glass transition temperature. From Fig. 1, it is clear that no change in ε' is observed as a
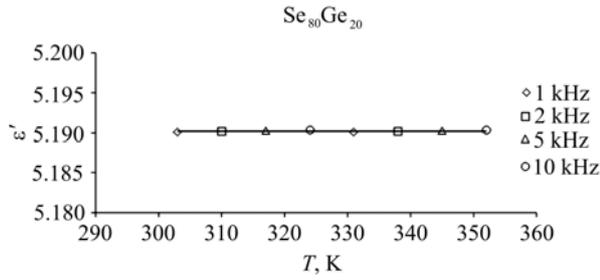
Fig. 1. Variation of dielectric constant ($\varepsilon^{'}$) with temperature at different frequencies in glassy $Se_{80}Ge_{20}$.

Fig. 3. Variation of dielectric loss ($\varepsilon^{''}$) with temperature at different frequencies in glassy $Se_{75}Ge_{20}Ag_5$.

function of temperature and frequency. This shows that dielectric relaxation does not exist in glassy $Se_{80}Ge_{20}$ alloy. The dielectric loss ε'' is also found to be negligible in this frequency range. Figs 2 and 3 show the results of the dielectric constant and dielectric loss measurements for $Se_{75}Ge_{20}Ag_5$ glassy alloy. These figures indicate that the temperature dependence of ε' and ε'' is appreciable only in the certain temperature range. At lower temperatures, ε' and ε'' are found almost constant. Only after a certain temperature, ε' and ε'' increase appreciably with temperature. In this glassy sample, dielectric constant increases with the increase in temperature, the increase being different at different frequencies. Thus, the temperature dependence of ε' and ε'' in the present chalcogenide glass is same as reported by various workers in other chalcogenide glasses [24-29].

4.2. Frequency dependence of dielectric constant (ε') and dielectric loss (ε'')

Fig. 4 shows the frequency dependence of dielectric constant ε' at different temperatures for $Se_{75}Ge_{20}Ag_5$. It is clear from the figure that ε' decreases with increasing frequency and increases with increasing temperature.
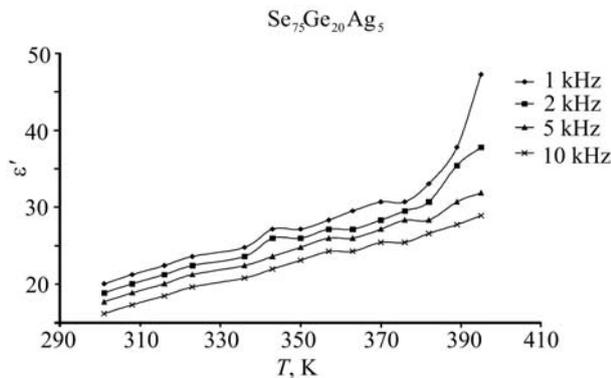
The increase of ε' with temperature can be attributed to the fact that the orientational polarization is connected with the thermal motion of molecules, so dipoles cannot orient themselves at low temperatures. When the temperature is increased the orientation of dipoles is facilitated and this increases the value of orientational polarization and this increases ε' with increasing temperature.

The frequency dependence of dielectric loss ε'' is shown in Fig. 5 at different temperatures for $Se_{75}Ge_{20}Ag_5$. From this figure, it is clear that ε'' is also found to decrease with increasing frequency and increase with increasing temperature according to the equation $\varepsilon'' = A\,\omega^m$, where A is a constant.

The values of power m, calculated from the slopes of straight lines in Fig. 5, are plotted as a function of temperature in Fig. 6. The values of m are negative and the magnitude of m decreases linearly (correlation coefficient $R^2 \approx 1$) with temperature (Figs 5 and 6). This is consistent with Eq. (2), which shows that the Guintini [19] theory of dielectric relaxation based on the hopping of charge carriers over a potential barrier as suggested by Elliott [20] is applicable in the case of present ternary glass. The slope of least fit square line is used for the calculation of W_m. Value of W_m obtained from the slope of the line of Fig. 5 is 0.383 eV.
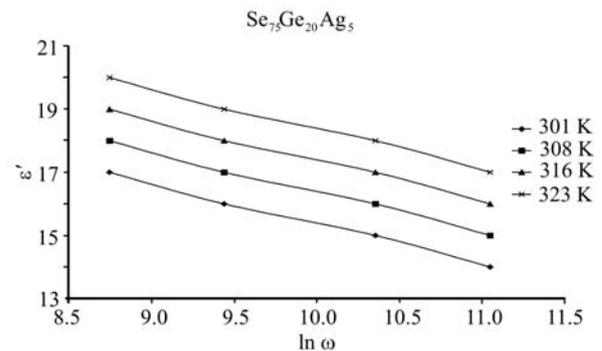

Fig. 2. Variation of dielectric constant ($\varepsilon^{'}$) with temperature at different frequencies in glassy $Se_{75}Ge_{20}Ag_5$.

Fig. 4. Frequency dependence of dielectric constant ($\varepsilon^{'}$) at certain fixed temperatures in glassy $Se_{75}Ge_{20}Ag_5$.
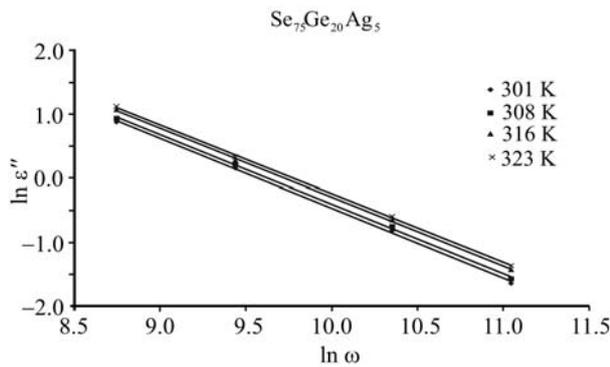
Fig. 5. Frequency dependence of dielectric loss (ε'') at certain fixed temperatures in glassy $Se_{75}Ge_{20}Ag_5$.

5. Discussion

The temperature dependence of ε' at various frequencies for the present glassy alloy indicated that ε' varies with temperature and then saturates at higher temperatures. This type of temperature dependence is generally observed in molecular solids where the Debye theory [30] for the viscosity dependence of relaxation time holds quite well. The observed behaviour is conveniently explained if one assumes that the present glassy alloys exist in the form of dipoles [31]. At higher temperatures, these dipoles get activated and attain freedom of rotation, even though the material remains in solid state. The molecular explanation of this temperature dependence is that the relative influence of the molecular interaction energy decreases with respect to that of the thermal energy at higher temperatures.

The above mentioned dipolar concept may be understood in terms of the charged defect states suggested by Mott and his collaborators [32, 33]. According to them, the dangling bonds can exist in paired defects states ($D^+ + D^-$) and are responsible for the density of states in the gap pinning the Fermi level.

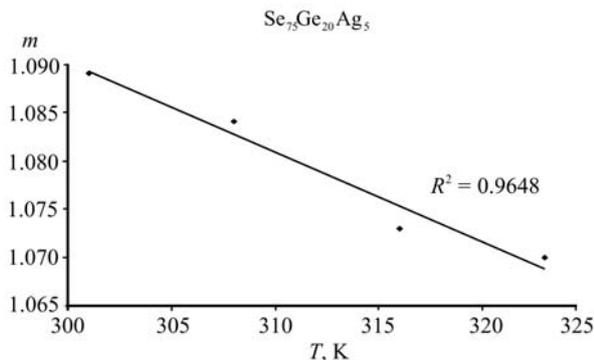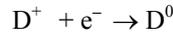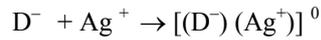It is well known that the dissolution of silver in chalcogenide glasses involves migration of Ag^+ ions and electrons [34]. Since there are a large number of D^+ and D^- sites in the chalcogenide glasses, one would eventually expect a new equilibrium to be set up after migration, i.e.,

$$D^+ + e^- \rightarrow D^0$$

and

$$D^- + Ag^+ \rightarrow [(D^-)\,(Ag^+)]^0$$

The above reaction suggests that, on doping, some of the D^- and Ag^+ couples together to form $[(D^-)\,(Ag^+)]$ dipoles which otherwise were not present in the undoped samples. The presence of above dipoles is probably responsible for the observed dipolar type relaxation in the present ternary glassy alloy.

6. Conclusions

Dielectric measurements made in chalcogenide glasses $Se_{80}Ge_{20}$ and $Se_{75}Ge_{20}Ag_5$ showed that dielectric dispersion does not exist in $Se_{80}Ge_{20}$ glassy alloy in the audio frequency range. However, the dielectric dispersion occurs in this material in the audio frequency range on addition of 5 at. % of Ag. The results of the dielectric constant and dielectric loss measurements show that Guintini's theory of dielectric dispersion of two electrons hopping over a potential barrier is applicable in the present case.

A detailed analysis of the data reveals that the results are well explained in terms of dipolar relaxation with a distribution of relaxation times, which is quite expected in case of non-crystalline systems. It is suggested that charged defect states present in silver doped chalcogenide glasses may be responsible for dipolar type behaviour.

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Fig. 6. Temperature dependence of m for glassy $Se_{75}Ge_{20}Ag_5$.

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