Role of metallic Zn and In additives in the electrical and dielectric properties of $Se_{0.85}Te_{0.15}$ glassy alloy

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Abstract

In this paper we report the effect of metallic Zn and In additives on the electrical and dielectric properties of $Se_{0.85}Te_{0.15}$ glassy system. The temperature and frequency dependence of the dielectric parameters in glassy $Se_{0.85}Te_{0.15}$, $Se_{0.75}Te_{0.15}In_{0.10}$ and $Se_{0.75}Te_{0.15}Zn_{0.10}$ alloys are studied by measuring capacitance and dissipation factor in the frequency range (1 kHz–5 MHz) and temperature range (300–350 K). Direct current (dc) measurements were also performed in the aforesaid temperature range to assess the dc conduction losses. Results are interpreted in terms of a theoretical model which is based on two electron hopping over a potential barrier and is applicable in the present case. Dielectric constant ε', dielectric loss ε'' and loss tangent δ are found highly frequency and temperature dependent. Dependence of electrical and dielectric parameters on the additives has also been found in the present glassy system and has been discussed in terms of electronegativity difference between the elements used in making the aforesaid glassy system.

1. Introduction

Selenium (Se) exhibits the unique property of reversible phase transformation [1]. Its various device applications like rectifiers, photocells, xerography, switching and memory, etc have made it attractive, but pure Se has disadvantages such as short lifetime and low photosensitivity. This problem can be overcome by alloying Se with Tellurium (Te). The effect of alloying Te into a-Se result in dissociation of long polymeric chains and eight member rings of a-Se [2].This makes Se-Te alloys more important as compared to a-Se due to distinct advantages (greater hardness, better photosensitivity, reduced ageing effects, etc.) and hence find various applications.

Similarly, Se-In glasses find application in optical and electronic communication, switching and memory devices, and photovoltaic applications. Various properties such as photoconductivity, charge conduction and optical absorption, solar cell applications have been reported in this system. Se-In also exhibits anomalous

features such as negative Seebek coefficient in certain composition [3], large Fermi level shift [4] and an anomalous rise of the photocurrent [5].

However in these glasses limited reversibility [6] and low crystallization temperatures are serious problems. These problems can be overcome by addition of third element as a chemical modifier. The addition of dopant can modify the lattice perfection. Several researchers [7–14] have reported the impurity effects in various chalcogenide glasses. Se-Te-In glassy systems have been relatively less investigated as compared the Se-In system. Structural study of Se-Te-In alloy using X-rays reveal that Selenium K- edge shift towards the lower energy side compared to Se-Te [15]. Recently [16–19], it has been reported that in these glasses the dielectric dispersion does exist at low frequencies even though these materials are covalently bonded semiconductors.

The electrical properties of chalcogenide glasses are not, in general, affected, appreciably by the incorporation of additives because the random network of atoms can accommodate an impurity without creating an extra electron-hole pair. This concept is based on the fact that an additive atom can satisfy its valance requirements by adjusting its nearest neighbour environment, thus causing negligible effect on electrical properties.

However experimental results reported by various workers have shown that the addition of impurity atoms does change the electrical properties significantly. They are situated in sites with unusual configurations which do not allowed their valance to be satisfied.They can therefore behave in an electrically active manner leading to donor-like or acceptor-like behavior.

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. 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 the understanding of the nature and origin of the losses occurring in these materials. Thus there is need to predict the suitability of various glass compositions, with the dielectric relaxation being a key parameter.

In view of the above we have decided to study the effect of Zn and In additive in the dielectric and electrical properties of $Se_{0.85}Te_{0.15}$ glassy system. The next section describes the experimental details of the measurements. The results are presented and discussed in the third section. The final section deals with the conclusions drawn from the present work.

2.   Experimental details

2.1.   Preparation of glassy alloys

Glassy alloys of $Se_{0.85}Te_{0.15}$, $Se_{0.75}Te_{0.15}In_{0.10}$ and $Se_{0.75}Te_{0.15}Zn_{0.10}$ systems were prepared by quenching technique. High purity (99.999%) materials were weighed according to their atomic percentages and were sealed in quartz ampoules (length $\sim$5 cm and internal diameter $\sim$8 mm) with a vacuum $\sim10^{-5}$ Torr. The ampoules containing the materials were heated to 900 $^\circ$C and held at that temperature for 10–12 hours. The temperature of the furnace was raised slowly at a rate $\sim$3–4 $^\circ$C/min. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This was done to obtain homogenous glassy alloys.

After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples were taken out by breaking the quartz

ampoules. Compositional analysis was performed using electron probe micro- analysis (EPMA) technique.

Pellets of diameter ~ 10 mm and thickness ~ 1–2 mm were prepared by compressing the finely grounded powder in a die in a hydraulic press under a load of ~ 3–4 tons. Measurements were performed after coating the pellets with indium film deposited by vacuum evaporation technique.

2.2. Dielectric relaxation measurements

A specially designed metallic sample holder was used for the measurements of dielectric parameters in a vacuum $\sim 10^{-3}$ Torr. The pellets were mounted in between two steel electrodes of the sample holder. The temperature was measured with the help of a calibrated copper-constantan thermocouple mounted very near to the sample, which could give measurements of temperature with an accuracy of 1 $^\circ$C. The temperature dependence of the dielectric constant ε' and dielectric loss ε'' were studied in a heating run at a heating rate of 1 K/min. The frequency dependence of ε' and ε'' was also measured by maintaining constant temperature inside the sample holder.

Dielectric measurements were made using a Hioki model 3532-50 LCR Hi Tester. The parallel capacitance and dissipation factor was measured, and then ε' and ε'' was calculated. Three terminal measurements were performed to avoid the stray capacitances.

To measure the dc conductivity of the sample, a dc voltage of 10 V was applied across the sample and the resulting current was measured via a Scientific Equipments Roorkee made Digital Picoammeter model DPM 111. These measurements were also made in the same sample holder in which the dielectric measurements were made. A vacuum of $\sim 10^{-3}$ Torr was also maintained during these measurements.

We preferred to measure dielectric behavior 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. [20], both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar dielectric behavior in chalcogenide glasses for the suspected in-homogeneities 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 ($\sim 10^{18}$ to 10^{19} eV$^{-1}\cdot$ cm^{-3}) in these glasses. Microsoft Excel programming has been used for more accurate calculations in the present study.

3. Results and discussion

3.1. Measurements of D. C. conductivity

Before studying the dielectric behavior, the temperature dependence of dc conductivity (σ_{dc}) was also measured for all glassy samples used in the present study. Interpretation of the data confirms that the conductivity in the present case is thermally activated having single activation energy. Figure 1 shows plots of ln σ_{dc} as a function of temperature are largely straight lines for various samples, which indicates that the conductivity increases with the increase of temperature, following a usual relation:

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

where ΔE is the activation energy for dc conduction and k_B is the Boltzmann's constant. Values of ΔE are calculated from the slopes of ln σ_{dc} vs. $1000/T$ curves; and the results are shown in Table 1. The same table also contains the value of σ_{dc} at 300 K for all the samples.
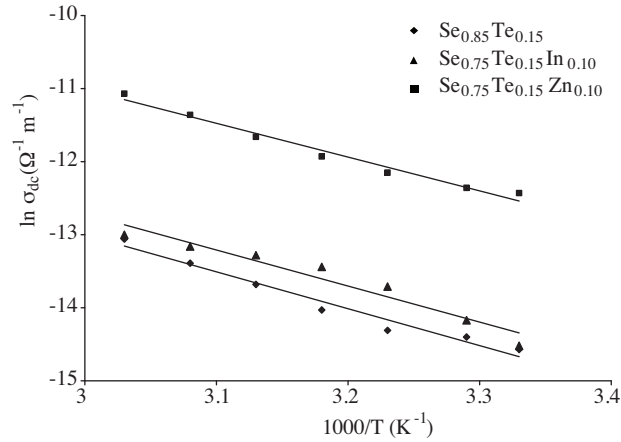
Figure 1. Temperature dependence of dc conductivity in a-Se$_{0.85}$Te$_{0.15}$, a-Se$_{0.75}$Te$_{0.15}$In$_{0.10}$ and a-Se$_{0.75}$Te$_{0.15}$Zn$_{0.10}$ glassy alloys.

Table 1. Values of σ_{dc} and ΔE for various glassy alloys.

Glassy alloys	$\sigma_{dc}(\Omega^{-1}\mathrm{m}^{-1})$ (at 300 K)	ΔE (eV)
Se$_{0.85}$Te$_{0.15}$	4.7×10^{-7}	0.43
Se$_{0.75}$Te$_{0.15}$In$_{0.10}$	5.0×10^{-7}	0.42
Se$_{0.75}$Te$_{0.15}$Zn$_{0.10}$	4.0×10^{-6}	0.39

3.2. Dielectric behavior of considered glassy alloys

Temperature dependence of ε' and ε'' was measured at various frequencies (1 kHz to 5 MHz) for various glassy alloys studied in present case. Measurements have been taken in the temperature range 300 K to 350 K. ε' and ε'' are found to be temperature dependent in the above frequency range in all the glassy samples studied here. Figures 2–7 show ε' and ε'' as functions of temperature for aforementioned glassy alloys. Note ε' and ε'' increase with temperature, the increase being different at different frequencies. This type of behavior has been reported by various workers [21] in chalcogenide glasses. This behavior can be attributed to the fact that orientational polarization is associated with the thermal motion of molecules. The orientation of the dipoles increases as the thermal energy increases, leading to the increase of ε'. The increase of ε'' with temperature may be due to increase in the conduction losses with temperature. The sum of electronic, ionic, dipolar and space charge represents the total polarisation of a dielectric material. In the present study, it is clear that the ionic polarisation does not show a pronounced effect in the total polarisation where the covalent nature of the studied composition is expected.

The degree of covalency of the studied compositions can be estimated according to the following relation [22]:

$$\text{The proportion of covalent character } = 100\% \cdot \exp[-0.25(\chi_A - \chi_B)^2], \tag{2}$$

where χ_A and χ_B are the electronegativities of atoms A and B, respectively. The values of covalent characters are listed in Table 2. When the applied field frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is further

increased the dipole will be completely unable to follow the field and the orientational polarization stopped, so ε' decreases approaching a constant value at a higher frequency due to the interfacial polarization.
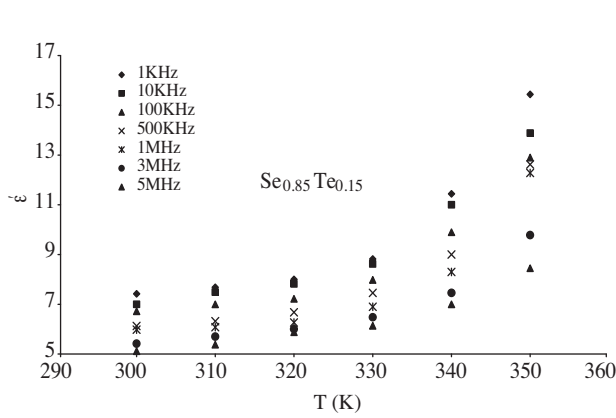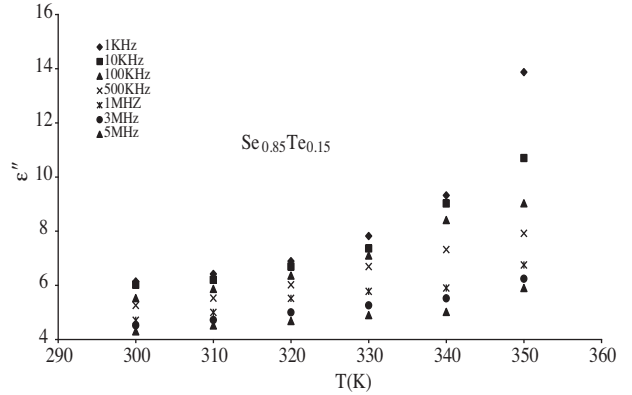

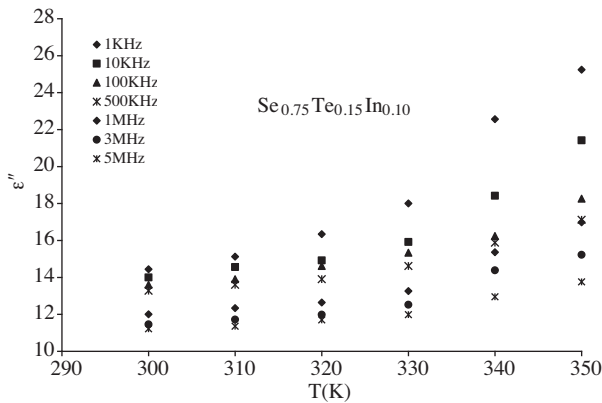**Figure 2.** Temperature dependence of dielectric constant (ε') in glassy $Se_{0.85}Te_{0.15}$ alloy.
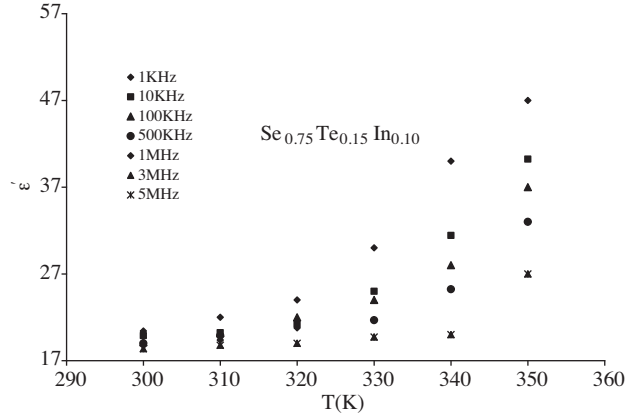
Figure 3. Temperature dependence of dielectric constant (ε') in glassy $Se_{0.75}Te_{0.15}In_{0.10}$ alloy.
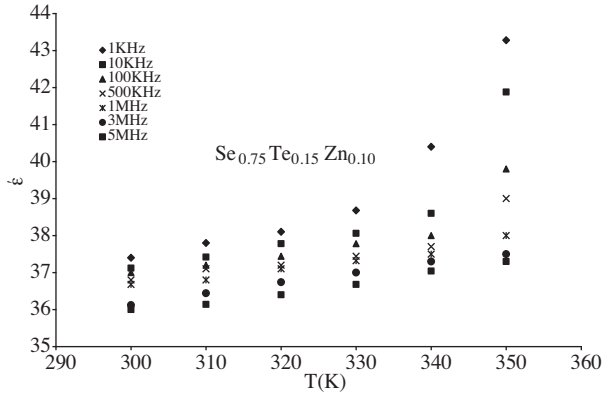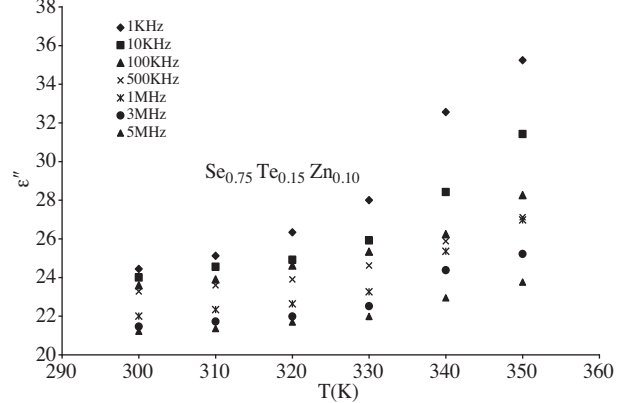

Figure 4. Temperature dependence of dielectric constant (ε') in glassy $Se_{0.75}Te_{0.15}Zn_{0.10}$ alloy.

Figure 5. Temperature dependence of dielectric loss(ε'') in glassy $Se_{0.85}Te_{0.15}$ alloy.

Figure 6. Temperature dependence of dielectric loss(ε'') in glassy $Se_{0.75}Te_{0.15}In_{0.10}$ alloy.

Figure 7. Temperature dependence of dielectric loss(ε'') in glassy $Se_{0.75}Te_{0.15}Zn_{0.10}$ alloy.

**Table 2.** Calculated covalent character of bonds for considered compositions.

| Bonds for bond type	% covalent character
Se-Se	100
Se-Te	97.78
Se-In	88.47
Se-Zn	85.21
Te-Te	100
Te-In	96.08
Te-Zn	93.94
Zn-Zn	100
Zn-In	99.75
In-In	100

The incorporation of metallic additive In and Zn in the binary $Se_{0.85}Te_{0.15}$ glassy alloy leads to increase the value of the dielectric constant as given in Table 3. This increase can be understood in terms of the nature of the bonding in the system. It may be supposed that the incorporation of impurity atom in the binary alloy may lead to decrease in the density of stronger bonds than other bonds in the network structure, i.e, increases the weaker bond density in the investigated compositions, which are more responsive to electric field than the stronger bonds. Thus the value of ε' increases with impurity incorporation in the studied system.

Table 3. Dielectric parameters of various glassy alloys.

Glassy alloys	ε' (1 kHz, 300 K)	ε'' (1 kHz, 300 K)	Wm (at 300 K)	Tan δ (at 300 K)
$Se_{0.85}Te_{0.15}$	7.42	6.14	0.31	0.83
$Se_{0.75}Te_{0.15}In_{0.10}$	20.42	14.44	0.35	0.71
$Se_{0.75}Te_{0.15}Zn_{0.10}$	37.40	24.44	0.69	0.65

Also, in the above glassy alloys, ε'' is found to follow a power law with frequency, i.e. $\varepsilon'' = A\omega^m$. Figures 8–10 (for $Se_{0.85}Te_{0.15}$, $Se_{0.75}Te_{0.15}In_{0.10}$ and $Se_{0.75}Te_{0.15}Zn_{0.10}$ glassy alloys) confirm this behavior where ln ε'' versus ln ω curves are found to be straight lines at various temperatures. The power m is calculated from the slopes of these curves and found that the values of m are negative at all measuring temperatures. The values of m at different temperatures for all glassy alloys are given in Table 4. The magnitude of m increases with the increase of temperature in all the samples studied at present (Figures 11–13) (for aforementioned glassy alloys).
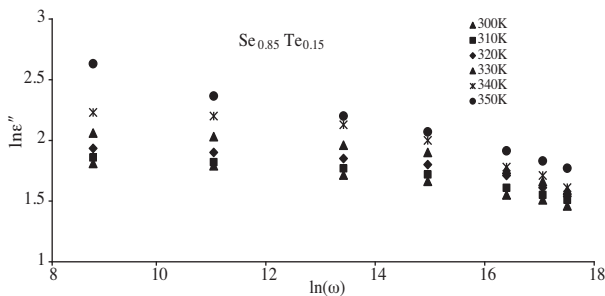
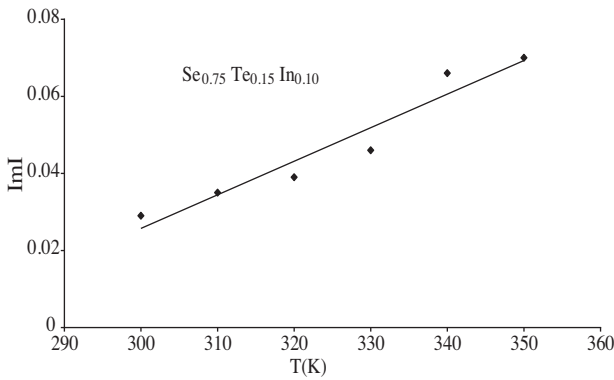**Figure 8.** Frequency dependence of dielectric loss(ε'') in glassy $Se_{0.85}Te_{0.15}$ alloy at certain fixed temperatures.
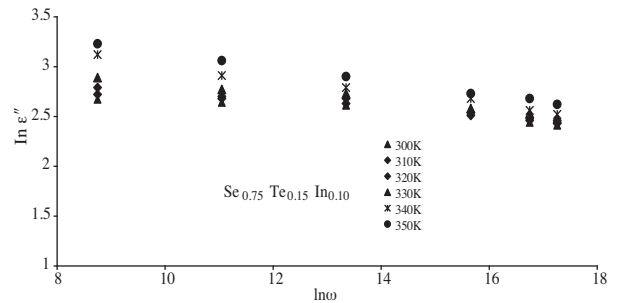
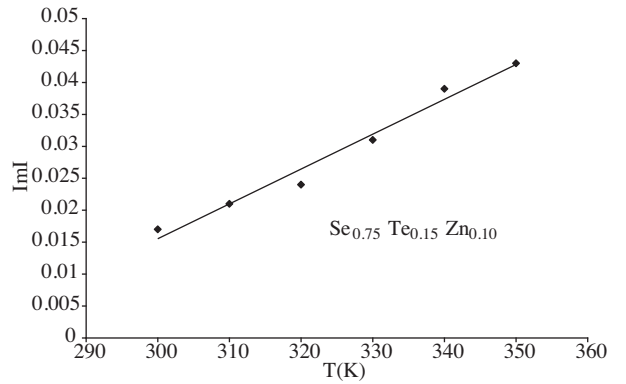**Figure 9.** $\ln\omega$ vs $\ln\varepsilon''$ curves in a-$Se_{0.75}Te_{0.15}In_{0.10}$ at certain fixed temperatures.
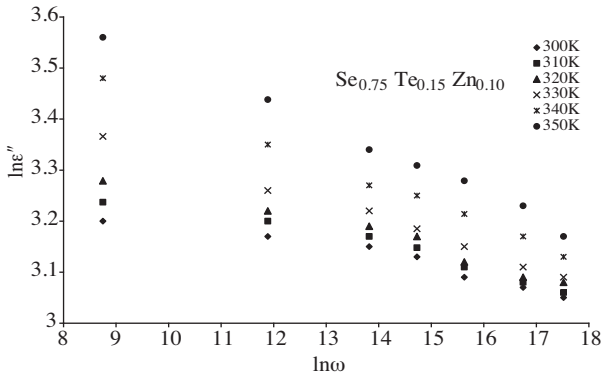
Figure 10. $\ln\omega$ vs $\ln\varepsilon''$ curves in a-$Se_{0.75}Te_{0.15}Zn_{0.10}$ at certain fixed temperatures.
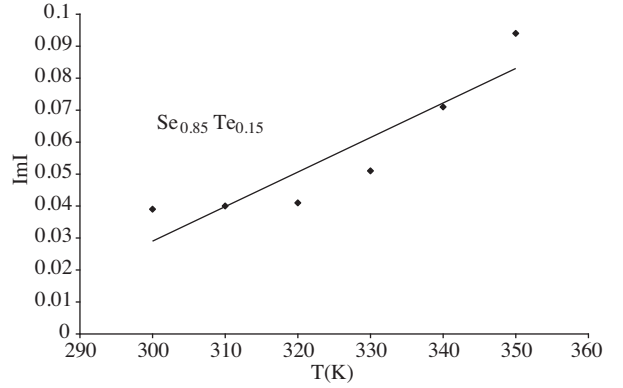
Figure 11. ImI versus T curve in glassy $Se_{0.85}Te_{0.15}$ alloy.

Figure 12. ImI versus T curve in glassy $Se_{0.75}Te_{0.15}In_{0.10}$ alloy.

Figure 13. ImI versus T curve in glassy $Se_{0.75}Te_{0.15}Zn_{0.10}$ alloy.

Table 4. Values of m at different temperatures for various glassy alloys.

T (K)	$Se_{0.85}Te_{0.15}$ m	$Se_{0.75}Te_{0.15}In_{0.10}$ m	$Se_{0.75}Te_{0.15}Zn_{0.10}$ m
300	-0.039	-0.029	-0.017
310	-0.040	-0.035	-0.021
320	-0.041	-0.039	-0.023
330	-0.051	-0.046	-0.031
340	-0.071	-0.066	-0.039
350	-0.094	-0.070	-0.043

Guintini et al. [23] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [24] of hopping of charge carriers over a potential barrier between charged defects states (D^+ and D^-). These defects are responsible not only for the position of the Fermi level, but also for the transport properties of the material. In addition they act as traps and recombination centers for carriers and (D^+/D^-) is assumed to form a dipole which has a relaxation time depending on its activation energy; the latter can be attributed to the existence of a potential barrier over which the carriers hop. This potential barrier, as proposed by Elliot, is due to the coulombic interaction between neighboring sites forming a dipole.

The relaxation time connected with a hop is given by

$$\tau = \tau_0 \exp(W/k_B T) \tag{3}$$

Combining the imaginary part of the permittivity with circular frequency ω of the applied electric field, we can write

$$\varepsilon''(\omega) = (\varepsilon_o - \varepsilon_\infty) 4\pi N \varepsilon_o k_B T / ne^2 \int\limits_0^\infty R^4 [\omega/(1 + \omega^2 \tau^2)] d\tau. \tag{4}$$

Here, $R = R(\tau)$ is the distance between localized sites . This integral has already been evaluated [24–25]. According to Guintini et al. [23], assuming $\omega\tau << 1$, ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by the relation

$$\varepsilon''(\omega) = (\varepsilon_o - \varepsilon_\infty) 2\pi^2 N (ne^2/\varepsilon_0)^3 kT \tau_0^m W_m^{-4} \omega^m. \tag{5}$$

Here, m is a power of angular frequency and is negative in this case and is given by

$$m = -4k_B T/W_m, \tag{6}$$

where 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 equation (5), 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 (6). This equation is consistent with the expression of $\varepsilon''(\omega)$ obtained from the Kramers-Kronig relations. In our samples, we also found that ε'' follows a power law with frequency at higher temperatures where dielectric dispersion occurs. The values of m at different temperatures are negative and follow a linear relation with temperature. Using the values of m, W_m is calculated and the results are given in Table 3. It is clear from this table that the value of W_m increases with additive incorporation.

From the above discussion it seems that the paired defect states (D^+ and D^-) behave as dipoles in the aforesaid glasses studied here. The present results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott [24] in case of chalcogenide glasses.

3.3.   Additive dependence of ε' and ε''

When isoelectronic atom Te is added to amorphous Selenium, [26] the density of defect states is increased and hence the residual potential increases in xerographic experiment. Onozuka et al., have therefore, observed that on introducing Cl to Se-Te system, the residual potential is decreased again. This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to small electronegativity of Te as compared to Se, while Cl atoms having higher electronegavity than Selenium [22] form negatively charged impurities, thereby compensating the effect of Te [26].

Along the same lines, one can expect that when In and Zn, having lower electronegativity than Se and Te [22], is introduced in $Se_{0.85} Te_{0.15}$, positive charged defects will be created, thus increasing the density of defect states in ternary Se-Te-In and Se-Te-Zn glassy system as compared to pure binary Se-Te glassy alloy.

The values of ε' and ε'' in aforesaid glassy alloys are given in Table 3. As the dielectric loss in these glasses depends upon the total number of localized sites, the increase of dielectric loss with the Zn and In

incorporation can be understood in terms of the increase of density of defects on addition of Zn and In to Se-Te glassy system. Due to the increased number of dipoles (D^+ and D^-) with Zn and In, the dielectric constant is also expected to increase as found by us in the present study.

4. Conclusion

The temperature and frequency dependence of the dielectric constants and the dielectric losses in various glassy systems in the frequency range (1 kHz–5 MHz) and temperature range (300 K–350 K) have been measured. It has been found that dielectric constant and the dielectric loss both are highly dependent on frequency and temperature and also found to be dependent with the nature of metallic additives in Se-Te glassy system. The frequency dependence of the dielectric loss in the above temperature range could be interpreted in terms of the hopping of charge carriers, over a potential barrier, between charged defect states (D^+ and D^-). It is clear from the results obtained that the addition of Zn and In increases the charged defect states in the pure Se-Te glassy network which also affects the dielectric properties. This change of the dielectric parameters with additive in $Se_{0.85}Te_{0.15}$ binary glassy system could also be explained on the basis of the electro-negativity difference and the nature of covalent character of bonds between the constituent elements used in making the above glassy alloys.

Acknowledgements

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