Chalcogenide Letters Vol. 6, No. 12, December 2009, p. 673 – 682

ROLE OF SOME METALLIC IMPURITIES (Pb, Sb, Te) ON DIELECTRIC PROPERTIES OF Se-In GLASSY ALLOYS

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In this paper we report the effect of impurity incorporation on the Dielectric properties of a-$Se_{75}In_{25}$ glassy alloy. The temperature and frequency dependence of the dielectric constants and the dielectric losses in Glassy $Se_{75}In_{25}$, $Se_{75}In_{10}Pb_{15}$, $Se_{75}In_{10}Sb_{15}$ and $Se_{75}In_{10}Te_{15}$ alloys are studied by both capacitance and dissipation factor measurements in the frequency range (1 K Hz - 5 M Hz) and temperature range (300 K – 350 K). A Debye like relaxation of dielectric behavior has been observed.A detailed analysis shows that the observed dielectric loss is in agreement with the Guintini's theory of dielectric dispersion based on two electron hopping over a potential barrier and is applicable in the present case. Dielectric constant and dielectric loss both are highly dependent on frequency and temperature. Dependence of these dielectric parameters over the metallic impurities has also been found in the present glassy system. The results have been interpreted in terms of increase in the density of defect states on incorporation of metallic additives and have also been correlated with the electronegativity difference between the elements used in making the aforesaid glassy system.

(Received December 2, 2009; accepted December 11, 2009)

Keywords: Chalcogenide glasses, Dielectric measurements, Defect states

1. Introduction

Shortcomings of a-Se can be overcome by the addition of other chalcogenides or metals of different group to get new binary, ternary or quaternary chalcogenide glasses with some modified/enhanced properties which makes them very useful in various applications. The addition of impurities to disordered systems has a pronounced effect on changing their conduction mechanism and their structures. This effect can be widely different for different impurities [1-6]. Impurities and defects are known to exert strong influence on the phase transition. From this point of view , the strength of these influences is determined by whether defects are centrosymmetric or have their own dipole moment and whether the dipoles are frozen or can readily change their orientation [7,8] . The dielectric relaxations are important to understand the nature and origin of the dielectric losses which , in turn , may be useful to determine the nature of defects in solids .The dielectric characterization has been considered as an important complementary efforts contributing to a better understanding of transport mechanism in amorphous semiconductors.

In Ge-Se and Se-In systems, some metallic additives have been found [9-14] to change conduction from p type to n type and hence these binary systems are of great importance.

The energy band gap of glassy Se-In alloys is about 1.3 eV at 300 K [15]. This value is close to the theoretical optimum for solar energy conversion and hence several attempts have been made to utilize glassy Se-In alloys in solar cells [16-17]. Therefore, glassy Se-In alloys are used to extend the utility of a-Se.

From the above point of view, different properties of glassy Se-In alloys have been reported by our group [18-23] and other workers in a series of papers [24-31]. Effect of high field

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in a-Se-In system has been studied by Kumar et al [18, 21]. Observation of M-N rule has been reported by the same group [19].Steady state and transient photoconductivity measurement on amorphous thin films of Se-In has also been studied by Kumar et al [22]. A. C. Conduction studies on Se-In system have been reported by Mehta et al [23]. Electrical conductivity and relaxation of Se-S-In glasses has been studied by Zulfequar et al [24]. Electrical conduction mechanism in Se-In-Pb has been studied by Khan et al [25]. Thermoelectric power measurements in glassy Se-In system have been made by Khan et al [28]. Optical band gap of amorphous thin films of Se-In has been determined by Man et al [29]. Enthalpy recovery during relaxation and crystallization kinetics before and after slow neutron radiation has also been reported in glassy $Se_{96}In_4$ alloy by Imran et al [30-31].

In the present paper we report the dielectric measurements in glassy Se-In alloys to study the effect of impurity incorporation in it. 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 $Se_{75}In_{25}$, $Se_{75}In_{10}Pb_{15}$, $Se_{75}In_{10}Sb_{15}$ and $Se_{75}In_{10}Te_{15}$ system were prepared by quenching technique. High purity (99.999 %) materials were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~ 5 cm and internal dia ~ 8 mm) with a vacuum ~ 10^{-5} Torr. The ampoules containing the materials were heated to 900°C and held at that temperature for 10 - 12 hours. The temperature of the furnace was raised slowly at a rate ~ 3 - 4 °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. The glassy nature of the materials was checked by XRD technique. 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 d. c. conductivity and dielectric parameters in a vacuum ~ 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 1^0C. The temperature dependence of the dielectric constant ($\varepsilon^{'}$) and dielectric loss ($\varepsilon^{''}$) were studied in a heating run at a heating rate of 1 K / min. The frequency dependence of $\varepsilon^{'}$ and $\varepsilon^{''}$ was also measured by maintaining constant temperature inside the sample holder.

Dielectric measurements were made using a “Hioki 3532-50 LCR Hi TESTER”. The parallel capacitance and dissipation factor was measured and then $\varepsilon^{'}$ and $\varepsilon^{''}$ was calculated with the help of it. Three terminal measurements were performed to avoid the stray capacitances.

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 [32], both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar dielectric behavior in chalcogenide glasses 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. Results and discussion

3.1. Dielectric behavior of various glassy alloys

Temperature dependence of $\varepsilon^{'}$ and $\varepsilon^{''}$ was measured at various frequencies (1 kHz to 5 MHz) for various glassy alloys studied in present case. Measurements have been taken between the temperature range 300 K to 350 K. $\varepsilon^{'}$ and $\varepsilon^{''}$ are found to be temperature dependent in the above frequency range in all the glassy samples studied here. (See Figs. 1-8 for aforesaid glassy alloys). $\varepsilon^{'}$ and $\varepsilon^{''}$ increase with the increase of temperature, the increase being different at different frequencies. This type of behavior has been reported by various workers [33] in chalcogenide glasses.

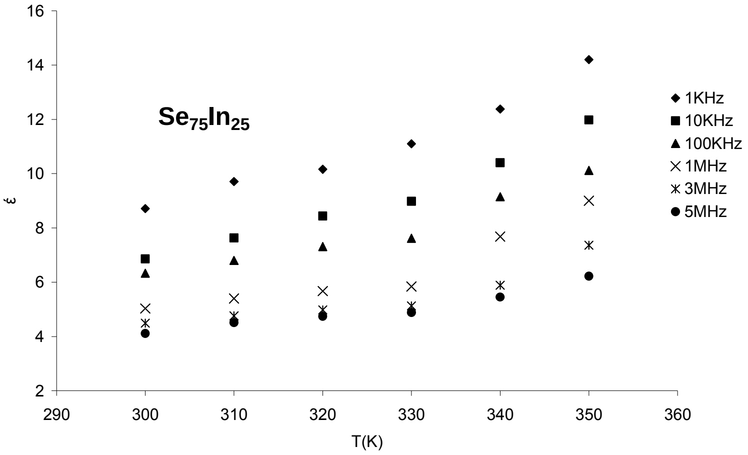

Fig.1. Temperature dependence of dielectric constant(έ) in glassy $Se_{75}In_{25}$ alloy

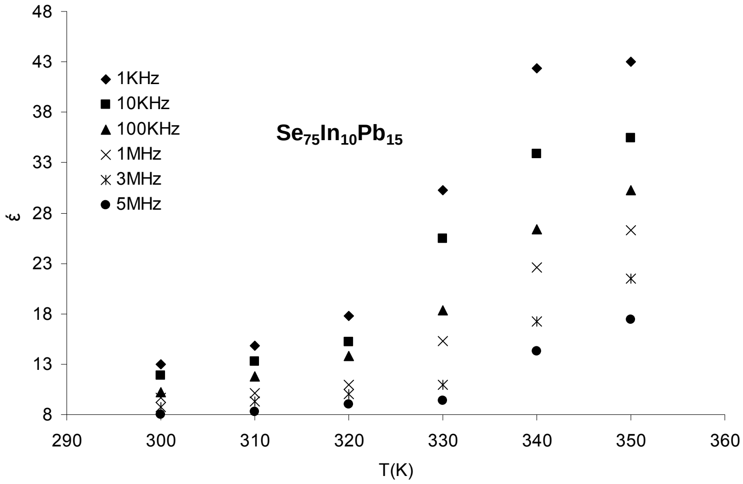

Fig.2. Temperature dependence of dielectric constant (έ) in glassy $Se_{75}In_{10}Pb_{15}$ alloy

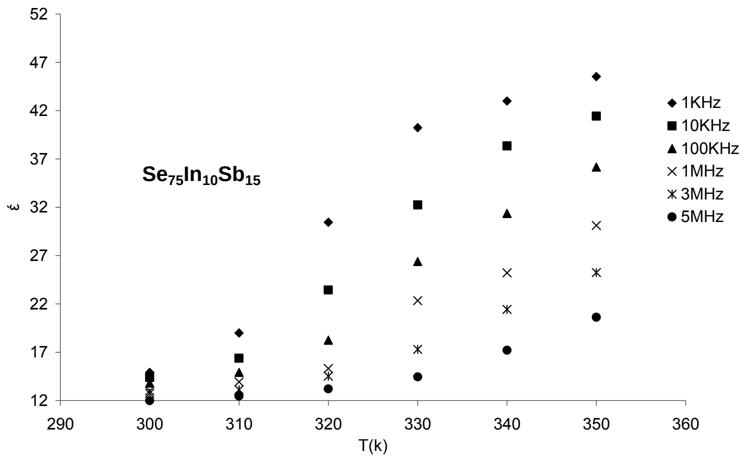

Fig.3. Temperature dependence of dielectric constant(ɛ́) in glassy $Se_{75}In_{10}Sb_{15}$ alloy

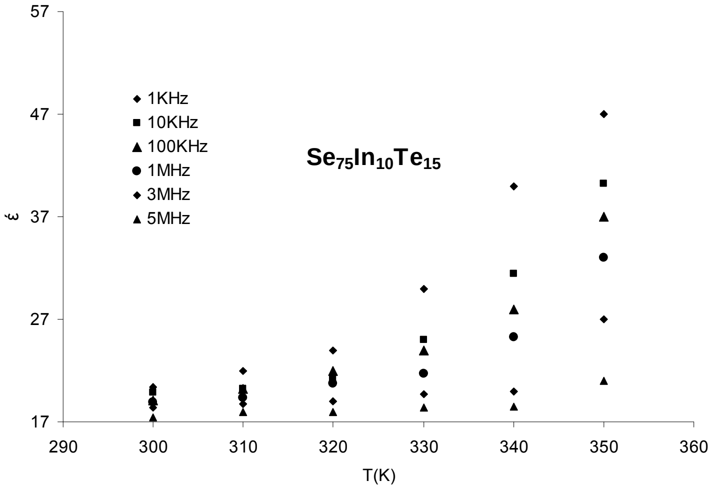

Fig.4. Temperature dependence of dielectric constant (ɛ́) in glassy $Se_{75}In_{10}Te_{15}$ alloy

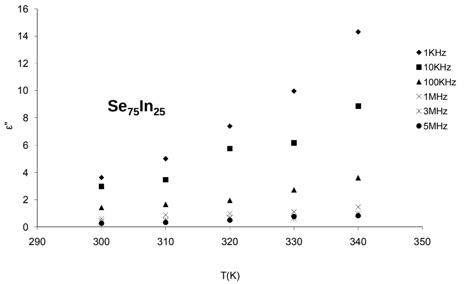

Fig.5. Temperature dependence of dielectric loss (ε") in glassy $Se_{75}In_{25}$ alloy

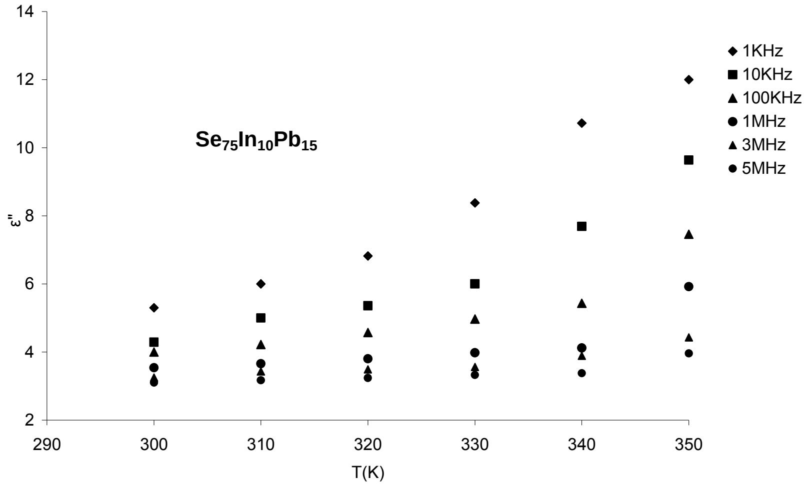

Fig.6. Temperature dependence of dielectric loss (ε") in glassy $Se_{75}In_{10}Pb_{15}$ alloy

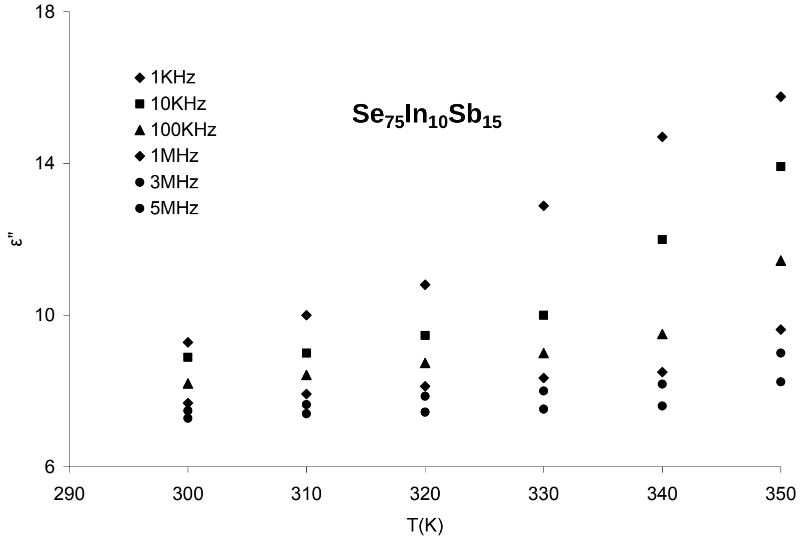

Fig.7. Temperature dependence of dielectric loss (ε") in glassy $Se_{75}In_{10}Sb_{15}$ alloy

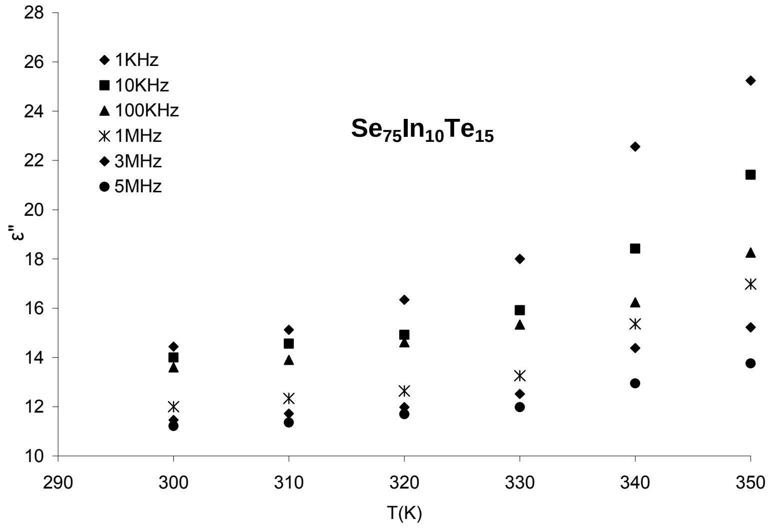

Fig.8. Temperature dependence of dielectric loss(ε") in glassy $Se_{75}In_{10}Te_{15}$ alloy

The different behaviour of dielectric constant at low and high frequencies may be due to semiconducting nature of the glassy alloys used in the present study. This may also be due to the fact that at higher frequencies the atomic nucleus ceases to follow the field and only the electronic polarization remains in the system. The dipolar contributions are small or almost negligible because of the inertia of molecules and ions.Increase in dielectric constant with increasing temperature at various frequencies is in accordance with the Debye's concept of viscosity dependence of relaxation time where the ε' should increase exponentially with temperature.

In above glassy alloys, ε'' is found to follow a power law with frequency, i.e., $\varepsilon'' = A\,\omega^m$. Figs. 9-10 (for a-$Se_{75}In_{10}Sb_{15}$ and $Se_{75}In_{10}Te_{15}$ glassy alloys) confirm this behavior where ln ε'' versus ln ω curves are found to be straight lines at various temperatures. Similar results are found for other samples also (results not shown here).

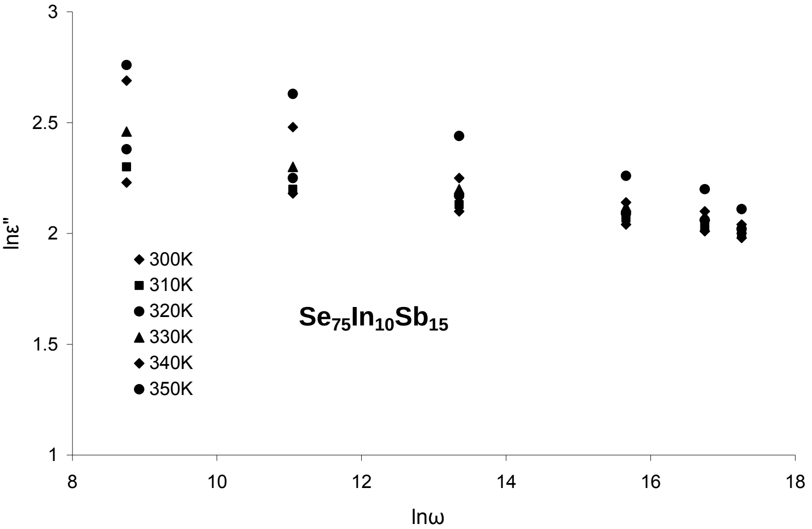

Fig.9. lnω vs lnε" curves in a-$Se_{75}In_{10}Sb_{15}$ at certain fixed temperatures

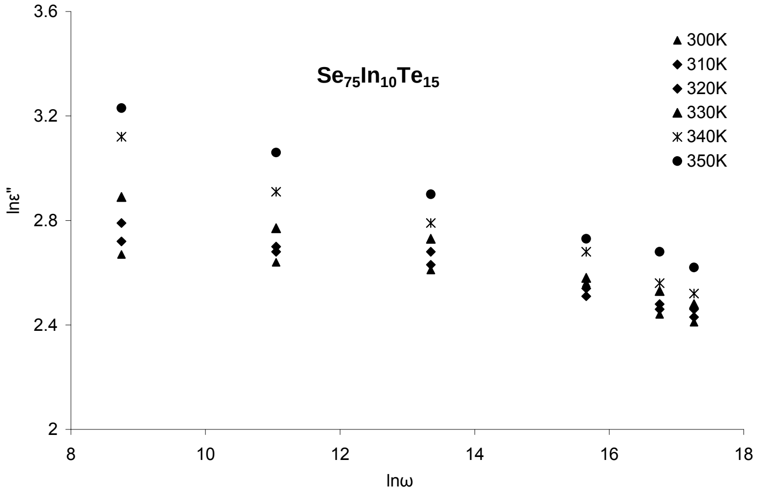

Fig.10. lnω vs lnε" curves in a-$Se_{75}In_{10}Te_{15}$ at certain fixed temperatures

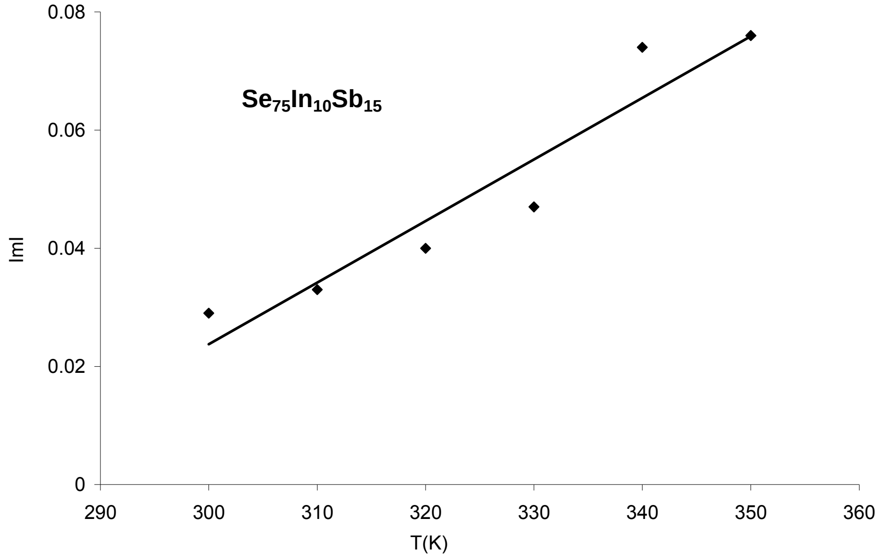

Fig.11. ImI vs T curve in glassy $Se_{75}In_{10}Sb_{15}$ alloy

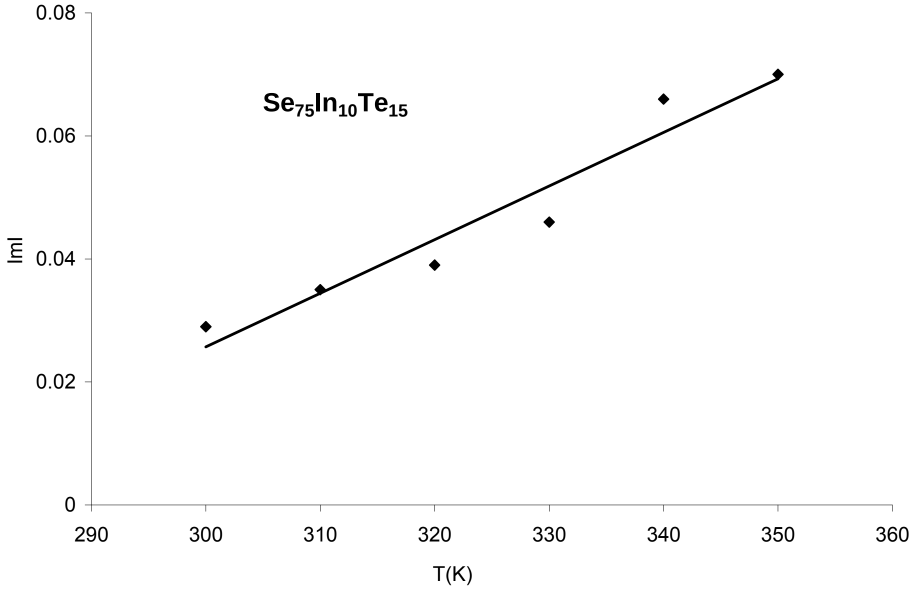

Fig.12. ImI versus T curve in glassy $Se_{75}In_{10}Te_{15}$ alloy

The power m is calculated from the slopes of these curves and found that the values of m are negative at all temperatures. The magnitude of m increases with the increase of temperature in all the samples studied. Guintini et al. [34] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [35] of hopping of charge carriers over a potential barrier between charged defects 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; the latter can be attributed to the existence of a potential barrier over which the carriers hop.

The relaxation time connected with a hop being $\tau = \tau_0 \exp(W/kT)$, we can combine the permittivity with circular frequency ω of the applied electric field.

$$\varepsilon''(\omega) = (\varepsilon_o - \varepsilon_\infty)\, 4\pi N \varepsilon_o kT/n\, e^2 \int_0^\infty R^4 [\omega/(1+\omega^2\tau^2)] d\tau$$

where R (a function of τ) is the distance between localized sites .This integral has already been evaluated [35,36]. According to Guintini et al. [34], assuming $\omega\tau<<1$, ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by

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

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

$$m = \square\ 4\, k\, T\, /\, W_M \qquad (2)$$

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 (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 (2). In our samples we found also 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 (see Figs. 11-12 for $Se_{75}In_{10}Sb_{15}$ and $Se_{75}In_{10}Te_{15}$ glassy alloys). Using the values of m, W_M is calculated and the results are given in Table 1. It is clear from this table that the value of W_M decreases with impurity 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 [35]in case of chalcogenide glasses.

3.2. Impurity dependence of ε' and ε''

When iso-electronic atom Te is added to amorphous Selenium, the density of defect states is increased and hence the residual potential increases in xerographic experiment. Onozuka et.al. [37] 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 [38], while Cl atoms having higher electronegavity than Selenium [38] form negatively charged impurities, thereby compensating the effect of Te [37].

Along the same lines, one can expect that when the impurity (Pb, Sb and Te) having lower electronegativity than Se [38] is introduced, positively charged defects will be created thus increasing the density of defect states in binary Se-In system as compared to pure Se.

Table 1. Values of W_M for various glassy alloys

Glassy alloys	W_M (eV)
$Se_{75}In_{25}$	0.49
$Se_{75}In_{10}Pb_{15}$	0.43
$Se_{75}In_{10}Sb_{15}$	0.38
$Se_{75}In_{10}Te_{15}$	0.35

Table 2. Dielectric parameters of various glassy alloys

Glassy alloys	ε' (1K Hz, 300 K)	ε'' (1 K Hz, 300 K)
$Se_{75}In_{25}$	8.71	3.63
$Se_{75}In_{10}Pb_{15}$	12.98	5.30
$Se_{75}In_{10}Sb_{15}$	14.92	9.28
$Se_{75}In_{10}Te_{15}$	20.42	14.44

From the above discussion it is clear that the impurity incorporation to Se-In system increases the number of charged defect states which may affect the dielectric properties. The values of $\varepsilon^{'}$ and $\varepsilon^{''}$ in aforesaid glassy alloys are given in Table-2.As the dielectric loss in these glasses depends upon the total number of localized sites, the increase of dielectric loss with the impurity incorporation can be understood in terms of the increased density of defects on addition of impurity to Se-In glassy system. Due to the increased number of dipoles (D^+ and D^-) with impurity, the dielectric constant is also expected to increase as found by us in the present study.

4. Conclusions

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 impurity incorporated in Se-In 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^-). The results have also been interpreted in terms of increase in the density of defect states which could also be correlated with the electronegativity difference in the incorporation of metallic additive in the aforesaid glassy system.

Acknowledgements

S. Kumar is grateful to U. G. C., New Delhi for providing a major research project during the course of this work.

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