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ROLE OF Pb ADDITIVE IN THE DIELECTRIC PROPERTIES OF $Se_{90}In_{10}$ and $Se_{75}In_{25}$ GLASSY ALLOYS

J. SHARMA, S. KUMAR*
Department of Physics, Christ Church College, Kanpur-208001, India

In this paper we report the effect of Pb incorporation in the dielectric properties of two well known binary Se-In glassy systems, comparing the properties of a-$Se_{90}In_{10}$, a-$Se_{75}In_{25}$ and a-$Se_{75}In_{10}Pb_{15}$ glassy alloys. The temperature and frequency dependence of the dielectric constants and the dielectric losses in glassy $Se_{90}In_{10}$, $Se_{75}In_{25}$ and $Se_{75}In_{10}Pb_{15}$ alloys are studied by measuring capacitance and dissipation factor 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 ($\varepsilon^{'}$), dielectric loss ($\varepsilon^{''}$) and loss tangent (Tan δ), are found highly frequency and temperature dependent. Dependence of these dielectric parameters over the metallic impurity Pb, has also been found in the present glassy system. The peculiar role of the third element Pb, as an impurity in the pure binary $Se_{90}In_{10}$ and $Se_{75}In_{25}$ glassy alloys, is also discussed in terms of electronegativity difference between the elements used in making the aforesaid glassy system.

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1. Introduction

The study of dielectric behavior of chalcogenide glasses is expected to reveal structural information which, in effect, can be useful for the understanding of 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 the understanding of the nature and origin of the losses occurring in these materials. Recently [1-4], it has been reported that in chalcogenide glasses the dielectric dispersion does exist at low frequencies even though these materials are covalently bonded semiconductors. Glassy Se-In alloys have drawn great attention because of their potential application in solar cells [5, 6]. The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction type from p to n as most of these glasses show p type conduction only. In Ge - Se and Se - In systems, some metallic additives have been found to change conduction from p type to n type and hence these binary systems are of great importance. However in these glasses limited reversibility 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.Thus there is need to predict the suitability of various glass compositions, with the dielectric relaxation being a key parameter.

From the above point of view, The effect of incorporation of some metallic impurity in glassy Se-In alloys have been reported by many workers in a series of papers [7-12]. Electrical conductivity and relaxation of Se-S-In glasses has been studied by Zulfequar et al [7]. Electrical conduction mechanism in Se-In-Pb has been studied by Khan et al [8]. Thermoelectric power measurements in glassy Se-In system have been made by Khan et al [9]. Optical band gap of amorphous thin films of Se-In has been determined by Man et al [10]. 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 [11-12].

In view of the above we have decided to study the effect of Pb as an impurity in the dielectric properties of two well-known binary $Se_{90}In_{10}$ and $Se_{75}In_{25}$ glassy systems. 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 $Se_{90}In_{10}$, $Se_{75}In_{25}$ and $Se_{75}In_{10}Pb_{15}$ 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 ~ 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. 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 ~ 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 [13], 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 (~ 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 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 between 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. (See Figs. 1-6 for aforesaid glassy alloys). ε' and ε'' increase with the increase of temperature, the increase being different at different frequencies. This type of behavior has been reported by various workers [14] 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 molecules of 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.

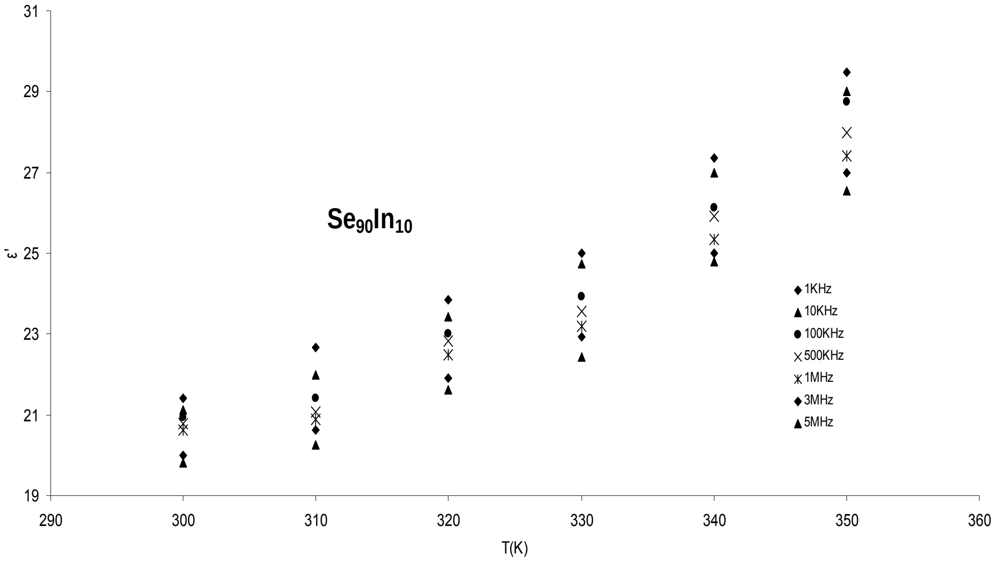

Fig. 1. Temperature dependence of dielectric constant (ε') in glassy $Se_{90}In_{10}$ alloy.

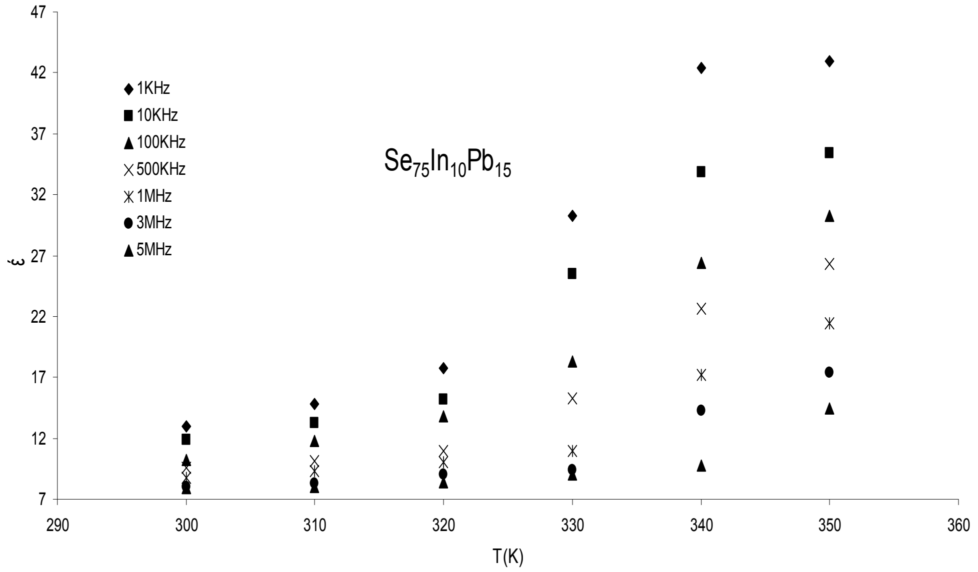

Fig. 2. Temperature dependence of dielectric constant (ε') in glassy $Se_{75}In_{10}Pb_{15}$ alloy.

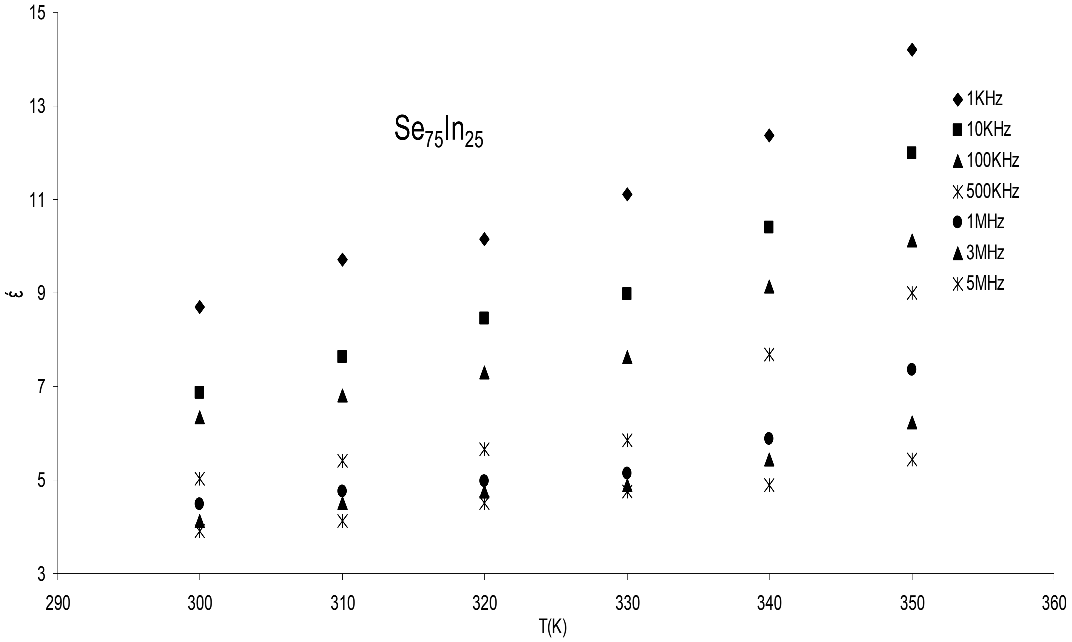

Fig. 3. Temperature dependence of dielectric constant (ε') in glassy Se$_{75}$In$_{25}$ alloy

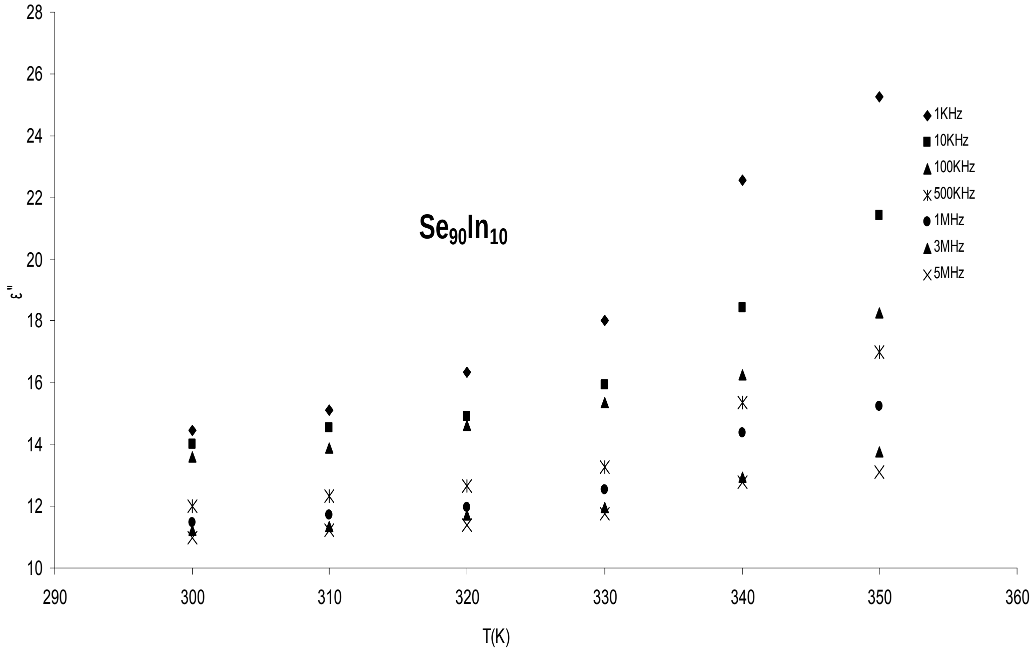

Fig. 4. Temperature dependence of dielectric loss (ε') in glassy Se$_{90}$In$_{10}$ alloy.

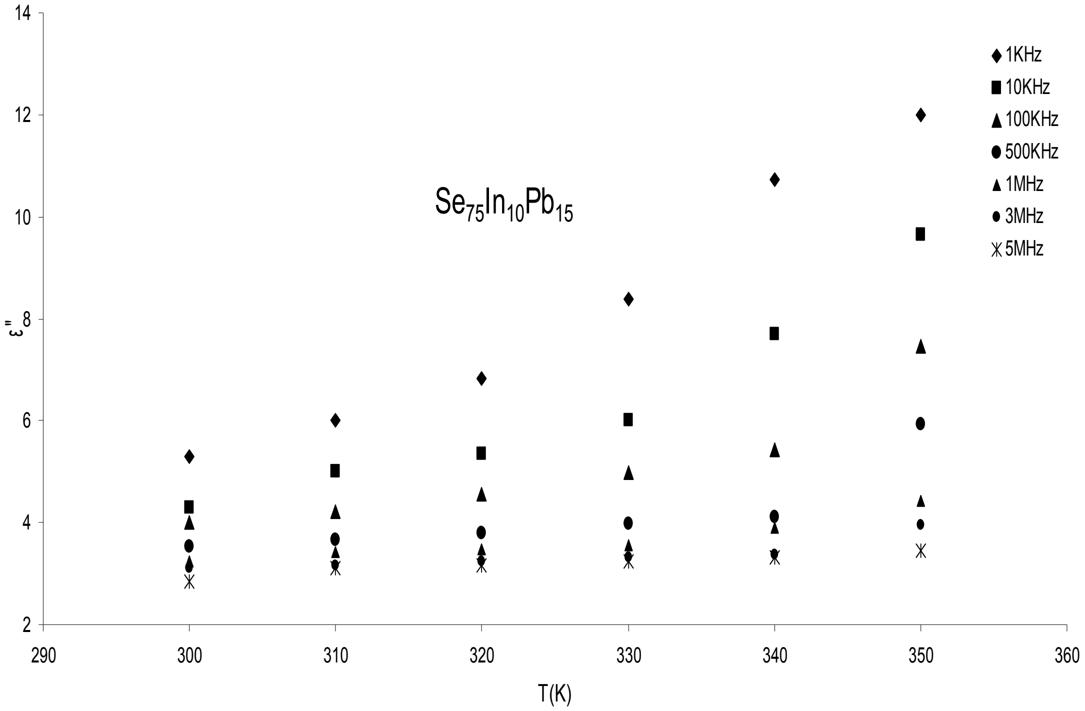

Fig. 5. Temperature dependence of dielectric loss (ε') in glassy $Se_{75}In_{10}Pb_{15}$ alloy.

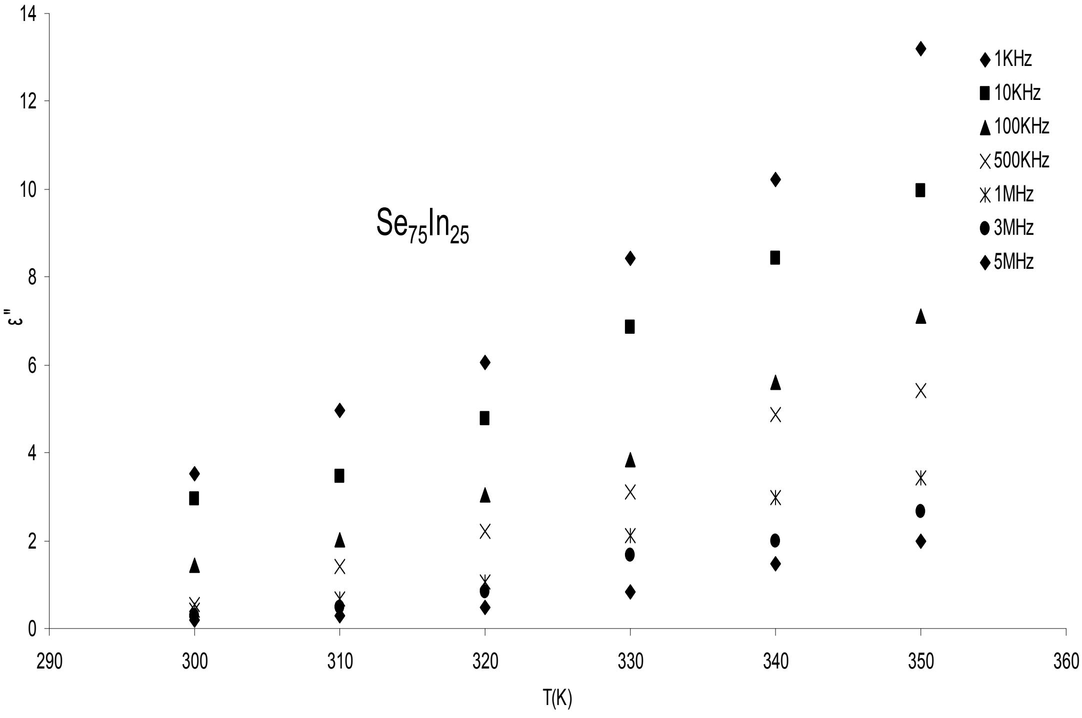

Fig. 6. Temperature dependence of dielectric loss (ε') in glassy $Se_{75}In_{25}$ alloy.

In above glassy alloys, ε'' is found to follow a power law with frequency, i.e., $\varepsilon'' = A\ \omega^{m}$. Figs. 7-9 (for aforesaid glassy alloys) confirm this behavior where ln ε'' versus ln ω curves are found to be straight lines at various temperatures.

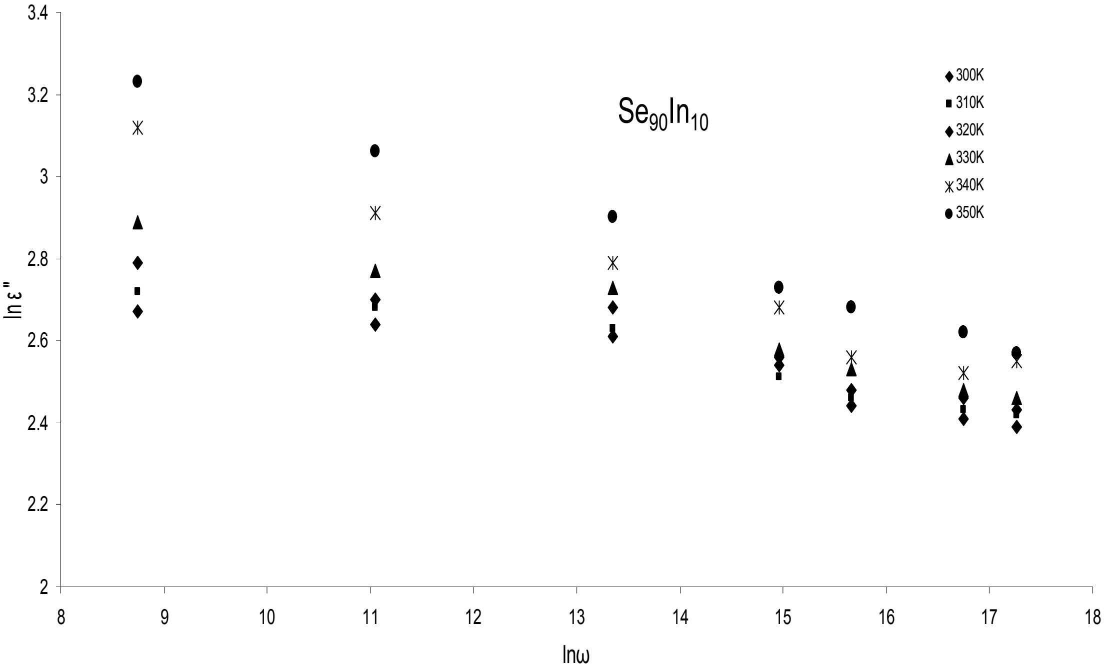

Fig. 7. Inω vs Inε'' in glassy $Se_{90}In_{10}$ alloy at certain fixed temperatures.

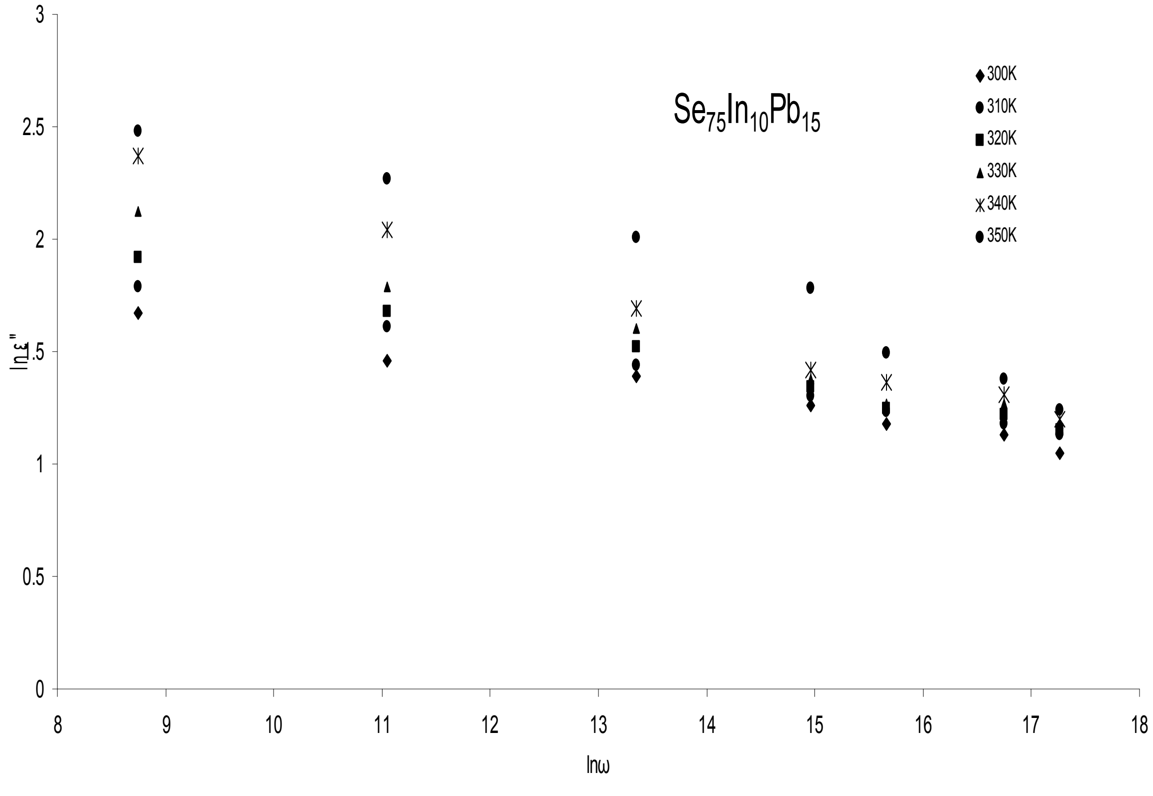

Fig. 8. Inε'' vs Inω curves in glassy $Se_{75}In_{10}Pb_{15}$ alloy at certain fixed temperatures.

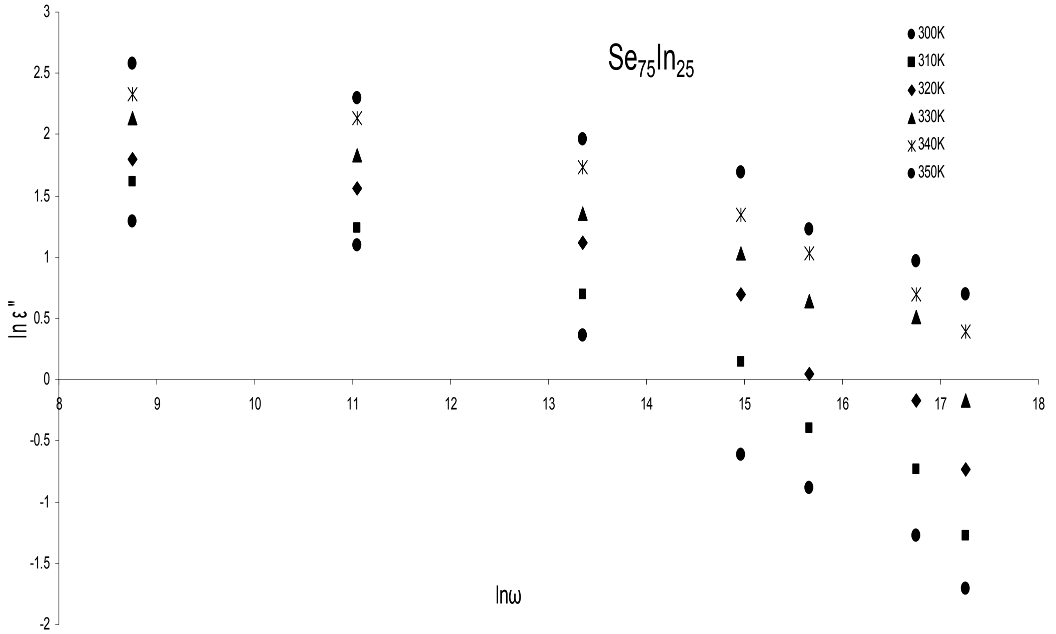

Fig. 9. Inε'' vs Inω curves in glassy $Se_{75}In_{25}$ alloy at certain fixed temperatures.

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 magnitude of m increases with the increase of temperature in all the samples studied at present. Guintini et al. [15] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [16] 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:

$$\tau = \tau_0 \exp (W/kT) \qquad (1)$$

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

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

where R (a function of τ) is the distance between localized sites .This integral has already been evaluated [16-17]. According to Guintini et al. [15], assuming $\omega\tau<<1$, ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by:

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

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

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

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 (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 (4).This equation is consistent with the expression of $\varepsilon''(\omega)$ obtained from the Kramers - Kronig relations. 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 Fig.10 for $Se_{75}In_{10}Pb_{15}$ glassy alloy). Similar results have been found for other glasses also. Using the values of m, W_m is calculated and plotted in Fig.11 (for $Se_{75}In_{10}Pb_{15}$). The values of loss tangent (Tan $\delta = \varepsilon''/\ \varepsilon'$) are also calculated and the results obtained are given in Table 1. It is clear from this table that the value of W_m increases while Tan δ decreases with impurity incorporation.

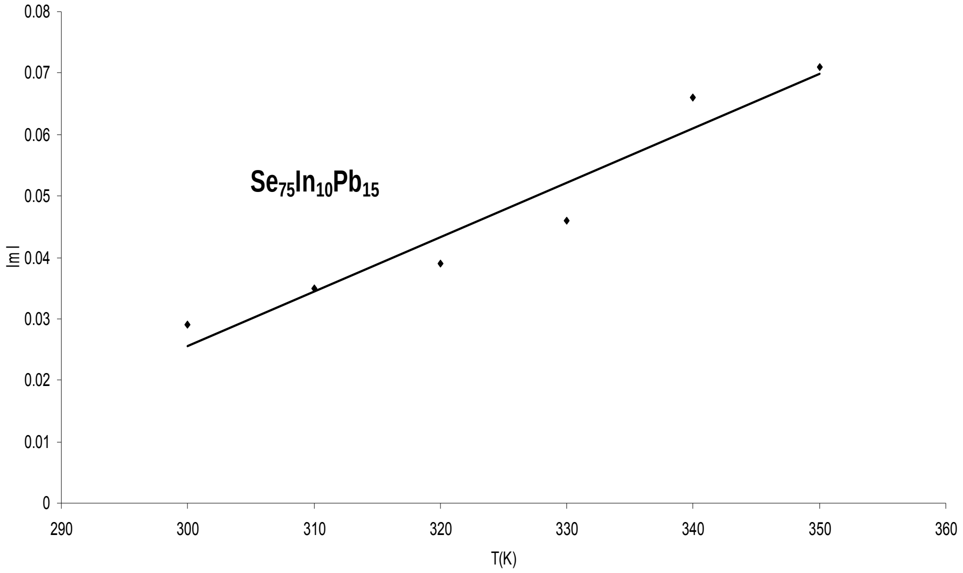

Fig. 10. Iml vs T curves in glassy $Se_{75}In_{10}Pb_{15}$ alloy.

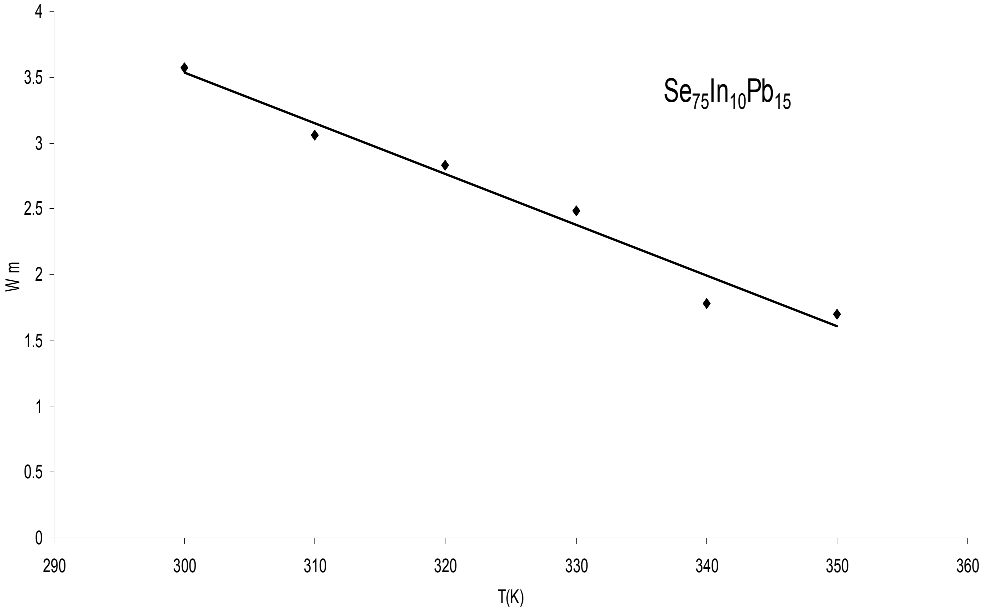

Fig. 11. Wm vs T curves in glassy $Se_{75}In_{10}Pb_{15}$ alloy.

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 [16] in case of chalcogenide glasses.

Table1. Values of W_m for various glassy alloys

Glassy alloys	W_m (eV)	Tan δ (1K Hz,300K)
$Se_{90}In_{10}$	0.35	0.67
$Se_{75}In_{10}Pb_{15}$	0.43	0.41
$Se_{75}In_{25}$	0.49	0.40

3.2. Impurity dependence of ε' and ε''

When iso-electronic atom Te is added to amorphous Selenium, [18] 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 [19] form negatively charged impurities, thereby compensating the effect of Te [18].

Table 2. Dielectric parameters of various glassy alloys.

Glassy alloys	ε' (1K Hz, 300 K)	ε'' (1 K Hz, 300 K)
$Se_{90}In_{10}$	21.42	14.44
$Se_{75}In_{10}Pb_{15}$	12.98	5.30
$Se_{75}In_{25}$	8.71	3.53

Along the same lines, one can expect that when Pb, having lower electronegativity than Se, is introduced in $Se_{90}In_{10}$ at the cost of Se, positive charged defects will be created, but the extent of their creation will be smaller since the amount of In is same in both. On the other hand, when the same Pb is incorporated in $Se_{75}In_{25}$ at the cost of In, density of defect states increases.

The values of ε' and ε'' in aforesaid glassy alloys are given in Table-2. It is evident from this table that the values of ε' and ε'' are found to be decreased and increased with Pb incorporation in $Se_{90}In_{10}$ and $Se_{75}In_{25}$ glassy systems respectively. As the dielectric loss in these glasses depends upon the total number of localized sites, the decrease of dielectric loss with the Pb incorporation can be understood in terms of the decrease of density of defects on addition of Pb to $Se_{90}In_{10}$ glassy system. Due to the decreased number of dipoles (D^+ and D^-) with , the dielectric constant is also expected to decrease as found by us in the present study. On the other hand, the increase in the same dielectric parameters may be due to increase in density of defect states with Pb incorporation in $Se_{75}In_{25}$ glassy system.

4. Conclusions

The temperature and frequency dependence of the dielectric constants and the dielectric losses in $Se_{90}In_{10}$, $Se_{75}In_{25}$ and $Se_{75}In_{10}Pb_{15}$ 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^-).It is clear from the results obtained that the addition of Pb affects the charged defect states in the pure Se-In glassy network which also affects the dielectric properties.The difference in order of change in defect states in the two $Se_{90}In_{10}$ and $Se_{75}In_{25}$ binary glassy system could be explained on the basis of the electro-negativity difference between the constituent elements used in making the above glassy alloys.

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