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Dielectric relaxation in glassy $Se_{75}In_{25-x}Pb_x$ alloys

J SHARMA and S KUMAR*
Department of Physics, Christ Church College, Kanpur 208 001, India
*Corresponding author. E-mail: dr_santosh_kr@yahoo.com

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Abstract. In this paper we report the effect of Pb incorporation in 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 $Se_{75}In_{25-x}Pb_x$ ($x = 0, 5, 10$ and 15) alloys in the frequency range (1 kHz–5 MHz) and temperature range (300–340 K) have been measured. A detailed analysis shows that the dielectric losses are dipolar in nature and can be understood in terms of hopping of charge carriers over a potential barrier as suggested by Elliott for the case of chalcogenide glasses. It has been found that both dielectric constant and the dielectric loss are highly dependent on frequency and temperature and also found to increase with increasing concentration of Pb in binary a-$Se_{75}In_{25}$ glassy system. The results have been interpreted in terms of increase in the density of defect states by the incorporation of Pb as a metallic additive in the aforesaid glassy system.

Keywords. Chalcogenide glasses; dielectric measurements; defect states.

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1. Introduction

Glassy Se–In alloys have drawn great interest because of their potential application in solar cells [1,2]. Incorporation of a third element in binary chalcogenides is interesting because it results in comparatively stable alloys. It also causes a change in the type of conduction from p to n as most of these glasses show p-type conduction only. In Ge–Se and Se–In systems, some metallic additives are found [3–8] to change conduction from p-type to n-type and hence these binary systems are of great importance.

The dielectric relaxations are important to understand the nature and the origin of the dielectric losses which, in turn, may be useful to determine the nature of defects in solids. Measurements of the dielectric properties of different substances have been the subject of many researches and various models have been proposed to interpret the experimental results [9,10]. Most of the dielectric measurements for chalcogenide glasses have been reported at audio and/or radiofrequencies. Literature survey of dielectric measurements shows that relatively very few measurements have been reported on these glasses when compared to other electrical properties.

It is also interesting to note the diversity in the findings reported by different investigators for the same material [11–15].

In view of the above, we have made dielectric measurements in glassy $Se_{75}In_{25}$ alloys to study the effect of Pb incorporation in a-Se–In binary system and to see the dielectric behaviour with concentration of Pb.

Section 2 describes the experimental details of sample preparation and dielectric measurements. The results are presented and discussed in §3. The last section deals with the conclusions drawn from the present work.

2. Experimental details

2.1 *Preparation of glassy alloys*

Glassy alloys of $Se_{75}In_{25-x}Pb_x$ ($x = 0, 5, 10$ and 15) system were prepared by the quenching technique. High purity (99.999%) components were weighed according to their atomic percentages and were sealed in quartz ampoules (length ∼5 cm and internal dia. ∼8 mm) in vacuum (∼10^{-5} Torr). The ampoules containing the components were heated to 900°C and kept at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate of ∼3–4°C/min. During heating, all the ampoules were constantly rocked, by rotating the ceramic rod to which the ampoules are tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 10 h, 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 microanalysis (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 DC conductivity and dielectric parameters in a vacuum of ∼10^{-3} Torr. The pellets were mounted 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°C. The temperature dependences 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 dependences of ε' and ε'' were 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 were measured and then ε' and ε''

were calculated with the help of these values. Three terminal measurements were performed to avoid the stray capacitances.

We preferred to measure dielectric behaviour 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* [16], both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar dielectric behaviour in chalcogenide glasses. No evidence of Maxwell–Wagner losses for the suspected inhomogeneities in the case of compressed pellets is found by them 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 ($\sim 10^{18}$–10^{19} eV^{-1} cm^{-3}) in these glasses. Microsoft Excel programming has been used in the present study for more accurate calculations.

3. Results and discussion

3.1 *Dielectric behaviour of glassy $Se_{75}In_{25-x}Pb_x$ alloys*

Temperature dependences of ε' and ε'' were measured at various frequencies (1 kHz–5 MHz) for various glassy alloys studied in the present case. Measurements have been taken in the temperature range of 300–340 K. ε' and ε'' are found to be temperature-dependent in the above frequency range in all the glassy samples studied here (see figures 1–4 for a-$Se_{75}In_{25}$ and a-$Se_{75}In_{15}Pb_{10}$ glassy alloys). Similar results are found for other samples (results not shown here). ε' and ε'' increase with the increase of temperature, the increase being different at different frequencies. This type of behaviour in chalcogenide glasses has been reported by various workers [17].

In glassy $Se_{75}In_{25-x}Pb_x$ alloys, ε'' is found to follow a power-law with frequency, i.e., $\varepsilon'' = A\omega^m$. Figures 5 and 6 (for a-$Se_{75}In_{25}$ and a-$Se_{75}In_{15}Pb_{10}$ glassy alloys) confirm this behaviour where $\ln\varepsilon''$ vs. $\ln\omega$ curves are found to be straight lines at various temperatures. Similar results are found for other samples also (results not shown here).

The power m is calculated from the slopes of these curves and it is 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 (see figures 7 and 8 for a-$Se_{75}In_{25}$ and a-$Se_{75}In_{15}Pb_{10}$ glassy alloys).

Guintini *et al* [18] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [19] of hopping of charge carriers over a potential barrier between charged defect 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, and the latter can be attributed to the existence of a potential barrier over which the carriers hop.

According to Guintini *et al* [18], ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by

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

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

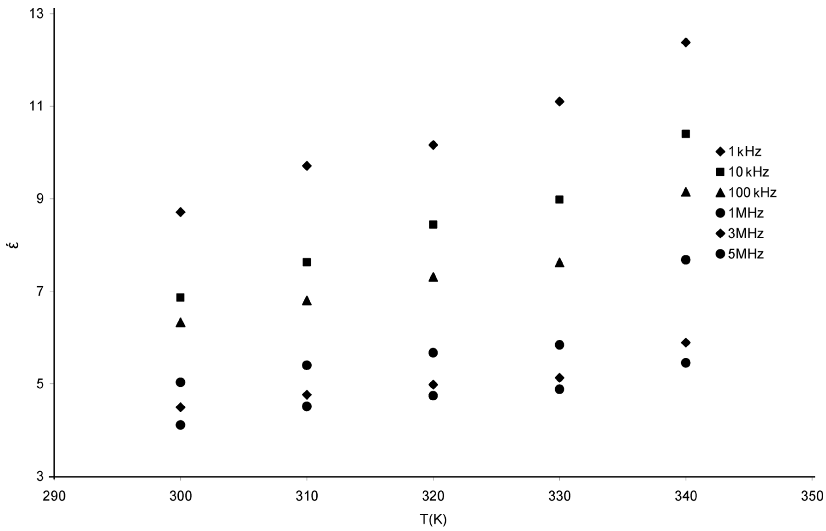

Figure 1. Temperature dependence of dielectric constant (ε') in a-$Se_{75}In_{25}$ glassy alloy at certain fixed frequencies.

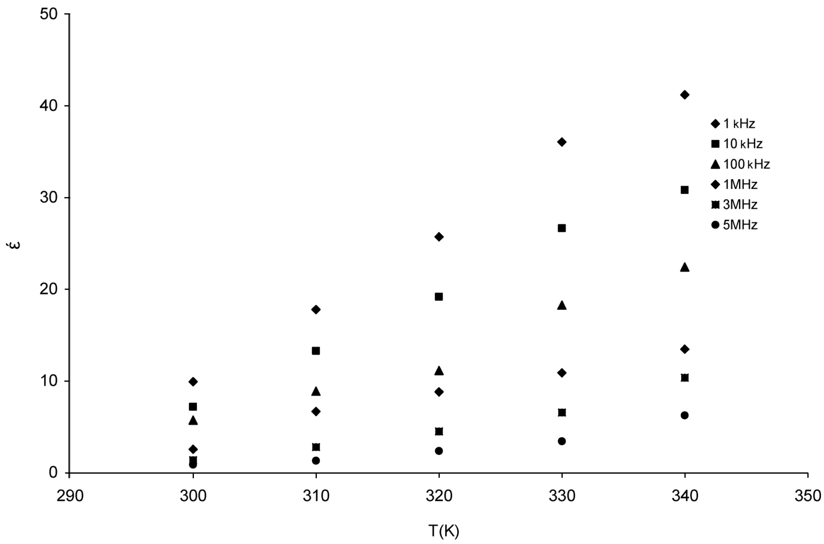

Figure 2. Temperature dependence of dielectric constant (ε') in a-$Se_{75}In_{15}Pb_{10}$ glassy alloy at certain fixed frequencies.

$$m = -4kT/W_m, \tag{2}$$

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.

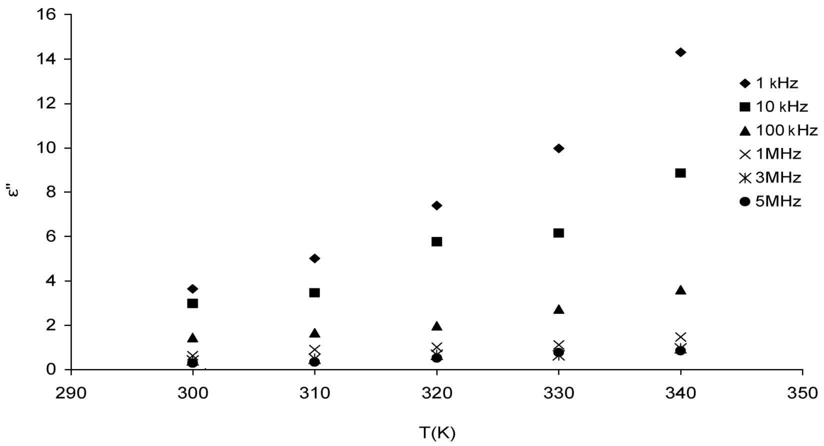

Figure 3. Temperature dependence of dielectric loss (ε'') in glassy a-$Se_{75}In_{25}$ alloy at certain fixed frequencies.

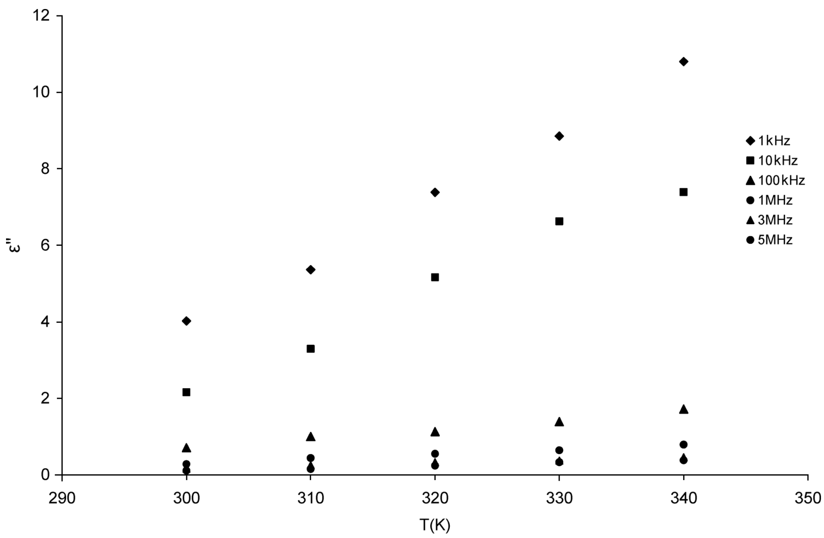

Figure 4. Temperature dependence of dielectric loss (ε'') in a-$Se_{75}In_{15}Pb_{10}$ glassy alloy at certain fixed frequencies.

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 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 as pointed out in the last section. The calculated values of m are given in table 1. The plot of power m as a function of Pb concentration is given in figure 9.

From the above discussion it seems that the paired defect states (D^+ and D^-) behave as dipoles in $Se_{75}In_{25-x}Pb_x$ glasses. The present results are in agreement

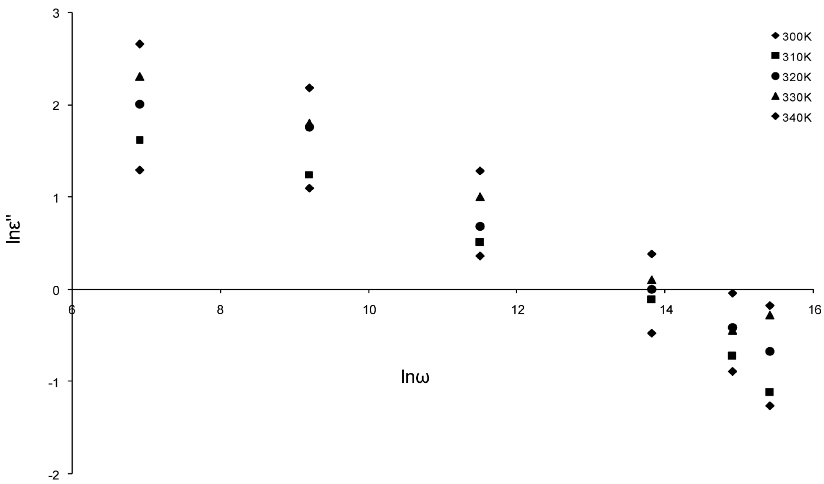

Figure 5. $\ln \varepsilon''$ vs. $\ln \omega$ curves in a-$Se_{75}In_{25}$ alloy at certain fixed temperatures.

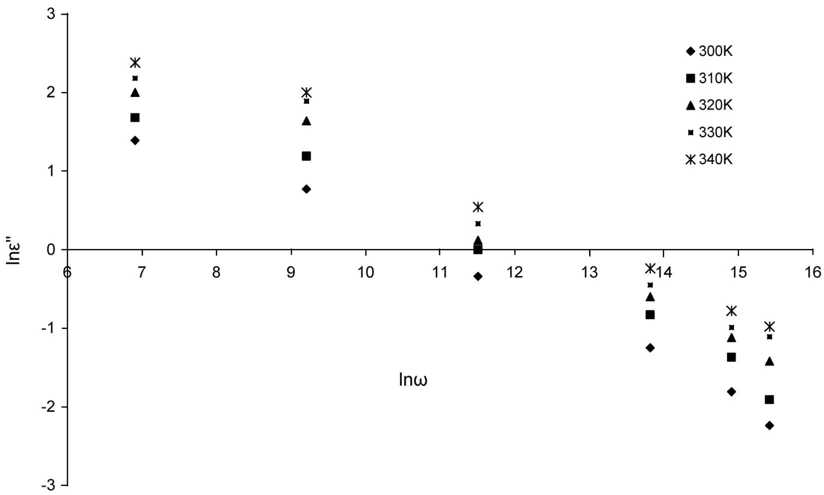

Figure 6. $\ln \varepsilon''$ vs. $\ln \omega$ curves in a-$Se_{75}In_{15}Pb_{10}$ glassy alloy at certain fixed temperatures.

with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott [19] in the case of chalcogenide glasses.

3.2 *Composition dependence of ε' and ε''*

When isoelectronic 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* [20] observed that, on introducing Cl to Se–Te system, the

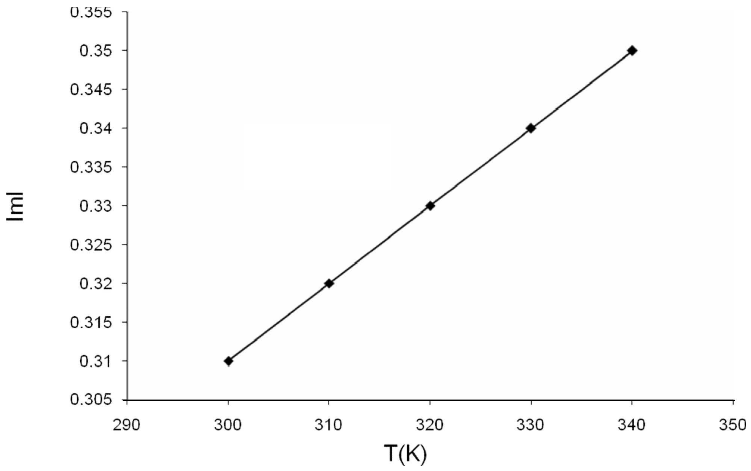

Figure 7. $|m|$ vs. T curve in glassy $Se_{75}In_{25}$ alloy.

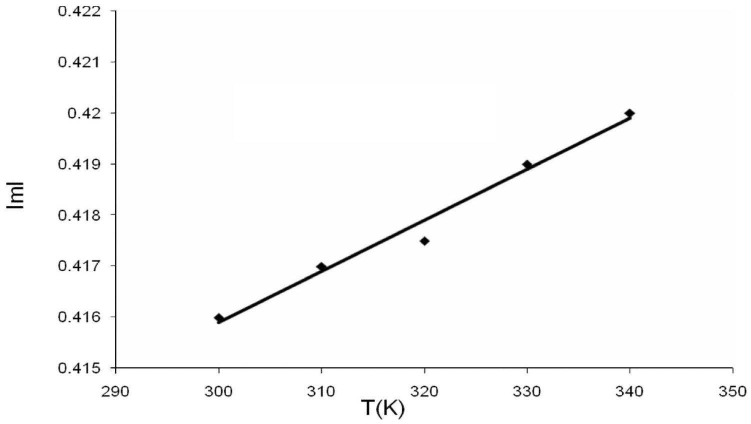

Figure 8. $|m|$ vs. T curve in glassy $Se_{75}In_{15}Pb_{10}$ alloy.

Table 1. Composition dependence of ε', ε'' and $|m|$ in $Se_{75}In_{25-x}Pb_x$ glassy alloys.

Samples	ε' (1 kHz, 300 K)	ε'' (1 kHz, 300 K)	$\|m\|$ (At 300 K)
$Se_{75}In_{25}$	8.7	3.6	0.31
$Se_{75}In_{20}Pb_5$	9.1	3.8	0.35
$Se_{75}In_{15}Pb_{10}$	9.9	4.0	0.42
$Se_{75}In_{10}Pb_{15}$	13.0	5.6	0.44

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 the small electronegativity of Te as compared to Se [21], while Cl

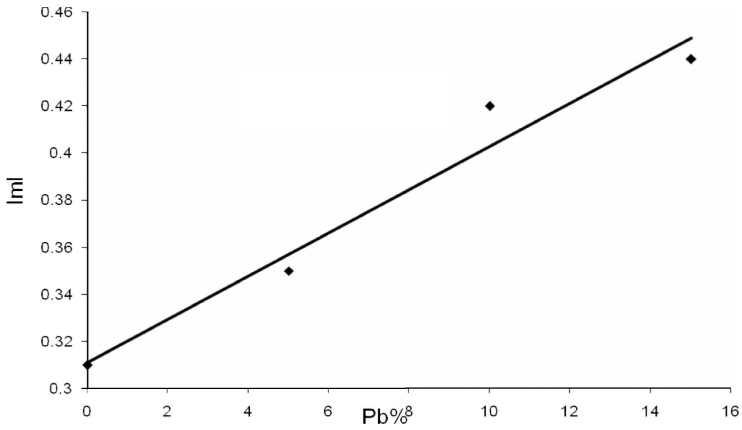

Figure 9. $|m|$ vs. Pb% in glassy $Se_{75}In_{25-x}Pb_x$ alloys.

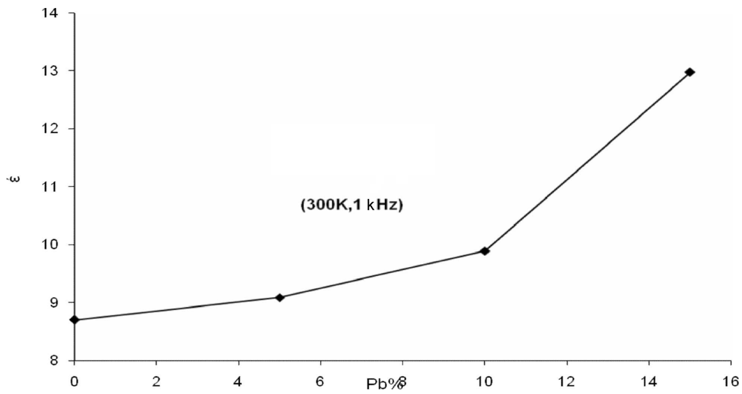

Figure 10. Composition dependence of dielectric constant (ε') in glassy $Se_{75}In_{25-x}Pb_x$ alloys.

atoms having higher electronegativity than selenium [21] form negatively charged impurities, thereby compensating the effect of Te [20].

Along the same lines, one can expect that when Pb having lower electronegativity than Se [21] 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.

From the above discussion it is clear that the addition of Pb to Se–In system increases the number of charged defect states which may affect the dielectric properties. Composition dependences of ε' and ε'' in $Se_{75}In_{25-x}Pb_x$ glassy alloys are given in table 1 and are plotted in figures 10 and 11. As the dielectric loss in these glasses depends on the total number of localized sites, the increase of dielectric loss with the increase of Pb concentration can be understood in terms of the increased density of defects on addition of Pb to Se–In glassy system. Due to the increased number of dipoles (D^+ and D^-) at higher concentration of Pb, the dielectric constant is also expected to increase with Pb concentration as we found in the present study.

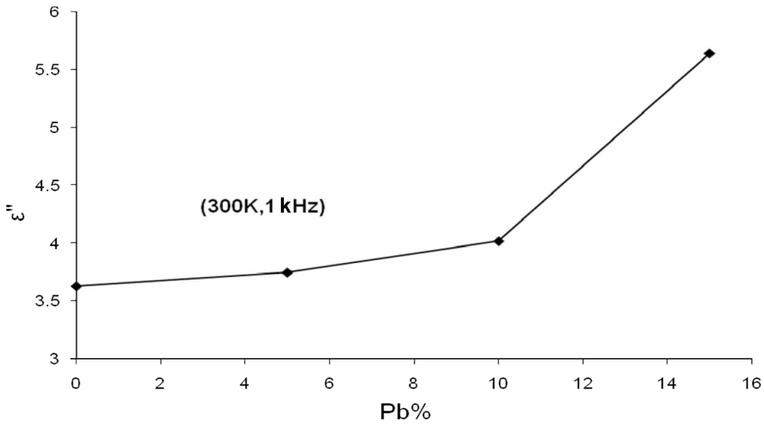

Figure 11. Composition dependence of dielectric constant (ε'') in glassy $Se_{75}In_{25-x}Pb_x$ alloys.

4. Conclusions

The temperature and frequency dependences of the dielectric constants and the dielectric losses in $Se_{75}In_{25-x}Pb_x$ glassy systems in the frequency range (1 kHz–5 MHz) and temperature range (300–340 K) have been measured. It has been found that both dielectric constant and dielectric loss are highly dependent on frequency and temperature and also found to increase with increasing concentration of Pb 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 by the incorporation of Pb as a metallic additive in the aforesaid glassy system.

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