

# Composition dependent of dielectric properties in $\text{Se}_{100-x}\text{Pb}_x$ glassy alloys

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Received 09.09.2008

## Abstract

In this paper we report the composition dependent of dielectric properties in  $\text{Se}_{100-x}\text{Pb}_x$  ( $x = 0, 2, 4, 6$  and  $10$ ) glassy alloys. The temperature and frequency dependence of the dielectric constants and the dielectric losses in the above glassy systems in the frequency range  $1\text{ kHz} - 5\text{ MHz}$  and temperature range  $300 - 340\text{ K}$  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 increased with increasing concentration of Pb in pure amorphous Se. The results have been interpreted in terms of increase in the density of defect states in the incorporation of Pb as a metallic additive in the aforesaid glassy system. Apart from this, the results have been also correlated in terms of a dipolar model which considers the hopping of charge carriers over a potential barrier between charged defect states.

**Key Words:** Dielectric properties, chalcogenide glasses, amorphous semiconductors.

## 1. Introduction

The electrical properties of Se-based glasses are very interesting, for these materials exhibit effects such as optical memory and photo darkening to which the study of their electrical behavior could shed light. It has been found that these alloys are useful due to greater hardness, high photosensitivity, higher crystallization temperature and smaller ageing effect compared to pure a-Se [1, 2]. The transport mechanism of charge carriers in amorphous semiconductors has been the subject of intensive theoretical and experimental investigations for the last few years. These studies have been stimulated by the attractive possibilities of using the structure disorder in amorphous semiconductors for the development of better, cheaper and more reliable solid state devices [3, 4].

The addition of impurities to disordered systems has a pronounced effect on changing their conduction mechanisms and their structures. This effect can be widely different for different impurities [5–7]. Investigation

of the influence of disorder produced by defects and impurities on phase transition has been a subject of intensive studies since 1970. Impurities and defects are known to exert strong influence on phase transition. From this point of view, the strength of these influences is determined by whether defects are Centro symmetric or have their own dipole moment and whether the dipoles are frozen or can readily change their orientation [8, 9]. 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 [10]. Most dielectric measurements for chalcogenide glasses have been reported at audio and/or radio frequencies. Literature survey of dielectric measurements show that relatively very few measurements have been reported on these glasses as 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  $\text{Se}_{100-x}\text{Pb}_x$  alloys to study the effect of Pb incorporation in pure a-Se and to see the dielectric behavior with concentration of Pb.

Section 2 describes the experimental details of sample preparation and dielectric measurements. The results are presented and discussed in section 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  $\text{Se}_{100-x}\text{Pb}_x$  ( $x = 0, 2, 4, 6$  and  $10$ ) were prepared by quenching technique. High purity (99.999 %) materials were weighed according to their atomic fractions and sealed in quartz ampoules (length  $\sim 5$  cm and internal diameter  $\sim 8$  mm) with a vacuum  $\sim 10^{-5}$  Torr. The ampoules containing the materials were heated to  $900^\circ\text{C}$  and held at that temperature for 10–12 hours. The temperature of the furnace was raised slowly at a rate  $\sim 3\text{--}4^\circ\text{C}/\text{min}$ . 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  $\sim 10$  mm and thickness  $\sim 1\text{--}2$  mm were prepared by compressing the finely grounded powder in a die in a hydraulic press under a load of  $\sim 3\text{--}4$  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  $\sim 10^{-3}$  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  $1^\circ\text{C}$ . The temperature dependence of the dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  were studied in a heating run at

a heating rate of 1 K/min. The frequency dependence of  $\epsilon'$  and  $\epsilon''$  was also measured by maintaining constant temperature inside the sample holder.

Dielectric measurements were made using a Hioki 3532-50 LCR HiTester. The parallel capacitance and dissipation factor was measured from which  $\epsilon'$  and  $\epsilon''$  were calculated. Three terminal measurements were performed to avoid the stray capacitances.

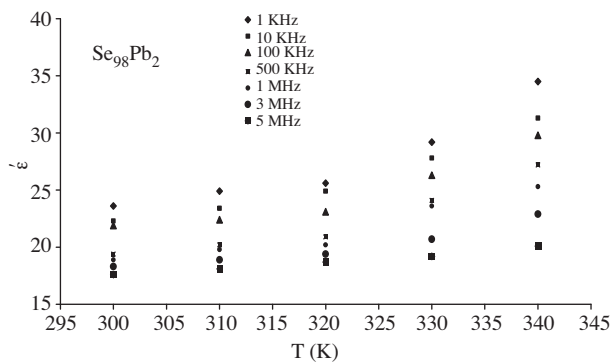
We preferred to measure dielectric behavior on the pellet rather than the bulk, as macroscopic effects (gas bubbles, etc.) may appear in the bulk during preparation. It has been shown by Goyal et al. [16], both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar 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 $^{-1}$  cm $^{-3}$ ) in these glasses. Microsoft Excel programming has been used for more accurate calculations in the present study.

### 3. Results and discussion

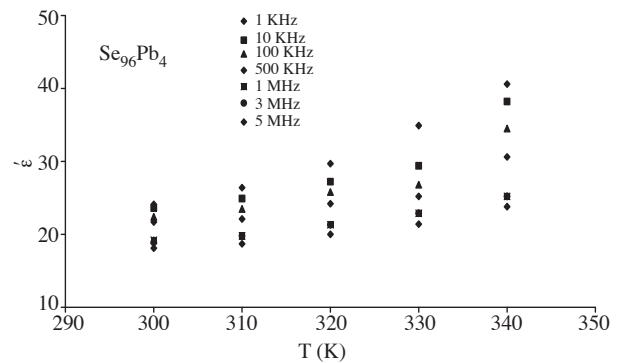
#### 3.1. Dielectric behavior of $\text{Se}_{100-x}\text{Pb}_x$ glassy alloys

Temperature dependence of  $\epsilon'$  and  $\epsilon''$  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 340 K.  $\epsilon'$  and  $\epsilon''$  are found to be temperature dependent in the upper frequency range in all the glassy samples studied here. (See Figures 1–4 for a- $\text{Se}_{98}\text{Pb}_2$  and a- $\text{Se}_{96}\text{Pb}_4$  glassy alloys). Similar results are found for other samples (results not shown here).  $\epsilon'$  and  $\epsilon''$  increase with the increase of temperature, the increase being different at different frequencies. This type of behavior has been reported by various workers [17] in chalcogenide glasses.

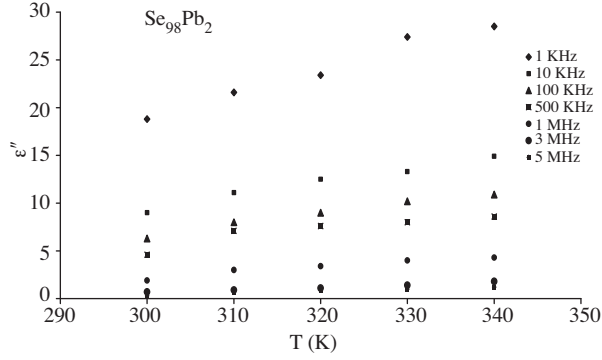
The different behavior of dielectric constant at low and high frequencies may be due to semiconducting nature of the glassy alloys used in the present study. This may also be due to the fact that at higher frequencies the atomic nucleus ceases to follow the field and only the electronic polarization remains in the system. The dipolar and the ionic contributions are small or almost negligible because of the inertia of molecules and ions.



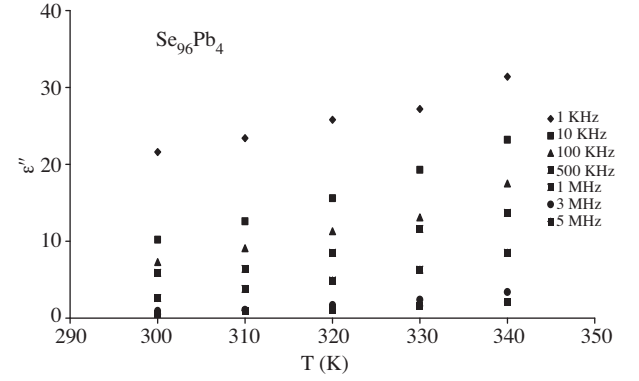
**Figure 1.** Temperature dependence of dielectric constant ( $\epsilon'$ ) at certain fixed frequencies



**Figure 2.** Temperature dependence of dielectric constant ( $\epsilon'$ ) at certain fixed frequencies.

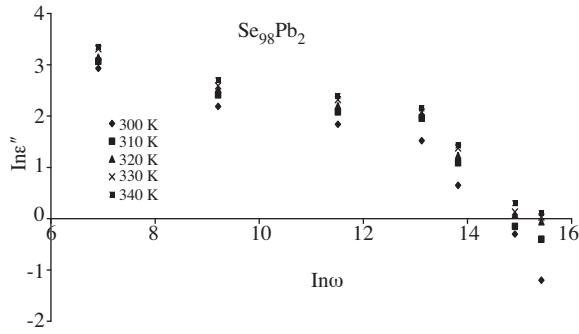


**Figure 3.** Temperature dependence of dielectric loss ( $\epsilon''$ ) at certain fixed frequencies.

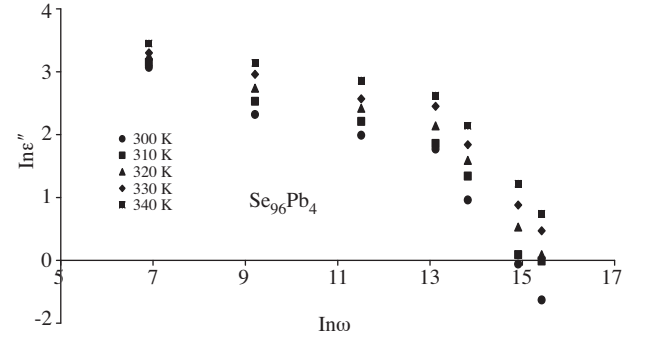


**Figure 4.** Temperature dependence of dielectric loss ( $\epsilon''$ ) at certain fixed frequencies.

In glassy alloys of  $\text{Se}_{100-x}\text{Pb}_x$ ,  $\epsilon''$  is found to follow a power law with frequency, i.e.,  $\epsilon'' = A\omega^m$ . Figures 5, 6 (for a- $\text{Se}_{98}\text{Pb}_2$  and a- $\text{Se}_{96}\text{Pb}_4$  glassy alloys) confirm this behavior; curves of  $\ln\epsilon''$  versus  $\ln\omega$  are found to be straight lines at various temperatures. Similar results are found for other samples also (results not shown here).



**Figure 5.**  $\ln\epsilon''$  versus  $\ln\omega$  curves at certain fixed temperatures.



**Figure 6.**  $\ln\epsilon''$  versus  $\ln\omega$  curves 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 temperatures. The magnitude of  $m$  increases with temperature in all the samples studied (results not shown here). 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; the latter can be attributed to the existence of a potential barrier over which the carriers hop.

According to Guintini et al. [18], at a particular frequency in the temperature range where dielectric dispersion occurs,  $\epsilon''$  is given by the relation

$$\epsilon''(\omega) = (\epsilon_o - \epsilon_\infty) 2\pi^2 N (ne^2 / \epsilon_o)^3 kT \tau_o^m W_m^{-4} \omega^m. \quad (1)$$

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

$$m = -4kT/W_M. \quad (2)$$

$n$  is the number of hopping electrons,  $N$  is the concentration of localized sites,  $\varepsilon_o$  and  $\varepsilon_\infty$  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 relation (1),  $\varepsilon''$  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  $\varepsilon''$  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. 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 Pb incorporation in pure a-Se. The value of  $|m|$  at certain temperature has also been given in the table for various glassy alloys studied at present.

**Table 1.** Composition dependence of  $\varepsilon'$  and  $\varepsilon''$  in  $\text{Se}_{100-x}\text{Pb}_x$  glassy alloys

Samples	$\varepsilon'$ (1 kHz, 300 K)	$\varepsilon''$ (1 kHz, 300 K)	$W_m$ (eV)	$ m $ (At 300 K)
a-Se	3.5	0.5	0.41	0.52
a-Se <sub>98</sub> Pb <sub>2</sub>	23.6	18.8	0.35	0.43
a-Se <sub>96</sub> Pb <sub>4</sub>	24.1	21.6	0.17	0.39
a-Se <sub>94</sub> Pb <sub>6</sub>	34.6	38.3	0.12	0.28
a-Se <sub>90</sub> Pb <sub>10</sub>	45.4	47.1	0.09	0.19

From the above discussion it seems that the paired defect states ( $D^+$  and  $D^-$ ) behave as dipoles in  $\text{Se}_{100-x}\text{Pb}_x$  glasses. The present results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott [19] in case of chalcogenide glasses.

### 3.2. Composition dependence of $\varepsilon'$ and $\varepsilon''$

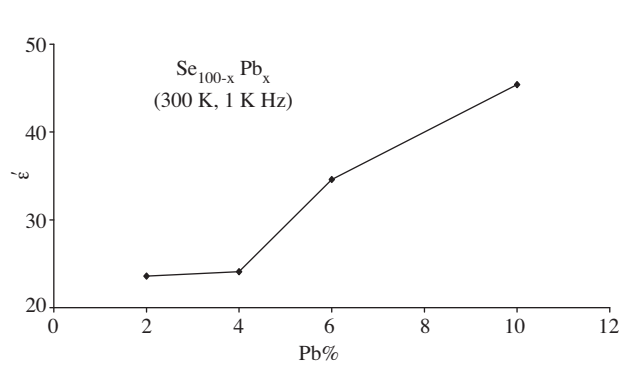
When iso-electronic atom Te is added to amorphous Selenium, the density of defect states is increased, hence the residual potential increases in xerographic experiment. Onozuka et al. [20] observed that, on introducing Cl to Se-Te system, the residual potential is decreased again. This result was interpreted 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 [21], while Cl 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-Pb system as compared to pure Se.

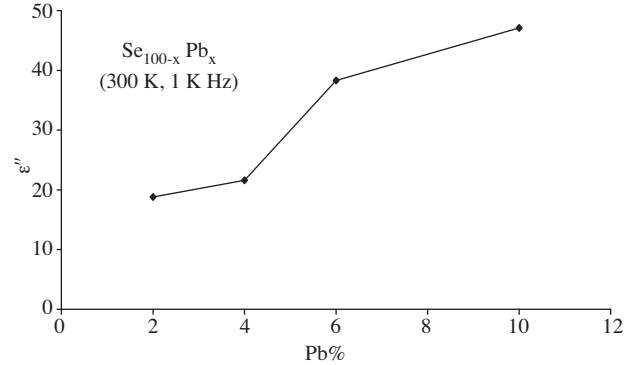
From the above discussion it is clear that the addition of Pb to Se increases the number of charged defect states which may affect the dielectric properties. Composition dependence of  $\varepsilon'$  and  $\varepsilon''$  in  $\text{Se}_{100-x}\text{Pb}_x$  glassy alloys are given in Table-1 and are plotted in

Figures 7, 8. As the dielectric loss in these glasses depends upon 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. 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 found in the present study.



**Figure 7.** Composition dependence of dielectric constant ( $\epsilon'$ ) in a- $\text{Se}_{100-x}\text{Pb}_x$  glassy alloys.



**Figure 8.** Composition dependence of dielectric loss ( $\epsilon''$ ) in a- $\text{Se}_{100-x}\text{Pb}_x$  glassy alloys.

## 4. Conclusion

The temperature and frequency dependence of the dielectric constants and the dielectric losses in  $\text{Se}_{100-x}\text{Pb}_x$  glassy systems in the frequency range (1 kHz–5 MHz) and temperature range 300–340 K have been measured. It has been found that dielectric constant and the dielectric loss both are highly dependent on frequency and temperature and also found to be increased with increasing concentration of Pb in pure amorphous Se. The frequency dependence of the dielectric loss in this 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 in the incorporation of Pb as a metallic additive in the aforesaid glassy system.

## Acknowledgements

S. Kumar is grateful to the University Grants Commission (U.G.C.), New Delhi, for providing major research support during the course of this work.

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