Composition dependent of dielectric properties in $Se_{100-x}Sn_x$ glassy alloys☆

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ABSTRACT

In this paper we report the composition dependence of dielectric properties in $Se_{100-x}Sn_x$ ($x = 0, 2, 4$ and 6) glassy alloys. The temperature and frequency dependence of the dielectric constant (ε') and the dielectric loss (ε'') in the above glassy systems, in the frequency range (1 kHz to 5 MHz) and temperature range (300–350 K) have been measured. It has been found that ε' and ε'' both are frequency and temperature dependent and are also found to increase with increasing concentration of Sn in pure amorphous Se. The role of Sn, as an impurity in the pure a-Se glassy alloy, has also been discussed in terms of electronegativity difference between the elements used in making the aforesaid glassy system. Apart from this, the results have also been correlated in terms of a dipolar model which considers the hopping of charge carriers over a potential barrier between charged defect states.

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1. Introduction

Amorphous Selenium has been emerged as promising material because of its potential technological importance. It is widely preferred in the fabrication of electrophotographic devices and more recently switching and memory devices [1]. It has been found that metal chalcogenides offer a range of optical band gaps suitable for various optical and optoelectronic applications. Se based alloys are useful due to greater hardness, high photosensitivity, higher crystallization temperature and smaller ageing effect compared to pure a-Se [2]. Among the compounds of IV–VI groups, Se–Sn has potential applications in memory switching devices, as efficient solar material and in holographic recording system [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]. 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. It has been reported that in chalcogenide glasses the dielectric dispersion does exist at low frequencies even though these materials are covalently bonded semiconductors [8,9]. 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].

In our earlier communications [11,12], we have reported dielectric measurements in $Se_{100-x}Ge_x$ and a-$Se_{100-x}Pb_x$ glassy systems and found that the dielectric parameters are highly temperature and frequency dependent. In view of the same, we have made dielectric measurements in glassy $Se_{100-x}Sn_x$ alloys to study the effect of Sn incorporation on the dielectric behavior of pure a-Se.

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 conclusion drawn from the present work.

2. Experimental details

2.1. Preparation of glassy alloys

Glassy alloys of $Se_{100-x}Sn_x$ ($x = 0, 2, 4$ and 6) 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 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 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 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 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.
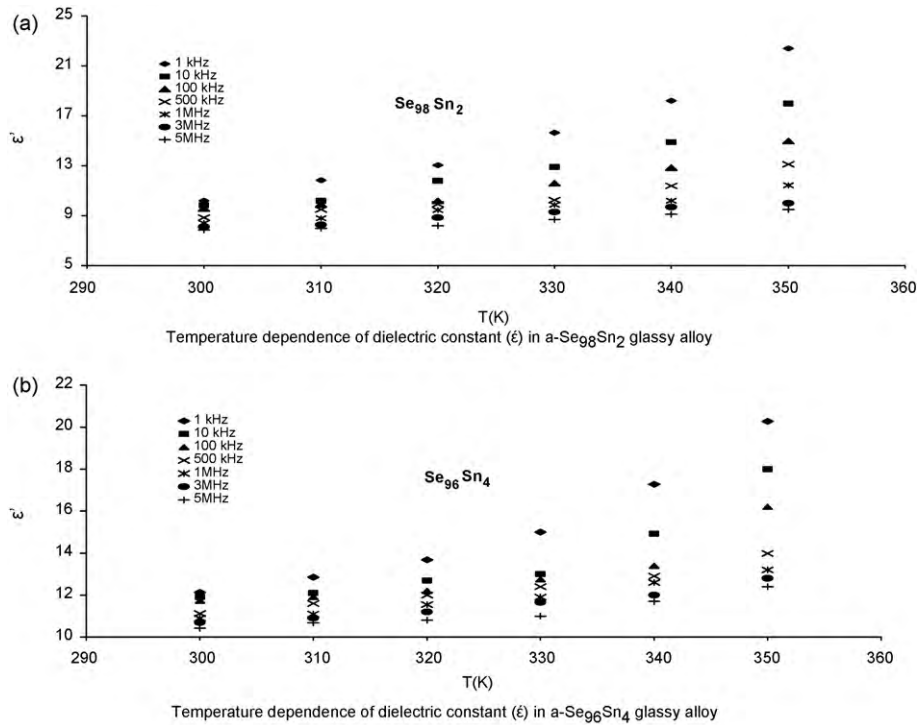
2.2. Dielectric relaxation measurements

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

Fig. 1. (a) Temperature dependence of dielectric constant (ε') in a-Se$_{98}$Sn$_2$ glassy alloy. (b) Temperature dependence of dielectric constant (ε') in a-Se$_{96}$Sn$_4$ glassy alloy.

sample, which could give measurements of temperature with an accuracy of 1 °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 3532-50 LCR Hi TESTER". The parallel capacitance and dissipation factor were measured and then ε' and ε'' were 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 ($\sim 10^{18}$–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 Se$_{100-x}$Sn$_x$ glassy alloys

Temperature dependence of ε' and ε'' was measured at various frequencies (1 kHz to 5 MHz) for various glassy alloys studied in the present case. Measurements have been taken in the temperature range 300–350 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 and 2 for a-Se$_{98}$Sn$_2$ and a-Se$_{96}$Sn$_4$ 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 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. 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

Table 1
Calculated covalent character of bonds for considered compositions.

Bonds for bond type	% Covalent character
Se–Se	100
Se–Sn	97.78
Sn–Sn	100

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 by the following relation [14], according to which:

The proportion of covalent character $= 100\% \exp[-0.25(\chi_A - \chi_B)^2]$

$$\text{(1)}$$

where χ_A and χ_B are the electronegativities of atoms A and B, respectively. The values of covalent characters are listed in Table 1. 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 polarisation stopped, so ε' decreases approaching a constant value at a higher frequency due to the interfacial polarisation. This type of behavior has been reported by various workers [15] in chalcogenide glasses.

The incorporation of metallic impurity Sn in a-Se glassy alloy leads to increase the value of the ε' as given in Table 2. This increase can be understood in terms of the nature of the bonding in the sys-

Table 2
Composition dependence of ε' and ε'' in Se$_{100-x}$Sn$_x$ glassy alloys.

Samples	ε' (1 kHz, 300 K)	ε'' (1 kHz, 300 K)
a-Se	3.5	0.5
a-Se$_{98}$Sn$_2$	10.20	3.04
a-Se$_{96}$Sn$_4$	12.13	5.62
a-Se$_{94}$Sn$_6$	16.40	11.15

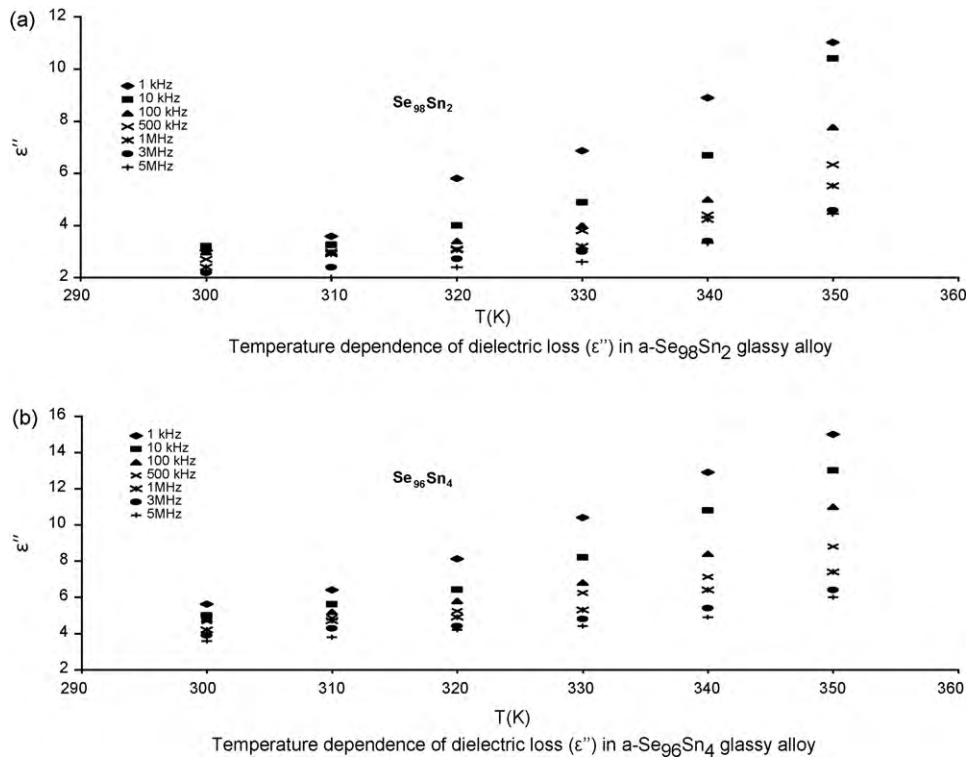**Fig. 2.** (a) Temperature dependence of dielectric loss (ε'') in a-Se$_{98}$Sn$_2$ glassy alloy. (b) Temperature dependence of dielectric loss (ε'') in a-Se$_{96}$Sn$_4$ glassy alloy.

tem. It may be supposed that the incorporation of impurity atom, Sn in pure a-Se may leads to decrease 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

In glassy alloys of Se$_{100-x}$Sn$_x$, ε'' is found to follow a power law with frequency, i.e., $\varepsilon'' = A\omega^m$. Fig. 3 (for a-Se$_{98}Sn_2$ and a-Se$_{96}$Sn$_4$

glassy alloys) confirms 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).

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 (See Fig. 4 for a-Se$_{98}$Sn$_2$ and a-Se$_{96}$Sn$_4$ glassy alloys). Guintini et al. [16] had proposed a dipolar model for dielec-
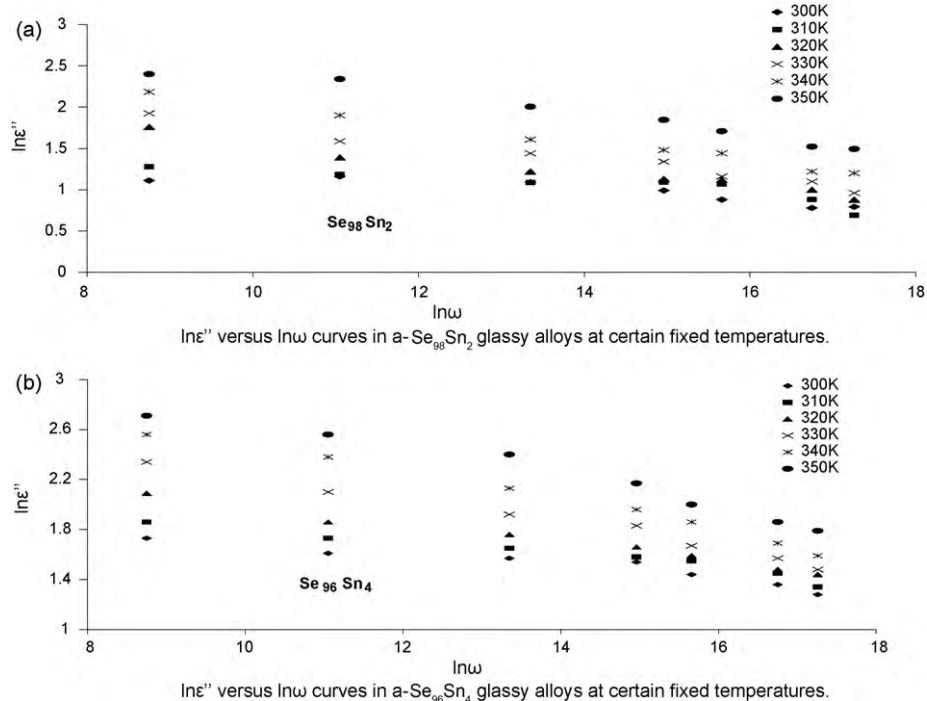

Fig. 3. (a) ln ε'' versus ln ω curves in a-Se$_{98}$Sn$_2$ glassy alloy at certain fixed temperatures. (b) ln ε'' versus ln ω curves in a-Se$_{96}$Sn$_4$ glassy alloys at certain fixed temperatures.
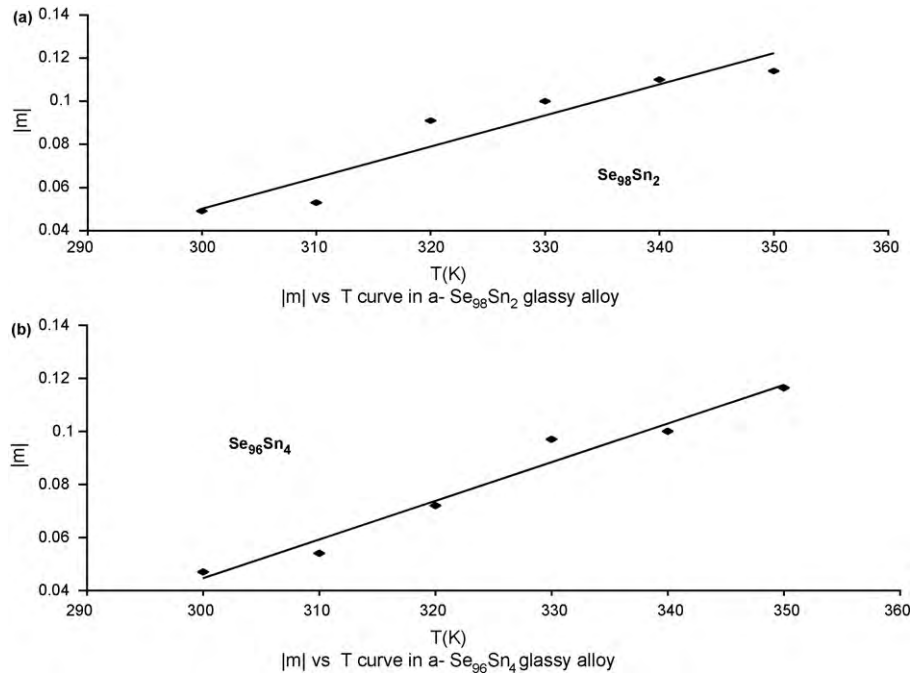
Fig. 4. (a) $|m|$ versus T curve in a-$Se_{98}Sn_2$ glassy alloy. (b) $|m|$ versus T curve in a-$Se_{96}Sn_4$ glassy alloy.

tric dispersion in chalcogenide glasses. This model is based on Elliott's idea [17] 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. [16], ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by:

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) 2\pi^2 N \left(\frac{ne^2}{\varepsilon_0}\right)^3 kT\tau_0^m W_m^{-4} \omega^m \tag{2}$$

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

$$m = -\frac{4kT}{W_m} \tag{3}$$

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 (2), 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 (3). In our samples also we 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. 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 decreases with impurity incorporation. The values of loss tangent

Table 3
Values of W_m and Tan δ at room temperature for various glassy alloys.

Samples	W_m (eV)	Tan δ
a-Se	0.41	0.30
a-$Se_{98}Sn_2$	0.25	0.34
a-$Se_{96}Sn_4$	0.23	0.46
a-$Se_{94}Sn_6$	0.19	0.68

(Tan δ) are also given in Table 3. The quantity Tan δ is a useful practical parameter since it is independent of the sample geometry. Further, it also incorporates the imaginary part of the conductivity.

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

3.2. Composition dependence of ε' and ε''

When iso-electronic atom Te is added to a-Se, the density of defect states is increased and hence the residual potential increases in xerographic experiment. Since Se and Te are elements of the same group of the periodic table. When Te is added to pure Se, some of the Te atoms may not be incorporated in chains. In this case, some of the Te atoms would act as ionized impurities. Since the electron affinity of Te is lower than that of Se, Te atoms are therefore expected to form positively charged localized states. Similarly, the addition of Sn can induce more positively charged localized states, since their electron affinities are much lower than those of Se and Te as observed by Onozuka et al. [18].

Along the same lines, one can expect that when Sn, having lower electronegativity than Se [19] is incorporated in a-Se, increases the density of defect states. Thus the increase in the density of defect states after incorporating of Sn in a-Se may therefore be understood in terms of the difference in electron affinities of impurity element.

From the above discussion it is clear that the addition of Sn to Se increases the number of charged defect states which may affect the dielectric properties. Composition dependence of ε' and ε'' in $Se_{100-x}Sn_x$ glassy alloys are given in Table 2 and are plotted in Fig. 5. As the dielectric loss in these glasses depends upon the total number of localized sites, the increase of dielectric loss with the increase of Sn concentration can be understood in terms of the increased density of defects on addition of Sn to Se. Due to the increased number of dipoles (D^+ and D^-) at higher concentration of Sn, the dielectric constant is also expected to increase with Sn concentration as found in the present study.
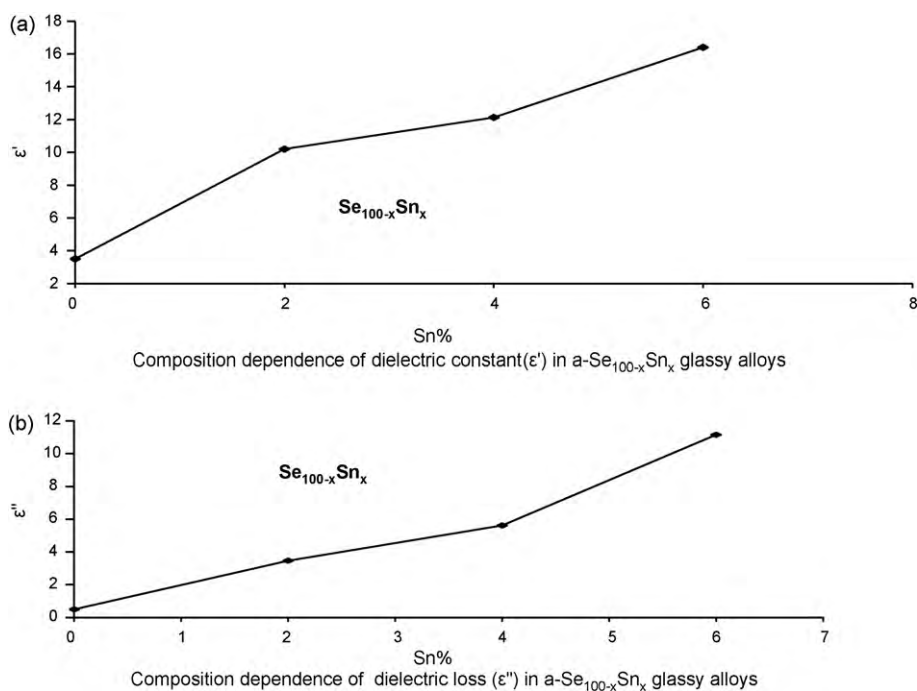
Fig. 5. (a) Composition dependence of dielectric constant (ε') in a-Se$_{100-x}$Sn$_x$ glassy alloys. (b) Composition dependence of dielectric loss (ε'') in a-Se$_{100-x}$Sn$_x$ glassy alloys.

4. Conclusions

The temperature and frequency dependence of the dielectric constants and the dielectric losses in Se$_{100-x}$Sn$_x$ glassy systems in the frequency range (1 kHz to 5 MHz) and temperature range (300–350 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 increased with increasing concentration of Sn 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$^-$). This change of the dielectric parameters with Sn in a-Se glassy system could also be explained on the basis of the electronegativity 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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