Effect of zinc incorporation on the density of defect states in a-Se$_{85}$Te$_{15}$ glassy alloy

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Abstract

Present work incorporates the study of d.c. conductivity measurements at high electric fields in vacuum evaporated thin films of Se$_{85-x}$Te$_{15}$Zn$_x$ ($x = 0$, 2, 4, 6 and 10) glassy alloys. Current-Voltage (I-V) characteristics have been measured at various fixed temperatures. In these samples, at low electric fields, ohmic behavior is observed. However, at high electric fields ($E \sim 10^4$ V/cm), non ohmic behavior is observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the glassy materials studied in the present case. From the fitting of the data to the theory of SCLC, the density of defect states (DOS) near Fermi level is calculated. It is found that the DOS is increasing with increase in concentration of Zn in pure binary Se$_{85}$Te$_{15}$ glassy system. The results obtained have been explained on the basis of some structural changes with third element Zn as an impurity in the pure binary Se$_{85}$Te$_{15}$ glassy alloy and have been correlated with the electronegativity difference between the elements used in making the aforesaid glassy systems.

Key Words: Chalcogenide glasses, thin films, SCLC, DOS

1. Introduction

Modern technological applications of chalcogenide glasses are widespread. Chalcogenide materials have been widely studied for their potential applications in active as well as passive solid-state electronics and optical devices, such as: switching memory, thermal imagining, chemical, ultra-high density phase-change storage and memory, integrated fiber optics, infrared photo detectors and photoreceptor [1–10]. The electrical properties of amorphous Se based chalcogenide glasses exhibit large Fermi level shift and large photo voltaic effects [11–12]. Current-Voltage (I-V) characteristics and consequent field effect study of several chalcogenide glasses have been reported by different investigators [13].

The common feature of chalcogenide glasses is the presence of localized states in the mobility gap due to the absence of long-range order as well as various inherent defects. These defects play a very important role in the suitability of the material for their respective devices. Hence, it is very much essential to have an exact determination of densities of localized states (DOS).

One particular chalcogenide material, amorphous Se-Te alloys, has gained much importance [14], for these alloys are found to be more photosensitive, harder, have a higher glass transition temperature and crystallization temperatures and exhibit less ageing effect than pure selenium. Properties of chalcogenide glassy semiconductors are often affected by the addition of a third element. One interesting problem involving the incorporation of a third element in binary chalcogenide glassy alloys [15–18] is getting relatively stable glassy alloys to change conduction from p- to n-type conduction.

High field effects are most readily observed in these materials because of their low conductivity (Joule heating is negligibly small at moderate temperatures) and have been studied by various groups working in this area [19–25]. The result of these workers have been interpreted in terms of heating effect, space charge limited conduction (SCLC) and high field conduction due to the Poole-Frenkel effect. This indicates that the interpretation of the high field data is highly intriguing in these materials and there is much to do in this field. One of the most useful methods for the determination of DOS involves the measurement of SCLC.

In an earlier communication, we applied SCLC technique to measure the DOS in some significant Se-Te based glassy alloys [26–30]. For us it was very much fruitful to see the variation of DOS with the third element as an impurity in the said binary alloy. In continuation of this prior work, in the present paper we report the high field conduction measurements in glassy Se-Te-Zn system, where the properties have been found to be highly composition dependent. The experimental data fits well with the theory of SCLC in the high electric field region. Section 2 describes the experimental details. The results have been presented and discussed in Section 3. Conclusions have been presented in the last section.

2. Experimental technique

2.1. Sample preparation

Glassy alloys of $Se_{85-x}Te_{15}Zn_x$ (where $x = 0, 2, 4, 6$ and 10) system were prepared by melt quenched technique. High purity elements (99.999% pure) of selenium, tellurium and zinc were weighed by electronic balance (Shimadzu, AUX 220) according to their atomic fractions with a least count of 10^{-4} g. The properly weighed materials were put into clean quartz ampoules (length $\sim$ 5 cm and internal diameter $\sim$8 mm) and then sealed under vacuum at 1.3×10^{-3} Pa. These sealed ampoules were heated in electric furnace up to 1000 °C and kept at temperature for 10–12 hours. The temperature of the furnace was raised slowly at a rate of 3–4 °C/min. During the heating process ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous glassy alloy.

After rocking for about 10 hours, as-obtained molten materials were rapidly quenched by removing the ampoules from the furnace and dropping into ice-cooled water. The quenched samples of the glassy alloys were taken out by breaking the quartz ampoules. The amorphous nature of sample was confirmed by the absence of any sharp peak in the X-ray diffraction pattern. Compositional analysis was performed using electron probe micro-analysis (EPMA) technique.

2.2. Thin film preparation

Thin films of glassy alloys of $Se_{85-x}Te_{15}Zn_x$ were prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the film is $\sim$500 nm. A planar geometry (length $\sim$1.2 cm and electrode

separation $\sim$0.12 mm) was used. A vacuum $\sim$1.3 Pa was maintained through the entire temperature range. The thin films were kept in the deposition chamber, in the dark, for 24 hours before mounting them in the sample holder. This was done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples, as suggested by Abkowitz [31].

2.3. Measurement procedure

For the measurement of SCLC the samples were mounted in a specially designed metallic sample holder. A vacuum $\sim$1.3 Pa was maintained throughout the measurements. Before measuring the d.c. conductivity, the films were annealed at 340 K (below their glass transition temperature, $\underline{T}_g$) for one hour. The temperature of the film was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film. A d.c. voltage (0–300 V) was applied across the sample to measure I-V characteristics. The resulting current is measured by a digital Pico-Ammeter. I-V characteristics were reported at various fixed temperatures for all glassy alloys under study. The heating rate was kept quite small (0.5 K/min) for these measurements.

3. Results and discussions

3.1. X-ray diffraction patterns of $Se_{85-x}Te_{15}Zn_x$ thin films

Figure 1 shows the X-ray diffraction pattern of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10) thin films. The absence of any sharp peak in the X-ray diffraction pattern confirms the amorphous nature of the samples.
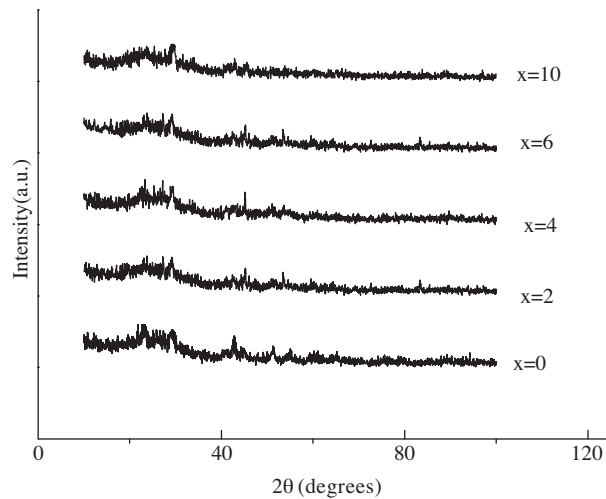
Figure 1. X-ray diffraction pattern of $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6, 10$).

3.2. Space charge limited conduction (SCLC) measurement

Results of I -V characterization at different temperatures show that, in the glassy samples studied here, ohmic behavior is observed at low voltages, i.e., up to 10 V. However, at higher voltages (E $\sim$ 10^4 V/cm), a super-ohmic behavior is observed in the samples. Here, plots of $\ln(I/V)$ as a function of V are found

to be straight lines at all measuring temperatures. Figures 2–6 show such curves for various compositions of $Se_{85-x}Te_{15}Zn_x$ glassy alloy. It is clear from these figures that the slopes S of $\ln(I/V)$ vs. V were temperature dependent. At low voltage the injected charge carrier density is lower than the thermally generated carrier density and that leads to the ohmic behavior. At higher voltage it may be suggested that the conduction in this region is dominated by a trap limited SCLC mechanism. According to the theory of SCLC, in the case of an uniform distribution of localized states having density g_0, the current I at a particular voltage V is given by [32]

$$I = (2eA\mu n_0 V/d)\exp(SV). \tag{1}$$

Here, e is the electronic charge, A is the cross sectional area of the film, n_0 is the density of thermally generated charge carriers, d is the electrode spacing and S is given by

$$S = 2\varepsilon_r\varepsilon_0/eg_0kTd^2, \tag{2}$$

where ε_r is the relative dielectric constant, ε_0 is the permittivity of free space, g_0 is the density of localized states near Fermi level and k is Boltzmann's constant.
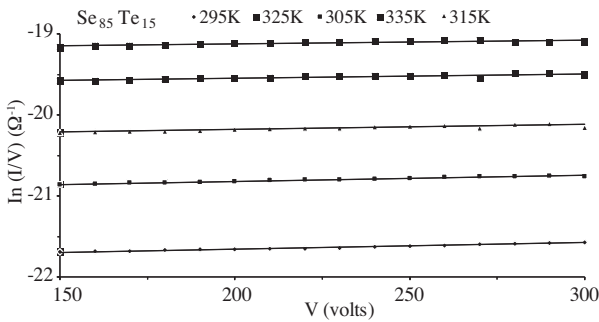

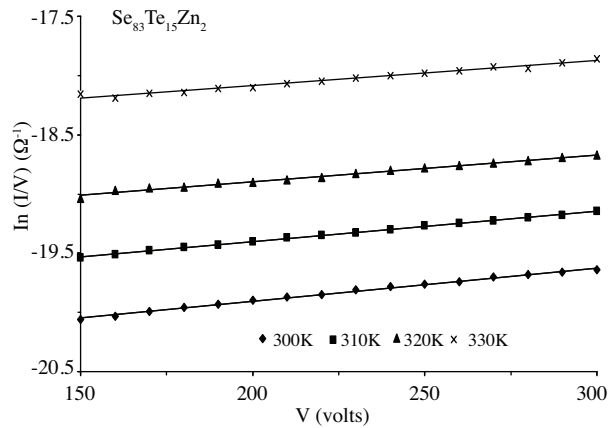**Figure 2.** ln(I/V) versus V curve for $Se_{85}Te_{15}$ glassy alloy at different temperatures.

Figure 3. ln(I/V) versus V curve for $Se_{83}Te_{15}Zn_2$ glassy alloy at different temperatures.

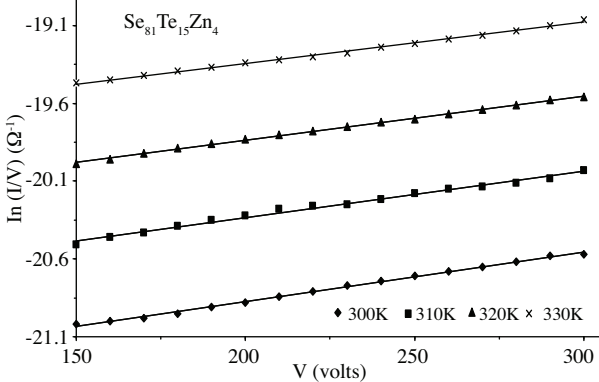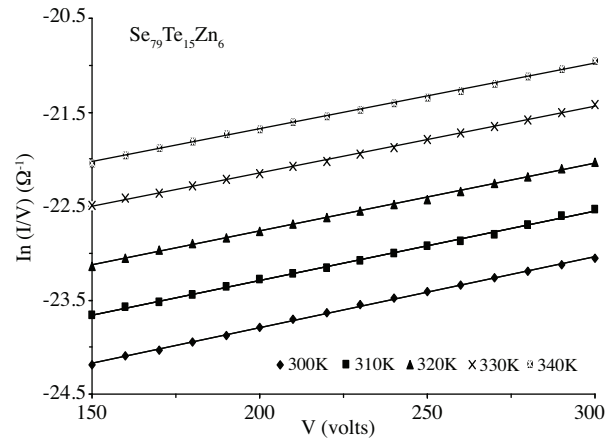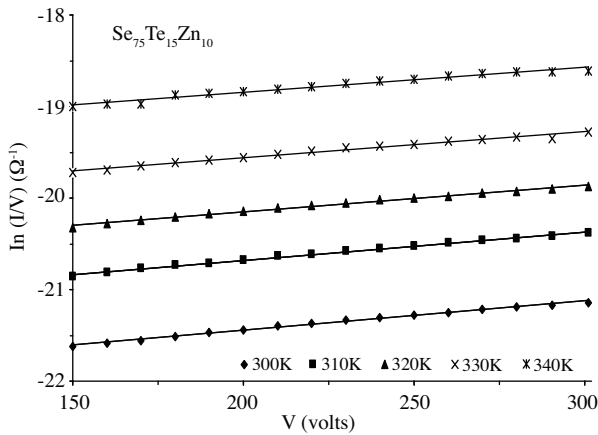**Figure 4.** ln(I/V) versus V curve for $Se_{81}Te_{15}Zn_4$ glassy alloy at different temperatures.

**Figure 5.** ln(I/V) versus V curve for $Se_{79}Te_{15}Zn_6$ glassy alloy at different temperatures.

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Thin films contain a large number of defects due to dangling bonds that give rise to large number of localized defect states. These localized states act as carrier trapping centers and after trapping the injected charge from electrodes, they become charged and thus are expected to build up a space charge. This build-up of space charge by the inherent native defects plays the key role in the determination of SCLC process.

According to equations (1) and (2), for SCLC, plots of $\ln(I/V)$ as a function of V should be straight lines whose slopes S should decrease with increasing temperature. It is clear from Figures 2–6 that the S are not the same at all observed temperatures. The values of these slopes are plotted as a function of temperature in Figure 7 for the glassy system used in the present study. It is clear from the figure that the slope S is inversely proportional to the temperature for all the glassy alloys studied. These results indicate the presence of SCLC in these samples.

Figure 6. $\ln(I/V)$ versus V curve for $Se_{75}Te_{15}Zn_{10}$ glassy alloy at different temperatures.
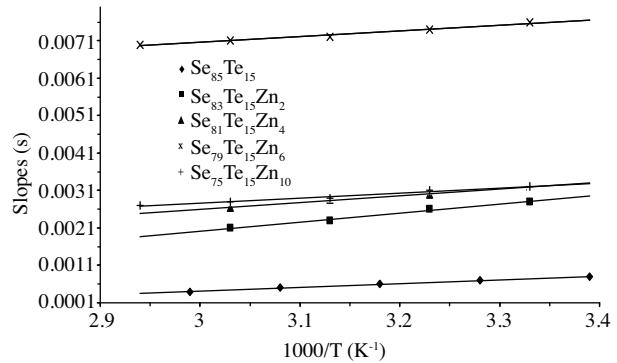
Figure 7. Slopes (s) of $\ln(I/V)$ versus V curve against $1000/T$ for a-$Se_{85-x}Te_{15}Zn_x$ thin films.

It may be mentioned here that in amorphous materials, non-ohmic behavior has also been explained in terms of high field conduction due to the Poole-Frenkel effect of screened charge intrinsic defects and field induced lowering of energy barriers for the charge-carrier hopping within localized states at the band edges [33–35]. According to this, the current I at a particular voltage V is given by the equation

$$\ln I = \text{Constant} + (e\beta V^{1/2})/(kTd^{1/2}). \tag{3}$$

The theoretical value of β is given by the relation

$$\beta = (e/\pi\varepsilon_r\varepsilon_o)^{1/2}. \tag{4}$$

According to equation (3), plots of $\ln(I)$ as a function of $V^{1/2}$ should yield a straight line at a particular temperature of measurement. The slope should, however, decrease with increasing temperature. In the present case, $\ln(I)$ vs. $V^{1/2}$ could be fitted to a straight line at various temperatures of measurements (see Figure 8 for the case of $Se_{83}Te_{15}Zn_2$). Similar plots were obtained for other glasses. The slopes of $\ln(I)$ vs. $V^{1/2}$ decreases linearly with temperature, as it is clear from the above Figure. This also confirms the validity of equation (3).
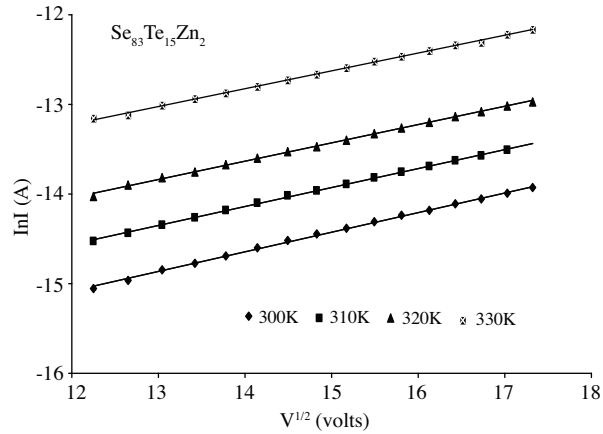
Figure 8. Plot of lnI versus $V^{1/2}$ curve for $Se_{83}Te_{15}Zn_2$ film at different temperatures.

To distinguish between these two processes the measurements on samples having different electrode gaps (scaling law) are necessary, according to which, in the case of field dependent conductivity, the plot of $\ln(I/V)$ vs. V must be independent of the electrode spacing d. On the other hand, for any SCLC mechanism, the same plot gives different curves for different values of d.

We have therefore measured I-V characteristics at room temperature for various samples having different electrode spacing. The results for one particular sample $Se_{83}Te_{15}Zn_2$ are given in Table 1 and plotted in Figure 9. (similar plots were obtained for other samples, also.) It is clear from this figure that different slopes are obtained at different electrode spacing. The values of these slopes are plotted against $1/d^2$ in Figure 10. This confirms the validity of equation (2) in the present case and excludes the possibility of any other high-field conduction processes mentioned above. Hence these measurements confirm the presence of SCLC in the present samples.
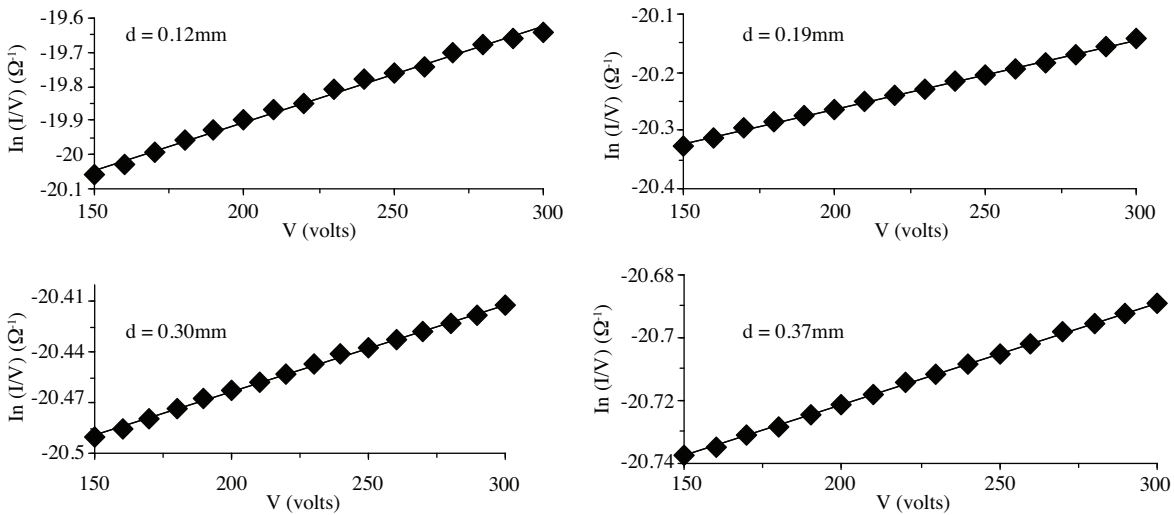
Figure 9. Plots of ln(I/V) versus V curve at room temperature having different electrode gaps for $Se_{83}Te_{15}Zn_2$ thin film.

Table 1. Values of slopes of ln I/V versus V curves at different electrode gaps for $Se_{83}Te_{15}Zn_2$ thin film.

Electrode gap d (mm)	$1/d^2$ (mm^{-2})	Slopes s of ln I/V versus V at T_{room} (300 K)
0.12	69.44	2.80×10^{-3}
0.19	27.70	1.18×10^{-3}
0.30	11.11	5.10×10^{-4}
0.37	7.31	3.22×10^{-4}
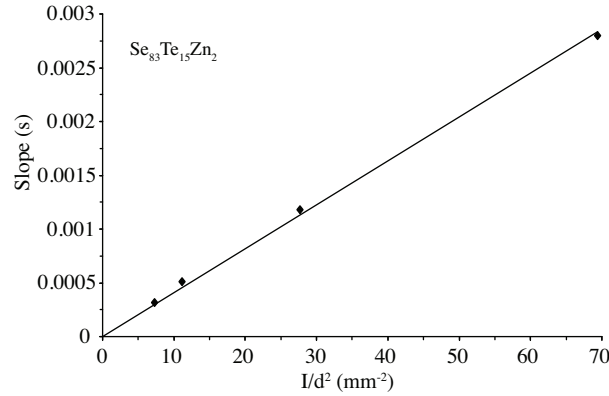

Figure 10. S vs. $1/d^2$ curve for different electrode gaps for $Se_{83}Te_{15}Zn_2$ glassy system.

Using equation (2), we have calculated the density of localized states g_0 from the slope of Figure 7. The value of the relative dielectric constant ε_r is measured by using capacitance measuring assembly model a Hioki 3532-50 LCR Hi TESTER, employing the four-terminal techniques. The results of these calculations are given in Table 2 and plotted in Figure 11. The results show that g_0 near mid-gap increases with increasing Zn impurity in the binary $Se_{85}Te_{15}$ glassy system.

Table 2. Density of localized states g_0 in various glassy alloys.

Glassy alloys	Slope S vs. $1000/T$	ε_r (at 120 Hz, T_{room})	g_0 (eV^{-1}cm^{-3})
$Se_{85}Te_{15}$	9.99×10^{-4}	7.78	6.93×10^{14}
$Se_{83}Te_{15}Zn_2$	2.40×10^{-3}	26.00	9.64×10^{14}
$Se_{81}Te_{15}Zn_4$	1.80×10^{-3}	32.00	1.58×10^{15}
$Se_{79}Te_{15}Zn_6$	1.53×10^{-3}	43.00	2.50×10^{15}
$Se_{75}Te_{15}Zn_{10}$	1.33×10^{-3}	55.00	3.68×10^{15}

While studying the effect of chlorine on electro-photographic properties of Se-Te, Onozuka et al. in [36] observed that the increase in residual potential caused by Te addition to Se is counteracted by addition of chlorine to Se-Te glassy alloy. The results were interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to small electro-negativity of Te as compared to Se; while chlorine atoms, having larger electro-negativity, formed negatively charged impurities, thereby compensating the effect of Te.
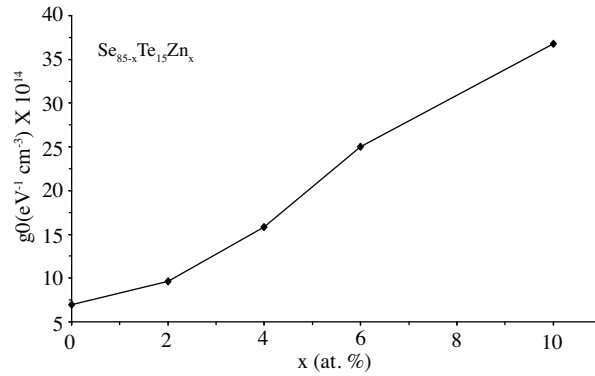
Figure 11. Density of localized states (g_0) versus Zn concentration in a-$Se_{85-x}Te_{15}Zn_x$ glassy system.

Along the same lines, one can expect that when a third element Zn, having lower electro-negativity (1.7) compared to Se (2.4) and Te (2.1) [37], is added into Se-Te glassy alloys, positively charged defects will be created thus increasing the density of defect states in ternary Se-Te-Zn system as compared to pure binary Se-Te glassy alloy. Our SCLC data also confirms the same.

4. Conclusion

I-V characteristics have been studied in amorphous thin films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6$ and 10) glassy system. At low fields, ohmic behavior is observed. However, at higher fields ($\sim 10^4$ V/cm) super ohmic behavior is observed.

Analysis of the observed data shows the existence of SCLC in the glassy samples used in the present study. From the fitting of the data in the theory of SCLC, the density of localized states near Fermi-level is calculated. It is found that the density of defect states is increasing with increase of Zn additive in pure binary $Se_{85}Te_{15}$ glassy system. The results obtained have been correlated with the electro-negativity difference between the constituent elements used in making the above glassy alloys.

Acknowledgements

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