

High Field Conduction in Thin Films of $a-(\text{Ge}_{.20}\text{Se}_{0.80})_{1-x}\text{Pb}_x$ Glassy Alloys*

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Abstract

The present paper reports d.c. conductivity measurements at high electric fields in vacuum evaporated amorphous thin films of $(\text{Ge}_{.20}\text{Se}_{0.80})_{1-x}\text{Pb}_x$ (where $x = 0, 0.02, 0.04, 0.06$ and 0.10) 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 Pb in pure binary $\text{Ge}_{0.20}\text{Se}_{0.80}$ glassy system. The peculiar role of third element Pb as an impurity in the pure binary $\text{Ge}_{0.20}\text{Se}_{0.80}$ glassy alloy is also discussed.

Key Words: Thin films, Chalcogenide glasses, SCLC, DOS.

1. Introduction

Because of their potential applications, thin films of chalcogenide glasses have been extensively studied in recent years. Attempts have been made to produce stable glasses which have good photosensitive properties and can be doped to n- or p-type. The effect of incorporating a third element in binary chalcogenide glassy alloys has always been an interesting problem towards achieving relatively stable glassy alloys, as well as to change the 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 have been found [1–7] to change conduction from p- type to n-type, hence their great importance.

Ge-Se-Pb chalcogenide glasses have also recently drawn great attention [8–11] for their own importance and, as we know that the density of localized states (DOS) is the key parameter to predict the suitability of these glasses, to use them in respective devices. Therefore, the determination of DOS has been a important issue in these glasses.

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 field [12–20]. Result of these workers have been interpreted in terms of heating effect, space charge

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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 much has to be done in this field.

Keeping this fact in mind we have decided here to measure the high field effects in the well known binary Ge-Se and ternary Ge-Se-Pb glassy alloys. Space charge limited conduction has been used as a tool to measure the DOS near Fermi level. Effect of adding Pb on the DOS in pure binary Ge-Se is also discussed.

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

Glassy alloys of $(\text{Ge}_{0.20}\text{Se}_{0.80})_{1-x}\text{Pb}_x$ (where $x = 0, 0.02, 0.04, 0.06$ and 0.10) systems are prepared by quench technique. High purity (99.999%) materials are weighed according to their atomic percentages and are sealed in quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum $\sim 1.3 \times 10^{-3}$ Pa. The ampoule containing the materials are heated to 1000 °C and held at that temperature for 10–12 hours. The temperature of the furnace is raised slowly at a rate of 3–4 °C/min. During heating, the ampoule is constantly rocked, by rotating a ceramic rod to which the ampoule is tucked away in the furnace. This is done to obtain homogenous glassy alloy.

After rocking for about 10 hours, the obtained melt is cooled rapidly by removing the ampoule from the furnace and dropping to ice-cooled water. The quenched sample of the glassy alloy is taken out by breaking the quartz ampoule. 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.

Thin film of these glasses is prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrode at bottom is used for the electrical contact. The thickness of the film is ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm) is used for the present measurements. A vacuum ~ 1.3 Pa is maintained over the entire temperature range (293 K to 363 K).

The thin films are kept in the deposition chamber and in the dark for 24 hours before mounting them in the sample holder. This is done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [21]. Before measuring the d.c. conductivity, the films are first annealed at 370 K (below their glass transition temperature, T_g) for one hour in a vacuum ~ 1.3 Pa.

As co-planar structure of the film is used for the present measurements, a d.c. voltage is applied across the electrodes to measure I-V characteristics and found to be linear and symmetric up to 10 V. The present measurements are, however, made by applying a voltage up to 300 V across the films. The resulting current is measured by a digital Pico-Ammeter. The heating rate is kept quite small (0.5 K/min) for these measurements. Thin film sample is mounted in a specially designed sample holder. A vacuum ~ 1.3 Pa is maintained throughout the measurements. The temperature of the film is controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film.

3. Results and Discussions

Results of I-V characteristics at different temperature shows that in the glassy sample 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, $\ln I/V$ vs. V curves are found to be straight lines. Figures 1–2 Show such curves in case of $(\text{Ge}_{0.20}\text{Se}_{0.80})_{1-x}\text{Pb}_x$ (where $x = 0$ and 0.10) glassy alloys. Similar

results have also been found for other glasses. According to the theory of SCLC, in the case of a uniform distribution of localized states having density g_0 , the current I at a particular voltage V is given by [22]

$$I = (2eA\mu n_0 V/d)[\exp(SV)]. \quad (1)$$

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

$$S = 2\varepsilon_r\varepsilon_0/eg_0kTd^2, \quad (2)$$

where ε_r is the static value of the dielectric constant, ε_0 is the permittivity of free space, g_0 is the density of traps near the Fermi level and k is Boltzmann's constant.

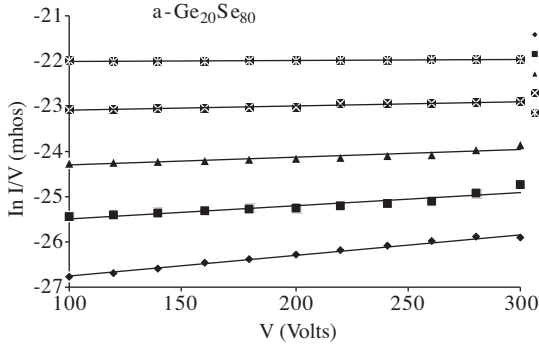


Figure 1. Plots of $\ln I/V$ vs. V curve for $a\text{-Ge}_{20}\text{Se}_{80}$ at different temperatures.

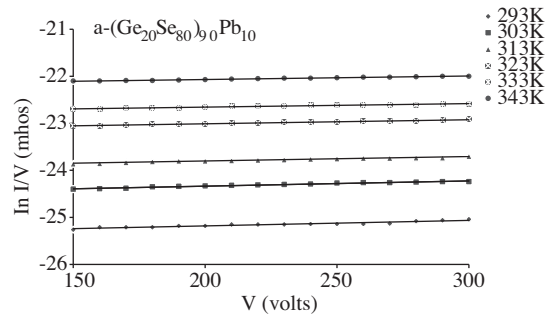


Figure 2. Plots of $\ln I/V$ vs. V curve for $a\text{-(Ge}_{20}\text{Se}_{80})_{90}\text{Pb}_{10}$ at different temperatures.

It should be noted that equation 1 is not an exact solution of SCLC equation, but is a very good approximation of the one carrier space charge limited current under the condition of a uniform distribution of traps. In the present case, the single carrier assumption is justified as these glasses are known to behave as p-type material. As present measurements scan a very limited range of energy near the Fermi level, the assumption of uniform distribution of traps is also not unjustified.

According to equation 1, lines of $\ln I/V$ as a function of V should be straight whose slope should decrease with increase in temperature, as evident from equation 2. It is clear from Figures (1)–(2) that the slope S of $\ln I/V$ vs. V is not the same at all measuring temperatures. The value of these slopes is plotted as a function of temperature in Figure 3 for the glassy systems used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature. These results indicate the presence of SCLC in the present samples.

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 [23–25], according to which the current I at a particular voltage V is given by:

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

The theoretical value of β is given by

$$\beta = (e/\pi\varepsilon_r\varepsilon_0)^{1/2}. \quad (4)$$

According to Equation 3, curves of $\ln I$ vs $V^{1/2}$ 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. $V^{1/2}$ curves could be fitted to a straight line at various temperatures of measurements [see Figure 4 for $(\text{Ge}_{20}\text{Se}_{80})_{0.90}\text{Pb}_{0.10}$]. Similar plots were obtained for other glasses also.

The slope s of $\ln I$ vs. $V^{1/2}$ curves decreases linearly with temperature as it is clear from the above Figure. This also confirms the validity of Equation 3.

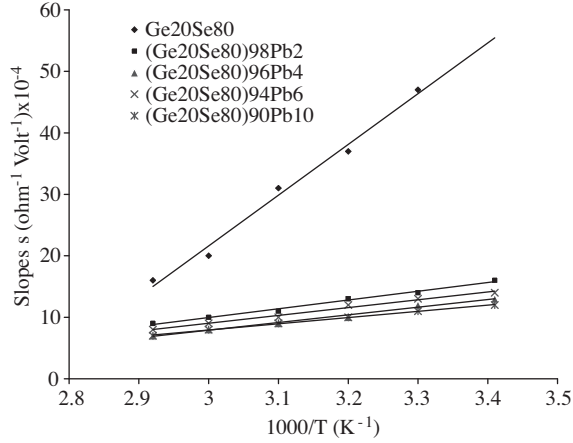


Figure 3. Plots of S vs. $1000/T$ curves for glassy $(\text{Ge}_{20}\text{Se}_{80})_{100-x}\text{Pb}_x$ (where $x = 0, 2, 4, 6$ and 10) systems.

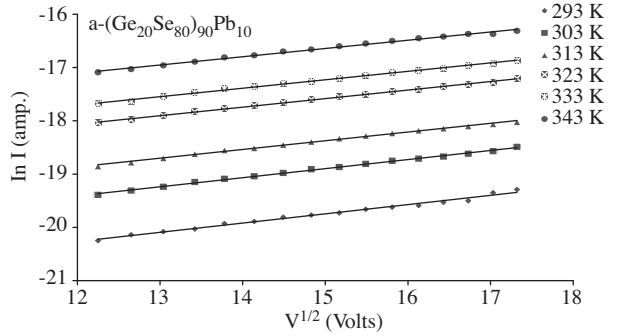


Figure 4. Plots of $\ln I$ vs $V^{1/2}$ curve for $a\text{-(Ge}_{20}\text{Se}_{80})_{90}\text{Pb}_{10}$ at different temperatures.

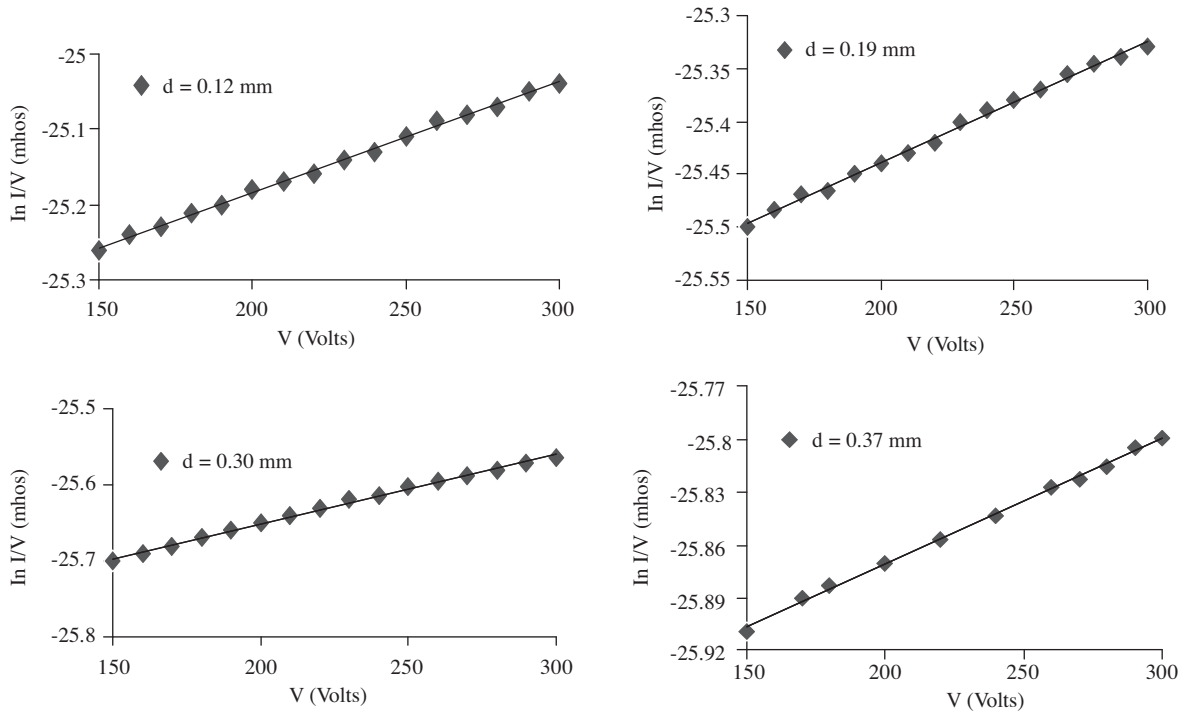


Figure 5. Plots of $\ln(I/V)$ vs. V curve at room temperature having different electrode gaps for $a\text{-(Ge}_{20}\text{Se}_{80})_{90}\text{Pb}_{10}$ glassy system.

Now 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 (293 K) for samples having different electrode spacing. The results

for $(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Pb}_{0.10}$ are plotted in Figure 5. Similar plots were obtained for other glasses 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 6. 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.

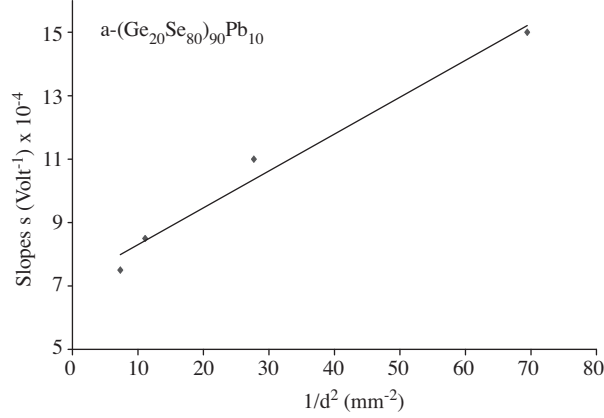


Figure 6. S vs. $1/d^2$ curve for different electrode gaps for $(\text{Ge}_{20}\text{Se}_{80})_{90}\text{Pb}_{10}$ glassy system.

Using equation 2, we have calculated the density of localized states from the slope of Figure 3. The value of the relative dielectric constant ϵ_r is measured by using capacitance measuring assembly model General Radio model 1620-AP capacitance measurement bridge, employing the three terminal techniques. The results of these calculations are given in Table 1. The results show that the density of defect states near mid-gap is increasing by the increase of a third element Pb to the binary Ge-Se glassy alloy. Since high concentration of Pb (10 at.%) is incorporated in Ge-Se system, these atoms can not be considered as impurities. The properties of such ternary materials must, therefore, be attributed to the modifications in structure of the host alloy on the addition of a third element.

Table 1. Density of localized states (g_0) in $a-(\text{Ge}_{0.20}\text{Se}_{0.80})_{1-x}\text{Pb}_x$ glassy system.

Glassy alloys	Slope S vs. $1000/T$ curves	ϵ_r (at 120 Hz, 305 K)	g_0 ($\text{eV}^{-1}\cdot\text{cm}^{-3}$)
$\text{Ge}_{0.20}\text{Se}_{0.80}$	8.3×10^{-3}	2.62	2.82×10^{13}
$(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.98}\text{Pb}_{0.02}$	1.4×10^{-3}	2.85	1.87×10^{14}
$(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.96}\text{Pb}_{0.04}$	1.3×10^{-3}	2.87	2.04×10^{14}
$(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.94}\text{Pb}_{0.06}$	1.2×10^{-3}	3.23	2.32×10^{14}
$(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Pb}_{0.10}$	9.6×10^{-4}	3.64	3.36×10^{14}

According to Phillips [26], Ge-Se alloys must be considered as small chemically ordered clusters embedded in a continuous network. Some of these clusters may be $(\text{Se})_n$ chains, $\text{Ge}(\text{Se}_{1/2})_4$ corner-sharing tetrahedral or $\text{Ge}(\text{Se}_{1/2})_6$ ethane-like structural units. The first two types of clusters may be predominant in Se-rich alloys (as in the present case). The addition of Pb at large concentration may modifies the $\text{Ge}(\text{Se}_{1/2})_4$ clusters, penetrating into them to form units containing all three elements, Ge, Pb and Se, as suggested by Pazin et al. [27] in the case of Bi in Ge-Se glassy alloys.

Incorporation of third element Pb to Ge-Se binary alloy is expected to modify the structure of the host alloy, with the new element entering into chemical bond formation with Ge and/or Se as reported by Shukla et al., [28] in their x-ray K-absorption studies in Ge-Se- M ($M = \text{Ag}, \text{In}, \text{Pb}$ and Cd) glassy alloys.

While studying the effect of chlorine on electro-photographic properties of Se-Te, Onozuka et al., [29] 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 electron affinity of Te as compared to Se while chlorine atoms having larger electron affinity formed negatively charged impurities, thereby compensating the effect of Te.

Along the same lines, one can expect that when a third element Pb having lower electro-negativity than Se [30] is added into Ge-Se glassy alloys, positively charged defects will be created thus increasing the density of defect states in ternary Ge-Se-Pb system as compared to pure binary Ge-Se glassy alloy.

Our SCLC data also confirms that the density of defect states is increasing with incorporation of Pb in pure binary $\text{Ge}_{.20}\text{Se}_{.80}$ glassy system.

4. Conclusion

I-V characteristics have been studied in amorphous thin films of $(\text{Ge}_{.20}\text{Se}_{.80})_{1-x}\text{Pb}_x$ (where $x = 0, 0.02, 0.04, 0.06$ and 0.10) 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 Pb additive in pure binary $\text{Ge}_{.20}\text{Se}_{.80}$ glassy system. This increase in DOS has been explained with the electro-negativity difference between the constituent elements used in making the above glassy system.

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