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Density of Defect States in $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ Glassy Alloys

The present paper reports the study of density of defect states in bulk glassy alloys of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x = 0, 2, 4, 6$ and 8). Space charge limited conduction technique is used for this purpose. I-V characteristics have been measured at various fixed temperatures in the range 300 K to 380 K. An ohmic behavior is observed at low electric fields upto 10^2 V/cm. However, superohmic behavior is observed at high electric fields ($10^3 - 10^4$ V/cm). High-field conduction theory of space charge limited conduction for uniform distribution of localized states in the mobility gap fits well with the experimental data. Using this theory, the density of defect states (DOS) near Fermi level is calculated for all the glassy alloys. A maxima is observed at 4 at. % of Ag, which is explained in terms of average co-ordination number.

Keywords: Chalcogenide glasses, Space charge limited conduction, Density of defect states

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1. Introduction

The chalcogenide glasses are one of the most widely known families of glasses and have been studied extensively over the past few decades because of their interesting properties and wide applications. It has been observed that Se based glassy alloys are more useful as compared to pure glassy Se due to their higher photo sensitivity, greater hardness, higher crystallization temperature and lower aging effect [1]. Se-Sb alloys are preferred over Se – Te alloys as the addition of small percentage of Sb is sufficient to cause crystallization of pure amorphous Se [2]. Recently, Ag is used as an additive in many chalcogenide systems because of their nature of conduction in Ag doped chalcogenide glasses. The electrical conductivity of Ag containing glasses changes by several orders of magnitude as compared to parent glassy alloy. Therefore, it is interesting to study the electrical properties of Ag doped chalcogenide glasses from the point of view of basic science and applications [3].

The common feature of chalcogenide glasses is the presence of localized states in the mobility gap due to the absence of long range order and also due to various inherent defects. Due to their low conductivity these materials are most suitable for high field conduction studies. Some such types of studies have been reported on chalcogenide glasses [4-6]. It is well known now that the density of defect states in the mobility gap controls many physical properties of chalcogenide glasses. One of the most direct methods for the determination of density of defect states in the mobility gap involves the measurements of space charge limited conduction (SCLC). This technique has already been applied in chalcogenide glasses by various workers [7-13].

In our previous work, we have used SCLC technique to study DOS in the bulk glassy system $\text{Se}_{90-x}\text{Sb}_x$ [8]. The present paper reports the

measurements of SCLC in bulk glassy $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x=0, 2, 4, 6$ and 8) with a objective to see the effect of Ag incorporation on DOS in binary $\text{Se}_{90}\text{Sb}_{10}$.

The next section describes the experimental details of material preparation and the details of the measurements. The results and discussions are presented in the third section. The last section deals with the conclusions drawn from the present experimental work.

2. Experiment

2.1 Material Preparation

Glassy alloys of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x=0, 2, 4, 6$ and 8) are prepared by quenching technique. High purity (99.999%) materials are weighted according to their atomic percentages and sealed in quartz ampoules (length ~5cm and internal diameter ~8mm) with a vacuum $\sim 10^{-5}$ Torr. The ampoule containing the material is held at 900°C for 10-12 hours where the ampoules are constantly rocked to make the melt homogeneous. The melt is cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water.

2.2 SCLC Measurements

The glassy alloys of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x=0, 2, 4, 6$ and 8) are ground to a very fine powder and pellets (diameter ~12mm and thickness ~0.5mm) are obtained by compressing the powder in a die at a load of 7-8 Tons. The pellet is mounted in between two steel electrodes of a metallic sample holder for SCLC measurements. A d. c. voltage (0 to 500 V) is applied across the sample and the resultant current is measured by a digital pico-ammeter. Current-Voltage (I-V) characteristics are measured at various fixed temperatures. The temperature of the pellet is controlled by mounting a heater outside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near to the

pellet. A vacuum of about 10^{-2} Torr is maintained during measurements.

3. Results and Discussion

In the present work, I-V characteristics of bulk glassy alloys of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x=0, 2, 4, 6$ and 8) are measured at various temperatures (300-380K). At low fields ($<10^2$ V/cm), Ohmic behavior is observed in all the samples and I versus V curves are found to be straight lines and at higher fields (10^3 - 10^4 V/cm), super Ohmic behavior is observed at all measuring temperatures as shown in Fig. 1.

Several glassy alloys exhibit at high electric field E, I vs V characteristics of the form [13, 14]:

$$I = I_0 \exp(\beta E^{1/2} / kT) \quad (1)$$

Here β is a constant and its value can be given by

$$\beta = (e^3 / \lambda \pi \epsilon_0 \epsilon_r)^{1/2} \quad (2)$$

Taking $\lambda=1$, Eq. (2) reduces to the Pool-Frenkel coefficient and its value is given by

$$\beta_{\text{PF}} = (e^3 / \pi \epsilon_0 \epsilon_r)^{1/2} \quad (3)$$

Taking $\lambda=4$, Eq. (2) reduces to the Schottky coefficient and its value is given by

$$\beta_{\text{Sch}} = (e^3 / 4 \pi \epsilon_0 \epsilon_r)^{1/2} \quad (4)$$

It is clear from the above that in Pool-Frenkel as well as in Schottky effect, $\ln(I)$ vs. $V^{1/2}$ curves are expected to be straight lines as expected from Eq. (1) and also there are some differences which distinguishes Pool-Frenkel effect and Schottky effect.

To test the above high field conduction theories in the present case, we have plotted $\ln(I)$ vs $V^{1/2}$ curves at various temperatures and found that these curves are not straight lines having good correlation coefficient in $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ glassy alloys. Hence, Pool-Frenkel and Schottky effect may not be responsible for super ohmic behavior in the present case.

In the present case we observed that, in the high field region, $\ln(I/V)$ versus V curves are found to be straight lines as shown in Fig. 2. type of behavior is expected if one considers the theory of space charge limited conduction (SCLC), for uniform distribution of localized states according to which, the current I at particular voltage is given by the relation [15] as given below:

$$I = (2 e A \mu n_0 V/d) \exp(S V) \quad (5)$$

where d is electrode spacing, n_0 is the density of the thermally generated charge carriers, μ is the mobility, e is the electronic charge, A is the area of cross section of pellet and slope (S) is given by:

$$S = 2 \epsilon_r \epsilon_0 / e g_0 k T d^2 \quad (6)$$

where g_0 is the DOS near Fermi level

As evident from equations (5) and (6), a plot of $\ln(I/V)$ versus V should be linear and slope of these lines should decrease inversely with temperature.

In the present case also, $\ln(I/V)$ versus V curves are found to be straight lines with good correlation coefficient at all the measuring temperatures as shown in Fig. 2. The slope S decreases with the increase in temperature as shown in Fig. 3.

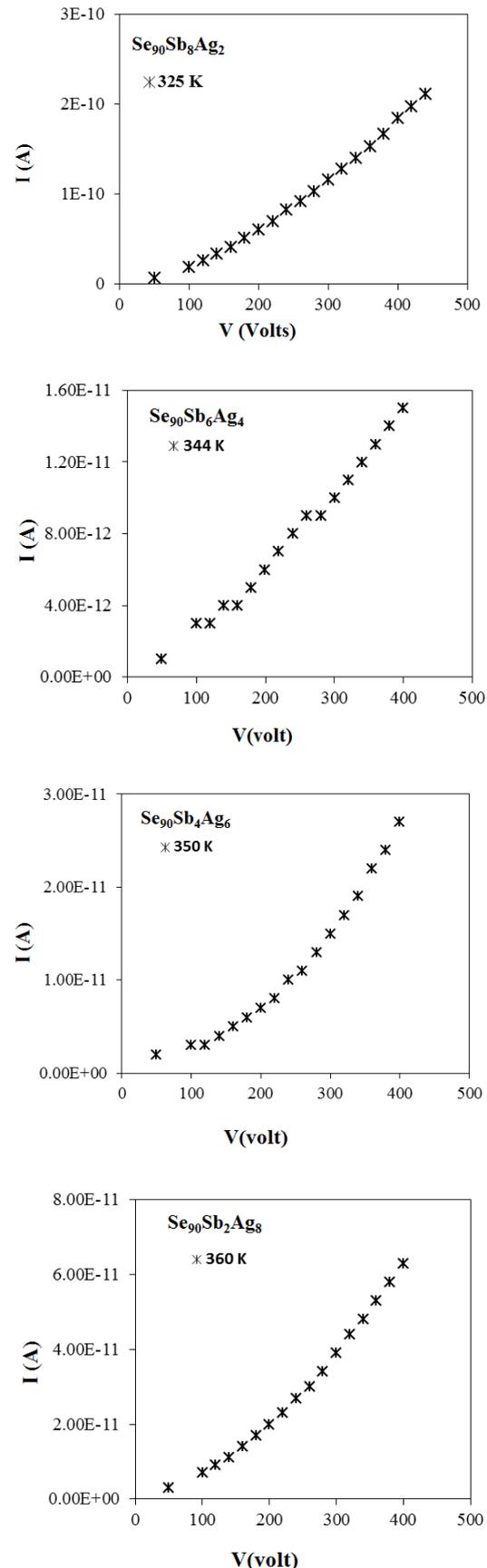


Fig. (1) Plots of I vs. V for $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ glassy system at different temperatures

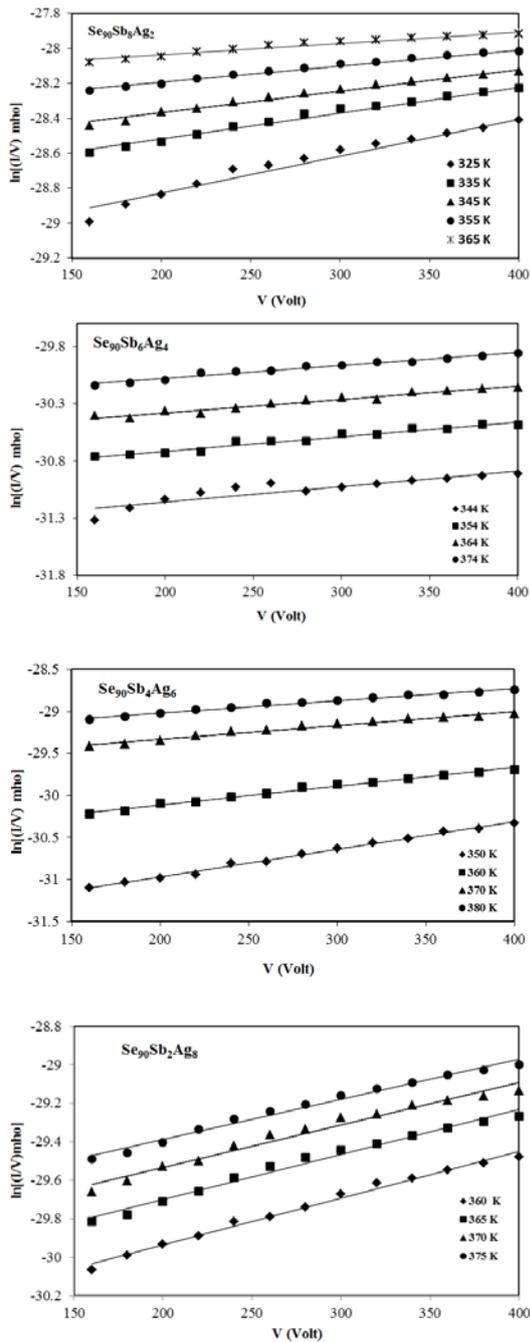


Fig. (2) Plots of $\ln(I/V)$ vs V for $Se_{90}Sb_{10-x}Ag_x$ glassy system at different temperatures

Using Eq. (6), we have calculated the density of localized states from the slope of the Fig. 3. The calculated values of density of localized states near Fermi level in $Se_{90}Sb_{10-x}Ag_x$ glassy alloys are given in Table (1) and plotted against concentration of Ag in Fig. 4. It is clear from this figure that g_0 does not change drastically up to 2 at.% of Ag. However, when the Ag concentration increases further, g_0 increases drastically at 4 at.% of Ag and then decreases again at higher concentrations. This type of discontinuity is observed in chalcogenide glasses in many physical properties [16-18] at a particular

concentration of the additive element when average co-ordination number reaches a certain value, e.g., 2.4 in Ge-Se glasses. According to Phillips and Thorpe model [19], structure below a certain average co-ordination number is floppy type and above this average co-ordination number it is mechanically optimized structure.

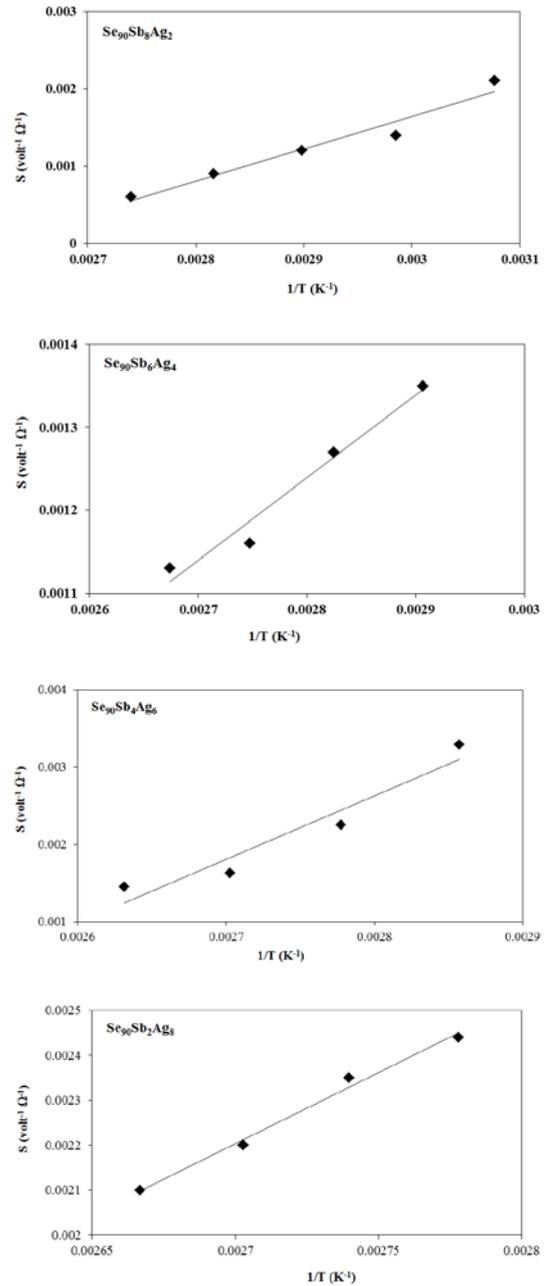


Fig. (3) Plots of slope (S) vs $1/T$ for $Se_{90}Sb_{10-x}Ag_x$ glassy system

The average co-ordination number $\langle z \rangle$ of the glasses studied has been evaluated using the standard procedure described by Tanaka [20].

Thus, for the glassy system $Se_aSb_bAg_c$ ($a+b+c=1$), the value of $\langle z \rangle$ is given by:

$$\langle z \rangle = (a Z_{Se} + b Z_{Sb} + c Z_{Ag}) / (a + b + c) \quad (7)$$

Table (1) Values of Slope of S vs (1/T) curves and density of defect states g_0 for $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ glassy system

No.	Samples	Slope of S vs. (1/T) curves	Density of defect states g_0 ($\text{eV}^{-1} \text{cm}^{-3}$)
1.	$\text{Se}_{90}\text{Sb}_{10}$	4.76	4.78×10^{13}
2.	$\text{Se}_{90}\text{Sb}_8\text{Ag}_2$	4.17	2.98×10^{13}
3.	$\text{Se}_{90}\text{Sb}_6\text{Ag}_4$	0.99	2.79×10^{14}
4.	$\text{Se}_{90}\text{Sb}_4\text{Ag}_6$	8.23	2.93×10^{13}
5.	$\text{Se}_{90}\text{Sb}_2\text{Ag}_8$	3.16	3.94×10^{13}

Using the co-ordination number 2, 3, 4 for Se, Sb and Ag respectively, the value of $\langle z \rangle$ is calculated for each glassy alloy. $\langle z \rangle$ varies from 2.10 to 2.18 in the present case. The $\langle z \rangle$ for the composition at which maxima occurs in Fig. 4, comes out to be 2.14. However, Phillips and Thorpe model shows threshold at $\langle z \rangle = 2.4$.

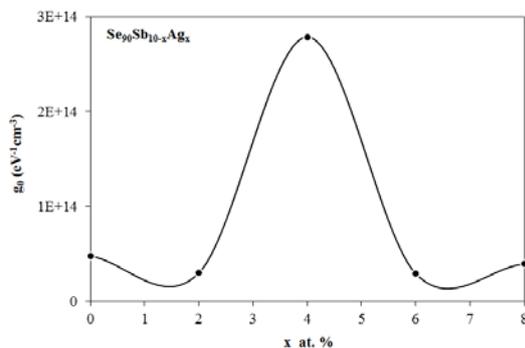


Fig. (4) Plot of density of defect states g_0 vs Ag concentration in $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ glassy system

The $\langle z \rangle$ value in the present case is slightly lesser than what is expected from the above model. This may be due to an important limitation of Phillips and Thorpe model. In this model, Phillips considered the interaction between atoms to be purely covalent while arriving at the balance condition. Such an assumption may be valid for Ge-Se glasses, but not for system containing heavier elements like Sb, Ag. The presence of such a heavier element may lead to partial covalent bonding. This can affect the balance condition.

4. Conclusions

I-V characteristics have been studied in glassy $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ (where $x=0, 2, 4, 6$ and 8). At low fields (10^2 V/cm), an Ohmic behavior is observed. However, at high fields (10^3 - 10^4 V/cm), a

superohmic behavior is observed. By fitting the data to the theory of SCLC for uniform distribution of localized states, the density of defect states has been calculated near Fermi level for each glassy alloy. The results indicate that a discontinuity in DOS vs Ag concentration is observed at 4 at.% of Ag which is explained in terms of the formation of mechanically stabilized structure at this composition.

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