

## A COMPARATIVE STUDY OF THE DENSITY OF DEFECT STATES IN THIN FILMS & BULK SAMPLES OF GLASSY $\text{Se}_{100-x}\text{Bi}_x$

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The present paper reports the composition dependence of the density of defect states (DOS) in glassy  $\text{Se}_{100-x}\text{Bi}_x$  ( $x = 0.5, 2.5, 4, 6, 10$ ) in thin films as well as in bulk samples to make a comparative study between bulk and thin film samples. DOS is determined by using space charge limited conduction measurements. The theory of uniform distribution of defect states has been used for this purpose. It is observed that DOS is highly composition dependent, showing a minima at 4 at % of Bi, in thin films as well as in bulk samples. However, thin film samples are found to have density of defect states two orders of magnitude higher than bulk samples.

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### 1. Introduction

There are numerous potential applications of chalcogenide glasses proposed in the civil, medical and military areas [1-6]. It is possible to produce electrical switches, xerographic and thermoplastic media, photo-resistant and holographic media, optical filters, optical sensors, thin films, waveguides, non-linear elements, etc. [1-6].

It has been found that Se based alloys are more useful as compared to pure Se, due to their greater hardness, high photosensitivity, higher crystallization temperature and smaller aging effect as compared to pure a-Se [7].

The transport mechanism of charge carriers in amorphous semiconductors has been the subject of intensive theoretical and experimental investigations for the last few decades. 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 [8-9].

A study of the electrical conduction of any medium gives us an insight in to the transport mechanism of the prevailing charge carriers. In low field conduction, the mobility and free carriers concentration are assumed to be constant with field. However, application of a high field to a free carrier system may influence both the mobility and the number of charge carriers. High field effects are most readily observed in materials with a small number of equilibrium carriers, since heating effects are kept reasonably small. For the same reason, the study of high field effects is particularly favored in low conductivity solids, e.g., amorphous semiconductors. High field effects have been studied in amorphous semiconductors [10-18]. However, more work is required in this direction.

The present paper reports the space charge limited conduction (SCLC) measurements in glassy system of  $\text{Se}_{100-x}\text{Bi}_x$ , where properties have been found to be highly composition dependent. Using SCLC theory for the case of uniform distribution of defect states, the density of defect states

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near Fermi level is calculated for the present system. The results obtained on thin films and on bulk samples have been compared. Though the composition dependence of the density of defect states is same in both the cases, the magnitude of the density of the defect states is found to be two orders of magnitude higher in thin films as compared to bulk samples.

## 2. Experimental

### 2.1 Materials preparation

Glassy alloys of  $\text{Se}_{100-x}\text{Bi}_x$  ( $x = 0.5, 2.5, 4, 6, 10$ ) are prepared by quenching technique. High purity 5 N materials are 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 are held at  $800^\circ\text{C}$  for 10-12 hours where the ampoules are constantly rocked to make the melt homogeneous. The melts are cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water.

### 2.2 Thin films preparation

Thin films of these glasses are prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom are used for the electrical contact. The thickness of the films is  $\sim 500$  nm. The co-planer structure (length  $\sim 1.2$  cm and electrode separation  $\sim 0.12$  mm) are used for the present measurements. For the measurements of high-field conduction the thin film samples are mounted in a specially designed sample holder where a vacuum of  $\sim 10^{-2}$  Torr could be maintained throughout the measurements.

### 2.3 Pellets preparation

The glassy alloys are ground to a very fine powder and pellets (diameter  $\sim 6$  mm and thickness  $\sim 1$  mm) are obtained by compressing the powder in a die at a load of 5 Tons. The pellets are mounted in between two steel electrodes of a metallic sample holder for d. c. conductivity measurements using a digital Pico-ammeter. A d. c. voltage (0 to 400 V) is applied across the sample (thin films & pellets) and the resultant current is measured by a digital Pico-ammeter. I - V characteristics are measured at various fixed temperatures. The temperature of the pellets & thin films is controlled by mounting a heater inside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near to the pellets & thin films. A vacuum of about  $10^{-2}$  Torr is maintained during measurements.

## 3. Results and discussion

In the present work, I – V characteristics of thin films & pellets of a-  $\text{Se}_{100-x}\text{Bi}_x$  ( $x = 0.5, 2.5, 4, 6, 10$ ) are examined at various temperatures. At low fields ( $<10^3$  V/cm), ohmic behavior is observed in all the samples where I vs V curves are found to be straight lines. However, at higher fields ( $\sim 10^4$  V/cm), non ohmic behavior is observed at all measuring temperatures where  $\ln(I/V)$  vs V curves are found to be straight lines.

According to the theory of space charge limited conduction, in the case of uniform distribution of localized states, where  $g(E) = g_0$ , the current I at particular voltage V is given by the relation:

$$I = (2 e A \mu n_0 V/d) \exp(S V) \quad (1)$$

Where d is electrode spacing,  $n_0$  is the density of the thermally generated charge carriers,  $\mu$  is the mobility, e is the electronic charge, A is the area of cross section of thin films & pellets, S is given by:

$$S = 2 \varepsilon_r \varepsilon_0 / e g_0 k T d^2 \quad (2)$$

As evident from equation (1) and (2), a plot of  $\ln I / V$  vs  $V$  should be linear and slope of these lines should decrease inversely with temperature.

In the present case also,  $\ln (I / V)$  vs  $V$  curves are found to be straight lines with good correlation coefficient at all the measuring temperatures as shown in Figs.1-2 for  $\text{Se}_{96}\text{Bi}_4$  thin films and pellets. The slope  $S$  decreases with the increase in temperature as shown in Figs 3-4. Similar results were obtained in other glassy.

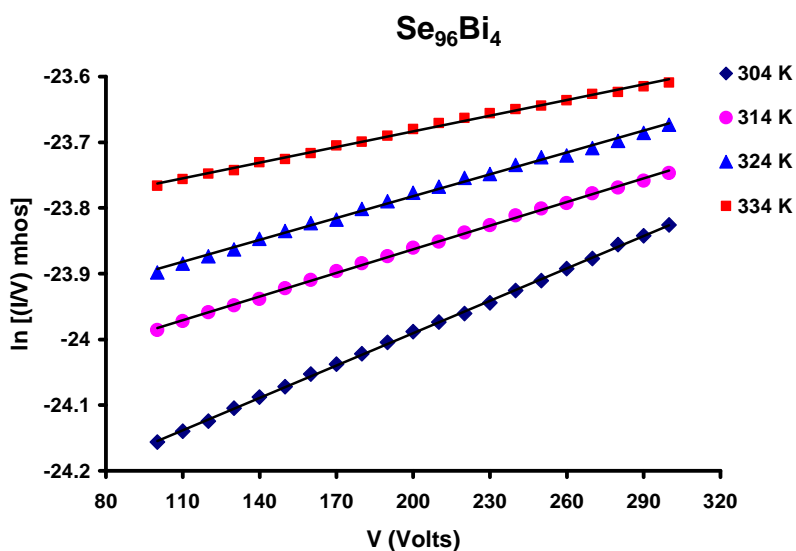


Fig.1. Plots of  $\ln (I / V)$  vs  $V$  for  $a\text{-Se}_{96}\text{Bi}_4$  thin films at different temperatures.

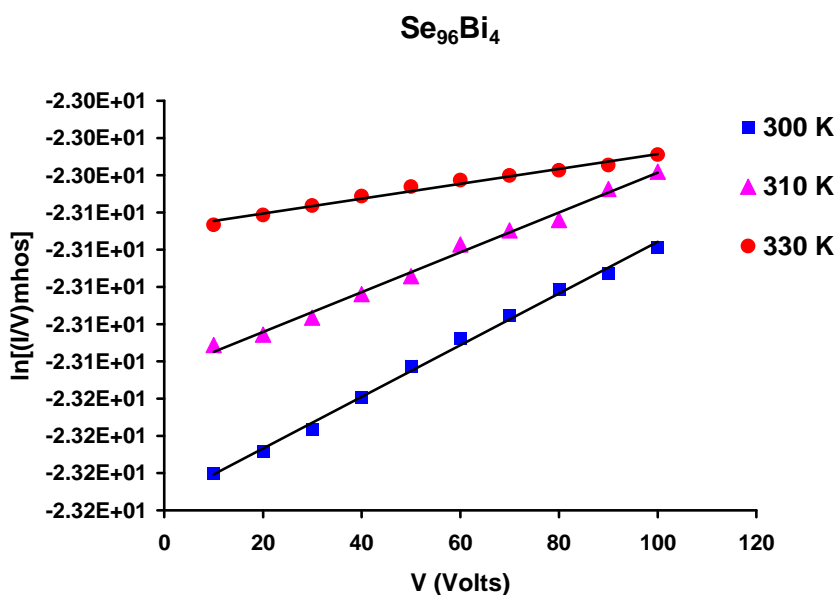


Fig.2. Plots of  $\ln (I / V)$  vs  $V$  for  $a\text{-Se}_{96}\text{Bi}_4$  pellets at different temperatures.

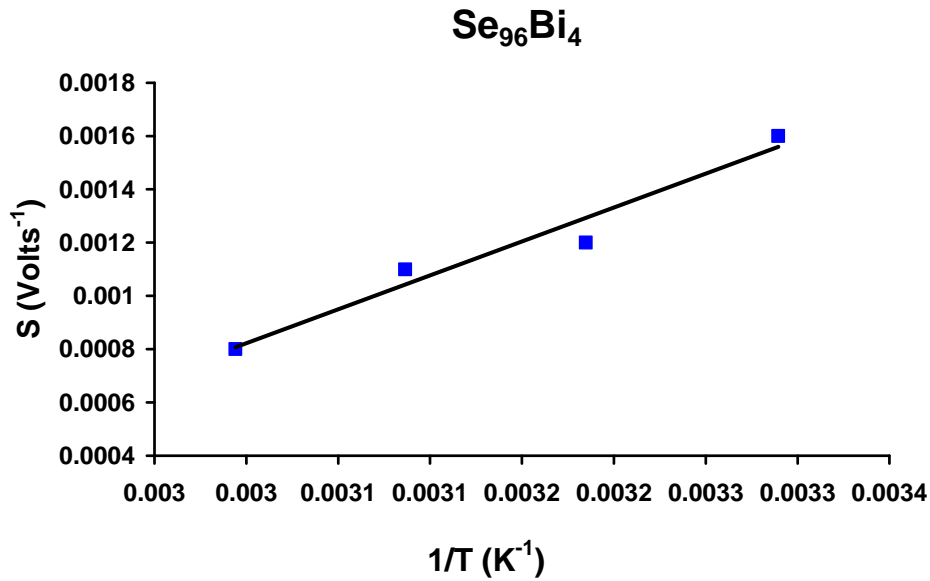


Fig.3. Plot of Slope  $S$  vs  $1/T$  for  $\alpha$ - $\text{Se}_{96}\text{Bi}_4$  thin films.

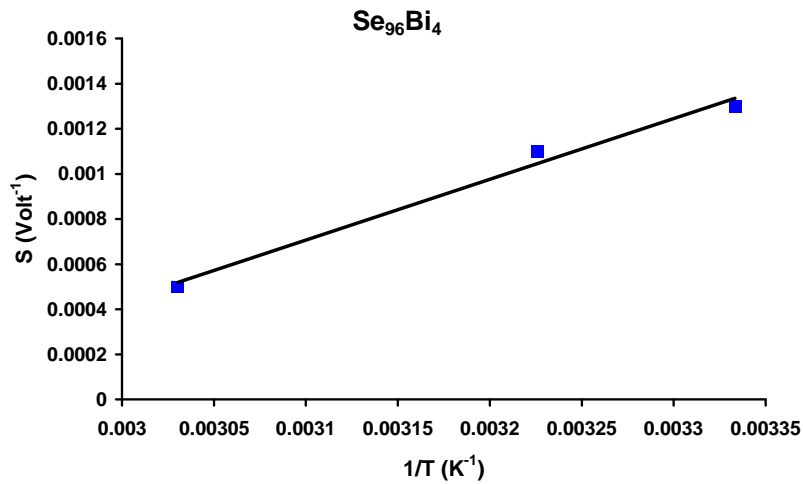


Fig.4. Plot of Slope  $S$  vs  $1/T$  for  $\alpha$ - $\text{Se}_{96}\text{Bi}_4$  pellets.

Using equation 2, we have calculated the density of localized states from the slope of the Figs.3-4. The value of relative dielectric constant  $\epsilon_r$  is taken to be 10 which is the dielectric constant value of glassy Se. The results of these calculations are given in Table 1-2 and density of defect states is plotted against concentration of Bi in Fig 5-6 for  $\text{Se}_{100-x}\text{Bi}_x$  thin films and pellets. It is clear from this table that thin film samples have density of defect states two orders of magnitude higher than bulk samples.

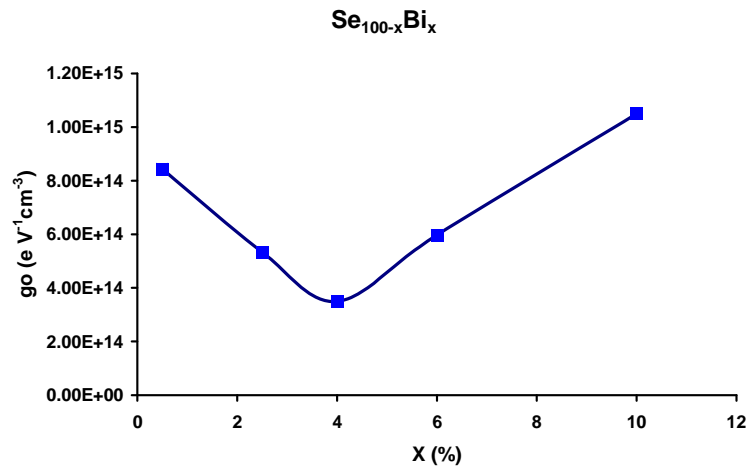


Fig.5. Plot of density of localized states ( $g_0$ ) vs Bi concentration in  $a$ - $Se_{100-x}Bi_x$  thin films.

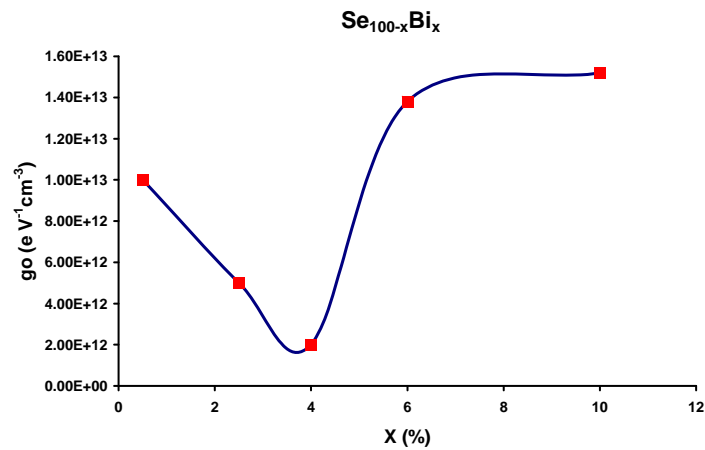


Fig.6. Plot of density of localized states ( $g_0$ ) vs Bi concentration in  $a$ - $Se_{100-x}Bi_x$  pellet

Table1. Composition dependence of density of localized states  $g_0$  in  $a$ - $Se_{100-x}Bi_x$  thin films.

Sample	Slope of S vs. $1/T$	$g_0$ (in units of $eV^{-1}.cm^{-3}$ )
$Se_{99.5}Bi_{0.5}$	1.0549	$8.44 \times 10^{14}$
$Se_{97.5}Bi_{2.5}$	1.669	$5.33 \times 10^{14}$
$Se_{96}Bi_4$	2.5436	$3.50 \times 10^{14}$
$Se_{94}Bi_6$	1.4916	$5.97 \times 10^{14}$
$Se_{90}Bi_{10}$	0.8408	$1.05 \times 10^{15}$

Table2. Composition dependence of density of localized states  $g_0$  in  $a$ - $Se_{100-x}Bi_x$  pellets.

Sample	Slope of S vs. $1/T$	$g_0$ (in units of $eV^{-1}.cm^{-3}$ )
$Se_{99.5}Bi_{0.5}$	4.2192	$1.0 \times 10^{13}$
$Se_{97.5}Bi_{2.5}$	5.8126	$5.0 \times 10^{12}$
$Se_{96}Bi_4$	3.0441	$2.0 \times 10^{12}$
$Se_{94}Bi_6$	2.5726	$1.3 \times 10^{13}$
$Se_{90}Bi_{10}$	0.8408	$1.5 \times 10^{13}$

In chalcogenide glasses, a discontinuity in various physical properties has been observed [19-21] at a particular composition when the average coordination number  $\langle z \rangle$  reaches 2.4. This is explained by Phillips and Thorpe [22] in terms of a mechanically optimized structure at a critical glass composition.

In the present case, the coordination number of Se is 2 and that of Bi is 4. Hence, at the composition  $\text{Se}_{96}\text{Bi}_4$ , where minima in  $g_o$  occurs,  $\langle z \rangle$  comes out to be nearly 2.1. However, Phillips and Thorpe show threshold at  $\langle z \rangle = 2.4$ . The  $\langle z \rangle$  value in the present case is slightly less. 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 Bi. 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 thin films & pellets of  $\text{Se}_{100-x}\text{Bi}_x$  ( $x = 0.5, 2.5, 4, 6, 10$ ). At low field ( $<10^3\text{V/cm}$ ), an ohmic behavior is observed. At high fields ( $\sim 10^4\text{V/cm}$ ), a super-ohmic behavior is observed.

The density of localized states near Fermi level is calculated by fitting the data to the theory of SCLC for the case of uniform distribution of localized state. It is clear from the results that DOS is highly composition dependent; showing minima at 4 at % of Bi, in thin films as well as in bulk samples. The results indicate that thin film samples have density of defect states two orders of magnitude higher than bulk samples.

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