Space-charge-limited conduction in $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy: observation of Meyer–Neldel rule

ANJANI KUMAR and A KUMAR*

Department of Physics, Harcourt Butler Technological Institute, Kanpur, India

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Abstract. The present paper reports the measurements of space-charge-limited conduction (SCLC) in glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ alloy. For this purpose, I – V characteristics have been taken at certain fixed temperatures. The results indicate that super-ohmic behaviour is observed at high electric fields. The results fit well with the theory of SCLC for the uniform distribution of traps. From the temperature dependence of conductivity, activation energy is obtained at different electric fields, which is found to be field dependent. Pre-exponential factor is found to depend on the activation energy and obeys Meyer–Neldel rule.

Keywords. Chalcogenide glasses; Meyer–Neldel rule; SCLC; pre-exponential factor.

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, nonlinear elements, etc. It has been found that Se-based alloys are more useful than pure Se, due to their greater hardness, high photosensitivity, higher crystallization temperature and smaller ageing 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 into 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, as heating effects are kept reasonably small. For the same reason, the study of high field effects is particularly favoured in low conductivity solids, e.g., amorphous semiconductors. High field effects have been studied in amorphous semiconductors

by various workers.^{10–13} However, more work is required in this direction.

In view of the above, the present paper reports the high field conduction measurements in bulk glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ alloy. Using SCLC theory for the case of uniform distribution of defect states, the density of defect states near Fermi level is calculated for the present system. The present research also included a study of temperature dependence of conductivity in the same glassy alloy at certain fixed electric fields, where the variation of activation energy with electric field could be observed. Using the field dependence of activation energy data, Meyer–Neldel (MN) relation is verified.

2. Experimental

2.1 Material preparations

Glassy alloy of $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ is prepared by quenching technique. High purity 5 N materials are sealed in quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum $\sim 10^{-5}$ Torr. The ampoule containing the material is held at 800°C for 10–12 h, where the ampoule is constantly rocked to make the melt homogeneous. The melt is cooled rapidly by removing the ampoule from the furnace and dropping into ice-cooled water.

2.2 Conductivity measurements

The glassy alloy of $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ is ground to a very fine powder, and pellets (diameter ~ 6 mm and thickness ~ 1 mm) are obtained by compressing the powder in a die at a load of 5 Tons. The pellet is 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 (0–400 V)

* Author for correspondence (dr_ashok_kumar@yahoo.com)

is applied across the sample and the resultant current is measured by a digital Pico-ammeter. 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

3.1 Observation of SCLC

In the present work, I - V characteristics of bulk glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ alloy are examined at various temperatures. In the present case, $\ln(I/V)$ vs. V curves are found to be straight lines with good correlation coefficient at all the measuring temperatures as shown in figure 1. The slope S decreases with the increase in temperature as shown in figure 2.

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

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

Figure 1. Plots of $\ln(I/V)$ vs. V for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy at different temperatures.

Figure 2. Plots of slope (S) vs. $1/T$ for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy.

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

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

As evident from equations (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 are linear (figure 1) and slope of these lines decreases inversely with temperature (figure 2).

On the other hand, for any SCLC mechanism, the same plot gives different curves for different values of d . Therefore, I - V characteristics were measured at fixed temperature (360 K) for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy having different electrode spacing (figure 3). The values of these slopes are given in table 1 and are plotted against $1/d^2$ in figure 4, which comes out to be a straight line. This confirms the validity of eq. (2) and also confirms the SCLC in the present case.

Using eq. (2), we have calculated the density of localized states from the slope of figure 2. The value of relative dielectric constant ε_r is taken to be 70, which is the measured dielectric constant value of glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$. The calculated value of density of localized states near Fermi level comes out to be $2.93 \times 10^{13} \text{ eV}^{-1} \text{ cm}^{-3}$.

3.2 Observation of MN rule

In another set of experiment, the temperature dependence of d.c. conductivity (σ) is studied at different electric fields. Figure 5 plots such results for glassy alloy of $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ from 350 to 380 K. This figure shows that $\ln \sigma$ vs. $1/T$ curves are straight lines at all the electric fields applied. These results indicate that d.c. conductivity is thermally activated and can be represented by the following equation:

$$\sigma = \sigma_0 \exp(-\Delta E/kT). \quad (3)$$

Here, ΔE is called activation energy and σ_0 is called the pre-exponential factor.

From the slope and the intercepts of figure 5, the values of activation energy (ΔE) and pre-exponential factor (σ_0) have been calculated and the results are shown in table 2. The activation energy is found to decrease with the increase in applied electric field. The decrease of activation energy with field applied in high field region may be understood in terms of the shift of Fermi level due to excess charge carriers injected by the electrodes. Due to injection of charge carriers from electrodes, SCLC is observed as reported in Section 3.1.

The values of σ_0 are also found to be different at different electric fields. Figure 6 shows a plot of $\ln \sigma_0$ vs. ΔE , which is a straight line indicating that σ_0 varies exponentially with ΔE , following the equation:

$$\sigma_0 = \sigma_{00} \exp(-\Delta E/E_{MN}). \quad (4)$$

Figure 3. Plots of $\ln(I/V)$ vs. V for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy at different electrode gaps.

Table 1. Values of slopes of $\ln(I/V)$ vs. V curves for different electrode gaps in $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy.

Electrode gap (d) in mm	$1/d^2$ (in mm^{-2})	Slope (S) of $\ln(I/V)$ vs. V
0.35	8.16	2.44×10^{-3}
0.42	5.67	2.41×10^{-3}
0.50	4.00	2.38×10^{-3}
0.61	2.69	2.23×10^{-3}

Figure 4. Plots of slope (S) vs. $1/d^2$ for different electrode gaps for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy.

Here σ_0 is a constant and E_{MN} is often called as the MN characteristic energy. Such type of rule, called MN rule, has also been reported in the case of other glassy

Figure 5. Plots of $\ln(\sigma)$ vs. $1/T$ for glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ at different electric fields.

Table 2. ΔE (eV) and $\ln \sigma_0 (\Omega^{-1} \text{cm}^{-1})$ for $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ glassy alloy.

Electric field (V cm^{-1})	ΔE	$\ln \sigma_0$
1.75×10^3	0.50	-17.18
3.51×10^3	0.49	-17.15
5.26×10^3	0.45	-18.42
7.02×10^3	0.44	-18.79

semiconductors.^{14–19} In the present case, we have changed the activation energy by changing electric field instead of composition. Even then, the MN rule could be observed.

Figure 6. Plots of $\ln(\sigma_0)$ vs. ΔE for glassy alloys $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$.

This shows that MN rule is more general in chalcogenide glasses and does not depend on how activation energy is varied. In the present case, we have estimated the value of MN characteristic energy as 39.03 meV.

4. Conclusion

The density of localized states near Fermi level is calculated in glassy $\text{Se}_{90}\text{Sb}_4\text{Ag}_6$ by fitting the data to the theory of SCLC for the case of uniform distribution of localized state. This comes out to be $2.93 \times 10^{13} \text{ eV}^{-1} \text{ cm}^{-3}$.

The temperature dependence of d.c. conductivity (σ) is studied at different electric fields. Activation energy is found to decrease with electric field. A correlation between activation energy and pre-exponential factor is also observed which is same as MN rule.

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