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Study of High field conduction in Se based Chalcogenide glasses

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The present work reports the study of high field conduction in thin films of $Se_{90}Ge_{10-x} In_x$ (x=2,6) because high field conduction in chalcogenide glasses is affected by the presence of localised states at the band edges as well as the defect states present in the mobility gap.To measure the density of states in these thin films , space charge limited conduction technique is used. I-V characteristics have been measured at various fixed temperatures. An ohmic behaviour is observed at low electric fields upto 10^2V/cm. Superohmic behaviour 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 localised states in the mobility gap fits well with the experimental data.Using this theory, the density of defect states near Fermi level is calculated for all glassy alloys.

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1. Introduction

Chalcogenide glasses belong to an important class of amorphous semiconductors category, which are prepared by the rapid cooling of the melt. They contain chalcogen element in large proportion and behave as semiconductor. These semiconductors have the energy band gap 1-3 eV. Chalcogenide glasses transmits the longer wavelengths in the IR region than silica and fluoride glasses. There are numerous optoelectronic applications in the civil, medical and military areas. In the present research work some new selenium-based chalcogenide glasses have been characterised to develop a promising material for the optical devices such as photonic devices, optical scanners, optoelectronic devices, optical printer, optical filters and optical memory effects.

Amorphous Selenium has emerged as a promising material because of its potential technological importance. It is widely preferred in the fabrication of electro photographic devices and, more recently, switching and memory devices [1]. It has been found that Se-based alloys are useful for their greater hardness, high photosensitivity, higher crystallization temperature and smaller aging effect compared to pure a-Se [2]. The transport mechanism of charge carriers in amorphous semiconductors has been the subject of intensive theoretical and experimental investigations for the last few years. 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 [3–4].

Due to their low conductivity, amorphous semiconductors are most suitable for high field conduction studies, as Joule heating is negligibly small in these materials at moderate temperatures. Some studies have been reported in chalcogenide glassy semiconductors [5–15] and the results have been interpreted in terms of Space charge-limited conduction (SCLC) or Poole-Frenkel conduction. One of the most direct methods for the determination of the density of the localised states g_0 in the mobility gap involves the measurements of SCLC, which can easily be observed at high fields in chalcogenide materials. Such a technique has already been applied to a-Si:H [16–18]. SCLC technique is not influenced by surface states, unlike field effect experiments where surface states may come into play.

Based on some physical properties the covalently bonded non crystalline semiconductors

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have been divided into two main categories (i) Ge type whichs shows ESR signal, paramagnectic behaviour and variable range hopping conduction (ii) Se type which does not show the above properties under normal conditions due to presence of paired defect states.The Ge_xSe_{1-x} system may belong to either of the categories depending upon value of x.

A study of I-V characteristics is a matter of importance for properly analysing the conduction mechanism, particularly in case of thin films .It is generally found that in case of chalcogenide glasses, I-V curves are straight lines at low voltages. However, at higher voltages, a nonlinearity is observed showing super ohmic behaviour. A nonlinear curve often may reveal the existence of different kinds of conduction mechanism.

Since density of states (DOS) in the mobility gap controls many physical properties of amorphous semiconductors, the determination of density of such states have become an important issue in these materials. The different authors on this topic reveal the fact that space charge limited conduction (SCLC) is established tool to find DOS in chalcogenide glasses because it was relatively simple to measure and could potentially yield bulk DOS near Fermi level.The SCLC measurement and analysis constitute a relatively simple straightforward and generally applicable method of obtaining the density of states in the gap of amorphous glassy chalcogenides.

The present work is an attempt to measure the DOS by using SCLC technique in vacuum deposited thin films of ternary chalcogenides glasses with an emphasis on preparation of those composition which have relatively lower DOS so that one could potentially use them in various devices.The result and discussion in a Se_xGe_{1-x} In_x (x=2,6) system are done in this work which shows the existence of SCLC in samples .

2. Experimental details

Chalcogenide glasses in the present work are prepared from the Melt Quenching Technique.The exact proportions of 5N pure elements, according to their atomic percentages, are weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm.The materials are sealed in evacuated (~10^{-5}Torr) quartz ampoules having length ~ 5cm and internal diameter ~ 8 mm, using a Diffusion pump for creating such a high vacuum. The ampoules containing the constituent elements are heated to ~ 1000°C and is heated for 12 hours with the increase of 3-4°C/ minute of furnace temperature .While heating, all the ampoules are intermittently rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This is done to obtain homogeneous glassy alloys. Quenching is done, by dropping the heated ampoules to the ice-cooled water. Materials were then taken out by breaking the ampoules.

Thin films of the glassy alloys are prepared by Vacuum Evaporation Technique using a standard coating unit (IBP-TORR, TYPE: EPR-002) .The coating unit consists of a deposition chamber inside which proper arrangement is done for the deposition of the desired materials.The micro slides of size 2.5 cm length; 1.0 cm width and 2.0 mm thickness are taken as substrates for Thin film deposition. In order to remove contaminations, if any, from the surface of the substrates, the slides are immersed into chromic acid for at least 48 hours. Then, they are rinsed in deionised water and finally, degreased in the vapors of isopropyl alcohol.

Thin films of glassy alloys are deposited at a base pressure~10^{-5} Torr, keeping substrates at room temperature. During the film preparation the thickness is controlled by means of a thickness monitor. The films thus grown have thickness of about 5000 Å. In order to get thermal equilibrium, films are kept as such in the deposition chamber for 2-3 days.

3. Results and Discussion

I-V characteristics are studied at various fixed temperatures in amorphous thin films of of $Se_{90}Ge_8In_2$ and $Se_{90}Ge_4In_6$ as given in Tables 1.1,1.2 and plotted in Figures 1, 2. An ohmic behaviour is observed at low electric fields ($E < 10^3$ V/cm) while, at high electric fields ($E \sim 10^4$ V/cm), a super ohmic behaviour is observed. In high field region, ln I/V vs. V curves are found to be straight lines as shown in figures 3 and 4.It is clear from these figures that the slopes S of ln(I/V) vs. V curves are temperature dependent.

At low voltage the injected charge carrier density is lower than the thermally generated carrier density which leads to the ohmic behaviour.At higher voltages, injected charge carrier density predominates and the conduction in this region may be dominated by a trap limited SCLC, in the case of a uniform distribution of localised states having (g_0), the current I at a particular voltage V is given by Equation

$$I=KV \exp (SV) \qquad (1)$$

where I is current ,V is voltage, K and S is given by

$$K= 2eAn_0\mu/d= \text{constant and S is given by} \qquad (2)$$

$$S= 2\varepsilon_r\varepsilon_0/eg_0kTd^2 \text{ where } \varepsilon_r \text{ is dielectric constant , } g_0 \text{ is density of localised states} \qquad (3)$$

Table 1. Values of current and voltages for $Se_{90}Ge_8In_2$.

S.No	Voltage (V)	Current (I)Amperes X10^{-10}			
		At 360K	At 367.5K	At 375 K	At 382.5K
1	220	1	2	4.1	6.4
2	240	1.1	2.2	4.5	7
3	260	1.3	2.5	4.9	7.6
4	280	1.4	2.9	5.4	8.3
5	300	1.5	3.1	5.8	9.2
6	320	1.7	3.3	6.2	9.7
7	340	1.8	3.5	6.8	10.3
8	360	1.9	3.9	7.3	11
9	380	2.1	4.	7.9	12
10	400	2.2	4.3	8.3	12.7
11	420	2.3	4.6	8.7	13.5
12	440	2.5	4.8	9.4	14.1
13	460	2.6	5	9.8	15.1

Table 2. Values of current and voltages for $Se_{90}Ge_4In_6$.

S.No	Voltage (V)	Current (I)Amperes X10^{-10}			
		At 355K	At 362.5K	At 370 K	At 377.5K
1	220	2.9	5.6	14.5	26.6
2	240	3.2	6	15.6	30
3	260	3.6	6.4	17.3	32.9
4	280	4	7.1	18.4	36
5	300	4.3	7.8	19.9	38.7
6	320	4.7	8.2	21.4	41.2
7	340	4.9	8.9	23	44
8	360	5.2	9.4	24.3	46.8
9	380	5.5	10.3	26.2	49.5
10	400	5.8	10.8	27.4	52.1
11	420	6.2	11.5	29.3	54.7
12	440	6.6	11.8	30.9	58.3
13	460	7	12.4	32.9	61.2

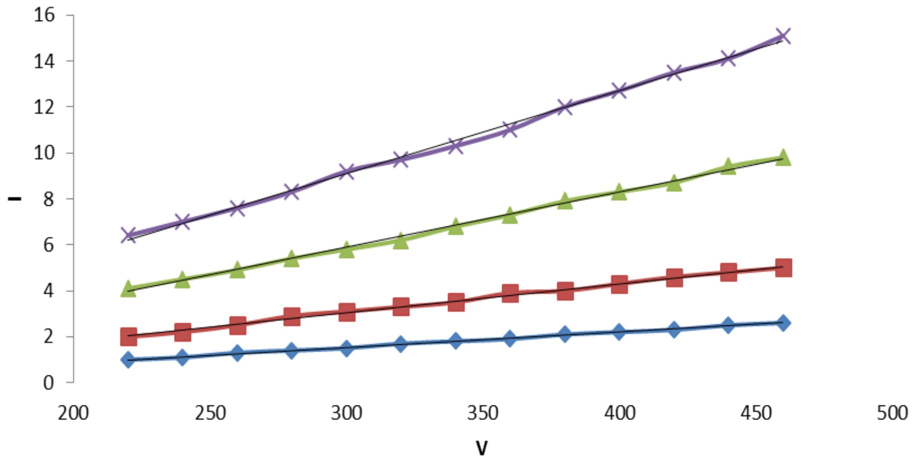

Fig. 1. Plot of V vs. I for $Se_{90}Ge_8In_2$ *at different temperature.*

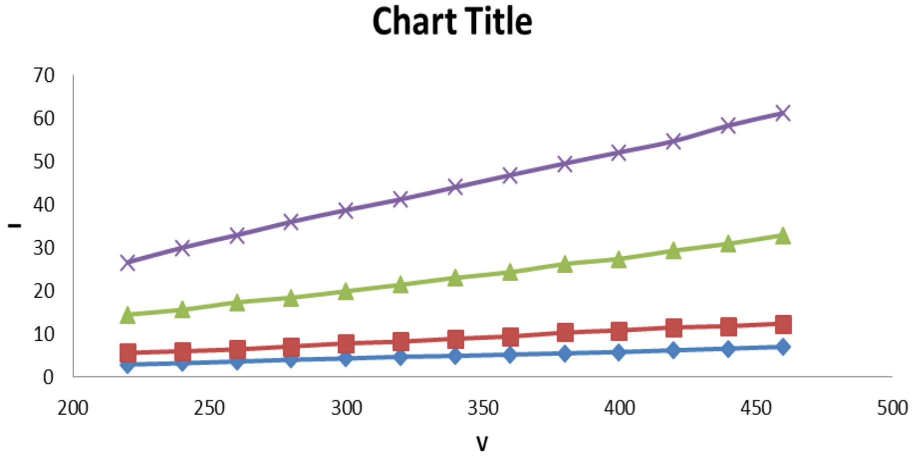

Fig. 2. Plot of V vs. I for $Se_{90}Ge_4In_6$ *at different temperature.*

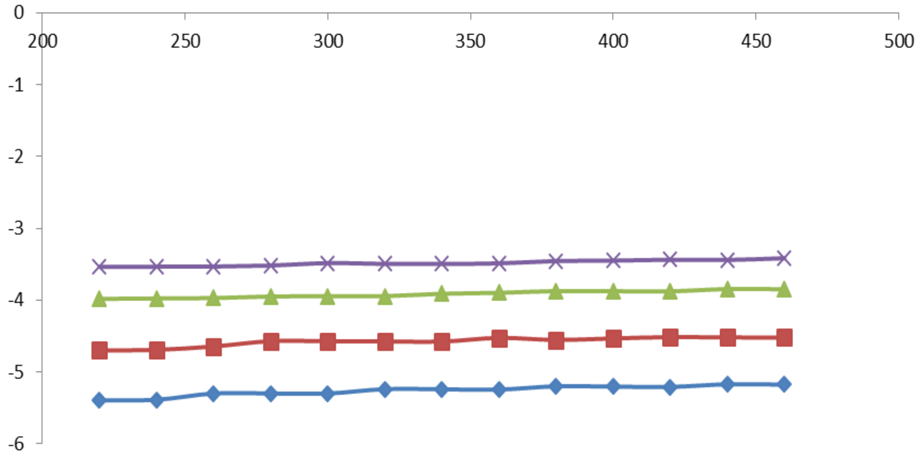

Fig. 3. Plots of ln(I/V) as a function of V for a $Se_{90}Ge_8In_2$ *at different temperature.*

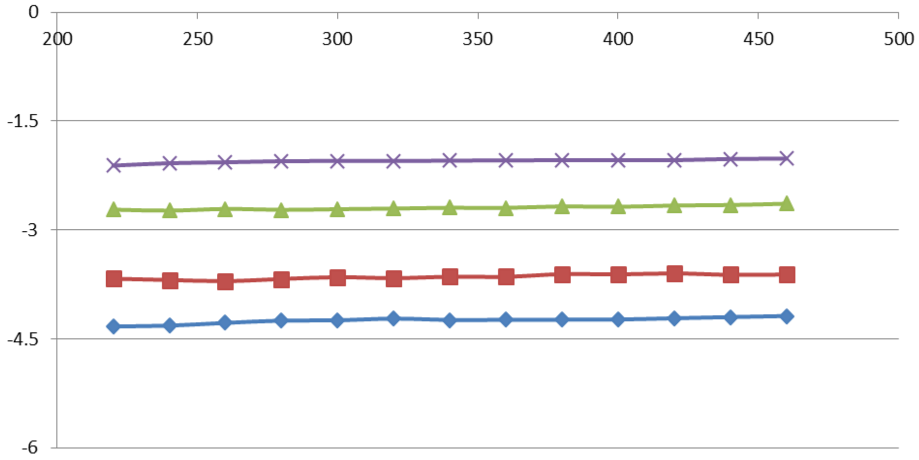

Fig. 4. Plots of ln(I/V) as a function of V for a $Se_{90}Ge_4In_6$ at different temperature.

According to above Equations (1),(2),(3), ln(I/V) vs. V curves should be straight lines and slope S of these curves should decrease with increase in temperature. The values of these slopes, in the present case are given in tables 3 and 4 and plotted as a function of temperature in figures 5 and 6 of $Se_{90}Ge_8In_2$ and $Se_{90}Ge_4In_6$ glassy system respectively. It is clear from these tables and figures that the slope S of ln(I/V) vs. V curves s inversely proportional to the temperature for all the samples. These results indicate the presence of SCLC in the present samples.

Table 3. Slope (s') of S vs (1/T) curve for $Se_{90}Ge_8In_2$.

S.No	Temperature (K)	Slope (S) of ln(I/V) vs. V	Slope of S vs.(1/T) curves
1	360	8.9×10^{-4}	2.36
2	367.5	7.7×10^{-4}	
3	375	6.2×10^{-4}	
4	382.5	5.1×10^{-4}	

Table 4. Slope (s') of S vs (1/T) curve for $Se_{90}Ge_4In_6$.

S.No	Temperature (K)	Slope (S) of ln(I/V) vs. V	Slope of S vs.(1/T) curves
1	355	4.8×10^{-4}	1.09
2	362.5	3.9×10^{-4}	
3	370	3.5×10^{-4}	
4	377.5	3.9×10^{-4}	

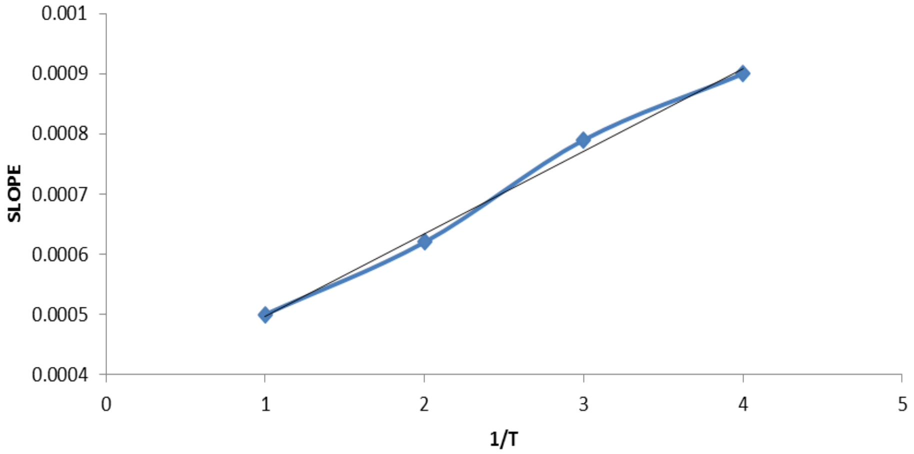

Fig. 5. Plots of slope as a function of (1T) for a $Se_{90}Ge_8In_2$.

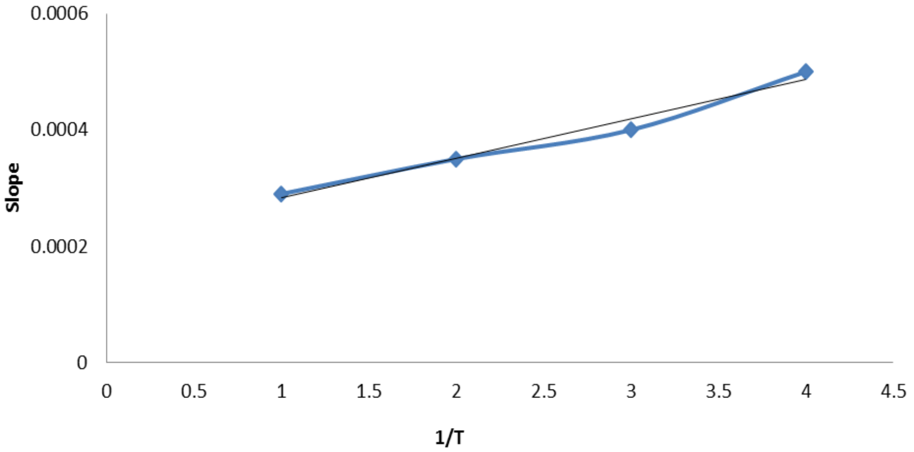

Fig. 6. Plots of slope as a function of (1T) for a $Se_{90}Ge_4In_6$.

Amorphous thin films contain a large number of defects due to dangling bonds that give rise to large number of localised defect states. These localised states act as carrier trapping centres and after trapping the injected charge from electrodes, they become charged and thereby expected to build up a space charge. This builds up of space charge [19,21] then play the key role in determination of SCLC process.

We have calculated the density of defect states from the slope (s') of S vs. 1/T plots. Here the value of relative dielectric constant (ε_r) is measured experimentally. The results of DOS are given in Table 5 for $Se_{90}Ge_8In_2$ and $Se_{90}Ge_4In_6$ samples. It is clear from the table that the density of defect states g_0 increases with In concentration in $Se_{90}Ge_{10-x}In_x$.

Table 5. Density of localised states (g_0) *in* $Se_{90}Ge_{10-x}In_x$ *(x=2,6).*

S.No	Samples	ε_r	Slope of S vs.(1/T) curves	G_0(eV^{-1} cm-3)
1	$Se_{90}Ge_8In_2$	10	2.36	2.80 X 10^{13}
2	$Se_{90}Ge_4In_6$	13	1.09	7.92 X10^{13}

Incorporation of third element In to Se-Ge binary alloy is expected to modify the structure of the host alloy, with the new element entering into chemical bond formation with Ge and Se as reported by Shukla et. Al. [22] in their X ray K absorption studiesin Ge –Se –M (M=Ag,In, Pb and Cd)glassy alloys.

While studying the effect of chlorine on electro photographic properties of Se –Te Onozuka et.al.[23] observed that on introducing Cl to Se Te system, the residual potential is decreased .This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to smaller electronegativity of Te as compared to S[24], while Cl atoms having electro negativity than selenium form negatively charged impurities , thereby compensating the effect of Te.

Along the same lines, one can expect that when concentration of In, having lower electro negativity than Se and Ge is increased in $Se_{90}Ge_{10}$, positively charged defects will be increased, thus increasing the density of defect states in ternary Se Ge In system with concentration of In in Ge Se binary glassy alloy. Our SCLC data also confirms that the density of defect states is increasing concentration of In in pure binary $Se_{90}Ge_{10}$ glassy system.

4. Conclusion

V characteristics have been studied in amorphous thin films of $Se_{90}Ge_8In_2$ and $Se_{90}Ge_4In_6$ glassy system. At low fields, ohmic behaviour is observed. At low fields ohmic behaviour is observed. At high fields (~10^4 V/ cm) superohmic behaviour is observed. Analysis of the observed data shows the existence of the SCLC in all the glassy samples used in the present study .From the fitting of the data to the theory of SCLC, the density of localised states near Fermi level is calculated. The results indicate that the density of defect states (g_0) increases with In concentration in $Se_{90}Ge_{10-x}In_x$. This is explained in terms of the electronegativity of the constituent atoms.

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