Temperature and composition dependence of electrical conductivity of $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) chalcogenide glasses

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ABSTRACT

Electrical conductivity of $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) glassy systems prepared by melt quenching technique has been studied at different temperature in bulk form through I-V characteristic curves. It has been observed that the electrical conductivity increases as the Sb concentration increases up to 4 atomic weight percentages and on further addition of Sb it reduces. The variation in electrical conductivity with Sb concentration is attributed to the Se-Sb bond concentration. Using the Arrhenius equation of conductivity, the activation energy of conduction is evaluated. The effect of Sb concentration on activation energy has also been studied. It is quite evident from results that Poole-Frankel and Rechardson-Schottky conduction mechanism hold good for conduction in these glasses.

Keywords: Chalcogenide glass, Se-In-Sb, Electrical conductivity, Activation energy

INTRODUCTION

Chalcogenide glasses are inorganic materials, which contain one or more of the chalcogen elements: S, Se and Te in conjunction with any (more) electropositive elements of group V of the period table [1]. These glasses are generally semi-conductor; opaque in visible region of the spectrum and chemical bonding of matrix is usually directional and covalent. The most important application of the amorphous semi-conductors is to utilize their metastable property [2]. In the above context chalcogenide glasses are the candidates for optoelectronic devices, infrared optical materials used for temperature monitoring, thermal imaging and power delivery of a CO or CO_2 laser [3]. These glasses have proved their potential applications for acousto-optic devices [4], X-ray imaging [5], photonics, inorganic photoreceptors, and optical wave-guides e.g. in welding and surgery [6].

Several investigators have studied the I-V characteristics of chalcogenide glasses and consequently their field effect [7-8]. These characteristics have been explained by many models such as Poole-Frankel effect [9], Small-Polaron Conduction [10], Tunneling Conduction [11], Hopping Conduction [12] and Space-Charge Limited

conduction [13]. Furthermore, many researchers have carried out studies of composition, temperature and field effect dependence of the conductivity of chalcogenide glasses [14, 15].

The aim of this paper is to report some electrical features, and determine the influence of Antimony (Sb) content on the electrical conductivity of the Se-In-Sb system and characterize its dependence on temperature. Selenium is selected because of its wide commercial application. Its device application like switching [16], memory [17] and xerography [18] have made it attractive. It also exhibits an interesting property of reversible phase transformation. This property makes it very useful in optical memory devices [19, 20]. But in pure state it has disadvantage because of its short lifetime and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms (Bi, Sb, Te etc.), which gives higher sensitivity, higher crystallization temperature and smaller ageing effects. The addition of In the to Se-Sb system is expected to modify the material properties to make it more suitable for reversible optical recording with an eraser time less then 1 micro second [21].

EXPERIMENTAL DETAILS

Glassy alloy of $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) were prepared by melt-quenching technique. High purity (99.999%) of all constituent materials in appropriate atomic weight proportions were weighed into a quartz ampoule. The content of the ampoule (5g) was sealed in a vacuum of 10^{-5} Torr and heated in a furnace where the temperature was raised at a rate of 3-4 ^{0}C per minute up to 900^{0}C and kept at that temperature for 15 hours. The ampoule was agitated frequently in order to intermix the constituents to ensure homogenization of the melt. The molten sample was rapidly quenched in ice-cooled water to get glassy state. The ingot of so produced glassy sample was taken out of the ampoule by breaking the ampoule and then grinded gently in mortar and pestle to obtain powder form. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using differactometer with FeK_α-radiation source (λ= 1.93 A^0). Fig. 1 shows the XRD pattern of $Se_{90}In_6Sb_4$ glass at room temperature.

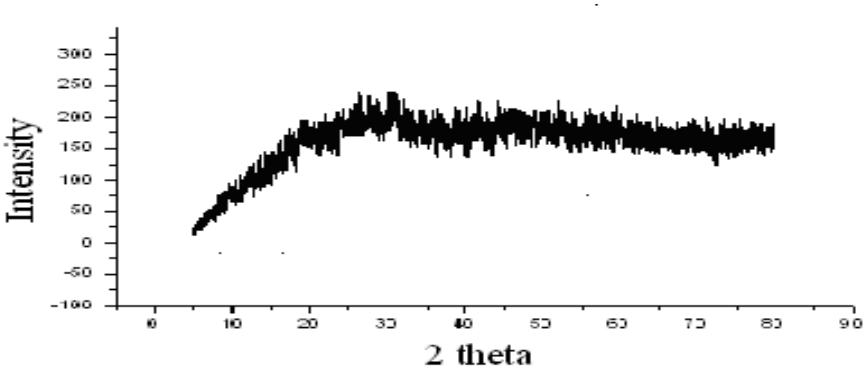

Fig. 1: XRD pattern of $Se_{90}In_6Sb_4$ chalcogenide glass at room temperature.

For I-V measurements in bulk, pellets of 13 mm diameter and thickness ≈ 1 mm were prepared under a load of 5 tons. These pellets were used in circuitry of Keithley electrometer 6517A in order to record the I-V

characteristics. I-V characteristics of $Se_{90}In_{10-x}Sb_x$ (x=0,2,4,6,8,10) glassy pellets were carried out in a temperature range from room temperature to 355 K. Fig.2 shows the temperature dependence of I-V characteristic of $Se_{90}In_6Sb_4$ as a representative case.

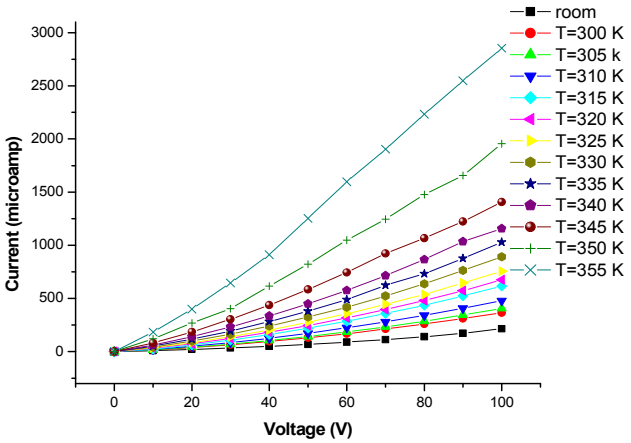

Fig.2: I-V characteristics of $Se_{90}In_6Sb_4$ glassy pellets at different temperature

RESULT AND DISCUSSION

In order to find the proper mechanism to explain the behavior of the observed I-V characteristics in these glasses, different mechanisms have been considered here and a discussion is initiated.

It can be noticed that the I-V curves show ohmic behavior in the region A-B. Above the point B the curve start to deviate from linearity and the relation between the current and the square root of the applied voltage is given by Jonsher and Hill [22]

$$I=I_{PF} \exp (\beta V^{1/2}/kT) \qquad (1)$$

where $\beta=(e^3/4\pi\varepsilon\varepsilon_0 d)^{1/2}$, ε_0 is the permittivity of the space ,ε is the relative permittivity of the sample, d is the inter-spacing between the filled and empty sites (jump distance) and I_{PF} (at V=0) is given by

$$I_{PF}= I_0 \exp (-\Phi/kT) \qquad (2)$$

Where Φ is the trap depth and I_0 = (Anedν), since A, n, e and ν are the electrode area, carrier concentration, electronic charge and phonon frequency, respectively. The constant υ is taken as 10^{13} s^{-1} [23].

Fig. 3 shows the plot between ln (I) vs $V^{1/2}$ for $Se_{90}In_{10-x}Sb_x$ glassy pellet. Linearity of ln(I) vs $V^{1/2}$ curves suggests that the conduction in such material obey the Poole-Frankel conduction mechanism. The observed linearity could be due to absence of space charge resulting in uniformity of field distribution between electrodes. The current in case of Poole-Frankel effect will practically remain unchanged when polarities of the electrodes are reversed. This is due to the fact that current does not depend upon the potential barrier at the interface. The Poole-Frankel conduction mechanism deals with the conduction in such materials where defect/ impurity generated electron, traps are involved. The structural defects in the material cause additional energy states close to the band edge called

'traps'. These traps restrict the current flow because of the capture and emission process, thereby becoming the dominant current mechanism.

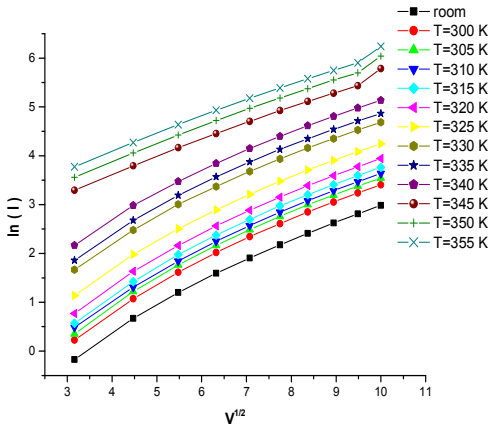

Fig.3 (a) $Se_{90}In_{10}$

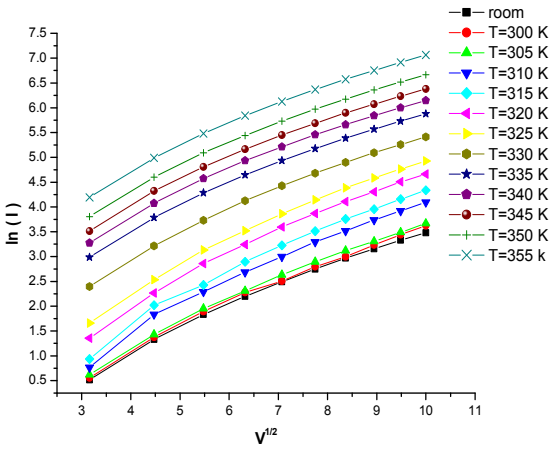

Fig.3 (b) $Se_{90}In_8Sb_2$

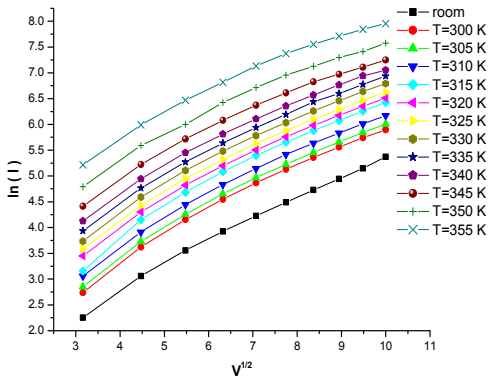

Fig.3 (c) $Se_{90}In_6Sb_4$

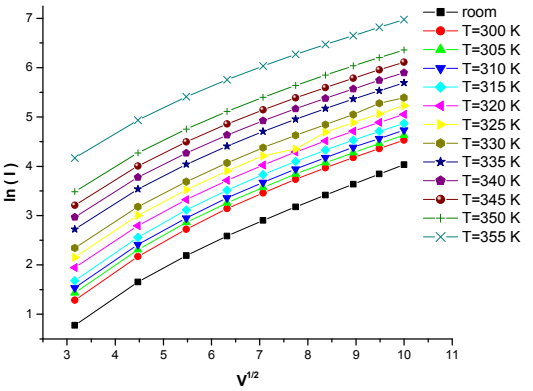

Fig.3 (d) $Se_{90}In_4Sb_6$

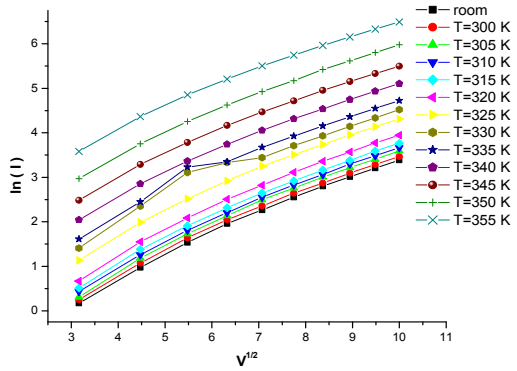

Fig.3 (e) $Se_{90}In_2Sb_8$

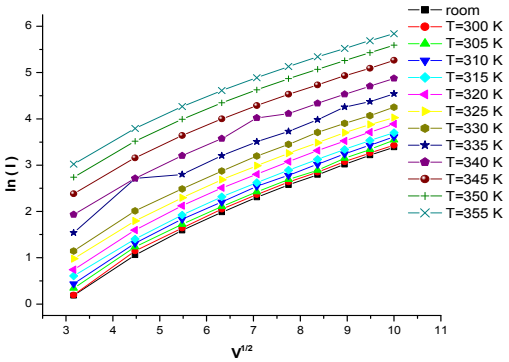

Fig.3 (f) $Se_{90}Sb_{10}$

Fig.3 ln (I) versus $V^{1/2}$ of the system $Se_{90}In_{10-x}Sb_x$ (x=0, 2, 4, 6, 8, 10) at different temperature

Rechardson-Schottky current voltage relation is given as:

$$J=AT^2 \exp(-\Phi/kT + \beta E^{1/2}) \quad (3)$$

$$\text{With } \beta= (e/kT)(e/4\pi\varepsilon\varepsilon_0 d)^{1/2} \quad (4)$$

where the symbol have their usual meanings. Fig.4 shows the plot of ln(J) against temperature for $Se_{90}In_6Sb_4$ glassy system and we get two linear region in this plot. The non-linearity or sharp increase in current between the temperature ranges 335 K to 355 K indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature, which may be regarded as glass transition temperature and it is also supported by DSC thermogram of the samples reported earlier [24]. As the temperature increases beyond 335 K i.e. glass transition range, nucleation and growth process starts and the glassy system leads to crystallization. With the growth of the grain, the size of grain increase with the narrowing down to grain boundaries which inturn affect the conduction process. This is due to the fact that available charge carriers will get the easier path to cross the grain boundaries, which is effectively responsible for the increment in the current in the temperature range beyond 335 K. Also this decrease in the resistance in this temperature range is caused due to the fact that glass is acquiring a more ordered state during the process of crystallization.

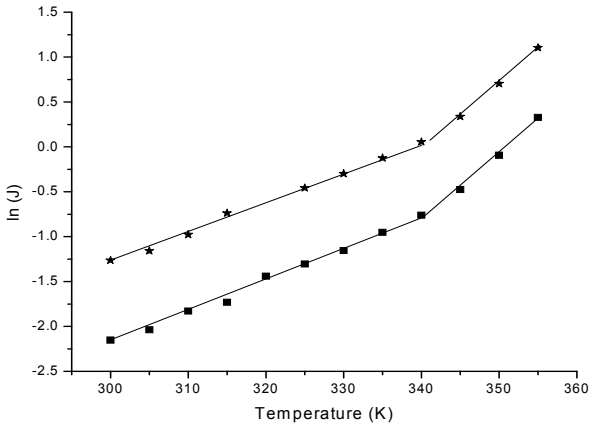

Fig.4 The plot of ln(J) against temperature for Se90In6Sb4 glassy system at two different voltages

DC electrical conductivity was calculated from the relation:

$$\sigma_{DC} = 1/\rho_{DC} = (1/R)(L/A) \quad (5)$$

where, R is the resistance of the sample, L is the thickness of the sample, A is the cross-sectional area of the sample and ρ_{DC} is the resistivity of the sample under test. It is well known that electrical conduction can take place by means of two parallel processes namely band conduction and hoping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states at high temperatures. The excitations of carriers into localized states at band edges cause the hoping conduction. Thus the total conductivity is given as:

$$\sigma = \sigma_i + \sigma_h \quad (6)$$

where, σ_i is the intrinsic conductivity and σ_h is the hoping conductivity.

Fig. 5 shows the composition vs conductivity plots at different temperatures. It has been indicated that in Se containing glass, there is a tendency to form polymerized network glasses and the homopolar bond is qualitatively suppressed [25]. Moreover, at lower percentage of Sb the system contains $SbSe_{4/2}$ tetrahedral units dissolved in a matrix composed of Se chains. With the increases of Sb content, the glassy matrix becomes heavily cross-linked and the steric hindrance increases. The Se-Se bonds (bond energy 205.8 KJ/mol) will be replaced by Sb-Se bonds, which have a higher bond energy (214.2 KJ/mol). Hence the cohesive energy of the system increases with increasing Sb content. It is found that electrical conductivity is maximum at 4 at % of antimony (Sb). This composition can be considered as a critical composition at which the system becomes a chemically ordered alloy containing high-energy Sb-Se hetropolar bonds. Further addition of Sb favours the formation of Sb-Sb bonds (bond energy 176.4 KJ/mol) thus reducing the Sb-Se bond concentration. Thus the cohesive energy decreases resulting a decrease of conductivity.

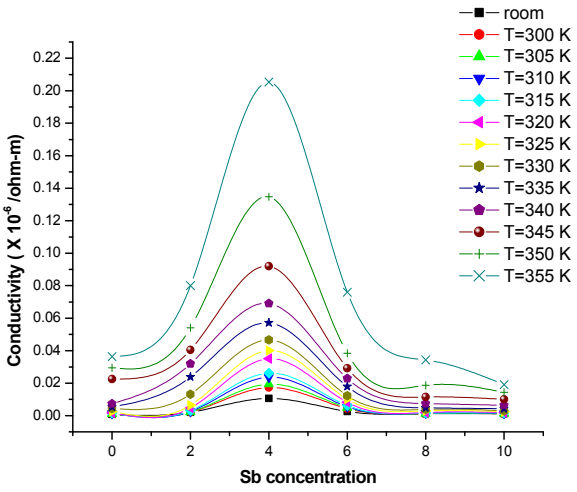

Fig. 5 Conductivity vs Sb concentration at different temperature

The variation of electrical conductivity with temperature of different glassy alloys is shown in Fig.6. It is found that at low temperature electrical conductivity increases linearly. The non-linearity or sharp increase in current between the temperature ranges 335 K to 355 K indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature as explained above.

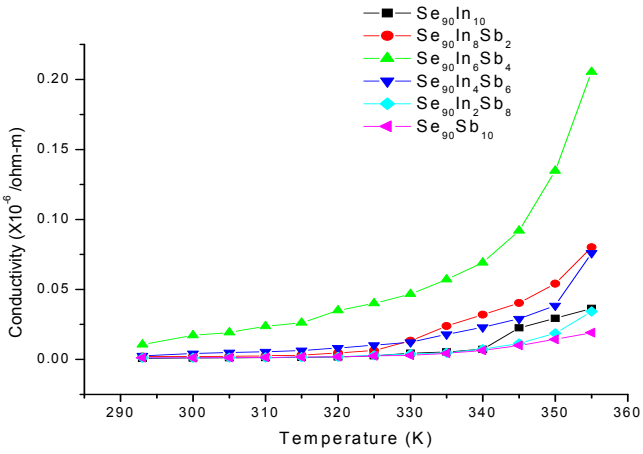

Fig.6 The variation of electrical conductivity with temperature of different glassy alloys

The Dc conductivity of the investigated samples is plotted against (1/T) and is found to satisfy the Arrhenius relation

$$\sigma = \sigma_0 \exp(-E_c / RT) \qquad (7)$$

where E_c is the activation energy of conduction and σ_0 is the pre-exponential factor. Fig.7 Shows the variation in ln(σ) as a function of $10^3/T$, for various Se-In-Sb glassy alloys. Fig.7 Shows break lines; their kinks illustrate two different values of activation energy for each sample. These may reveal two different conduction mechanisms, depending on the temperature range. The activation energies at low and high temperature ranges, for each sample, have been deduced and given in Table1.

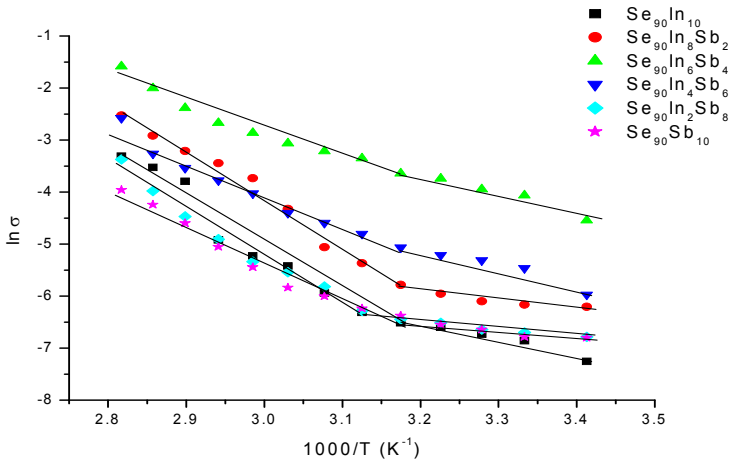

Fig.7 Shows the variation in ln(σ) as afunction of $10^3/T$, for various Se-In-Sb glassy alloys

Table 1- The activation energies at the low and high temperature ranges.

Sample	335-355 K		Room temp –335 K	
	E_c (KJ/mol)	σ_0 (x 10^3 /ohm-m)	E_c (KJ/mol)	σ_0 (x 10^3 /ohm-m)
$Se_{90}In_{10}$	80.28	3.17	25.31	1.17
$Se_{90}In_8Sb_2$	77.68	3.04	22.35	1.04
$Se_{90}In_6Sb_4$	44.16	2.58	30.90	2.11
$Se_{90}In_4Sb_6$	53.46	2.72	30.15	1.87
$Se_{90}In_2Sb_8$	69.50	2.99	11.47	0.74
$Se_{90}Sb_{10}$	74.90	3.07	21.98	0.73

It can be seen that the activation energy in the low temperature range is almost composition independent for all the samples. This may mean that, in low temperature range, the sensitivity of the investigated samples for conduction is somewhat weak at high concentration of Sb. The activation energy in the high temperature range decreases as the Sb concentration increase upto 4 atomic weight percentages and more addition of Sb reduces the activation energy. As the antimony content increases beyond 4, more Sb-Sb and Se-Sb bonds may be formed, this increases the cross-link density in the structure. This is turn increases the compactness of the structure, which consequently results in an increase of the activation energy for conduction. Fig.8 shows variation of activation energy with Sb concentration in 335-355-temperature range.

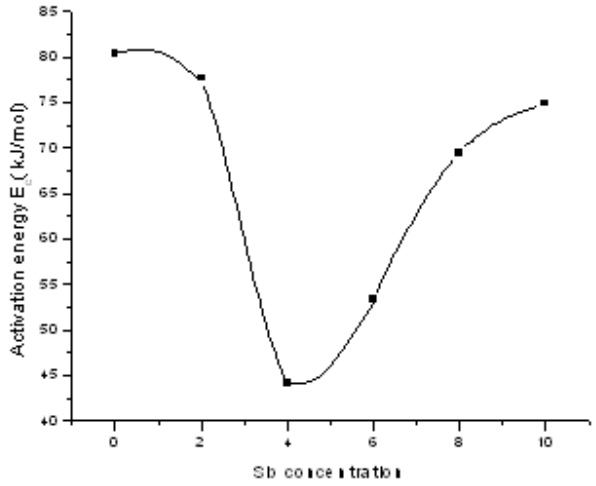

Fig.8 Variation of activation energy with Sb concentration in 335-355-temperature range.

CONCLUSION

The I-V characteristics of $Se_{90}In_{10-x}Sb_x$ have been discussed and explained in terms of their parent structure related to Se-In system in the addition of Sb inclusion. Also the conduction is explained qualitatively in terms of Poole Frankel and Rechardson-Schottky conduction mechanism. More precisely we conclude that:

1. The electrical conductivity increases upto 4 at. wt % of Sb and decreases on further addition of Sb.
2. The electrical conductivity increases with the increase in temperature, which confirms the semi conducting nature of the samples.
3. The activation energy of conduction of these glassy alloys has been calculated using Arrehinius equation in two different temperature ranges. In low temperature range activation energy is almost independent of Sb concentration but in high temperature range the activation energy decreases upto 4 at. Wt. % of Sb and increases on further addition of Sb.

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