
CHAPTER - III

RESULTS AND DISCUSSION

SUMMARY CONCLUSIONS

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The bulk samples of chalcogenide glasses of the system $As_{33}Se_{67-x}Sn_x$ (where $x = 0, 1, 3, 5, 7\%$ atomic weight of Sn) were studied for their I-V characteristics, DC electrical conductivity, thermo-electric power (TEP) and magnetic susceptibility measurements. The amorphous nature of the material is confirmed from X-ray diffraction pattern. The pattern consists of broad halos.

The current-voltage (I-V) characteristics of different compositions are shown in Fig. 2.9. The I-V curves are symmetric in nature. The current at low voltages is linear and follows Ohm's law. As the voltage increases it becomes non-linear i.e. the current suddenly increases at certain high voltage. This is the on-state for the material. The nonlinear current-voltage characteristics has been explained in the literature by different mechanism [1-4]. The non-linear I-V behaviour in amorphous semiconducting Se-Te alloys has been reported by Zope [5] on the basis of charged defect states existing in the material. Muragi et al. [6] have reported mechanism of non-linear I-V behaviour in Se-Te-Sn system based on micro-crystalline model. For our system we are discussing the non-linear I-V behaviour on the basis of charged defect states. To understand the nature of defect states, Kastner [7] proposed that in amorphous semiconductors,

the lowest energy defect states are positively charged three-fold co-ordinated C_3^+ and negatively charged one-fold co-ordinated C_1^- chalcogen atoms. These charged centres are present in equal concentration. A high density of such inherent defects is observed in many amorphous semiconductors. When an electric field is applied to an amorphous semiconducting material, electrons and holes are injected from the cathode and anode into the material. Initially the injected electrons and holes do not move in the structure as there is no internal built up electric field. Hence they are held up at the electrodes only. At the cathode the electrons are trapped by the C_3^+ (donor) centres which transform to C_3^0 neutral centres. At the anode, the C_1^- centres capture the holes and transform to C_3^0 neutral centres. The electrons are captured at a faster rate than the holes because the mobility of electrons is higher than that of the holes. This will create higher concentration of C_1^- centres as compared to that of C_3^+ centres. Thus, at the anode, a high field exists and the holes drift towards the cathode, where they are captured by the C_3^0 neutral centres thus creating C_3^+ centres at the cathode. This increases the field at the cathode and thus electrons drift from the cathode towards the anode where they are again captured by the C_3^0 centres and C_1^- are formed. When the On-state is reached at higher injection, the electrons and holes drift through the bulk of the material without much recombination.

The experimental conductivity data of five samples of the system $As_{33}Se_{67-x}Sn_x$ (where $x=0,1,3,5,7\%$ atomic weight of Sn) is shown in Fig. 2.11. The graphs are straight line in nature. The conducti-

vity is expressed by Mott's equation,

$$\sigma(T) = \sigma_0 \exp. (-E_{\sigma}^* / KT) \quad \dots (3.1)$$

where E_{σ}^* is the activation energy of the carriers and σ_0 is the conductivity preexponential factor. The conduction is due to the motion of carriers in the extended states as the observations are taken above room temperature (300°K). For all samples conductivity increases with increasing temperature. The pre-exponential factor σ_0 was obtained by extrapolating the curves in Fig. 2.11. It is likely that there may be some errors in σ_0 factor due to large extrapolation involved in the calculation. One can get an idea about its variation due to addition of tin in the sample. The values of σ_0 are tabulated in Table 3.1. The σ_0 values are found to decrease with increasing Sn concentration in the sample.

The variation of room temperature conductivity with Sn concentration is represented in Fig. 2.12. It is found that the conductivity decreases with increasing Sn concentration in the sample.

The activation energy for each sample is obtained by taking the slopes of the curves $\ln \sigma$ versus $10^3/T$ which are shown in Fig. 2.11. The values of activation energies are tabulated in Table No. 3.1. The variation of room temperature conductivity with activation energy is shown in Fig. 2.13. From the Fig. 2.13 it is seen that the conductivity increases with decrease in activation energy. This relationship between conductivity and activation energy has been reported by Majid [8] for the system $(As_2-Se)_{1-x}(Tl_2-Se_3)_x$.

He showed that the conductivity and activation energy are inversely related.

The dependence of activation energy on Sn concentration is represented in Fig. 2.14. The linear variation of activation energy with Sn concentration is observed. It is found that the activation energy increases with increasing Sn concentration in the sample. For $\text{As}_{33}\text{Se}_{67}$ the activation energy is 0.64 eV and increases to 0.71 eV for $\text{As}_{33}\text{Se}_{60}\text{Sn}_7$.

Many attempts have been made to see the variation of activation energy on addition of metal in chalcogenide glasses. Nagels and Sakai [9,10] have reported the DC conductivity of Se-Te-Sb as a function of temperature. The electrical and optical properties of As-Se-In and Ge-Se-In have been reported by Kosek and Karpova [11]. The electrical properties of silver doped As-Se glasses have been reported by Kazuo ABAI et al [12]. Gadkari and Zope [13] have reported the electrical properties of Se-Te-In system. All above studies show that the activation energy decreases with increasing metal content in the chalcogenide glasses. In our case the activation energy is found to increase with increasing Sn concentration in the system. This behaviour of activation energy is not found in chalcogenide glasses but the same behaviour of activation energy has been reported recently in other systems.

The widening of band gap in heavily Sn doped In_2O_3 has been reported by I. Hamberg et al. [14]. They showed that the band-gap

can be altered by local strain induced by impurities, point defects and poor crystallinity. In the doped material one has to consider three different effects :

1. The shapes of valence and conduction bands may not be accounted for, by precisely the same effective masses as in the undoped material. Indeed, it has been found [15,16] that m_c^* is weakly dependent on the electron concentration. A corresponding variation for m_v^* cannot be ruled out.
2. Above the Mott critical density, the partial filling of the conduction band leads to blocking of the lowest states and hence widening of the optically observed band-gap.
3. Again above the Mott critical density the valence and conduction bands are shifted in energy as a result of electron-electron and electron-impurity scattering. There may be smearing effects due to local deformations of the lattice as a result of the randomly oriented Sn ions.

It has been reported by R.V.Kruzelecky et al. [17] that the incorporation of bonded hydrogen into a-Si network results in widening of band-gap. They showed that the idealized band edges are perturbed by random potential fluctuations arising from disorder. The conduction band states below E_c (Valence band states above E_v) are broadened into a band of tail states. Deeper lying states are weakly perturbed. The incorporation of bonded hydrogen widens the band-gap from about 1.8 eV to 2.0 eV at higher hydrogen contents. In the quantum well model, Brodsky [18] has proposed that, Si-H sites are associated with

correlated potential fluctuations in valence and conduction bands that increase the effective gap near the vicinity of Si-H bond. The increase in band-gap upon hydrogenation reflects the additional compositional disorder and deeper potential fluctuations associated with the incorporation of bonded hydrogen. Moreover, the presence of other impurities such as oxygen bonded to Si with high Si-X bonding energies may result in potential fluctuations that widen the band-gap.

The band-gap widening in our system may be :

1. As a result of electron-electron and electron-impurity scattering.
2. The smearing effects due to local deformations of the lattice as a result of randomly oriented Sn ions.
3. Due to the compositional disorder and deeper potential fluctuations associated with incorporation of Sn in chalcogenide glasses.

The variation of thermo e.m.f. (ΔV) with temperature difference (ΔT), between the two ends of the sample upto (20°C) is shown in Fig. 2.18. From Fig.2.18 the thermo e.m.f. is found to vary linearly with temperature difference. As the observed thermo e.m.f. is positive, the carriers are holes and the sample is p-type in nature. This graph is used to calculate the values of thermoelectric power $S = \Delta V/\Delta T$. Then the graph between thermoelectric power S and $10^3/T$ for each sample is plotted, which is represented in Fig. 2.19. The thermoelectric power increases with increasing Sn concentration in the sample.

The electrical conductivity and thermoelectric power measurements of the system As-Se-Tl have been reported by Strunk [19]. He showed that thermoelectric power decreases with increasing Tl content in the sample. He also pointed out that the conductivity increases with increasing Tl content. In our case the conductivity decreases while thermoelectric power increases with increasing Sn concentration in the sample.

The thermoelectric power is expressed by Fritzsche's [20] equation,

$$S(T) = \pm \frac{k}{q} \left[\frac{E_s^*}{KT} + A \right] \quad \dots (3.2)$$

where A is scattering factor and $A = 1$ for most of the chalcogenide glasses, q is charge of the carrier. The positive sign is taken for hole and negative is for electron. Fig. 2.20 shows variation of $\ln \sigma$ (obtained from Fig. 2.11) with S (obtained from Fig. 2.19). The $\ln \sigma$ values are found to decrease with increasing values of S .

Overhof and Beyer [21] combined equation (3.1) and (3.2) to define a new quantity,

$$Q(T) = \ln \sigma (T) + \frac{q}{K} S(T) \quad \dots (3.3)$$

and obtained an equation,

$$Q(T) = Q_0 - \frac{E_Q}{KT} \quad \dots (3.4)$$

where $E_Q = E_\sigma^* - E_s^*$.

The variation of $Q(T)$ with $10^3/T$ is represented in Fig. 2.21. The values of $Q(T)$ are obtained by using equation (3.3) and Fig. 2.20.

The Q_0 values are obtained by taking the intercept on $Q(T)$ axis in Fig. 2.21. The Q_0 values are listed in Table No. 3.1. It is seen that the Q_0 values increase with increase in Sn concentration in the sample. The reported [21] value of Q_0 is 10. In our case the Q_0 values are less than 10. This deviation from reported value may be due to the large extrapolation involved in calculating Q_0 values.

The activation energy E_s^* for each sample is calculated by taking the slopes of the curves S versus $10^3/T$ which are shown in Fig. 2.19. The E_s^* values are tabulated in Table No. 3.1. The activation energy is found to increase with increasing Sn concentration in the sample.

The activation energies calculated from DC conductivity and TEP measurements differ by 0.13 eV. The values of $E_Q = E_\sigma^* - E_s^*$ are listed in Table 3.1. Several models have been proposed to interpret this difference [21,22]. For chalcogenide P. Nagel[22] proposed ambipolar transport mechanism to interpret this difference. Overhof and Beyer [21] have reported a difference between activation energies of the order of 0.1 eV to 0.2 eV for chalcogenide glasses. Our results are in agreement with those reported in the literature [21-24].

The non-zero value of E_Q is due to the long range static potential that modulates the energy of the mobility edge in space [21]. The origin of this potential could be the electrostatic potential of the charged centres which are randomly distributed in the bulk.

The magnetic susceptibility for each sample is calculated by using formula,

$$\chi_s = \left(\frac{\chi_r ds - 0.029 \times 10^{-6}}{\Delta W_r} \right) \cdot \frac{\Delta W_s (W_r - C)}{W_s dr} + \frac{0.029 \times 10^{-6}}{ds} \dots (3.5)$$

The χ_s values are tabulated in Table No. 2.15. The magnetic susceptibility for all samples is negative. The dependence of magnetic susceptibility on Sn concentration is shown in Fig. 2.2. The diamagnetic susceptibility is found to increase with increasing Sn concentration in the sample.

The magnetic susceptibility of semiconductive glasses of the system As-Se-Tl has been reported by Funtikov et al. [25]. They showed that the glasses of the system As-Se-Tl are diamagnetics and the absolute magnetic susceptibility increases with the Tl content. The increase is due to an increase in the diamagnetic component of the susceptibility. The magnetic properties of amorphous semiconductors have been reported by White et. al [26]. They identified two mechanisms as possible sources of the diamagnetic enhancement of the susceptibility of amorphous semiconductors. One of these is the presence of large orbits associated with localized states close to the mobility edge. The other is the reduction in the paramagnetic Van Vleck contribution arising from the loss of long-range order.

The temperature dependence of magnetic susceptibility is represented in Fig. 2.2. The magnetic susceptibility is found to be independent of temperature. M. Matyas [27] reported the temperature and compositional dependence of magnetic susceptibility in some semiconducting glasses. They showed that the diamagnetic susceptibility is independent of temperature. They interpreted their results on the

fact that semiconducting glass is formed from atoms bound together by covalent bonds. This glass is considered as a big molecule having no magnetic moment in the ground state and having some unsaturated bonds.