CHAPTER IV

RESULT AND DISCUSSION

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The electrical transport properties of amorphous semiconducting Se-Te-Sb system, are discussed here. Amorphous structure of the material, under study is confirmed from the X-ray diffraction pattern, which consist of broad rings, vanishing rapidly with increasing angle, without any evidence of spots or sharp rings, which would indicate some degree of crystallinity. The X-ray diffraction pattern show diffused rings. This means that Se-Te-Sb is amorphous in nature.

Current voltage characteristics are measured for sample $Se_{70}Te_{30}$, and $Se_{70}Te_{30-x}$-Sb_x (where X=1,3,5,7,9% atomic weight). The same characteristics of the sample Se_{70}-Te_{25}-Sb_5 with different thickness (0.130, 0.144, 0.180, 0.234, 0.300 cm.) were also studied.

The current voltage characteristics at different compositions are shown in [Figure 3·11]. The I-V curves are usually symmetric in nature, when applied field is very low, it appears atmost across the contacts and the interelectrode bulk field is also very low, and therefore, the current in the circuit is very less, i.e. current in (μA) is observed. At this low current value, the resistance of the material is very high. This is the off state regime. The low current obtained may be due to the thermally generated carriers from the defect states, existing in the bulk of the material. Therefore, the curves at low field are ohmic in nature.

When the applied field is increased, the current density becomes very high, at the threshold field [250] volts. At this point the resistance of the sample becomes low, this is the ON state of the material. High currentat ON state is due to the free charges and released charges from the traps. Normally the negative charges and positive charges are equal in magnitude. At high field the dense electron-hole Plasma would be injected from each side of the electrode The ON state would be maintained as long as injection rate is equal to recombination rate4.1. If the injection rate becomes smaller than recombination rate than the ON state will not be maintained, because the holding current will decrease in the circuit 4.2. At this stage, the material goes from nonconducting state to conducting state. It is the ON state. Such mechanism has been proposed by several authors 4.3, 4.4. Some authors have involved, mechanism of carrier multiplication in various forms 4.5, 4.6.

Here we would like to discuss the non-linear I-V behaviour on the basis of charge defect states introduced by Kastner and Hudgens [4.2]. They proposed that in amorphous semiconductors the lower energy defect states are positively charged threefold coordinate C_3^+ and negatively charged One-fold coordinate C_1^- chalcogen atoms. When an electric field is applied to an amorphous semiconductor, electrons and holes are injected from the cathode and anode into the material.

Initially the injected electrons and holes are held up at the electrodes, as there is no internal electric field. At the cathode the electrons are trapped by C_3^+ (donors) centres which transform to C_3° neutral centres. At the cathode the C_1^- centres capture the holes and transform to C_3° neutral centres. The electrons are captured at faster rate than holes, because of the mobility of the electrons is higher than that of holes. This will result in creating a higher concentration of C_1^- centres as compared to that of C_3^+ centres. Thus at the anode a high field exists, and holes drift towards the cathode, where they are captured by the C_3° neutral centres, thus creating C_3° centres at the anode. 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° centres and C_1^- are formed.

The current voltage characteristics of Se_{70} -Te_{25} -Sb_5 for different sample thiknesses are shown in figure (3.12). The nature of curves for different thicknesses of the material is the same and it can be explained by the same mechanism given above. The only difference, we observed that as the thickness increases the current in the circuit decreases for the same field value it may be explained that in a thin sample the voltage required to inject the required amount of charges for building up an internal field is less because of small distance between the electrode and smaller value of resistance of the sample. While in the thick sample, the voltage required to inject the same density of charges, for building up the internal field is large because of the large distance between electrodes and greater value of resistance of the thick sample. Therefore, as the thickness of the sample decreases, the conductivity of the sample increases.

D.C. Conductivity

The experimental conductivity data of six samples of the system Se_{70}-$Te_{30-x}$$Sb_x$ (where X=1,3,5,7,9% atomic weight) is listed in table (4.1). The conductivity is represented by Mott's equation

$$\sigma = C \exp.\left(\frac{E_\sigma^*}{KT}\right) \qquad (4.1)$$

the value of activation energies E_σ^* obtained from the curves drawn between logσ against 1/T and the preexponential factor C, are listed in table (4.1). It is observed that conductivity increases with increase in antimony concentration in the samples. For Se_{70} -Te_{30} , activation energy is 0.6341 ev and increases to 0.9702 ev. for Se_{70} -Te_{23}-Sb_7. It is suggestd by Haisty and Krab [3] that the incorporation of Sb in Se-Te is regarded as forming mixed rings and strong covalent bonds, between the atoms in the rings. The addition of Sb leads to cross-linking between the chains promoting theformation of three dimensional net work. The addition of Sb weakens the bonds in rings which will influence the band structure of the material and hence electrical properties. Therefore, we must get increase in conductivity with increase in Sb concentration. Such type of behaviour is observed for our system. It is found that, with increase Sb concentration, the conductivity increases up to Se_{70} $-Te_{23}$ $-Sb_{7}$.

But for the sample Se_{70} $-Te_{21}$ $-$ Sb_{9} it is found that activation energy decreases. This type of behaviour may be due to some changes in the bulk of the material. It may be due to the higher concentration of antimony. The material may be converted from amorphous to crystalline phase. The X-ray diffraction study [Fig. 3.7] of the same sample also support to the above nature. In X-ray diffraction pattern, we get some peaks which indicates the crystallinity of the sample. The I-V characteristics study also supports to above observed fact, for sample Se_{70} $-Te_{21}$ $-Sb_{9}$ in which current decreases.

We can also explain the above Result with the help of, sample (Si-H) with Al.

The influence of Aluminium upon electronic transport of amorphous (Si-H) has been reported by Fortuna and Marshall4.7. They have observed that the activation energy decreases as percentage of Aluminium in the sample increases, indicating thereby that the conductivity of the sample increases. They have explained this on the basis of formation of Aluminium islands in the semiconducting medium. The conduction takes place between two islands, when the carriers move in the medium. The material does not become completely matallic but the current value increases because of increase in Aluminium content and conductivity increases. For our sample $Se_{70}Te_{30}$ the conductivity increases as the percentage of antimony increases in the sample. But at higher concentration of Sb the amorphous material may be slowely converted in to crystalline form, as a result thereby decrease of conductivity value.

Fig. (3.14) shows variation of room temperature conductivity, with variation of antimony concentration. It is seen from figure that, conductivity increases with increasing antimony concentration.

Fig.(3.15) shows, variation of pre-exponential factor 'C' against concentration of antimony. From this curve we find that the pre-exponential factor 'C' is not constant but depends upon glass composition. The value of 'C' lies between (-3.2×10^{-7} to 3.83×10^{-6}) for different concentrations of antimony in Se-Te. Mott and Davis (4) argued that, there is no definite correlation between the intercept 'C' and activation energy E_{σ}^{*} of amorphous semiconductors. However the present investigations show that 'C' decreases with increase in activation energy. According to Mott and Davis the intercept 'C' is related to density of localized state. As 'C' decreases the density of localized states increases. Thus observed in 'C' with composition probably suggests the formation of glass composition with higher degree of discorder. This behaviour is also explained by Majid et al(4).

Fig.(3.16) shows variation of room temperature conductivity with activation energy. It has been observed that the conductivity increases with increase in activation energy and high concentration of Sb with decrease in activation energy, which is in agreement with observaions given by Majid(4), for the system $(As_2-Se)_{1-x}(Ti_2Se\ )_x$.

The variation of E_σ^* with concentration X and E_σ^* with 'C' is shown in figure (3.17,3.18). Figure (3.17) shows that as antimony concentration increases in the sample, the activation energy increases, it means, the conductivity of the sample decreases as the antimony concentration increases.

Fig.(3.22-) in sample Se_{70} Te_{23} Sb_7 shows variation of conductivity with field strength, at different temperatures. It is observed that, the conductivity increases with increase in field strength, at room temperature. This increase in conductivity at room temperature is found to depend, on antimony concentration in Se-Te system. As antimony concentration is increased, less increase in conductivity is found. It is found that, above 60°C, the conductivity becomes independent of field strength.

At room temperature the charge carriers are accelerated, due to applied field. As field is increased, more and more charges reach to anode, resulting increase in current. At high temperature the number of charge carriers are more as compared to room temperature, but the effect of field is not predominent.

Thermo-e.m.f.

Figure[3.21] shows variation of e.m.f. with temperature difference. It shows that the thermo e.m.f. varies linearly with temperature difference. As we get positive thermo e.m.f. for the sample, the charge carriers are holes, and the material is p-type in nature.

The variation of thermoelectric power with $\frac{1}{T}$/°K is shown in fig.(3.22). It is observed that the thermoelectric power varies linearly in all the samples. There is increase in thermoelectric power with increase of antimony in Se-Te.

The thermoelectric power equation given by Fritzsche[6]

$$S = \frac{K}{e} \left[\frac{E_s^*}{KT} + A \right] \tag{4.2}$$

is used to calculate the activation energy. For most of the chalcogenide glasses A=1. The activation energy calculated from the curves comes out to be 0.4951 ev. for Se_{70}-Te_{30} and increases to 0.8184 ev. for Se_{70}-Te_{23}-Sb_7.

The activation energy increases as the percentage of antimony in Se-Te system increases. The difference in activation energy, calculated from the conductivity and thermoelectric power measurement is

$$(E_Q = E^*_\sigma - E^*_S) \approx 0.1 \text{ ev.}$$

The values E^*_S and E_Q are listed in table no.4.1. Several models have been proposed to explain the features found experimentally for the difference in activation energy, calculated from conductivity and thermoelectric power. For chalcogenide P.Nagels[7] proposed ambipolar transport. This difference in activation energy (E_Q), could represent an activation energy in the mobility, $\mu(T)$ which enters the expression for σ i.e.

$$\sigma = \int_{\infty}^{+\infty} g(E)\ f(E)\, e\, \mu(E)\, dE \qquad (4.3)$$

But not for S. In that case, conduction could be due to small-polaron hopping. However the conductivity data appear to require sufficiently large mobilities, that this mechanism is highly unlikely [8]. At the present time, none of the three standard transport properties σ, S, and R_H can be considered to be understood. It is clear that σ can be modulated over many orders of magnitude both by n-type and p-type dopping. Overhof andBeyer[9] have reported difference between activation energies as 0.1 eV to 0.2

eV. for chalcogenide glasses, and α-Si-H. They have also discussed various transport modes considering the transport properties of both chalcogenide and a Si-H, simultaneously. They have defined Q(T) by the follwoing relation

$$Q(T) = \ln\sigma(T) + q/k\ S(T) \qquad (4.4)$$

with $q = -|\varrho|$ for electron and

$q = +|\varrho|$ for holes.

They have also shown that both for silicon and chalcogenide, the Q(T) curves are generally well represented by

$$Q(T) = Q_0 - E/KT \qquad (4.5)$$

Following Overhof and Bayer, we have plotted the graph of Q(T) against T^{-1} K for our system as shown in fig.[3.23]. The slope of curve yields Qo values which are presented in table(4.1). Many attempts have been made to explain the non-zero value of E_Q [9]. When transport takes place in the extended states, above the mobility edge,

$$Q(T) = \ln(\sigma_{min}\ \Omega^{-1}\ cm^{-1}) + 1 \qquad (4.6)$$

The value of E_Q obtained from above equation are in agreement with value reported in the literature [10].

The non-zero slope of Q(T) is due to long range static potential that modulates the energy of mobility edge in space[9]. The origin of this potential could be electrostatic potential of charged centres which are probably not homogeneously distributed in space than random distribution. In this case variation of E_Q with preparation and doping level had to be attributed to long range potential. It has been reported that, in highly doped or more disordered samples E_Q may as large as 0.25 eV, while for undoped sample E_Q = 0.05 eV [11].

The plot of lnσ against S is shown in fig.[3.24]. The slope of which enables to calculate σ_o . It seems to us that further work both theoretical and experimental is necessary to determine σ_o .

The conductivity is given by

$$\sigma = \sigma_o \text{ exp. } \left[- \frac{E_c - E_F}{KT} \right] \tag{4.7}$$

at zero temperature

$$\sigma_o = \frac{0.03\, e^2}{h\, l_1}$$

Where l_1 is inelastic diffusion length, σ_o is obtained from the slope of lnσ against S. curves the values of l_1 are listed in table 3.1.

Table No. 4.1

Values of activation energy E^*_σ, E^*_s, the intercept 'C' Room temperature conducivity $\sigma \Omega^{-1}cm^{-1}$ Energy difference, EQ, the factor Qo, preexponential factor σo, and inelastic diffusion length 1 for bulk of the sample Se_{70}-Te_{30}-Se_{70}-Te_{30-x} -Sb_x.

Glass Composition	Concentration X in% of atomic Wt.	Activation Energy E^*_σ eV	Activation Energy E^*_s eV	Intercept ln C ($\Omega^{-1}cm^{-1}$)	Room Temp. Conductivity $\sigma \Omega^{-1}cm^{-1}$	Energy difference $E_Q = E^*_\sigma - E^*_s$	Factor Qo	Preexp. factor σ_o $\Omega^{-1}cm^{-1}$	Inelastic diffusion length L_1 cm.
$Se_{70}Te_{30}$	0	0.6341	0.4951	-15.75	2.03×10^{-9}	0.1390	8.55	6.43	8.59×10^{-8}
$Se_{70}Te_{29}Sb_1$	0.1	0.7186	0.5543	-15.00	2.38×10^{-9}	0.1643	7.94	5.71	7.63×10^{-8}
$Se_{70}Te_{27}Sb_3$	0.3	0.8300	0.6619	-14.20	2.44×10^{-9}	0.1681	6.25	7.61	10.16×10^{-8}
$Se_{70}Te_{25}Sb_5$	0.5	0.9103	0.7491	-13.40	3.72×10^{-9}	0.1612	3.50	5.25	7.01×10^{-8}
$Se_{70}Te_{23}Sb_7$	0.7	0.9702	0.8184	-12.25	3.97×10^{-9}	0.1518	2.78	5.34	7.13×10^{-8}
$Se_{70}Te_{21}Sb_9$	0.9	0.7699	0.6105	-14.85	7.90×10^{-10}	0.1594	- -	-	-

Result and discussion of
(Sb - Se - Cu)

Current voltage characteristics at different compositions are show in fig.(3.25). The I-V curves are symmetric in nature. At low field the interelectrode bulk field is very low, and therefore current in the circuit is in (μA) ramge. The resistance of the sample is very high. This is the Off state of highimpedance state. The low current obtained may be due to the thermally generated carriers from the defect state, existing in the bulk of the material. Therefore, the curves at low field are ohmic in nature.

Here we would like to discuss the non-linear I-V behaviour on the basis of charge defect states, introduced by Kastner and Hudgnes$^{4.4}$. The defect states introduced by above scientisits are discussed in series Se_{70}-$Te_{30-x}Sb_x$.

The measurement of d.c. conductivity in the case of amorphous semiconductors have yielded valuable information about the transport mechanism. The majority of amorphous semiconductor at high temperature show an activated temperature dependence in accordance to the relation

$$\sigma = \sigma_0 \exp.\left(\frac{E_\sigma^*}{kT}\right) \qquad 4.8$$

Where E_σ^* and σ_0 are the conductivity activation energy and pre-exponential factor respectively.

The experimental conductivity data of sample of system Sb_{70}-Se_{25}-Cu_5 and Se_{70}-$Se_{23}Cu_7$ are shown in fig.[3.20,21].

The value of activation energies $E\sigma^*$ obtained from the curves drawn between $\log\sigma$ against 1/T are listed in table [3.27]. or

The observed variation of d.c. conductivity with reciprocal temperature ($\log\sigma$ Vs T^{-1}) for various bulk amorphous samples of $Sb_{70}Se_{25}C_5$ and $Sb_{70}Se_{23}C_7$ in the temperature range (300° K to 350° K) is shown in fig.[3.26]. It can be observed that for samples with $0.4 < x < 0.9$, the conductivity is not singly activated in the entire temperature range investigated in fact, the data are characterized by slightly curved lines with gradually increasing activation energy with increasing temperature.

It is observed that there is an decrease in conductivity with increase in Cu in the sample $Sb_{70}Se_{30-x}.Cu_x$

The addition of Cu weaknes the bonds in rings which will influence the band structure of the material and hence electrical properties.

This decrease in conductivity due to increase of Cu in the sample, may be thought on the basis of Cu islands formed due to addition of Cu in to the sample. These is Islands may be of acceptar type in the amorphous field.

Figure (3.26) shows variation of room temperature conductivity σ with Cu concentration. It is seen from the figure that conductivity decreases with increasing Cu concentration.

This glass obey the log σ against T^{-1} °K relation over entire range of temperature. The amorphous Sb-Se-Cu system was obey this linear relation for 300°K to 340°K .

Fig.(   ) shows variation of pre-exponential factor 'C' against concentration of Cu. From this curve we find that the pre-exponential factor 'C' is not constant but depends upon the glass composition. Mott and Davis[4.11] argued that there is no definite correlation between the intercept C and activation energy E_σ^* of amorphous semiconductors. However the present investigations show that 'C' increases with decrease in activation energy. According to Mott and Davis the intercept 'C' is related to density of localized state.

Fig.(   ) shows variation of room temperature conductivity with activation energy. It has been observed that the conductivity increases with decrease in activation energy, which is agreement with observations given by Majid(4) for the system $(AS_2-S_1)_{1-x}(Te_1-Se_3)_x$

The variation of E_σ^* with concentration X is shown in figures or Table No. 4.2 .

Fig.(4.2) shows that as cupper concentration increases in the sample, the activation energy is decreases in our sample Sb-Se-Cu

Fig.(3.28) shows variation of conductivity with field strenght, at different temperatures. It is observed that, the conductivity increases with increase in field strength, at room temperature. This increase in conductivity at room temperature is found to depend, on cupper concentration in Sb-Se system. As cupper concentration is increased, less increase in conductivity is found. It is found that, above 50 C, the conductivity becomes independent of field strength.

At room temperature the charge carriers are accelerated, due to applied field. As field is increased, more and more charges reach to anode, resulting increase in current. At high temperature the number of charge carriers are more as compared to room temperature, but the effect of field is not predominent.

Fig.(3.29) shows variation of thermo e.m.f. with temperature difference. It is found that thermo-e.m.f. varies -e linearly with temperature difference. The variation of thermoelectric power with 1/T K is shown in fig.(3.29). It is observed that the thermoelectric power varies linearly in all the samples.

There is decrease in thermoelectric power with increase in copper in Sb-Se.

The activation energy calculated from the curves comes out to be0.5416 ev for Sb_{70}-Se_{25}-Cu_5 and decrease to 0.4568eV for Sb_{70} -Se_{23} -Cu_7. Therefore difference in activation energy, calculated from the conductivity and thermoelectric power measurement is ($E_a = E_\sigma^* - E_S^*$) $\simeq$ 0.1 eV. The values os E_σ^* and E_S^* are listed in table no.(4.2). Several models have been proposed to explain the features found experimentally for the difference activation energy, calculated from conductivity and thermoelectric power. For chalcogenide P. Nagels(7) proposed ambipolar transport. This difference in activation energy (E_a), could represent on activation energy in the mobility, μ(T), which enters the expression for i.e.

$$\sigma = \int_{-\infty}^{+\infty} N(E)\ f\ (E)\ e\,\mu(E)\ dE \qquad \cdots\cdots\cdots\cdots 4.9$$

but not for S. In that case, conduction could be due to small-polaron hopping.

TABLE NO. 3.27

Compound	E_σ^* (eV)	E_s^* (eV)	$E_Q=E_\sigma^* - E_s^*$ (eV)	Intercept $\ln C\,\Omega^{-1}\,cm^{-1}$	Factor Qo	σo $\Omega^{-1}\,cm^{-1}$	L_1
Se Se Cu	0.5416	0.3692	0.1724	-5.75	9.142	0.44	0.5962×10^{-8} cm
Se Se Cu	0.4568	0.275	0.1818	-4.55	11.13	0.30	0.4065×10^{-8} cm