

TEMPERATURE AND COMPOSITION DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN a- $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ THIN FILMS

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In the present paper D.C. conductivity measurements have been made on $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($x = 0, 2, 8$) thin films in the temperature range 255-360K. Two regions have been observed in the entire temperature range. One such region is at low temperatures 255K to 305K and other region is in high temperature range 310K to 360K. In the high temperature range conductivity is thermally activated having single activation energy. Electrical parameters (activation energy (ΔE) and pre-exponential factors σ_0) have been calculated for each sample. It has been observed that the activation energy decreases on increasing concentration of Zn. Composition dependence of conductivity shows that conductivity decreases at 2% of Zn. However on further incorporation of Zn, conductivity increases. Same behavior has been observed for pre-exponential factor (σ_0). In low temperature range (255-305K) variable range hopping conduction is observed. Mott parameters and density of localized states near Fermi level have been calculated. Density of localized states decreases at 2% of Zn and then increases with the further increases in Zn concentration.

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1. Introduction

Amorphous selenium (a-Se) is a very useful material for application point of view due to its current use as photoconductors in TV vidicon pick-up tubes [1] and particularly in xerography [2]. However, it has limited applications due to certain shortcomings such as low crystallization temperature (T_c), low photosensitivity, lesser durability and more aging effects. So, to extend the utility of a-Se for higher T_c and photosensitivity, Te is added to it. It has been reported that the addition of Te to a-Se changes its properties drastically until a critical concentration of Te is reached above which it loses glass forming ability and the quenched melt become crystalline.

Glassy alloys of Se-Te system have become materials of considerable commercial, scientific and technological importance. They are widely used for various applications in many fields as optical recording media because of their excellent laser writing sensitivity, xerography, and electrographic applications such as photoreceptors in photocopying and laser printing, infrared spectroscopy, laser fibre techniques [3-5]. Pure a-Se is believed to consist predominantly of a mixture of two structural species, long helical chains and eight member rings, held to each other by weak forces, perhaps of the Vander-Waals type. Strong covalent bonds exist between the atoms in the chains and rings. The relative proportions of the two species, as well as the length of the chains, are expected to depend on the conditions, of preparations, which can be either by melt quenching or by vacuum evaporation. Long polymeric chains and eight members ring of a-Se are dissociated by the addition of Te [6-7], which makes Se-Te alloys more important due to their attractive advantages as compared to pure a-Se. however these alloys have some significant problems when used as a recording layer material in optical phase change technique (PC) [8-9].

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The two serious problems are the limited reversibility [10], low glass transition and crystallization temperature. These problems can be removed by adding third element as a chemical modifier in Se-Te binary alloys. A lot of work has been done on ternary chalcogenide glasses having different compositions like Se-Te-Sb, Se-Te-Ge, Se-Te-In [11-13]. In the present work, Zn has been added as a third element in binary Se-Te alloys. The reason for the selection of Zn as a chemical modifier in Se-Te system is based on its attractive and important applications in chalcogenide glasses. Like Ag, Zn can also be used for photo - doping in chalcogenide glasses [14-19]. There are successful reports of doping of Zn $\text{Se}_x\text{Te}_{1-x}$ in the literature that are suitable for the development of light emitting diodes and lasers. The major draw back of amorphous semiconductor over their crystalline counter part is the presence of defect states. The density of states (DOS) in the mobility gap controls many physical properties of amorphous semiconductors. Thus the determination of density of states has therefore been an important issue of these materials.

The present paper reports the measurements of conductivity as a function of temperature. Conductivity data in the low temperature region has been used to determine the density of states near Fermi level using the theory of variable range hopping conduction.

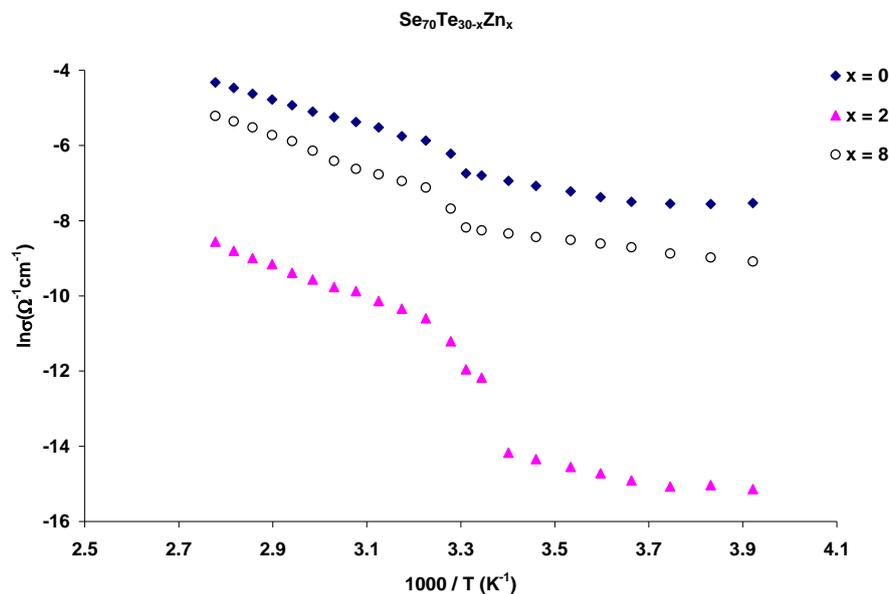


Fig. 1. Temperature dependence of conductivity plotted as $\ln\sigma$ vs $1000/T$ in a - $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ thin film

Section 2 describes the experimental details. The results have been presented and discussed in section 3. The conclusions have been presented in the last section.

2. Experimental details

2.1 Synthesis of materials

Glassy alloys of $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$ ($x = 0, 2, 8$) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Zn elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800°C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of $3 - 4^\circ\text{C} / \text{minute}$. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous

glassy alloy. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction. For this, X-ray diffraction (XRD) patterns of samples were taken at room temperature by using an X-ray diffractometer (Philips, PW 1140/09). The copper target was used as a source of X-rays with $\lambda = 1.54 \text{ \AA}$ ($\text{Cu K}\alpha_1$).

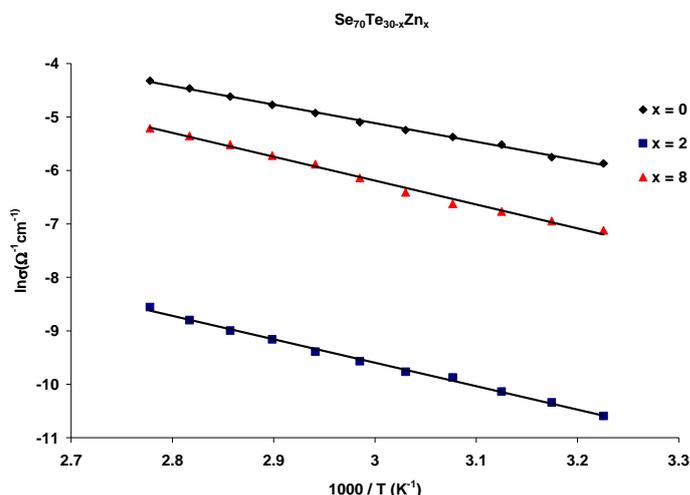


Fig. 2. $\ln\sigma$ vs $1000/T$ in the temperature range where the Arrhenius behaviour is observed.

2.2 Thin films preparation

Thin films of the glassy material were prepared by Vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for electrical contacts. The thickness of the films was $\sim 500 \text{ nm}$. The coplanar structures (length $\approx 1.2 \text{ cm}$ and electrode separation $\approx 0.5 \text{ mm}$) were used for the present measurements.

For the measurement of electrical conductivity, thin film samples were mounted in a specially designed sample holder which has a transparent window to shine light for these measurements in a vacuum $\sim 10^{-3}$ Torr. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper - constantan thermocouple mounted very near to the films. The low temperature was obtained by cooling the samples using liquid nitrogen.

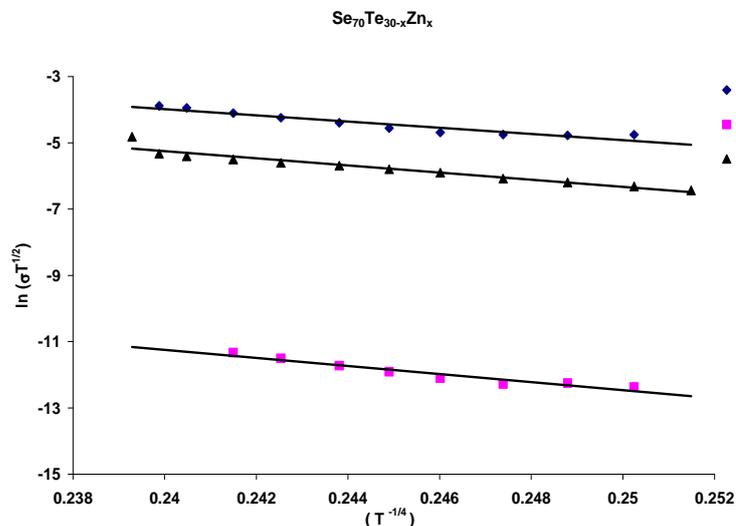


Fig. 3. $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ plot at various concentration of Zn in a- $Se_{70}Te_{30-x}Zn_x$.

The d. c. conductivity is measured by a digital Electrometer (Keithley, model 614). The heating rate was kept quite small (0.5 K/min) for these measurements.

Before measuring the dark conductivity, the films were first annealed below glass transition temperature T_g for two hours in a vacuum $\sim 10^{-3}$ Torr. I-V characteristics were found to be linear in all the glasses studied. The present measurements were made by applying only 10 V across the films.

3. Results and discussion

The electrical conductivity of $Se_{70}Te_{30-x}Zn_x$ ($x = 0, 2, 8$) thin films has been measured in the temperature range 255 K to 360K in dark and a plot of $\ln\sigma$ versus $1000/T$ is shown in Fig.1. This figure shows that $\ln\sigma$ vs $1000/T$ curve is not a straight line in the entire temperature range of measurements. Only in the high temperature range, such curves are straight lines indicating that from 310K to 360K, the Arrhenius behaviour is observed where conductivity increases exponentially with temperature following the relation:

$$\sigma = \sigma_0 \exp(-\Delta E / k T) \quad (1)$$

where, ΔE is the activation energy for conduction and k is the Boltzmann's constant.

The $\ln \sigma$ vs. $1000/T$ curves for a- $Se_{70}Te_{30-x}Zn_x$ thin films have been plotted separately in Fig.2 in the temperature range (310-360K). The exponential variation of conductivity with temperature indicates that the conductivity in these glasses is due to a thermally activated process. The values of conductivity σ at a particular temperature 305 K, pre-exponential factor σ_0 and ΔE for different compositions of $Se_{70}Te_{30-x}Zn_x$ glassy alloys are given in Table1.

Table.1. D.C. conduction parameters in the high temperature range in a- $Se_{70}Te_{30-x}Zn_x$

Zn (%)	σ ($\Omega^{-1}\text{cm}^{-1}$) at 305 K	ΔE (eV)	σ_0 ($\Omega^{-1}\text{cm}^{-1}$)
0	1.99×10^{-3}	0.30	2.0×10^2
2	1.35×10^{-5}	0.36	3.4×10^1
8	4.63×10^{-4}	0.39	1.8×10^2

Table 2. Mott's Parameters in the low temperature region in a- $Se_{70}Te_{30-x}Zn_x$

Zn (%)	A ($\text{K}^{1/4}$)	T_0 (K)	$N(E_F)$ ($\text{eV}^{-1}\text{cm}^{-1}$)	$\alpha \times 10^7$ (cm^{-1})	R (cm)	W (eV)	αR
0	93.66	7.7×10^7	1.69×10^{20}	4.0	1.5×10^{-7}	0.148	8.4
2	121.57	2.2×10^8	1.45×10^{18}	1.2	8.1×10^{-7}	0.192	10.9
8	108.43	1.4×10^8	1.60×10^{20}	4.7	2.1×10^{-7}	0.171	9.7

In the low temperature region, data is plotted in Fig.3 in terms of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ to see the applicability of Mott's variable range hopping (VRH) conduction model in our case. In such a case, the conduction can be attributed to the hopping of the charge carriers between localized states near Fermi level and the conductivity can be expressed as [20-21]:

$$\sigma T^{1/2} = \sigma_1 \exp(AT^{-1/4}) \quad (2)$$

and

$$A^4 = T_0 = \lambda \alpha^3 / k N(E_F) \quad (3)$$

where $N(E_F)$ is the density of localized states at E_F , α^{-1} the degree of localization, T_0 the degree of disorder. λ and A are dimensionless constants. The value of pre-exponential term σ_1 of eq.2 as obtained by various workers is given by

$$\sigma_1 = 3e^2 \gamma [N(E_F) / 8\pi\alpha kT]^{1/2} \quad (4)$$

where 'e' is electronic charge and the ' γ ' Debye frequency ($=10^{13}$ Hz). A simultaneous solution of eq.(3) and (4) yields

$$\alpha = 22.52\sigma_0 A^2 (\text{cm}^{-1}) \quad (5)$$

and

$$N(E_F) = 18 \alpha^3 / k A^4 (\text{cm}^{-3}\text{eV}^{-1}) \quad (6)$$

The hopping distance and hopping energy is given by

$$R = [9 / 8\pi\alpha kT N(E_F)]^{1/4} \quad (7)$$

$$W = 3/4 \pi R^3 N(E_F) \quad (8)$$

In the present case, $\ln \sigma T^{1/2}$ vs $T^{-1/4}$ plot is found to be a straight line (see Fig.3) which indicates the validity of hopping conduction mechanism. This is in good agreement with Mott's VRH model. The slope of these curves gives the value of $N(E_F)$ and other Mott's parameters are calculated from eq. (2 -8) and are given in Table 2.

It is evident from Table 2 that the density of localized states decreases at 2% of Zn. However, on further incorporation of Zn, DOS near Fermi level increases. Same trend has been observed for the conductivity. Figs 4-5 show the composition dependence of DOS and conductivity respectively.

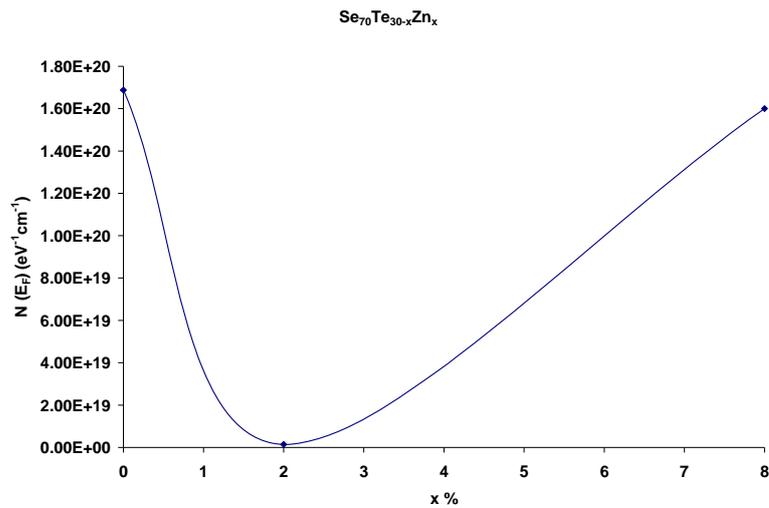


Fig. 4. Composition dependence of DOS near Fermi level in a- $Se_{70}Te_{30-x}Zn_x$ thin films

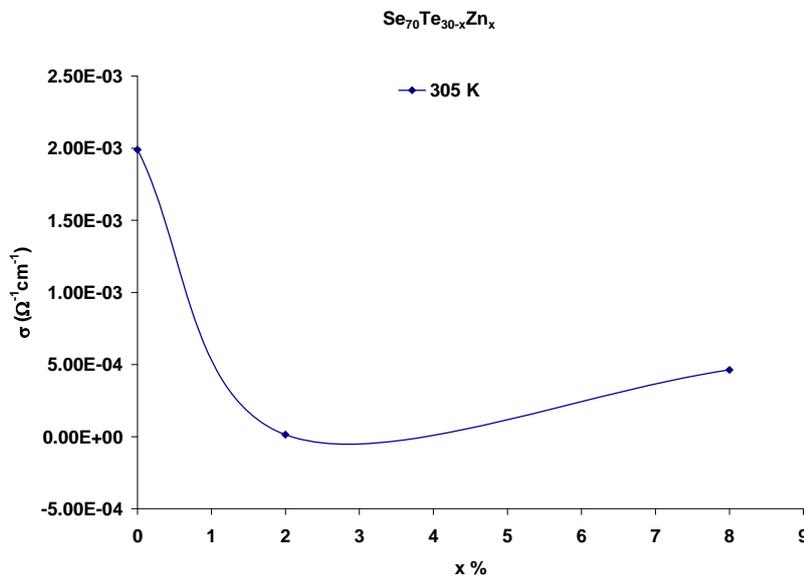


Fig. 5. Composition dependence conductivity in a- $Se_{70}Te_{30-x}Zn_x$ thin films at temperature 305K.

Thus, from the above experimental results in, one can expect that the charge transport in the low temperature range can be attributed to the hopping of the charge carriers in the localized states near Fermi level.

4. Conclusions

Electrical parameters as well as Mott parameters have been calculated in a- $Se_{70}Te_{30-x}Zn_x$ thin film prepared by vacuum evaporation technique. Composition dependence of conductivity and density of states near Fermi level, shows that conductivity, and DOS near Fermi level both decrease at 2 % of Zn. However, on further incorporation of Zn, the value of conductivity as well as DOS increases, which is quite consistent with our earlier results where DOS has been calculated by two different methods namely thermally stimulated (TSC) conductivity and space charge limited conduction (SCLC) [22-23].

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