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I-V MEASUREMENTS OF Se-Te-Sb GLASSY BULK AND THIN FILM SAMPLES

Vibhav K. Saraswat[a,b*], V. Kishore[a,b], Deepika[b], N.S. Saxena[b], T.P. Sharma[a], L.I. Singh[c], P.K. Saraswat[d]
[a]*Deptt. of Physics, AIM & ACT, Banasthali University, Banasthali- 304022 India.*
[b]*Semi-conductor & Polymer Science Laboratory, 5-6, Vigyan Bhawan, Deptt. of Physics, University of Rajasthan, Jaipur- 302004, India.*
[c]*Deptt. of Physics, Imphal College, Imphal, Manipur, India*
[d]*Deptt. of Physics, N.D. College, Shikohabad, Firozabad- 205135, India.*

I-V characteristic curves of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) glassy system prepared by melt quenching have been studied at different temperatures in bulk and at room temperature in thin film form. Experimental results indicate that the conduction mechanism in these systems is of Poole-Frenkel type. The change in dc electrical conductivity is attributed to the Se-Sb bond concentration in the Se-Te-Sb system. The electrical conductivity vs composition plots are found to have very similar trend as the thermal conductivity vs composition. Also the composition containing Sb 4 at. wt.% shows the minimum resistance in both the cases i.e. in bulk and thin film form. As these electrical measurements have a strong agreement with reported measurements of thermal conductivity, it has been claimed that $Se_{81}Te_{15}Sb_4$ is the most thermally stable composition for electrical applications and hence is coined as “Magic Composition” in the proposed series. Higher resistance in thin films as compared to bulk is attributed to the higher density of surface defects and lower thickness in the films.

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1. Introduction

Amorphous semi-conductors are non- crystalline. They lack long-range periodic ordering of their constituent atoms. This is not to say that amorphous semi-conductors are completely disordered on the atomic scale. Local chemistry provides almost rigorous bond- length and to a lesser extent bond-angle constraints on the nearest neighbour environment. Unlike amorphous metals, amorphous semi-conductors do not consist of closely packed atoms, but rather they contain covalently bonded atoms arranged in an open network with correlation ordering up to the third or fourth nearest neighbours [1]. The short-range order is directly responsible for observable semi-conductor properties such as absorption edges and activated electrical conductivities.

The common feature of these glasses is the presence of localized state in the mobility gas as a result of the absence of long-range order as well as various inherent defects. Recently, the investigation of electron transport in disordered system has gradually been developed and the investigation of gap states is of particular interest because of their effect on the electrical properties of semi- conductors [2-3]. The effect of impurity in an amorphous semi- conductor may be widely different, depending upon the conduction mechanism and the structure of the material [4]. While

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[*] Corresponding author: vibhu_saraswat@hotmail.com

in crystalline semi- conductors the effect of a suitable impurity is always to provide a new donor or acceptor states, this is not essential in amorphous semi- conductor [5]. Instead of providing a localized impurity level in the forbidden gap, an impurity may merely alter the mobility of the charge carriers or may introduce structural change [6] in the amorphous material with or without modification of the localized states in the forbidden gap. Investigations of the temperature dependence of conductivity, the effect of impurities on the activation energy, and the effect of high electrical field on the conduction mechanism is a subject of great interest, because the result of such studies provide methods to control effectively the conductivity of amorphous semi-conductors. So, the present work incorporates the study of temperature dependence of I-V characteristics of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) glasses in bulk form at different temperatures and in thin films at room temperature.

2. Experimental details

First of all the constituent materials (i.e. Se, Te & Sb) of high purity (99.999%) were taken in their elemental powder form in proper atomic weight percentage according to the proposed composition $Se_{85-x}Te_{15}Sb_x$ (where x= 2, 4, 6, 8 & 10). Chalcogenide glasses belong to substances which have an incongruent melting point, exhibit a high partial vapour pressure during melting and are susceptible to oxidation and hydrolysis and therefore the synthesis must be carried out in sealed evacuated quartz ampoule. The synthesis conditions are widely varied – they depend on the glass composition, glass-forming region, glass forming ability and the melting temperature of the constituents etc. The necessary chemical and physical purity of prepared glass should be about 10^{-5} mol% for the presence of OH, SH, SeH groups and the concentration of physical defects in the range 10^2- 10^3 per cm^3 [7] The powders of Se, Te and Sb, in appropriate at. wt. % proportions, were weighed and sealed in a quartz ampoule (10 mm inner dia. and 12 mm outer dia.) under a vacuum of 10^{-6} Torr to avoid oxidation at higher temperatures. Ampoules were slowly heated (rate 3-4 K/min) to 950 K and kept there for 10 hrs. at the maximum temperature, ampoules were frequently shaken to homogenize the melt. Quenching was done in the ice-cooled water to get glassy state. The ingot was taken out of the ampoule by breaking the ampoule and then was gently grinded in a mortar and pestle to its powder form. The X-ray diffraction (XRD) patterns of powders were taken on Philips Mode PV 1840 diffractometer with an Iron K_α radiation source (λ = 1.937355 Å), which confirmed the glassy nature of the materials. Figure 1 shows the XRD pattern of $Se_{75}Te_{15}Sb_{10}$ glass. These powders were used to make pellets of dimensions as thickness ≈ 1mm and diameter 12mm. Thin films were deposited by Vacuum Flash Evaporation technique.

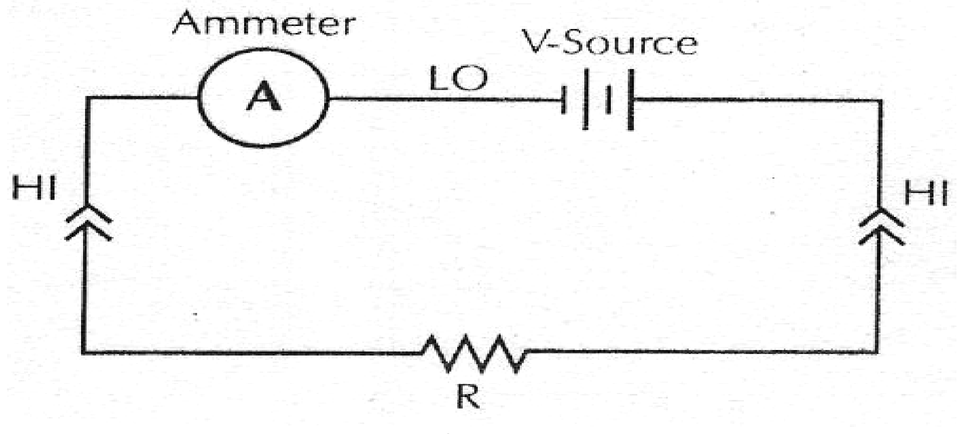

Fig.1. XRD of $Se_{75}Te_{15}Sb_{10}$ glass.

Measurements of I-V characteristics of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) were performed on Keithley High Resistance Meter/ Electrometer 6517A at different temperatures. Electrometer (6517A) was used to apply the voltage across the sample and to measure the current through the sample as it has an in- built capability of output independent voltage source of ± 1000 V. The indigenously designed sample holder with copper electrodes was used in the circuitry for bulk pellets and the thin films were used with silver paste contact in circuitry. The basic circuit diagram, used for this study, is shown in figure 2.

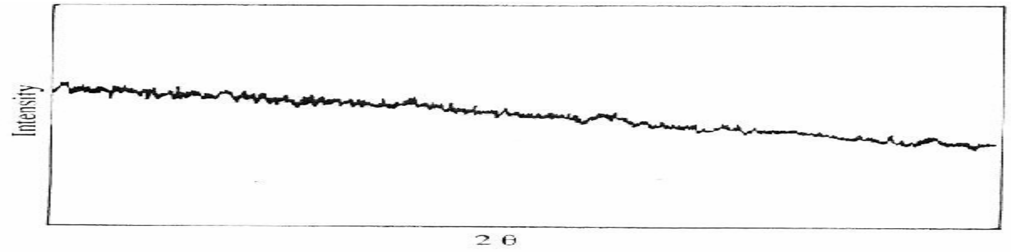

Fig. 2. Electrical circuit diagram used for I-V measurements

3. Result and discussion

Typical I-V characteristics of glassy pellets and thin films of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) were measured at different temperatures (room, 40, 50, 60, 65, 70, 75, 80 & 85 °C) (voltage range 10 – 200 V) and at room temperature (voltage range 10 – 100 V), respectively. Figure 3 shows the temperature dependence of I-V characteristics of $Se_{81}Te_{15}Sb_4$ glassy pellet as a representative case and figure 4 shows the I-V characteristics of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) thin films at room temperature.

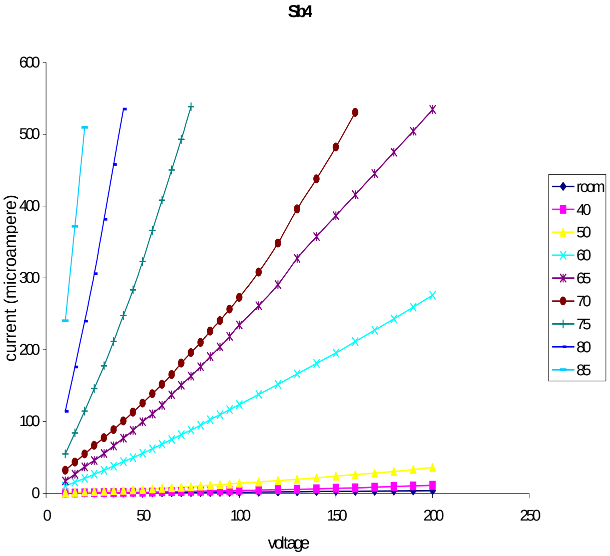

Fig. 3. I-V characteristics of $Se_{81}Te_{15}Sb_4$ glassy pellet at different temperatures.

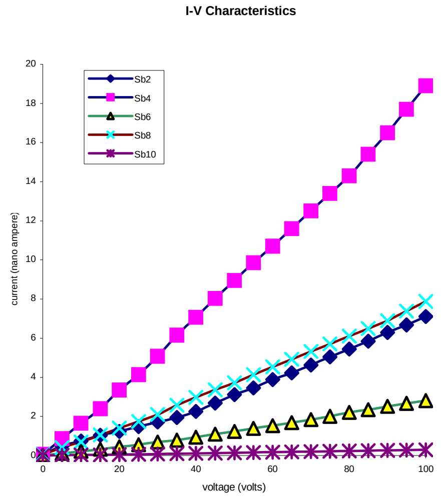

Fig. 4. I-V characteristics of $Se_{85-x}Te_{15}Sb_x$ (x = 2, 4, 6, 8 & 10) glassy thin films at room temperature.

Three main observations from figure 3 & 4 are as follows:

1. These I-V characteristics do not follow the power law i.e. $I = kV^m$; where k and m are constants.
2. There is a decrease in resistance with the increase in temperature and voltage. A temperature dependence of conductivity is observed in bulk samples.
3. Material has higher resistance in the form of thin films than that of pellets (bulk).

All the above made observations could be explained in the following manner. In case, where the power law is not obeyed for the I-V characteristics, different mechanisms can be applied to understand the conduction process in such materials e.g. Fowler-Nordheim, Rechardson, Schottky-Rechardson and Poole-Frenkel mechanisms etc.

The resistance of the glassy pellets and thin films has been calculated by the slope of the I-V characteristics curves and the conductivity using,

$$\sigma = 1/\rho = (1/R)*(L/A) \qquad (1)$$

where symbols have their usual meanings.

First of all we will elaborate the observed I-V characteristics according to different conduction mechanisms to find the proper mechanism to explain these characteristics. The Fowler-Nordheim relation [8] for current density is

$$J = AV^2e^{-\phi/V} \qquad (2)$$

$$\text{So that, } \ln (J/V^2) = \ln A - \phi/V \qquad (3)$$

where the basic idea is that quantum mechanical tunneling from the adjacent conductor into the insulator limits the current through the structure. According to eq. (3) the ln (J/V^2) vs 1/V is expected to be linear with negative slope. Figure 5 shows the plot of ln (J/V^2) vs 1/V for $Se_{81}Te_{15}Sb_4$ glassy pellet. These plots are very near to straight line with positive slope, indicating that there is no tunneling current in the samples as suggested by Fowler-Nordhiem relation.

Rechardson current voltage relationship is given as:

$$J = AT^2 \exp(-\phi/kT + \beta E^{1/2}) \qquad (4)$$

where the symbols have their usual meanings and hence the plot of ln (J/T^2) vs 1/kT should be straight line with negative slope. Figure 6 shows the plot between ln (J/T^2) and 1/kT for $Se_{81}Te_{15}Sb_4$ glassy pellet at different voltages, which does not appear to be straight line, and is indicative of the fact that the mechanism in these glassy samples does not obey the Rechardson's mechanism.

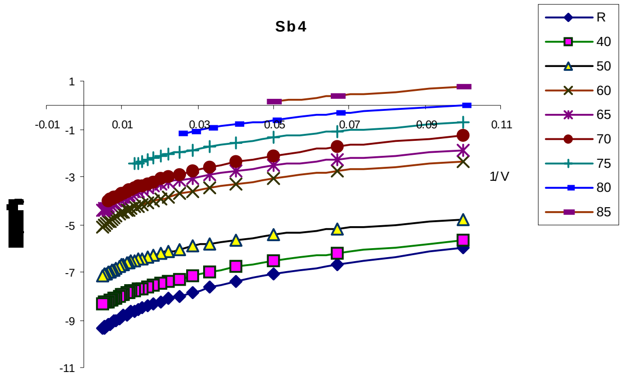

Fig. 5. Disagreement with Fowler-Nordheim mechanism.

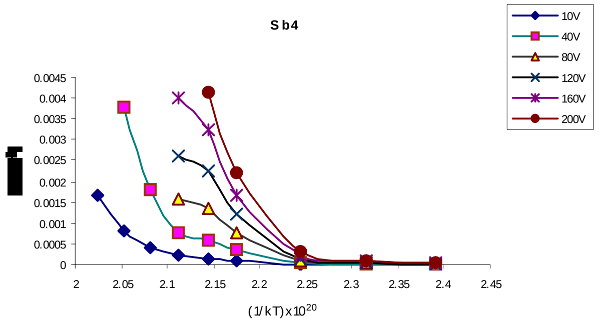

Fig. 6. Disagreement with Richardson mechanism.

The temperature dependence of the current density may be given in the form of plots between ln (J) and T. Figure 7 shows that these plots are not straight line which is suggestive of the fact that the conduction mechanism is not in good agreement with Schottky-Rechardson mechanism. The non-linearity of these plots indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature. In figure 7 curves show linearity near to room temperature and as the temperature increases towards a particular value (glass transition temperature), as mentioned above, these curves show a trend towards some saturation. The process of glass transition is a endothermic process and material absorbs heat to complete this process. Therefore, as soon as, our experiment enters into vicinity of glass transition, the effect of increasing current diminishes. This is due to the heat absorbed by the material in glass transition process increases the resistance, resulting a saturation in ln(J) vs T plots in the said temperature range. As this temperature range of glass transition is over, the curves show the increasing behaviour of current due to decrease in resistance of the material. This decrease in the resistance is caused on account of liberation of heat from the sample and hence decrease of heat contents of the material.

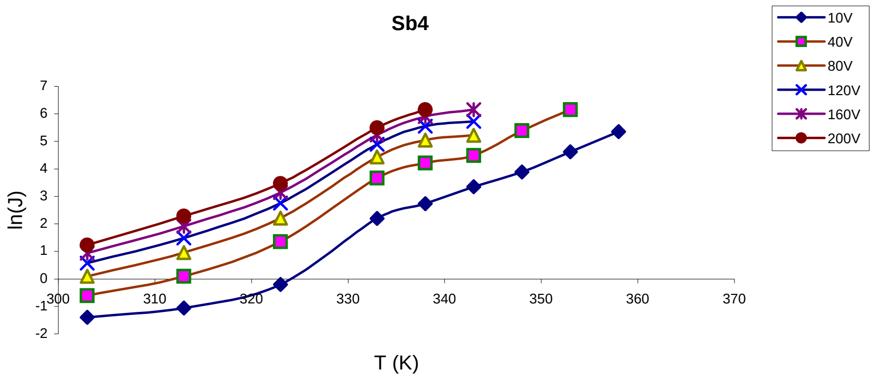

Fig. 7. Disagreement with Schottky-Richardson mechanism.

The relation between the current and the square root of applied voltage as given by Jonschere and Hill [9],

$$I = I_{PF} \exp (\beta V^{1/2}/kT) \tag{5}$$

$$\text{where, } \beta = (e^3/4\pi\varepsilon\varepsilon_0 d)^{1/2} \tag{6}$$

Eq. (6) has been used to plot variation of ln(I) with square root of applied voltage. Figure 8 shows the plot between ln (I) and $V^{1/2}$ for $Se_{81}Te_{15}Sb_4$ glassy pellet. These plots are linear with positive slope and this linearity is suggestive of the fact that the conduction mechanism in these glassy samples is of Poole-Frenkel type [10]. This linearity between ln (I) and $V^{1/2}$ is due to the absence of space charge resulting in a uniformity of field distribution between electrodes [11].The current in case of Poole-Frenkel effect will practically remain unchanged when polarities of electrodes are reversed. This is due to the fact that current does not depend upon the potential barrier at the interface. In case of thin films Poole-Frenkel conduction mechanism also holds good. Figure 9 shows the ln (I) vs $V^{1/2}$ plots for the thin films at room temperature for different compositions of Se-Te-Sb glassy system. The Poole- Frenkel 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 flow of current because of a capture and emission process, thereby becoming the dominant current mechanism.

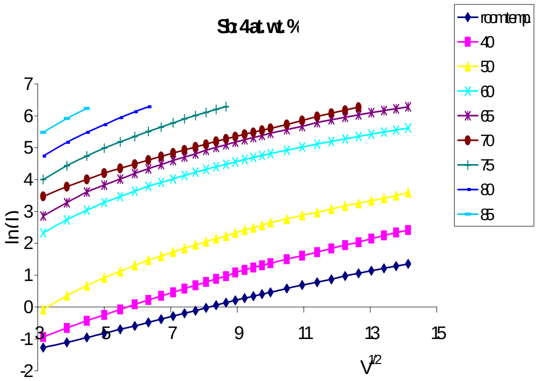

Fig. 8. Verification of Poole-Frenkel mechanism for $Se_{81}Te_{15}Sb_4$ glassy pellet as a representative case at different temperatures.

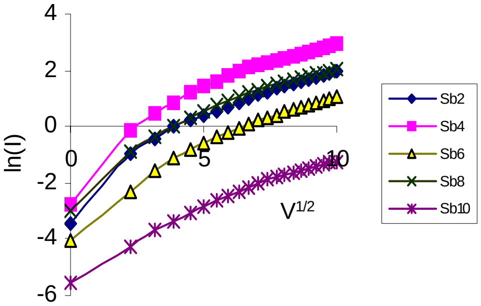

Fig. 9. Verification of Poole-Frenkel mechanism for $Se_{85-x}Te_{15}Sb_x$ *(x = 2, 4, 6, 8 & 10) glassy thin films at room temperature.*

Now we will discuss how this conduction takes place in amorphous materials. If we assume that a periodic structure of a crystalline material disarrayed and is concerted into glass; the conduction and valance bands may still exist but the disordered structure has two following effects:

1. Disorderness gives rise to a large density of states in the forbidden energy gap, which are localized at or near particular atomic sites. The density of these localized states is high near the band edges and decreases roughly exponentially with energy into the forbidden gap. These localized states act as traps for electrons and they may be regarded as originating from the small deviations in bond lengths and bond angles which perturbs the periodic structure of the crystal and lead to the disordered structure characteristics of a glass.
2. The deviations from periodicity decrease the mean free path of the carriers in the allowed bands. In allowed states near the edges of the bonds the mean free path may be reduced to the order of atomic spacing.

In thermal equilibrium the non-localized states in the conduction and valance bands and the localized traps will be occupied with their respective equilibrium number of charge carriers. An electron, say, which happens to be trapped can now migrate either by activation to the conduction band and eventual retrapping at some other site, or by direct hopping to another trap if there is one close enough.

These two processes are fundamentally different and glasses like chalcogenides there is evidence for both mechanisms occurring in appropriate circumstances. Thus the total conductivity in such materials is given as,

$$\sigma_{total} = \sigma_i + \sigma_h \tag{7}$$

where, σ_i is the intrinsic conductivity and σ_h is the hopping conductivity. The DC behaviour of these materials, for example, is similar in many ways to ordinary semi-conduction in semi-conductors and the present view is that the DC conduction involves carrier generation across a forbidden gap and migration via the allowed states just within the respective bands. Because of the small mean free path and frequent trapping of carriers, the mobility, and hence the conductivity, is lower than would otherwise be the case.

It is a well-established fact that glasses containing Se have a tendency to form polymerized network and the homopolar bond is qualitatively suppressed [12]. The structure of Se-Te system prepared by melt quenching is regarded as a mixture of Se_8 member rings, Se_6Te_2 mixed rings and Se-Te chains. A strong covalent bond exists between the atoms in the ring, whereas in between chains only the Van der Waal's forces are dominant [13]. The addition of a small amount of Sb (2 at. wt. %) to the Se-Te system leads to its entry into the cross-link chains and hence increasing the stability in the glass. This stability of the system increases upto 4 at. wt. % of Sb. Further increment in at. wt. % of Sb lowers the stability of the system. One can infer that the composition $Se_{81}Te_{15}Sb_4$ has maximum density of Sb-Se bonds. Since the stability and the conductivity are directly related, which is quite evident from figure 10. Figure 10 shows the composition vs conductivity plots at different temperatures for bulk samples. The same explanation also holds good for the case of thin films. Figure 11 shows the composition vs resistance plot for thin films of proposed glassy system at room temperature. At lower percentage of Sb the system contains $SbSe_{4/2}$ tetrahedral units dissolved in the matrix composed of Se- chains. With the increase of Sb content, glassy matrix becomes heavily cross-linked and the steric hindrance increases. The Se-Te bonds (bond energy 205.8 kJ/mol) [14] are replaced by Sb-Se bonds, which have higher bond energy (214.2 kJ/mol) favouring the increment in thermal conductivity as well as electrical conductivity. Further addition of Sb favours the formation of Sb-Sb bonds (bond energy 176.4 kJ/mol) thus reducing the Se-Sb bond concentration also resulting the decrement in electrical conductivity as well as thermal conductivity for bulk [11,14], because the unsaturated bonds, produced as a result of insufficient number of atoms in amorphous material [15], form defects in material. Such defects produce the localized states in the band gap of amorphous material, which causes the observed variation in resistance in case of thin films (Figure 11).

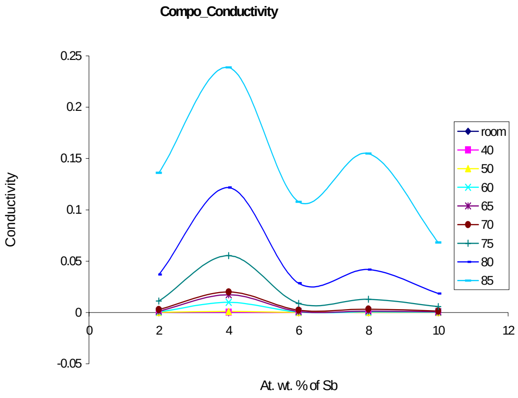

Fig. 10. Composition vs conductivity plots at different temperatures for pellets

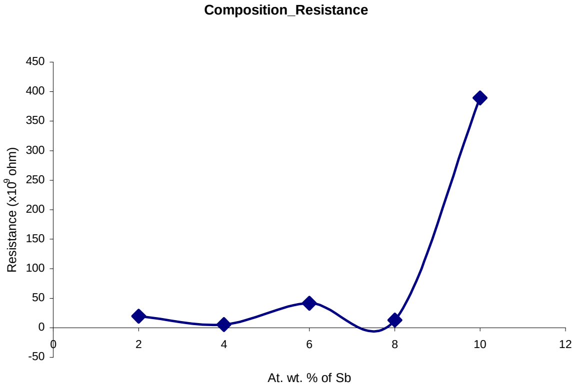

Fig. 11. Composition vs resistance plot at room temperature for thin films

Now we come to our second observation. Decrement in resistance is quite visible in figure 3 with increasing voltage and temperature for bulk samples and with increasing voltage in figure 4 for thin films. It is a strong support for the well-established fact that generally chalcogenide glasses are semi-conducting in nature. At higher voltages there may be two contributory factors for thermal effects in case of temperature dependence of pellets. One is due to the increasing temperature and second one is due to higher voltage induced thermal effects. Being the semi-conducting in nature I-V characteristics are not exactly linear.

Third and last observation for the present study, thin films are less conducting than that of bulk samples, can be attributed to the more surface defects and less thickness in thin films as compared to bulk samples. Defects act as scattering centers in the conduction process and it is quite clear form I-V curves, where the current in pellets is of microampere (μA) order and in thin films current is of the order of nanoampere (nA). One can infer that these two factors (surface defects and less thickness in thin films) decrease the current by 10^3 order of magnitude in thin films as compared with bulk pellets.

3. Conclusions

Taking into consideration the above discussion, it has been concluded that the conduction mechanism in these materials is of Poole-Frenkel type. The composition $Se_{81}Te_{15}Sb_4$ shows maximum dc electrical conductivity at all temperatures in bulk form. This composition is more thermally conducting against its counterparts reported in its thermal conductivity measurements elsewhere [14]. Role of surface defects in electrical conduction in thin films and more stability of material in bulk with higher current is suggestive of the fact that the use of material in appliances in bulk form with a proper composition as mentioned above (i.e. Sb 4 at. wt.%) has an advantage over thin films and hence it will be a potential candidate for electrical applications as compared to other counterparts of the present series. Keeping all these in view, here we coin this composition as “Magic Composition”.

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