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Electrical measurements of $Se_{85-x}Te_{15}Sb_x$ glasses

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Temperature dependence of *I-V* characteristics and *dc* conductivity of $Se_{85-x}Te_{15}Sb_x$ (where *x*= 2, 4, 6, 8 and 10) glasses in the form of thin pellets has been studied. The pellets have been prepared from the ingots of glasses in the powder form. It is quite evident from *I-V* characteristics that the glass containing 4 at wt % of Sb allow maximum current to pass through itself as compared to its other counterparts of the series. The linear relationship between ln (*I*) and $V^{1/2}$ strongly suggests the type of conduction as the Poole-Frenkel. The deviation from ohmic behaviour at lower voltages towards the non-ohmic behaviour at higher voltages is due to the additional thermal effects at higher temperatures induced in the sample. The electrical conductivity of these samples for the above-mentioned compositions using their *I-V* characteristics has been determined. The variations of electrical conductivity with composition at all temperatures show that $Se_{81}Te_{15}Sb_4$ glass has the maximum conductivity. This variation is explained using the bonding between Se and Sb at different compositions. Hence, the composition $Se_{81}Te_{15}Sb_4$ is more chemically ordered and electrically conducting as compared to other members of the series.

Keywords: Glass, Critical composition, Bulk, Se-Sb bonding, Poole-Frenkel conduction mechanism
IPC Code: G01R

1 Introduction

The current interest in chalcogenide materials centers on X-ray imaging[1] and photonics. The investigation of electrical and optical properties of Se based chalcogenide glasses have been a subject of interest for both researchers and electronic engineers for their applications as photovoltaics[2] and memory switching[3] materials. Many amorphous semiconductor glasses, especially Se, show a unique property of reversible transformation[4], which makes them very useful in optical memory devices. Moreover, they are interesting as core materials for optical fibers for transmission especially when short length and flexibility are required[5].

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 semiconductors[6]. The effect of impurity in an amorphous semiconductor may be widely different, depending upon the conduction mechanism and the structure of the material[7]. While in crystalline semiconductors the effect of a suitable impurity is always to provide a new donor or acceptor states, this is not essential in amorphous semiconductor[8]. 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[9] 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 are a subject of great interest, because the results of such studies provide ways to control effectively the conductivity of amorphous semi-conductors. So, the present work incorporates the study of temperature dependence of *I-V* characteristics and *dc* conductivity of $Se_{85-x}Te_{15}Sb_x$ (where *x*= 2, 4, 6, 8 and 10) glasses along with their composition dependence in thin pellet form.

2 Experimental Details

Bulk $Se_{85-x}Te_{15}Sb_x$ (where *x*= 2, 4, 6, 8 and 10) glassy materials were prepared using the well-established melt-quenching technique. The details

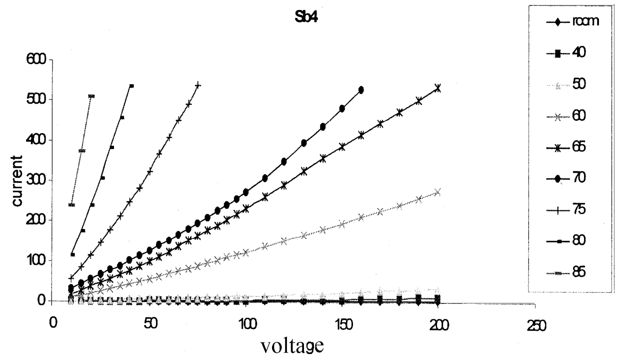

Fig. 1—*I-V* characteristics of $Se_{81}Te_{15}Sb_4$ glass

about sample preparation and characterization have been discussed elsewhere[10].

3 Results and Discussion

The typical *I-V* characteristics were recorded at different temperatures (room, 40, 50, 60, 65, 70, 75, 80 and 85°C) in order to investigate the temperature and composition dependence of the *dc* electrical conductivity of samples. It is quite evident from *I-V* characteristics that at lower voltages the curves show the ohmic nature while at higher voltages the curves deviate from linearity i.e. they tend to show non-ohmic behaviour. Fig. 1 shows the *I-V* characteristics at different temperatures for 4 at wt % of Sb content in Se-Te-Sb system.

One can infer that the composition $Se_{81}Te_{15}Sb_4$ allows the maximum current flow or in other words one can say that it has maximum conductivity as compared to other counterparts of this series. It is also clear that with the increasing voltage, the resistance is decreasing. The resistance could be calculated by the slope of *I-V* characteristics. One can observe the decreasing nature of resistance with respect to increasing temperature, by which it is inferred that the conductivity is increasing with the increase in the temperature, showing the semiconducting nature of these samples.

The conduction mechanism in the sample under test can be divided into two parts, out of which first can be related with the composition dependence and second can be related with temperature dependence of conductivity. It is well-established fact that electrical conduction can take place by means of two parallel processes *viz* band conduction and hopping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states at high temperatures. The excitation of the carriers into localized states at band edges causes the hopping conduction[11]. It is known that unsaturated bonds are produced as a result of insufficient number of atoms in the amorphous material[12]. These bonds are responsible for the formation of some defects in the material. Such defects produce localized states in the band gap of amorphous solid. Thus, the total conductivity is given by:

$$\sigma = \sigma_i + \sigma_h \quad \ldots (1)$$

where σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

Many researchers have established that in the glass containing Se, there is a tendency to form polymerized network and the homopolar bond is qualitatively suppressed[13]. 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 inbetween chains only the Vander Waals forces are dominant[14]. 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 up to 4 at wt % of Sb and Se-Te-Sb glass containing 4 at wt % of Sb has been reported[15] as the most stable glass in the system. Further increment in at wt % of Sb lowers the stability of the system. 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[16] (bond energy 205.8 kJ/mol) 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. Figure 2 shows the composition dependence of electrical

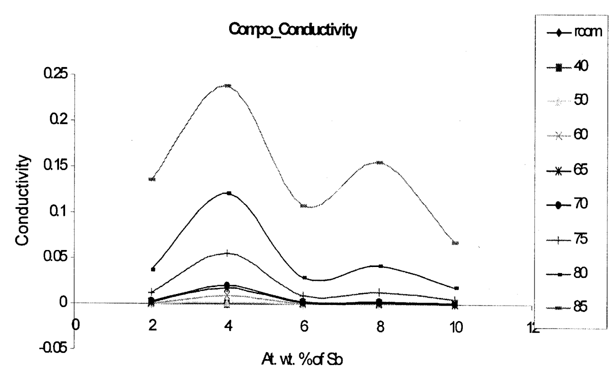

Fig. 2—Composition versus conductivity at different temperatures

conductivity for Se-Te-Sb glassy system for different temperature (from room to 85°C). It is clear that at all temperatures the system containing Sb 4 at wt % allows the maximum current flow. It could be inferred that composition $Se_{81}Te_{15}Sb_4$ is thermally stable for electrical conduction as compared to its other counterparts of the series. Also it has similar trend as for thermal conductivity plotted against the composition for Se-Te-Sb glassy system elsewhere[15].

Hence, this composition can be considered as a critical composition at which the system has maximum density of Sb-Se bonds. 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. However, at 8 at wt% of Sb in the Se-Te the electrical conductivity increases. This increase in electrical conductivity is nominal at room temperature as also seen in thermal conductivity measurement on the same sample[15] but increases sharply at higher temperature (~ 90°C). This might be due to the formation of some rigid structure at this concentration of Sb in Se-Te-Sb system. Besides the contributory factor of stronger bond, the effect of voltage applied, temperature and the induced thermal effects due to higher voltage also contribute to the electrical conduction in such type of materials[10].

The materials of different composition show the semiconducting nature, as the conductivity of semiconductor increases with increasing temperature. Fig. 2 shows the temperature dependence of the conductivity of different samples. It is also supported by the *I-V* characteristics of these samples (Fig. 1). At higher voltages, there may be two contributory factors for thermal effects. One is due to the increasing temperature and other is due to the higher voltage induced thermal effects. Due to these effects, *I-V* characteristics are changing their behaviour in the higher voltage regions, showing the non-ohmic behaviour. The relation between the current and the square root of applied voltage as given by Jonschere and Hill[17] is:

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

where, $\beta = (e^3/ 4\pi\epsilon\epsilon_0 d)^{1/2} \quad \ldots (3)$

ϵ_0 is the permittivity of the space, ϵ the relative permittivity of the sample, d is the inter spacing between filled and empty sites (jump distance) and I_{PF} (at V=0) is given by:

$$I_{PF} = I_0 \exp (-\phi / kT) \quad \ldots (4)$$

where, ϕ is the trap depth and

$$I_0 = Anedv \quad \ldots (5)$$

In Eq. (5), A is the electrode area, n the carrier concentration and e the electronic charge and υ is the phonon frequency, respectively[18].

One can obtain linear plot between ln (I) and $V^{1/2}$, which suggests that the conduction mechanism in such materials is of Poole-Frenkel type[19]. Fig. 3 shows the plot between ln (I) and $V^{1/2}$ for $Se_{81}Te_{15}Sb_4$ glass as representative case in this proposed study.

This linearity could be due to the absence of space charge resulting in a uniformity of field distribution between electrodes. The current in case of Poole-Frenkel effect remains 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. 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 current flow because of a capture and emission process, thereby becoming the dominant current mechanism.

4 Conclusion

The slight non-linearity of *I-V* characteristics of $Se_{85-x}Te_{15}Sb_x$ (where x= 2, 4, 6, 8 and 10) glassy materials indicate that these characteristics do not follow the power law $I = kV^m$, where k and m are constants. This variable rate of increasing current is an evidence for: (a) the increment in current with increasing applied voltage at a constant temperature, and (b) the increment in current with the increment in temperature at a constant voltage. It is a strong support

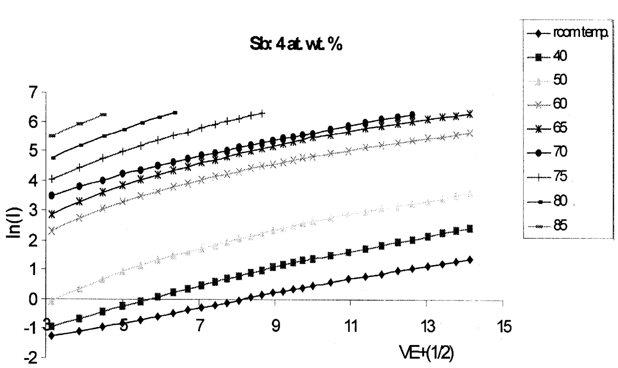

Fig. 3—$V^{1/2}$ versus ln(I): verification of Poole-Frenkel conduction mechanism for $Se_{81}Te_{15}Sb_4$ glass

of the materials to be semiconducting nature and hence the conduction mechanism is discussed qualitatively in terms of Poole-Frenkel effect. Also, the linear relationship between ln (I) and $V^{1/2}$ confirms this type of conduction mechanism. The composition versus conductivity plots are suggestive of the fact that composition $Se_{81}Te_{15}Sb_4$ is the magic composition allowing maximum current and also has been reported as most stable composition in thermal conductivity experiments[15], hence, become the most thermally stable for electrical conduction. This composition will be useful for their electrical applications bearing more temperatures (to be degraded) as compared to other members of the series.

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