Conduction mechanism and defect density of states in amorphous $Te_{15}(Se_{100-x}Bi_x)_{85}$ glassy alloys

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The present paper reports the dc conductivity measurement up to 100 V for pallets of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at %) glassy alloys in temperature range (303-343 K). The dc conductivity is calculated from the I-V characteristics curves of the pellets of bulk samples prepared by melt quenching technique. The samples obey Ohm's law in the lower (0-25 V) voltage range whereas the behaviour in the higher (25-100 V) voltage range is non-ohmic. The experimental results for all the samples fit well with the theory of space charge limited conduction SCLC for uniform distribution of localized states in the mobility gap. The density of defect states is calculated for the glassy alloys and is found to increase with Bi content. The increase in defect density of states can be explained on basis of electro negativity difference of Bi as compared to host elements. The increase in dc conductivity is probably due to Se-Bi bond concentration in the Se-Te-Bi glasses.

Keywords: Chalcogenide glasses, Space charge limited conduction, Localized states, Density of states

1 Introduction

The chalcogenide glasses are formed when chalcogen elements S, Se and Te are doped with elements such as Bi, Ge, Sb and Ga etc.[1] These materials have applications such as optical fibre memory devices, reversible phase change optical recording materials and memory switching[2-5]. Chalcogenide glasses are mostly selenium based because of its glass forming ability, unique property of reversible transformation and applications like switching, optical memory and xerography etc.[6, 7]. Pure Se has disadvantages such as short life time and low photosensitivity. These problems can be overcome by alloying Se with impurities atoms like Te, Ge, Ga, As etc.[8, 9]. It has been found that substitution of Te for Se breaks the Se_8 ring structure and slightly increases the chain fraction but reduces the chain length[10]. Se-Te glassy alloys have gained much importance because of their high photosensitivity, greater hardness, high crystallization temperature and smaller aging effects[11].

Addition of third element expands the glass forming area and also creates compositional and configurational disorder in the system. The energy band gap of the material plays an important role in preparing a device for a particular wavelength which can be modified by the addition of a dopant[12]. So, the influence of additive

on electrical properties has been an important issue in chalcogenide glasses. A systematic study of electrical properties of chalcogenide glasses provides useful information about the band gap, density of states, mechanism of conduction, type of dominant charge carriers, recombination kinetics and defect states etc. of the material[13,14]. We have chosen Bi as the third element because it produces remarkable changes in the optical and thermal properties of the Se-Te glasses, decreasing the optical band gap[15] and increasing the glass transition temperature[16]. The density is found to increase indicating the increase in rigidity and hence density of defect states[17]. Further, the addition of Bi to Se-Te glasses changes the conductivity from p type to n type[18-21]. The investigation of density of defect states (DOS) is of interest because of its effect on electrical properties of glassy semiconductors. The common feature of these glasses is the presence of localised states in the mobility gap because of the absence of long range order and various inherent defects. The significant localised states in mobility gap in chalcogenide glasses are the D^+ and D^- states[22]. The density of states can be found using different methods. One of the most direct methods for measuring DOS is measurement of space charge limited conduction (SCLC). In chalcogenides glasses, the DOS reported by various workers is of the range[23-27] 10^{12} to 10^{17} $eV^{-1}cm^{-3}$. The present paper reports the SCLC measurements in Se-Te-Bi glassy alloys.

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2 Experimental Procedures

Bulk multicomponent glassy materials Te_{15} $(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4 at. %) have been prepared by the melt quenching technique. Selenium, Tellurium and Bismuth of high purity (99.999 %) were weighed according to their atomic percentages and were sealed in cleaned quartz ampoules of length 10 cm and internal diameter 0.8 cm at a vacuum of 10^{-3} Pa. The ampoules were kept in a vertical furnace and heated to a temperature of 1073 K at a heating rate of 3-4 K/min. The ampoules were heated at this temperature for 12 h. During heating the ampoules were frequently rocked to make the melt homogenous. The quenching was done in ice cold water. The ingots of glassy materials were obtained after breaking the ampoules. The ingots were grinded to get the powder of the materials. The pellets of thickness 1 mm were made from the powder by applying a load of 5 tons. For the measurement of the I-V characteristics the samples were mounted in a specially designed sample holder, in which a vacuum of 10^{-3} Pa was maintained throughout the measurements. The pellets were coated with silver paste on both sides to confirm good electrical contact with the electrodes of the sample holder. A dc voltage (0-100 V) was applied across the sample and the resulting current was measured by a digital picometer (Keithley, model 6487) for a temperature range 303-343 K.

3 Results and Discussion

The I-V characteristics of glass alloys were recorded in the voltage range (0-100 V) and temperature range (303-343K). The I-V graphs for all compositions at temperature 303 K are shown in Fig. 1. The curves show linear behaviour in the voltage range (0-25 V) and in the higher voltage r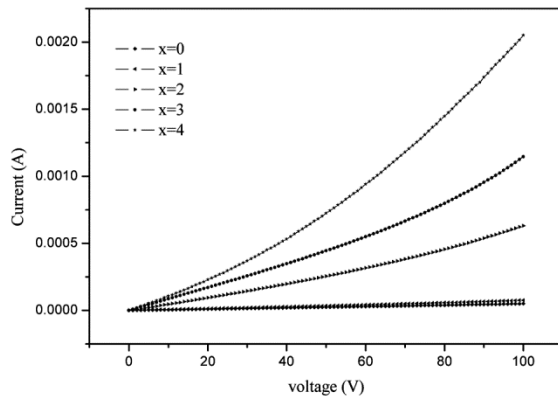ange there are deviations from the linearity means the samples show non ohmic behaviour. The resistance of the samples was found from the slope of I-V curves and reported in Table 1. It has been observed that the resistance goes on decreasing in the higher voltage range. The dc electrical conductivity of the samples in ohmic region was calculated using the relation:

$$\sigma_{DC} = \frac{1}{\rho_{DC}} = \left(\frac{1}{R}\right)\left(\frac{L}{A}\right) \qquad \text{... (1)}$$

Where, R is resistance, L is thickness and A is area of cross-section and ρ_{DC} is the resistivity of the glassy pellets. The values of dc conductivity for all the samples in the different voltage ranges are given in Table 1. The electrical conduction can take place by two parallel processes: (i) by band conduction and (ii) by hopping conduction in the localized states.

The band conduction occurs in the high temperature range. In this mode the carriers excited beyond the mobility edges into the localized states dominate the transport whereas in the hopping conduction the carriers excited into the localized states at the band edges dominate the transport[28]. The total conductivity is:

$$\sigma = \sigma_i + \sigma_h \qquad \text{... (2)}$$

σ_i is the intrinsic conductivity and σ_h is the hopping conductivity. As pointed earlier the behaviour upto 25 V is Ohmic but with further increase in voltage across the sample, the thermal effects may be induced resulting as increase in electrical conductivity. As a result the I-V characteristics change their behaviour towards the non-Ohmic region. The plots of ln(I/V) versus V are straight lines for all the samples at all the temperatures suggesting space charge limited conduction, SCLC, mechanism in the samples. According to this mechanism the current and voltage are related[29] by:

$$I = \left(eA\mu n_0 V / d\right)\exp\left(SV\right) \qquad \text{... (3)}$$

Where, d is the electrode spacing, n_0 is the density of thermally generated charge carriers, μ is the mobility, e

Fig. 1 — I-V characteristics of Te_{15} $(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at 303 K.

Table 1 — Resistance and dc conductivity values of Te_{15} $(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys at 303 K.

Composition	R ($\times 10^4\,\Omega$) (0-25 V)	R ($\times 10^4\,\Omega$) (25-100 V)	σ_{dc} $(\Omega\,cm)^{-1}$ (0-25 V)	σ_{dc} $(\Omega\,cm)^{-1}$ (25-100 V)
x=0	223	210	5.78×10^{-8}	5.82×10^{-8}
x=1	157	141	9.99×10^{-8}	1.04×10^{-7}
x=2	21.9	17.6	7.94×10^{-7}	8.02×10^{-7}
x=3	11.6	10.0	1.38×10^{-6}	1.44×10^{-6}
x=4	9.35	5.53	2.60×10^{-6}	2.67×10^{-6}

is electronic charge, A is area of cross section of the pallets. The slope S of these ln(I/V) versus V plots is given by:

$$S = 2\varepsilon_0\varepsilon_r / eg_o kTd^2 \qquad ... (4)$$

Where, g_0 is the density of localized states, DOS, near the Fermi level, ε_r is the relative dielectric constant of the samples. ε_0 is the permittivity of free space and k is the Boltzmann constant. Figure 2-4 shows ln(I/V) versus V plots for x=0, 1, 4. Similar, results are obtained for other samples as well.

The slope S of these graphs is found inversely proportional to temperature suggesting SCLC mechanism in all the samples. The DOS has been calculated using Eq. 4. The S versus 1000/T plots are shown in Figs. 5-6 for x=0 and x=3. Similar trends were observed for other samples. The values of dielectric constant of the samples have been measured using Impedance Analyser Wayne-Kerr 6500 B. The calculated values of DOS and relative dielectric constant are reported in Table 2. Due to dangling bonds the chalcogenide materials have large number of defect states which acts as carrier trapping centres. After trapping the injected charge from the electrodes these centres become charged and thus, build the space charge. When isoelectronic atom Te is added to
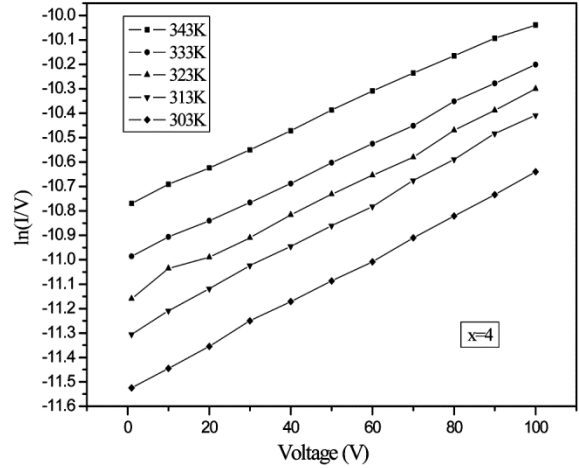

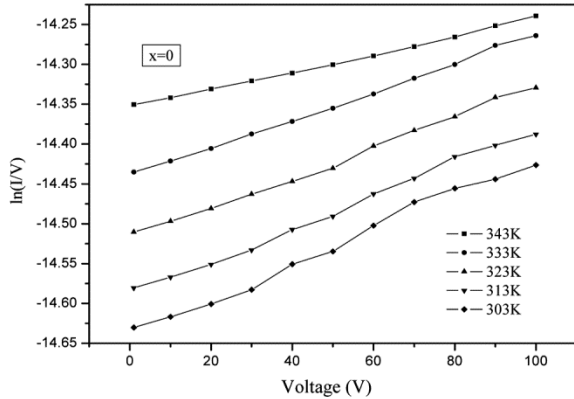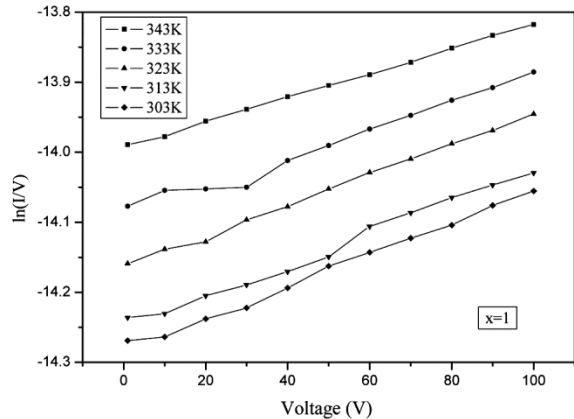Fig. 4 — Plot between ln(I/V) and V of $Te_{15}(Se_{100-x}Bi_x)_{85}$ for x=4.

Fig. 5 — Plot between slope S and 1000/T of $Te_{15}(Se_{100-x}Bi_x)_{85}$ for x=0.
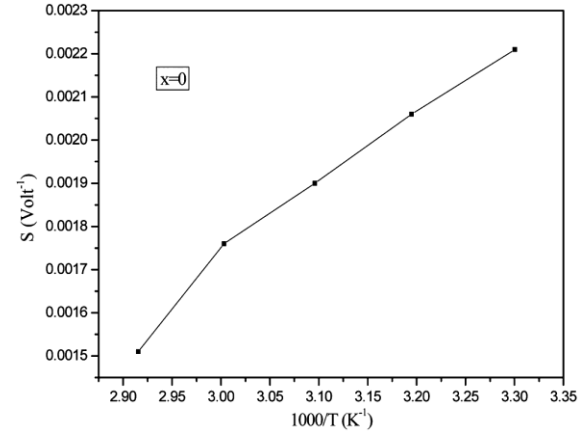
Fig. 2 — Plot between ln(I/V) and V of $Te_{15}(Se_{100-x}Bi_x)_{85}$ for x=0.

Fig. 6 — Plot between slope S and 1000/T of $Te_{15}(Se_{100-x}Bi_x)_{85}$ for x=-3.

Fig. 3 — Plot between ln(I/V) and V of $Te_{15}(Se_{100-x}Bi_x)_{85}$ for x=1.
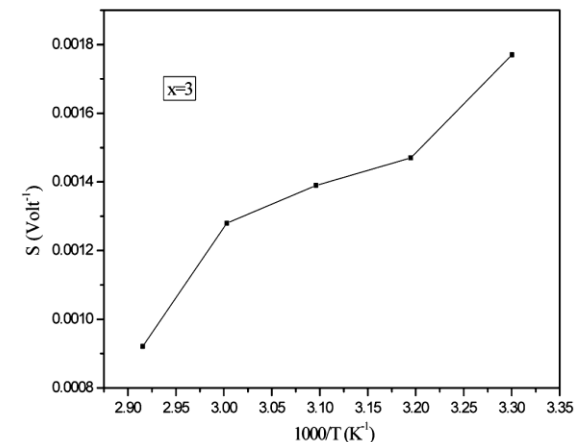
Table 2 — Dielectric constant and DOS of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys.

Composition	Dielectric constant (303 K, 100 kHz)	Density of states ($eV^{-1}cm^{-3}$)
x=0	5.15	9.91×10^{12}
x=1	6.10	1.17×10^{13}
x=2	23.97	4.61×10^{13}
x=3	28.33	5.45×10^{13}
x=4	40.92	7.87×10^{13}

amorphous Se, the DOS is increased. The results are explained on the basis of electro negativity difference of atoms involved[30]. Te being less electronegative (2.1) than Se (2.4) is assumed to form positive charged impurities. The addition of Bi to Se-Te system induces structural changes in the host network. Bi, being less electronegative (2.0) than Se, increases the concentration of positively charged defects which further increases the DOS with Bi addition in the samples.

4 Conclusions

The study of I-V characteristics of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0,1, 2, 3, 4 at.%) glass shows that the glasses exhibit both the ohmic and non-ohmic behaviour in the studied voltage range. The resistance of the glasses is found to decrease with increase in Bi content. The linearity of graph between ln(I/V) and V shows that the conduction mechanism is of SCLC type. The DOS for the samples were measured using space charge limited conduction mechanism. The DOS were found to increase with Bi concentration in all the samples. This is explained according to structural defect model based on electro negativity difference of Bi as compared to Se-Te.

Acknowledgements

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