JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Conduction process and estimation of defect density of states in $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4 at.%) amorphous semiconductors using AC conductivity measurements

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Abstract

The ac conductivity of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) amorphous glassy alloys in bulk has been studied using Wayne Kerr 6500B, impedance analyser at different temperatures and frequencies. The experimental results indicate that ac conductivity of samples is frequency dependent. The ac conductivity is found to increase with frequency of applied voltage obeying the ω^s law. Due to defects in the amorphous materials, a good density of defect states has been observed in the middle of the band gap. The defects in these materials probably arise as a result of under-coordination or over-coordination of atoms in the materials and are responsible for these states. These states can be analysed in terms of dangling bonds and valance alternation pairs. In the present paper the defect density of states in the band gap between the valence and conduction bands has been estimated. The correlated barrier hopping model (CBH) has been used to explain the frequency dependence of ac conductivity and estimation of density of defect states.

Key words: AC conductivity, amorphous materials, defect states, dangling bonds.

1. Introduction

Amorphous semiconducting materials containing pure S, Se and Te, generally called glassy alloys, have great potential in applications such as optical fibre memory devices, reversible phase change optical recording materials and memory switching [1-3]. The study of conduction mechanism in these samples reveal the presence of localised states in the band gap between the valance and conduction bands due to absence of long range order in amorphous materials. Good density of these states exists in the band gap due to defects like dangling bonds and valance alternation pairs in the glassy alloys [4,5]. Electronic picture of a material is governed by the distribution of density of electronic states. Recently, the study of electron transport in disordered systems has gradually been developed and the investigation of density of defect states is of interest because of their effect on electrical properties of glassy semiconductors. The significant localised states in mobility gap in amorphous glasses are the D^+ and D^- states [6]. The hopping conduction can be easily distinguished from that of band conduction by measuring the frequency dependence of ac conductivity. Therefore, the measurement of ac conductivity of amorphous glasses can be used to obtain information about these states. Amorphous 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. [7,8]. Generally, the pure Se show low values of electrical conductivity, which would mean a serious limit to its technological applications. Pure Se also 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. [9,10]. We have chosen Te as the second alloying element. 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 [11]. Se-Te glassy alloys have gained much importance because of their high photosensitivity, greater hardness, high crystallization temperature and smaller aging effects [12].

Certain more additives are used to improve the properties of the samples.The 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 [13]. So the influence of additive on electrical properties has been an important issue in amorphous glasses. A systematic study of electrical properties of amorphous 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 [14,15]. We have chosen Bi as the third element because it has produced remarkable changes in the optical and thermal properties of the Se-Te glasses. The optical band gap of Se-Te glasses decreases with Bi addition [16] and the glass transition temperature increases [17]. The density

is found to increase indicating the increase in rigidity and hence density of defect states [18]. Further, the addition of Bi to Se-Te glasses changes the conductivity from p type to n type [19-22]

The present work incorporates the study of effect of Bi addition on the ac conductivity, dielectric properties of the glassy pellets in temperature range (315-350K). From this study the defect density of states are calculated for these samples.

2. Experimental procedure

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, Telurium 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 hours. 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 amorphous nature was confirmed as no sharp peak was observed in their x-ray diffraction spectra (X-Pert PRO), Fig.1. The prepared glasses were grounded to make fine powder for DTA studies. The thermal behaviour of the samples was recorded using Shimadzu DTG-60 system. DTA thermograms for x=3 composition at different heating rates are shown in Fig.2. In each study approximately 20-25 mg bulk material was used. Four heating rates of 10, 15, 20 and 25 K/min were chosen for the present study to get glass transition temperature T_g.

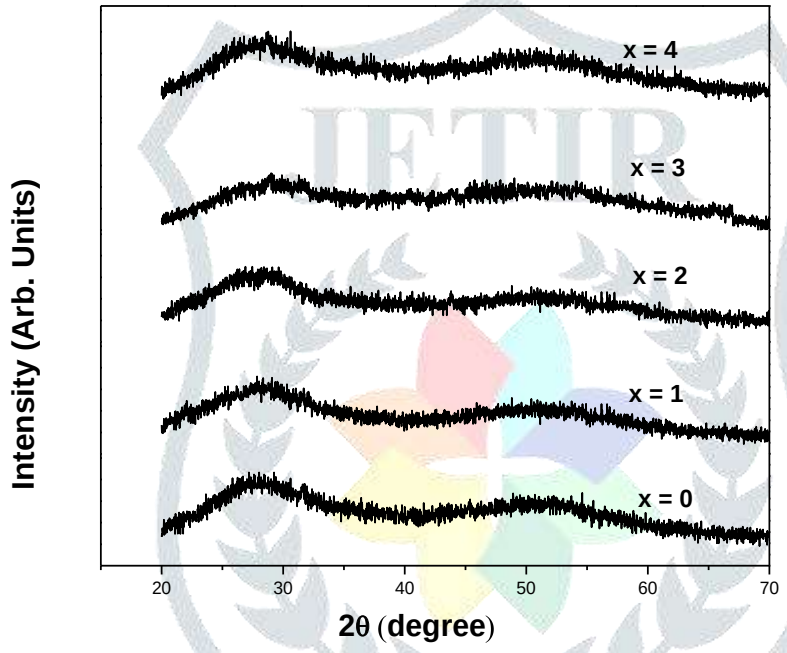


Fig. 1 X-ray diffraction profiles of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

The ingots were grinded in pestle and mortar to get the powder of the materials. The pellets were made from the powder by applying a load of 5 tons. An Impedance analyser (Wayne Kerr 6500B) was used for ac conductivity and dielectric properties measurements. The ac conductivity and dielectric constant of the pellets was measured in the frequency range 10 kHz to 100 kHz in temperature range (315-350K).

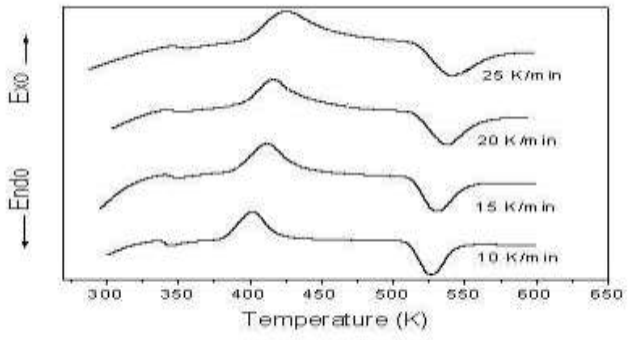


Fig. 2 DTA thermograms for $Te_{15}(Se_{100-x}Bi_x)_{85}$ glassy alloys for (x = 3 at%) at heating rates of 10, 15, 20, 25 K/min.

3. Results and Discussion

3.1Temperature dependence of a.c. conductivity:

The temperature dependence of a.c. conductivity was studied for all samples at different frequencies. Fig. 3 shows the plot of $\ln\{\sigma_{ac}(\omega)\}$ versus 1000/T for x=3. Similar trends are also observed for other compositions. The increase in a.c. conductivity with temperature suggests that a.c. conductivity like d.c. conductivity is thermally activated process. The a.c. conductivity is found to obey the equation

$$\sigma_{ac}(\omega) = \sigma_0(\omega)\exp\left(-\frac{\Delta E(\omega)}{K_B T}\right) \quad (1)$$

The ac activation energy $\Delta E(\omega)$ is calculated from the slope of $\ln\{\sigma_{ac}(\omega)\}$ versus 1000/T plot. The ac activation energy has been calculated and reported in table 1. It decreases with increase in Bi content in amorphous semiconductors.

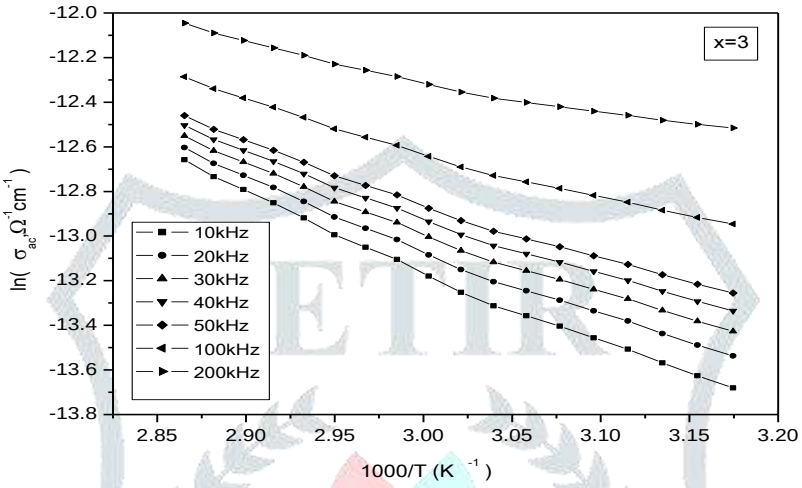
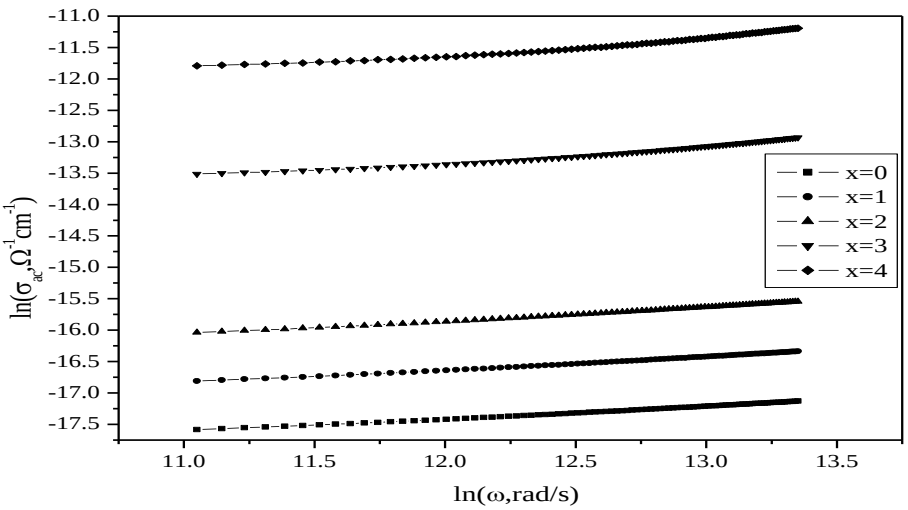


Fig.3 Temperature dependence of ac conductivity for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4at.%) at different frequencies.

3.2 Frequency dependence of a.c. conductivity:

There exist localized electronic states in the amorphous materials due to disorder in atomic configuration. As the charge carriers are localised the ac techniques are useful to probe their behaviour [23-25]. The ac conductivity measurements have been widely used to investigate the nature of defect centres in disordered systems since it is assumed that these are responsible for such type of conduction. The general behaviour in such type of materials is of $A\,\omega^s$ type over a wide range of frequencies. Where s is the frequency exponent. Values of frequency exponent *s* were calculated from the slope of straight line graphs between $\ln\{\sigma_{ac}(\omega)\}$ and $\ln(\omega)$, Fig.4. The frequency exponent *s* is found to be temperature dependent and has value less than 1. Various models have been formulated to explain this behaviour and classical approach has been used to explain the ac and dc conduction separately.
The Correlated Barrier Hopping (CBH) model [26] has been extensively applied to the glassy semiconductors. According to this model the conduction occurs via a bipolaron hopping process, where two electrons simultaneously hop over the potential barrier between two charged defect states (D^+ and D^-) and the barrier is correlated with the inter-site separation via a Colombian interaction. At higher temperatures, D^0 states are produced by thermal excitation of D^+ and D^- states and single polaron (one electron hopping between D^0 and D^+ states and a hole hopping between D^0 and D^- states) hopping becomes a dominant process



[27].

Fig.4 Frequency dependence of ac conductivity for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4at.%) at room temperature.

The frequency dependence of ac conductivity in semiconductors and other disordered systems is due to conduction in localized states. The almost straight line graph between $\ln\{\sigma_{ac}(\omega)\}$ and $\ln(\omega)$ suggest that the a.c. conductivity obeys the relation [28]

$$\sigma_{ac}(\omega) = A_0\omega^s \qquad (2)$$

where ω is the angular frequency, A_0 is a constant and *s* is the frequency exponent. The value of a.c. conductivity is found to increase with frequency for all compositions.

Fig. 4 shows frequency dependence of ac conductivity at room temperature for all compositions. The increase in ac conductivity with frequency has been ascribed to relaxation caused motion of electrons or atoms. Such motion can involve hopping or tunnelling between equilibrium sites. Determination of ac conduction mechanism means study of frequency exponent with temperature. The plot of frequency exponent with temperature for all compositions is shown in Fig.5.The calculated value of *s* lies between (0.16 and 0.95). The increase in *s* at low temperature indicate that small polaron tunnelling is the dominant mechanism where as correlated barrier hopping (CBH) is the conduction mechanism involved at high temperature [29]. The frequency dependence of a.c. conductivity can be explained on the basis of correlated barrier hopping model (CBH) [30, 31], according to which the electrons in the defect states hop over a Coulombic barrier given by

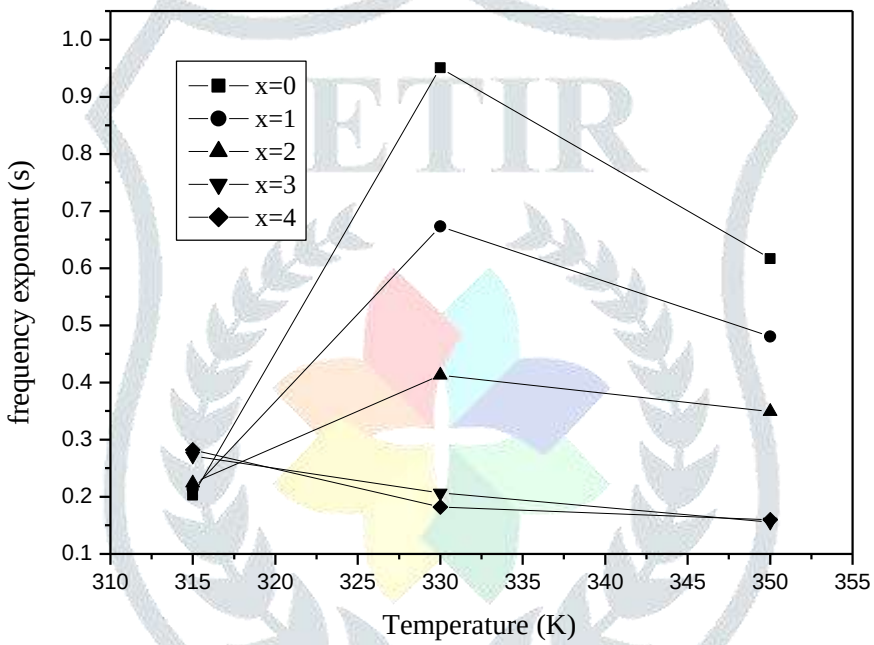


Fig.5 Temperature dependence of average value of frequency exponent for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4 at.%) amorphous glasses.

$$W = W_m - \left(\frac{ne^2}{\pi\varepsilon\varepsilon_0 r}\right) \qquad (3)$$

where *W* is the barrier height and its maximum value is W_m . ε is dielectric constant and ε_0 permittivity of free space and *r* is distance between hopping sites. The variation of dielectric constant with frequency for x=3 composition is shown in Fig.6 and the calculated values are recorded in table 1.

The relaxation time for electron hopping over the barrier as per CBH is given by

$$\tau = \tau_0 \exp\left(\frac{W}{k_B T}\right) \qquad (4)$$

where τ_0 is the characteristic relaxation time approximately of the order of vibrational time period of an atom. The ac conductivity is given by

$$\sigma_{ac}(\omega) = \frac{1}{6} n\pi^3 \varepsilon\varepsilon_0 N^2 \omega (R_\omega)^6 \exp\left(\frac{e^2}{4\pi\varepsilon\varepsilon_0 T_g R_\omega}\right) \quad (5)$$

N is the defect density of states, T_g is the glass transition temperature, reported in table 2, n=1 and 2 respectively for single and bipolaron hopping.

R_ω is the hopping distance and is given by [32]

$$R_\omega = \left(\frac{ne^2}{\pi\varepsilon\varepsilon_0 W_m}\right) \frac{1}{\left[1+\left(\frac{k_B T}{W_m \ln(\tau_0 \omega)}\right)\right]} \quad (6)$$

T is temperature below glass transition temperature and k_B is Boltzmann constant. For single polaron hopping the ac conductivity and R_ω are given by [33]

$$\sigma_{ac}(\omega) = \frac{1}{6} \pi^3 \varepsilon\varepsilon_0 N^2 \omega (R_\omega)^6 \quad (7)$$

$$R_\omega = \left(\frac{e^2}{\pi\varepsilon\varepsilon_0 W_m}\right) \frac{1}{\left[1+\left(\frac{k_B T}{W_m \ln(\tau_0 \omega)}\right)\right]} \quad (8)$$

The values of N^2 are calculated by adjusting the fit of theoretical curves to the experimental curves of $\ln\{\sigma_{ac}(\omega)\}$ versus 1000/T . The theoretical curve is a combined curve for single polaron n=1 and bipolaron n=2. The theoretical and experimental graphs between $\ln\{\sigma_{ac}(\omega)\}$ and 1000/T for x=3 are shown in Fig.7. The calculated values of *N* are reported in table 2.

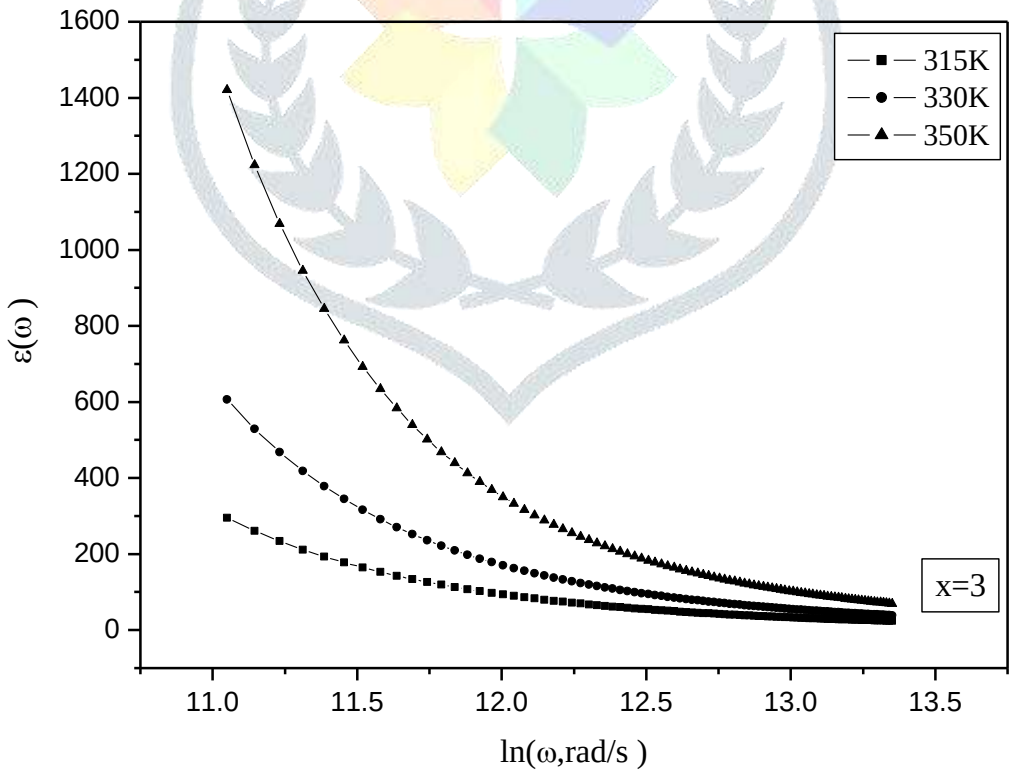


Fig.6 Frequency dependence of dielectric constant $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 3 at.%) amorphous glasses.

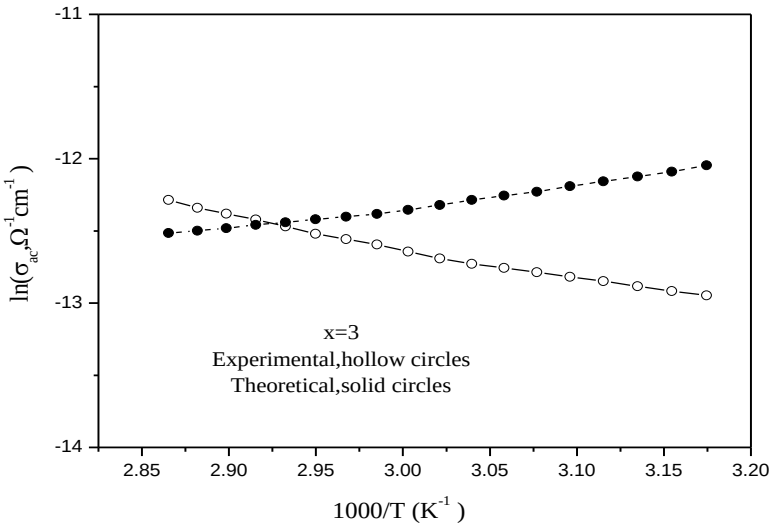


Fig.7 Experimental and theoretical plots of $\ln\{\sigma_{ac}(\omega)\}$ versus 1000/T for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 3 at.%) amorphous glasses.

Composition	ΔE (eV)	ε (315K,100kHz)	m (315 K)
X=0	0.68	5.15	0.2028
X=1	0.63	6.10	0.2135
X=2	0.54	23.97	0.2239
X=3	0.43	28.33	0.2713
X=4	0.35	40.92	0.2820

Table1 Values of activation energy (ΔE), dielectric constant (ε), and frequency exponent m for amorphous glasses $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4 at.%).

Composition	T_g (K)	N (cm^{-3})
X=0	341.15	$4.08X10^{13}$
X=1	342.11	$5.67X10^{14}$
X=2	343.17	$6.62X10^{14}$
X=3	344.19	$7.78X10^{14}$
X=4	345.10	$9.98\ X10^{14}$

Table 2 Values of T_g at the heating rate of 10 K/min and N for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

4. Conclusion:

The ac conductivity and the dielectric properties studied in the frequency range (10-100kHz) and temperature range (315-50K) are found to be frequency and temperature dependent for the $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4 at.%) glassy alloys. The ac conductivity increases both with temperature and frequency. The frequency dependence of ac conductivity suggests that the conduction is due to hopping conduction mechanism. The temperature dependence of frequency exponent implies that the CBH model is applicable to these samples. The dielectric constant is found to increase with temperature and decrease with frequency. The frequency and temperature dependence of dielectric constant are due to interfacial and orientational polarizability respectively. The defect density of states for these samples has been found by comparing the experimental and theoretical plots of a.c. conductivity versus temperature. The defect density of states increases with increase in Bi content in Se-Te host.

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