A.C. Conductivity of Ag Incorporated Se-Te-Bi Glassy Alloy

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Effect of Ag addition on the *a.c.* conductivity as a function of frequency in $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ ($y = 1.0$, 1.5 and 2.0 at. %) glassy alloy has been investigated in the temperature range 300-355 K. The electrical conductivity is measured as a function of frequency (ω) of an alternating electric field in the frequency range 1-500 kHz, using Wayne Kerr 6500 B Impedance Analyzer. *A.C.* conductivity $\sigma(\omega)$ is found to increases with an increase in frequency for the entire range of temperature in all compositions. The frequency exponent *s* is found to decrease with an increase in temperature which indicates that the correlated barrier hopping is the possible conduction mechanism in the investigated samples.

Keywords: A.C. conductivity, Chalcogenide glasses, Activation energy, Frequency exponent.

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1. INTRODUCTION

Multinary amorphous semiconducting materials are the subject of growing interest because they contain the characteristic features of disordered materials and some properties of crystalline semiconducting materials. These chalcogenide semiconductors possesses fast, accurate, low cost and quality device applications [1, 2]. They have been proposed [3-6] for prospective applications in photoelectronics, solid-state electrolytes for lithium secondary batteries and thermoelectric devices. These materials have numerous applications in optical memories, optical coating such as imaging, display, communication, sensing, manufacturing of anti reflection coating and filters [7-9] etc. The properties of chalcogenide glasses which depend on chemical composition are of special interest in considering the effect of average coordination number and the number of covalent bonds per atom [10]. The effect of impurity atoms in chalcogenide glasses depends upon the chemical nature of impurity, composition of the glass and the value of impurity concentration. The nature of defect centers in these glasses is supposed to be responsible [11] for the type of conduction mechanism in these materials. The chalcogenide glasses shows *p*-type conduction [12] based on the asymmetry of conduction and valance band. The disorder has larger effect on antibonding states than on non-bonding states which results in a deeper tail for the conduction band. However, the conductivity of chalcogenide glasses switches from *p* to *n* type due to the addition of Bi in Se-Te system [12-14]. From application point of view it will be useful to study the affect of metal impurities on the properties of Se-Te glasses. The addition of an impurity like Bi, Sn, Sb, Ag, etc. to this alloy is found to improve its various properties like higher glass transition temperature, higher crystallization temperature and thermal stability [15-17]. The optical and electrical data available suggest that the addition of Bi produces localized states near the conduction band edge so the electrical properties are influenced by the hopping of electron in the localized states at the conduction band edge. It is found that Ag diffuses easily in the chalcogenide system by bridging the chalcogenide chains and makes the system stable [18]. Addition of Ag results in various structural changes in the materials which in turn modify the band structure and hence electrical properties due to its ionic nature. Ag containing chalcogenide glasses have attracted much attention in glass science and technology due to their potential device applications in chemistry, optoelectronics, biology and in optics [19-21]. They can be used as optical memory, holography and membranes of sensors for potentiometric determination [19, 22-24].

In the present work we aim to study the effect of Ag on the electrical properties, especially, the a.c. conductivity of Se-Te-Bi semiconducting glassy alloys and to highlight some new features of these chalcogenide materials for their applications. The frequency and temperature dependence of A.C. conductivity is studied in the frequency range 1-500 kHz over the temperature range 300-355 K, using parallel impedance measurements. The A.C. conductivity $\sigma(\omega)$ as a function of frequency, at different temperatures, is found to increases with an increase in frequency whereas the frequency exponent *s* is found to decrease with an increase in temperature for all compositions. The correlated barrier hopping (CBH) model has been used to describe the temperature dependence of *A.C.* conductivity and the frequency exponent *s*.

2. EXPERIMENTAL DETAILS

The glassy alloys of $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ ($y = 0$, 1.0, 1.5 and 2.0 at. %) in bulk form were prepared by melt quenching technique. High purity (99.999 %) elemental substances were weighed according to their atomic percentages and were sealed in quartz ampoules evacuated to a vacuum of 10^{-5} Torr. The sealed ampoules were heated in a vertical furnace at an appropriate temperature of 1323 K for 15 hours by gradually increasing the

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temperature at the rate of 3-4 K·min^{-1}. The ampoules were rocked frequently during heating in order to ensure homogenization of the melt. The ampoules were quenched in ice cooled water to obtain the glassy alloy. The samples were taken out from the ampoules by dissolving the ampoules in HF + H$_2$O$_2$ solution for about 48 h. The amorphous state of the bulk samples was confirmed by X-ray diffraction as no prominent peak was observed in the spectra. The glassy alloy so prepared was grinded to a fine powder and the samples in the form of pellets of diameter about 10 mm and thickness between 1-2 mm were prepared by compressing the powder in a good quality steel die under a load of 5 tons. The pallets were coated, both sides, with air drying conducting silver paste in order to obtain the good quality contact with the electrodes of the sample holder. The coated pellets were mounted between two steel electrodes inside a specially designed sample holder which is connected to Wayne Kerr 6500 B Impedance Analyzer. To determine the *a.c.* conductivity of Se$_{80.5}$Bi$_{1.5}$Te$_{18-y}$Ag$_y$ alloys the impedance parameter *Z* and conductance *G* were measured in the frequency range 1 to 500 kHz at different temperatures ranging from 300 to 355 K. All the measurements are done in vacuum so as to avoid the effect of moisture on the dielectric properties. The measurements were done under identical experimental conditions for all the samples so that the results could be compared.

3. RESULTS AND DISCUSSION

In general, total measured conductivity at a given frequency, consisting of *D.C.* and *A.C.* components, can expressed as

$$\sigma_{Total}(\omega) = \sigma_{D.C.} + \sigma(\omega) \qquad (1)$$

The *A.C.* conductivity $\sigma(\omega)$, can be calculated by measuring total conductivity at a given frequency and then subtracting *D*.C. conductivity from it. In chalcogenide glasses the *D.C.* conductivity arises due to the band conduction by carriers in extended states beyond the mobility edge and $\sigma(\omega)$ arises due to the relaxation processes. If both *D.C.* and *A.C.* conduction are taking place then $\sigma_{D.C.}$ is simply given by

$$\sigma_{D.C.} = \lim_{\omega \to 0} t\sigma(\omega) \qquad (2)$$

$\sigma(\omega)$ in amorphous semiconductors increase monotonically with frequency and usually depends on temperature. The pure *A.C.* component of conductivity tends to dominate at high frequency or at low temperature. Generally, all amorphous semi-conductors exhibit frequency dependence of conductivity which increases almost linearly with frequency in a given range $10^2 < \omega < 10^8 \sec^{-1}$.

3.1 Frequency Dependence of A.C. Conductivity

The frequency dependence of *A.C.* conductivity in semiconductors and some disordered systems is expected due to the conduction in localized states [27]. The low temperature *A.C.* conduction can be explained by considering bipolaron hopping between D^+ and D^-
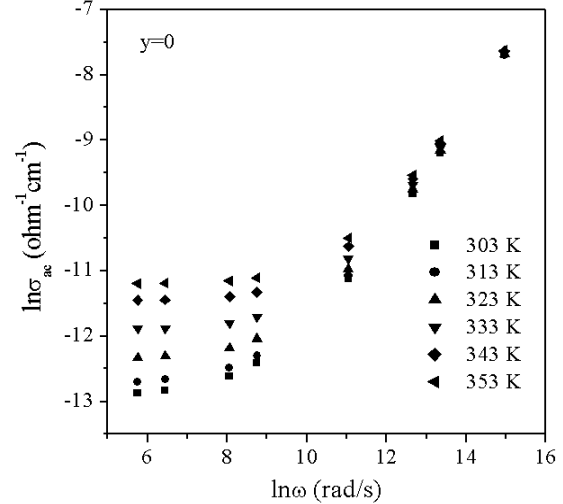

Fig. 1 – Variation of ln(σ) versus ln(ω) for Se$_{80.5}$Bi$_{1.5}$Te$_{18}$ glass at different temperatures
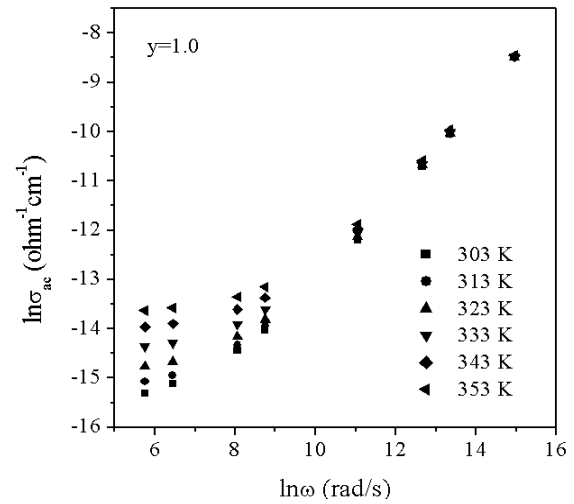

Fig. 2 – Variation of ln(σ) versus ln(ω) for Se$_{80.5}$Bi$_{1.5}$Te$_{17}$Ag$_1$ glass at different temperatures

centers whereas the higher temperature behavior is due to thermally activated single polaron hopping.

At higher temperatures a number of thermally generated D^0 centers are produced with a temperature dependent concentration [28]. The *A.C.* conductivity, $\sigma(\omega)$, in these materials is found to obey the relation.

$$\sigma_{A.C.}(\omega) = A\omega^S , \qquad (3)$$

In equation (6) s (≤ 1) is a frequency exponent and is given [29] as

$$s = \frac{d(\ln \sigma_{A.C.}(\omega))}{d \ln \omega} = 1 - \frac{6k_B T}{W_m} . \qquad (4)$$

Here, W_m is the maximum barrier height over which the electron hop, *T* is the absolute temperature and k_B is the Boltzmann constant.

The plots of the *A.C.* conductivity $\sigma_{A.C.}(\omega)$ as a function of frequency for the investigated compositions, at different temperatures, are shown in Fig. 1-4. Fig. 1-4 reveals that $\sigma(\omega)$ increases with an increase in frequency at different temperatures.
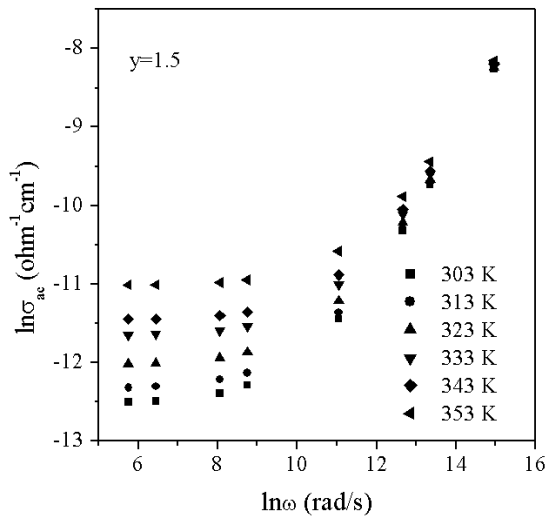
Fig. 3 – Variation of $\ln(\sigma)$ versus $\ln(\omega)$ for $Se_{80.5}Bi_{1.5}Te_{16.5}Ag_{1.5}$ glasses at different temperatures

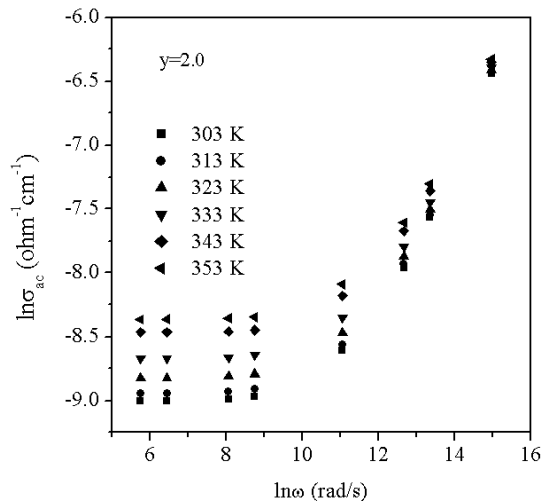**Fig. 5** – Variation of s with Temperature (K) for $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ $(y = 0, 1.0, 1.5$ and $2.0)$ glasses

355 K at different frequencies. The obtained *A.C.* conductivity $\sigma(\omega)$ as a function of temperature for different compositions is plotted in Fig. 6-9. Fig. 6–9, show that *A.C.* conductivity increases with an increase in temperature as well as with frequency for all compositions. This shows that the *A.C.* conductivity is a thermally activated process from different localized states in the gap or its tail. Our results for temperature dependence of *A.C.* conductivity are in agreement with the results reported for other amorphous materials [29, 34-35]. The compositional variation of $\sigma(\omega)$ as a function of temperature at a frequency of 1 kHz is shown in Fig. 10.

Fig. 4 – Variation of $\ln(\sigma)$ versus $\ln(\omega)$ for $Se_{80.5}Bi_{1.5}Te_{16}Ag_2$ glass at different temperatures

The values of frequency exponent s is calculated from the slope of the curves plotted between $\ln \sigma_{A.C.}(\omega)$ and $\ln(\omega)$. The mean value of the frequency exponent for all compositions is plotted as a function of temperature in Fig. 5. From Fig. 5 it evident that s lies between 0.20 to 0.75 and decrease with an increase in temperature. Our results for s are in agreement with the earlier reported results for other chalcogenide glasses [27, 29-33]. The variation of s with temperature indicates that the correlated barrier hopping (CBH) is the possible conduction mechanism in the investigated samples [28]. According to *CBH* model, the values of frequency exponent s should decreases with increase in temperature. Hence, our results show that the conduction mechanism in the system under study can be explained in terms CBH model.

3.2 Temperature Dependence of *A.C.* Conductivity and Activation Energy of Conduction

The temperature dependence of *A.C.* conductivity $\sigma(\omega)$ for $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ $(y = 0, 1.0, 1.5$ and $2.0)$ glasses is studied in the temperature range of 300 to
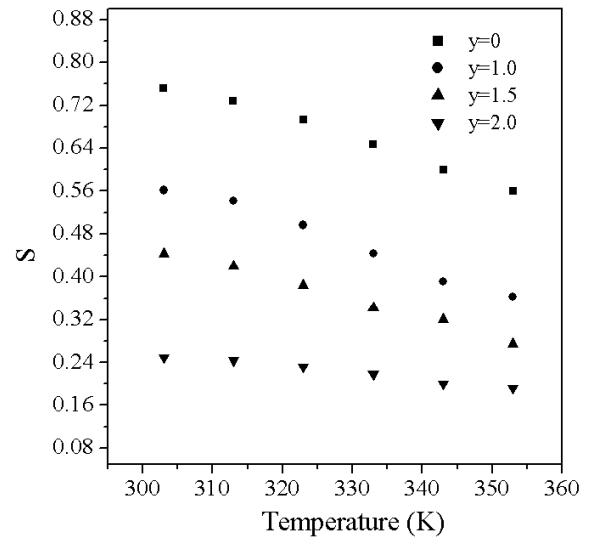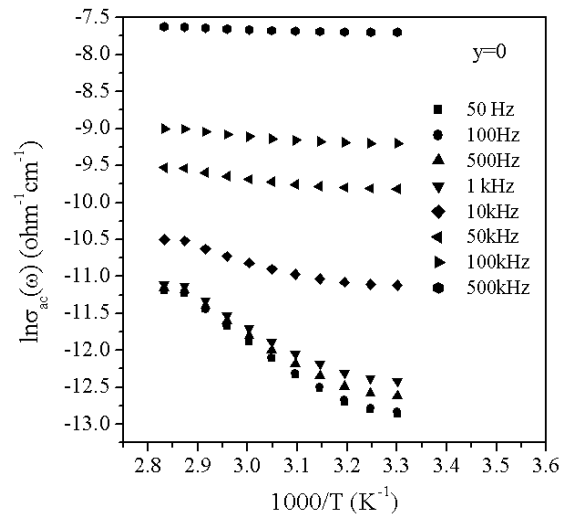

Fig. 6 – Variation of $\ln \sigma_{A.C.}(\omega)$ versus $1000 / T$ at different frequencies for $Se_{80.5}Bi_{1.5}Te_{18}$ glass

The *A.C.* activation energy of conduction for $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ glasses is calculated from the slopes of plots of $\ln \sigma_{A.C.}(\omega)$ versus $1000 / T$ by using well known relation [32]

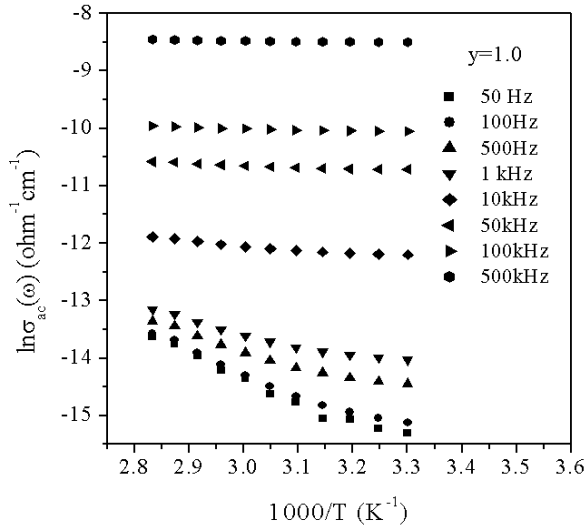$$\sigma(\omega) = \sigma_0(\omega) \exp\left[-\frac{\Delta E_{A.C.}(\omega)}{kT} \right] \qquad (5)$$

Fig. 7 – Variation of ln $\sigma_{A.C.}(\omega)$ versus $1000/T$ at different frequencies for $Se_{80.5}Bi_{1.5}Te_{17}Ag_1$ glass

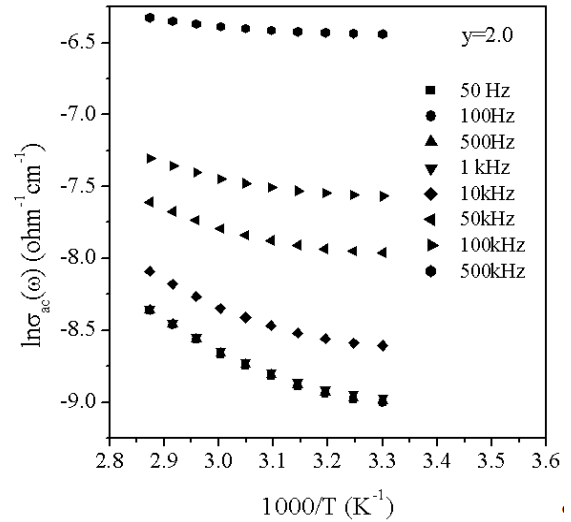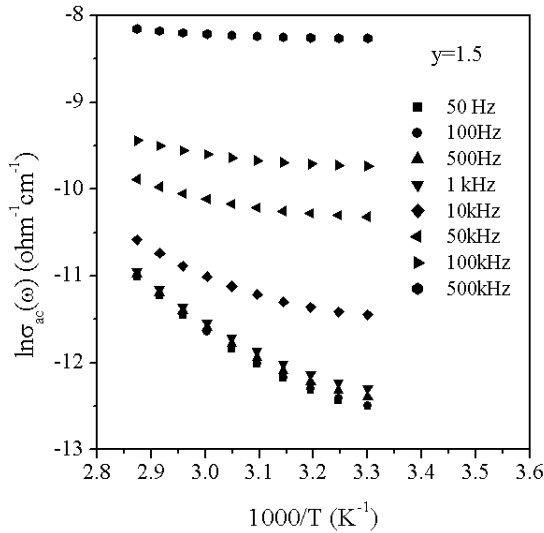**Fig. 9** – Variation of ln $\sigma_{A.C.}(\omega)$ versus $1000/T$ at different frequencies for $Se_{80.5}Bi_{1.5}Te_{16}Ag_2$ glass

Fig. 8 – Variation of ln $\sigma_{A.C.}(\omega)$ versus $1000/T$ at different frequencies for $Se_{80.5}Bi_{1.5}Te_{16.5}Ag_{1.5}$ glass

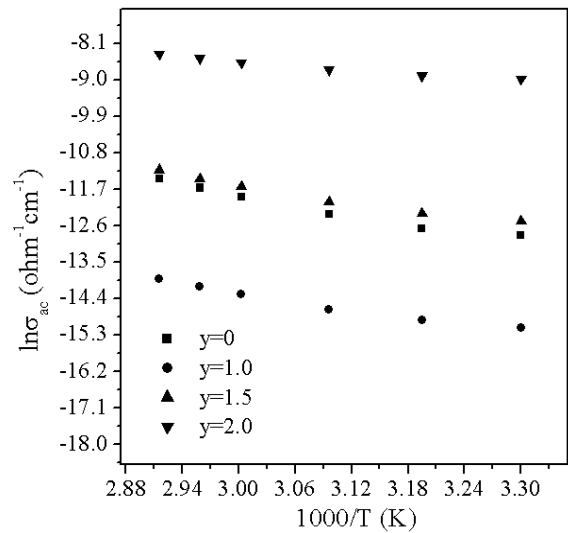**Fig. 10** – Variation of ln $\sigma_{A.C.}$ with temperature $1000/T$ in $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ glasses at 1 kHz

Table 1 – Values of activation energy $\Delta E_{A.C.}(\omega)$ at different frequencies for $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ glasses

Frequency	$\Delta E_{A.C.}(\omega)$			
	$Se_{80.5}Bi_{1.5}Te_{18}$	$Se_{80.5}Bi_{1.5}Te_{17}Ag_1$	$Se_{80.5}Bi_{1.5}Te_{16.5}Ag_{1.5}$	$Se_{80.5}Bi_{1.5}Te_{16}Ag_2$
50 Hz	3.37234	3.29806	2.97486	1.36003
100 Hz	2.94961	3.22515	2.95997	1.3584
500 Hz	2.0437	2.85743	2.79491	1.33799
1 KHz	1.61295	2.53763	2.64512	1.31188
10 KHz	0.56483	1.17601	1.63319	1.07895
50 KHz	0.2464	0.53787	0.79083	0.72308
100 KHz	0.17217	0.36606	0.53681	0.53233
500 KHz	0.08137	0.13485	0.19615	0.22927

here $\Delta E_{A.C.}(\omega)$ is the *A.C.* activation energy and $\sigma_0(\omega)$ is the pre exponential factor. The values of activation energy $\Delta E_{A.C.}(\omega)$ at different frequencies are reported in the Table 1.

It is found that a.c. activation energy $\Delta E_{A.C.}(\omega)$ decreases with an increase in frequency which is in accor-

dance with the earlier results [27, 36]. This decrease may be attributed to the increase in applied field frequency, which enhances the electronic jump between localized states. The obtained results of *A.C.* activation energy for the samples support the hopping conduction mechanism.

4. CONCLUSIONS

The effect of Ag incorporation on the *A.C.* conductivity has been studied in $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ ($y = 0$, 1.0, 1.5 and 2.0) alloys in the frequency range 1-500 *kHz* over the temperature range 300-355 *K*, using parallel impedance measurements. The temperature dependence of *A.C.* conductivity and the exponent *s* are discussed in terms of the correlated barrier hopping (CBH) model which indicates that *A.C.* conductivity $\sigma(\omega)$ is proportional to ω^s, $s < 1$ and decreases with increasing temperature.

A.C. conductivity $\sigma(\omega)$ as a function of frequency, at different temperatures, is found to increases with an increase in frequency for all compositions. The frequency exponent *s* is found to decrease with an increase in temperature which indicates that the correlated barrier hopping is the possible conduction mechanism in the investigated samples. The frequency dependence of *A.C.* conductivity and temperature dependence of *s* (frequency exponent) show that these glasses exhibit the hopping conduction type mechanism. Hence, correlated barrier hopping (CBH) model may be employed to describe the conduction mechanism in the investigated compositions.

ACKNOWLEDGEMENT

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