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Electrical conductivity of silver bismuth borate tellurite glasses

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Abstract

The AC electrical conductivity of $(Ag_2O)_x\,(Bi_2O_3)_{30}\,(B_2O_3)_{60-x}\,(TeO_2)_{10}$ glass ($x = 0$, 2, 4, 5, 10, 15 and 20) were measured at different temperatures and frequencies. The results obtained indicated that glasses containing silver < 5 mol% have values nearly approximately equal to AC electrical conductivity. A slight decrease was observed with increasing Ag_2O concentration up to 4 mol%. However, the AC electrical conductivity values increase with increasing silver content, i.e. $\geqslant 5$ mol%. The AC electrical conductivity values, increased with increasing frequency and follow the power law, $\sigma_{AC} = A\omega^s$. The frequency exponent s was found to be dependent on frequency and temperature. The s values tended to increase to unity as the temperature decreased. Such results suggest that the correlated barrier-hopping (CBH) model is appropriate for explaining the AC electrical conductivity in these glasses. A pronounced increase in the dielectric loss values was observed with increasing silver content. These reflect the effect of Ag^+ ions charge carriers on the electrical conductivity of such glasses.

Keywords: Conductivity; Silver bismuth borate tellurite; Glasses

1. Introduction

Heavy metal oxide glasses, e.g. Bi_2O_3, TeO_2 and PbO, have been studied extensively in the recent years. These glasses have wide range of applications because of their high refractive index, infrared transmission, non-linear properties, low melting temperature and high dielectric constant [1–4]. The electrical properties of glass depend not only on chemical composition and structural features but also on the degree of molecular order [5]. Tellurium oxide (TeO_2) is a conditional glass former [6] and forms glass only with a modifier such as alkali, alkaline earth and transition metal oxides (TMOs) or other glass formers. In a binary tellurite glasses, the basic structural unit of TeO_4 is the trigonal bipyramid (tbp) with lone pair of electrons and the structural units take the Te–O–Te bond for glass formation [7].

B_2O_3 is a typical glass former whereas Bi_2O_3 is a conditional glass former [8]. Singh [9] found that the electrical conductivity of Li_2O–B_2O_3–Bi_2O_3 glasses is ionic conductor when the Bi_2O_3 content is $\leqslant 20$ mol%. He attributed this behavior to the electronic conduction mechanism in semi conducting glasses as proposed by Souquet [10] takes into account a small polaron hopping. The hopping occurs between an occupied site (donor level) and an empty site (acceptor level). In case of transition metal oxide glasses, the d orbitals are involved. For Bi_2O_3 containing glasses, Bi^{3+} could be a donor and Bi^{5+} is an acceptor. If Bi_2O_3 content is $\leqslant 20$ mol%, only BiO_6, units (IR results) could be detected. These units are bonded together in micro-molecular chains and are accordingly of ionic nature. Beyond 25 mol% Bi_2O_3, the increase in the formation of BiO_3, units may give rise to a number of acceptor levels, which in turn enhances the polaron hopping and thereby increases the electronic part of conductivity. These results are in agreement with those observed in the case of V_2O_3, added to Li_2O–B_2O_3 [11]. Sanghi et al. [12] reported that in calcium bismuth borate glasses, the DC conductivity is found to decrease with the addition of Bi_2O_3 content up to 30 mol%, beyond which it increases. The initial decrease in conductivity could be interpreted in terms of the decrease in mobility and proportion of Ca^{2+} ions available for

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conduction, because Ca^{2+} ions may be interacting with $[BiO_6]^{3-}$ and $[BiO_5]^{2-}$ units. The conductivity in such glass is ionic with no contribution from electronic conductivity. Beyond 30 mol% Bi_2O_3, in such glass the electronic contribution to the total conductivity becomes relevant. For Bi_2O_3-containing glasses, a donor could be Bi^{3+} and an acceptor is Bi^{5+}. Beyond 30 mol% Bi_2O_3, the increase in BiO_3 units may give rise to a number of acceptor levels. Such an increase enhances the polaron hopping and thereby increases the electronic conductivity [9].

The present work was undertaken to obtain a comprehensive understanding of the influence of silver ions on the AC conduction of B_2O_3–Bi_2O_3–TeO_2 glasses and this was achieved by the dielectric constant (ε), the dielectric loss (δ) and the AC conductivity (σ) of glasses in this system in the frequency range 200–10^5 Hz and in the temperature range 298–645 K.

2. Experimental

2.1. Glass preparation

The $(Ag_2O)_x$ $(Bi_2O_3)_{30}$ $(B_2O_3)_{60-x}$ $(TeO_2)_{10}$ glasses with ($x = 0, 2, 4, 5, 10, 15$ and 20) were prepared by melting the appropriate mixtures of Analar grade Ag_2O, Bi_2O_3, H_3BO_3 and TeO_2 using in general alumina crucibles heated in an electric furnace open to the atmosphere. The mixture was heated first at 400 °C for 1 h in order to reduce any tendency toward volatilization and then transferred to another furnace which was held at 800 °C for 1 h. The glass melts were stirred occasionally with an alumina rod to achieve good homogeneity. The highly viscous melt was cast into a cylindrically shaped split-mold of mild steel. The glass produced was then annealed at 300 °C in a furnace for 1 h. Finally, the furnace was switched off and the glass was allowed to cool gradually in situ for 24 h. The glass samples were cut in the form of disks of 1 cm diameter and were ground and polished by usual techniques to a thickness of 0.2 cm for conductivity measurements.

2.2. AC conductivity measurements

The cell for the electrical measurements consists of a silica tube surrounded by nickel chrome wire as a heater. A (chromel–alumel) thermocouple (inside the tube) was used for temperature measurement. The cell was surrounded by metallic shielding to eliminate noise. The AC conductivity as measured by applying a complex impedance technique. A constant AC voltage (1 $V_{r.m.s}$) was applied to the sample and the current through the sample was determined by measurement of potential difference across an ohmic resistor using a lock-in amplifier (Stanford Research System SR510). The lock-in amplifier simultaneously measures the voltage across the resistor and the phase difference between this voltage and the applied voltage. The AC conductivity σ_{AC} was determined from the out of phase current. To overcome the effect of humidity, the electrical conductivities were measured under vacuum. The measurements were made from room temperature 298 to 645 K.

3. Results and discussion

The temperature dependence of the AC conductivity of the silver-free glass and the silver-containing glasses is shown in Figs. 1a and b. The AC conductivity was measured at temperature in the range 298–645 K and at a frequency in the range 0.2–100 KHz.

The AC conductivity of the silver-free glass and the silver-containing glasses up to 5 mol% Ag_2O, slightly increases as the temperature increases from room temperature to 495 K. A marked increase in the conductivity was observed beyond 495 K. Silver glasses containing more than 5 mol% Ag_2O show an obvious increase in the AC conductivity with increasing the temperature.

Fig. 2 plots the variation of the AC conductivity as a function of Ag_2O content of the glass. It is noted that the conductivity decreases and reaches a minimum value for glasses containing 4 mol% Ag_2O. Further Ag_2O additions were predicted to lead to a further decrease in the AC conductivity, but this is not the case. Fig. 2 shows that the conductivity increases with increasing Ag_2O content beyond 4 mol%.

The electrical conductivity of paratellutrite (α-TeO_2) at temperatures below 300 °C has been ascribed by different authors [13,14] to the presence of oxygen vacancies and to an electronic contribution. However, the AC and DC conductivity measurements showed that TeO_2 glass is ionic conductor when the modifier is a monovalent alkali oxide [15,16]. As mentioned before in calcium bismuth borate glasses, containing more than 30 mol% Bi_2O_3 an increase in the electronic conductivity was reported [12]. Montani et al. [17,18] studied the effect of the Ag_2O on the conductivity of vanadium tellurite and vanadium–molybdenum tellurite glasses in a wide range of temperatures. The obtained results confirm the existence of a transition from a typically electronic (polaronic) conductive regime when the molar fraction ($x<5$) of Ag_2O to an ionic conductive regime when $x>5$. This transition is characterized by a deep minimum in the electrical conductivity of about three orders of magnitude. They discussed two models to explain this transition in the conductivity. The first one was proposed by Bazan et al. [19] for sodium–molybdenum phosphate glasses, where a kind of interaction between ion and polaron was assumed. The argument is as follows: mobile electrons or polarons formed by the capture of the moving electron by a V (IV) atom are attracted to the oppositely charged Ag1 ions. This so formed cation–polaron pair tends to move together as a neutral entity. Then, the migration of these pairs does not involve any net displacement of charge, so this process does not contribute to the electrical conductivity.

The other explanation proposed has been given by Jayanasinghe et al. [20] for sodium vanadium tellurite

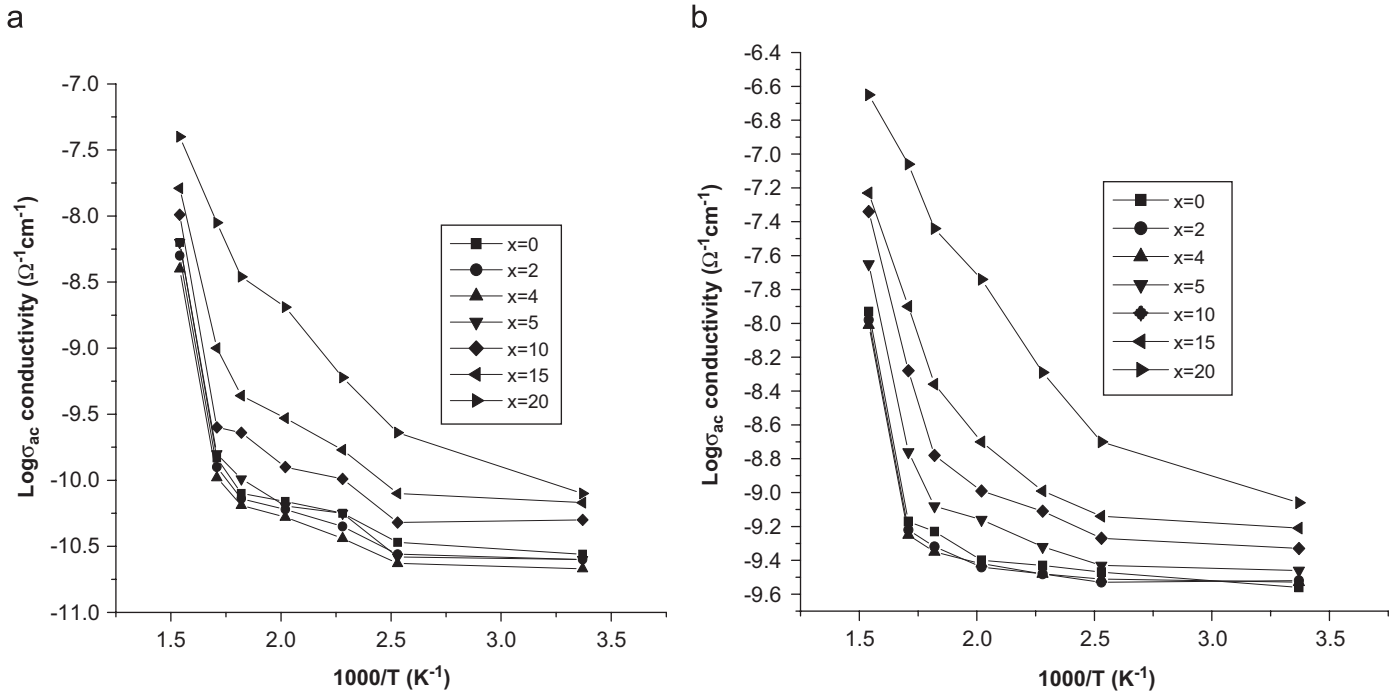

Fig. 1. (a) Variation of $\mathrm{Log}\,\sigma_{AC}$ conductivity with reciprocal of temperature at frequency (a) 200 Hz and (b) 60 kHz for several glass compositions (Ag_2O mol%).

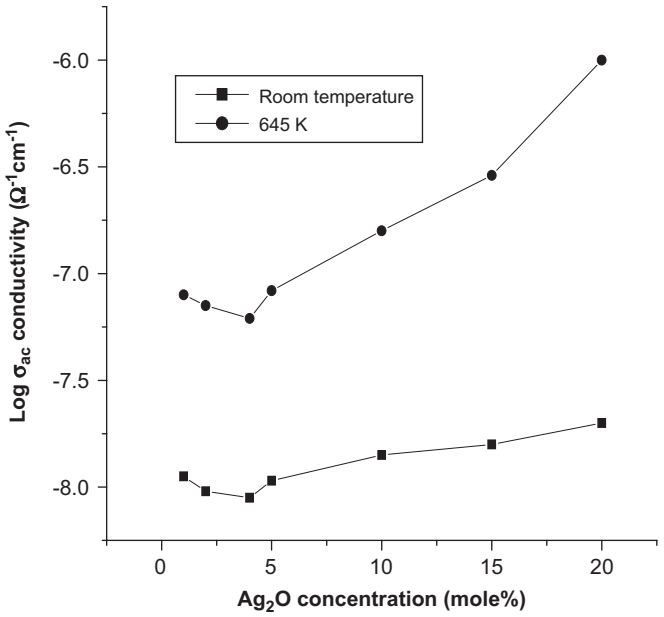

Fig. 2. Variation of $\mathrm{Log}\,\sigma_{AC}$ conductivity with Ag_2O concentration (mol%) at frequency = 60 kHz.

glasses, who suggested the existence of two kinds of independent migrating paths: one kind of path consisting of an electronic transfer in the chain (IV) V (V) and the other kind of path made by the regular position of non-bridging oxygen along the network-former chains allowing the ion displacement. So, when adding Ag_2O the electronic paths are progressively blocked, causing an inhibition of the electronic current. These two suggestions provide an explanation for the variation in the AC conductivity of silver bismuth borate tellurite glasses as a function of silver concentration in the glass Fig. 2. As mentioned before, it is well established for silver-free bismuth borate tellurite glass. The electronic conduction when adding the network modifier (Ag^+) up to 4 mol% Ag_2O, the electronic paths are progressively blocked causing the electronic conductivity to fall down. With further increase of Ag_2O content beyond 4 mol%, the active centers for ionic conduction, mainly formed by non-bridging oxygen, become closer and the ionic (cationic) transport starts and progressively increases. Consequently, the relative minimum in the AC conductivity, Fig. 2, reflects the change of the mechanism of the electrical transport process in these glasses with the variation of Ag_2O content from electronic to ionic.

The frequency dependence of AC conductivity for some studied glasses is presented in Fig. 3a–d, which shows that this type of dependence satisfies the universal empirical relation:

$$\sigma_{AC} = A\omega^s, \tag{1}$$

where A is the temperature-dependent constant and the frequency exponent s is $\leqslant 1$ [21]. It is noticed that the AC conductivity increases linearly with increasing frequency for all compositions on different isotherm.

The values of the exponent s (the slope of linear dependence of $\mathrm{Log}\,\sigma$ versus $\mathrm{Log}\,\omega$) are plotted as a function of temperature in Fig. 4, which reveals that the s values depend on the temperature and glass composition. The values of s are almost less than unity and decrease with temperature. The numerical values of s at room

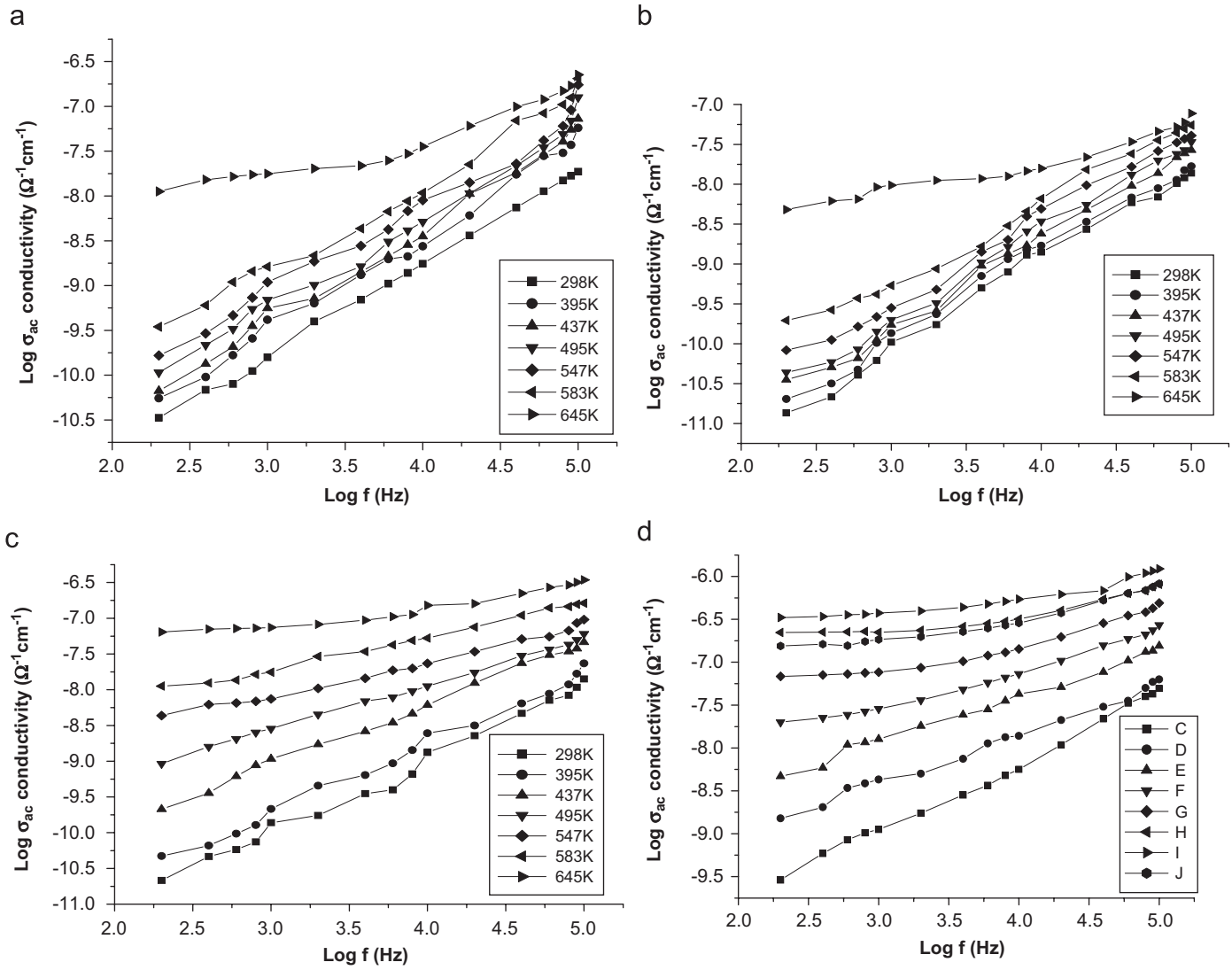

Fig. 3. (a) The relation between Log frequency and Log σ_{AC} (a) sample 1, (b) sample 2, (c) sample 6 and (d) sample 7.

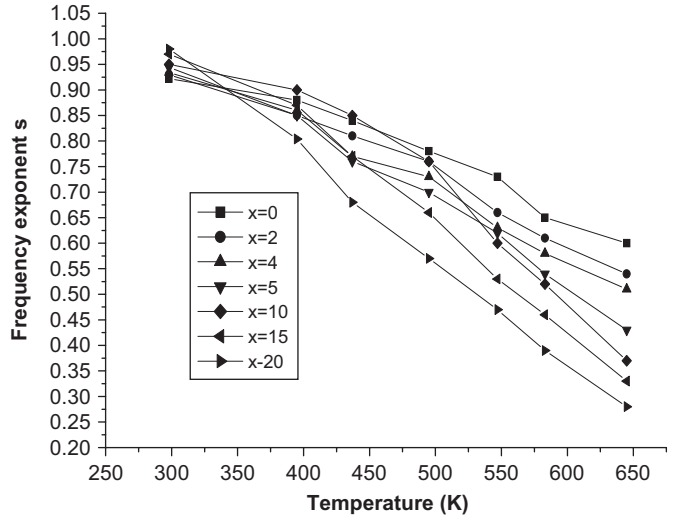

Fig. 4. Variation of frequency exponent s with temperature for several glass compositions (x = Ag_2O).

temperature are in the range $0.98 < s < 0.91$, Table 1, which are closely associated with proven carrier transport: hopping electrons [22]. It has been established that a value of s close to unity is to be associated with lattice responses [23]. The distinction between lattice and carrier responses corresponds to some impurities or injected carriers as a result of the existence of transition metal ions.

Elliot and Hen [24] suggested that evaluation of the s value is only possible at lower temperatures. They also stated that the s value increases with increasing concentration of carriers (i.e. sodium cations). This explains the increase of the s value with increasing concentration of Ag_2O in the glass as represented in Table 1.

The AC conductivity in many non-crystalline materials has been considered by many authors, and different models were proposed to account for its dependence on temperature and frequency. Owen [25] reported that the electrical properties of glass in a periodic field depend not only on the mobile ions (electrons or ions), which give rise to DC

Table 1
The calculated values of the frequency exponent s, the exponent β, the AC conductivity σ_{AC}, and the density of state N at room temperature and at a frequency of 200 Hz for the $Ag_xBi_5B_{85-x}Te_{10}$ ($x = 0, 2, 4, 5, 10, 15$ and 20) glass system

Ag_2O (mol%)	Exponent s	Exponent β	W_m (eV)	σ_{AC} ($\Omega^{-1}\,cm^{-1}$)	$N \times 10^{15}$
0	0.922	0.078	1.973	2.71×10^{-11}	2.625
2	0.935	0.065	2.199	2.51×10^{-11}	3.154
4	0.940	0.060	2.368	2.23×10^{-11}	3.363
5	0.944	0.056	2.749	2.39×10^{-11}	3.921
10	0.959	0.041	3.755	5.03×10^{-11}	6.898
15	0.968	0.032	5.132	6.76×10^{-11}	13.130
20	0.980	0.020	7.698	7.94×10^{-11}	20.362

conductivity but also on other relatively immobile ions or dipoles, which form part of the glass network. Polak and Geballe [26] proposed the quantum mechanical tunneling model to interpret impurity conduction in n-type silicon. In this model the exponent s is temperature independent but frequency dependent in contrast to the obtained results, Fig. 4. Hill and Jonscher [27] studied the AC conductivity in a wide range of materials, and reported that the exponent s typically coverd the range 0.5–1 at room temperature. Elliot [22] proposed the correlated barrier-hopping (CBH) model and applied it to glassy semiconductors. According to this model, barrier hopping of bipolaron (i.e. two electrons hopping between charged defects D^+ and D^-) has been proposed to interpret the frequency dependence of conductivity in glass. Thus electrons in the charged defect state hop over the columbic barrier whose height is given as W according to

$$W = W_m - \frac{4ne^2}{\varepsilon R}, \tag{2}$$

where W_m is the maximum height of energy of the energy band, ε is an effective dielectric constant; e is electronic charge, n the number of electrons that hop. In the case of glass $n = 2$ [22] and R is the distance between the hopping sites. The relaxation time τ for the electron hop over a barrier of height W is given by

$$\tau = \tau_0 \exp(-W/k_B T), \tag{3}$$

where τ_0 is the order of atomic vibration period $= 10^{-13}$ and k_B is Boltzmann constant. The final expression for the AC conductivity can be expressed

$$\sigma_{AC} = \left[\frac{\pi^2 N^2}{24}\varepsilon\left(\frac{8e^2}{\varepsilon W_m}\right)\frac{s}{\tau_0^{\beta}}\right], \tag{4}$$

where N is the concentration of localized states and β is given by

$$\beta = \frac{6}{W_m}kT. \tag{5}$$

And s is given by

$$s = 1 - \beta. \tag{6}$$

Using Eqs. (4)–(6) the density of state N can be calculated. The values of N, s, β and W for the studied glasses at room temperature and at a frequency equal to 1 kHz are listed in Table 1. The value of N increases with increasing the concentration of Ag_2O due to the increase in non-bridging oxygen ion content with increasing Ag^+ ion concentration. Thus, increasing the number of free bonds leads to an increase in the density of state [28]. The observed increase in N values suggests that the model proposed by Jayasinghe [20] seems appropriate to explain the influence of silver ions on the AC conductivity of B_2O_3–Bi_2O_3–TeO_2 glasses.

Figs. 5a and b represents the variation of the dielectric loss ($\tan\delta$) with frequency at both room temperature and 645 K. Low-frequency dependence of $\tan\delta$ values was observed at room temperature Fig. 5a. However, apparent frequency dependence of $\tan\delta$ values was observed at 645 K Fig. 5b. $\tan\delta$ values increase with decreasing frequency and increasing Ag^+ ion concentration in the glass. Von Hippel et al. [29] stated that there is a close connection between the dielectric loss at low frequencies and the alkali concentration. Increased proportions of alkali, particularly sodium was found to cause a marked increase in $\tan\delta$ in much the same way it decreases the DC resistivity.

Fig. 6 represents the variation of dielectric constant (ε) versus Ag_2O concentration. The dielectric constant increases with increasing temperature and concentration of Ag_2O. Owen and Douglas [30] reported that in commercial glasses the increase in the amount of alkali increases the dielectric constant. They noticed also that at room temperature, the value of dielectric constant was between 5 and 9 and it changed slightly with frequency. As the temperature increases, a point is usually reached at which the dielectric constant value began to increase markedly showing a pronounced increase with frequency. The results obtained in Fig. 6 are in agreement with the observation of Owen and Douglas [30]. The observed increase in the value of dielectric constant in glasses containing 2–4 mol% Ag_2O (Fig. 6) can be attributed probably to the change in the conductivity mechanism, which is associated with the small addition of Ag_2O to bismuth borate tellurite glass.

4. Summary and conclusion

The AC electrical conductivity of $(Ag_2O)_x$ $(Bi_2O_3)_{30}$ $(B_2O_3)_{60-x}$ $(TeO_2)_{10}$ glass ($x = 0, 2, 4, 5, 10, 15$ and 20),

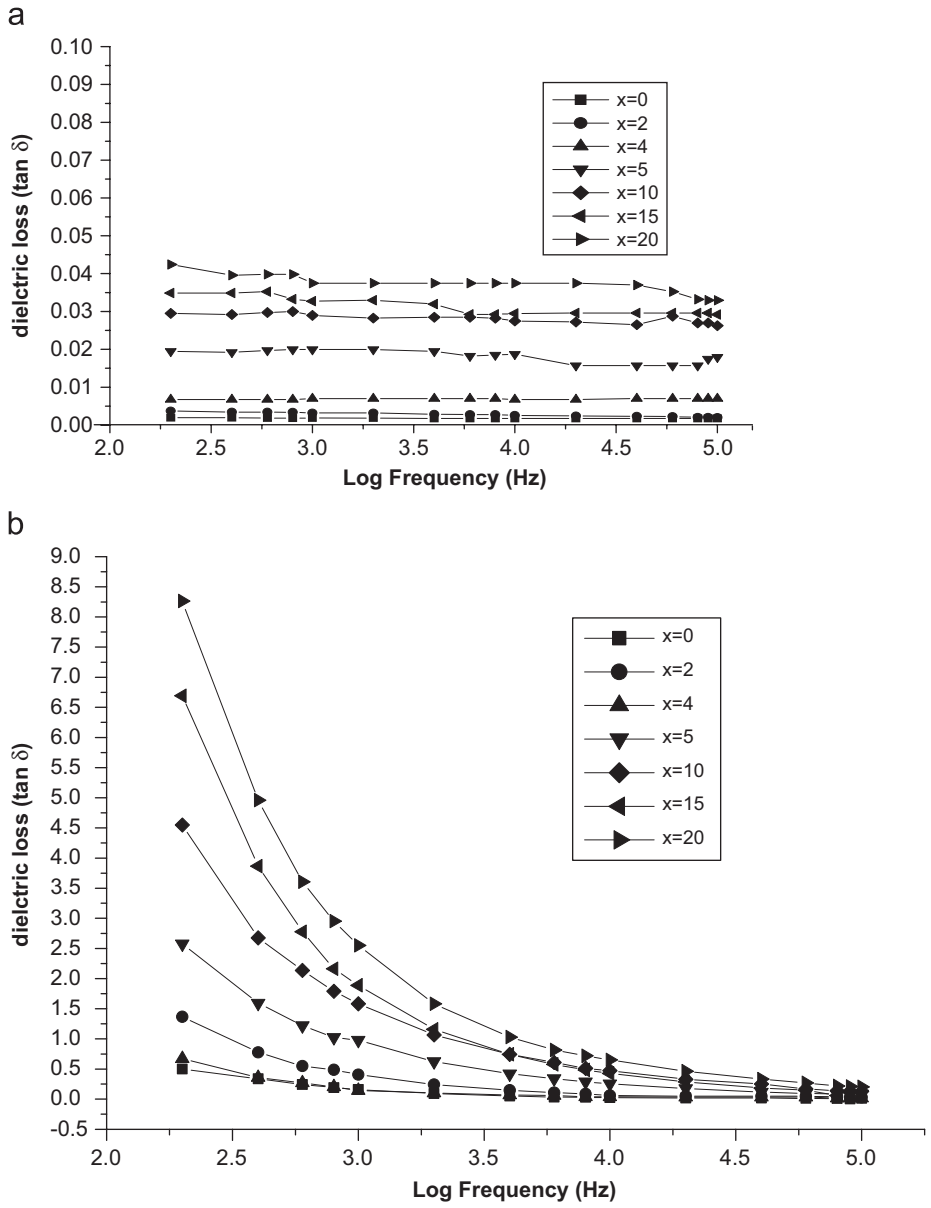

Fig. 5. (a) The relation between Log frequency and dielectric loss at (a) 298 K and (b) 645 K for different glass compositions (x = Ag_2O).

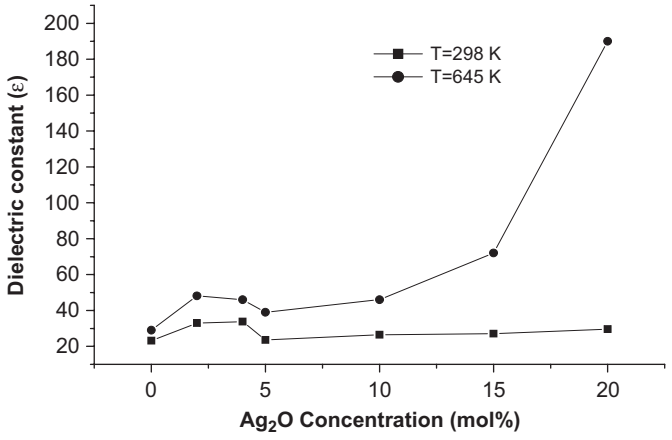

Fig. 6. Variation of the dielectric constant (ε) with Ag_2O concentration (mol%) in glass at 298 K and 645 K.

was measured at temperatures in the range 298–645 K and in the frequency range 0.2–100 KHz. This work was conducted to shed light on the effect of the Ag_2O on the mechanism of the electrical conduction of bismuth borate tellurite glasses. It was found that the relationship between the AC conductivity and Ag_2O content showed a minimum at $\approx$4 mol% Ag_2O. This behavior suggests two conduction mechanisms in conformity with Jayanasinghe et al [20]. The first mechanism is the electronic conduction in silver-free bismuth borate tellurite glasses, whereas the second mechanism is associated with the regular position of non-bridging oxygen along the network-former chains, which allows ion displacement. Then with the addition of the network modifier (Ag^+) the electronic paths are progressively blocked causing the electronic conductivity to fall down, up to 4 mol% Ag_2O. With the further increasing

concentration of Ag_2O beyond 4 mol% Ag_2O the active centers for ionic conduction are mainly formed. The AC conductivity is found to increase with increasing frequency according to the power law $\sigma_{AC} = A\omega^s$. The exponent s values decreased with increasing temperature. The s can take a value between 0.98 and 0.91 at room temperature. These results suggest that, the correlated barrier-hopping (CBH) model is appropriate for explaining the AC conductivity as a function of frequency and temperature. The concentration of localized states calculated using the CBH model is found to increase with increasing Ag_2O concentration. This result supports the suggestion of the presence of two conduction mechanisms in the glass. At high temperature, both of the dielectric loss and the dielectric constant values show apparent increase with increasing the frequency and Ag_2O concentration, respectively.

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