The Conduction Mechanism and Dielectric Behavior of Sodium Borate Glasses Containing Fe and Bi ions

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Glasses in the system $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ with x=0,5,15 and 25 mol % were prepared. A.c. Conductivity ($\sigma_{a.c}$) of the prepared samples has been measured in the frequency range (0.5-20 kHz). The measurements were carried out in the temperature range (290-420K). The obtained results showed that, $\sigma_{a.c.}$ obey the relation $\sigma_{a.c}(\omega)=A\omega^s$, and the exponent (s) was found to decrease with increasing temperature. The values of s of all the investigated samples lie between 0.3 and 0.7. The analysis of the results reveals that, the a.c. conductivity of the investigated samples follow the correlated barrier hopping (C.B.H) model. The dependence of the dielectric constant (έ) and dielectric loss (tanδ) on both temperature and frequency are also discussed in the framework of the current theories. The effect of composition on both conductivity and dielectric constant is also discussed.

1. Introduction:

Oxide glasses containing transition metal ions (TMI) were first reported by A.E. Dale et. al.[1]. Many glasses containing (TMI), for instance iron or vanadium, are electronic conducting semiconductors [2,3]. A general condition for semiconducting behaviour is the coexistence of transition metal ions in more than one valence state, for instance Fe^{2+} and Fe^{3+}, so that conduction can take place by a transfer of electrons from low to high valence ions. Charge transport in these glasses is usually considered in terms of small-polaron hopping model[4,5]. Many authors[6-8] have investigated the dielectric properties of various TMI glasses and concluded that dielectric relaxation is consistent with the mechanism of electron hopping in pairs of transition metal ions. Experimental evidence of this behaviour is a power law of a.c. conductivity $\sigma_{a.c.} = A\omega^s$ observed over many decades of frequency. The interpretation usually involves analysis of the temperature dependence of s(T), which makes it possible to find out the conduction mechanism [9].

The objective of the present study is to examine the a.c. conductivity of sodium borate glasses containing different concentrations of Fe and Bi ions, with a view to understand their conduction mechanism and dielectric behaviour.

2. Experimental Procedure:

Samples used in the present study had the molar formula [$(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$, x=0,5,15 and 25 mol%] were prepared from high purity (99.99%) chemicals. The finely mixed batches were melted in porcelain crucibles at 1000 ^oC for about 2 h under air atmosphere. The melts were then cast in the form of discs onto a warmed stainless-steel plate, and were subsequently annealed at 300 ^oC in order to avoid mechanical strain.

The a.c. conductivity ($\sigma_{a.c}$), dielectric constant (έ) and dielectric loss tangent (tanδ) measurements were obtained using a PM 6304 programmable automatic RLC (Philips) meter at the frequency range (0.5-20 kHz). Samples temperature was varied in the range (290-420K) as measured using chrome alumel type k thermocouple placed near the sample. The disc shaped samples were polished on both surfaces to be parallel, and were then fixed to the double electrode. The sample holder and silver paste was used as measuring electrodes. Thickness of the samples and area of contacting electrodes were determined.

3. Results and Discussion:

3.1. A.c. conductivity

A common feature of all semiconductor materials is the frequency dependent conductivity $\sigma_{a.c.}(\omega)$, which increases linearly with frequency in the frequency range $10 < \omega < 10^8$ Hz ,i.e.

$$\sigma_{a.c.}(\omega) = \sigma(\omega) - \sigma_{d.c.} = A\omega^s \qquad (1)$$

where $\sigma_{d.c.}$ is the d.c. part of the total conductivity σ, A is a constant and ($s \leq 1$) is the frequency exponent. The phenomenon has variously been ascribed to the relaxation caused by the motion of electrons or atoms, hopping or tunneling, between the equilibrium sites [9]. The complex dielectric constant of a material medium is represented by two parts ε=έ+ ″ε, where έ is the real part (dielectric constant) and ″ε is the imaginary part (dielectric loss). The relation between έ and ″ε defines a dielectric loss tangent i. e. tanδ= ″ε ⁄ έ.

The a.c. conductivity, dielectric constant έ and loss tangent tanδ of glasses in the system $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ with x=0,5,15 and 25 mol% have been measured in the frequency range (0.5-20 k Hz) and in the temperature range (290-420K). Generally the temperature dependence of d.c. conductivity $\sigma_{d.c.}$ and a.c. conductivity $\sigma_{a.c.}$ can be expressed by the following relation :- $\sigma=\sigma_o$ exp.$(-\Delta E / kT)$, where σ_o is a constant, ΔE is the activation energy and k is the Boltzmann constant.

The frequency dependence of a.c. conductivity $\sigma_{a.c}$ at various temperatures is shown in Fig. (1) for the composition containing 5 mol% Bi_2O_3 as a representative example for the investigated system. All other samples show the same behaviour. It can be seen that, values of $\sigma_{a.c.}$ for the investigated samples obey the general relation: -

$$\sigma_{a.c.}(\omega)= A\omega^s$$

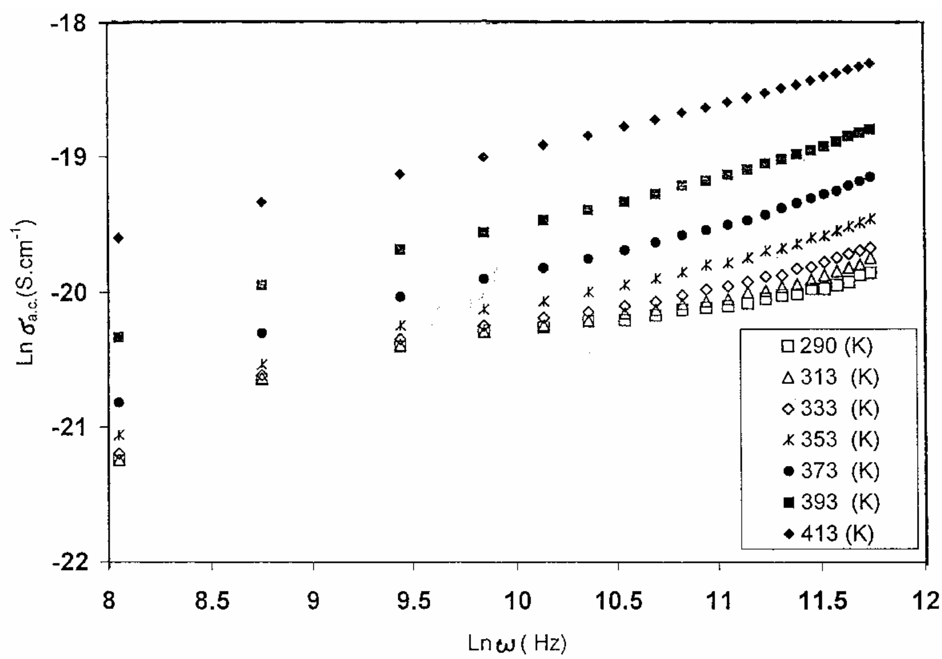

Fig. (1): Frequency dependence of a.c. conductivity $\sigma_{a.c.}$ for $(Na_2B_4O_7)_{75}$ $(Fe_2O_3)_{20}$ $(Bi_2O_3)_5$ sample.

The values of the exponent s as determined from the experimental data using the equation [s= d (Ln $\sigma_{a.c.}(\omega)) / $ d (Ln (ω))] are presented in Fig.(2) as a function of temperature. It can be seen that, the values of the exponent s lie between 0.3 to 0.7 and decreases with increasing temperature for all the samples under investigation.

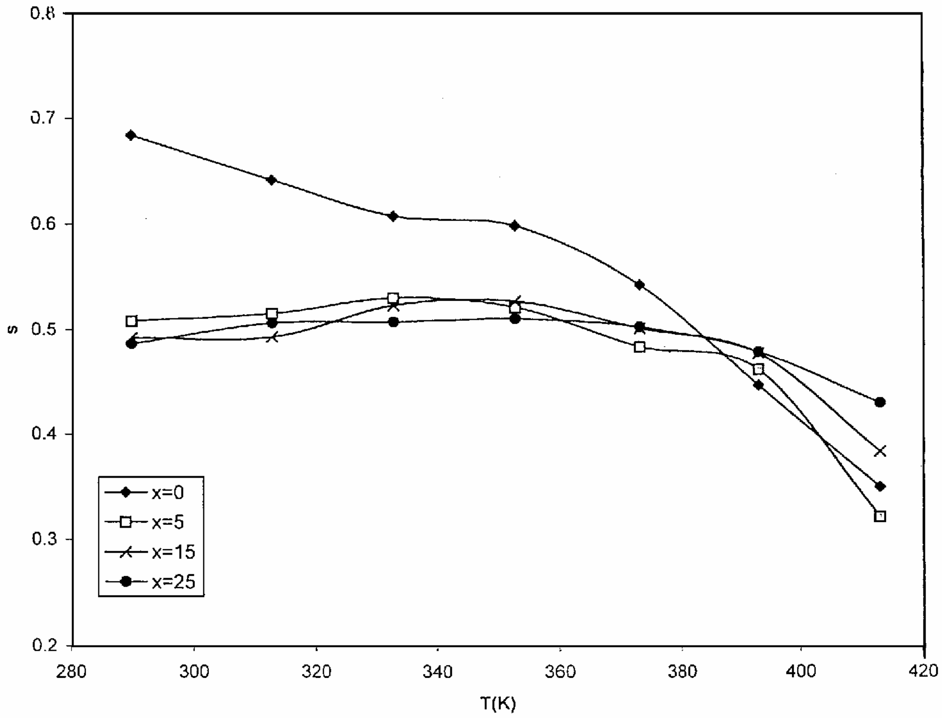

Fig. (2): Temperature dependence of frequency exponent (s) for $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ glass system.

Different models have been developed to explain the a.c. conductivity of amorphous semiconductors. Among these models, the quantum mechanical tunneling (Q.M.T.)[5,10], the correlated barrier hopping (C.B.H.)[9,11-13] and the overlapping large - polaron (O.L.P.) are the most applicable models. According to Q.M.T. model, the a.c. conductivity originates from the tunneling of carriers between the different valence states. In this model the expression of the a.c. conductivity and frequency exponent are respectively given by the following equations: -

$$\sigma_{a.c.}(\omega) = Ce^2 a\, k\, T[N(E_f)]^2\, \omega\, R_\omega^4 \qquad \text{------}\rightarrow(2)$$

$$s = 1 - 4 / \mathrm{Ln}(1/\omega\tau_0) \qquad \text{---------}\rightarrow(3)$$

Where N (E_f) is the density of states at Fermi level, R_ω is the hopping length at frequency ω, τ_0 is the atomic vibration period and a is the localized radius. Equation (3) predicts that s= 0.81 for ($\omega=10^4$ Hz and $\tau_0 = 10^{-13}$s) and is independent of temperature. The obtained values of s as shown in Fig. (2), are found to decrease with increasing temperature. This appears to be in disagreement with the (Q.M.T.) model. Therefore, the experimental data will be discussed in the frame of the (C.B.H.) model. According to this model, the conduction occurs via the hopping carriers over a potential barrier between two different valence states. The a.c. conductivity and frequency exponent expressions due to the (C.B.H.) model are given by the following equations: -

$$\sigma_{a.c.}(\omega) = (1/24)\,\pi^3\varepsilon' N^2\varepsilon_o\,\omega\,R^6_\omega \qquad \text{-------}\rightarrow(4)$$

$$s = 1-\{6kT/\,[W_H+kT\ln(1/\omega\tau o]\} \qquad \text{- -------}\rightarrow(5)$$

Where ε_o the free-space dielectric permittivity, ε' is the dielectric constant and W_H is the maximum barrier height. Equation (5) predicts that, s decrease with increasing temperature. Therefore the (C.B.H.) is the involved conduction mechanism for all the investigated samples.

Figure (3) shows the temperature dependence of a.c. conductivity at fixed frequency (10 kHz). It is observed that, $\sigma_{a.c.}$ increases with increasing temperature for all investigated samples. On the other hand, Fig. (3) also shows that $\sigma_{a.c.}$ decreases with increasing Bi_2O_3 content and reaches a minimum value at 15 mol %. Further increase in Bi_2O_3 content up to 25 mol % (i.e. total replacement of Fe_2O_3 by Bi_2O_3) brings about an increase in the a.c. conductivity. This behavior can be attributed to the high concentration of Fe^{+2} and Fe^{+3} ions, which are responsible for the increase of $\sigma_{a.c}$ in the Bi_2O_3 free sample. On addition of Bi_2O_3 at the expense of Fe_2O_3, the concentration of Fe^{+2} and Fe^{+3} ions decreases and $\sigma_{a.c.}$ goes to its minimum value [14]. The values of activation energy (ΔE) as determined from the experimental data using the equation: - $\sigma_{a.c} = \sigma_o \exp.(-\Delta E/kT)$ are listed in Table (1). It was found that, ΔE values decrease as $\sigma_{a.c.}$ values increase.

Table (1): Values of a.c. conductivity $\sigma_{a.c.}$ and activation energy ΔE, calculated at T=303K and frequency f= 10 k H for $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ glass system.

Comp. (mol %)	$\sigma_{a.c.}$ (S. cm^{-1})	ΔE (eV)
X=0	1.54 X10^{-9}	0.35
X=5	1.11 X10^{-9}	0.37
X=15	0.74 X10^{-9}	0.41
X=25	1.34 X10^{-9}	0.39

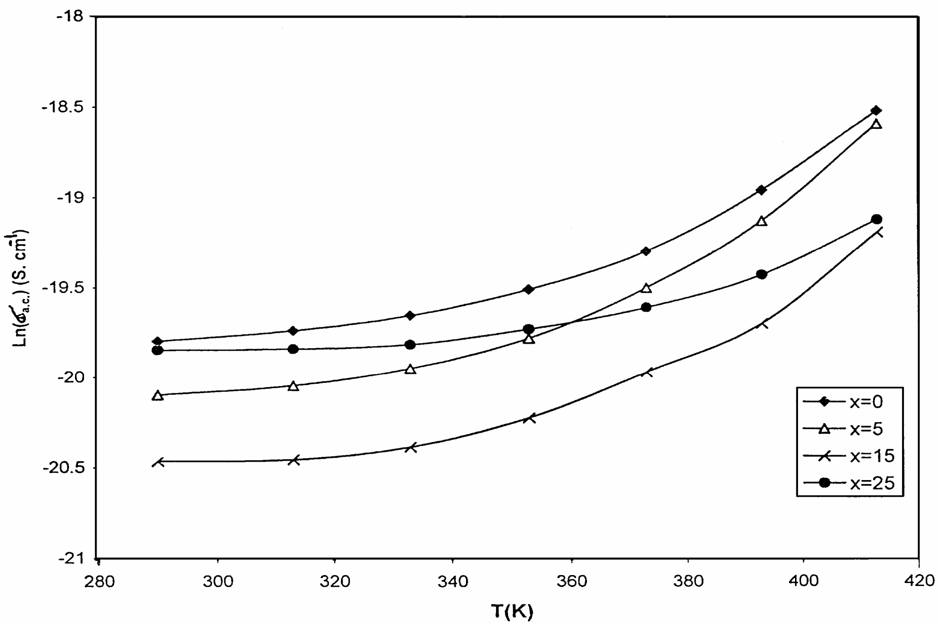

Fig. (3): Temperature dependence of a.c. conductivity $\sigma_{a.c.}$ at frequency 10 k Hz for $(Na_2B_4O_7)_{75}\,(Fe_2O_3)_{25-x}\,(Bi_2O_3)_x$ glass system.

3.2. Dielectric Behaviour

The dielectric behaviour of ion conducting glasses arises mainly from ionic motions. The free energy barriers impeding the ionic diffusion are expected to vary from site to site in glassy semiconductors, so there are different ionic motions in such glasses. The first is the rotation of ions around their negative sites. The second is the hopping of ions from sites with low free energy up to sites with high free energy in the direction of electric field or slowly oscillates between the sites with high free energy in a fast alternating electric field. Both the first and the second motions make a contribution to the dielectric constant έ of glasses [15,16]. Figures (4,5) shows the temperature dependence of the dielectric constant έ of the studied samples. All the samples show the same behaviour. It is observed that, the dielectric constant slowly increases as the temperature increases and no maximum is observed over the temperature and frequency ranges studied for all the samples. This behaviour is an indication of non-ferroelectric behaviour of all the samples[17]. It also observed that έ increases as the frequency increases. This can be accounted for by considering the relatively low flexibility of ions at low frequency. By increasing frequency, the flexibility of ions increases which could lead to the increase of έ [18]. On the other hand, the dielectric constant decreases as Bi_2O_3 content increases up to 15 mol %, then starts to increase again in the sample containing 25 mol % Bi_2O_3 (Iron free sample). This behavior is consistent with the behavior of a.c. conductivity with composition (figure3). These variations of the dielectric constant with composition could be attributed to the fact that, the value of έ is affected by the presence of the polarized space charge. In the sample that contains the largest amount of iron ions (free of Bi_2O_3), it is supposed that there are iron–rich clusters, which give rise to an extra-polarized space charge. In the Bi_2O_3 free sample, about 60% of iron ions in the glass network act as network formers (NWF), while 30% enter as network modifiers (NWM) and 10% appears as precipitated Fe_2O_3 dispersed in the whole sample. The addition of 5 mol% Bi_2O_3 at the expense of Fe_2O_3 causes the disappearance of the precipitated phase. Also some of the polarized space charges are eliminated and έ goes to its minimum value. With further addition of Bi_2O_3, bismuth ions may replace the iron ions in the NWF positions and hence increase the distortion of the glass network [19]. Figures (6,7) shows the temperature dependence of the dielectric loss tangent (tanδ) for all the studied samples. All the samples show the same behavior where tanδ increases with increasing temperature and no maximum was obsorved in the investigated temperature range. On the other hand tanδ decreases as Bi_2O_3 content increases up to 15 mol %, then starts to increase again in the sample contaning 25 mol % Bi_2O_3 (Iron free sample).

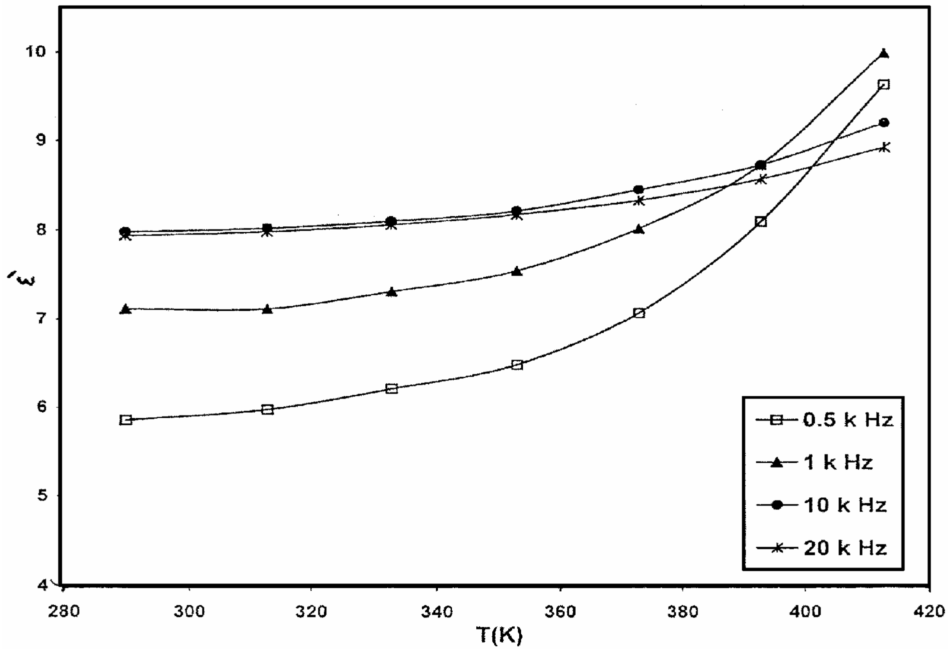

Fig. (4): Temperature dependence of the dielectric constant (ε) for $(Na_2B_4O_7)_{75}$ $(Fe_2O_3)_{20}$ $(Bi_2O_3)_5$ glass system.

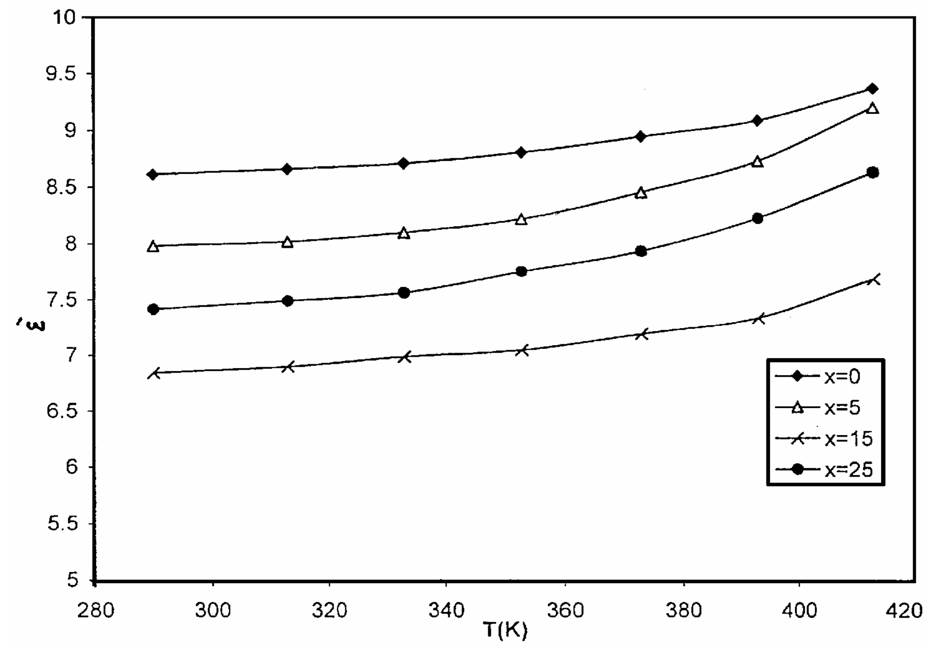

Fig. (5): Temperature dependence of the dielectric constant (ε) at 10 kHz for $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ glass system.

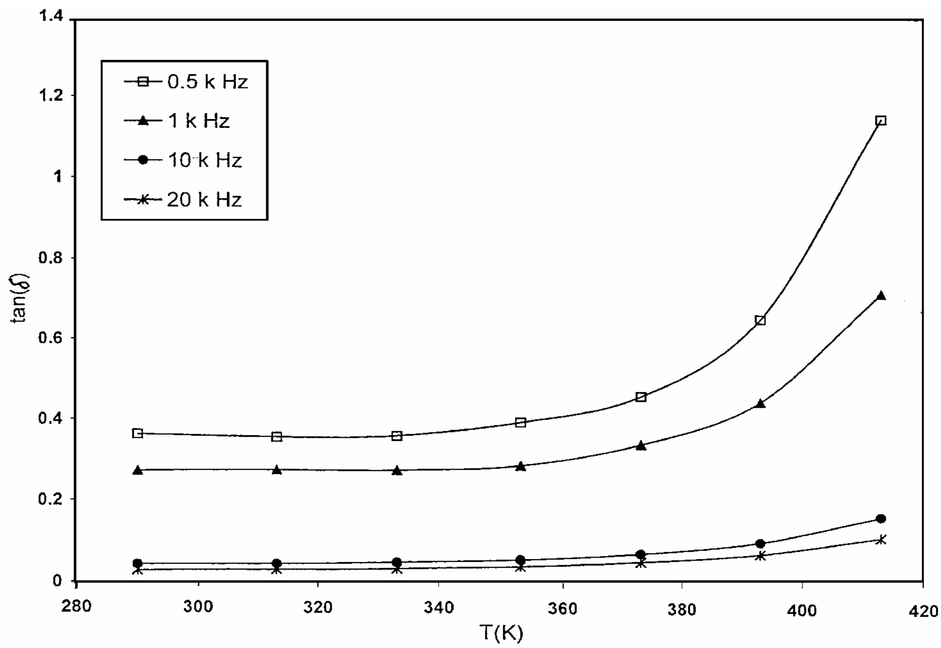

Fig. (6): Temperature dependence of the dielectric loss (tan δ) for $(Na_2B_4O_7)_{75}(Fe_2O_3)_{20}(Bi_2O_3)_5$ glass system.

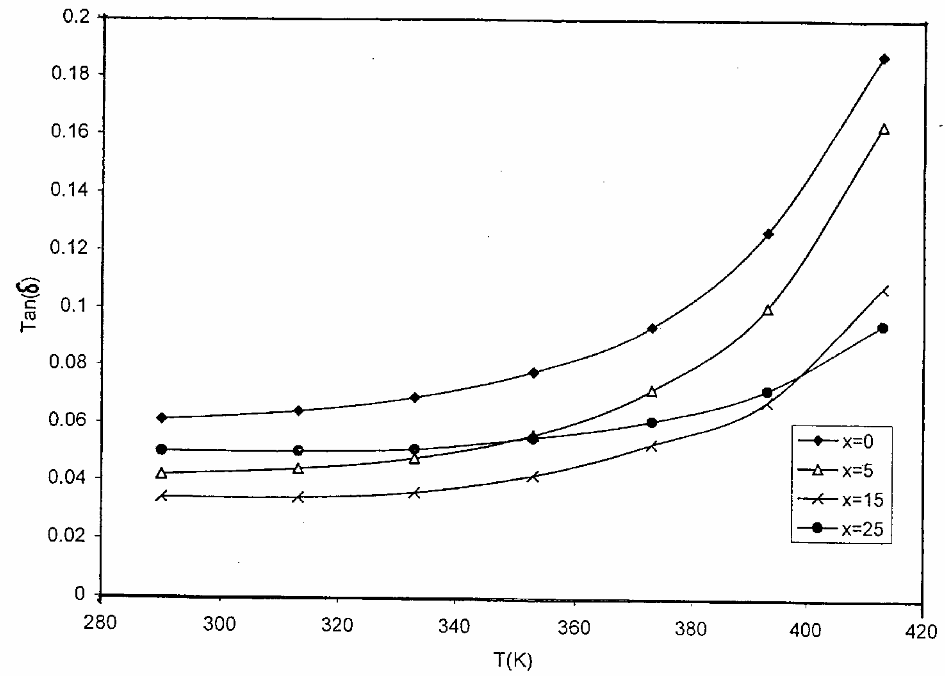

Fig. (7): Temperature dependence of the dielectric loss (tan δ) at 10 kHz for $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ glass system.

Conclusion:

Samples of $(Na_2B_4O_7)_{75}(Fe_2O_3)_{25-x}(Bi_2O_3)_x$ were prepared in the form of discs with different concentrations x=0,5,15 and 25 mol%. A.c. conductivity in the frequency range (0.5–20 kHz) over the temperature range (290–420 K) was used to study the conduction mechanism of the prepared samples. The different parameters of a.c. conductivity were obtained and the data was found to be in a good agreement with the recent published works. A.c. conductivity showed a linear relation with frequency. The frequency exponent s found to be decrease with increasing temperature, which indicates that the correlated barrier hopping (C.B.H.) is the most probable mechanism. On the other hand, a.c. conductivity and dielectric constant were found to be decrease with increasing Bi_2O_3 content up to 15 mol %, and then starts to increase with further increase of Bi_2O_3 up to 25 mol% (Iron free sample). This behaviour can be attributed to the high concentration of Fe^{+2} and Fe^{+3} ions, which responsible for the increase of $\sigma_{a.c.}$. On addition of Bi_2O_3 at the expense of Fe_2O_3, the concentration of Fe^{+2} and Fe^{+3} ions decreases and $\sigma_{a.c.}$ goes to its minimum value.

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