**Conductivity measurements of transition metal doped mixed alkali bismuth borate glasses**

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**Abstract:** In this paper, we report the conductivity measurements of transition metal doped mixed alkali bismuth borate glasses prepared by melt quenching technique. The AC conductivity was studied in the frequency range 100Hz-1MHz. At room temperature the AC conductivity increased with the increase in frequency. For all the glass samples, dielectric constant and dielectric loss decreased with increase in the frequency. The DC conductivity measurement has been carried out by two probe method in the temperature range 403 to 573K. The DC conductivity values for all the prepared glass samples was observed to lie in the range $10^{-8}$ - $10^{-6}$ S m\(^{-1}\). Activation energy values were calculated using the conductivity data. The conductivity was found to increase with the increasing temperature exhibiting the semiconducting nature of the prepared glasses.

**Key words:** DC conductivity, transition metal, activation energy, bismuth borate glasses.

1. **Introduction**

Heavy metal oxide like bismuth borate glasses have been used in the area of linear and non linear optics [1-3]. The classical glass formers like lithium borate glasses have been studied [4,5]. In glasses, the electrical conduction may be due to ionic or electronic or both [6,7]. The electrical conduction in alkali oxide glasses is due to the motion of alkali ions in interstitial positions within the glass network. Among various oxide glasses, sodium ions and lithium ions are quite mobile[8]. In these glasses, ionic transport is interpreted in terms of ionic jumping over an energy barrier between sites by a thermal activation process[9]. The transition metal oxide (TMOs) such as Fe\(_2\)O\(_3\) and V\(_2\)O\(_5\) doped glasses exhibit semiconducting nature. In such glasses, the electrical conduction is due to the small polaron hopping (SPH) [10-13]. Glasses containing Fe\(_2\)O\(_3\) are used in electro chemical, electronic, electro-optic and memory switching devices[14]. Shapaan and Ebrahim studied the AC conductivity in the glass system (80-x)B\(_2\)O\(_3\)-xBi\(_2\)O\(_3\)-20Fe\(_2\)O\(_3\) (x=10, 15 and 20) and observed decrease in $\sigma_{dc}$ and increase in $(\theta_D /2)$ with increasing Bi\(_2\)O\(_3\) content [15]. Mahmoud et.al [16] studied dielectric constant, dielectric loss tangent and electric modulus as a function of temperature of xBi\(_2\)O\(_3\)-(75-x)B\(_2\)O\(_3\)-25Li\(_2\)O glasses.

To the best of our knowledge, there are no reports in the literature on the AC and DC conductivity measurements of transition metal doped mixed alkali bismuth borate glasses. The aim of the present work was therefore, to study the AC and DC electrical conductivity of ferric oxide doped lithium sodium bismuth borate glasses.
2. Experimental

The starting materials used in the preparation of glasses i.e., $\text{Bi}_2\text{O}_3$, $\text{H}_3\text{BO}_3$, $\text{Li}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3$ and $\text{Fe}_2\text{O}_3$ were of pure AR grade. The glass samples of composition $x\text{Fe}_2\text{O}_3+25\text{Li}_2\text{O}+5\text{Na}_2\text{O}+15\text{Bi}_2\text{O}_3+(55-x)\text{B}_2\text{O}_3$ where ($x=0,2,4,6$) were prepared by melt quenching technique. The chemicals were weighed and mixed thoroughly and ground for 2h to make powder in an agate mortar. The powder was taken in silica crucible and melted at 1100 $^\circ$C for 30 min. The melt was then suddenly quenched by pouring it on a steel plate and pressing it with one more steel plate in air at room temperature. The glasses so formed were annealed at 300$^\circ$C for 3 h to release the thermal stress in the glasses.

The DC conductivity for prepared glasses was measured in the temperature range 403-573 K by two probe method. The glass samples were coated with silver which served as electrodes. A constant voltage was applied to the glass samples using a stabilized power supply and the current at different temperatures was measured using a digital nano ammeter. The DC conductivity was determined using the relation,

$$\sigma = \frac{I}{hV}$$  \hspace{1cm} (1)

where, I is the current through the sample, h is the thickness, V is the voltage and A is the cross section area of the glass samples.

The DC conductivity of all prepared glass samples obeys the Arrhenius equation,

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right)$$  \hspace{1cm} (2)

where $\sigma_0$ is the pre-exponential factor, k is the Boltzmann constant and W is the activation energy for conduction. The conductivity and dielectric measurements for all the glasses with varying frequency at room temperature were done using computer controlled precision impedance analyzer (Wayne Kerr, 6500B). Using the AC measurement, values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) have been calculated using following relation [17];

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (3)

$$\varepsilon'' = \varepsilon' \tan\delta$$  \hspace{1cm} (4)

$$\sigma_{ac} = \omega\varepsilon_0 \varepsilon''$$  \hspace{1cm} (5)

where $d$ is glass thickness, A area of glass and $\varepsilon_0$ permittivity of free space, C is capacitance, $\omega=2\pi f$ with f being applied frequency.

3. Results and discussion

The DC conductivity values for all the prepared glass samples from 403 to 573K was observed to lie in the range $10^{-8}$ - $10^{-6}$ S m$^{-1}$. The relationship between the log $\sigma_{dc}$ and 1/T with a negative slope indicate that the mechanism of conductivity is ionic in nature. The linear relationship between log $\sigma_{dc}$ and 1/T is as shown in figure 1. The slope of this curve gives the activation energy. The activation energy is the average value of the heights of the potential energy barriers that the mobile ion must overcome in its jumps. At low temperature region, electrical conduction is contributed by electrons, while at high temperature, conduction is contributed by mobile ions. Similar work was reported in the literature for some iron containing alkali phosphate and borate glasses [18, 19]. The values of DC conductivity, pre-exponential factor and activation energy are shown in table 1.
The DC conductivity at 523K is more for 2FLNBiB glasses and less for 6FLNBiB glasses. The DC conductivity increased with increasing temperature and it was also observed that the electrical conduction was maximum when activation energy was minimum. The activation energy values were observed to lie in the range $0.405 - 0.450$ eV. Sayer and Mansing observed activation energy for glass $80V_2O_5$-$20P_2O_5$ to lie in the range $0.09 - 0.35eV\[20\].

The DC conductivity and activation energy values show mixed transition ion effect when $Fe_2O_3$ is replaced by $B_2O_3$. The Lithium ions were available for conduction, Li ions may be interacting with $Fe_2O_3$ rather than taking part in the conduction. The increase of $Fe_2O_3$ ions show a “blocking effect”. A similar result was reported in vanadyl doped $Bi_2O_3$-$K_2O.B_2O_3$ and $Bi_2O_3$.Li$_2O$.B$_2$O$_3$ glass samples [21 – 24]. The activation energy and DC conductivity variation with $Fe_2O_3$ content at 523K is as shown in figure 2.

| Sample Code | $\sigma_{dc}$ (S m$^{-1}$) at 423K ($\times 10^{-8}$) | $\sigma_{dc}$ (S m$^{-1}$) at 523K ($\times 10^{-6}$) | $\log\sigma_0$ (S m$^{-1}$) | W (eV) |
|-------------|---------------------------------|---------------------------------|------------------|--------|
| 0FLNBiB     | 3.0906                          | 6.9864                          | 0.680            | 0.450  |
| 2FLNBiB     | 3.7692                          | 8.3847                          | 0.627            | 0.424  |
| 4FLNBiB     | 4.4424                          | 7.6950                          | 0.522            | 0.405  |
| 6FLNBiB     | 2.4230                          | 5.3030                          | 0.603            | 0.421  |

Table 1. DC conductivity $\sigma_{dc}$, pre exponential factor, $\log\sigma_0$, activation energy (W) for prepared glass samples

![Figure 1](image-url)  

**Figure 1** Variation of $\log \sigma$ with temperature
Figure 2 Compositional variations of W and log $\sigma_{dc}$ with Fe$_2$O$_3$

The AC electrical conductivity $\log \sigma_{ac}$ Vs log f is as shown in figure 3. The AC conductivity increased with increase in frequency which give the information about semiconducting nature of glasses. Similar type of behaviour was reported with Li$_2$O doped glass by Abbas et al.[25]and Bih et al. [26] with glass compositions Li$_2$O-Na$_2$O-MoO$_3$-P$_2$O$_5$ and Li$_2$O-Na$_2$O-WO$_3$-P$_2$O$_5$, respectively. The V$_2$O$_5$ doped glass showed similar result [27]. The non linear plot of $\log \sigma_{ac}$ Vs log f gave frequency exponent S. The S values are in the range 0.408 to 0.760. The values of S at room temperature are tabulated in table 2. The dielectric properties of glasses arise due to ionic motion. The variation of dielectric constant with frequency is as shown in figure 4. Dielectric constant decreased with increase in frequency. All the samples show the same behaviour. The change in the dielectric constant may be due to polarized space charge. By applying an external field, space charges can move and create lots of dipole moments. By applying low frequencies, the dipole moment can easily follow the change of electric field giving rise to low energy losses, resulting in a high value of polarization and there by a high value of dielectric constant. As frequency of the applied field increase, a point will be reached where the space charge cannot sustain with the field and hence polarization decreases.

Table 2. Frequency exponent (S) at room temperature

| Sample Code | S  |
|-------------|----|
| 0FLNBiB     | 0.408 |
| 2FLNBiB     | 0.677 |
| 4FLNBiB     | 0.481 |
| 6FLNBiB     | 0.760 |

The plot of dielectric loss ($\varepsilon''$) versus frequency for prepared glasses at room temperature is shown in figure 5. The dielectric loss decreased as frequency increased and in all the samples same behaviour is observed.
4. Conclusion

The glass samples of composition $x\text{Fe}_2\text{O}_3+25\text{Li}_2\text{O}+5\text{Na}_2\text{O}+15\text{Bi}_2\text{O}_3+(55-x)\text{B}_2\text{O}_3$ where $(x=0,2,4,6)$ were prepared by melt quenching technique. The DC conductivity was found to increase with temperature confirming thereby the semiconducting nature of glasses. The data has been analysed using Arrhenius expression and activation energies of glasses were determined. The DC conductivity values from 403 to 573K were observed to lie in the range $10^{-8} - 10^{-6}$ S m$^{-1}$. The AC conductivity increased with increase in frequency. At room temperature, the frequency exponent $S$ values are in the range 0.408 to 0.760. The dielectric constant and dielectric loss decreased with increase in frequency.

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