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Effect of the Transition Metal Oxides addition on the electrical Conductivity of Lithium Borosilicate glass system

Thomas Philip
Department of Physics,
Hislop College, Nagpur – 440001,
India.
Email: philipnagpur@gmail.com

V.K. Deshpande
Department of Applied Physics,
Visvesvaraya National Institute of Technology,
Nagpur – 440010,
India.

Abstract: In this study Li_2O_3 : B_2O_3 : SiO_2 glass system is used as a base system due to its better glass formability and chemical stability. This base system is used as a potential solid electrolyte material in solid state batteries. The electrical properties of certain transition metal oxide doped glass systems have been studied earlier. The TMOs (Transition Metal Oxides) MnO_2, Fe_2O_3 are here added to the base system in the present study. The a.c conductivity analysis of the glass samples was studied in the temperature range from 533 K to 593 K by using high resolution impedance analyzer. The scaling of the modulus spectra shows that the overlapping of the spectra for a given concentration indicates the temperature independence of the conduction mechanism. The dielectric constant of these glass samples has also been studied. The dielectric constant of lithium borosilicate glasses slightly increases with addition of TMOs. The Mn containing glass exhibiting high dielectric constant among the samples studied here. This glass sample could be developed further as a dielectric material.

Key words: a. c. conductivity, modulus spectra, dielectric constant.

INTRODUCTION

Lithium conducting glasses are prospective electrolyte materials for solid state batteries and have been studied widely in last few decades. When the transition metal oxides are added in glass system, it gives different coloring mechanism and also they increase electronic conductivity of the systems [1,2]. The electrical conductivity by ionic conduction is due to motion of alkali ion and electronic conduction is due to small polaron hopping between transition metal ions. The dc and ac conductivity studies have been reported in a number of transition metal ions doped alkali borate glasses. Transition Metal ions are also used as a probe of the glass structure. The valences and coordination of transition metals in glass can be understood on the analysis of electron spectra. Hence in the present work, the influence of MnO_2 and Fe_2O_3 addition on the electrical properties of lithium borosilicate glass have been studied.

Methodology:

The finely ground mixture $_{of}$ the chemicals of high purity melted in Platinum crucible at 1050^0C in a muffle furnace for one and a half hour. The melts were stirred from time to time to attain homogeneity and quenched on an aluminium mould at room temperature in air. The glass so prepared was annealed at 400^0C for two hours, in order to relieve the mechanical stresses, if any present. X-ray diffraction studies confirmed the glassy nature.

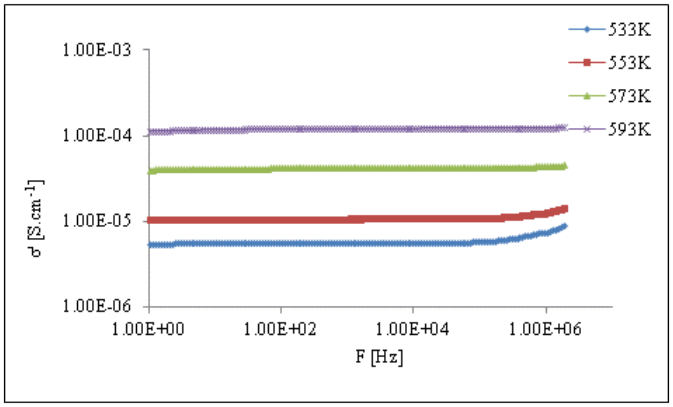
Results and Discussions:

Electrical conductivity studies:

The analysis of a.c. conductivity and modulus spectra of some of the representative glass samples have been attempted here. The analysis of the frequency dependence of real part of conductivity, σ', for some representative glass samples from among the studied glasses, has been given here. Jonscher's power law, which was originally enunciated for the frequency dispersion of dielectric systems but found to be equally applicable to conducting materials as well, has been applied in the present work. It is described by the equation,

$$\sigma'_T(\omega) = \sigma_0 + A(\omega)^s$$

Based on the observed results, extraction of related information about the conduction dynamics has been attempted. Roling et al [3] have reported that it may be more meaningful to discuss conductivity relaxations in terms of log - log dependence of the conductivity on frequency since it takes into account the mobility and the number density of charge carriers. This analysis is called as 'time - temperature superposition of conductivity'. In the present work all the glasses studied contain lithium as the mobile charge carrier and transition metal cation. It has been discussed earlier that the transition metal ions have practically no mobility as compared to that of Li^+ ions.



.Fig. 1: Frequency dependence of the electrical conductivity for glass sample I at different temperatures.

Figure 1 depicts the conductivity spectra for the glass sample I (i.e., $30Li_2O$: (70 – 5) ($6/7B_2O_3$:$1/7SiO_2$): $5MnO_2$). The curves exhibit typical power law behavior. However, it is seen that the major portion of the conductivity isotherms exhibits d.c. plateau in the mid frequency region. It is only at the lower temperatures that conductivity dispersion is observed. The power law region, where σ' is proportional to F^s, is observed in the curves at lower temperatures in the high frequency region.

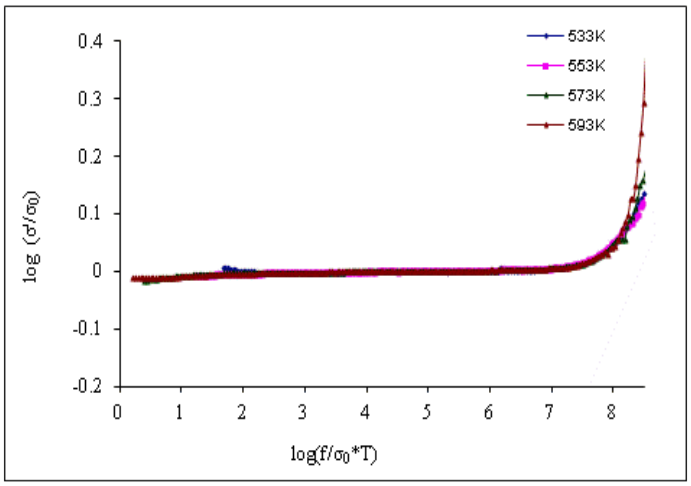


Fig. 2: Scaling of the data of Fig. 1

Figure 2 displays the result of scaling of the data of Figure 1 as discussed earlier. The σ' axis is normalized by the d.c. conductivity σ_0 while the frequency axis, by the product (σ_0*T). It is observed that there is a good overlapping of the data. Similar results have been reported in the literature for different ionic conductors. The observed collapse of the data into one single curve indicates the time - temperature superposition and a subsequent independence of the conduction mechanism and mobile carrier concentration with respect to temperature.

Figure 3 depicts the variation of σ', the real part of the complex conductivity σ (F, T), with frequency at different temperatures for the glass sample II (i.e., $30Li_2O$: (70 – 5) ($6/7B_2O_3$:$1/7SiO_2$): $5Fe_2O_3$). These conductivity spectra describe the power law behavior as discussed earlier.

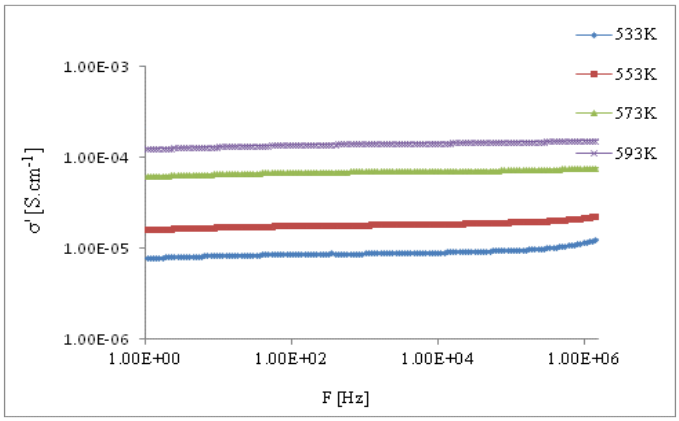


Fig. 3: Frequency dependence of the electrical conductivity for glass sample II at different temperatures.

It is observed that the isotherms have very similar shapes, i.e. the nature of frequency dispersion of the conductivity does not change with temperature. The frequency corresponding to the crossover between the d.c. and dispersive behavior shifts to higher values with increase in temperature.

As mentioned earlier, Figure 4 has been derived by the use of scaling function suggested by Roling et. al. From this figure it is seen that all the isotherms collapse into a single master curve, as discussed earlier for glass sample I. According to this procedure one gets the time - temperature superposition of the conductivity of ion conducting materials by using the Summerfield scaling and observed similar collapse of the data into a single curve [4]. According to them the scaling procedure implies that the only effect of temperature is either to speed up or slow down the ionic hopping processes, leaving the conduction or relaxation mechanism and number of mobile ions unchanged. This suggests that the carrier concentration in a particular glass is independent of temperature.

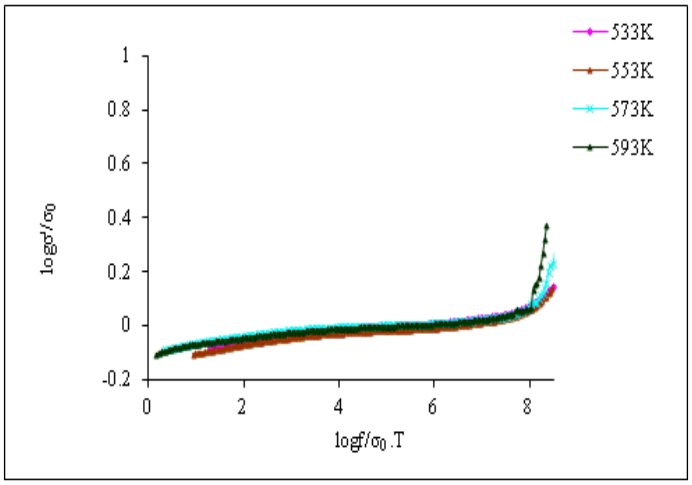


Fig. 4: Scaling of the data of Fig. 3.

Thus the increase in the conductivity of a glass sample as a function of temperature may be attributed to the increase in the mobility of the charge carriers as has been observed in the present study also.

After having discussed the results of a.c. conductivity, we now turn our attention towards the analysis based on modulus formalism. Here the M" spectra and their scaling has been tried for these glass samples.

Modulus spectra studies:

Figure 5 depicts the modulus spectra (M" – imaginary part of the complex dielectric modulus function, M*) for the glass sample I (i.e., $30Li_2O$: (70 – 5) ($6/7B_2O_3$:$1/7SiO_2$): $5MnO_2$) at various temperatures.

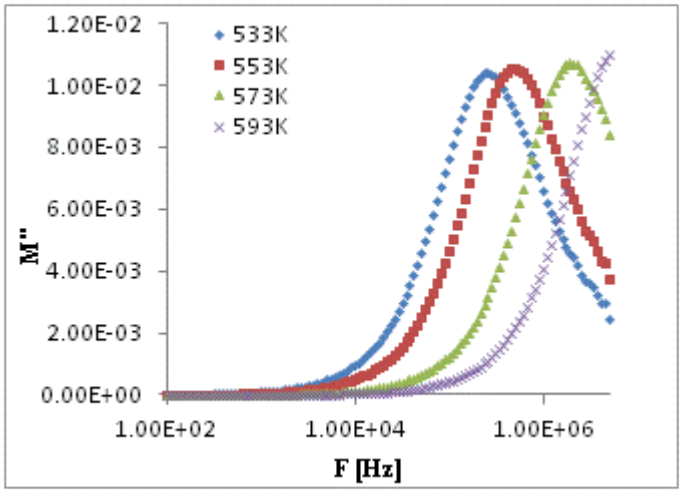


Fig. 5: Modulus spectra for the glass sample I

It is observed that these spectra are characterized by a maximum at a particular frequency and this frequency shifts towards higher values with increase in temperature while the height of the maximum slightly increases. There is an asymmetry in the spectrum when one compares the low frequency and high frequency regions.

Figure 6 shows the data of Figure 5 after scaling. The frequency axis has been scaled with F_{max}, the frequency corresponding to the maximum in the spectrum for a given temperature, while the M" axis has been normalized by the factor $M"_{max}$.

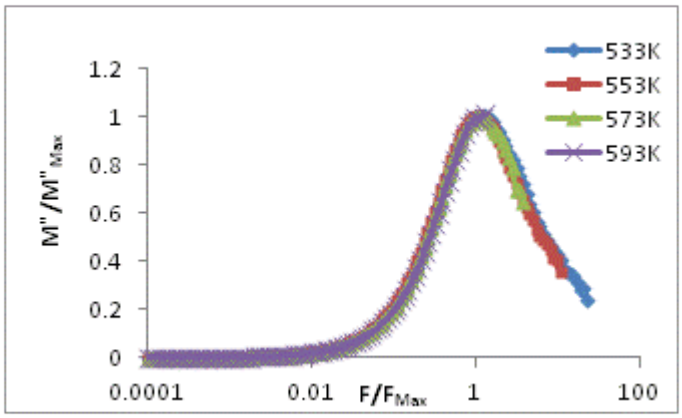


Fig. 6: Scaling of the data of Fig. 5

It can be seen from this figure that there is a good overlap of the data in which the peaks in different spectra of the previous figure collapsed into a single peak, except for some dispersion at the high frequency end. Many have reported the scaling of M" spectra of different glass samples and pointed out that the overlapping of these spectra for a given concentration indicates the temperature independence of the conduction mechanism. This finding also supports our results of a.c. conductivity analysis [5].

Figure 7 depicts the modulus spectra (M" – imaginary part of the complex dielectric modulus function, M*) for the glass sample II (i.e., $30Li_2O$: (70 – 5.0) ($6/7B_2O_3$:$1/7SiO_2$): $5Fe_2O_3$) at various temperatures.

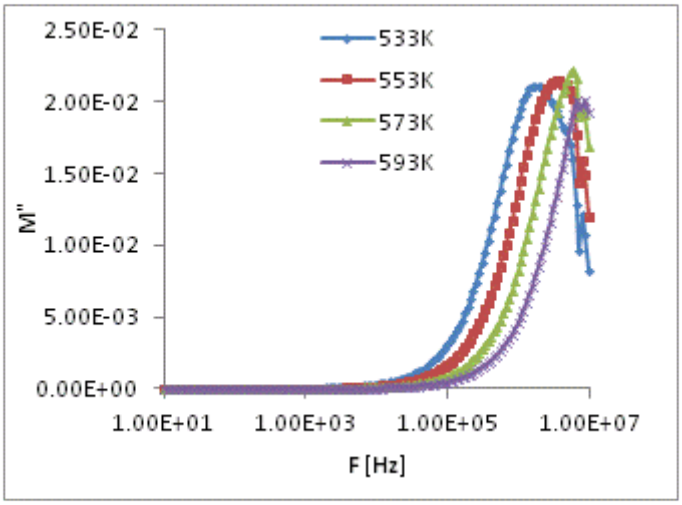


Fig. 7: Modulus spectra for the glass sample II.

It is observed that these spectra are characterized by a maximum at a particular frequency and this frequency shifts towards higher values with increase in temperature while the height of the maximum slightly increases. There is an asymmetry in the spectrum when one compares the low frequency and high frequency regions.

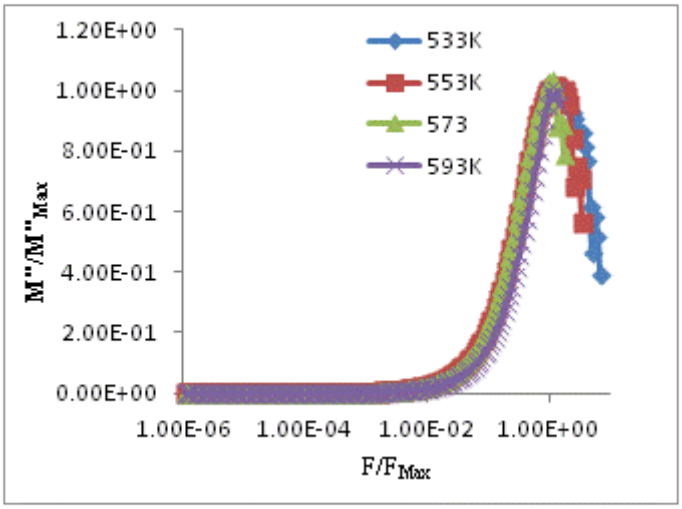


Fig. 8: Scaling of the data of Fig. 7.

Figure 8 shows the data of Figure 7 after scaling. The frequency axis has been scaled with F_{max}, the frequency

corresponding to the maximum in the spectrum for a given temperature, while the M" axis has been normalized by the factor M''_{max}. It can be seen from this figure that there is a good overlap of the data in which the peaks in different spectra of the previous figure collapsed into a single peak, except for some dispersion at the high frequency end.

Hence on the basis of the observed results and supporting evidences in the literature (mentioned earlier), it may be said that the conduction mechanism is composition dependent. On the basis of observed trends in modulus spectra it may be said that the scaling indicates temperature independence of the conduction mechanism in the TMO added lithium borosilicate glasses.

Dielectric Constant Studies:

The dielectric properties of various TMO containing glasses have been investigated by many research groups [6,7].

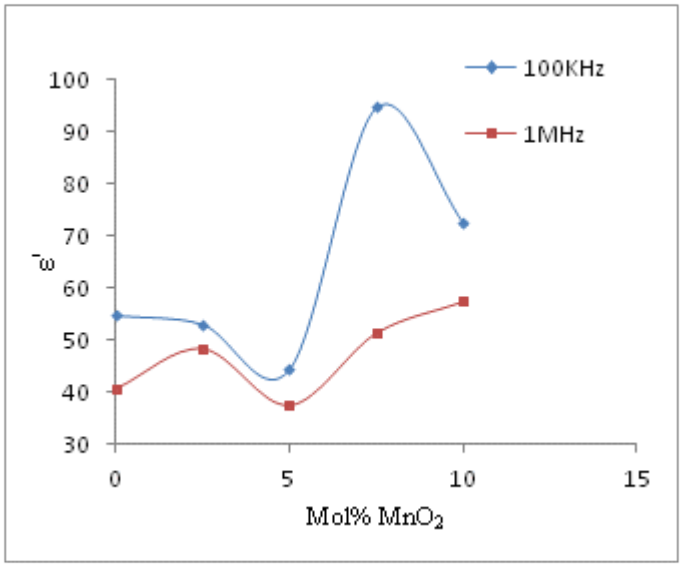


Fig. 9: Dielectric constant ε' at 573 K as a function of mol% MnO_2 (0 – 10)

The variation of dielectric constant ε' at 573 K with mol% MnO_2 added glass samples is depicted in Figure 9. The maximum value is observed at 7.5mol% of MnO_2. This may be due to the increase in polarizability as expected from similar studies.

Figure 10 shows the dielectric constant ε' variation at 573 K with mol% Fe_2O_3 added glass samples. The dielectric constant ε' increases at 5 mol% and 10 mol% Fe_2O_3 addition. For low concentrations (less than 5 mol%) of TMO, the ions occupy preferentially substitutional positions in the glass network reinforcing the covalent bonds between the TM and glass former. This reduces the polarization, reducing therefore the dielectric constant. Iron ions, in these glasses, are expected to exist in the Fe^{3+} state; however, as the concentration (around 5 mol%) of Fe_2O_3 increases. There is a possibility for a gradual conversion of these ions into Fe^{2+} states that occupy interstitial positions, contributing to the polarization.

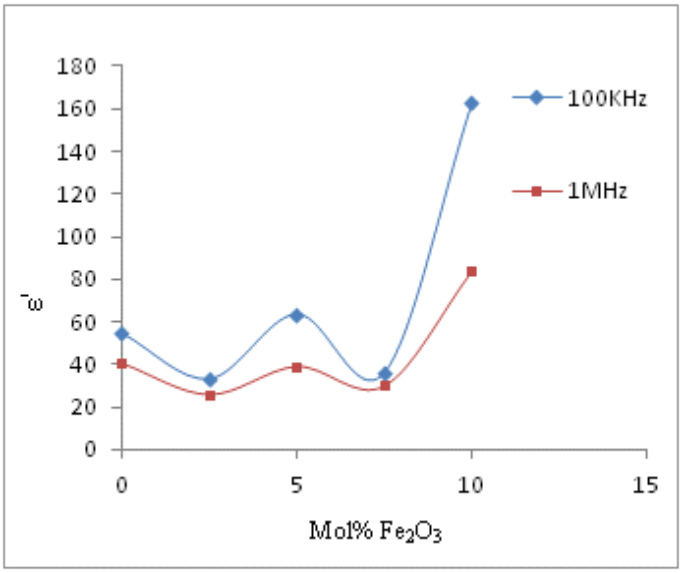


Fig. 10: Dielectric constant ε' at 573 K as a function of mol% Fe_2O_3 (0 – 10).

The dielectric constant is higher for lower frequencies, as shown in the figure. The response of the permanent dipoles decreases as the frequency increases. It has been reported that at microwave frequencies, some permanent dipoles could still be capable of polarization, following fast field variations, as shown by the increasing dielectric constant values. Therefore the valance state of the transition metal oxide plays an important role on the polarization mechanism in the glasses. However, for in deep understanding, it needs to be probed thoroughly.

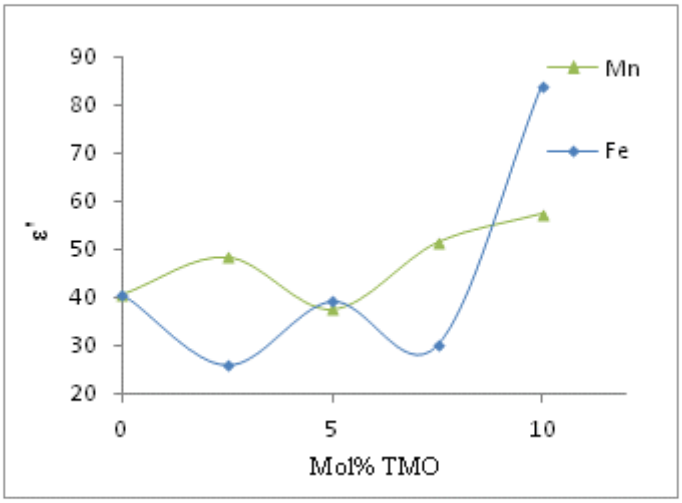


Fig. 11: Variation of dielectric constant ε' with mol% TMO at I MHz (at 573K).

The Figure 11 shows the comparison of variation of dielectric constant as a function of mol% TMO for the glasses containing MnO_2 and Fe_2O_3 at 5 mol% at 1 MHz at 573K. The Mn added glass samples show better dielectric constant as compared to Fe type. The different behavior observed for the addition of Fe is probably due to the appearance of Fe clusters for concentrations higher than 7.5mol% as reported for different iron doped oxide glasses.

Conclusion:

The TMO doped lithium borosilicate glass samples were prepared and confirmed by X-ray diffraction. The temperature dependent a.c. electrical conductivity was investigated. It was discussed based on Jonscher's formula. The scaling of the data has been done with the frequency dependence of $\sigma'(\omega)$ at various temperatures. It is found to be collapsed into a single master curve. At higher frequencies, deviation from the master curve is seen. A.C. conductivity is composed of conduction of the charge carriers and conduction related polarization governed by the relaxation time.

It is found that the Mn containing glass exhibiting higher dielectric constant than the Fe containing glass. It can be further studied to be developed as dielectric materials.

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