

# Dielectric studies on Fe<sub>2</sub>O<sub>3</sub> doped Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> glasses

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**Abstract :** The structure of 30 Li<sub>2</sub>O – (10-x)(ZnO-CdO) -60 B<sub>2</sub>O<sub>3</sub>: x Fe<sub>2</sub>O<sub>3</sub> glass system with  $0 \leq x \leq 2$  mol% was prepared. The dielectric properties indicates that the the density of the defect energy states is found to increase with increase in the concentration of Fe<sub>2</sub>O<sub>3</sub> beyond 0.8 mol % indicating an increasing disorder in the glass network

**IndexTerms:** Alkali borate glasses, Dielectric studies, Dielectric losses

## I. INTRODUCTION

The transition metal ions dissolved in Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> glass matrix even in very small quantities make these glasses coloured and have strong influence over the insulating character and optical transmission of these glasses. It may be useful to compare the environment of manganese ions in various other glass systems like silicates, fluorides, borate, arsenates etc., with that of the present glass system. The objective of the present investigation is to have a comprehensive understanding over the topology and valence states of Ferrous ions in Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> glass network, by a systematic study of various dielectric properties like dielectric constant, loss tanδ, over a moderately wide range of frequency and at room temperature.

## II. EXPERIMENTAL

The following compositions of glasses with the chemical formula Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> were chosen for the present study.

- M<sub>0</sub>: 30 Li<sub>2</sub>O - 10 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub> (pure)  
 M<sub>1</sub>: 30 Li<sub>2</sub>O - 9.8 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 0.2 Fe<sub>2</sub>O<sub>3</sub>  
 M<sub>2</sub>: 30 Li<sub>2</sub>O -9.6 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 0.4 Fe<sub>2</sub>O<sub>3</sub>  
 M<sub>3</sub>: 30 Li<sub>2</sub>O -9.4 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 0.6 Fe<sub>2</sub>O<sub>3</sub>  
 M<sub>4</sub>: 30 Li<sub>2</sub>O -9.2 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 0.8 Fe<sub>2</sub>O<sub>3</sub>  
 M<sub>5</sub>: 30 Li<sub>2</sub>O -9.0 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 1 Fe<sub>2</sub>O<sub>3</sub>  
 M<sub>6</sub>: 30 Li<sub>2</sub>O -9.4 (50ZnO-50 CdO) -60 B<sub>2</sub>O<sub>3</sub>: 1.2 Fe<sub>2</sub>O<sub>3</sub>

The glasses used for the present study are prepared by the melt- quench method.. Batch materials to produce 10 g of each glass were accurately weighed, thoroughly mixed in an agate mortar and melted in a platinum crucible. Appropriate amounts (all in mol %) of reagent grades of H<sub>3</sub>BO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, ZnO, CdO and MnO powders were thoroughly mixed in an agate mortar and melted in Porcelain crucible in the temperature range 950-1050°C. The glasses were melted for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould held at room temperature and subsequently annealed at 300° C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.4 cm. For dielectric measurements thin films of silver were coated on these samples using sputtering technique. The dielectric measurements on the Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub>: Fe<sub>2</sub>O<sub>3</sub> glasses were carried out on HOCI LCR HITESTER3532-50 meter at 1 kHz– 1 MHz in the temperature range 30 – 300° C.

## III. RESULTS AND DISCUSSION

The dielectric constant ε' and loss tan δ at room temperature (~ 30 °C) of pure Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> glasses at 100 kHz are measured to be 12.649 and 0.0064 respectively; the values of ε' and tan δ of the glasses are found to increase considerably with decrease in frequency. Fig. 1 represents the variation of dielectric constant and loss of Li<sub>2</sub>O-ZnO-CdO-B<sub>2</sub>O<sub>3</sub> glasses containing different concentrations of Fe<sub>2</sub>O<sub>3</sub>, with frequency, measured at room temperature; the parameters, ε' and tan δ are observed to decrease with the concentration of Fe<sub>2</sub>O<sub>3</sub> slowly up to 0.8 mol % and beyond this concentration, the parameters are found to increase at faster rates.

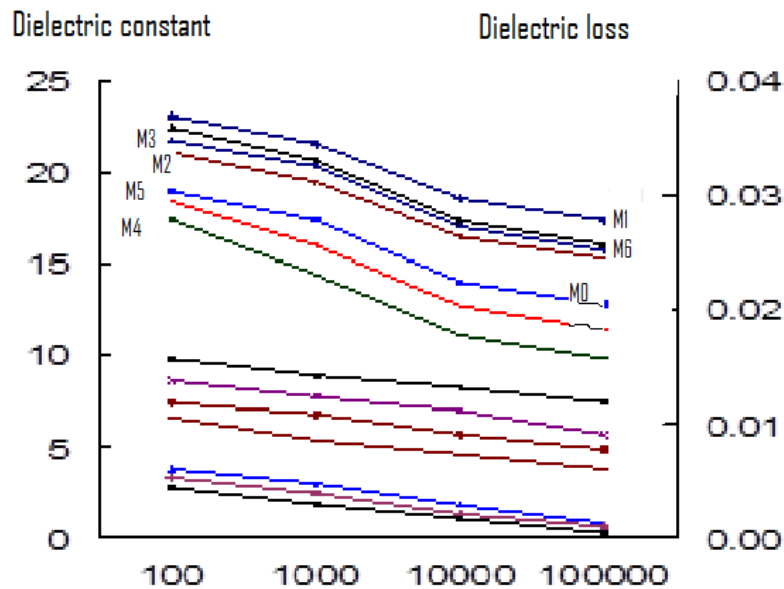


Fig.1. Variation of dielectric constant and loss with the frequency at room temperature.

The temperature dependence of  $\epsilon'$  at different frequencies of the glasses containing different concentrations of  $\text{Fe}_2\text{O}_3$  at 15 kHz are shown in Figs. 2 respectively.

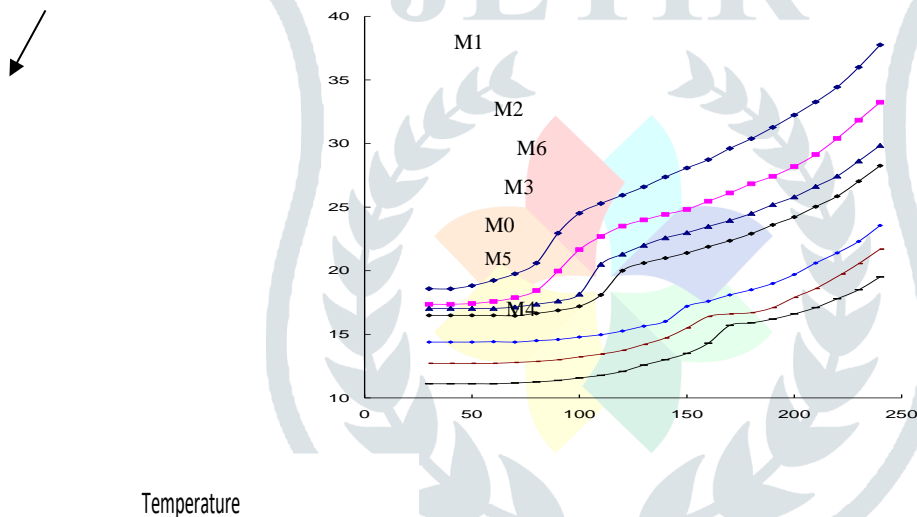


Fig.2 A comparison plot of variation of dielectric constant with temperature at 15 kHz for  $\text{Li}_2\text{O-ZnO-CdO-B}_2\text{O}_3$  glasses containing different concentrations of  $\text{Fe}_2\text{O}_3$

The value of  $\epsilon'$  is found to exhibit a considerable increase at higher temperatures especially at lower frequencies; however the rate of increase of  $\epsilon'$  with temperature is found to be the highest for the glass containing the highest concentration of  $\text{Fe}_2\text{O}_3$ .

A comparison plot of variation of  $\tan \delta$  with temperature, measured at a frequency of 100 kHz is presented in Fig. 3.

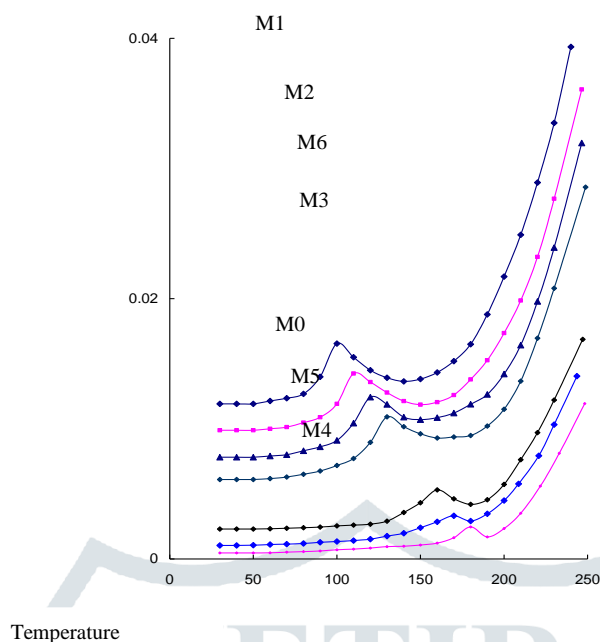


Fig.3.. Variation of dielectric loss with temperature measured at 100 kHz.

The curves of both the pure and  $\text{Fe}_2\text{O}_3$  doped glasses have exhibited distinct maxima; with increasing frequency the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher frequency, indicating the dielectric relaxation character of dielectric losses of these glasses. Further, the observations on dielectric loss variation with temperature for different concentrations of  $\text{Fe}_2\text{O}_3$  indicate an increase in the broadness and  $(\tan \delta)_{\max}$  of relaxation curves with increase in the concentration of  $\text{Fe}_2\text{O}_3$  beyond 0.4 mol %. The summary of the data on the relaxation effects of  $\tan \delta$  with  $\text{Fe}_2\text{O}_3$  concentration is presented in Table 1.

**Table 1 Data on dielectric loss of  $\text{Li}_2\text{O-ZnO-CdO-B}_2\text{O}_3\text{: Fe}_2\text{O}_3$  glasses**

Glass	$(\tan \delta_{\max})_{\text{avg}}$	Temperature region of relaxation ( $^{\circ}\text{C}$ )	Activation energy for dipoles(eV)
M <sub>0</sub>	0.0041	140-156	2.11
M <sub>1</sub>	0.0165	85-125	1.68
M <sub>2</sub>	0.0156	82-129	1.68
M <sub>3</sub>	0.013	104-135	1.72
M <sub>4</sub>	0.004	157-179	2.98
M <sub>5</sub>	0.005	132-173	3.05
M <sub>6</sub>	0.018	86-128	1.78

In the present measurements of  $\epsilon'$  and  $\tan \delta$  on  $\text{Li}_2\text{O-ZnO-CdO-B}_2\text{O}_3\text{: MnO}$  glasses, we notice, a large increase of these parameters with temperature beyond the relaxation region; such a behavior can only be attributed to space charge polarization due to the bonding defects of the type mentioned earlier in these glasses [3].

The values of  $\epsilon'$  and  $\tan \delta$  also are found to increase at any frequency and temperature with increase in the concentrations of  $\text{Fe}_2\text{O}_3$  beyond 0.8 mol %. In this concentration range Ferrous ions act as modifiers and create bonding defects. The defects thus produced create easy path ways for the migration of charges that would build up space charge polarization leading to an increase in the dielectric parameters as observed [4]. In the concentration ranges of  $0 \leq \text{Fe}_2\text{O}_3 \leq 0.8$  the values of dielectric parameters have showed a decreasing trend. Such tendency suggests that Ferrous ions occupy single site symmetry, cross link with the other structural units and increase the rigidity of the glass network. In other words such cross linkages decrease the concentration of free charge carriers as a result there may be a decrease in the space charge polarization [5].

$\tan \delta$  versus temperature curves for  $\text{Li}_2\text{O-ZnO-CdO-B}_2\text{O}_3\text{: Fe}_2\text{O}_3$  glasses show dipolar relaxation effects. In general, the dielectric relaxation effects are observed only when the metal ions are present in divalent state. As evident in the literature, the divalent may form dipoles and such types of dipoles are responsible for the observed dielectric relaxation effects; with increase in the concentration of  $\text{Fe}_2\text{O}_3$  up to 0.8 mol %, the value of  $\tan \delta_{\max}$  is observed to decrease while value of activation energy for dipoles is observed to increase. These trends suggest a decreasing degree of freedom for dipoles to orient in the field direction. Indirectly, it leads to the conclusion, that there is an increasing hardness of the glass network.

## IV . CONCLUSIONS

The dielectric parameters viz.,  $\epsilon'$  and  $\tan\delta$  are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of  $\text{Fe}_2\text{O}_3$  beyond 0.8 mol %; this has been attributed to the increasing presence of  $\text{Fe}^{3+}$  ions. Finally, the analysis of the results of various studies on dielectric properties of  $\text{Li}_2\text{O}-\text{ZnO}-\text{CdO}-\text{B}_2\text{O}_3$  glasses doped with different concentrations  $\text{Fe}_2\text{O}_3$  indicates that there is a possibility of conversion of a part of  $\text{Fe}^{3+}$  ions into  $\text{Fe}^{2+}$  ions, especially when the concentration of  $\text{Fe}_2\text{O}_3$  is approximately more than 0.8 mol %. Such ions mostly act as glass modifiers.

## V.. ACKNOWLEDGMENTS

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## VI. REFERENCES

- [1] M. Srinivasa Reddy, G. Murli Krishna, N. Veeraiah, "Spectroscopic and magnetic studies of manganese ions in  $\text{ZnO}-\text{Sb}_2\text{O}_3-\text{B}_2\text{O}_3$  glass system", Journal of Physics and Chemistry of Solids, Volume 67, Issue 4, pp. 789-795, April 2006.
- [2] Cutroni, M., A. Mandanici, A. Piccolo, C. Fanggao, G.A. Saunders, P. Mustarelli, 1996. Frequency and temperature dependence of a.c. conductivity of vitreous silver phosphate electrolytes Original Research Article. Solid State Ionics., 90: 167-172.
- [3] Dutta, B., N.A. Fahmy, I.L. Pegg, 2005. Effect of mixed transition-metal ions in glasses. I. The  $\text{P}_2\text{O}_5-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$  system. J. Non-Cryst. Solids., 351: 1958-1966.
- [4] El. Mkami, H., B. Deroide, R. Backov, J.V. Zanchetta, 2000. dc and ac Conductivities of  $(\text{V}_2\text{O}_5)_x(\text{B}_2\text{O}_3)_{1-x}$  oxide glasses. J. Phys. Chem. Solids., 61: 819-826. Gedam, R.S., V.K. Deshpande, 2006.
- [5] An anomalous enhancement in the electrical conductivity of  $\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{Al}_2\text{O}_3$  glasses. Solid State Ionics., 177: 2589-2592. Ghosh, A., 1990.
- [6] Frequency-dependent conductivity in bismuth-vanadate glassy semiconductor. Phys. Rev. B, 41: 1479.
- [7] Ghosh, A., 1993. Complex ac conductivity of tellurium cuprate glassy semiconductors. Phys. Rev. B. 47: 15537-15542.
- [8] Jain, H., J.N. Mundy, 1987. Analysis of ac conductivity of glasses by a power law relationship. J. Non-Cryst. Solids., 91: 315-323.
- [9] Kumar, B., T. Vijaya, Sankarappa, M. Santosh Kumar, P.J. Prashant Kumar, R. Sadashivaiah, Ramakrishna Reddy, 2006. Dielectric properties and conductivity in  $\text{CuO}$  and  $\text{MoO}_3$  doped borophosphate glasses. Physica, B 404: 3487-3492
- [10] Mahmoud, K.H., F.M. Abdel-Rahim, K. Atef, Y.B. Saddeek, 2011. Dielectric dispersion in lithium-bismuthborate glasses. Current Applied Physics, 11: 55-60.
- [11] Nagaraja, N., T. Sankarappa, M. Prashant Kumar, 2008. Electrical conductivity studies in single and mixed alkali doped cobalt-borate glasses. J. Non-Cryst. Solids., 354: 1503-1508