

# Dielectric studies of Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glasses doped with copper ions

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## ABSTRACT

The structure of 30 Li<sub>2</sub>O – (10- x) ZnO–60B<sub>2</sub>O<sub>3</sub>: x CuO glass system with 0 ≤ x ≤ 6 mol% was prepared. Dielectric properties, viz., dielectric constant ε', loss Tan δ and a.c. conductivity σ<sub>a.c.</sub> in the frequency range 10<sup>2</sup> to 10<sup>5</sup> Hz and in the temperature range 30 to 300° C. The analysis of the results of dielectric properties of Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>: CuO glasses indicates that there is a possibility of conversion of a part of Cu<sup>2+</sup> ions into Cu<sup>+</sup> ions, leading to decrease in the total concentration of Cu<sup>2+</sup> ions (that take part in modifying positions). As a result an increase the rigidity of the glass network may be achieved when the content of CuO is greater than 0.3 mol % in the glass matrix.

**KEY WORDS:** Glasses, Copper ions, Dielectric Properties.

## 1. INTRODUCTION

The TM ions such as copper doped in Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glass matrix even in very little quantities create these glasses coloured and improve the insulating character and OT of these glasses. It is useful to compare the environment of copper ions in different glass systems like silicates, fluorides, borate, arsenates etc., with the present glass system. CuO containing oxide glasses are known as semi- conducting glasses since a long time. These ions present in different environment (ionic, covalent) in glass matrices. Cu<sup>2+</sup> ions are well-known paramagnetic ions. The objective of this is to study valence states of copper ions (when present in small quantities) in Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glass network, by a systematic study of various dielectric properties (dielectric constant, loss tan δ, a.c conductivity σ<sub>a.c.</sub>).

## 2. MATERIALS AND METHODS

**Glass Preparation:** Within the glass-forming region of Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glass system, the following particular compositions are chosen for this study:

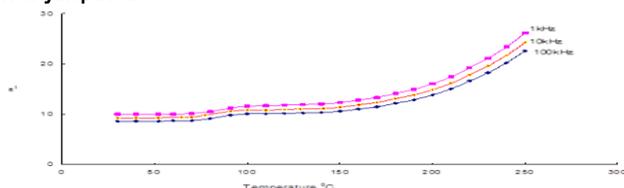
Type of glass	Percentage of each ingredient			
	Li <sub>2</sub> O	ZnO	B <sub>2</sub> O <sub>3</sub>	CuO
C <sub>0</sub>	30	10	60	0
C <sub>1</sub>	30	9.9	60	0.1
C <sub>2</sub>	30	9.8	60	0.2
C <sub>3</sub>	30	9.7	60	0.3
C <sub>4</sub>	30	9.6	60	0.4
C <sub>5</sub>	30	9.5	60	0.5
C <sub>6</sub>	30	9.4	60	0.6

The glasses used for the present study are prepared by the melt quenching techniques. Batch materials to produce 10 g of each glass were accurately weighed. 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 and CuO powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 1000-1050°C. The furnace used was a PID temperature controlled furnace. The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200° 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 0.2 cm.

**Dielectric Properties:** The dielectric measurements on the Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>: MnO glasses were carried out on HP 4263B LCR Meter in the frequency range 10<sup>2</sup> - 10<sup>5</sup> Hz in the temperature range 30 – 300° C.

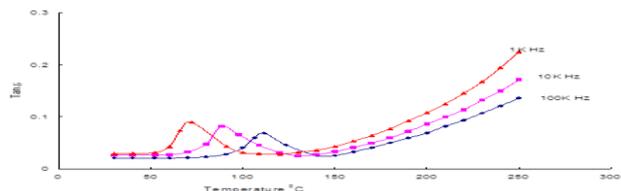
## 3. RESULTS

With the addition of CuO, the value of ε' is observed to raise up to 0.3 mol % and beyond this concentration a reverse trend was observed. The dielectric loss, tanδ at room temperature with the concentration of CuO has followed same trend. Figure 1 shows the temperature effect of dielectric constant at different frequencies for glass C<sub>1</sub>. Figure 2 shows the temperature effect of dielectric constant for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>: CuO glasses measured at 1 kHz. The rate of increase of dielectric constant with temperature has maximum value for the glass containing the 0.3 mol % of CuO and minimum value for the glass containing 0.6 mol %).



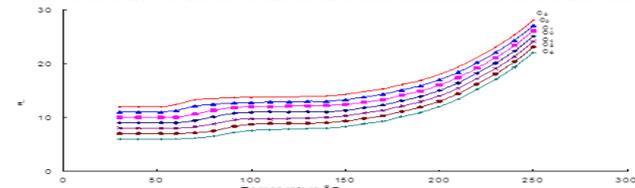
**Figure.1. Variation of dielectric constant with temperature at different frequencies for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glasses containing 0.1 mol% of CuO**

The temperature effect of dielectric loss at various frequencies for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>: CuO glasses containing 0.2 mol % of CuO is shown in Figure.3, Figure.4 shows the temperature dependence of dielectric loss for all the glasses measured at 10 kHz.

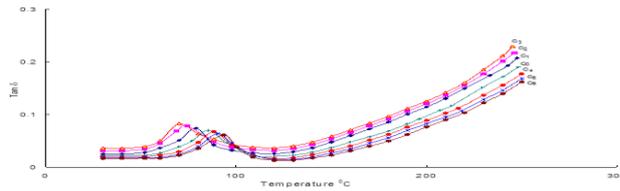


**Figure.3. Variation of dielectric loss with temperature at different frequencies for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glasses containing 0.2 mol% of CuO (glass C<sub>2</sub>)**

The temperature effect of dielectric loss of pure and copper contained glasses have exhibited distinct maxima indicating the dielectric relaxation character of dielectric loss of copper doped Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glasses. With the raise in the concentration of CuO up to 0.3 mol % the relaxation intensity is observed to increase beyond that concentration a reverse trend is observed. The effective activation energy,  $W_d$ , for the dipoles, evaluated using  $f = f_0 \exp(-W_d/KT)$ , is observed to be highest for glass C<sub>6</sub> and low for glass C<sub>3</sub> (Table 1).



**Figure.2. A comparison of variation of dielectric constant (at 1 kHz) with the temperature for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>:CuO glasses**



**Figure.4. A comparison plot of variation of dielectric loss (at 10 kHz) with the temperature for Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>:CuO glasses**

**Table.1. Data on dielectric loss of Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub>: CuO glasses**

Glass	( $\tan \delta_{\max}$ ) <sub>avg</sub>	Temp. region of relaxation (°C)	Activation energy for dipoles (eV)
C <sub>1</sub>	0.0211	82-162	1.41
C <sub>2</sub>	0.0200	88-157	1.45
C <sub>3</sub>	0.0177	100-152	1.49
C <sub>4</sub>	0.0182	108-153	1.55
C <sub>5</sub>	0.0120	148-198	1.56
C <sub>6</sub>	0.0171	121-172	1.59

## DISCUSSION

Variations of  $\epsilon'$  and  $\tan \delta$  with temperature are observed to be the highest for the glasses containing CuO about 0.3 mol %. This indicates a boost in the lattice distortion in Li<sub>2</sub>O-ZnO-B<sub>2</sub>O<sub>3</sub> glasses with raise in CuO concentration this resulting an enhancement of the space charge polarization, that ultimately causes a larger raise of  $\epsilon'$  and  $\tan \delta$  values.

For higher concentration of CuO (more than 0.3 mol %) we observed that the dielectric constant and loss to decrease; this is vividly due to the decrease in the concentration of copper (2+) ions that take modifying positions. Our observations as mentioned earlier, indicate that the rate of increase of  $\epsilon'$   $\tan \delta$  with temperature is gradually raised with raise in the concentration of CuO up to 0.3 mol % and beyond that a reversal trend is observed. Since the values of  $\epsilon'$  and  $\tan \delta$  with temperature is the maximum for the glass C<sub>3</sub>. These observations reveal that, there is a raise in the disorderliness in the glass network when there is an increment in the concentration of CuO (up to 0.3 mol %) in the glass matrix and an enhancement in the insulating strength is observed when the concentration of CuO is beyond this 0.3 mol%.

## 4. CONCLUSION

The values of dielectric constant and dielectric loss are observed to increase and the activation energy for ac conduction is observed to decrease with the raise in the concentration of CuO up to 0.3 mol %, revealing that increase in the concentration of copper (2+) ions that act as modifiers in this concentration range. Finally these analysis indicates that there is a raise in the rigidity of the glass network may be achieved for higher concentrations.

## REFERENCES

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