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Dielectric and spectroscopic studies on Li_2O-ZnO-B_2O_3 glasses doped with copper ions

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ABSTRACT

Alkali oxy borate glasses are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices. Transition metal ions are very interesting ions to probe in the glass network because they exist in different valence states and influence the physical properties of the glasses to a substantial extent. Different concentrations of Cu^{2+} doped (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol %) Li_2O-ZnO-B_2O_3 glasses were prepared using melting and quenching technique. The prepared material was characterized by optical absorption spectra and physical, dielectric properties were measured. From optical absorption spectra the prepared sample was tetragonally distorted octahedral symmetry.

KEYWORDS

Li_2O-ZnO-B_2O_3 glasses;
Copper ions;
Dielectric and
Optical Spectra.

INTRODUCTION

Glass is an inorganic solid material that is usually clear or translucent with different colors. It is hard, brittle and stands up to the effects of wind, rain or sun. Alkali oxy borate glasses are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices. These glasses are relatively moisture resistant, posse's high mechanical strength when compared with the pure borate glasses[1,2]. Glass has been used due to its chemical and physical-chemical characteristics such as good behavior during fusion, homogeneity, durability and stability to several environmental conditions. In addition, glass shows an open amorphous structure and can easily be incorporated with a great number of elements of the periodic table. These characteristics are also interesting to the inertization of galvanic waste in the glass matrix that contains several diûerent metals in its composition[3].

Transition metal ions are very interesting ions to probe in the glass network because they exist in different valence states and influence the physical properties of the glasses to a substantial extent[4-6]. Among various transitional metal ions, copper ion, when dissolved in glass matrix in very small quantities, influences the optical property and dielectric properties of the glasses significantly. CuO containing oxide glasses are known as semi- conducting glasses since a long time. It may be useful to compare the environment of copper ions in various other glass systems like silicates, fluorides, borate, arsenates etc., with that of the present glass system. The transition metal ions such as copper dissolved in Li_2O-ZnO-B_2O_3 glass matrix even in very small quan-

tities make these glasses colored and have strong influence over the insulating character and optical transmission of these glasses[7]. A study of the physical properties including spectroscopic, dielectric properties etc., of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view[8-10].

The objective of the present investigation is to have a comprehensive understanding over the topology and valence states of copper ions in Li_2O-ZnO-B_2O_3 glass network, by a systematic study of various dielectric properties (dielectric constant έ, loss tanδ, a.c conductivity $\sigma_{a.c}$, over a moderately wide range of frequency and temperature) coupled with optical absorption. In the present work, different concentrations of Cu^{2+} doped (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol%) Li_2O-ZnO-B_2O_3 glasses were prepared using melting and quenching technique. The prepared materials were characterized by different spectroscopic studies.

EXPERIMENTAL

The chemicals Li_2O, ZnO, B_2O_3 and CuO were purchased from Merck Chemicals, Mumbai, India. All of the chemical reagents used in this experiment were analytical grade and used without further purification. The appropriate amounts of the compounds were thoroughly mixed in an agate mortar and melted in a platinum crucible. The prepared sample is placed in a proportional-integral-derivative (PID) temperature controlled furnace at 1000-1050^{0}C for 20 min. till a bubble free liquid is formed. Resultant melt was poured on a rectangular brass mould and annealed at 200^0 C in another furnace. The approximate dimensions of the glasses used are 1 cm x 1 cm x 0.2 cm. Glass samples are formed and these samples are optically polished, finally we get copper ions doped Li_2O-ZnO-B_2O_3 glasses.

The detailed compositions of the prepared samples are

- C_0 : 30 Li_2O — 10 ZnO - 60 B_2O_3 (pure)
- C_1 : 30 Li_2O — 9.9 ZnO - 60 B_2O_3: 0.1 CuO
- C_2 : 30 Li_2O — 9.8 ZnO - 60 B_2O_3: 0.2 CuO
- C_3 : 30 Li_2O — 9.7 ZnO - 60 B_2O_3: 0.3 CuO
- C_4 : 30 Li_2O — 9.6 ZnO - 60 B_2O_3: 0.4 CuO
- C_5 : 30 Li_2O — 9.5 ZnO - 60 B_2O_3: 0.5 CuO
- C_6 : 30 Li_2O — 9.4 ZnO - 60 B_2O_3: 0.6 CuO

Optical absorption spectrum is recorded at room temperature on JASCO V-670 spectrophotometer in the wavelength region of (300-1100 nm). Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum of the prepared sample in the region 1600 - 400cm^{-1}. Physical properties of the prepared sample were calculated.

RESULTS AND DISCUSSION

Physical and dielectric properties

Some physical parameters useful for characterization Li_2O-ZnO-B_2O_3: CuO glasses are estimated from the measured value of density (d) and the average molecular weight $\overline{M}$, using the following Eqs.[11]

The transition metal ion concentration (N_i) could be obtained from:

$$N_i\ (10^{22}\ \text{ions/cm}^3) = N_A\, M\ (\text{mol\%})\, d / \overline{M} \qquad (1)$$

From the N_i values obtained, the polaron radius (r_p) and inter-ionic distance (r_i) of transition metal ions could be evaluated:

$$\text{Inter - ionic distance } r_i\ (\text{Å}) = \left[\frac{1}{N_i}\right]^{1/3} \qquad (2)$$

$$\text{Polaron radius } r_p\ (\text{Å}) = \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3} \qquad (3)$$

From the measured values of the density and average molecular weight M of the samples, various other physical parameters such as transition metal ion concentration N_i, inter-ionic distance r_i, polaron radius r_p for all the glass samples were evaluated and presented in TABLE 1.

Figure 1 shows a comparison plot of the temperature dependence of 'e' for Li_2O-ZnO-B_2O_3 glasses doped with different concentrations of CuO measured at 1 kHz. The rate of increase of 'e' with temperature is found to be the highest for the glass containing the 0.3 mol % of CuO and the lowest for the glass containing

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TABLE 1 : Physical properties of Cu^{2+} doped Li_2O-ZnO-B_2O_3 glasses

Glass	Conc. CuO (mol%)	Density (g/cm^3)	Avg. mol. wt $\overline{M}$	Conc. Cu ions N_i (x 10^{21} ions/cm^3)	Inter ionic distance of Cu ions r_i(A^0)
C_0	0	2.5040	58.874	0	0
C_1	0.1	2.5174	58.872	0.257547	33.8622
C_2	0.2	2.5206	58.870	0.525766	26.8647
C_3	0.3	2.5228	58.869	0.774337	23.4615
C_4	0.4	2.5264	58.867	1.03396	21.3059
C_5	0.5	2.5295	58.864	1.2941	19.7702
C_6	0.6	2.5339	58.863	1.55565	18.5936

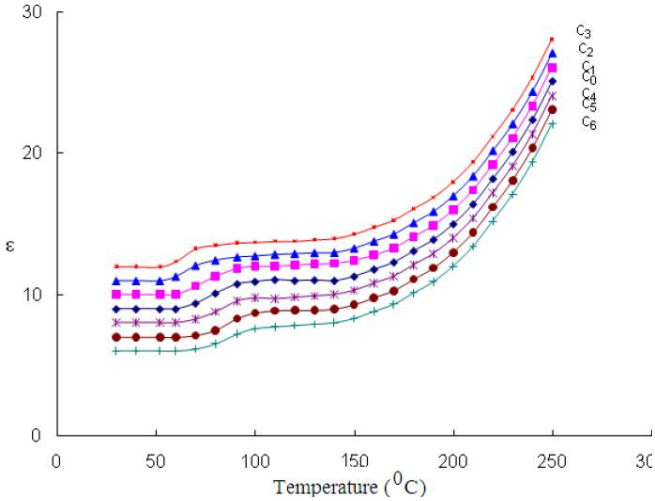

Figure 1 : A comparative plot of variation of dielectric loss (1 KHz) with temperature

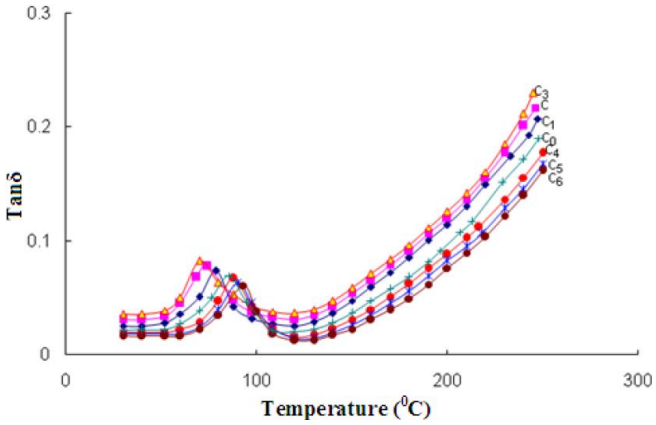

Figure 2 : A comparative plot of variation of dielectric loss (10 KHz) with temperature

0.6 mol %. Figure 2 shows the temperature dependence of tand for the glasses doped with different concentrations of CuO measured at 10 kHz. The temperature dependence of dielectric loss tan d of pure and Cu^{2+} doped Li_2O-ZnO-B_2O_3 glasses have exhibited distinct maxima and with increasing temperature the frequency maximum shifts towards higher frequencies, indicating the dielectric relaxation character of dielectric loss of Li_2O-ZnO-B_2O_3: CuO glasses. With the increase in the concentration of CuO up to 0.3 mol% the relaxation intensity is observed to increase.

The dielectric parameters viz., 'e', tand and $s_{a.c}$ are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of CuO up to 0.3 mol %, indicating an increase in the concentration of Cu^{2+} that act as modifiers in this concentration range. The high temperature part of the conductivity is explained on the basis of random cite model whereas the quantum mechanical tunneling model seems to be appropriate for the low temperature part of the conductivity. Variation of tan δ with temperature has exhibited dipolar relaxation effects; the spreading of relaxation with the set of relaxation times t has been observed with the doping of CuO. The relaxation effects are attributed to the association of divalent copper ions. TABLE 2 shows the data on dielectric loss of Li_2O-ZnO-B_2O_3: CuO glasses.

Optical absorption studies

Figure 3 represents the optical absorption spec-

TABLE 2 : Data on dielectric loss of Li_2O-ZnO-B_2O_3: CuO glasses

Glass	$(\tan d_{max})_{avg}$	Temperature region of relaxation (°C)	Activation energy for dipoles (eV)
C_1	0.0211	82-162	1.41
C_2	0.0200	88-157	1.45
C_3	0.0177	100-152	1.49
C_4	0.0182	108-153	1.55
C_5	0.0120	148-198	1.56
C_6	0.0171	121-172	1.59

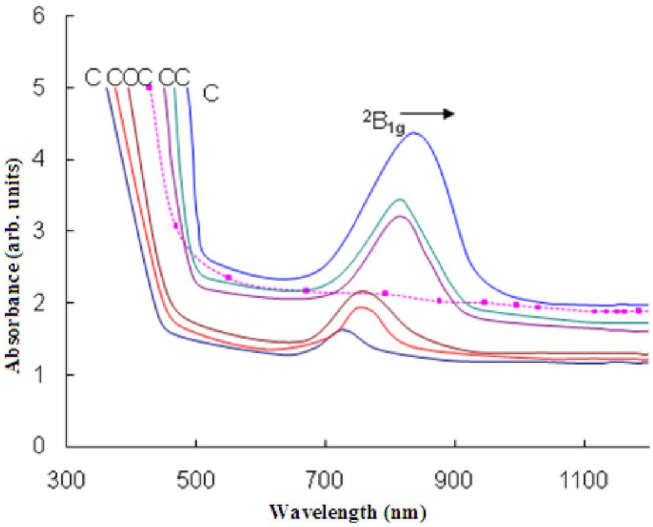

Figure 3 : Optical absorption spectra of Li_2O-ZnO-B_2O_3: CuO glasses

tra of Li_2O-ZnO-B_2O_3: CuO glasses recorded at room temperature in the wavelength region 300-1200 nm. The absorption edge is observed at 424 nm for glass C_0 (pure glass). It is observed to shift slightly to higher wavelength side with increase in the concentration of CuO up to 0.3 mol % and beyond this concentration the edge is observed to shift towards lower wavelength. The spectrum of glass C_4 has exhibited a broad absorption band at 750 nm corresponding to $^2B_{1g}$'!$^2B_{2g}$ transition of Cu^{2+} ions, with an increase in the concentration of CuO up to 0.3 mol%, the intensity of the band is found to increase with a shift in the peak position slightly towards higher wavelength. Beyond this concentration, the intensity of the band is noticed to decrease with the shifting of the peak position towards lower wavelength. The optical absorption measurements on these glasses indicate the presence of copper ions mostly in tetragonally distorted octahedral positions[12]. The analysis of this data further indicates with an increase

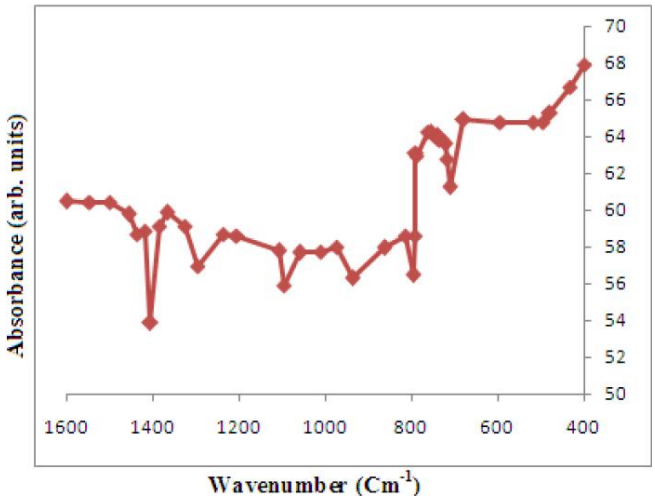

Figure 4 : FT-IR spectrum of Li_2O-ZnO-B_2O_3: CuO glasses

TABLE 3 : IR data of Li_2O-ZnO-B_2O_3: CuO glasses

S.No.	Band Positions	Band Assignments
1	710	B-O-B linkage
2	795	P-O-P Symmetric
3	936	PO_4^{3-}- BO_4 units
4	1095	P-O-P Asymmetric
5	1295	PO^{2-} units
6	1405	BO_3 units

in the concentration of CuO (above 0.3 mol%) a gradual adaptation of Cu^{2+} from ionic environment to covalent environment.

FT-IR studies

Figure 4 show the FT-IR spectrum of Li_2O-ZnO-B_2O_3: CuO glasses recorded at room temperature in the region 400-1600 cm^{-1}. The spectrum exhibit bands characteristic of symmetric and asymmetric stretching and bending vibrations borate groups, triply degenerate modes of phosphate ion PO_4^{3-}, P-O-P modes of vibrations. The band observed at 710 cm^{-1} is due to B-O-B linkage. The band observed at 795 cm^{-1} is due to symmetric mode of P-O-P. The band observed

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at 936 cm^{-1} is due to PO_4^{3-}- BO_4 units[13]. The band observed at 1095 cm^{-1} is due to asymmetric mode of P-O-P. The band observed at 1295 cm^{-1} is due to PO^{2-} units. The band observed at 1405 cm^{-1} is due to BO_3 units[14]. The IR band positions and their assignments are presented in TABLE 3.

CONCLUSIONS

Cu^{2+} doped Li_2O-ZnO-B_2O_3 glasses were prepared using melting and quenching technique. The dielectric parameters viz., 'e', tand and $s_{a.c}$ are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of CuO up to 0.3 mol %, indicating an increase in the concentration of Cu^{2+} ions that act as modifiers in this concentration range. The high temperature part of the conductivity is explained on the basis of random cite model whereas the quantum mechanical tunneling model seems to be appropriate for the low temperature part of the conductivity. Variation of tan δ with temperature has exhibited dipolar relaxation effects; the spreading of relaxation with the set of relaxation times t has been observed with the doping of CuO. The relaxation effects are attributed to the association of divalent copper ions. The optical absorption measurements on these glasses indicate the presence of copper ions mostly in tetragonally distorted octahedral positions. The analysis of this data further indicates with an increase in the concentration of CuO (above 0.3 %) a gradual adaptation of Cu^{2+} ions from ionic environment to covalent environment. Finally, the analysis of the results of various studies viz. optical absorption and dielectric properties of Li_2O-ZnO-B_2O_3: CuO glasses indicates that there is a possibility of conversion of a part of Cu^{2+} ions into Cu^{+} ions, leading to decrease in the total concentration of Cu^{2+} 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. FT-IR spectra showed the characteristic vibrational modes of the prepared samples.

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