Optical Absorption Spectra of Li_2O-Zno-B_2o_3 Glasses Doped With Copper Ions

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Abstract

The structure of 30 Li_2O – (10- x) ZnO–60B_2O_3: x CuO glass system with 0 $\leq x \leq$ 6 mol% was prepared and investigated by optical absorption spectra. The optical absorption measurements on these glasses indicate the presence of copper ions mostly in octahedral distorted tetragonally positions.

Keywords: Glasses, Copper Ions, Optical Absorption Spectra

Introduction

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, posses' high mechanical strength when compared with the pure borate glasses. Extensive studies on various properties like ESR studies, optical properties of various alkali borate glasses doped with different transition and rare earth metal ions are available [1-5]. Addition of alkali-earth oxides like CaO, BaO, MgO etc., in to these glass matrices is expected to increase the resistance of the glasses to the moisture. Spectroscopic studies on alkali metal borate glasses have revealed that the structure of alkali metal borate glasses is dependent not only upon the content of the alkali metal ion but also upon the difference in the alkali metal ions [6]. Copper ions have strong bearing on electrical and optical properties of glasses. These ions subsist in different surroundings (ionic, covalent) in glass matrices. The content of copper in different environments exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the position of the copper ion and the electrical properties of the glass is highly interesting. Cu^{2+} ions are well-known paramagnetic ions and it is also quite likely for copper ions to have link with arsenic groups; strengthen the glass structure and may raise the chemical resistance of the glass. Though considerable number of studies is available on some CuO containing glasses most of them are restricted to spectroscopic studies [7-9]. The study of the optical absorption can be used for

revealing the structural details of these glasses since these are very sensitive to the local symmetry, the character of the chemical bond and other structural properties.

Experimental Work

Glass Preparation

Within the glass-forming region of Li_2O-ZnO-B_2O_3 glass system, the following particular compositions with successive increase in the concentration of CuO are chosen for the present study:

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

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_3BO_3, Li_2CO_3, 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^{o} 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.\

X-Ray Diffraction

As glassy or amorphous materials do not have long range order, a diffraction pattern containing sharp peaks is not expected as in crystalline materials. The X-ray diffraction pattern for some of the Li_2O-ZnO-B_2O_3: CuO glasses recorded in the range $10^{O} \leq 2\theta \leq 80^{O}$ is shown in Fig.1. The absence of sharp peaks in the pattern indicates the amorphous nature of the samples.

Optical Absorption

The optical absorption spectra of the glasses were recorded using a JASCO Model V-670 Spectrophotometer in the wavelength range 300-2200 nm.

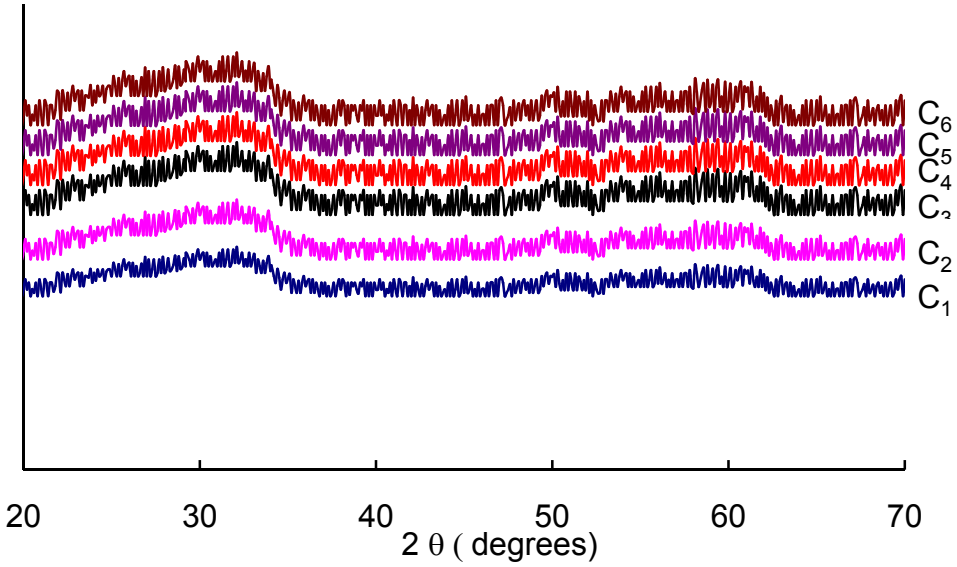

Fig.1X-ray diffraction patterns of Li_2O-ZnO-B_2O_3 : CuO

Result and Discussion

Fig.2 represents the optical absorption spectra of Li_2O-ZnO-B_2O_3: CuO glasses recorded at room temperature in the wavelength region 300-1200 nm. The absorption edge observed at 424 nm for glass C_0 (pure glass) 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 $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions [26-28]; 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. From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot.

Fig.3 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap (E_o) obtained from the extrapolation of these curves are presented in Table 1. The value of E_o is found to decrease with the increase in concentration of CuO up to 0.3 mol % and after the E_o is found to increase.

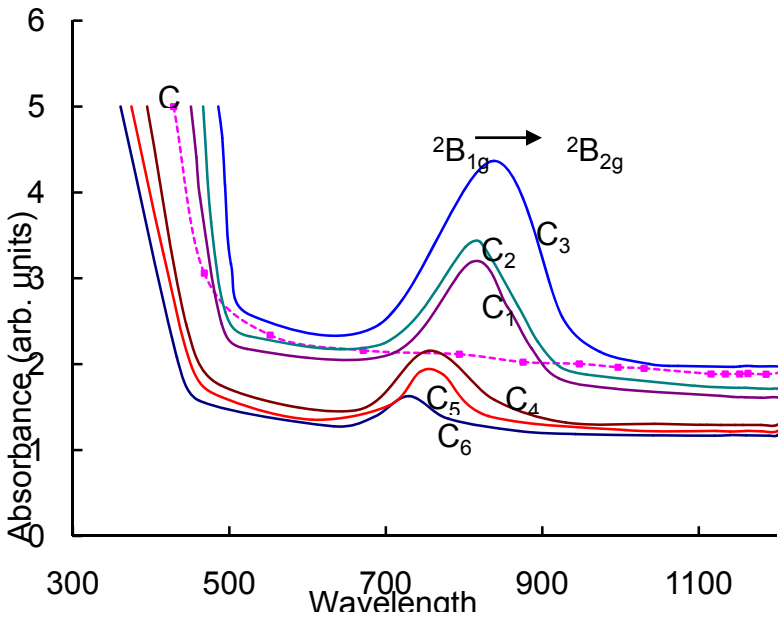

Fig. 2 Optical absorption spectra of Li_2O-ZnO-

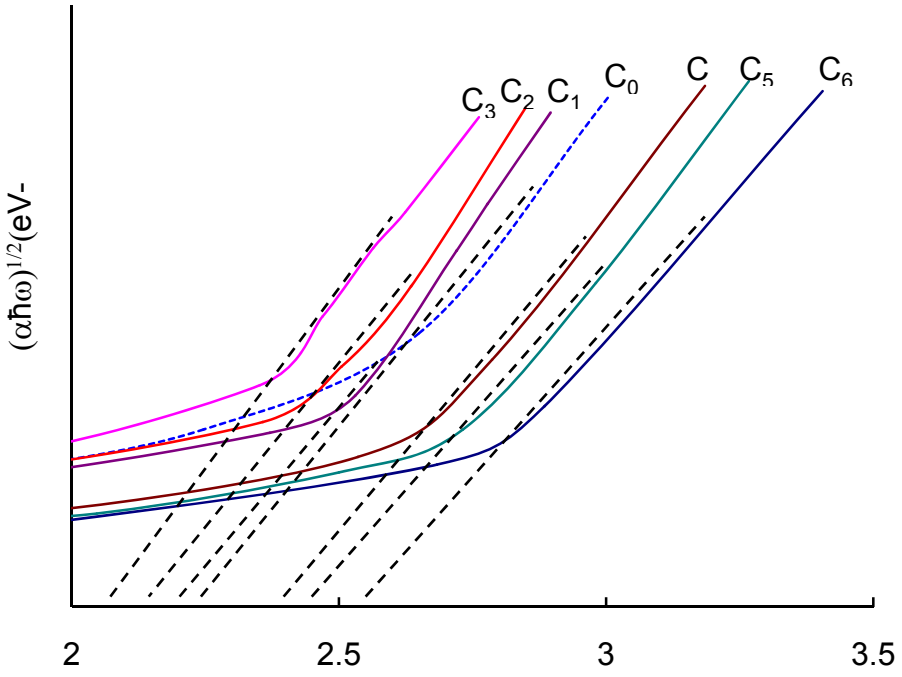

Fig.3 Urbach plot for Li_2O-ZnO-B_2O_3 :

Table 1 Summary of Data On Optical Absorption Spectra of Li_2O-Zno-B_2O_3: Cuo Glasses.

Glass	Optical Band Gap	Cut-Off Wavelength	Position of E_0 (Ev)
	(Nm)	$^2b_{1g} \rightarrow {}^2B_{2g}$ Band	(nm)
C_0	2.20	424	-----
C_1	2.16	446	805
C_2	2.12	461	816
C_3	2.04	481	833
C_4	2.36	390	750
C_5	2.40	370	739
C_6	2.52	356	725

The optical absorption spectra of CuO doped Li_2O-ZnO-B_2O_3glasses exhibited a broad absorption band at about 800 nm. This is the characteristic of distorted octahedral symmetry. Thus the band can be assigned to $^2B_{1g}$ $^2B_{2g}$ transition [10, 11]. When the concentration of CuO is increased beyond 0.3 mol %, a gradual decrease in the intensity of optical absorption band is observed. This observation indicates a gradual decrease in the concentration of Cu^{2+} ions that take modifier positions in the glass network. In this concentration range of CuO. The lower the concentration of modifying Cu^{2+} ions, the lower is the concentration of NBO's in the glass matrix leading to a decrease of the disorder in the glass network. Such a decrease of disorder in the network results an increase in the optical band gap and shifts the absorption edge towards low wavelength side as observed (Figs.2 and 3) for the glasses C_3 to C_6.

Conclusions

The optical absorption measurements on these glasses indicate the presence of copper ions mostly in octahedral distorted tetragonally positions. The analysis of these 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.

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