

XRD, EPR and FT-IR Studies of Zinc Aluminium Lithium Borate (ZALB) Glasses Doped with Cu²⁺ Ions

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In this study, zinc aluminum lithium borate (ZALB) glasses of different compositions doped with Cu²⁺ ions were prepared using conventional melt quenching technique. X-Ray diffraction (XRD), electron paramagnetic resonance (EPR), and Fourier transform infrared (FT-IR) studies were carried out for ZALB glasses. The XRD pattern of the ZALB glass confirmed the amorphous structure of the glass matrix. The EPR spectra of the Cu²⁺ doped zinc aluminium lithium borate glass system, $g_{\parallel} > g_{\perp}$, determined the position of the Cu²⁺ ion in the glasses at the tetragonally elongated octahedral (D_{4h}) site. FT-IR spectra showed that the increment of copper oxide led to the cleavage of B-O-B bonds and formation of more new bonds. In addition, FT-IR findings also confirmed the both EPR results and the findings from the optical absorption. Our results highlight the major role of copper oxide in the formation of cross-linking bands.

Keywords: Borate glasses, XRD, EPR, FT-IR spectroscopy

INTRODUCTION

Recent technological preparation, investigation, and applications of the oxide glasses are important due to the structural differences of these materials, and their especial properties such as high-quality transparency and excellent corrosion resistance [1-4]. Among these glasses, borates have a high refractive index and low dispersion characteristics. Due to these exclusive properties, borates have been widely used for laboratory glassware, optical lenses, glass discharge tubes, and solar energy technologies [5]. Borate glasses with copper oxides have fascinating properties due to the some oxidation states of these ions in the glass matrix. Copper notably affects the optical properties, strengthens the glass structure, leads to an

increase in the chemical resistance of the glasses for being used in several applications [6]. The chemical durability of the glasses has been improved due to the introduction of modifier cum network former zinc, lithium is an important alkali cation and aluminum is an important metal ion. The zinc lithium aluminum system has been of interest in the last few years because of its important industrial and scientific applications. Zinc-aluminum-lithium borate glasses have many technological uses, including batteries and micro-electronic packing [7,8]. In the present research, spectroscopic studies were carried out for Cu²⁺ doped zinc aluminium lithium borate glasses in order to determine the bond character, understand the glass structure occurrence, and attain the glass network's microscopic perspective using XRD, EPR, and FT-IR spectroscopy.

The elementary and most appropriate dopants for glass systems are transition metal ions as they are distinguished

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by *d* shells which are partially filled. Glasses with copper oxide have stronger semi conductive quality and this makes them suitable for being used in many technological applications [9]. Copper may exist in glass at various oxidation states, namely in the form of Cu²⁺ and Cu¹⁺. This element is one of the glass structure modifiers. Cu²⁺ is a well-known coloring agent in different glasses [10-12]. In order to determine the local structure of transition metal ions in glasses, spectroscopic methods such as Electron Paramagnetic Resonance (EPR) and optical absorption spectral methods have been used [13,14].

EXPERIMENTAL

Suitable amounts of analaR grade chemical agents; boric acid, lithium carbonate, zinc oxide, aluminum oxide and copper oxide were added to every composition of glass. The powdered compound, in each case, was thoroughly mixed in an agate mortar and subjected to melt in a porcelain crucible in a furnace with high temperature between 950-1050 °C for about one hour until a bubble free liquid was formed. The resulting molten liquid was quenched at room temperature (30 °C), poured onto a brass material, and then annealed at 300 °C for 3 h. The compositions of the glass samples used in the study are given in Table 1. The amorphous nature of the present samples was carried using the CuK α radiation ($\lambda = 0.15406$ nm) of a XRD-6100 SHIMADZU X-ray diffractometer. The EPR spectra of the present samples were recorded on a JES-FA 200 series of EPR spectrometer operating in the X-band frequencies (9.16 GHz), with a field modulation of 100 kHz. SHIMADZU 8201 PC FT-IR spectrophotometer was used to record FT-IR spectra of the present samples in the wavelength rang of 4000-400 cm⁻¹. Determination of the properties in the present study is based on the procedures and formulae mentioned by the researches in the literature [15].

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

Figure 1 displays the XRD pattern (TGC3) for Cu²⁺ doped zinc aluminum lithium borate glass. No major crystalline peak (Bragg Peaks) was recorded in the patterns,

Table 1. Compositions of the Glass Samples (Mole %)

Glass sample	Composition
TGC1	10ZnO-5Al ₂ O ₃ -19.8Li ₂ O-65B ₂ O ₃ -0.2CuO
TGC2	10ZnO-5Al ₂ O ₃ -19.6Li ₂ O-65B ₂ O ₃ -0.4CuO
TGC3	10ZnO-5Al ₂ O ₃ -19.4Li ₂ O-65B ₂ O ₃ -0.6CuO
TGC4	10ZnO-5Al ₂ O ₃ -19.2Li ₂ O-65B ₂ O ₃ -0.8CuO

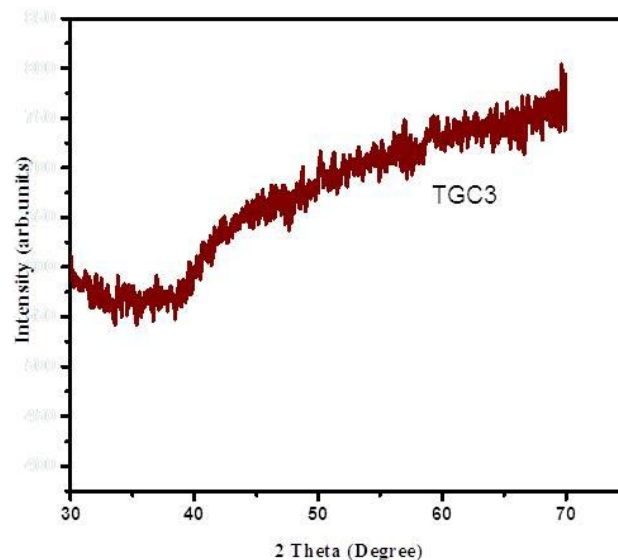


Fig. 1. XRD spectrum of the Cu²⁺ doped ZALB glass.

which confirms the amorphous nature of the glass samples.

EPR Spectral Studies

Due to the absence of the paramagnetic components, no resonance signal was observed in the EPR spectrum of undoped glasses. Once the Cu²⁺ ions were injected into the base glass, the characteristic resonance of Cu²⁺ was obtained in the EPR spectra of all the glass samples. The EPR sample spectrum analyzed at room temperature is shown in Fig. 2. The EPR spectra of the glasses doped with Cu²⁺ ions were studied using an axial spin-Hamiltonian of the form:

$$H = \beta [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

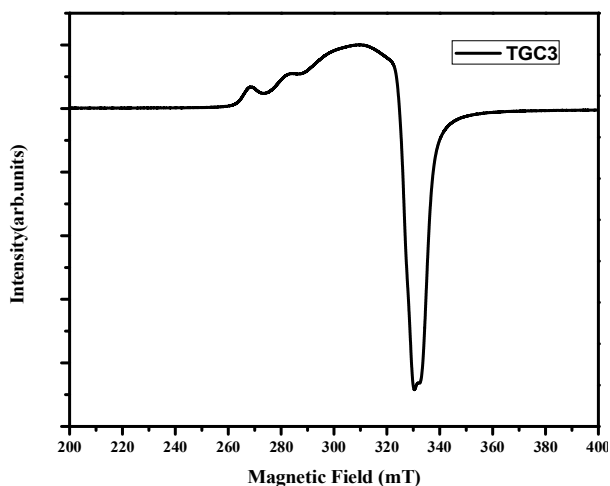


Fig. 2. EPR spectra of Cu²⁺ doped ZALB glasses.

Table 2. Spin-Hamiltonian Parameters of Cu²⁺ Doped ZALB Glasses

Glass sample	$g_{ }$	g_{\perp}	$A_{ }$ (10^{-4} cm^{-1})
TGC1	2.326	2.071	128
TGC2	2.335	2.070	136
TGC3	2.349	2.068	134
TGC4	2.356	2.082	137

Where β is Bohr magneton; $g_{||}$ and g_{\perp} are parallel and perpendicular components of the anisotropic g-tensor; $A_{||}$ and A_{\perp} are parallel and perpendicular components of the hyperfine components of the hyperfine tensor A; z is the symmetry axis; B_x, B_y, B_z are the static components of the magnetic field; S and I are the electron and nuclear spin operators.

The spin-Hamiltonian parameters of present EPR spectra are shown in Table 2. It is clear from Table 2 that the values of $g_{||}$, g_{\perp} and g_e are in the order of $g_{||} > g_{\perp} > g_e$, indicating the presence of Cu²⁺ ion in the octahedral sites with tetragonal distortions. For different glass compositions, the variance of $g_{||}$ and $A_{||}$ was nonlinear. This was due to the tetragonal distortion shift. Variations in $g_{||}$ and $A_{||}$ values may be related to the changes in the Cu²⁺ setting, which is due to the structural changes in the strength of the ligand field at Cu²⁺ site in the glass. Therefore, an increase in the amount of copper oxide in the glass influenced the Cu²⁺ site

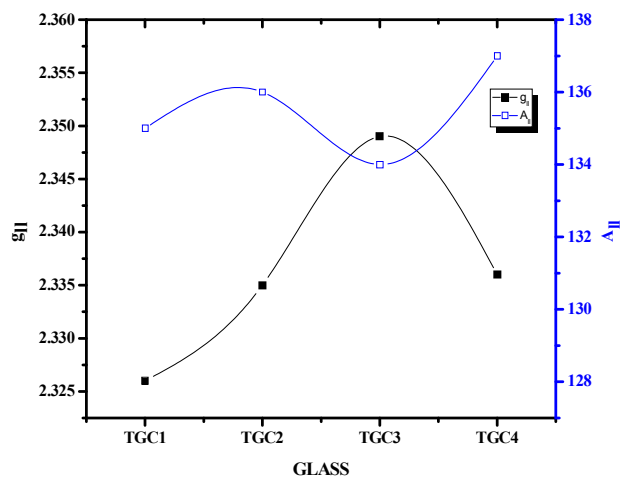


Fig. 3. Compositional dependence of the spin-Hamiltonian parameters.

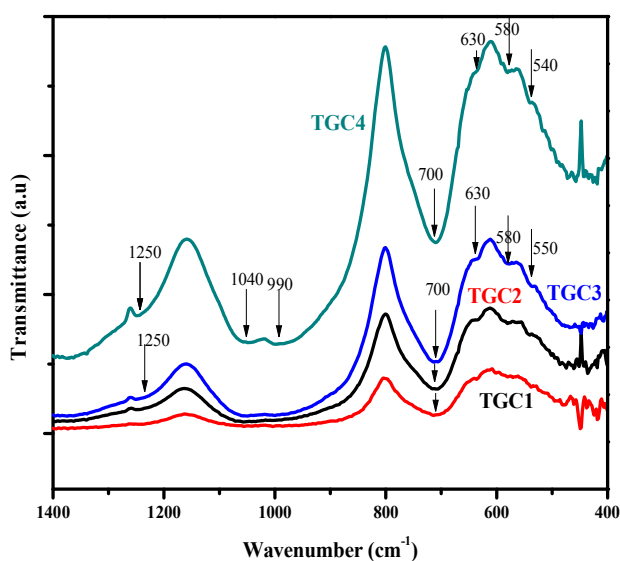


Fig. 4. FTIR spectra of Cu²⁺ doped ZALB glasses.

leading to the nonlinear variance of the Hamiltonian spin parameters as shown in Fig. 3.

FTIR Spectral Studies

Fourier transform infrared spectroscopy is a highly sensitive and widely used method for examining the local order to characterize the vitreous materials such as glass. Typical FTIR spectra of Cu²⁺ doped zinc aluminium lithium borate glasses are shown in Fig. 4. The fundamental infrared

Table 3. Summary of the Data Obtained for the FT-IR Spectra of the Cu²⁺ Doped ZALB Glasses

Glass sample				Band assignments
TGC1	TGC2	TGC3	TGC4	
540	550	550	550	The vibrations of Li ⁺ cations against their network
580	580	580	580	Bending mode of Zn–O vibrations
700	700	700	700	Bending vibration of B-O-B linkage in borate networks
-	-	990	990	Vibration of boron atoms attached to NBO's in the form of BO ₄ vibrations
-	1040	1040	1040	B-O stretching vibration of BO ₄ units
1250	1250	1250	1250	=B-O-B≡ linkage with one of the boron in tetrahedral coordination

absorption peaks of borate vibrational modes were found for the Cu²⁺ doped zinc aluminium lithium borate series of glasses.

The bands at about 1250 cm⁻¹ are assigned to =B-O-B≡ linkage with one of the boron having tetrahedral coordination. The bands at 1040 cm⁻¹ are attributed to the B-O stretching vibration of BO₄ units in tri-tetra and pent borate groups [16]. The bands at 990 cm⁻¹ may be due to vibration of boron atoms attached to NBO's in the form of BO₄ vibrations [17]. The absence of a band at around 800 cm⁻¹ in all the recorded glass samples indicates the absence of boroxol ring in the glass network [18].

This indicates that ZALB glass structure consists of BO₃ and BO₄ groups. The band at 700 cm⁻¹ is assigned to the bending vibration of B-O-B linkage in borate networks [19, 20]. The vibrational modes observed at 580 cm⁻¹ are due to bending mode of Zn–O vibrations, and the bands at 550 cm⁻¹ are attributed to the vibrations of Li⁺ cations against their network. The addition of CuO breaks the boroxol rings (B₃O₆) leading to formation of more BO₃ and BO₄ groups [21]. By changing the composition, there is no much variation in peak position and band shapes. A successive change in the intensity of the bands related to symmetrical borate structural units was obtained by a gradual increase in the concentration of the dopants CuO in the ZnO-Al₂O₃-Li₂O-B₂O₃ glass; this is due to the asymmetrical groups. FTIR observations clearly shows that an increase in the CuO concentration led to an increase in rigidity (or) and a decrease in disorder of the glass. The observed FTIR spectral bands of ZALB glasses are shown in Table 3.

CONCLUSIONS

The XRD pattern of ZALB glass confirmed the amorphous structure of the glass matrix. Using EPR spectra of Cu²⁺ doped zinc aluminum lithium borate glass system, $g_{\parallel} > g_{\perp}$, the position of the Cu²⁺ ion in the glasses at the tetragonally elongated octahedral (D_{4h}) site was determined. FTIR spectra showed that the increment of copper oxide led to the cleavage of B-O-B bonds and formation of more new bonds. Furthermore, FTIR findings also confirmed the both EPR results and the findings of optical absorption, which highlights the major role of copper oxide in the formation of cross-linking bands.

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