IR, EPR and Optical Absorption Studies of xCuO-(1-x) B_2O_3 Glasses

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Abstract– Synthesis of xCuO-(1-x)B₂O₃ with 0.06≤ x ≤ 0.16 was performed by sol-gel method. The amorphous nature of the samples was ascertained by the XRD studies. The room temperature IR spectral studies show the presence of octahedral [CuO₆/₂] and planar [BO₃/₂] units in the glasses. The X-band electron paramagnetic resonance (EPR) and optical absorption studies were carried out at room temperature to understand the nature and symmetry for Cu²⁺ ions in the glasses. The spin Hamiltonian parameters have been calculated. The trend in g-values g∥>g⊥>gₑ (gₑ=2.0023) calculated from the observed electron paramagnetic resonance lineshapes show that the paramagnetic site is Cu²⁺(3d⁹) which is in a tetragonally elongated octahedron [O₁/₂-CuO₄/₂.O₁/₂] with orbital singlet ²B₁g (3dₓ²₋y²) as the ground state having D₄h symmetry. The molecular bonding parameters evaluated by correlating optical and EPR data show that bonding between the central metal ion and ligands is partially covalent.

Keywords– Bonding parameters, EPR, Glasses, Optical absorption.

I. INTRODUCTION

The study of borate glasses has received considerable attention due to their structural peculiarities. In borate glasses, Diboron trioxide, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and trivalent nature of B. In borate glasses, B^{3+} ions triangularly coordinated by oxygen, form glasses easily [1]. Borate is one of the most important glass former and has been incorporated in many kinds of glass systems to achieve chemical and physical properties. Copper (II) oxide, CuO can enter the glass network both as a network former and also as a network modifier and due to this the structure of this glass is expected to be different from other glasses such as alkali borate, phosphates and silicates. Glasses containing mixed-valence transition metal ions are important for their electronic as well as magnetic properties. **Electron paramagnetic resonance (EPR) studies of transition metal ions in oxide glasses is of scientific interest and gives information concerning the state of the ligands, the glass structure, nature** of bonding, and site symmetry around metal ion. The changes in the composition of the glass may change the local environment of the transition metal ion into the glass, leading to ligand field changes which may be reflected in the IR, EPR and optical absorption spectra. The aim of the present investigation is to study the nature of the site symmetry and bonding of Cu^{2+} in copper oxide-borate glasses from the nature and splitting of EPR and optical bands as a function of mol % of CuO.

II. EXPERIMENTAL

The starting materials copper (II) nitrate, $[Cu(NO_3)_2]$ and trihydrooxidoboron, $[H_3BO_3]$, used in the preparation of the samples, were of Analar grade quality. **The samples were prepared by sol-gel method via nitrate-citrate gel route [2] using reagent grade chemicals.** Three samples were prepared with x= 0.06, 0.11 and 0.16 and labeled as A1, A2 and A3. Calculated amounts of copper (II) nitrate, $[Cu(NO_3)_2]$ and boric acid, $[H_3BO_3]$ were dissolved in dil. HNO_3, nitric acid (hydroxidodioxidonitrogen) to prepare 0.05 M solutions. These solutions were then mixed with 2 M citric acid (2-Hydroxypropane-1, 2, 3-tricarboxylic acid) solution to prepare the sol. The resulting sol was air dried by heating ~ 60 °C to prepare the gel which was then decomposed at ~120 °C and a black powder was obtained. Finally, the samples were prepared by melting them in alumina crucibles in the range 1073-1133 K and then quenching in air. The glass formation was confirmed by powder X-ray diffraction recorded with a Phillips type PW 1050 diffractometer using Cu Kα radiation. The IR spectra of the samples at room temperature were recorded in the range 400-4000 cm⁻¹ by a SHIMADZU FTIR-8700 spectrometer using KBr pellet technique. The EPR spectra were recorded on an EPR spectrometer (JEOL-FE-1X) operating in the X-band frequency (≈9.200GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power used was 5 mW. A powdered glass sample of 100 mg was placed in a quartz tube for EPR measurements. The optical absorption spectra of the glasses were recorded using a JASCO UV–VIS–NIR spectrophotometer in the

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wavelength region 300 - 900 nm.

III. RESULTS AND DISCUSSION

Powder XRD spectra recorded for the three glassy samples is shown in Fig.1. The observed XRD pattern of the samples indicates amorphous nature as well as long range structural disorder of the glasses. This figure exhibits no detectable peaks which confirmed the proper preparation of glass samples. Infrared spectroscopy has been extensively employed over the years to investigate the structure of glasses. Fig. 2 shows the IR-spectra of the samples A1-A3 recorded in the range 400-4000 cm^{-1} at 300 K. In copper phosphate glasses, it is reported in literature [3] that copper exists as Cu^+ and Cu^{2+} ions, and the environment of the paramagnetic Cu^{2+} ion is tetragonally distorted octahedron, $[O_{1/2}-CuO_{4/2}-O_{1/2}]$ [4] due to Jahn-Teller distortion. On the other hand, B_2O_3-containing systems exhibit even more complex geometries. Apart from the trigonal $[BO_{3/2}]$ units, the six-membered boroxol rings help in the formation of triborate and
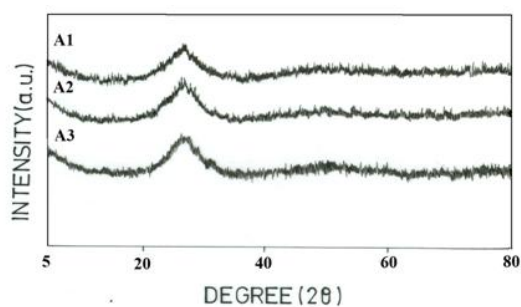

Fig.1. X-ray diffraction pattern of A1-A3 glasses of $xCuO-(1-x) B_2O_3$ ($0.06 \leq x \leq 0.16$) at room temperature.

pentaborate groups (joined in pairs which are equivalent to two tetraborate groups) and as well as diborate groups[5]. The sharp peak around 542-549 cm^{-1} in the samples is due to symmetric bending mode [6] of O-B-O bonds of the trigonal $[BO_{3/2}]$ unit. The intense peak in the range 637-645 cm^{-1} is due to the Cu-O stretching mode[7] in the network. The weak peak in the range 799-807 cm^{-1} in all the samples is due to the symmetric stretching [7] of the out of plane π-bonding of the trigonal $[BO_{3/2}]$ unit, while the very weak peak at ~ 886 cm^{-1} is due to the asymmetric stretching mode[7] of the octahedral $[CuO_{6/2}]^{4-}$ unit. The sharp peak in the range 1190-1197 cm^{-1} in all the samples is attributed to the asymmetric stretching vibrations of B-O bonds in $[BO_{3/2}]$ unit from pyroborate and orthoborate groups [8], [9]. The band at ~ 1455 cm^{-1} is assigned to B-O stretching vibrations in $[BO_{3/2}]$ units in borate rings [8], [9]. The bands [10] above 1600 cm^{-1} are due to the moisture in KBr pellet.
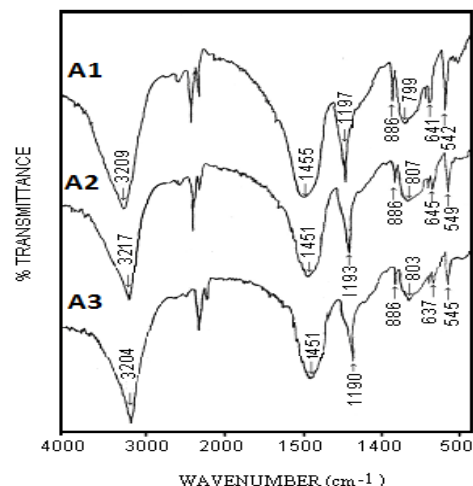

Fig.2. IR spectra of A1-A3 of $xCuO-(1-x) B_2O_3$ ($0.06 \leq x \leq 0.16$) at room Temperature.

The EPR spectra of glassy samples exhibit multiple absorption lines. Cu^{2+} ions with S=1/2 have a nuclear spin of I = 3/2 for both ^{63}Cu (natural abundance is 69%) and ^{65}Cu (natural abundance 31%). Therefore (2I+1), i.e. four parallel and four perpendicular hyperfine components are expected. The EPR spectra of glasses, recorded at room temperature are shown in Fig. 3. The observed lineshapes of the glassy samples show poorly resolved four parallel lines and unresolved perpendicular line typical of $^{63\ or\ 65}Cu$ (I=3/2) system. For Cu^{2+} ions, a regular octahedral site may not exist, as the cubic symmetry is disturbed by the electronic hole in the degenerate d_{x2-y2} orbital and this produces the tetragonal distortion. The EPR spectra of Cu^{2+} ions in tetragonally distorted octahedral environment are analysed by using an axial spin Hamiltonian [11].

$$H = \beta_e g_{\parallel} B_z S_z + \beta_e g\perp (B_x S_x + B_y S_y) + A_{\parallel} I_z \quad S_z + A\perp (S_x I_x + S_y I_y) \qquad (1)$$

The solution of the spin Hamiltonian gives the expressions for the peak positions related to the principal 'g' and 'A' tensors [12]. The spin Hamiltonian parameters, evaluated from EPR spectra for the glass samples are: A1 glass: $g_{\parallel}$ = 2.35, $g\perp$ = 2.05, $A_{\parallel}$ = 136 x 10^{-4} cm^{-1} and $A\perp$ = 31 x 10^{-4} cm^{-1}; A2 glass: $g_{\parallel}$ = 2.36, $g\perp$ = 2.06, $A_{\parallel}$ = 137 x 10^{-4} cm^{-1} and $A\perp$ = 31 x 10^{-4} cm^{-1} ; and A3 glass: $g_{\parallel}$ = 2.36, $g\perp$ = 2.06, $A_{\parallel}$ =137 x 10^{-4} cm^{-1} and $A\perp$ =31 x 10^{-4} cm^{-1}. The observed $g_{\parallel}$ and $g\perp$ values are characteristic for Cu^{2+} ions in octahedral coordination. The evaluated spin Hamiltonian parameters are in good agreement with those reported earlier [13], [14]. As $g_{\parallel}$ > $g\perp$ >g_e (free electron g value), the ground state of the unpaired electron is $3d_{x2-y2}$ ($^2B_{1g}$), the Cu^{2+} ion being located in distorted octahedral sites (D_{4h}) elongated along the z-axis[15], [16].
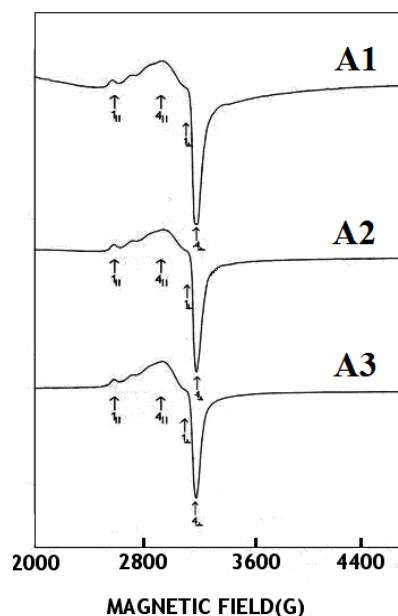
Fig.3. X- band EPR spectra of A1-A3 glasses of xCuO-(1-x) B_2O_3 (0.06≤x≤0.16) at room temperature.

This observation also suggests that Cu^{2+} ions are subjected to tetragonally elongated distortion. The spin Hamiltonian parameters for the three glassy samples are very close to each other with respect to variable CuO concentrations. These spin Hamiltonian parameters are compared with other glass systems and are in good agreement with those reported in the literature. From spin Hamiltonian parameters, it is clear that the coordination structure of Cu^{2+} complexes keeps approximately the same symmetry. From the spin Hamiltonian parameters, the dipolar term (P) and the Fermi-contact term (κ) are calculated using the expression [17], [18].

$$P = 2\gamma_{Cu} \beta_0 \beta_N \langle r^{-3}\rangle = 0.036 \text{ cm}^{-1} \qquad (2)$$

$$\kappa = (A_o / P) + \Delta g_0 \qquad (3)$$

where γ_{Cu} is the magnetic moment of copper; β_0 is the Bohr magneton; β_N is the nuclear magneton; r is the distance from the central nucleus to the electron; A_o= (1/3) ($A_\parallel$ + $A\perp$); Δg_0 = (g_e - g_o); $g_{0 = (1/3)}$ ($g_\parallel$ + 2 $g\perp$) and g_e is the free electron g-value (2.0023). The Fermi contact term is a measure of the polarization produced by the uneven distribution of d-electron density on the inner core s-electron. These changes are due to structural changes taking place with composition and also modification of the boron network with CuO content.

The optical absorption spectra of Cu^{2+} ions in glasses at room temperature have been recorded in the wavelength region 300 - 900 nm and are shown in Fig. 4.
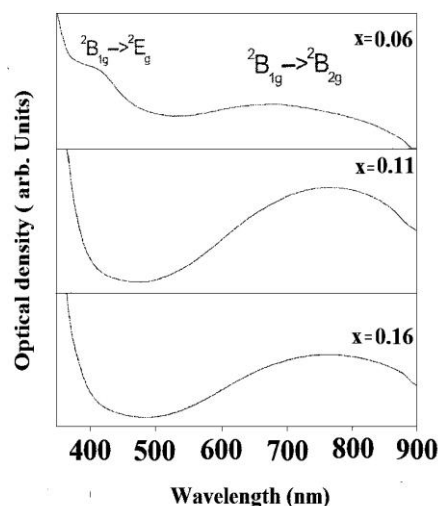

Fig.4. Optical absorption spectra of A1- A3 glasses of xCuO-(1-x) B_2O_3 (0.06≤x≤0.16) at room temperature.

The ^2D ground state of Cu^{2+} ($3d^9$) splits into ^2Eg and $^2T_{2g}$ in a ligand field of octahedral symmetry as shown in Fig.5. The ground state of Cu (II) ion in an elongated tetragonally distorted octahedral crystal field of D_{4h} symmetry is described as a single electron in d_{x2-y2} (b_{1g}) orbital, or a $^2B_{1g}$ spectroscopic state. Thus, ^2E_g ground state splits into $^2B_{1g}$ and $^2A_{1g}$ and the $^2T_{2g}$ state to $^2B_{2g}$ and ^2E_g due to Jahn-Teller distortion as shown in Fig.5. The energy difference between $^2A_{1g}$ and $^2B_{2g}$ depends on the amount of distortion. More than one band owing to a low-symmetry ligand field component of Jahn-Teller distortion is predicted which occurs at energies higher than the octahedral transitions [19]. The optical absorption spectra of all the samples are similar, showing one strong band as a result of the transition $^2B_{1g} \rightarrow ^2B_{2g}$ except A1 (x = 0.06). For A1 (x = 0.06), two bands have been observed for the Cu^{2+} ion and a broad band as a result of the transition ($^2B_{1g} \rightarrow ^2B_{2g}$) at 14240 cm^{-1} and a weak band as a result of the transition ($^2B_{1g} \rightarrow ^2E_g$) at 22,115 cm^{-1} on the higher energy side. For A2 and A3 (x = 0.11, 0.16), the band $^2B_{1g} \rightarrow ^2E_g$ is not observed, and the strong band shifts slightly to the lower energy side, centered in the range 14,240 - 12,935 cm^{-1}. This strong band shift can be ascribed to the increase in ligand field around Cu^{2+} ion with increase in x. The transition $^2B_{1g} \rightarrow ^2B_{2g}$ is a measure of 10 Dq. The broad and asymmetric band is due to Jahn-Teller distortion. The appearance of the additional band at 22,115 cm^{-1} ($^2B_{1g} \rightarrow ^2E_g$) for Cu^{2+} ions in A1 (x = 0.06) glass may be due to sites of lower symmetry around the Cu^{2+} ion. The observed absorption bands obtained in the present work are in good agreement with those reported by earlier workers [20]-[24].
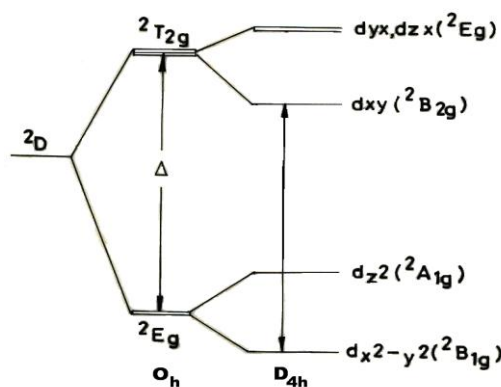
Free Octahedral Tetragonal
ion crystal field elongation

Fig.5. Splitting of ^2D state in octahedral and tetragonal crystal field giving $^2B_{1g}$ ground state.

The metal-ligand bond nature can be described using the parameters α^2, β^2 and β_1^2 [25], [26]. The parameters α^2 and β_1^2 represent the contribution of 3d atomic orbitals of the cupric ion to the B_{1g} and B_{2g} anti bonding orbitals respectively. The bonding coefficients α^2, β_1^2 and β^2 (=1.00) characterize, respectively, the in-plane σ bonding, in-plane π bonding and out-of-plane π bonding of the Cu^{2+} ligand bond in the glasses. The values of these parameters lie between 0.5 and 1.0, the limits of pure covalent and pure ionic bonding. A value of 0.5 represents a pure covalent bond while a value of zero or unity represents purely ionic bonding [27]. The value of β^2 may be expected to lie sufficiently close to unity to be indistinguishable from unity in the bonding coefficient calculations [28]. The expression α^2 given in equation [29] is the bonding coefficient due to the covalency of the σ bonds with the equatorial ligands which measures the electron density delocalized on the ligand ions and β_1^2 accounts for covalency of π anti-bonding between ligands and the excited $^2B_{2g}$ state. The bonding coefficient α^2 (i.e., the in-plane σ bonding) can be calculated from the EPR data using the expression given by Kuska et al [30].

$$\alpha^2 = (g_{\|} - g_e) + 3/\mathbf{7}(g_{\perp} - g_e) - A_{\|}/\,0.036 + 0.04 \quad (4)$$

where P = 0.036 cm^{-1} and A = (1/3 $A_{\|}$ +2/3$A_{\perp}$). The α^2 values calculated for copper oxide borate glasses are presented in Table I.

Table. I. Molecular orbital coefficients

Glass sample x	α^2	β_1^2	Γ_σ (%)	Γ_π (%)
0.06	0.78	0.95	48	10
0.11	0.80	0.96	44	08
0.16	0.80	0.96	44	08

The EPR and optical absorption spectral data can be correlated to evaluate the bonding coefficients as follows [26]:

$$g_{\|} = 2.0023 \,[1 - 4\lambda\alpha^2\beta_1^2 / E_1] \quad (5)$$

$$g_{\perp} = 2.0023 \,[1 - \lambda\alpha^2\beta^2 / E_2] \quad (6)$$

E_1 and E_2 are the energies corresponding to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ respectively, and λ is the spin-orbit coupling constant (= -828 cm^{-1}) [31]. From the equations (5) and (6) it can be seen that to determine Cu^{2+} bonding coefficients one needs, in addition to the EPR parameters, the energy positions of the absorption bands of Cu^{2+} which indicate the values of E_1 and E_2. β_1^2 is a direct measure of the covalency of the in-plane π-bonding between copper and its ligands. Thus β_1^2 is more sensitive to variations in covalency than α^2 and is therefore a better indicator of the covalent character. The α^2 values indicate an intermediate ionic bond for the Cu^{2+}-O$^-$ in-plane σ bonding. The value of β_1^2 depends strongly on the network former. In the present work, the β_1^2 value is lower in A1 and higher in A2 and A3. This change in β_1^2 is related to the change in B-O bonds. The values of the calculated parameter α^2 and β_1^2 obtained for various glasses indicate that the in-plane σ bonding is moderately covalent whereas the in-plane π bonding is significantly ionic in nature. From the calculated values of α^2 and β_1^2, two more variables that give an idea about the basicity of the oxide ion can be calculated. The normalized covalency (Γ_π) of the Cu(II)-O in-plane bonding of σ and π symmetry is expressed [32] in terms of bonding coefficients α^2 and β_1^2.

$$\Gamma_\sigma = 200 \,(1-S) \,(1- \alpha^2) /\, (1 - 2S) \,\% \quad (7)$$

$$\Gamma_\pi = 200 \,(1- \beta_1^2) \,\% \quad (8)$$

where S is the overlapping integral ($S_{oxygen} = 0.076$). The normalized covalency values of the Cu(II)-O in-plane bonding of π symmetry indicates the basicity of the oxide ion. The calculated values of the covalency of the in-plane σ bonding Γ_σ and the covalency of in-plane π bonding Γ_π are given in Table 1 and it is seen that in-plane bonding of π symmetry is high in A1 and decreases in A2 and A3. The changes in β_1^2 are related to the changes in B-O bonds; there is a decrease in the strength of B-O bonds resulting in the increase of covalency of Cu (II)-O bonds. The Cu (II)–O bonds may be affected by the direct adjacent B-O bonds as well as by the slightly more distant ones [21].

IV. CONCLUSION

The IR spectral results at room temperature show the presence of octahedral $[CuO_{6/2}]^{4-}$ and trigonal planar $[BO_{3/2}]^-$ units in the glassy samples. EPR and optical absorption studies show that the Cu^{2+} ions are in

tetragonally distorted octahedral sites (D4h) elongated along the z-axis in all the glass samples with d_{x2-y2} ($^2B_{1g}$) ground state. Only one band is observed for A2 and A3. It is interesting to note that for A1 (x= 0.06), two bands, i.e., a strong band corresponding to the transition $^2B_{1g} \rightarrow ^2B_{2g}$ at (14240 cm^{-1}) and a weak band corresponding to the transition $^2B_{1g} \rightarrow ^2E_g$ (22115 cm^{-1}) on the higher energy side are observed. The additional band on the higher energy side is due to sites of lower symmetry around the Cu^{2+} ion. For A2 and A3 (x = 0.11 and 0.16), the $^2B_{1g} \rightarrow ^2E_g$ band is vanished. The molecular orbital values α^2 and β_1^2 obtained for three glasses in the present work indicate that the in-plane σ bonding is moderately covalent and in-plane π bonding is significantly ionic in nature.

V. REFERENCES

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