



IR, EPR and Optical Absorption Studies of $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ Glasses

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Glasses with composition $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ have been synthesized over the range $0.6 \leq x \leq 0.8$ mol % by sol-gel method. The IR studies show that the glassy system contains $[\text{BiO}_6]$ octahedral and $[\text{BiO}_3]$ pyramidal units. The X-band electron paramagnetic resonance and optical absorption studies were carried out to understand the nature of bonding, symmetry and local structure around Cu^{2+} ions in the glasses. The spin-Hamiltonian parameters have been calculated. The trends in g-values $g_{\parallel} > g_{\perp} > g_e$ (2.0023), calculated from the observed EPR spectra show that Cu^{2+} ions are coordinated with six ligand atoms in a distorted octahedron elongated along z-axis and the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital ($^2\text{B}_{1g}$ state) having D_{4h} symmetry. The optical absorption spectra of all the glass samples show a broad band corresponding to $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ transition of Cu^{2+} ion. By correlating the EPR and optical absorption spectral data, the molecular orbital coefficients, α^2 and β_1^2 have been evaluated.

Keywords: Glasses, IR, Electron paramagnetic resonance, Bonding parameters, Optical absorption.

INTRODUCTION

CuO -containing glasses draw special attention because of their different electrical conductivity [1] and structure-property behaviour [2,3] compared to the glasses containing V_2O_5 [4] and MoO_3 [5]. In the case of CuO , during the reduction process by citric acid for gel formation [6], Cu^+ ($3d^{10}$) ions are formed. The Cu^{2+} ($3d^9$) ion is an interesting paramagnetic site to study the nature of bonding and site symmetry [7] by electron paramagnetic resonance (EPR) spectroscopy. Electron paramagnetic resonance investigations of Cu^{2+} ions in glasses are interesting and have received a considerable attention due to the sensitivity of parameters to local symmetry and have been studied in wide variety of glasses [8]. Furthermore, in the case of Bi_2O_3 -containing glasses, the structural complications involving the different units in the network, makes it interesting to study the structural-property relations in such systems. Unconventional glasses containing Bi_2O_3 as glass former are of great interest because of their potential applications in industry and many allied areas [9]. By correlating the electron paramagnetic resonance and optical absorption spectra, we obtain information regarding the bond parameters that determine the metal-ligand bond nature in the glasses. In this paper we study the changes in IR, electron paramagnetic resonance and optical absorption parameters as a result of the variation in glass composition.

EXPERIMENTAL

In the present study, three glass samples of compositions $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ ($0.6 \leq x \leq 0.8$) were prepared by sol-gel method via nitrate-citrate gel route using reagent grade chemicals $[\text{Bi}(\text{NO}_3)_3]$, $[\text{Cu}(\text{NO}_3)_2]$ and citric acid. Three samples were labeled as A1, A2 and A3. Calculated amounts of $[\text{Cu}(\text{NO}_3)_2]$ and $[\text{Bi}(\text{NO}_3)_3]$ were dissolved in dil. HNO_3 to prepare 0.05 M solutions. These solutions were then mixed with 2 M citric acid solution to prepare the sol. The resulting sol was air dried by heating at about 60°C to prepare the gel which was then decomposed at $\sim 120^\circ\text{C}$. Finally, the samples were prepared by melting them in alumina crucibles in the range 1073-1133 K. The melt was air quenched by pressing between two ice cold aluminum plates to prepare the glass. The glass formation was confirmed by powder X-ray diffraction recorded with a Phillips type PW 1050 diffractometer using CuK_α radiation. The IR spectra of the samples at room temperature were recorded in the range $4000-400\text{ cm}^{-1}$ 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 ($H \approx 9.200\text{ GHz}$) with a field modulation frequency of 100 kHz. 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 UV-visible spectrophotometer in the wavelength region 500-900 nm.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) spectra of glass samples are shown in Fig. 1. A broad peak around 30° in 2θ vanishing at higher diffraction angles is characteristic of a glass. The absence of sharp peaks in XRD patterns exhibit that the glass samples do not possess long range periodic lattice arrangement of a crystal. A broad hump observed in the XRD patterns further confirms that the samples show amorphous nature. In Fig. 2 we show the room temperature IR spectra of glasses A1-A3 in the range $4000\text{--}400\text{ cm}^{-1}$.

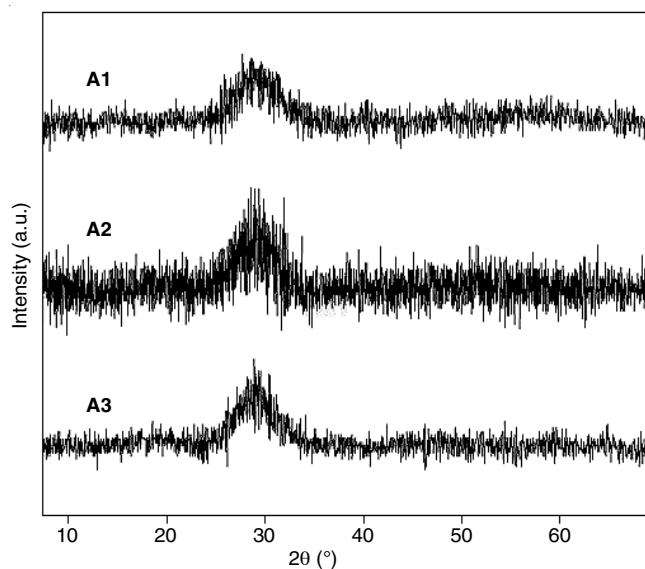


Fig. 1 XRD patterns of $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ ($0.6 \leq x \leq 0.8$) glasses

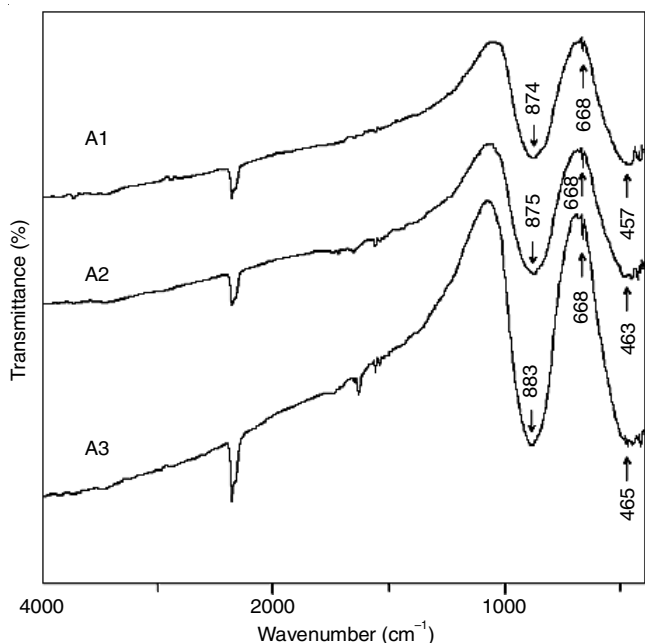


Fig. 2. FTIR spectra of $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ ($0.6 \leq x \leq 0.8$) glasses

In copper phosphate glasses, it is reported in literature [1] that copper exists as Cu^+ and Cu^{2+} ions and the environment of Cu^{2+} ion is tetragonally distorted octahedron, $[\text{O}_{1/2}\text{--CuO}_{4/2}\text{--O}_{1/2}]$ [10]. It is also reported in literature [11] that Bi_2O_3 cannot form glasses by itself, in the presence of conditional glass

formers such as V_2O_5 , CuO , *etc.* or a strong polarizing cation such as Si^{4+} , it reduces its coordination number from six in the $[\text{BiO}_6]$ octahedral to three in $[\text{BiO}_3]$ pyramidal units and forms the glass network. The sharp and intense peak in the range $883\text{--}874\text{ cm}^{-1}$ in A1-A3 is due to the symmetric stretching [11] vibration mode of $[\text{CuO}_6]$ octahedral unit and has approximately the same intensity for A1-A3. The weak peak in the range $457\text{--}465\text{ cm}^{-1}$ in A1-A3 is ascribed to the symmetric bending mode [12] of $[\text{BiO}_3]$ pyramidal units. The peak at 668 cm^{-1} in A1-A5 is due to the symmetric stretching mode [13] of $[\text{BiO}_6]$ octahedral unit in the matrices.

The room temperature X-band EPR spectra of the present glasses are shown in Fig. 3. Cu^{2+} ions with $S = 1/2$ have a nuclear spin of $I = 3/2$ for both ^{63}Cu (natural abundance 69 %) and ^{65}Cu (natural abundance 31 %). For Cu^{2+} ions, a regular octahedral site may not exist, as the cubic symmetry is disturbed by the electronic hole in the degenerate $d_{x^2-y^2}$ orbital and this produces the tetragonal distortion. The EPR spectra of Cu^{2+} ions in glasses can be analyzed by using an axial spin-Hamiltonian of the form:

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

where the symbols have their usual meaning [14]. The nuclear quadrupole and nuclear Zeeman interaction terms are ignored due to their negligible contribution. From the Fig. 3 it is observed that the absorption spectra are asymmetric, characteristic of Cu^{2+} ($3d^9$) ions in axially distorted octahedral symmetric sites. It is observed that the EPR lineshapes in the compositional range ($0.6 \leq x \leq 0.8$) exhibit high structural stability of the glassy matrix. The spectra show the hyperfine structure due to the interaction of the unpaired electron spin with the nuclear one, $I = 3/2$, characteristic of Cu^{2+} . The hyperfine structure shows poorly resolved parallel band of the spectra and unresolved perpendicular line typical of ^{63}Cu or ^{65}Cu system. Three

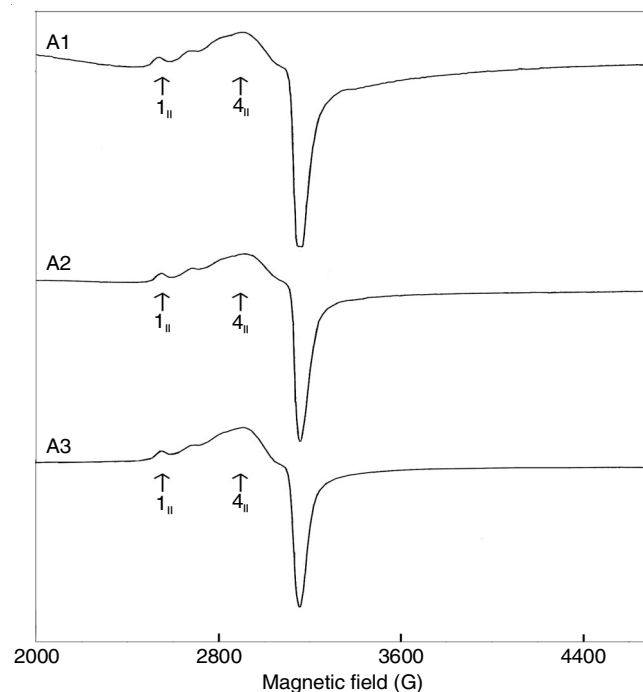


Fig. 3. EPR spectra of $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ ($0.6 \leq x \leq 0.8$) glasses

hyperfine lines are observed on the parallel features of the spectrum. The hyperfine lines are not observed on the perpendicular features of the spectrum as a result of individual line broadening which is due to the increased dipolar interactions with the ligand field fluctuations around the paramagnetic ion. The values of spin-Hamiltonian parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} were estimated from the spectra and are given in Table-1.

TABLE-1
EPR AND OPTICAL PARAMETERS OF THE
GLASS SYSTEM $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$

Parameters	$x = 0.6$	$x = 0.7$	$x = 0.8$
g_{\parallel}	2.367	2.354	2.355
g_{\perp}	2.055	2.056	2.056
$A_{\parallel} \times 10^{-4} (\text{cm}^{-1})$	147	146	147
$A_{\perp} \times 10^{-4} (\text{cm}^{-1})$	33	33	33
$\lambda (\text{nm})$	690	690	700
$\Delta E_{xy} (\text{cm}^{-1})$	14493	14493	14286
α^2	0.836	0.820	0.824
β_1^2	0.95	0.94	0.92
$\Gamma_{\sigma} (\%)$	36	39	38
$\Gamma_{\pi} (\%)$	10	12	16

The change in spin Hamiltonian parameters with composition can be attributed to the variation of ligand field around Cu^{2+} . The observed values of g_{\parallel} and g_{\perp} suggest that the Cu^{2+} ions in the glasses are coordinated by six ligands that form an octahedron elongated along the Z-axis [15,16]. As $g_{\parallel} > g_{\perp} > g_e (= 2.0023)$, it is confirmed that ground state for Cu^{2+} ions is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state), the Cu^{2+} ion being located in distorted octahedral site (D_{4h}) elongated along the Z-axis. The optical absorption spectra of glassy system are shown in Fig. 4. A single absorption band in near-infrared region is observed in all samples, which are attributed to $d-d$ transition band due to Cu^{2+} ions [17]. Cu^{2+} undergoes a Jahn-Teller distortion, which leads to the splitting of energy levels in terms of ligand field theory [18]. It is observed that the elongated structures are usually more energetically favoured than the compressed ones [19]. Hence, in the present study, the observed broad and asymmetric band for the samples (A1-A3) is due to overlap of $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transitions. The optical absorption spectra of all the samples (A1-A3) are similar, showing one strong band as a result of the transition $^2B_{1g} \rightarrow ^2B_{2g}$ at 14286 cm^{-1} . Most of the authors [20,21] assigned the observed optical peak to the $^2B_{1g} \rightarrow ^2B_{2g}$ transition and have used this value in the evaluation of the bond parameters. The intensity of absorption band is maximum in A3 ($x = 0.8$). The transition $^2B_{1g} \rightarrow ^2B_{2g}$ is a measure of $10 Dq$. The observed absorption bands obtained in the present work are in good agreement with those reported by earlier workers [22-24]. We determine the bonding coefficients of Cu^{2+} from the absorption frequencies of optical absorption bands. By correlating EPR and optical absorption data, we evaluate the bonding coefficients of Cu^{2+} . The bonding between the Cu^{2+} ion and its ligands can be described in terms of the covalency parameters α^2 and β_1^2 ; where α^2 describes the in-plane σ bonding with the copper $d_{x^2-y^2}$ orbital and the β_1^2 is a measure of the in-plane π bonding with the d_{xy} orbital. The values of α^2 lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding, respectively.

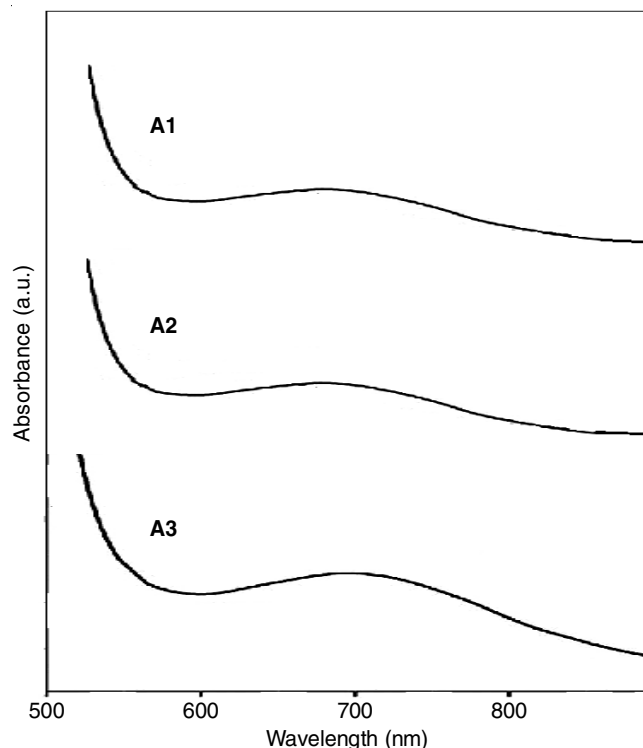


Fig. 4. Optical absorption spectra of $x\text{CuO}-(1-x)\text{Bi}_2\text{O}_3$ ($0.6 \leq x \leq 0.8$) glasses

The bonding parameters were evaluated using the equations [25] given below:

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

where P , the dipolar hyperfine coupling parameter = 0.036 cm^{-1} and $A = (1/3 A_{\parallel} + 2/3 A_{\perp})$.

The bonding coefficients of Cu^{2+} are evaluated using the following equations [26] by correlating EPR and optical absorption data.

$$g_{\parallel} = 2.0023 \left(1 - \frac{4\lambda\alpha^2\beta_1^2}{\Delta E_{xy}} \right) \quad (3)$$

ΔE_{xy} is the energy corresponding to the transitions $^2B_{1g} \rightarrow ^2B_{2g}$ and λ is the spin-orbit coupling constant ($= -828 \text{ cm}^{-1}$) [27]. In the present work, values of α^2 and β_1^2 are similar in A1-A3 in the composition range ($0.6 \leq x \leq 0.8$). The calculated values of the parameter α^2 and β_1^2 given in Table-1, show an ionic nature for the Cu (II)-O in-plane σ bonding and the in-plane π bonding. 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 of the Cu(II)-O in-plane bonding of σ and π symmetry is expressed [28] in terms of bonding coefficients α^2 and β_1^2 .

$$\Gamma_{\sigma} (\%) = 200 (1-S) (1-\alpha^2)/(1-2S) \quad (4)$$

$$\Gamma_{\pi} (\%) = 200 (1-\beta_1^2) \quad (5)$$

where S is the overlapping integral ($S_{\text{oxygen}} = 0.076$). The normalized covalency (Γ_{π}) of Cu(II)-O bonding of π symmetry indicates the basicity of the oxide ion. We observe that the covalency of the in-plane σ bonding (Γ_{σ}) is constant whereas the covalency of in-plane π bonding (Γ_{π}) increases.

Conclusion

The IR spectral analysis confirms the presence of $[\text{BiO}_6]$ octahedral and $[\text{BiO}_3]$ pyramidal units in the glass. From the spin-Hamiltonian parameters of EPR and optical absorption data, it is observed that Cu^{2+} ions in all the samples have occupied tetragonally distorted octahedral sites elongated along z-axis with $d_{x^2-y^2}$ orbital (${}^2\text{B}_{1g}$ state) as the ground state. The optical absorption spectra of the glasses show a single broad band due to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition of Cu^{2+} ions in axially elongated octahedral sites. The values of the molecular orbital bonding parameters show that in-plane σ bonding and the in-plane π bonding are ionic in nature. The covalency of in-plane σ bonding (Γ_σ) is constant, whereas the covalency of in-plane π bonding (Γ_π) increases.

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