**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 V2O5 [4] and MoO3 [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\(_2\)O\(_3\)-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\(_2\)O\(_3\) 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.
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 4000-400 cm⁻¹.

In copper phosphate glasses, it is reported in literature [1] that copper exists as Cu⁺ and Cu²⁺ ions and the environment of Cu²⁺ ion is tetragonally distorted octahedron, [O₁/₂-CuO₄/₂-O₁/₂] [10]. It is also reported in literature [11] that Bi₂O₃ cannot form glasses by itself, in the presence of conditional glass formers such as V₂O₅, CuO, etc. or a strong polarizing cation such as Si⁴⁺, it reduces its coordination number from six in the [BiO₆] octahedral to three in [BiO₃] pyramidal units and forms the glass network. The sharp and intense peak in the range 883-874 cm⁻¹ in A1-A3 is due to the symmetric stretching [11] vibration mode of [CuO₆] octahedral unit and has approximately the same intensity for A1-A3. The weak peak in the range 457-465 cm⁻¹ in A1-A3 is ascribed to the symmetric bending mode [12] of [BiO₃] pyramidal units. The peak at 668 cm⁻¹ in A1-A5 is due to the symmetric stretching mode [13] of [BiO₆] octahedral unit in the matrices.

The room temperature X-band EPR spectra of the present glasses are shown in Fig. 3. Cu²⁺ ions with S = 1/2 have a nuclear spin of I = 3/2 for both ⁶³Cu (natural abundance 69 %) and ⁶⁵Cu (natural abundance 31 %). For Cu²⁺ ions, a regular octahedral site may not exist, as the cubic symmetry is disturbed by the electronic hole in the degenerate dₓ²−y² orbital and this produces the tetragonal distortion. The EPR spectra of Cu²⁺ ions in glasses can be analyzed by using an axial spin-Hamiltonian of the form:

\[ H = \beta g_s B_s S_z + \beta g_\perp (B_x S_x + B_y S_y) + A_s I_z S_z + A_\perp (S_x I_x + S_y I_y) \]

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 Cu²⁺ (3d⁹) ions in axially distorted octahedral symmetric sites. It is observed that the EPR lineshapes in the compositional range (0.6 ≤ x ≤ 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 Cu²⁺. The hyperfine structure shows poorly resolved parallel band of the spectra and unresolved perpendicular line typical of ⁶³Cu or ⁶⁵Cu system. Three

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**Fig. 1** XRD patterns of xCuO-(1-x)Bi₂O₃ (0.6 ≤ x ≤ 0.8) glasses

**Fig. 2** FTIR spectra of xCuO-(1-x)Bi₂O₃ (0.6 ≤ x ≤ 0.8) glasses

**Fig. 3** EPR spectra of xCuO-(1-x)Bi₂O₃ (0.6 ≤ x ≤ 0.8) glasses
The change in spin Hamiltonian parameters with composition can be attributed to the variation of ligand field around Cu$^{2+}$. The observed values of $g_{||}$ 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 $g_{||} > g_{\perp} > g_{e}$ (= 2.0023), it is confirmed that ground state for Cu$^{2+}$ ions is $d_{\alpha \beta \gamma}$ orbital ($\Gamma_{\pi}$ state), the Cu$^{2+}$ ion being located in distorted octahedral site (Dm) 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 $^3\text{Bi}_{\pi} \rightarrow ^3\text{A}_{\pi 1}$ and $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ transitions. The optical absorption spectra of all the samples (A1-A3) are similar, showing one strong band as a result of the transition $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ at 14286 cm$^{-1}$. Most of the authors [20,21] assigned the observed optical peak to the $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ 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 $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ 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 $\alpha^2$ and $\beta_1^2$; where $\alpha^2$ describes the in-plane $\pi$ bonding with the copper $d_{\alpha \beta \gamma}$ orbital and the $\beta_1^2$ is a measure of the in-plane $\pi$ bonding with the $d_{\sigma}$ orbital. The values of $\alpha^2$ lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding, respectively.

### Table 1: EPR and Optical Parameters of the Glass System $xCuO-(1-x)Bi_2O_3$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$x = 0.6$</th>
<th>$x = 0.7$</th>
<th>$x = 0.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{</td>
<td></td>
<td>}$</td>
<td>2.367</td>
</tr>
<tr>
<td>$g_{\perp}$</td>
<td>2.055</td>
<td>2.056</td>
<td>2.056</td>
</tr>
<tr>
<td>$A_\pi \times 10^{-4}$ (cm$^{-1}$)</td>
<td>147</td>
<td>146</td>
<td>147</td>
</tr>
<tr>
<td>$A_\sigma \times 10^{-4}$ (cm$^{-1}$)</td>
<td>33</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>$\lambda$ (nm)</td>
<td>690</td>
<td>690</td>
<td>700</td>
</tr>
<tr>
<td>$\Delta E_\sigma$ (cm$^{-1}$)</td>
<td>14493</td>
<td>14493</td>
<td>14286</td>
</tr>
<tr>
<td>$\alpha^2$</td>
<td>0.836</td>
<td>0.820</td>
<td>0.824</td>
</tr>
<tr>
<td>$\beta_1^2$</td>
<td>0.95</td>
<td>0.94</td>
<td>0.92</td>
</tr>
<tr>
<td>$\Gamma_\alpha$ (%)</td>
<td>36</td>
<td>39</td>
<td>38</td>
</tr>
<tr>
<td>$\Gamma_\pi$ (%)</td>
<td>10</td>
<td>12</td>
<td>16</td>
</tr>
</tbody>
</table>

The change in spin Hamiltonian parameters with composition can be attributed to the variation of ligand field around Cu$^{2+}$. The observed values of $g_{||}$ 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 $g_{||} > g_{\perp} > g_{e}$ (= 2.0023), it is confirmed that ground state for Cu$^{2+}$ ions is $d_{\alpha \beta \gamma}$ orbital ($\Gamma_{\pi}$ state), the Cu$^{2+}$ ion being located in distorted octahedral site (Dm) 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 $^3\text{Bi}_{\pi} \rightarrow ^3\text{A}_{\pi 1}$ and $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ transitions. The optical absorption spectra of all the samples (A1-A3) are similar, showing one strong band as a result of the transition $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ at 14286 cm$^{-1}$. Most of the authors [20,21] assigned the observed optical peak to the $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ 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 $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ 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 $\alpha^2$ and $\beta_1^2$; where $\alpha^2$ describes the in-plane $\pi$ bonding with the copper $d_{\alpha \beta \gamma}$ orbital and the $\beta_1^2$ is a measure of the in-plane $\pi$ bonding with the $d_{\sigma}$ orbital. The values of $\alpha^2$ lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding, respectively.

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

$$\alpha^2 = (g_{||} - g_{e}) + 3/7(g_{\perp} - g_{e}) - A/0.036 + 0.04$$

where P, the dipolar hyperfine coupling parameter = 0.036 cm$^{-1}$ and $A = (1/3 A_1 + 2/3 A_\perp)$.

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

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

$\Delta E_{xy}$ is the energy corresponding to the transitions $^3\text{Bi}_{\pi} \rightarrow ^3\text{B}_{\pi 2}$ and $\lambda$ is the spin-orbit coupling constant (≈ -828 cm$^{-1}$) [27]. In the present work, values of $\alpha^2$ and $\beta_1^2$ are similar in A1-A3 in the composition range (0.6 ≤ x ≤ 0.8). The calculated values of the parameter $\alpha^2$ and $\beta_1^2$ given in Table-1, show an ionic nature for the Cu (II)-O in-plane $\sigma$ bonding and the in-plane $\pi$ bonding. From the calculated values of $\alpha^2$ and $\beta_1^2$, 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 $\sigma$ and $\pi$ symmetry is expressed [28] in terms of bonding coefficients $\alpha^2$ and $\beta_1^2$.

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

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

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

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**Fig. 4.** Optical absorption spectra of $xCuO-(1-x)Bi_2O_3$ (0.6 ≤ x ≤ 0.8) glasses

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorbance (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>A1</td>
</tr>
<tr>
<td>600</td>
<td>A2</td>
</tr>
<tr>
<td>700</td>
<td>A3</td>
</tr>
<tr>
<td>800</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion

The IR spectral analysis confirms the presence of [BiO₆] octahedral and [BiO₃] pyramidal units in the glass. From the spin-Hamiltonian parameters of EPR and optical absorption data, it is observed that Cu²⁺ ions in all the samples have occupied tetragonally distorted octahedral sites elongated along z-axis with dₓ²ᵧ² orbital (2B₁g state) as the ground state. The optical absorption spectra of the glasses show a single broad band due to 2B₁g→2B₂g transition of Cu²⁺ 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 (Γₗ) is constant, whereas the covalency of in-plane π bonding (Γₜ) increases.

REFERENCES