CHAPTER – 4

SPECTROSCOPIC STUDIES OF Cu$^{2+}$ DOPED ALKALI FLOUROBOROROPHOSPHATE GLASSES
4.1 INTRODUCTION

The electron paramagnetic resonance (EPR) and optical spectroscopy allow investigating the electron and local structure of point defects in crystals and corresponding glasses. Structural and corresponding spectroscopic data for crystalline analogies are needed for an interpretation of the EPR and optical spectra in complex oxide glasses [1,2]. Adding copper ions in the content of oxide glasses made it very interesting due to their electrical and magnetic properties [3].

In the +1 state, most of the simple compounds and complexes of copper are diamagnetic and colourless because the ions have a d\(^{10}\) configuration. There are a few coloured compounds, for example, Cu\(_2\)O is yellow or red, Cu\(_2\)CO\(_3\) is yellow and CuI is brown in colour. In these cases, the colour arises from charge transfer bands and not from d-d spectra. The +2 state is the most stable and important for Cu. The cupric ion (Cu\(^{2+}\)) has the electronic configuration d\(^8\) and has an unpaired electron. Its compounds are typically coloured due to d-d spectra and the compounds are paramagnetic. This ion has the characteristic blue colour associated with copper salts and has a distorted octahedral shape [4].

The paramagnetic ion Cu\(^{2+}\) enters easily into a number of host lattices. Therefore this ion is preferred to study in different borate and phosphate doped glasses to determine the effect of the symmetry of metal ion [5-20]. In the present investigations on Cu\(^{2+}\) doped AFBP glasses are carried out by EPR, optical and FT-IR studies.
4.2 EXPERIMENTAL

The starting materials used in the present study are Analar grade CuO (99.9%), Na$_2$HPO$_4$ (99.9%), AlF$_3$·3H$_2$O (99.9%), B$_2$O$_3$ (99.9%) and LiF (99.9%). The glass samples in the present work are obtained by the classical melt quenching technique. 50Na$_2$HPO$_4$ + 10B$_2$O$_3$ + 20AlF$_3$·3H$_2$O +( 20 - X) LiF + X CuO (X = 1,2,3 mol%). For 1 mol%, 2 mol% and 3 mol% doped glasses are denoted as AFBPCu1, AFBPCu2 and AFBPCu3 respectively. All these chemicals are mixed in an agate mortar and then transferred to porcelain crucible heated in an electrical furnace in air at 980$^\circ$C for 30min. The melt was then quenched at room temperature in air by pouring it into a polished plate. Colored transparent glasses have been obtained with good optical quality. Finally the vitreous samples have been annealed at 300K for two hours to relieve internal stress and slowly cooled to room temperature. Polycrystalline EPR investigations are carried out at room temperature on JEOL JES TE 100 ESR spectrometer at X-band frequency with 100 kHz field. Optical absorption spectra are recorded on JASCO V670 spectrophotometer in the region of 200-1400 nm. FT-IR spectra are recorded using KBr pellets on Thermo Nicolet 6700 FT-IR spectrophotometer in the region 400 - 4000 cm$^{-1}$. 
4.3 THEORY

\( \text{Cu}^{2+} \) (\( d^9 \)) in octahedral crystal field has electronic configuration \( t_{2g}^6e_{g}^3 \) which is equivalent to one electron missing from the \( e_g \) orbit. Thus the configuration gives rise to \( ^2E_g \) term as the ground state. On excitation, one of the electrons of \( t_{2g} \) orbital is promoted to \( e_g \) orbital. The resulting electronic configuration \( t_{2g}^5e_{g}^4 \) gives rise to \( ^2T_{2g} \) state. For \( \text{Cu}^{2+} \) ion in pure octahedral symmetry, only one transition \( ^2E_g \rightarrow ^2T_{2g} \) is expected. According to the Jahn-Teller effect \( \text{Cu}^{2+} \) will never have a regular octahedral symmetry due to the degeneracy of its ground state. The degeneracy of \( ^2E_g \) state cannot be removed by trigonal distortion. It can be removed either by tetragonal or rhombic distortions.

If the site symmetry is tetragonally distorted octahedral (\( C_{4v} \)), the ground state \( ^2E_g \) splits into \( ^2B_1 \) and \( ^2A_1 \), and upper state \( ^2T_{2g} \) also splits into two states \( ^2A_2 \) and \( ^2E \). Therefore for \( \text{Cu}^{2+} \) in tetragonal site, three bands are expected due to the transitions from the ground state to the other three excited states. In the case of rhombic distortion (\( C_{2v} \)) gives four bands, the lower state \( ^2E_g \) splits into \( ^2A_1 \) (\( d_{x^2-y^2} \)) and \( ^2A_1 \) (\( d_{z^2} \)), and \( ^2T_{2g} \) splits into \( ^2A_2 \) (\( d_{xy} \)), \( ^2B_1 \) (\( d_{xz} \)) and \( ^2B_2 \) (\( d_{yz} \)). The correlation of different electronic states in octahedral (\( O_h \)), tetragonal (\( C_{4v} \)) and rhombic (\( C_{2v} \)) symmetries are shown in Fig.4.3.1.
Fig. 4.3.1 Energy level diagram for $d^0$ configuration.
4.4 RESULTS AND DISCUSSIONS

4.4.1. EPR SPECTRA OF Cu$^{2+}$ DOPED AFBP GLASSES

No resonance signal is detected in the EPR spectrum of un-doped glasses. Hence it confirms the diamagnetic nature for un-doped glass. When Cu$^{2+}$ ions are introduced into the present composition of alkali fluoroborophosphate glasses, the EPR spectra of glass samples exhibit multiple absorption lines recorded at room temperature. The EPR spectra of Cu$^{2+}$ doped mixed alkali fluoroborophosphate glasses are shown in Fig.4.4.1. for 1mol%, 2mol% and 3mol% named as AFBPCu1, AFBPCu2 and AFBPCu3 respectively.

The EPR spectra are analyzed using the spin-Hamiltonian

\[ H = g \parallel \beta H z S z + g \perp \beta (H x S x + H y S y) + A \parallel I z S z + A \perp (I x S x + I y S y) \]  \hspace{1cm} \ldots \hspace{1cm} (1) \]

where the symbols have their usual meanings [19]. The hyperfine peak positions are related to the principal values of \( g \) and \( A \) tensors by the solutions of the spin-Hamiltonian. The parallel hyperfine peaks are resolved in the present glasses and perpendicular hyperfine peaks are unresolved. Three hyperfine lines are observed on the parallel features of the spectrum.
Fig. 4.4.1. EPR spectra of Cu$^{2+}$ doped AFBP glasses.

(Cu-1: AFBPCu1, Cu-2: AFBPCu2, Cu-3: AFBPCu3).
EPR spectra of Cu\(^{2+}\) ion doped AFBPCu1, AFBPCu2, and AFBPCu3 glasses. From the spectrum, the spin-Hamiltonian and hyperfine splitting values evaluated for all three glasses are given in Table 4.4.1. These spin-Hamiltonian values are in good agreement with those reported for borate and phosphate glasses [5-20]. The fact that $g_\parallel > g_\perp$ suggests that Cu\(^{2+}\) ions are subjected to tetragonally elongated distortion.

From the spin-Hamiltonian parameters, the dipolar term ($P$) and the Fermi-contact term ($\kappa$) are calculated using the expressions [21, 22].

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

$$\kappa = \frac{A_0}{P} + \Delta g_0 \quad \text{..... (3)}$$

Here $\gamma_{Cu}$ is the magnetic moment of the copper, $\beta_0$ is the Bohr magneton, $\beta_N$ is the nuclear magneton and $r$ is the distance from the central nucleus to the electron. $A_0 = (A_\parallel + 2A_\perp)/3$, where $A_\parallel$ and $A_\perp$ are the hyperfine coupling constants in the parallel and perpendicular directions to the field. $g_\parallel$ and $g_\perp$ are the g-values parallel and perpendicular to the field and $\Delta g_0 = (g_0 - g_e)$, where $g_0 = (g_\parallel + 2g_\perp)/3$ and $g_e$ is the free ion g-value (2.0023). The Fermi contact term $\kappa$ is a measure of the polarization produced by the uneven distribution of d-electrons density on the inner core S-electron. The evaluated value for the all the compositions are given in Table 4.3.1. and the values of $\kappa$ is in tune with order of $\kappa$ [23].
4.4.2. OPTICAL ABSORPTION SPECTRA OF Cu$^{2+}$ DOPED AFBP GLASSES

The optical absorption spectra of copper doped AFBP glasses are shown in Fig. 4.4.2, Fig. 4.4.3 and Fig. 4.4.4 for AFBPCu1, AFBPCu2, and AFBPCu3 glasses respectively. In all the glasses, a broad band is observed at 820 nm (12192 cm$^{-1}$), 825 nm (12118 cm$^{-1}$) and 815 nm (12267 cm$^{-1}$) for AFBPCu1, AFBPCu2, and AFBPCu3 glasses respectively, which are characteristic of distorted octahedral symmetry [18]. Thus these broad bands are assigned to $^2B_1 \rightarrow ^2B_2$ transition.
Fig. 4.4.2. Optical absorption spectrum of Cu$^{2+}$ doped AFBPCu1 glasses.
Fig. 4.4.3. Optical absorption spectrum of Cu$^{2+}$ doped AFBPCu2 glasses.
Fig. 4.4.4. Optical absorption spectrum of Cu$^{2+}$ doped AFBPCu3 glasses.
By correlating EPR and optical absorption data, the molecular orbital coefficients $\gamma^2$ and $\beta_1^2$ are expressed by using the formulae given in the literature [21, 24-26] as follows:

$$\gamma^2 = \frac{7}{4}(A_{\parallel}/P - A/P + 2/3 \cdot g_{\parallel} - 5/21 \cdot g_{\perp} - 6/7) \quad \text{…. (4)}$$

$$g_{\parallel} = 2.0023 \left[1 - 4\lambda \gamma^2 \beta_1^2/E\right] \quad \text{…. (5)}$$

where $A = (A_{\parallel} + A_{\perp})/3$, $E_i$ is the energy corresponding to the $^2B_{1g}$ \rightarrow $^2B_{2g}$ transition, $P$ is a constant (0.036 cm$^{-1}$), $\lambda$ is the spin-orbit coupling constant (-830 cm$^{-1}$ for the Cu$^{2+}$ ion) and $g_e$ is the free electron g-value, ($g_e = 2.0023$). The parameters $\gamma^2$ and $\beta_1^2$ can be taken as a measure of the in-plane $\sigma$ - bonding and in-plane $\Pi$ - bonding between the d orbital of the central metal ion and p orbitals of the ligands [27-29]. Using the above equations (4) and (5), the values of $\gamma^2$ and $\beta_1^2$ are calculated for all the compositions and are given in Table 4.3.1. Both $\gamma^2$ and $\beta_1^2$ are smaller than unity and they indicate the covalent or ionic character of bonding between metal and ligand orbitals. If their values are in the order $\beta_1^2 < \gamma^2$, the in-plane $\Pi$ - bonding is more covalent than the in-plane $\sigma$ - bonding, otherwise $\sigma$ - bonding is more covalent and the $\Pi$ - bonding becomes significantly ionic [25,29-32]. The evaluated values shows that the molecular orbital coefficients obtained by correlating EPR and optical data indicate that the in-plane $\sigma$ - bonding is more covalent, whereas the
in-plane Π-bonding is more ionic for lower concentration of TM ions. For higher concentration, these values are in former case.

The normalized covalency of Cu$^{2+}$–O in-plane bonding of $\sigma$ or $\pi$ symmetry is expressed as [33]

$$\Gamma_{\sigma} = 200 \left( 1 - S \right) \left( 1 - \alpha^2 \right) \left( 1 - 2S \right) \%$$  \hspace{1cm} \text{\ldots(6)}

$$\Gamma_{\pi} = 200 \left( 1 - \beta_1^2 \right) \%$$  \hspace{1cm} \text{\ldots(7)}

where $S = 0.076$ cm$^{-1}$ for oxygen ligands and the normalized covalency ($\Gamma_{\pi}$) of Cu$^{2+}$–O bonding of Π symmetry indicates the basicity of the oxide ion. Generally the covalency of the in-plane $\sigma$-bonding ($\Gamma_{\sigma}$) decreases, while the covalency of in-plane $\Pi$-bonding ($\Gamma_{\pi}$) increases. The evaluated values $\Gamma_{\sigma}$ for AFBPCu1, AFBPCu2 and AFBPCu3 are 33.3%, 39.3% and 66.3 % respectively. The evaluated values of $\Gamma_{\pi}$ are 75.8%, 69.8% and 17.2% with respect to AFBPCu1, AFBPCu2 and AFBPCu3 glasses respectively. Since only one band is observed in optical absorption spectrum of both the glasses, the nature of the out of plane Π-bonding could not be inferred.
Table. 4.4.1. Spin-Hamiltonian, hyperfine splitting parameters and bonding parameters of Cu$^{2+}$ doped AFBP glasses.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AFBPCu1</th>
<th>AFBPCu2</th>
<th>AFBPCu3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_\parallel$</td>
<td>2.2891</td>
<td>2.2949</td>
<td>2.3468</td>
</tr>
<tr>
<td>$g_\perp$</td>
<td>2.07116</td>
<td>2.07160</td>
<td>2.1183</td>
</tr>
<tr>
<td>$A_\parallel$</td>
<td>183 X 10$^{-4}$ cm$^{-1}$</td>
<td>177 X 10$^{-4}$ cm$^{-1}$</td>
<td>142 X 10$^{-4}$ cm$^{-1}$</td>
</tr>
<tr>
<td>$A_\perp$</td>
<td>33 X 10$^{-4}$ cm$^{-1}$</td>
<td>43 X 10$^{-4}$ cm$^{-1}$</td>
<td>74 X 10$^{-4}$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.3720</td>
<td>0.3881</td>
<td>0.4616</td>
</tr>
<tr>
<td>$\gamma^2$</td>
<td>0.8472</td>
<td>0.8197</td>
<td>0.6956</td>
</tr>
<tr>
<td>$\beta_l^2$</td>
<td>0.6208</td>
<td>0.6506</td>
<td>0.9139</td>
</tr>
<tr>
<td>$\Gamma_\sigma$</td>
<td>33.3%</td>
<td>39.3%</td>
<td>66.3%</td>
</tr>
<tr>
<td>$\Gamma_\pi$</td>
<td>75.8%</td>
<td>69.8%</td>
<td>17.2%</td>
</tr>
</tbody>
</table>
4.4.3. FT-IR STUDIES OF Cu$^{2+}$ DOPED AFBP GLASSES

Alkali fluoroborophosphate glasses doped with copper is shown in Fig.4.4.5, Fig.4.4.6 and Fig.4.4.7 and the analysis of their vibrational group assignments are summarized in Table 4.4.2.

The characteristic absorption bands for crystalline CuO [33] and vitreous B$_2$O$_3$ [34, 35] were used in this discussion. The characteristic absorption bands for crystalline CuO were identified at ~ 410, ~ 500 and ~ 610 cm$^{-1}$ and for crystalline CuO were Cu$_2$O they were identified at ~ 615 cm$^{-1}$ [33]. The absorption band centered at ~ 490 cm$^{-1}$ is characteristic B-O-B bond-bending vibrations [34-36]. The absorption band at ~715 cm$^{-1}$ has been assigned to BO$_3$-O-BO$_3$ bending vibrations [35, 37]. The bands in the spectral range 400-550 cm$^{-1}$ are sensitive to alkali (Na, Li) environment [33]. The P-O-P bending vibration at 574 cm$^{-1}$ [38, 39] and ν of deformation modes of P-O$^-$ (PO$_4^{3-}$) groups [40-42]. The absorption bands at 670 cm$^{-1}$ are B-O-B bond bending vibrations of triborate groups [34-36]. The absorption bands at 900 cm$^{-1}$ are asymmetric P-O-P stretching vibrations [44, 45]. The bands at 1050 cm$^{-1}$ are ν(PO$_3$)$_5^{2-}$ vibrations [41, 46] and the bands at 1150 cm$^{-1}$ are P-O$^-$ ionic & (PO$_2$) stretching vibrations [40,45,47,48]. Stretching vibrations of B-O bonds in BO$_3$ units [45, 49] and (P=O) stretching vibrations are from 1200 – 1400 cm$^{-1}$ [50-53]. These borate and phosphate bond
vibrations overlap and form characteristic borophosphate vibration bands from 890 – 1400 cm$^{-1}$.

The vibrational bands around 1660 cm$^{-1}$ are assigned to bending vibrations of P-O-H [54]. Absorption bands near 2350 cm$^{-1}$ are assigned to characteristic stretching modes of P-O-H and vibrations of tetrahedral PO$_4^{3-}$ ion [56, 54]. IR vibrations at 3350 cm$^{-1}$ are assigned to the characteristic molecular and water vibrations [55-57].
Fig. 4.4.5. FT-IR spectrum of Cu$^{2+}$ doped AFBPCu1 glasses.
Fig. 4.4.6. FT-IR spectrum of Cu$^{2+}$ doped AFBPCu2 glasses.
Fig. 4.4.7. FT-IR spectrum of Cu$^{2+}$ doped AFBPCu3 glasses.
Table 4.4.2 FTIR analysis Cu$^{2+}$ doped AFBP glasses

<table>
<thead>
<tr>
<th>AFBPCu1</th>
<th>AFBPCu2</th>
<th>AFBPCu3</th>
<th>Vibrational assignments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>492</td>
<td>451</td>
<td>476</td>
<td>B-O-B bond bending vibrations. Specific vibrations of Cu-O bonds.</td>
<td>[33]</td>
</tr>
<tr>
<td>592</td>
<td>608</td>
<td>550</td>
<td>Bending vibrations of P-O-P. Deformation modes of P-O$^-$ ions in (PO$_4^{3-}$).</td>
<td>[38-42]</td>
</tr>
<tr>
<td>633</td>
<td>691</td>
<td>608,666</td>
<td>Alkali bond vibrations. B-O-B bending vibrations.</td>
<td>[34-36]</td>
</tr>
<tr>
<td>707</td>
<td>749</td>
<td>724</td>
<td>O$_3$B-O-BO$_3$ bending vibrations.</td>
<td>[35, 37]</td>
</tr>
<tr>
<td>898</td>
<td>923</td>
<td>915</td>
<td>Asymmetric stretching of P-O-P.</td>
<td>[44,45]</td>
</tr>
<tr>
<td>1006,1097</td>
<td>1006,1080</td>
<td>981,1055,1189</td>
<td>ν(PO$_3$)$_2^-$ vibrations. P-O$^-$ &amp; ν(PO$_2$)$_5^-$ vibrations.</td>
<td>[41,46]</td>
</tr>
<tr>
<td>1213,1329, 1395</td>
<td>1271,1321, 1395,1486</td>
<td>1288,1428</td>
<td>Stretching vibrations of B-O bonds in BO$_3$ units. ν(P=O) stretching vibrations</td>
<td>[45, 49-53]</td>
</tr>
<tr>
<td>1652</td>
<td>1660</td>
<td>1685</td>
<td>Bending vibrations of P-O-H.</td>
<td>[54]</td>
</tr>
<tr>
<td>2340</td>
<td>2340</td>
<td>2356</td>
<td>Stretching vibrations of P-O-H. Vibrations of tetrahedral PO$_4^{3-}$ ion.</td>
<td>[56][54]</td>
</tr>
<tr>
<td>3433,3508</td>
<td>3334,3417, 3492</td>
<td>3326,3442</td>
<td>Molecular, water groups.</td>
<td>[55, 56,57]</td>
</tr>
</tbody>
</table>
4.5 CONCLUSIONS

From the EPR, Optical absorption and FT-IR studies of Cu$^{2+}$ doped AFBP glasses, the following conclusions are drawn:

From the EPR spectral studies, the evaluated spin-Hamiltonian and hyperfine splitting parameters are in tune with the other reported borate and phosphate glass systems. The g-values ($g_\parallel > g_\perp$) indicates tetragonally elongated octahedral site for Cu$^{2+}$ ion in these glass systems. The values of $g_\parallel / A_\parallel$ increasing trend of the present glass systems indicate that site symmetry of Cu$^{2+}$ ions is distorted octahedron.

The analysis of the optical absorption spectra confirms the tetragonally distorted octahedral coordination of Cu$^{2+}$ ions in the host lattices. By correlating EPR and optical results, the evaluated parameters indicate the partial covalency of in-plane $\sigma$ ($\gamma^2$) and in-plane $\pi$ - bonding ($\beta_1^2$) between copper ions and its ligands. The parameters $\Gamma_\sigma$ and $\Gamma_\pi$ are in accordance with the complexes expected that of basicity character. From the FT-IR spectra of the all these glasses exhibited the distortion of $T_d$ symmetry of both Phosphate and Borate molecules. It clearly indicates that the metal ion and fluorine vibrations are also compositionally varied.
4.6 REFERENCES


