CHAPTER 3
CHAPTER 3
SPECTROSCOPIC STUDIES ON COPPER ION DOPED IN
MIXED ALKALI CADMIUM PHOSPHATE GLASSES

3.1 INTRODUCTION

The phenomenon of mixed-alkali effect in glasses have been
attracted much attention in recent years. This is due to their technological
and theoretical interests in describing physics and chemistry of glasses. A
number of mixed-alkali glass systems have been demonstrated non-linearity in electrical conductivity, viscosity, thermal properties and
chemical durability. Many physical properties measured in mixed-alkali
systems show initial non-linear growth and subsequent reversal in trends
leading to maxima or minima as a function of modifier fraction [1].
Mixed-alkali glasses contain more than one type of modifying cation [1-2].
The studies concerned with the structure and properties of phosphate
glasses are rather limited. This limitation is due to the hygroscopic nature
of phosphate glasses and the volatility of P2O5 at elevated temperatures [3].

By changing the chemical composition, the local environment of the
transition metal (TM) ion incorporated into the vitreous network can also
be changed, leading to local ligand field inhomogeneities. These structural
modifications are well reflected in the EPR and absorption spectra of
transition metal paramagnetic ions in glasses. Oxide glasses formed with
heavy metal ions have received significant attention owing to their interesting optical applications. These glasses are better competitors for optical transmission studies due to their long infrared cut-off [4]. Cadmium phosphate based glasses have been used as matrices for the growth of Cadmium selenide quantum dots. Recently spectroscopic investigations of certain transition metal doped phosphate glasses have been reported earlier [5-13]. The experimental and theoretical investigations on Mixed Alkali Effect (MAE) of several glasses are reported in literature [14-16]. The MAE in Li and Na aluminophosphate glasses is reported recently [17]. However, the MAE is not yet investigated so far in cadmium phosphate glasses. In addition, EPR and optical investigations on these glasses are also rare, even though these studies are important and useful to gain insight into the microscopic mechanisms responsible for the effect. Hence, the aim of the present investigations are to study the nature of the site symmetry of Cu$^{2+}$ in lithium-sodium mixed alkali cadmium phosphate glasses (here after referred to as Cu1, Cu2 and Cu3 glass) from the nature and splittings of EPR and optical bands along with MAE.

The element Copper shows oxidation states of +1, +2 and +3. Cu$^{1+}$ ions has $S = 0$ and hence can not give any ESR signal. Cu$^{3+}$ ion has $S = 1$ and is observable at very low temperatures only. But Cu$^{2+}$ is very common
and ESR is observable even at high temperatures. \( \text{Cu}^{2+} \) has spin \( S = \frac{1}{2} \) and nuclear spin \( I = 3/2 \) for both isotopes, \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\). The number of lines observable \((2I+1)\) is equal to four. So, the ESR spectrum of \( \text{Cu}^{2+} \) in most oxide glasses is distinctive and easily recognized on the basis of the principal ‘\( g \)’ values \((g_{||} = 2.3, g_{\perp} = 2.06)\) and a four line hyperfine splitting due to \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\). The ionic radius of \( \text{Cu}^{2+} \) is \(0.72\text{Å} \).

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, \(\text{Cu}_2\text{O}\) is yellow or red, \(\text{Cu}_2\text{CO}_3\) is yellow and \(\text{CuI}\) 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 \((\text{Cu}^{2+})\) has the electronic configuration \(d^9\) 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 [17a]

The paramagnetic ion \(\text{Cu}^{2+}\) enters easily into a number of host lattices. Therefore this ion is preferred to study the effect of the symmetry of the crystal fields on the d-electrons.
As a part of the investigations on the effects of descent in symmetry on the energy levels of the transition metal ions in solids, the present studies on the optical and EPR spectra of copper doped mixed alkali phosphate glasses are undertaken.

3.2 THEORY

\[ \text{Cu}^{2+} (d^9) \text{ in octahedral crystal field has electronic configuration } t_{2g}^6e_g^3 \text{ which is equivalent to one electron missing from the } e_g \text{ orbit. Thus the configuration gives rise to } ^2E_g \text{ term as the ground state. On excitation, one of the electrons of } t_{2g} \text{ orbital is promoted to } e_g \text{ orbital. The resulting electronic configuration } t_{2g}^5e_g^4 \text{ gives rise to } ^2T_{2g} \text{ state. For } \text{Cu}^{2+} \text{ ion in pure octahedral symmetry, only one transition } ^2E_g \rightarrow ^2T_{2g} \text{ 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 (\( C_{2v} \)) the lower state \( ^2E_g \)
splits into $^2A_1 \left( d_{x^2-y^2} \right)$ and $^2A_1 \left( d_z \right)$, and $^2T_{2g}$ splits into $^2A_2 \left( d_{xy} \right)$, $^2B_1 \left( d_{x^2} \right)$ and $^2B_2 \left( d_{yz} \right)$. Therefore four bands are expected due to the transition from the ground state to the other four excited states. The correlation of different electronic states in octahedral ($O_h$), tetragonal ($C_{4v}$) and rhombic ($C_{2v}$) symmetries are shown in Fig.3.1.

In the present investigation, Cu$^{2+}$ ion is considered as octahedrally coordinated by six oxygen atoms and the octahedron is tetragonally distorted. In the tetragonally distorted octahedron environment, the $^2E_g$ level splits into $^2A_1$ and $^2B_1$, and $^2T_{2g}$ level into $^2E$ and $^2B_2$, the ground state being $^2B_1$. With this model, the EPR spectra are explained on the basis of the conventional spin-Hamiltonian [18].

$$H = \beta_e B \cdot g \cdot S + S \cdot A \cdot I$$

here $\beta_e$ is the Bohr magneton, $S = 1/2$ for Cu$^{2+}$ ion and $I = 3/2$ for copper nucleus, $^{63}\text{Cu}/^{65}\text{Cu}$. The first term represents electron Zeeman interaction and second term represents interaction of unpaired electron spin with the nuclear spin.
3.3 EXPERIMENTAL

The starting materials used in the present study are Analar grade Li₂CO₃ (99.9%), Na₂CO₃ (99.9%), CdO (99.9%) and P₂O₅ (99.9%). The host glass composition is taken in the ratio of x Li₂O + (20-x) Na₂O + 20 CdO + 59.5 P₂O₅ + 0.5 CuO (5 ≤ x ≤ 15) to get the glasses. Each batch is first sintered at 700K and then melted in an electric furnace at 1250K for
nearly 2h, using Platinum crucibles. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are annealed at 550K for 30 minutes. For X-ray diffraction the PHILIPS XPERTPRO X-RAY diffraction system of 60 kV, Cu Kα radiation (angle range is 0-70°) was used to check for possible crystallinity of the sample after quenching and annealing. All samples are found to be completely amorphous in nature. EPR spectra of Copper-doped glasses are recorded at room temperature on JES-FA series X-band EPR spectrometer having 100 kHz field modulations. Optical absorption spectra of glasses are also recorded at room temperature on JASCO (V-550) spectrophotometer in the wavelength range 200-900 nm.

3.4 RESULTS AND DISCUSSIONS

Powder XRD spectra are recorded for the three Cu$^{2+}$ doped mixed alkali cadmium phosphate glass samples and a typical one for a glass sample is shown in Fig.3.2. The observed X-ray pattern of the samples studied in the present investigation indicates amorphous nature for all combinations of glasses. Hence, the formation of glass in these samples is confirmed in amorphous nature.
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 phosphate glasses, the EPR spectra of glass samples exhibit multiple absorption lines. The EPR spectra of Cu$^{2+}$ doped mixed alkali cadmium phosphate glasses, recorded at room temperature, are shown in Fig. 3.3. (a: Cu1 glass; b: Cu2 glass; c: Cu3 glass.)
Fig 3.3a Polycrystalline EPR spectra of Cu$^{2+}$ doped Li-Na cadmium phosphate Cu1 glass ($\nu=9.445$ GHz)
Fig 3.3b Polycrystalline EPR spectra of Cu$^{2+}$ doped Li-Na cadmium phosphate Cu2 glass ($\nu$=9.445 GHz)
Fig 3.3c Polycrystalline EPR spectra of Cu$^{2+}$ doped Li-Na cadmium phosphate Cu3 glass (ν=9.445 GHz)
The spectra, given in Fig. 3.3(a,t,c), reveal two sets of well resolved lines, one each in low and mid fields, corresponding to spin Hamiltonian parameters in the parallel and perpendicular directions of the applied magnetic field, i.e., $g_\parallel$ and $g_\perp$.

The spin-Hamiltonian parameters evaluated from EPR spectra for the glass samples are shown Table 3.1:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_\parallel$ cm$^{-1}$</th>
<th>$A_\perp$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1 glass</td>
<td>2.437</td>
<td>2.096</td>
<td>117 x $10^{-4}$</td>
<td>26 x $10^{-4}$</td>
</tr>
<tr>
<td>Cu2 glass</td>
<td>2.441</td>
<td>2.083</td>
<td>121 x $10^{-4}$</td>
<td>25 x $10^{-4}$</td>
</tr>
<tr>
<td>Cu3 glass</td>
<td>2.433</td>
<td>2.096</td>
<td>125 x $10^{-4}$</td>
<td>32 x $10^{-4}$</td>
</tr>
</tbody>
</table>

The observed $g_\parallel$ and $g_\perp$ values are characteristic of Cu$^{2+}$ ions coordinated by six ligands, which form an elongated octahedron along the Z-axis [19-20] and as $g_\parallel > g_\perp > g_e$ (free electron $g$ value), the ground state of the unpaired electron is $d_{x^2-y^2}$ ($^2B_{1g}$ state). The fact that $g_\parallel > g_\perp$ suggests that Cu$^{2+}$ ions are subjected to tetragonally elongated distortion. As the EPR spectra of the glasses indicate a single magnetically inequivalent Cu$^{2+}$ ion, one can assume on charge compensating grounds that the dopant ion might have entered the glass structure by replacing Cd$^{2+}$
ion. However, as the spin Hamiltonian parameters for the three glass samples are very close to each other with respect to variable Li$_2$O/Na$_2$O concentrations, the replacement of Cu$^{2+}$ for Lithium and Sodium is also ruled out. Similarly, in the present systems, if the small changes in the spin Hamiltonian parameters are considered, the glass sample with $x = 10$ shows diversion, i.e., a minima or maxima. For example, the $g_{\parallel}$ value is maximum and $g_{\perp}$ value is minimum for this concentration ($x = 10$). However, the trend in A values is not on expected lines, since the hyperfine lines are somewhat broad to measure very accurate spin Hamiltonian parameters (A values). These evaluated spin- Hamiltonian parameters are intune with the other reported glass systems given in Table 3.2
Comparison table of $g$ and $A$ values for various borate and phosphate glasses

Table 3.2. Comparison of spin-Hamiltonian parameters of Cu$^{2+}$ ions in different systems.

<table>
<thead>
<tr>
<th>System</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_\parallel$ $10^4$ cm$^{-1}$</th>
<th>$A_\perp$ $10^4$ cm$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O–B$_2$O$_3$</td>
<td>2.328</td>
<td>2.050</td>
<td>157</td>
<td>24.9</td>
<td>[26]</td>
</tr>
<tr>
<td>Na$_2$O–B$_2$O$_3$</td>
<td>2.327</td>
<td>2.065</td>
<td>150</td>
<td>26.0</td>
<td>[27]</td>
</tr>
<tr>
<td>ZnO–B$_2$O$_3$</td>
<td>2.321</td>
<td>2.039</td>
<td>159</td>
<td>—</td>
<td>[28]</td>
</tr>
<tr>
<td>PbO–B$_2$O$_3$</td>
<td>2.323</td>
<td>2.042</td>
<td>152</td>
<td>—</td>
<td>[28]</td>
</tr>
<tr>
<td>Li$_2$O–Na$_2$O–B$_2$O$_3$</td>
<td>2.382</td>
<td>2.061</td>
<td>162</td>
<td>22.5</td>
<td>[29]</td>
</tr>
<tr>
<td>Na$_2$O–K$_2$O–B$_2$O$_3$</td>
<td>2.333</td>
<td>2.044</td>
<td>140</td>
<td>23.7</td>
<td>[30]</td>
</tr>
<tr>
<td>CdSO$_4$–B$_2$O$_3$</td>
<td>2.422</td>
<td>2.084</td>
<td>77</td>
<td>—</td>
<td>[31]</td>
</tr>
<tr>
<td>Li$_2$SO$_4$–CdSO$_4$–B$_2$O$_3$</td>
<td>2.421</td>
<td>2.089</td>
<td>77</td>
<td>—</td>
<td>[31]</td>
</tr>
<tr>
<td>Na$_2$SO$_4$–CdSO$_4$–B$_2$O$_3$</td>
<td>2.420</td>
<td>2.086</td>
<td>77</td>
<td>—</td>
<td>[31]</td>
</tr>
<tr>
<td>K$_2$SO$_4$–CdSO$_4$–B$_2$O$_3$</td>
<td>2.420</td>
<td>2.089</td>
<td>77</td>
<td>—</td>
<td>[31]</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$–CdSO$_4$–B$_2$O$_3$</td>
<td>2.421</td>
<td>2.086</td>
<td>77</td>
<td>—</td>
<td>[31]</td>
</tr>
<tr>
<td>PbO–B$_2$O$_3$</td>
<td>2.369</td>
<td>2.068</td>
<td>124</td>
<td>20.4</td>
<td>[35]</td>
</tr>
<tr>
<td>MgO–P$_2$O$_5$</td>
<td>2.417</td>
<td>2.059</td>
<td>109</td>
<td>—</td>
<td>[32]</td>
</tr>
<tr>
<td>Na$_2$O–P$_2$O$_5$</td>
<td>2.423</td>
<td>2.088</td>
<td>107</td>
<td>—</td>
<td>[33]</td>
</tr>
<tr>
<td>CaO–P$_2$O$_5$</td>
<td>2.408</td>
<td>2.059</td>
<td>109</td>
<td>—</td>
<td>[32]</td>
</tr>
<tr>
<td>SrO–P$_2$O$_5$</td>
<td>2.342</td>
<td>2.063</td>
<td>109</td>
<td>—</td>
<td>[32]</td>
</tr>
<tr>
<td>BaO–P$_2$O$_5$</td>
<td>2.408</td>
<td>2.058</td>
<td>108</td>
<td>—</td>
<td>[32]</td>
</tr>
<tr>
<td>ZnO–P$_2$O$_5$</td>
<td>2.415</td>
<td>2.058</td>
<td>109</td>
<td>—</td>
<td>[34]</td>
</tr>
<tr>
<td>CdO–P$_2$O$_5$</td>
<td>2.404</td>
<td>2.058</td>
<td>109</td>
<td>—</td>
<td>[34]</td>
</tr>
<tr>
<td>Li$_2$O–Na$_2$O–CdO–P$_2$O$_5$ 1</td>
<td>2.437</td>
<td>2.096</td>
<td>117</td>
<td>26</td>
<td>[Present]</td>
</tr>
<tr>
<td>Li$_2$O–Na$_2$O–CdO–P$_2$O$_5$ 2</td>
<td>2.441</td>
<td>2.088</td>
<td>121</td>
<td>25</td>
<td>[Present]</td>
</tr>
<tr>
<td>Li$_2$O–Na$_2$O–CdO–P$_2$O$_5$ 3</td>
<td>2.433</td>
<td>2.096</td>
<td>125</td>
<td>32</td>
<td>[Present]</td>
</tr>
</tbody>
</table>
From the spin-Hamiltonian parameters, the dipolar term (P) and the Fermi-contact term (κ) are calculated using the expressions [21-22].

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

\[ \kappa = \frac{A_0}{P} + \Delta g_0 \]

Here \( \gamma_{Cu} \) is the magnetic moment of Copper, \( \beta_0 \) is the Bohr magneton, \( \beta_N \) is the nuclear magneton, \( r \) is the distance from the central nucleus to the electron. \( A_0 = \frac{(A_\parallel + 2A_\perp)}{3}, \Delta g_0 = g_0 - g_e \), where \( g_0 = \frac{(g_\parallel + 2g_\perp)}{3} \) and \( g_e \) is the free electron g-value (2.0023). The Fermi contact term \( \kappa \) is a measure of the polarization produced by the uneven distribution of d-electron density on the inner core s-electron. The evaluated value of \( \kappa = 0.364 \) for Cu1 glass, 0.360 for Cu2 glass and 0.331 for Cu3 glasses are in tune with the general order of \( \kappa \) [23].

The optical absorption spectra of copper doped Li-Na cadmium phosphate glasses are shown in Fig.3.4 (a, b, c). In all the glasses, a broad band is observed at 860 nm for Cu1 glass, 875 nm for Cu2 glass and 860 nm for Cu3 glass, which are characteristic of distorted octahedral symmetry [19]. Thus these broad bands are assigned to \( ^2B_1 \rightarrow ^2B_2 \) transition. The covalency parameter for the in plane \( \sigma \) - bonding is evaluated from the expression [21].
Absorbance (arbitrary units)

Fig. 3.4a Optical spectra of Cu$^{2+}$ doped Li-Na cadmium phosphate Cu$_1$glass
Fig. 3.4b Optical spectra of Cu$^{2+}$ doped Li-Na cadmium phosphate Cu$_2$glass
Fig. 3.4c Optical spectra of Cu\textsuperscript{2+} doped Li-Na cadmium phosphate Cu\textsubscript{3}glass
The value of $\alpha^2$ thus evaluated are 0.840, 0.849 and 0.858 respectively for Cu1, Cu2 and Cu3 glasses. By correlating EPR and optical absorption data, bonding parameter $\beta_1^2$ is calculated using the formula

$$g_{\|} = 2.0023 - 8Q \left[ \alpha \beta_1 - \frac{1}{(2)} \alpha' (1 - \beta_1^2)^{1/2} T(n) \right]$$

where $Q = (\lambda_o \alpha \beta_1 / \Delta E)$. $T(n) = 0.220$ is a function involving metal ligand hybridization constant and the effective nuclear charges for the ligand 2s, 2p orbitals and the metal 3d orbitals. $\Delta E$ is the transition energy between the $^3B_1 \rightarrow ^3B_2$ and $\lambda_o$ is the spin-orbit coupling constant (-828 cm$^{-1}$) [18].

$\alpha'$ can be evaluated from the normalization conditions on the ground state $b_1$ orbital as

$$\alpha' = (1 - \alpha^2)^{1/2} + \alpha S$$

In the above equation, S is the overlap integral between $d_{x^2-y^2}$ orbital and normalized ligand orbital. A value of S equal to 0.076 for oxygen ligands is used in the present investigation [21]. Accordingly the parameters evaluated are: $\beta_1^2 = 0.89, 0.87, 0.86$ and $\alpha' = 0.47, 0.46, 0.45$ for Cu1, Cu2 and Cu3 glasses respectively. These values are shown in Table 3.3.
Table 3.3 Evaluated bond parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\kappa$</th>
<th>$\alpha^2$</th>
<th>$\alpha'$</th>
<th>$\beta_1^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1 glass</td>
<td>0.364</td>
<td>0.840</td>
<td>0.47</td>
<td>0.89</td>
</tr>
<tr>
<td>Cu2 glass</td>
<td>0.360</td>
<td>0.849</td>
<td>0.46</td>
<td>0.87</td>
</tr>
<tr>
<td>Cu3 glass</td>
<td>0.381</td>
<td>0.858</td>
<td>0.45</td>
<td>0.86</td>
</tr>
</tbody>
</table>

$\alpha^2$ refers to the covalency of the in-plane $\sigma$ bonding between copper and its ligands. $\alpha'$ is a parameter for normalization of $b_1$ orbital and indicates the extent of overlap between $d_{xz, yz}$ orbital of the central metal ion and the normalized ligand orbital. This intermediate parameter is used to evaluate another important parameter $\beta_1^2$, which is a direct measure of the covalency of the in-plane $\pi$-bonding between copper and its ligands. Thus $\beta_1^2$ is more sensitive to variations in covalency than $\alpha^2$ and is therefore better indicator of the covalent character. The $\alpha^2$ values indicate an intermediate ionic bond for the $\text{Cu}^{2+}$-$\text{O}^-$ in-plane $\sigma$ bonding.

From the calculated parameters $\alpha^2$, $\beta_1^2$ of investigated glasses systems and using value of $S (=0.076)$ in oxide ligands, two more variables that give an idea about the basicity of the oxide ion can be calculated. The normalized covalency of $\text{Cu}^{2+}$-$\text{O}$ in-plane bonding of $\sigma$ or $\pi$ symmetry is expressed as [25]
\[ \Gamma_\sigma = 200 \left(1 - S\right) \left(1 - \alpha^2\right)/(1 - 2S) \% \]
\[ \Gamma_\pi = 200 \left(1 - \beta_1^2\right) \%
\]
Here, the normalized covalency (\(\Gamma_\pi\)) of Cu\(^{2+}\)-O bonding of \(\pi\) 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 are shown in Table 3.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Gamma_\sigma)</th>
<th>(\Gamma_\pi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1 glass</td>
<td>34.9%</td>
<td>21.8%</td>
</tr>
<tr>
<td>Cu2 glass</td>
<td>32.9%</td>
<td>25.4%</td>
</tr>
<tr>
<td>Cu3 glass</td>
<td>30.9%</td>
<td>28.7%</td>
</tr>
</tbody>
</table>

The values show the mixed alkali effect [25] in the glass samples. Since only one band is observed in optical absorption spectrum, the nature of the out of plane \(\pi\)-bonding could not be inferred.
3.5 CONCLUSIONS

From the EPR and optical absorption studies of Cu$^{2+}$ doped mixed alkali cadmium phosphate glasses, the following conclusions are drawn:

For Cu$^{2+}$ ion, the site symmetry is suggested to be axially elongated tetragonally distorted octahedral in all these glasses. Only one band is observed for Cu1 glass and Cu3 glass. It is interesting to note that for Cu2 glass ($x = 10$ glass), two bands, i.e., a strong band corresponding to the transition $^2B_{1g} \rightarrow ^2B_{2g}$ at $(11425 \text{ cm}^{-1})$ and other band corresponding to the transition $(^2B_{1g} \rightarrow ^2E_g)$ $(12045 \text{ cm}^{-1})$, were observed. The additional band was due to sites of lower symmetry around the Cu$^{2+}$ ion. In other glass samples, the $^2B_{1g} \rightarrow ^2E_g$ band was vanished. One can assume that Cu$^{2+}$ ions substitute in place of Cd$^{2+}$ ions in the glasses.

By correlating EPR and optical results, the evaluated parameters indicated the partial covalency of in-plane $\sigma$ ($\alpha^2$) and in-plane-$\pi$ bonding ($\beta_1^2$) between copper ions and its ligands. When comparing the parameters $\Gamma_\sigma$ and $\Gamma_\pi$, one can also conclude that the glass becomes more ionic as the lithium content was increased. The in-plane $\pi$ bonding has an ionic component and $\beta_1^2$ varies as lithium content increases. Mixed alkali effect has been noticed in these systems.
REFERENCES


