ESR, infrared and optical absorption studies of Cu$^{2+}$ ion doped in 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (M = Zn, Cd) glasses

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ESR, IR and optical absorption studies on 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (where M=Zn, Cd) glasses containing Cu$^{2+}$ spin probe have been carried out. The IR results prove the distribution of trigonal bipyramids (TeO$_6$) which determines the network and the distribution of borate triangles (BO$_3$) and borate tetrahedral (BO$_4$) groups. Structural changes take place with variation of PbO content in BTZP and BTCP series. ESR results show that the $g_{||}$, $g_{\perp}$ indicating that the Cu$^{2+}$ ion is in tetragonal distorted octahedral site and its ground state is $d_{x^2-y^2}$. There are considerable changes in $g_{||}$, $g_{\perp}$ and $A_{\parallel}$ values with the increasing concentration of PbO in both BTZP and BTCP glass systems. The optical absorption spectra results show that the absorption peak of Cu$^{2+}$ is a function of composition. The observed optical absorption peak of Cu$^{2+}$ has been found to be maximum at 813 nm for x=30 mol% of PbO content. Bonding parameters are calculated from both optical and ESR data. All these variations clearly indicate the structural changes in the present glass systems with varying PbO content.

Keywords: IR, ESR, Optical absorption spectra, Glasses, Cu$^{2+}$ spin probe

1 Introduction

Over the past decade, a great deal of work has been carried out in the preparation and analysis of different kinds of glasses which were based on oxides, bismuthates, borates and tellurites. Parallel to this work, some attention has been focused on the preparation and characterization of borotelurite glasses. According to the earlier works, it has been found that addition of TeO$_2$ into the glass matrices enhance glass quality with an improvement in transparency, refractive index, durability towards moisture and enhancement in the IR transmission. In the present work in order to understand spectroscopic properties of borotelurite glasses containing Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ ions.

A number of studies on various physical and optical properties have been done on some TeO$_2$ and B$_2$O$_3$ based glass systems$^{1-3}$. Among the three modifier oxides, viz., ZnO, CdO and PbO, ZnO is expected to shorten the time taken for solidification of glasses during the quenching process. Both ZnO and CdO are thermally stable, sublime and appreciably covalent in character$^4$. Addition of PbO into the glass matrix produce low rates of crystallization, since PbO has the ability to form stable glasses due to its dual role; one as glass former, if Pb-O is covalent and the other as modifier, if Pb-O is ionic$^{5,6}$. In view of these qualities, all the three modifier oxides are interesting oxides and make the glasses more stable against devitrification and resistant to moisture.

Transition metal ions are being greatly used in the present days to probe the glass structure since their outer $d$-electron orbital function has a broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. Among various transition metal ions, the copper ion, a para-magnetic metal ion, when dissolved in glass matrices in very small quantities makes the glasses coloured and has a strong influence over the optical properties of the glasses.

In the present study, preparation and characterization of 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (where M=Zn, Cd) glasses (x=0 to 30 mol%) has been done by using ESR, infrared and optical absorption studies.

2 Experimental Details

Appropriate amounts of analar grade reagents of TeO$_2$ (99.9% pure, sigma-Aldrich), H$_3$BO$_3$, PbO, ZnO, CdO and 1 mole % of CuO was added as an impurity to each glass composition. The powdered mixture, in each case was thoroughly mixed in an agate mortar and was melted in a platinum crucible between 1000-1050°C in high temperature furnace for about half an hour until a bubble free liquid was formed. The resultant molten liquids were air-
quenched at about 200°C, by pouring on stainless steel disc and subsequently annealed at 200°C for 8 h to relieve mechanical strains and cracking of the glass samples. The compositions of the glass samples employed in these studies are given in Table 1.

X-ray diffractogram of powdered glass samples were recorded using a copper target (k_{α}=1.54Å) on a Philips PW (1140) diffractometer at room temperature. Infrared spectra of powdered glass samples were recorded using a Perkin-Elmer FT-IS spectrometer model 1605. ESR spectra were recorded for all glass samples at the X-band using JEOL-JM Fe3, ESR spectrometer with 100 KHz field modulation at room temperature. Optical absorption spectra of all the glass samples (1mm thick) were recorded on a Shimadzu UV-3100 spectrometer in the wavelength range 300-1000 nm at room temperature using air as the reference medium. The peak-pick facility provided in the spectrometer was used to measure the peak position.

3 Results and Discussion

3.1 XRD and infrared spectra

The X-ray diffraction spectra show no peaks, indicating that the samples are amorphous. The infrared transmittance spectra of the glasses were taken on a Perkin-Elmer FT-IS spectrometer model 1605 in the frequency region 4000-400 cm\(^{-1}\). The IR spectra of the glasses (Fig. 1 and Fig. 2) are characterized by intense absorption bands in the frequency regions 3436-3450, 1333-1390, 950-1085, 665-687 and 458 cm\(^{-1}\) for samples BTZP4 and BTCP4. Observed absorption peaks for all the compositions are presented in Table 2.

Intense absorption in the high frequency region of the spectrum with maximum in the 3436-3450 cm\(^{-1}\) region belongs to O-H stretching vibrations\(^7\). In the present glass systems (both BTZP and BTCP) the disappearance of the absorption peak at 806 cm\(^{-1}\) indicates the absence of boroxol ring formation and thus clearly indicating the presence of triborate \(\text{BO}_3\) and tetra borate \(\text{BO}_4\) groups. Intense absorption band in the 950-1085 cm\(^{-1}\) in all the glasses are due to stretching vibrations of \(\text{BO}_4\) tetrahedra\(^8,9\). Intense absorption band with maximum in the 1330-1390 cm\(^{-1}\) can be attributed to B-O vibrations of \(\text{BO}_3\) units\(^10\).

[Table 1—Glass compositions]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTZP1</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-30\text{ZnO})</td>
</tr>
<tr>
<td>BTZP2</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-20\text{ZnO}-10\text{PbO})</td>
</tr>
<tr>
<td>BTZP3</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-10\text{ZnO}-20\text{PbO})</td>
</tr>
<tr>
<td>BTZP4</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-30\text{PbO})</td>
</tr>
<tr>
<td>BTCP1</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-30\text{CdO})</td>
</tr>
<tr>
<td>BTCP2</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-20\text{CdO}-10\text{PbO})</td>
</tr>
<tr>
<td>BTCP3</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-10\text{CdO}-20\text{PbO})</td>
</tr>
<tr>
<td>BTCP4</td>
<td>(60\text{B}_2\text{O}_3-10\text{TeO}_2-30\text{PbO})</td>
</tr>
</tbody>
</table>

Table 2—Peak frequencies from IR spectra for \(60\text{B}_2\text{O}_3-10\text{TeO}_2-(30-x)\text{MO}-x\text{PbO} (M=\text{Zn, Cd})\) glasses

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak positions (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTZP1</td>
<td>668 1022 1342 3448</td>
</tr>
<tr>
<td>BTZP2</td>
<td>668 1081 1342 3448</td>
</tr>
<tr>
<td>BTZP3</td>
<td>687 1085 1344 3448</td>
</tr>
<tr>
<td>BTZP4</td>
<td>667 1022 1333 3450</td>
</tr>
<tr>
<td>BTCP1</td>
<td>667 984 1391 3450</td>
</tr>
<tr>
<td>BTCP2</td>
<td>679 967 1384 3436</td>
</tr>
<tr>
<td>BTCP3</td>
<td>685 953 1378 3448</td>
</tr>
<tr>
<td>BTCP4</td>
<td>667 1022 1333 3450</td>
</tr>
</tbody>
</table>
The absorption band with maxima at 667 cm\(^{-1}\) indicates the presence of tellurium-oxygen groups. The structure pattern of tellurium-containing glasses is determined by trigonal pyramids (TeO\(_3\)) and bipyramids (TeO\(_4\)). The absorption in the range of 600-700 cm\(^{-1}\) in such glasses is determined by the stretching vibrations of Te-O bonds in TeO\(_3\) and TeO\(_4\) groups. The absorption of TeO\(_3\) groups has a high-frequency position than TeO\(_4\) groups. In general case, the absorption band range of TeO\(_3\) groups correlates with frequencies of 650-700 cm\(^{-1}\), and that of TeO\(_4\) groups\(^{11,12}\) correlates with 600-650 cm\(^{-1}\). Analyzing the obtained results and comparing them to the published data\(^3\), it is clear that TeO\(_3\) is present in the structure of the glass system (both BTZP and BTCP series) because of the absorption band with maximum at 667-685 cm\(^{-1}\). For lower concentration of PbO (20 mole %), the substitution of PbO for ZnO in BTZP series causes changes in the structure of the test glasses, which is apparent in a shift of the maximum indicated absorption band to higher frequencies up to 687 cm\(^{-1}\). Usually a shift of absorption bands to higher frequencies occurs as a result of an increase in the degree of polymerization of the structural network (TeO\(_3\)) of the glass. Absorption band at 687 cm\(^{-1}\) shifted to the lower frequency side, as the mole percentage of PbO increased from 20 to 30. The above reasoning may be held valid for 60B\(_2\)O\(_3\)-10TeO\(_2\)-(30-x)CdO-xPbO (samples BTCP1 to BTCP4) glasses in which PbO was substituted for CdO similar to the substitution of PbO for ZnO in BTZP glasses.

In Fig. 1, the peak around 1022 cm\(^{-1}\) in BTZP1 increases up to 1085 cm\(^{-1}\) as the content of PbO increases up to 20\%, and the peak around 1085 cm\(^{-1}\) decreases up to 1022 cm\(^{-1}\) as the content of PbO increases from 20 to 30\%. In lead borate glasses\(^4\), at low concentrations (15-20\%) PbO acts as a modifier of the structural network in the form of PbO\(_6\) groups and promotes conversion of BO\(_3\) groups to BO\(_4\) tetrahedra. Above 15-20\% PbO some lead enters the structure as network former in the form of PbO\(_4\) pyramids. The absorption bands at 458 cm\(^{-1}\) in BTZP4 probably belong to the PbO\(_4\) structural vibrations\(^5\). Thus the fraction of BO\(_3\) units increases as the content of PbO increases up to 20\%. It is clear from Fig. 1, that there is no significant change in position but there is clear evidence of a decrease in the intensity of the absorption band around 1342 cm\(^{-1}\) and corresponding increase in the intensity of the BO\(_4\) peak at 1022 cm\(^{-1}\) is observed in the spectra of all the glasses in BTZP series. This is possible only if the number of BO\(_3\) units decreases and the fraction of BO\(_4\) units increases as the content of PbO in the glasses increases.

In Fig. 2, the absorption band peak around 984 cm\(^{-1}\) due to BO\(_4\) units in BTCP1 decreases up to 953 cm\(^{-1}\) as the content of PbO increases up to 20\% and then the band around 953 cm\(^{-1}\) in BTCP3 increases up to 1022 cm\(^{-1}\) as the content of PbO increases from 20 to 30\%, similarly peak around 1391 cm\(^{-1}\) in BTCP1 decreases continuously up to 1333 cm\(^{-1}\) as the content of PbO increases up to 30\%. Thus the fraction of BO\(_3\) groups decreases and the fraction of BO\(_4\) units increases as the content of PbO increases.

### 3.2 ESR spectra

The ESR spectra of both the series of glasses doped with Cu\(^{2+}\) ions are shown in Fig. 3 and 4. The spectrum closely resembles that of the Cu\(^{2+}\) ion in most oxide glasses\(^1,2,3\). From the spectral analysis, the spin-Hamiltonian parameters are calculated using the equation due to Dance et al.\(^6\) and are presented in Table 3.

From Table 3, it is clear that \(g_\parallel > g_\perp\) i.e., Cu\(^{2+}\) is in an octahedral coordination with tetrahedral distortion and the ground state of Cu\(^{2+}\) is \(d_{x^2-y^2}\). Also \(g_\parallel\) and \(g_\perp\)

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**Fig. 3**—ESR spectra of Cu\(^{2+}\) in 60B\(_2\)O\(_3\)-10TeO\(_2\)-(30-x)ZnO-xPbO for BTZP1-BTZP4 glass systems.
Hamiltonian:

The ESR spectra were analyzed using spin Hamiltonian parameters of Cu$^{2+}$ ion in 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (M=Zn, Cd) glasses.

Table 3—Spin Hamiltonian parameters of Cu$^{2+}$ ion in 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (M=Zn, Cd) glasses

<table>
<thead>
<tr>
<th>Samples</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_1$ (10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTZP1</td>
<td>2.346</td>
<td>2.089</td>
<td>134</td>
</tr>
<tr>
<td>BTZP2</td>
<td>2.341</td>
<td>2.078</td>
<td>141</td>
</tr>
<tr>
<td>BTZP3</td>
<td>2.336</td>
<td>2.059</td>
<td>144</td>
</tr>
<tr>
<td>BTZP4</td>
<td>2.353</td>
<td>2.073</td>
<td>129</td>
</tr>
<tr>
<td>BTCP1</td>
<td>2.336</td>
<td>2.123</td>
<td>142</td>
</tr>
<tr>
<td>BTCP2</td>
<td>2.329</td>
<td>2.090</td>
<td>147</td>
</tr>
<tr>
<td>BTCP3</td>
<td>2.338</td>
<td>2.073</td>
<td>145</td>
</tr>
<tr>
<td>BTCP4</td>
<td>2.353</td>
<td>2.073</td>
<td>129</td>
</tr>
</tbody>
</table>

and $A_\parallel$ values change with the composition PbO in BTZP and BTCP glasses and $g_\parallel$ reaches to a maximum for BTZP4, minimum for BTCP2, $g_\perp$ reaches to a maximum for BTZP1, minimum for BTZP3 and $A_\parallel$ reaches to a maximum for BTCP2, minimum for BTZP4, indicating continuous structural change in the glass system. Thus, from Fig. 3 and Table 3, it is clear that the ESR spectra of 60B$_2$O$_3$-10TeO$_2$-(30-x)MO-xPbO (M=Zn,Cd) glasses are strongly concentration dependent.

The ESR spectra were analyzed using spin Hamiltonian:

$$H = g_\parallel \beta H_x S_x + g_\perp \beta (H_y S_y + H_z S_z) + A_\parallel S_x I_x$$

$$+ A_\perp (S_x I_y + S_y I_x)$$

Here $Z$ is the symmetry axis, $\beta$ the Bohr magneton, $S$ and $I$ are the electron and nuclear spin operators, $H_x$, $H_y$, and $H_z$ are the static magnetic field components, $g_\parallel$ and $g_\perp$ are the parallel and perpendicular components of the $g$ tensor and $A_\parallel$ and $A_\perp$ are the parallel and perpendicular components of the hyperfine tensor $A$. The values of $A_\parallel$ are calculated using the following equation due to Kivelson:

$$H_\parallel (-3/2) - H_\parallel (+3/2) = 3A$$

From Table 3, it is clear that $g_\parallel$ and $g_\perp$ values decrease and reach a minimum in BTZP1 to BTZP3 glasses at about 20% PbO and $g_\parallel$ and $g_\perp$ values increase abruptly and reach a maximum at about 30% PbO. It also clear from Table 3 that $A_\parallel$ value increases with increase of PbO up to 20% and there is considerable decrease in $A_\parallel$ at about 30% PbO. This indicates that the distortion around Cu$^{2+}$ ion is changing with the increasing content of PbO and also indicates a continuous structural change in the glass system (BTZP1-BTZP4). In the case of BTCP1-BTCP4 samples, it is clear that $g_\parallel$ value decrease with the increase of PbO up to 10%, there after $g_\parallel$ value increase with increase of PbO up to 30%. Similarly $g_\perp$ value decrease with the increase of PbO up to 20% and thereafter $g_\perp$ value slightly increase with the increase of PbO up to 30% and $A_\parallel$ value increase with increase of PbO up to 10% and thereafter there is a considerable decrease in $A_\parallel$ value with the increase of PbO up to 30%. This indicates that the distortion around Cu$^{2+}$ ion is changing with the increasing content of PbO and also indicates a continuous structural change in the glass system (BTCP1-BTCP4).

The variation in spin-Hamiltonian parameters with increasing concentration of PbO up to 30% in both BTZP and BTCP series is due to structural change in the glass system. This behaviour agrees with the IR spectra data which reveal the partial conversion of BO$_3$ units into BO$_4$ units as the PbO content increases up to 30%. The ESR parameters of Cu$^{2+}$ ion in present glasses (both BTZP and BTCP series) are compared with other oxide glasses and are in good agreement with earlier reported values.

3.3 Optical absorption spectra

Optical absorption spectra for all the glass compositions exhibit a single broad peak (Fig. 5 and Fig. 6) in the range 780-813 nm, which can be attributed to the presence of Cu$^{2+}$ ion in the glass. This absorption can be assigned to the
The absorption peak of Cu$^{2+}$ goes through a maximum in both BTZP and BTCP glasses at x=30 mole % of PbO. The variation in peak position with PbO concentration indicates the fluctuation in ligand field around the Cu$^{2+}$ probe ion, which is related to change in polarizability of oxygen ions surrounding the Cu$^{2+}$ and its dependence on field strength of network formers. The absorption of the maximum (Table 4) in optical absorption peak in the present system can be explained on the basis of structural change in the glasses with variation of composition of PbO. With increasing PbO content, structural changes take place due to partial conversion of BO$_3$ units into BO$_4$ units. The bonding parameters are calculated using ESR and optical data by the following equations:

$$g_{\parallel} = 2.0023 \left[ 1 - 4 \lambda \alpha^2 \beta_1^2 / \Delta E_{xy} \right]$$

$$g_{\perp} = 2.0023 \left[ 1 - \lambda \alpha^2 \beta_2^2 / \Delta E_{xz, yz} \right]$$

where $\lambda$, spin orbit coupling parameter is equal to 828 cm$^{-1}$ for Cu and $\beta_2 = 1$ for octahedral environment. $\Delta E_{xy}$ and $\Delta E_{xz, yz}$ are the heights of the $d_{xy}$ and $d_{xz, yz}$ and molecular orbital levels above the ground state $d_{x^2-y^2}$ respectively and these values are estimated from optical absorption spectra. In optical absorption spectra, the position of observed absorption maximum of Cu$^{2+}$ indicates the value of $\Delta E_g$. From Table 4, it is observed that the bonding parameters are changing with the percent of PbO. The bonding coefficients $\alpha$, $\beta_1$ and $\beta_2$ characterize respectively, the in-plane $\sigma$ bonding, in-plane $\pi$ bonding and out-of-plane $\pi$ bonding of the copper (II) complex, their values lie between 0.5 and 1.0, the limits of pure covalent and pure ionic bonding. From Table 4, it is clear that, the present system has ionic in nature.

### 4 Conclusions

From IR results it is clear that the boron ions exists as BO$_3$ and BO$_4$ groups, tellurium ions as TeO$_3$ groups and probably lead ions in octahedral coordination PbO$_6$ and tetrahedral coordination PbO$_4$ within the glass structural network. Increasing the PbO content in both BTZP and BTCP glasses causes partial conversion of the boron ions from trigonal coordination to tetrahedral coordination. ESR results...
indicate that \( g_{||} > g_{\perp} \), indicating that Cu\(^{2+}\) is present in octahedral coordination with a tetrahedral distortion and the ground state of Cu\(^{2+}\) ion is \( d_{x^2-y^2} \). The structural changes take place as the concentration PbO varies. The \( g_{||} \), \( g_{\perp} \) and \( A_{||} \) values are changing with PbO composition. From the optical absorption studies it is clear that the optical absorption around 813 nm can be assigned to \( ^2E_g(D) \rightarrow ^2T_{2g}(D) \) transition of Cu\(^{2+}\) ion. The absorption peak position reaches a maximum at \( x = 30 \text{ mol}\% \) of PbO. The bonding parameters calculated from both optical and ESR data are found to change with PbO concentration. Thus it is concluded that structural changes are taking place in the present system (both BTZP and BTCP glasses) with the varying PbO content.

Acknowledgement
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References
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