ESR, IR and optical absorption studies of Cu$^{2+}$ spin probe in $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ ternary glasses

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ESR, IR and optical absorption studies on $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ ternary glasses containing Cu$^{2+}$ spin probe have been carried out. The absence of band at 806 cm$^{-1}$ in the IR spectra indicates the absence of boroxol rings. Thus, the present glass system consists of borate triangles [BO$_3$] and borate tetrahedral [BO$_4$] structural units. It was also observed that structural changes are taking place with variation of Na$_2$O and ZnO contents. The hyperfine splittings in the parallel features of ESR spectra of Cu$^{2+}$ are recorded for all compositions. 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 is considerable variation in $g_{||}$ and $A_{||}$ values with the increasing concentration of Na$_2$O, whereas no perceptible changes have been observed in $g_{\perp}$ and $A_{\perp}$ values. The observed optical absorption peak of Cu$^{2+}$ has been found to be at 800 nm for $x=25$ mol% of Na$_2$O content. Bonding parameters are calculated from both optical and ESR data. All these variations clearly indicate the structural changes in the present glass system with varying Na$_2$O content.

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

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1 Introduction

Spectroscopic techniques like ESR, IR and optical absorption are most suitable experimental techniques among the various sampling methods to study the structural information of the glasses. Alkali borate glasses are an ideal case in comparison to other glass forming systems to demonstrate the effectiveness of the spectroscopic techniques in the glass science. Alkali borate glasses containing divalent oxides such as MgO and ZnO show interesting behaviour$^{16}$. During the last few years, these glasses have attracted the attention of many researchers as they can be used as solid-state electrolytes in the fabrication of solid-state batteries. Glasses doped with transition metal ions like Cu$^{2+}$ and Mn$^{2+}$ have attracted considerable interest because of their memory and photo conducting properties.

B$_2$O$_3$ is one of the best and well known glass formers and is present in almost all commercially important glasses. When modifiers like Na$_2$O and ZnO added to the B$_2$O$_3$ glass, some of the BO$_3$ units present as boroxal rings are converted to the BO$_4$ units until certain modifiers limit after which non-bridging oxygens are formed with increasing the modifier oxide. Being this transformation ability of boron in the presence of the modifier, existing in three and four oxygen co-ordinate environments and the high strengths of covalent B-O bonds enable borates to form stable glass.

The infrared spectra of vitreous boron oxide and sodium borate glasses were studied earlier by Borrelli$^{7}$. The temperature and pressure dependence studies of Na$^+$ ion conductivity on Na$_2$O-ZnO-B$_2$O$_3$ glasses have indicated that Zn$^{2+}$ prefer net work-forming position$^8$. More recently, elastic and spectroscopic studies of Na$_2$O-ZnO-B$_2$O$_3$ glass system have been reported by Veeranna Gouda$^{9}$ indicated that Zn$^{2+}$ ions are incorporated into the network as a glass former, presumably in the form of ZnO$_4$ tetrahedral.

In the present study, the authors report the preparation and characterization of $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ glass system using ESR, IR and optical absorption studies.

2 Experimental Details

Glass samples were prepared using analar grade sodium carbonate (Na$_2$CO$_3$), zinc oxide (ZnO) and boric acid (H$_3$BO$_3$) in the composition range $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ where $x$ ranged from 0 to 50 mol %. 1 mol % of CuO is added to each composition as a spin probe. Appropriate amounts of
weighed chemicals were ground thoroughly in a mortar to produce homogeneous mixture and melted in a porcelain crucible in a high temperature furnace at 1100°C for about 30 min. The molten liquids were stirred frequently for homogeneity. The molten liquids were air quenched at 300°C, by pouring on a stainless steel block and pressed with another steel disk. The compositions of the glass system employed in these studies are given in Table 1.

All the glass samples were transferred into annealing furnace and annealed at 300°C for 4 hours to avoid cracking of the glasses. Glass samples were cooled to room temperature to relieve the thermal strains of the glass samples. X-ray diffraction patterns of the glass samples were recorded using copper target (Kα = 1.54Å) on Philips Panaltic X’ Pert at room temperature.

Infrared transmittance spectra of the powdered glass samples were recorded by KBr disc technique using a Perkin-Elmer FT-IS spectrometer model 1605, in the wavenumber range 400-4000 cm⁻¹ at room temperature. ESR spectra of the all glass samples were recorded on X-band JEOL-JES FE 3X ESR Spectrometer, at room temperature, with 100 kHz field modulations. The organic radical α,α-diphenyl-β-picrylhydrazyl (DPPH) was used as a standard g marker.

Optical absorption spectra of the glasses were recorded on Shimadzu UV-VIS spectrometer in the wavelength range 200-1000 nm at room temperature, taking air as a 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

In the X-ray diffraction spectra, no peaks have been observed, which confirms the amorphous nature of the samples of the present glass system.

A knowledge of the infrared spectra of the ternary Na₂O-ZnO-B₂O₃ glasses would be helpful in identifying and understanding various boron-oxygen arrangements at different modification levels in alkali borate glasses. Figure 1 shows IR spectra, absorption bands around 3430-3443 cm⁻¹, 1504-1613 cm⁻¹, 1384 cm⁻¹, 1000 cm⁻¹, 690-714 cm⁻¹, 502-520 cm⁻¹ and 461-485 cm⁻¹ for samples NZB1-NZB7. Observed absorption peaks for all the compositions are presented in Table 2.

The bands recorded around 3430-3443 cm⁻¹ can be attributed to O-H stretching vibrations¹⁰. The bands recorded between 1504 and 1613 cm⁻¹ are due to the asymmetric stretching relaxation of the B-O band of the trigonal BO₃ units¹¹. The band around 1595 cm⁻¹ may be attributed to presence of Cu²⁺ ion in the present system¹².

Bands observed around 1384 cm⁻¹ are due to B-O bond stretching of the tetrahedral BO₄ units¹¹. The shoulder at 1021 cm⁻¹ can be referred to stretching vibrations of BO₄ tetrahedra¹³. The band around 1000 cm⁻¹ to the formation of diborate group in the present glass system. In IR spectra of PbO-ZnO-B₂O₃ glasses, the band at 993 cm⁻¹ was attributed to a stretching vibration of B-O-Pb linkage¹⁴. The similar absorption

![Fig. 1—Infrared transmittance spectra of Cu²⁺ in xNa₂O-(50-x)ZnO-50B₂O₃ for NZB1 & NZB4 & NZB7 glass systems](image-url)
band was observed in the present glass system at 990 cm\(^{-1}\) and is assigned to the stretching vibration of B-O-M (B-O-Na) linkage, where M represents a metal ion. The absorption band observed around 700 cm\(^{-1}\) is due to the bending of B-O-B linkages in the borate networks\(^{14}\). The low frequency band around 455 cm\(^{-1}\) in the spectra of investigated glasses can be attributed to vibrational metal cations\(^{13}\) such as Zn\(^{2+}\)/Na\(^{2+}\).

The band at 555 cm\(^{-1}\) can be attributed to the ZnO\(^4\) stretching vibrations. It can be seen from Fig. 1, the shift of the Zn-O stretching vibrations is observed towards the higher wavelength side from 502 cm\(^{-1}\) to 555 cm\(^{-1}\) with addition of the Na\(_2\)O content up to 25\% mol and further these vibrations are shifted to lower wavelength side. The initial shifting towards the higher wavelength is due to the formation of Na-O-Zn or B-O-Zn linkages in the glass matrix and shift in lower wavelength side is due to the decreasing amount of the ZnO content which in turn has not affected the glass structure as compared to 25\% mol ZnO content and above. Similar behaviour was also observed with ZnO-B\(_2\)O\(_3\)-SiO\(_2\) glass system\(^{14}\).

The well known 806 cm\(^{-1}\) band characteristic of vitreous B\(_2\)O\(_3\) is assigned to the symmetric breathing vibration of the boroxol ring. So, it is generally accepted that pure boron oxide glass is built up from networks of boroxol rings. Interestingly, when ZnO was added to the B\(_2\)O\(_3\) in the present glass system. The peak at 806 cm\(^{-1}\) disappeared clearly indicating the presence of triborate BO\(_3\) and tetra borate BO\(_4\) groups. These groups may be attached in the form of random network\(^{13}\).

Addition of alkali metal oxide to ZnO containing B\(_2\)O\(_3\) was found to cause the transformation of neutral borate tringles BO\(_3\), into charged borate tetrahedral BO\(_4\), where O indicates an oxygen atom bridging two boron atoms\(^{11}\). The addition of one molecule of alkali oxide to boron oxide results in the formation one triborate group and one penta borate group, which tends to occupy adjacent positions in the network. The formation of triborate-penta borate pairs continues upon further alkali oxide additions until a concentration of 20-mol \% is reached. At 20-mol \%, the structure consists mainly of two interpenetrating networks of alternating penta borate and triborate groups. On further additions, the number of diborate groups will increase at the expense of the penta borate-triborate pairs\(^{15}\). When triborate and penta borate groups are paired, they form a tetra borate group. Each added oxygen converts two BO\(_3\) units into BO\(_4\) tetrahedra. The glass system is hold up to about 30-40 mol \% alkali oxide, i.e. when the concentration of boron-oxygen tringles and tetrahedra are roughly equal. Above that concentration, the number of tetrahedral decreases with increasing alkali oxide concentration and non-bridging oxygen are formed with increasing number. However, the IR spectra appear to be not useful in identifying the non-bridging oxygen (NBO) containing groups.

### 3.2 ESR spectra

The ESR spectra for the samples NZB1, NZB4 and NZB7 of glass system are shown in the Fig. 2. From the spectral analysis, the spin Hamiltonian parameters are calculated and presented in Table 3, and found to be similar with most of the oxide glasses\(^{12,16,17}\). From the tabulated results it is clear that \(g_{||} > g_{\perp}\), i.e. Cu\(^{2+}\) is in an octahedral coordination with tetrahedral distortion. The ground state of Cu\(^{2+}\) is \(d_{x^2-y^2}\), no perceptible changes observed in \(g_{\perp}\) and \(A_{\perp}\). From Table 3, it is clear that the \(g_{||}\) and \(A_{||}\) values change with the composition Na\(_2\)O and \(A_{||}\) reaches to a maximum for NZB4, indicating continuous structural change in the glass systems. Thus, from Fig. 2 and Table 3, it is clear that the ESR spectra of xNa\(_2\)O-(50-x)ZnO-50B\(_2\)O\(_3\) glasses are strongly concentration dependent.

The ESR spectra were analyzed using spin Hamiltonian.

\[
H = g_{||} \beta H S_{||} + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{||} S_I I_x + A_{\perp} (S_x I_x + S_y I_y)
\]
Fig. 2—ESR spectra of Cu$^{2+}$ in $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ for NZB1 & NZB4 & NZB7 glass systems

Table 3—Spin Hamiltonian parameters of $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ glasses

<table>
<thead>
<tr>
<th>Sample</th>
<th>$g_1$ (±0.002)</th>
<th>$g_2$ (±0.002)</th>
<th>$A_\parallel$ (10$^{-4}$ cm$^{-1}$)</th>
<th>$A_\perp$ (10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZB1</td>
<td>2.337</td>
<td>2.070</td>
<td>143±2</td>
<td>20±2</td>
</tr>
<tr>
<td>NZB2</td>
<td>2.337</td>
<td>2.070</td>
<td>140±2</td>
<td>19±2</td>
</tr>
<tr>
<td>NZB3</td>
<td>2.332</td>
<td>2.069</td>
<td>143±2</td>
<td>19±2</td>
</tr>
<tr>
<td>NZB4</td>
<td>2.328</td>
<td>2.069</td>
<td>155±2</td>
<td>20±2</td>
</tr>
<tr>
<td>NZB5</td>
<td>2.317</td>
<td>2.068</td>
<td>143±2</td>
<td>20±2</td>
</tr>
<tr>
<td>NZB6</td>
<td>2.325</td>
<td>2.068</td>
<td>147±2</td>
<td>21±2</td>
</tr>
<tr>
<td>NZB7</td>
<td>2.328</td>
<td>2.069</td>
<td>140±2</td>
<td>21±2</td>
</tr>
</tbody>
</table>

Here $Z$ is the symmetry axis, $\beta$ the Bohr magneton, $S$ and $I$ are the electron and nuclear spin operators, $H_z$, $H_y$, and $H_x$ are the static magnetic field components, $g_1$ and $g_2$ are the parallel and perpendicular components of the $g$ tensor and $A_\parallel$ and $A_\perp$ are parallel and perpendicular components of the hyperfine tensor $A$.

The values of $A_\parallel$ and $A_\perp$ are calculated using the following equations due to Kivelson$^{18}$

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

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

The ESR parameters of Cu$^{2+}$ ion in present glass are compared with other oxide glasses and are in good agreement with earlier reported values$^{12,16,17}$ and variation of spin Hamiltonian parameters are of similar in nature. The distortion around the Cu$^{2+}$ ion is changing with increasing concentration of Na$_2$O.

3.3 Optical absorption spectra

The optical absorption spectra of Cu$^{2+}$ ion in $x$Na$_2$O-(50-$x$)ZnO-50B$_2$O$_3$ glass system for sample NZB1-NZB7 as shown in Fig. 3, show a single broad peak around 760 nm, which clearly indicates the presence of Cu$^{2+}$ in these glasses$^{19,20}$. This absorption peak can be assigned to $^2E_g(D) \rightarrow ^2T_{2g}(D)$ transition of Cu$^{2+}$. The close study of dependence of absorption peak position indicates that, the peak wavelength changes with Na$_2$O concentration and passes through a maximum at $x=25$ mol %. The variation in peak position with Na$_2$O 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$^{19-23}$.

The observation of the maximum (Table 4) in optical absorption peak wavelength in the present system can be explained on the basis of structural change in the glasses with variation of composition of Na$_2$O. With increasing Na$_2$O content, structural changes take place by producing non-bridging oxygen (NBO) ions. The bonding parameters are calculated using ESR and optical data by the following equations$^{18,24}$:

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

\[
g_\perp = 2.0023 \left[ 1 - \lambda \alpha^2 \beta^2 / \Delta E_{xz,yz} \right]
\]
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 $\Delta E_{x2y2}$ are the heights of the $d_{xy}$ and $d_{x2y2}$ and molecular orbital levels above the ground state $d_{z2}$ respectively and these values are estimated from optical absorption spectra$^{15}$. In optical absorption spectra, the position of observed absorption maximum of Cu$^{2+}$ indicates the values of $\Delta E_{xy}$.

From Table 4 it is observed that the bonding parameters are changing with the per cent of Na$_2$O. The bonding coefficients $\alpha^2$, $\beta^2$ 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
The ESR, IR, and optical absorption studies have been carried out on Cu$^{2+}$ doped in $x$Na$_2$O-(50-x)ZnO-50B$_2$O$_3$ glass system. From IR results it is clear that there exist [BO$_4$], [BO$_3$] units in the present system. The absence of absorption band at 806 cm$^{-1}$, clearly indicates that the absence of boroxol ring in the glass structure. ESR results indicate that $g_{||} > g_{\perp}$ indicating Cu$^{2+}$ is in octahedral coordination with tetrahedral distortion. The ground state of Cu$^{2+}$ ion is $d_{x2-y2}$. Structural changes are taking place as the concentration of Na$_2$O varied. The $g_{||}$ and $A_{||}$ values also change with the variation of Na$_2$O composition, however, there is no perceptible change in $A_{\perp}$ and $g_{\perp}$ values. From the optical absorption studies it is clear that the observed absorption peak at around 760 nm can be assigned to $^2E_g(D) \rightarrow ^2T_{2g}(D)$ transition of Cu$^{2+}$. The absorption peak wavelength reaches a maximum at $x = 25$ mol % of Na$_2$O. The bonding parameters calculated from both optical and ESR data are found to change with Na$_2$O concentration. Thus, it can be concluded that structural changes are taking place in the present system with the varying Na$_2$O content.

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References