



ESR, IR & OPTICAL ABSORPTION STUDIES OF Cu^{+2} SPIN PROBE IN $x\text{Na}_2\text{O}-(50-x)\text{ZnO}-50\text{B}_2\text{O}_3$ TERNARY GLASSES

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ABSTRACT

ESR, IR and Optical absorption studies on $x\text{Na}_2\text{O}-(50-x)\text{ZnO}-50\text{B}_2\text{O}_3$ 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 non-presence of boroxol rings. Thus the present glass system consists of tri borate $[\text{BO}_3]$ and tetra borate $[\text{BO}_4]$ structural units. It was also observed that structural changes are taking place with variation of Na_2O 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 $g_{\parallel} > g_{\perp}$ indicating that the Cu^{+2} ion is in tetragonal distorted octahedral site and its ground state is $d_{x^2-y^2}$. There is good variation in g_{\parallel} and A_{\parallel} values with the increasing concentration of Na_2O , whereas no perceptible changes observed in g_{\perp} and A_{\perp} values. The observed optical absorption peak of Cu^{+2} is found to be maximum at 800 nm for $x=25$ mol% of Na_2O content. Bonding parameters are calculated from the both Optical and ESR data. All these variations clearly indicates the structural changes in the present glass system with varying Na_2O content.

1. INTRODUCTION

Spectroscopic techniques like ESR, IR & optical absorption are most suitable experimental techniques among the various sampling methods to study the structural information of the glasses¹⁻⁶. Alkali Borate glasses are an ideal case in comparison to other glass forming system to demonstrate the effectiveness of the spectroscopic techniques in the glass science. Alkali Borate glasses containing divalent oxide such as MgO and ZnO show interesting behavior. During the last few years many research workers showing much interest in these glasses because they can be used as solid-state electrolytes in the fabrication of solid-state batteries.

Glasses doped with transition metal ions like Cu^{+2} , Mn^{+2} have attracted considerable interest because of their memory and photo conducting properties.

B_2O_3 is one of the best glass former known and is present in almost all commercially important glasses. The ability of boron 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 by N.F.Borrelli et.al.⁷ The Temperature and pressure dependence studies of Na^+ ion conductivity on $\text{Na}_2\text{O}-\text{ZnO}-\text{B}_2\text{O}_3$ glasses has indicated that Zn^{+2} prefer net work-forming position.⁸ More recently, Elastic and spectroscopic studies of $\text{Na}_2\text{O}-\text{ZnO}-\text{B}_2\text{O}_3$ glass system have been reported by Veeranna Gouda et.al

⁹ indicated that Zn^{+2} ions are incorporated into the network as glass a former presumably in the form of ZnO_4 tetrahedral.

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

2. EXPERIMENTAL

Glass samples were prepared using analar grade Sodium carbonate (Na_2CO_3), Zinc oxide (ZnO) and Boric acid (H_3BO_3) in the composition range $x\text{Na}_2\text{O}-(50-x)\text{ZnO}-50\text{B}_2\text{O}_3$ 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 were 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 the Table-1.

All the samples were transferred for annealing furnace and annealed at 300°C for 4 hours to avoid cracking in the samples. Samples were cooled to room temperature to relieve the thermal strains in the samples.

X-ray diffraction patterns of the powdered glass samples were recorded using copper target ($K_\alpha = 1.54^\circ\text{\AA}$) on Phillips panaltic X' Pert at room temperature.

Infrared transmittance spectra of the powdered glass samples were recorded using Perkin-Elmer FT-IR Spectrometer model 1605, in the wave number range $400-4000\text{ cm}^{-1}$ at room temperature.

ESR Spectra of the glass samples were recorded on X-band JEOL-JES FE 3X ESR Spectrometer, at room temperature, with 100KHz 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 ShimadzuUV-VIS spectrometer in the wavelength range 200 to 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 & 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.

Infrared transmittance spectra of all samples are shown in Fig.1, which was recorded as a function of wave number versus percentage of transmittance. IR spectra shows absorption bands around $3430-3443\text{ cm}^{-1}$, $1504-1613\text{ cm}^{-1}$, 1384 cm^{-1} , 1000 cm^{-1} , $690-714\text{ cm}^{-1}$ $461-485\text{ cm}^{-1}$ for sample NZB1-NZB7. The bands recorded around $3430-3443\text{ cm}^{-1}$ can be attributed to O-H stretching vibrations¹⁰ while the bands recorded between $1504-1613\text{ cm}^{-1}$ are due to the B-O bond stretching of the tetrahedral BO_4 units. The band around 1595 cm^{-1} may be attributed to presence of Cu^{+2} ion in the present system¹¹. Bands observed around 1384 cm^{-1} are due to the symmetric stretching relaxation of the B-O band of trigonal BO_3 units. The band around 1000 cm^{-1} to the vibration of

some boron atoms attached to the non-bridging oxygen in the form of tetra borate BO_4 ¹². In the present glass system the absence of the absorption peak at 806 cm^{-1} indicates the absence of the boroxol ring formation. The absorption bands are observed around 700 cm^{-1} and is due to the bending of B-O-B linkages in the borate net works¹³. In pure B_2O_3 glass, the 806 cm^{-1} frequency is a characteristic of boroxol ring in the glass structure, indicating the presence of BO_3 and BO_4 groups. This corresponds to progressive substitution of boroxol ring by BO_3 and BO_4 groups. This type of behavior is observed in $\text{B}_2\text{O}_3\text{-Li}_2\text{O}_3$ glass by Kulkarni.et.al.¹⁴. The low frequency band around 455 cm^{-1} in the spectra of investigated glasses can be attributed to Vibrational metal cations such as $\text{Zn}^{+2}/\text{Na}^{+2}$. The intensity of the peak at 1000 cm^{-1} corresponding to BO_4 units increases with increasing of Na_2O concentration indicating an increase in production of BO_4 units⁹.

3.2 Optical absorption spectra

The optical absorption spectra of Cu^{2+} ion in $x\text{Na}_2\text{O} - (50-x) \text{ ZnO} - 50 \text{ B}_2\text{O}_3$ glass system for sample NZB1-NZB7 show a single broad peak around 800 nm , which clearly indicates the presence of Cu^{2+} in these glasses.^{14,15} This absorption peak can be assigned to ${}^2\text{E}_g(\text{D}) \rightarrow {}^2\text{T}_{2g}(\text{D})$ transition of Cu^{2+} . The close study of dependence of absorption peak position indicates that, the peak wavelength changes with Na_2O concentration and passes through a maximum at $x=25 \text{ mol}\%$. The variation in peak position with Na_2O 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.¹⁵⁻¹⁹

The observation of the maximum (Table-2) 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_2O . With increasing Na_2O content, structural changes takes place by producing Non-Bridging Oxygen (NBO) ions. The bonding parameters are calculated using ESR and optical data by the following equations.^{20,21}

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

$$g_{\perp} = 2.0023 [1 - 4 \lambda \alpha^2 \beta_1^2 / \Delta E_{xz, yz}]$$

Where λ , spin orbit coupling parameter is equal to 828 cm^{-1} for Cu and $\beta^2 \cong 1$ for octahedral environment. ΔE_{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 spectra²². In optical absorption spectra, the position of observed absorption maximum of Cu^{+2} indicates the values of ΔE_{xy}

As shown in Table-2, the bonding parameters are changing with the composition of Na_2O . The bonding coefficients α^2 , β_1^2 and β^2 characterize respectively, the in-plane σ bonding, in-plane π bonding and out-of plane π 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-2 it is clear that, the present system has ionic in nature.

3.3 ESR Spectra.

Studies on ESR spectra of the binary transition metal oxide (TMO) glasses have been reported by several workers.²³. The ESR spectra for the samples NZB1, NZB4 & NZB7 of glass system are shown in the Fig. 2. From the spectral analysis the spin Hamiltonian parameters are calculated and

tabulated in Table-3, and found to be similar with most of the oxide glasses.²² From the tabulated results it is clear that $g_{\parallel} > g_{\perp}$ 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_{\parallel} and A_{\parallel} values are changes with the composition, indicating continuous structural change in the glass systems. Thus, from Fig.2 and Table-3, it is clear that the ESR spectra of $x\text{Na}_2\text{O} - (50-x) \text{ZnO} - 50 \text{B}_2\text{O}_3$ glasses are strongly concentration dependent.

The ESR spectra was analyzed using Spin Hamiltonian.

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y).$$

Where the symbols have their usual meanings.²⁴

The values of A_{\parallel} and A_{\perp} are calculated using the following equations due to Kivelson²⁰

$$\begin{aligned} H_{\parallel} (-3/2) - H_{\parallel} (+3/2) &= 3A_{\parallel} \\ H_{\perp} (-3/2) - H_{\perp} (+3/2) &= 3A_{\perp} \end{aligned}$$

The ESR parameters of Cu^{2+} ion in present glass is compared with other oxide glasses and are in good agreement with earlier reported values²¹ 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_2O .

4. CONCLUSIONS

The ESR, IR, and optical absorption studied have been carried out on Cu^{2+} doped in $x\text{Na}_2\text{O} - (50-x) \text{ZnO} - 50 \text{B}_2\text{O}_3$ glass system. From IR results it is clear that there exists $[\text{BO}_4]$, $[\text{BO}_3]$ 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 $g_{\parallel} > g_{\perp}$ indicating that Cu^{2+} is present in octahedral coordination with tetrahedral distortion. The ground state of Cu^{2+} ion is $d_{x^2-y^2}$. The structural changes takes place as the concentration Na_2O varies. The g_{\parallel} and A_{\parallel} values are also changes with Na_2O composition, however there is no perceptible change in A_{\perp} and g_{\perp} values. From the optical absorption studies it is clear that the optical absorption can be assigned to $2E_g (D) \rightarrow 2T_{2g} (D)$ transition of Cu^{2+} . The absorption peak wavelength reaches a maximum at $x = 25 \text{ mol\%}$ of Na_2O . The bonding parameters calculated from both optical and ESR data are found to change with Na_2O concentration. Thus it can be concluded that structural changes are taking place in the present system with the varying Na_2O content.

5. ACKNOWLEDGEMENT

The authors thank the DRDO/DST, New Delhi for the financial support.

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TABLES

Table-1: Composition of $x\text{Na}_2\text{O}$ - (50-x) ZnO -50 B_2O_3 glass system

Glass No.	Composition
NZB1	50 ZnO +50 B_2O_3 :Cu
NZB2	10 Na_2O + 40 ZnO +50 B_2O_3 :Cu
NZB3	20 Na_2O + 30 ZnO +50 B_2O_3 :Cu
NZB4	25 Na_2O + 25 ZnO +50 B_2O_3 :Cu
NZB5	30 Na_2O + 20 ZnO +50 B_2O_3 :Cu
NZB6	20 Na_2O + 10 ZnO +50 B_2O_3 :Cu
NZB7	50 Na_2O + 50 B_2O_3 :Cu

Table-2: Absorption peak of Cu^{+2} , bonding parameters and % of bonding symmetry of Cu^{+2} doped in $x\text{Na}_2\text{O}$ - (50-x) ZnO -50 B_2O_3 glass system

Glass No	Cu^{+2} peak (nm)	α^2	β^2	β_1^2	τ_π (%)	τ_σ (%)
NZB1	742	0.8048	0.9521	0.8294	37.04	41.88
NZB2	780	0.7961	0.9669	0.8112	37.36	44.69
NZB3	735	0.8041	0.9597	0.8544	29.12	41.84
NZB4	800	0.7970	0.9650	0.7702	45.96	44.23
NZB5	760	0.8188	0.9393	0.7625	47.50	39.48
NZB6	800	0.8048	0.9556	0.7557	48.86	42.53
NZB7	780	0.7964	0.9655	0.8148	34.12	44.36

Table- 3 Spin Hamiltonian parameters of $x\text{Na}_2\text{O}$ - (50-x) ZnO -50 B_2O_3 glasses.

Sample	$g_{ }(\pm 0.002)$	$g_{\perp}(\pm 0.002)$	$A_{ } (10^4 \text{cm}^{-1})$	$A_{\perp} (10^4 \text{cm}^{-1})$
NZB1	2.337	2.070	143 \pm 2	20 \pm 2
NZB2	2.337	2.070	140 \pm 2	19 \pm 2
NZB3	2.332	2.069	143 \pm 2	19 \pm 2
NZB4	2.328	2.068	143 \pm 2	20 \pm 2
NZB5	2.317	2.069	155 \pm 2	20 \pm 2
NZB6	2.325	2.068	147 \pm 2	21 \pm 2
NZB7	2.328	2.068	140 \pm 2	21 \pm 2

FIGURES

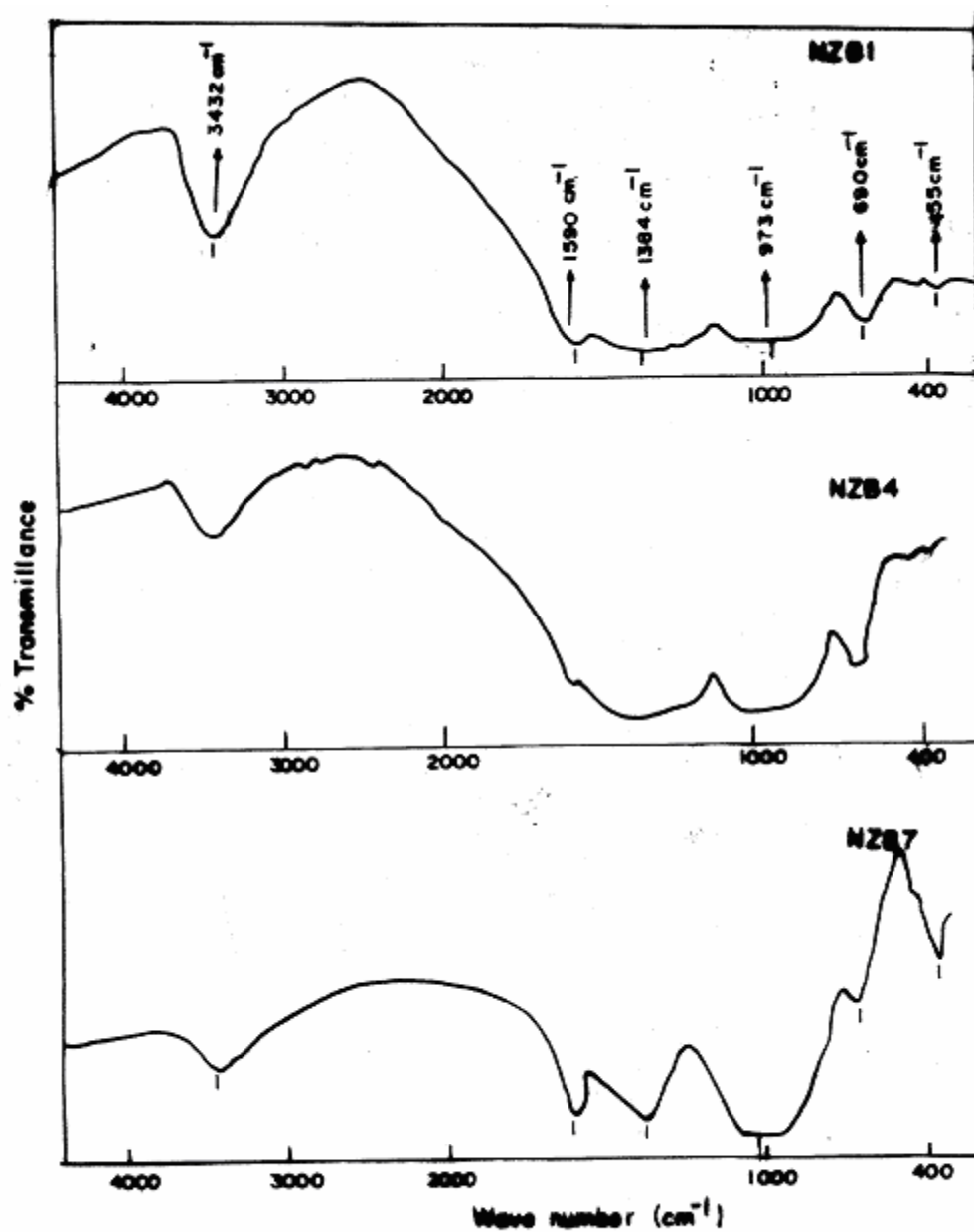


Fig.1. The infrared transmittance spectra of Cu^{2+} in $x\text{Na}_2\text{O}-(50-x)\text{ZnO}-50\text{B}_2\text{O}_3$ for NZB1, NZB4 & NZB7 glass system.

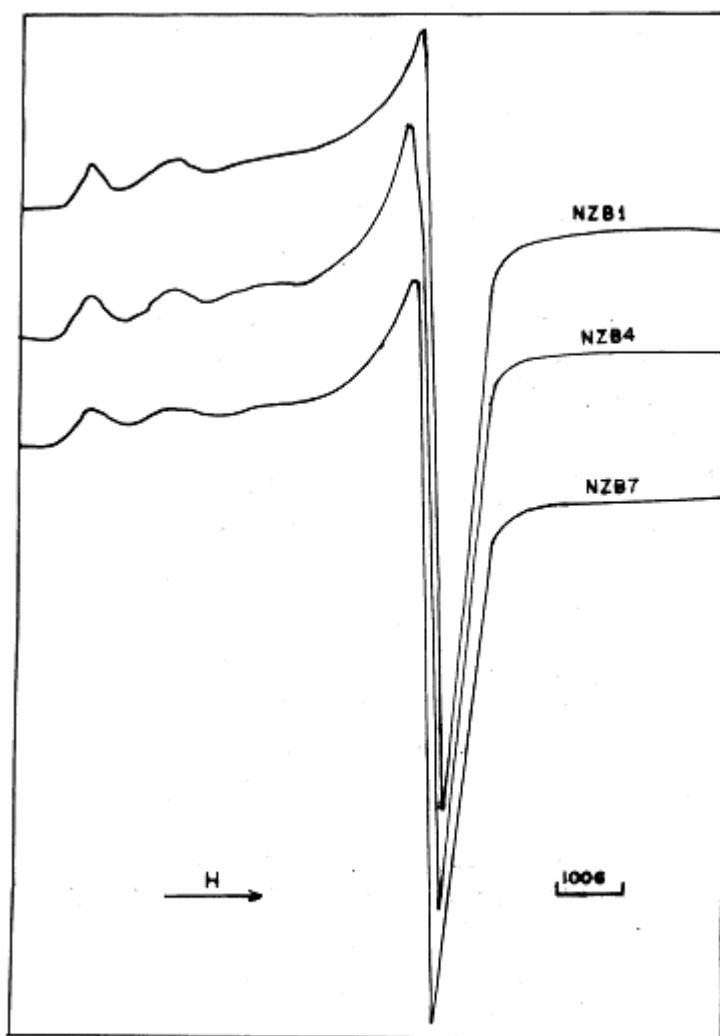


Fig. 2. The ESR spectra of Cu²⁺ in $x\text{Na}_2\text{O}-(50-x)\text{ZnO}-50\text{B}_2\text{O}_3$ NZB1, NZB4 & NZB7 glass systems.