

Electron Paramagnetic Resonance and Optical Absorption Studies of Cu^{2+} Probe in $\text{Li}_2\text{O}-\text{TeO}_2-\text{CdO}-\text{As}_2\text{O}_3-\text{B}_2\text{O}_3$ Glasses

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ABSTRACT

Electron paramagnetic resonance (EPR) and Optical absorption studies of $x\text{Li}_2\text{O}-(30-x)\text{TeO}_2-5\text{As}_2\text{O}_3-5\text{CdO}-59\text{B}_2\text{O}_3-1\text{CuO}$ (where $x=5, 10, 15, 20$ and 25 mol%) glasses were carried out by introducing Cu^{2+} ion as the spin probe. The glasses were prepared by the melt quenching method. The EPR spectra of all the glass samples were recorded at room temperature and at X-band frequencies. The EPR spectra exhibited similar spectral features. The spin-Hamiltonian parameters were calculated from the EPR spectra using standard procedures. The Cu^{2+} ions are in well defined axial sites but subjected to small distortion leading to the broadening of the spectra. It was observed that $g_{\parallel} > g_{\perp} > 2.0023$ and $A_{\parallel} > A_{\perp}$. The spin-Hamiltonian parameter values indicated that the ground state of Cu^{2+} ion is $d_{x^2-y^2}$ orbital ($2B_{1g}$) and the site symmetry around Cu^{2+} ions is tetragonally distorted octahedral. The optical spectra were recorded in the range 300-800nm. By correlating EPR and optical data, the bond parameters were evaluated and the values show purely ionic nature for the in-plane σ bonding and in-plane π bonding. The out-of-plane π bonding is moderately covalent. The theoretical optical basicity parameter values were evaluated and it was observed that the value of Γ_{σ} increases, whereas Γ_{π} decreases with the increase in optical basicity.

Keywords: Arsenate Glasses, Optical Absorption, Basicity, Spin Density, Susceptibility

I. INTRODUCTION

Boron oxide (B_2O_3) is one of the most common glass network formers and has received great attention from researchers due to its interesting technological applications like electrical, optical, structural, luminescent, physical, chemical durability, thermal stability, etc.[1]. The ability of boron to exist in both three- and four-coordinated environments and the high strength of the covalent B-O bonds impart borates to form stable glasses. Borate glasses still

require the incorporation with modifiers such as alkali or alkaline oxide to improve the mechanical stability and reduce the hygroscopic property of their glass network. Lithium in borate glass leads to the conversion of sp^2 planer BO_3 units to more stable sp^3 tetrahedral BO_4 units and is possible to create the non-bridging oxygens. The addition of alkali oxides can improve many properties of B_2O_3 glasses and modify, even their preparation conditions[2]. Tellurite glasses with good glass forming oxides like B_2O_3 are of scientific and technical interest on

account of their various properties like high refractive index, low melting temperature range and high optical non linearity. Tellurite glass has low thermal stability and borate glass has high phonon energy, but the B₂O₃ and TeO₂ combination gives excellent features like high thermal stability, low hygroscopic nature, and low phonon energy. Borotellurite glasses have a scientific and technological application in microelectronics and opto-acoustics due to their more suitable electrical and optical properties [1-4].

Electron spin resonance (ESR) spectroscopy is a sensitive technique for the study of transition metal (TM) ions in solids. It provides information concerning the valence state of TM ions, their concentration, local environment and the nature of interaction between them [5]. Glasses containing TM ions exhibits memory and photo conducting properties.

Optical absorption of transition metal ions in glasses is effected by the host construction into which the transition metal ions are incorporated. In oxide glasses, the TM ions mostly form coordination complexes with doubly charged oxygen as the ligands. The actual symmetry will depend on the composition of the glass system [6]. By correlating the optical and EPR spectra, one can get details concerning the bond parameters which determine the metal-ligand bond in the glasses. The properties of glass can often be altered by the addition of a network modifier to the basic constituents. The commonly used network modifiers are the alkali and alkaline earth oxides [7]. It was observed that the properties of an alkali oxide glass show a non-linear behavior when one kind of alkali is gradually replaced by another. This departure from linearity is called the mixed alkali effect [8]. Similar observations were made in the case of mixed alkali-alkaline earth oxide glasses [9]. This phenomenon is called mixed oxide effect. In this paper, we report EPR and optical absorption studies of Cu²⁺ spin probe in the quaternary glass system xLi₂O-(30-x)TeO₂-5As₂O₃-5CdO-59B₂O₃-1CuO (where x=5, 10, 15, 20 and 25 mol%). The influence of varying the concentrations of Li₂O and TeO₂,

which acts as network modifiers on the spin-Hamiltonian parameters, is discussed.

II. Experimental

A batch of approximately 15 g of chemicals in powder form was weighed using a digital balance with an accuracy of ±0.01mg. The relative weights of the components were calculated according to the molar formula xLi₂O-(30-x)TeO₂-5As₂O₃-5CdO-59B₂O₃-1CuO, where x ranged between 5 and 25 mol%. Appropriate amounts of reagent grade Li₂CO₃, As₂O₃, CdO, H₃BO₃, and TeO₂ were well-mixed and melted in porcelain crucibles in the temperature range of 1150-1200 °C, depending on the glass composition, in an electrical muffle furnace for about 60 minutes. The porcelain crucibles containing glass melt was swirled frequently to insure the homogeneity. The clear liquid (free of bubbles) was quickly cast in a stainless steel mould kept at 200 °C and pressed with another steel disc maintained at same temperature. Later, the samples were annealed 100 °C below their respective glass transition temperature for about 24 hours and slowly cooled to laboratory temperature.

EPR spectra were recorded on dry and perfectly powdered glass samples at room temperature (310 K) using EPR spectrometer (JEOL FEIX) operating at X-band frequency (9.205 GHz) with a modulation frequency of 100 kHz. The magnetic field was scanned between 0.23 and 0.43 T. Uncertainty in the measurement of *g* and *A* values were about ± 0.002 and ± 2 × 10⁻⁴ cm⁻¹ respectively. The optical absorption spectra of the glasses containing copper were recorded at room temperature (310 K) using UV-VIS spectrometer (shimadzu) in the wavelength region 300 nm to 1100 nm. The uncertainty in the measurement was about ± 1nm.

III. Results and Discussion

The room temperature Cu²⁺ ion doped EPR spectra of the present glasses were shown in Figure 1. The Cu²⁺ ion, with $S = \frac{1}{2}$, has a nuclear spin $I = \frac{3}{2}$ for both ⁶³Cu

and ^{65}Cu . Hence, $(2I+1)$ i.e. four parallel and four perpendicular hyperfine components were expected. In the present work, three weak parallel components were observed in the lower field region and the fourth parallel component was overlapped with the perpendicular component. The perpendicular components in the high field region were not resolved. It is found that the high field side of the spectra was more intense than the low field side. The EPR spectra of Cu^{2+} ions glasses studied could be analyzed by using an axial spin-Hamiltonian of the form [10, 11]:

$$H = g_{\parallel}\beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y) \quad (1)$$

Where β is the Bohr magneton, S_x, S_y and S_z and I_x, I_y and I_z are the components of the spin operators of the electron and nucleus, g_{\parallel} and g_{\perp} are the parallel and perpendicular principal components of the g tensor, H_x, H_y and H_z are the components of the magnetic field, z is the symmetry axis of individual Cu^{2+} complex and A_{\parallel} and A_{\perp} are the parallel and perpendicular principal components of the hyperfine coupling tensors respectively [12]. The nuclear quadrupole contribution is neglected. The calculated spin-Hamiltonian parameters are given in Table 1. From the figure it is observed that the obtained absorption spectra are asymmetric, characteristics of Cu^{2+} ($3d^9$) ions in axially distorted octahedral symmetric sites. It is found that the spectra keep their overall aspect in the entire composition range, suggesting high structural stability of the glassy matrix to accept Cu^{2+} ions. The spectra show the hyperfine structure due to the interaction of the unpaired electron spin with the nuclear one, $I = 3/2$, characteristic of Cu^{2+} . The hyperfine structure is resolved in the parallel band of the spectra and the perpendicular component is unsolved. Three hyperfine lines were observed on the features of the spectrum. The variations in the hyperfine line widths can be attributed to the functions in the coordination sphere surrounding the probe Cu^{2+} ion. The general nature of the ligand coordination can be obtained

from the fact that $g_{\parallel}, g_{\perp}, A_{\parallel}$ and $A_{\perp} g_{\parallel} > g_{\perp} > 2.0023$ [13]. Only an environment elongated along one of the cube axes can yield this result. In the present investigation, it is observed that $g_{\parallel} > g_{\perp} > g_e$. Therefore, from the g values and shape of the EPR spectra, it can be concluded that the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital, the Cu^{2+} ions being located in tetragonally distorted octahedral sites [14].

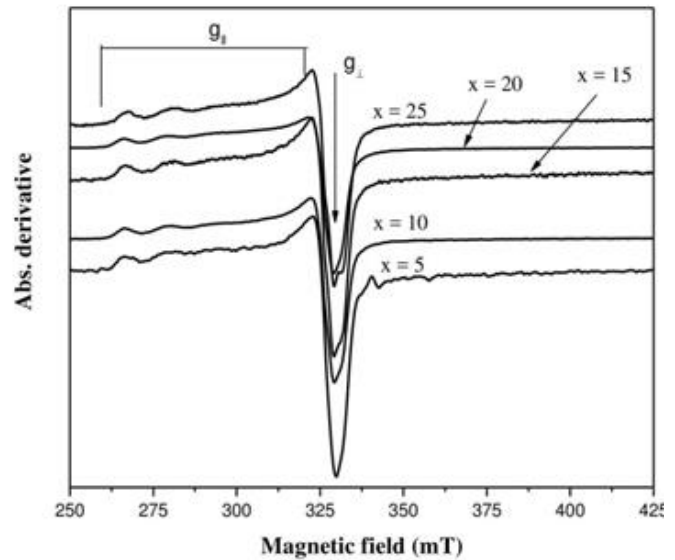


Figure 1. EPR spectra of Cu^{2+} in the present glass system

The variation of g_{\parallel} and A_{\parallel} with Li_2O content is shown in Figure 1. g_{\parallel} and A_{\parallel} varies non-linearly as the Li_2O content increases: g_{\parallel} decreases and then increases, whereas A_{\parallel} increases and then decreases indicating the change in the tetragonal distortion of Cu^{2+} ions [25]. The variation in g_{\parallel} and A_{\parallel} values may be associated with the change in the environment of Cu^{2+} . In the borate glasses, the addition of network modifiers leads to an increase in the coordination number of a certain portion of the boron atoms from 3 to 4. It is assumed that the resulting glass is composed of both triangular and tetrahedral units which form a relatively open network with holes between the oxygen atoms of sufficient size to accommodate the Li and Mg ions [15]. The solubility of the Cu^{2+} increases with the addition of the network modifiers presumably due to the coordination of the

metal ion by the extra oxygen ions. Thus, incorporation of Li₂O into the glass will influence the field at the site of Cu²⁺, which in turn will reflect in the non-linear variation of the spin Hamiltonian parameters as observed in the present glass system.

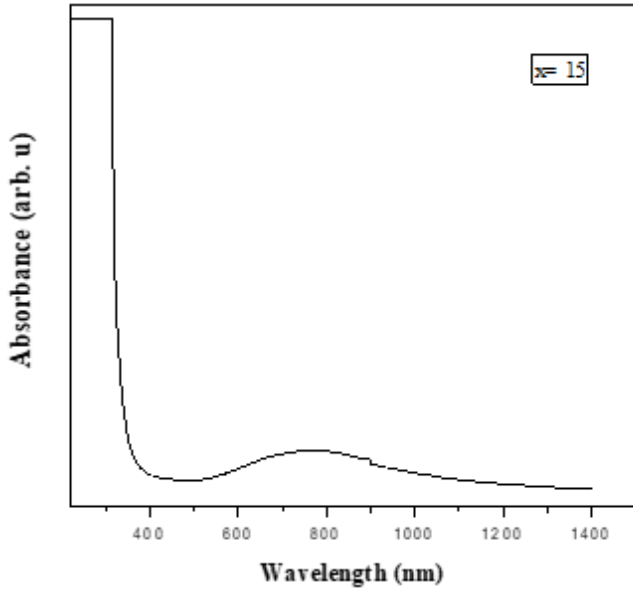


Figure 2. Optical absorption spectra of X= 15 mol% glasses

The optical absorption spectra of the present glasses are shown in Figure 2. The optical absorption spectra of all glasses studied reveal only a broad absorption band. The optical absorption peak position values are determined by peak pick facility of the spectrometer. It is observed that the elongated structures are usually more energetically favored than the compressed ones and the cupric ion exists in solution, solids and glasses in octahedral symmetry with a tetragonal distortion. For Cu²⁺ in elongated octahedral symmetry, more than one band will be observed [15,16]. But only a single optical absorption maximum was observed in most of the cases [17-24]. This single optical band was interpreted as the overlap of all the three transitions. Hence, in the present investigation, the observed asymmetric band around 13,192 cm⁻¹ is due to the overlap of ²B_{1g}→²A_{1g} and ²B_{1g}→²B_{2g} transitions. Nearly all the authors assigned the observed optical peak to the ²B_{1g}→²B_{2g}

transition (ΔE_{xy}) and have used this value in the evaluation of the bond parameters.

Table 1. EPR and optical parameters of xLi₂O-(30-x)TeO₂-5CdO-5As₂O₃-59B₂O₃-1CuO glass system.

Parameter	x=0	x=5	x=10	x=15	x=20	x=25
g	2.351	2.368	2.379	2.373	2.359	2.366
g _⊥	2.075	2.093	2.085	2.076	2.080	2.081
A (10 ⁻⁴ cm ⁻¹)	140.16	136.48	127.07	113.20	136.95	139.47
A _⊥ (10 ⁻⁴ cm ⁻¹)	17.96	19.24	22.10	17.96	20.67	19.22
λ (nm)	748	749	752	761	768	775
ΔE _{xy} (cm ⁻¹)	13369	13351	13298	13141	13021	12903
α ²	0.812	0.829	0.807	0.759	0.814	0.828
β ²	0.947	0.928	0.928	0.982	0.945	0.929
β ₁ ²	0.805	0.887	0.936	0.967	0.862	0.855

The EPR and optical absorption data can be related to evaluating the bonding coefficients of Cu²⁺. The bonding between the Cu²⁺ ion and its ligands can be described in terms of the covalency parameters α², β² and β₁² where α² describes the in-plane σ bonding with the copper d_{x²-y²} orbital, β² describes the out-of-plane π bonding with the d_{xz} and d_{yz} orbital and the β₁² parameter is a measure of the in-plane π bonding with the d_{xy} orbital. EPR results give rise to a new parameter (G), if G is greater than 5, a strong exchange coupling takes place among the magnetically non-equivalent Cu(II) ions in the unit cell. Truly compressed structures are relatively rare when compared to elongated structures. The calculated values of, α², β₁² indicate moderate covalency for the in-plane σ and π - bonding respectively, while the β² value indicated that the out-of-plane π-bonding is slightly ionic in nature. The calculated values are presented in Table 1, and Γ_σ, Γ_π are illustrated.

IV. CONCLUSION

The quaternary glass system of 1mole% CuO of xLi₂O-(30-x)TeO₂-5As₂O₃-5CdO-59B₂O₃ (5 ≤ x ≤ 25) were prepared, and their optical and EPR measurements have been studied. The following conclusions were made: EPR and optical data it is

clear that Cu^{2+} ions are present in all the glasses investigated and they exist on tetragonally distorted octahedral sites with $d_{x^2-y^2}$. The spin-Hamiltonian parameters are influenced by the composition of glass which may be attributed to the change of ligand field strength around Cu^{2+} . With increasing Li_2O content the ligand field strength is reduced around the Cu^{2+} ion due to the modification of the boron-oxygen network. The bond parameter values show purely ionic nature of the in-plane σ bonding and in-plane π bonding. The out-of-plane π bonding is moderately covalent. The value of Γ_σ increases, whereas Γ_π decreases with the increase in optical basicity and hence the covalency between Cu^{2+} ions and oxygen ligands decreases.

V. REFERENCES

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