

Research Article

EPR and Optical Absorption Spectral Investigations of Cu^{2+} in Bi_2O_3 - ZnO - B_2O_3 - Li_2O Glasses

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Received 25 February 2012; Accepted 28 March 2012

Academic Editors: W. A. Badawy, J. Casado, and M. Mączka

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Electron paramagnetic resonance and optical absorption studies of Bi_2O_3 - ZnO - B_2O_3 - Li_2O glasses were made by introducing Cu^{2+} as spin probe. The EPR spectra of Cu^{2+} in all the glass samples recorded in the X-band frequency have similar spectral features. The variation in glass composition influences the spin Hamiltonian parameters calculated from the spectra. The spin Hamiltonian parameters indicate that the Cu^{2+} ions are coordinated with six ligand atoms in a distorted octahedron elongated along one of the axes and the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital. The optical absorption spectra exhibited a broad band corresponding to d-d transition bands of Cu^{2+} ion. The values of bonding parameters indicate a covalent nature for the in-plane σ bonding and pure ionic nature for the in-plane and out-of-plane π bonding. 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.

1. Introduction

Electron paramagnetic resonance (EPR) studies of transition metal ions in oxide glasses is of scientific interest and gives information concerning the state of the ligands, the glass structure, nature of bonding, and site symmetry around metal ion [1–4]. The electron paramagnetic resonance (EPR) spectroscopic technique was first applied to glassy materials by Sands [1]. Unconventional glasses containing Bi_2O_3 as glass former are of great interest because of their potential applications in industry and many allied areas [5–7]. EPR investigations of Cu^{2+} ions in glasses are interesting and have received a considerable attention due to the sensitivity of parameters to local symmetry and have been studied in wide variety of glasses [8–13]. Optical absorption of transition metal (TM) ions in glasses is influenced by host structure 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. By correlating the EPR and optical absorption spectra, one can obtain information regarding the bond parameters that determine the metal-ligand bond in the glasses.

In this paper EPR and optical absorption properties of 1 mole % copper-doped $(60-x)\text{Bi}_2\text{O}_3$ - 25ZnO - $15\text{B}_2\text{O}_3$ - $x\text{Li}_2\text{O}$

glasses ($0 \leq x \leq 15$) are studied. The influence of Li_2O on the EPR and optical absorption parameters will be discussed. The variation of these parameters will be correlated with optical basicity of the glasses.

2. Experimental

In the present study copper-(1 mole %) doped glass samples of compositions $(60-x)\text{Bi}_2\text{O}_3$ - 25ZnO - $15\text{B}_2\text{O}_3$ - $x\text{Li}_2\text{O}$ ($0 \leq x \leq 15$) were prepared by melt quench technique using reagent grade chemicals Bi_2O_3 , ZnO , H_3BO_3 , Li_2CO_3 , and CuO . The mixture of these chemicals is taken in porcelain crucibles and was calcinated at 450°C for 1 h and then melted at 1100 – 1200°C depending on the glass composition. The liquids were agitated for 1 h to ensure homogeneity in the mixture. The clear liquid was quickly cast in a stainless steel mould kept at 200°C and pressed with another steel disc to obtain glass. All samples were transparent and greenish in colour. The glasses were chemically stable and nonhygroscopic. Thus, the obtained glasses were annealed at 200°C for 12 h to remove thermal stress and strain.

The room temperature EPR spectra of powdered glass samples were recorded using a JEOL-1X-EPR spectrometer

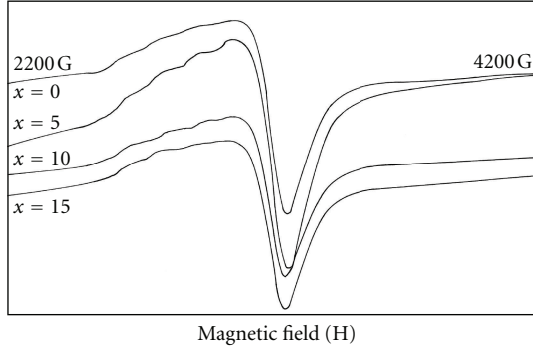


FIGURE 1: EPR spectra of Cu^{2+} in $(60-x)\text{Bi}_2\text{O}_3\text{-}25\text{ZnO-}15\text{B}_2\text{O}_3\text{-}x\text{Li}_2\text{O}$ glasses.

in the range 2200 G–4200 G operating in the X-band and employing a field modulation of 100 kHz. DPPH was used as the standard g marker for the determination of magnetic field.

The optical absorption spectra of the present glass samples were recorded at room temperature using a double-beam Shimadzu spectrometer (model UV-3100) in the wavelength range 500–800 nm. The uncertainty in the observed wave length is about ± 1 nm.

3. Results and Discussion

3.1. EPR Spectra. The room temperature EPR spectra of the present glasses containing Cu^{2+} are shown in Figure 1. Each spectrum was analysed using the spin Hamiltonian:

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

where the symbols have their usual meaning [14]. From the figure it is observed that the obtained absorption spectra are asymmetric, characteristic 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 unresolved. Three hyperfine lines were observed on the parallel features of the spectrum. The variations in the hyperfine line widths can be attributed to the fluctuations in the coordination sphere surrounding the probe Cu^{2+} ion [15]. The values of spin Hamiltonian parameters g_{\parallel} , g_{\perp} , A_{\parallel} , and A_{\perp} were estimated from the spectra and are given in Table 1. The estimated values of g_{\parallel} and g_{\perp} satisfy the relationship $g_{\parallel} > g_{\perp} > g_e (=2.0023)$ characteristic of Cu^{2+} ions coordinated with six ligand atoms in a distorted octahedron, elongated along one of the axes and the ground state of the Cu^{2+} is $d_{x^2-y^2}$ orbital. This configuration satisfies the conditions for

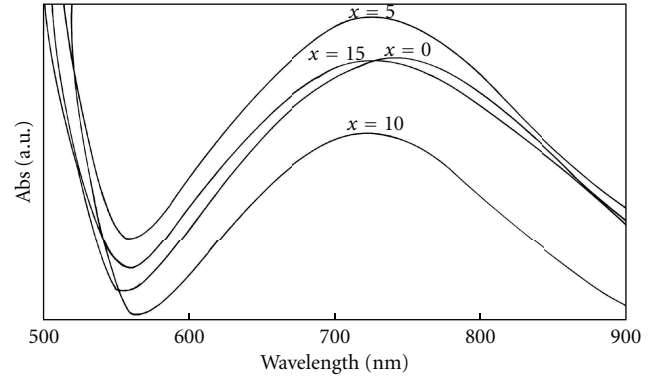


FIGURE 2: Optical absorption spectra of $(60-x)\text{Bi}_2\text{O}_3\text{-}25\text{ZnO-}15\text{B}_2\text{O}_3\text{-}x\text{Li}_2\text{O}$ glasses.

applying the analysis developed by Maki and McGarvey [16] and modified by Kivelson and Neiman [17]. The change in spin Hamiltonian parameters with composition can be attributed to the variation of ligand field around the probe ion.

3.2. Optical Absorption Spectra. Figure 2 presents the optical absorption spectra of Cu^{2+} ions in the present glasses. A single absorption band in the near-infrared region was observed for all samples. This band in the near-infrared region can be identified as d-d transition band due to Cu^{2+} ions [18] and can be described in terms of ligand field theory [19]. In glasses it is assumed that due to vitreous state disorder, no site is perfectly cubic. Therefore, tetragonal distortions are endemic to the vitreous state, which leads to the splitting of energy levels. It is observed that the elongated structures are usually more energetically favoured than the compressed ones [20]. Hence, in the present investigation the observed asymmetric band is due to overlap of ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. Most of the authors [16, 17, 21, 22] assigned the observed optical peak to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition (ΔE_{xy}) and have used this value in the evaluation of the bond parameters.

3.3. Bond Parameters. To determine the bonding coefficients of Cu^{2+} , one needs to know the absorption frequencies from the optical absorption bands. In a given glass, ΔE_{xy} is the frequency of an intense absorption band of Cu^{2+} in the optical spectrum. By correlating EPR and optical absorption data, one can evaluate the bonding coefficients of Cu^{2+} . The bonding between the Cu^{2+} ion and its ligands can be described in terms of the covalency parameters α^2 , β^2 , and β_1^2 where α^2 describes the in-plane σ bonding with the copper $d_{x^2-y^2}$ orbital, β^2 describes the out-of-plane π bonding with the d_{xz} and d_{yz} orbitals, and the β_1^2 parameter is a measure of the in-plane π bonding with the d_{xy} orbital. The values of α^2 lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding, respectively. The terms β^2 and β_1^2 can be interpreted similarly.

TABLE 1: EPR and optical parameters of the glass system (60- x)Bi₂O₃-25ZnO-15B₂O₃- x Li₂O.

Parameters	$x = 15$	$x = 10$	$x = 5$	$x = 0$
$g_{ }$	2.337	2.332	2.333	2.312
g_{\perp}	2.127	2.127	2.079	2.056
$A_{ } \times 10^{-4}$ (cm ⁻¹)	160	114	108	99
$A_{\perp} \times 10^{-4}$ (cm ⁻¹)	49	60	48	55
λ (nm)	717	712	719	727
ΔE_{xy} (cm ⁻¹)	13947	14044	13908	13755
α^2	0.875	0.743	0.707	0.651
β_1^2	0.803	0.939	0.980	0.986
β^2	0.656	0.797	0.837	0.909
Γ_{σ} (%)	27	56	63	76
Γ_{π} (%)	39	12	3	2
Λ_{th}	0.954	0.963	0.973	0.982

The bonding parameters were evaluated using the equations given below [23]:

$$\begin{aligned}\alpha^2 &= \left| \frac{A_{||}}{P} \right| + (g_{||} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0.04, \\ \beta_1^2 &= \left[\left(\frac{g_{||}}{g_e} \right) - 1 \right] \frac{\Delta E_{xy}}{3312\alpha^2}, \\ \beta^2 &= \left[\left(\frac{g_{\perp}}{g_e} \right) - 1 \right] \frac{\Delta E_{xz,yz}}{828\alpha^2},\end{aligned}\quad (2)$$

where P is the dipolar hyperfine coupling parameter, ΔE_{xy} is the energy corresponding to the transition $^2B_{1g} \rightarrow ^2B_{2g}$, and λ is the spin-orbit coupling constant ($\lambda = -828$ cm⁻¹).

The corresponding value of $\Delta E_{xz,yz}$ was calculated using the approximation [24]

$$\Delta E_{xz,yz} = \frac{1656k^2}{(g_{\perp} - g_e)}, \quad (3)$$

where k^2 is the orbital reduction factor ($=0.77$).

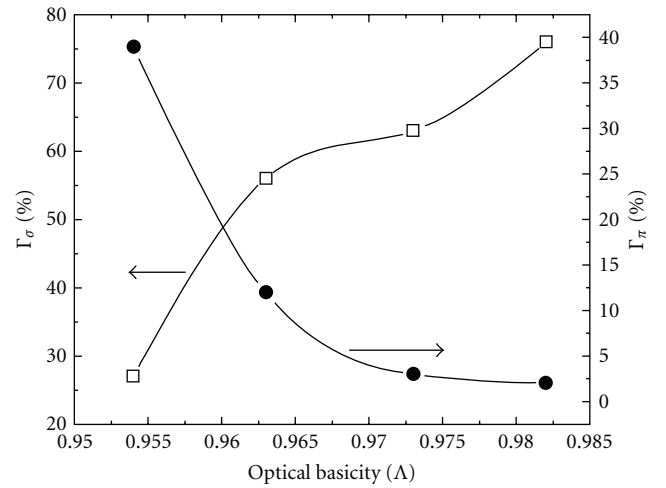
The normalized covalencies of Cu (II)-O in-plane bonds of σ and π symmetry are expressed in terms of bonding coefficients α^2 and β_1^2 as follows [16]:

$$\Gamma_{\sigma} = \frac{200(1-S)(1-\alpha^2)}{(1-2S)}\%, \quad \Gamma_{\pi} = 200(1-\beta_1^2)\%, \quad (4)$$

where S is the overlap integral ($S_{oxy} = 0.076$).

The calculated values of α^2 , β_1^2 , β^2 , Γ_{σ} , and Γ_{π} are presented in Table 1. The normalized covalency of Cu(II)-O in-plane bonding of π symmetry (Γ_{π}) indicates the basicity of the oxide ion. The values of α^2 , β_1^2 , and β^2 indicate a covalent nature for the in-plane σ bonding and pure ionic nature for the in-plane and out-of-plane π bonding.

3.4. Optical Basicity. The optical basicity (Λ) of an oxide medium as proposed by Duffy and Ingram [25] is a numerical expression of the average electron donor power of the oxide species constituting the medium. It is used as a measure of the acid-base properties of oxides, glasses, alloys, molten salts, and so forth. Theoretical optical basicity (Λ_{th}), for the

FIGURE 3: Variation of Γ_{σ} and Γ_{π} with optical basicity (Λ).

present glasses, can be calculated using the following equation, which is based on the approach proposed by Duffy [26]:

$$\Lambda_{th} = X_{Li_2O}\Lambda_{Li_2O} + X_{ZnO}\Lambda_{ZnO} + X_{Bi_2O_3}\Lambda_{Bi_2O_3} + X_{B_2O_3}\Lambda_{B_2O_3}, \quad (5)$$

where X_{Li_2O} , X_{ZnO} , $X_{Bi_2O_3}$, and $X_{B_2O_3}$ are the contents of individual oxides in mole %. Λ_{Li_2O} , Λ_{ZnO} , $\Lambda_{Bi_2O_3}$, and $\Lambda_{B_2O_3}$ are the theoretical optical basicity values assigned to oxides present in the glass. The values $\Lambda_{Li_2O} = 1$, $\Lambda_{ZnO} = 8.2$, $\Lambda_{Bi_2O_3} = 1.19$, and $\Lambda_{B_2O_3} = 0.42$ are used in the present study [26, 27]. The Λ_{th} values calculated using the above equation for the present glasses are given in Table 1. It can be seen from Table 1 that the theoretical optical basicity increases slightly with increasing Bi₂O₃ content, which can be attributed to the high polarizability of bismuth ions. Similar observations were reported earlier [6, 28]. The variation of Γ_{σ} and Γ_{π} with optical basicity is represented in Figure 3. It is observed that there is an overall increase in Γ_{σ} whereas Γ_{π} decreases with the increase in optical basicity. The optical basicity can also be used to classify the covalent/ionic ratios of the glasses since an increase in the optical basicity indicates decreasing

covalency. Therefore, in the present investigation, with the increase in Bi_2O_3 content, optical basicity increases and hence the covalency between Cu^{2+} ions and oxygen ligands decreases, which is clear from Γ_π values. Similar observation was reported by [11, 29].

4. Conclusions

From the values $g_{||} > g_{\perp} > g_e$ (2.0023), it is concluded that the ground state of Cu^{2+} ions in all the samples under study in the present paper is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state) and the site symmetry around Cu^{2+} ion is tetragonally distorted octahedral sites.

From the nature and position of the absorption band observed, it can be inferred that the band corresponds to $^2B_{1g} \rightarrow ^2B_{2g}$ transition.

The values of the bonding parameters indicate that the in-plane sigma bonding is covalent whereas the in-plane and out-of-plane π bonding is ionic in nature. The change in the spin Hamiltonian parameters with Li_2O content is attributed to the change in local structure.

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.

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