

Electron Paramagnetic Resonance and Optical Absorption Studies of $\text{PbF}_2\text{-SrO-B}_2\text{O}_3\text{-LiF}$ Glasses Containing Cu^{+2} Ions

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ABSTRACT

Electron paramagnetic resonance (EPR) and Optical absorption studies of $x\text{PbF}_2\text{-(30-x) LiF-15SrO-54B}_2\text{O}_3\text{-1CuO}$ glasses have been done by introducing a transition metal ion Cu^{+2} ion as a spin probe with fixed mole% in the given glass composition. Glasses containing transition metal (TM) ion give the information of site symmetry around the Cu^{+2} ion of the host glass. The EPR spectra of Cu^{+2} in all glass samples recorded in the X-band frequency have similar features. The spin-Hamiltonian parameters have been calculated, the observed values are $g_{\parallel} > g_{\perp} > g_e$ and $A_{\parallel} > A_{\perp}$. It suggests the site symmetry around Cu^{+2} ion is tetragonal distorted octahedral and the ground state of Cu^{+2} is $d_{x^2-y^2} ({}^2B_{1g})$ orbital. The Cu^{+2} ion is coordinated with six ligand atoms in a distorted octahedron site symmetry. Calculated bonding parameters suggest the covalent nature of in-plane σ -bonding (α^2) and pure ionic nature for out of a plane (β^2) and in-plane π -bonding (β_1^2). This data is correlated with the theoretical optical basicity (Λ_{Th}) values and it is observed that Γ_{σ} value increases whereas Γ_{π} values decrease with increasing Λ_{Th} .

Keywords : Lead glasses, XRD, EPR, Optical absorption, Cu^{+2} ion.

I. INTRODUCTION

Glasses are highly disordered material they can be prepared easily compared to ordered crystal structures. Borate glasses have higher thermal stability, good transparency, high rare earth solubility, higher Raman gain coefficient and better non-linear optical properties [1,2]. Borate glasses having a wide range of glass forming ability accepts a variety of glass formers such as B_2O_3 and GeO_2 , network modifiers such as Bi_2O_3 , ZnO , WO_3 , Er_2O_3 , etc, to improve the network connectivity. The effects of halides in the base lead glasses have been studied to some extent [4]. The addition of B_2O_3 to PbO glasses shows remarkable changes in physical and optical properties. The

influence of Bi_2O_3 , B_2O_3 in GeO_2 and lead glasses have been observed in various glasses like $\text{B}_2\text{O}_3\text{-TeO}_2\text{-Li}_2\text{O-CoO}$, $\text{TeO}_2\text{-ZnO-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$, $\text{TeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$, $\text{TeO}_2\text{-MoO}_3\text{-Bi}_2\text{O}_3$, $\text{TeO}_2\text{-ZnO-Nb}_2\text{O}_5\text{-Gd}_2\text{O}_3$, $\text{GeO}_2\text{-PbO-Nb}_2\text{O}_5$, $\text{GeO}_2\text{-PbO-CaCO}_3$ and $\text{Li}_2\text{O-GeO}_2\text{-P}_2\text{O}_5$ [5-8].

In the present paper EPR and optical absorption properties of 1mole% copper doped $x\text{PbF}_2\text{-(30-x) LiF-15SrO-54B}_2\text{O}_3$ glasses ($x=5,10,15,20$ and 25) are of interest. The influence of PbO on the EPR and optical absorption studies has been discussed. The variation in these parameters is correlated with optical basicity.

II. Experimental

Glass samples with composition $x\text{PbF}_2\text{-(30-x) LiF-15SrO-54B}_2\text{O}_3\text{-1CuO}$ ($x=5,10,15,20$ and 25) has been

prepared by melt quenching method using appropriate amounts of reagent grade LiF, As₂O₃, CuO, H₃BO₃, and PbF were well mixed and melted in porcelain crucibles in the temperature range of 750–800 °C, depending on the glass composition, in an electrical muffle furnace for about 60 minutes. The porcelain crucibles containing glass melt was stirred frequently to ensure the homogeneity. The clear liquid (free of bubbles) was quickly cast in a stainless steel mold kept at 200 °C and pressed with another steel disc maintained at the same temperature. Later, the samples were annealed 200 °C below their respective glass transition temperature for about 24 hours and slowly cooled to laboratory temperature.

The room temperature EPR spectra of present glass samples were recorded using a BRUKER, EPR spectrometer in the range 2200G – 4200G 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 the magnetic field. The optical absorption spectra were recorded at room temperature using a Shimadzu spectrometer (model JASCO V670) in the wavelength region 200 – 1000nm.

Results and Discussions

Lead fluoro borate glasses containing Cu²⁺ ions with the formula xPbF₂-(30-x) LiF-15SrO-54B₂O₃ were characterized using Electron Paramagnetic Resonance studies. No EPR signal was detected in the glass samples without Cu²⁺ ions. An EPR signal is observed for all the prepared glass samples containing Cu²⁺ which is shown in Figure 1. The Cu²⁺ ion has effective spin S=1/2 and nuclear spin I=3/2 for both ⁶³Cu and ⁶⁵Cu. Hence, (2I+1) i.e. four parallel and four perpendicular hyperfine (hf) components were expected. In the present work, three weak hyperfine parallel components were observed in the lower field region and fourth parallel component was overlapped with the perpendicular component. The perpendicular components were not resolved and a single intense line was observed. The high field side

of the spectra is more intense than the low field side. In most of the cases, the isotopic splits are not resolved owing to the nearly identical nuclear moments, and large line widths resulting from the random orientation of magnetic complexes in the glasses.

The EPR spectra can be analyzed by the spin-Hamiltonian [9] given by the following equations

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

where Z is the axis of symmetry, β is the Bohr magneton, S and I are the electron and nuclear spin operators, H_x, H_y, H_z are the static magnetic field components, g_∥, g_⊥ are parallel and perpendicular components of g tensor A_∥, A_⊥ are parallel and perpendicular components of the hyperfine tensor A. The nuclear quadrupole contribution is neglected.

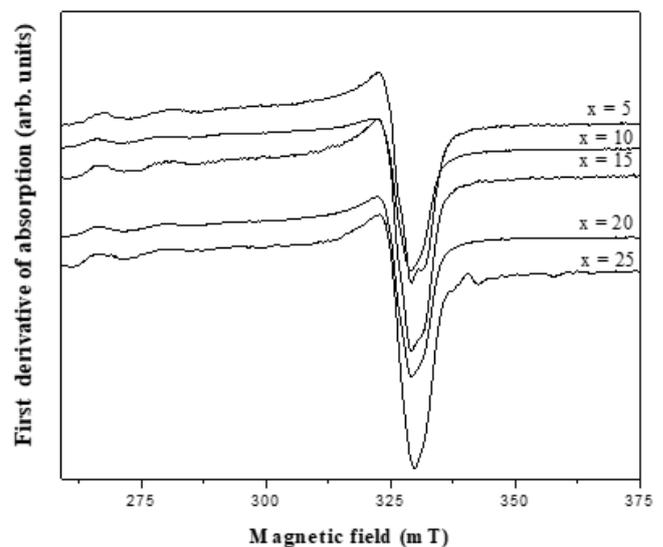


Figure 1: EPR spectra of Cu²⁺ in the present glass system.

The spin-Hamiltonian parameters of Cu²⁺ ion xPbF₂-(30-x) LiF-15SrO-54B₂O₃ glasses were determined and are presented in Table 1. g_∥ values of PFPBC system are in the range 2.343 to 2.363 are far away from free spin (g_e=2.0023) value. This indicates that Cu²⁺ ion is

subjected to large tetragonal distortion. g_{\perp} values are in the range 2.060 to 2.069 which are observed for most of the glasses. The observed 'g' and 'A' values and shape of the EPR spectra suggest that the Cu in all the glasses exist as Cu^{2+} ion with $3d^9$ configurations. In the present work it was noticed that $g_{\parallel} > g_{\perp} > g_e$ ($g_e = 2.0023$) and $A_{\parallel} > A_{\perp}$. From these results it can be concluded that the ground state of Cu^{2+} ion is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state), the Cu^{2+} ions being located in tetragonally distorted octahedral sites. To have an idea of tetragonal distortion around Cu^{2+} ion a plot is drawn between g_{\parallel} and A_{\parallel} for varying concentration of PbF_2 . From this Figure it was observed that the variation of g_{\parallel} and A_{\parallel} with PbF_2 content was found to be nonlinear which suggest that there is a change in the tetragonal distortion of Cu^{2+} ion.

Bonding Parameters

For all the glass samples, a single asymmetric broadband near IR region (~750nm) was observed which is shown in **Figure 2**. This band can be identified as d-d transition band due to Cu^{2+} ion. In the present investigation the observed optical absorption band can be assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transition (ΔE_{xy}). The EPR and Optical data were used for the calculation of the covalency parameters (α^2, β^2 and β_1^2), which describe the bonding between the Cu^{2+} ion and its ligands. The bonding between ligand (oxygen) and copper $d_{x^2-y^2}$ orbital is determined by the in plane σ – bonding represented by α^2 . The bonding between the ligand and copper $d_{xz,yz}$ orbital is represented by β^2 , it describes the in-plane Π – bonding. β_1^2 is out of plane Π -bonding.

The bonding parameters were evaluated using the equations given below.

$$\alpha^2 = -\left(\frac{A_{\parallel}}{P}\right) + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0.04 \quad (2)$$

$$\beta^2 = \left[\frac{g_{\perp}}{g_e} - 1\right] \frac{\Delta E_{xz,yz}}{828\alpha^2} \quad (3)$$

$$\beta_1^2 = \left[\frac{g_{\parallel}}{g_e} - 1\right] \frac{\Delta E_{xy}}{3312\alpha^2} \quad (4)$$

where P is the dipolar hyperfine coupling parameter ($=0.036 \text{ cm}^{-1}$), ΔE_{xy} and $\Delta E_{xz,yz}$ are the heights of the d_{xy} and $d_{xz,yz}$ molecular orbital levels above the ground state, $d_{x^2-y^2}$ respectively. The position of the observed absorption maximum of Cu^{2+} indicates the ΔE_{xy} value. The corresponding value of $\Delta E_{xz,yz}$ was calculated using the approximation [9].

$$\Delta E_{xz,yz} = \frac{1656K^2}{g_{\perp} - 2.0023} \quad (5)$$

where K^2 is the orbital reduction factor ($=0.77$). An error of 20% in this optical transition assignment ($\Delta E_{xz,yz}$) may introduce a 5% error in the measurement of β^2 [10].The bonding coefficients' were evaluated using equations and are presented in Table 1. From the Table 1 it was observed that α^2 values are in the range 0.784 to 0.817 indicating moderate covalent nature for in plane σ -bonding. While β^2 values are lying between 0.941 to 0.982 showing that in plane π -bonding is ionic in nature. β_1^2 values indicate that the out of plane π -bonding is moderately ionic.

The number of spins (N) participating in the resonance and the magnetic susceptibility (χ) were calculated. The number of spins (N) per Kg participating in resonance was calculated using the area under the absorption curves of the EPR signal of the sample and reference ($CuSO_4.5H_2O$) by using the formula given by Weil et al [11].

$$N = \frac{A_x(scan_x)^2 G_{std}(B_m)_{std}(g_{std})^2 [S(S+1)]_{std}(P_{std})^{1/2}}{A_{std}(scan_{std})^2 G_x(B_m)_x(g_x)^2 [S(S+1)]_x(P_x)^{1/2}} [std] \quad (6)$$

where A is the area under the absorption curve which can be obtained by double integrating the first derivative absorption curve, scan is the magnetic field corresponding to unit

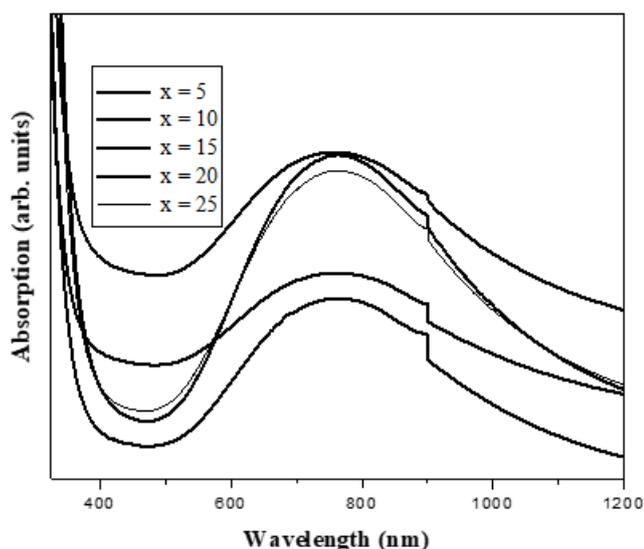


Figure 2 presents the optical absorption spectrum of Cu²⁺ ions in the present glasses.

length of the chart, G is the gain, B_m is the modulation width, g is the 'g' factor. S is the spin of

the system in its ground state, P is the power of the microwave used. The subscripts x and std represent the corresponding quantities for the glass samples and $[std]$ is the number of CuSO₄.5H₂O molecules in the reference taken. The EPR data was also used to calculate the paramagnetic susceptibility (χ) of the sample using the formula [12].

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3K_B T} \tag{7}$$

where N is the number of spins per Kg, J is the total angular momentum quantum number, β is the Bohr magneton, K_B is the Boltzman constant, T is the absolute temperature and 'g' [$g = (g_{||} + 2g_{\perp})/3$] is the Lande g factor. The values of N and (χ) are calculated and are given in Table 2.

Table 1. Spin-Hamiltonian parameters of Cu²⁺ions in xPbF₂-(30-x) LiF-15SrO-54B₂O₃-1CuO glasses

Parameter	x=5	x=10	x=15	x=20	x=25
$g_{ }$	2.375	2.358	2.377	2.374	2.355
g_{\perp}	2.052	2.077	2.087	2.067	2.084
$A_{ }$ (x 10 ⁻⁴ cm ⁻¹)	145	136	122	117	127
A_{\perp} (x 10 ⁻⁴ cm ⁻¹)	18	17	21	19	24
ΔE_{xy} (cm ⁻¹)	13396	13315	13289	13114	13022
$\Delta E_{xy, yz}$ (cm ⁻¹)	16118	16319	13154	15455	17277

Table 2. Optical parameters and bonding coefficients for Cu²⁺ions in the present glasses.

Parameter	x=5	x=10	x=15	x=20	x=25
λ_c	346	375	374	324	333
Indirect band gap (n =2)	2.691	2.518	2.543	2.531	2.439
ΔE	0.334	0.342	0.354	0.352	0.332
λ_{Max} (² E _g → ² T _{2g})	753	751	763	745	779
α^2	0.795	0.871	0.841	0.882	0.892
β_1^2	0.916	0.946	0.836	0.845	0.877
β^2	0.988	0.948	0.932	0.938	0.883
Γ_{σ} (%)	78	48	54	71	55
Γ_{Π} (%)	18	14	29	23	27
N	3.519	3.252	3.812	3.263	3.424
χ	5.719	5.999	6.742	7.212	5.685

The values of N are in the range $(3.252 \text{ to } 3.812) \times 10^{22}$ per Kg, while χ values lie in between $(5.685 \text{ to } 7.212) \times 10^{-3} \text{m}^3/\text{Kg}$. From the EPR spectra it is clear that the first derivative absorption intensity is found to be less for PFSBC3 and PFSBC5 which is reflected in the N values. The values of N depend on the glass composition, value and they vary in a non-linear manner with the composition PbF_2 .

III. CONCLUSION

The present glasses $x\text{PbF}_2-(30-x) \text{LiF}-15\text{SrO}-54\text{B}_2\text{O}_3-1\text{CuO}$ (5,10,15,20 and 25) were prepared, and their EPR and optical properties have been studied. The following conclusions were made: The values $g_{\parallel} > g_{\perp} > g_e (2.0023)$, it is accomplished that the ground state of Cu^{2+} ions in all the samples is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state) and all six ligands bonded around Cu^{2+} ion in the tetragonally distorted octahedral site (D_{4h}). The nature and position of the optical absorption band can be attributed to that, the band corresponds to $^2B_{1g} \rightarrow ^2B_{2g}$ transition. The bonding parameters indicate that the in-plane sigma bonding (α^2) is ionic whereas the in-plane and out-of-plane π bonding are moderately covalent in nature. The value of Γ_{σ} decreases whereas Γ_{π} increases with the decrease in optical basicity and hence the covalency between Cu^{2+} ions and oxygen ligands increases the same thing supported by bond parameter values.

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Cite this article as :

M. Srinivasa Reddy, "Electron Paramagnetic Resonance and Optical Absorption Studies of $\text{PbF}_2\text{-SrO-B}_2\text{O}_3\text{-LiF}$ Glasses Containing Cu^{2+} Ions", International Journal of Scientific Research in Science, Engineering and Technology (IJSRSET), Online ISSN : 2394-4099, Print ISSN : 2395-1990, Volume 6 Issue 2, pp. 710-714, March-April 2019.
 Journal URL : <http://ijsrset.com/IJSRSET207493>