

EPR, Infrared and Optical Absorption Studies of Cu^{2+} Ion Doped in $\text{LiF-Li}_2\text{O-SrO-Bi}_2\text{O}_3$ Glasses

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ABSTRACT

EPR, IR and optical absorption studies on $x\text{LiF-(50-x)Li}_2\text{O-20SrO-30Bi}_2\text{O}_3$ (where $x= 0, 5, 10, 15,$ and 20) glasses containing Cu^{2+} spin probe have been carried out. The IR results prove the distribution of trigonal pyramids (BiO_6) which determines the network and the distribution of borate triangles (BiO_3) and borate tetrahedral (BiO_6) groups. EPR 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 are considerable changes in g_{\parallel} , g_{\perp} and A_{\parallel} values with the increasing with increases of LiF content. The optical absorption spectra results show that the absorption peak of Cu^{2+} is a function of composition. Bonding parameters are calculated from both optical and EPR data. All these variations clearly indicate the structural changes in the present glass systems with varying LiF content.

Keywords: IR, EPR, Optical absorption spectra, Glasses, Cu^{2+} spin probe

I. INTRODUCTION

Heavy metal oxide (HMO) based glasses such as bismuth oxide glasses have attracted the scientific community due to their important applications in thermal and mechanical sensors, reflecting windows, glass ceramics, etc. [1–4]. Bi_2O_3 possesses high refractive index, and exhibits high optical basicity, large polarizability and large nonlinear optical susceptibility [5-7], which make it an ideal candidate for various applications such as infrared transmission components, ultra fast optical switches and photonic devices. Moreover, the HMO such as lead or bismuth oxide containing glasses shows extremely high radioactive resistance because of their high density and atomic number. Bismuth oxide alone cannot be considered as a network former due to small field strength ($z/a^2=0.53$, where z = formal valency and a =

internuclear distance) of Bi^{3+} ion [8]. However, in combination with other glass formers, the glass formation is possible in a relatively larger composition range [9].

We have undertaken the present work to investigate the influence of Cu^{2+} ion on the structure and optical properties of the present glasses. With the composition of the glass, the local environment of the transition metal (TM) ion incorporated into the glass network can be changed, leading to the local ligand field in homogeneities. Margaryan et al. [10] has discussed the spectroscopic properties of Cu^{2+} in bismuth and lead contained fluorophosphate glasses. In view of these characteristics, the valency of Cu^{2+} ions has strong effects on optical properties of the glasses. Thus, the study of such glasses with various spectroscopic techniques such as electron

paramagnetic resonance (EPR) and optical absorption etc. will give valuable information on these systems.

In the present paper EPR and optical absorption properties of 1mole% copper doped $x\text{LiF}-(50-x)\text{Li}_2\text{O}-20\text{SrO}-30\text{Bi}_2\text{O}_3$ glasses ($x=0,5,10,15$, and 20) are of interest. The influence of PbO on the EPR and optical absorption studies has been discussed.

II. Experimental

One series of glass with the molar formula $x\text{LiF}-(50-x)\text{Li}_2\text{O}-20\text{SrO}-30\text{Bi}_2\text{O}_3$ was prepared. Reagent grade LiF , Li_2O , SrO and Bi_2O_3 obtained from Sigma-Aldrich were used to form the samples. The latter was first heated in Al_2O_3 crucible at 300°C for 1 h for the purpose of excluding water and ammonia. Appropriate amounts of LiF and SrO were then added and the mixture was melted in an electric furnace at a temperature ranging between 900 and 1100°C depending on the glass composition. The melt was left for 30min under the atmospheric condition in the furnace. The melt was swirled periodically to insure homogeneity. Once melting was complete, the melt was poured and pressed between two stainless steel plates to form disks of 1–2 mm thickness. The glasses were labeled and stored in a desiccator until required.

The room temperature EPR spectra of present glass samples were recorded using a BRUKER, EPR spectrometer in the range $2200\text{G} - 4200\text{G}$ 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 the magnetic field.

III. Results and Discussions

Figure 1 shows that the X-ray diffraction spectra of present glasses. From figure it is clear that no sharp peaks were appeared which indicating that the samples are amorphous in nature. The x-ray diffraction pattern of the reference glasses with

system of $x\text{LiF}-(50-x)\text{Li}_2\text{O}-20\text{SrO}-30\text{Bi}_2\text{O}_3$ are given in the Figure 1. The peak free X-ray diffractograms indicated amorphous nature of the glass samples.

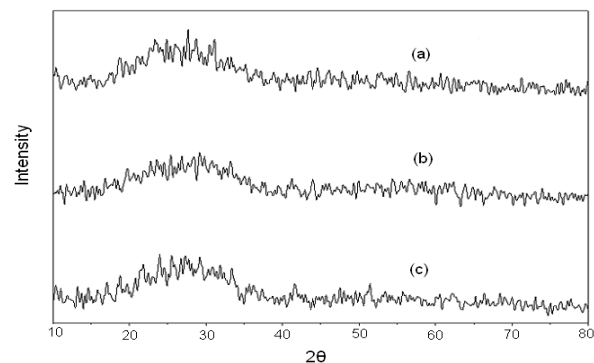


Figure 1. X-ray diffraction spectra

3.1 EPR spectra

No EPR signal was observed for the undoped (without Cu^{2+}) glasses indicating the absence of any transition metal ions. An EPR signal was observed for all the glasses containing Cu^{2+} ions. Figure represents the EPR spectra of $x\text{LiF}-(50-x)\text{Li}_2\text{O}-20\text{SrO}-30\text{Bi}_2\text{O}_3$ glasses. The high field side of the spectrum was found to be more intense than the low field side. The EPR spectra observed in the present study are similar to those reported earlier for Cu^{2+} ions in other glass systems.

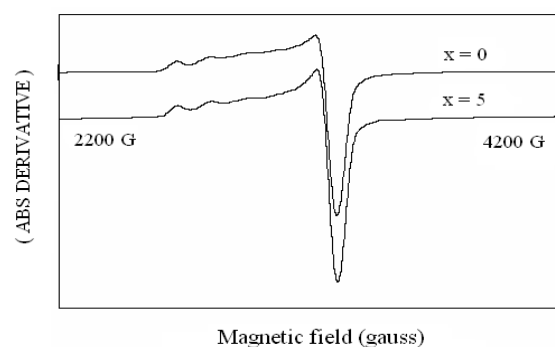


Fig. 2 EPR spectra of Cu^{2+} doped present glasses

The Cu^{2+} ion has a nuclear spin ($I=3/2$) for both ^{63}Cu (natural abundance 69 %) and ^{65}Cu (natural abundance 31 %) and therefore $(2I+1)$, i.e. four parallel and four perpendicular hyperfine lines could be observed. In most of the cases, however, the

isotopic splittings are not resolved owing to the nearly identical nuclear moments and the large line widths resulting from the random orientation of magnetic complexes in glasses. In all the EPR spectra recorded in the present investigation three weak parallel components were observed in the low field region. However, the perpendicular components are not resolved leading to the intense line in the high field region. It can be observed that the high field side of the spectrum is more intense than the low field side. Such spectral features are characteristic of Cu²⁺ ions present in axially distorted octahedral sites. The ESR spectra were analyzed using spin Hamiltonian:

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

Here *Z* is the symmetry axis, β the Bohr magneton, *S* and *I* are the electron and nuclear spin operators, *H_x*,

Table 1. Spin-Hamiltonian parameters of Cu²⁺ ions in the present glasses

Glass Composition	g_{\parallel} (±0.001)	g_{\perp} (±0.001)	$A_{\parallel}(\times 10^{-4})\text{cm}^{-1}$ (±2 x 10 ⁻⁴)	$A_{\perp}(\times 10^{-4})\text{cm}^{-1}$ (±2 x 10 ⁻⁴)
50Li ₂ O-20SrO-30Bi ₂ O ₃	2.332	2.127	113	28
5LiF-45Li ₂ O-20SrO-30Bi ₂ O ₃	2.314	2.025	126	31
10LiF-40Li ₂ O-20SrO-30Bi ₂ O ₃	2.306	2.047	129	27
15LiF - 35Li ₂ O -20SrO-30Bi ₂ O ₃	2.321	2.302	131	38
20LiF - 30Li ₂ O -20SrO-30Bi ₂ O ₃	2.331	2.025	125	35

IV. CONCLUSIONS

The present glasses xLiF-(50-x)Li₂O-20SrO-30Bi₂O₃ (0,5,10,15, and 20) 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 Cu²⁺ ions in all the samples is *d_{x²-y²}* orbital (²B_g state)

H_y and *H_z* are the static magnetic field components, g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the *g* tensor and A_{\parallel} and A_{\perp} are the parallel and perpendicular components of the hyperfine tensor *A*. The values of A_{\parallel} are calculated using the following equation due to Kivelson.

$$H_{\parallel}(-3/2) - H_{\parallel}(+3/2) = 3A$$

The spin-Hamiltonian parameters are presented in table 1. From the *g* values it is observed that $g_{\parallel} > g_{\perp} > 2.0023 (=g_e)$. Therefore it is concluded that Cu²⁺ has an octahedral environment along one of the cube axes, and the ground state of Cu²⁺ is *d_{x²-y²}*. The anisotropic hyperfine structure is due to John-Teller distortion [11]. The changes in the spin-Hamiltonian parameters with varying concentration of lithium ions are due to the change in electron cloud density at the Cu²⁺ ion as the Li₂O enters the glass network.

and all six ligands bonded around Cu²⁺ 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_g → 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.

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