Physical, Optical absorption and EPR studies on fluoro-bismuthate glasses

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ABSTRACT: Glasses of the xLiF-(50-x)Li2O-20SrO-30Bi2O3 system, with 0 \leq x \leq 20 mole % were studied by EPR and Optical measurements. The changes in both density and molar volume indicate structural modifications occur due to addition of LiF. The glass transition temperatures are observed to decrease with an increase in LiF content in the compositions. The local structure around Cu\textsuperscript{2+} ions has been examined by means of electron paramagnetic resonance and optical absorption measurements. It is observed that the spin-Hamiltonian parameters calculated from the EPR spectra are influenced by the glass composition. The Cu\textsuperscript{2+} ions are in well-defined axial sites but subjected to small distortion leading to the broadening of the spectra. The spin-Hamiltonian parameter values indicate that the ground state of Cu\textsuperscript{2+} is \textit{S}=1/2 and the site symmetry around Cu\textsuperscript{2+} ions is tetragonally distorted octahedral. The optical absorption spectra exhibited a broad band corresponding to the d-d transition bands of Cu\textsuperscript{2+} ion. By correlating EPR and optical absorption data, the bond parameters are evaluated.

1. INTRODUCTION

Bismuthate glasses have been the subject of renewed interest because of their manifold possible applications [1, 2]. These glasses were found to be an efficient \gamma-ray absorber [3] and also considered for use in scintillation detectors for high energy physics [4, 5]. Studies of EPR and optical properties of transition metal ions in glasses have made it possible not only to interpret the energy levels involved in the observed transitions, but also to comment on the chemical and structural environments about the metal ion center. The presence of transition metal ions (TMIs) in glasses is detected by optical absorption and electron paramagnetic resonance (EPR) studies by identifying the relevant absorption band.
positions due to TMIs. Copper can be present in glasses as the Cu$^{2+}$ ion (d$^9$), the Cu$^{+}$ ion (d$^{10}$), and under some circumstances as metallic Cu$_0$, the latter occurring in the so-called copper-ruby glass as a colloidal suspension [7]. The data obtained from EPR and optical absorption can be correlated to obtain information regarding the bond parameters which determine the metal-ligand bond nature in the glasses. There are reports from our laboratory regarding EPR and optical absorption studies of Cu$^{2+}$ containing heavy metal oxide glasses [8, 9].

2. EXPERIMENTAL

Pure and 1 mole % copper doped xLiF-(50-x) Li$_2$O-20SrO-30Bi$_2$O$_3$ glasses, (0 ≤ x ≤ 20) are prepared by conventional melt quench technique. Details of the preparation and characterization of the present glasses are given in ref. [10]. The glass transition temperature, T$_g$, was measured in all samples using a temperature modulated differential scanning calorimeter (TA Instruments, DSC 2910). All samples were heated at the standard rate of 10 oC min$^{-1}$ in aluminum pans. 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 400-800 nm. The uncertainty in the observed wave length is about ±1 nm. The room temperature EPR spectra of copper doped powdered glass samples were recorded using a JEOL-1X- EPR spectrometer 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.

![X-ray diffraction pattern for different glasses xLiF-(50-x)Li$_2$O-20SrO-30Bi$_2$O$_3$ system.](image)

Fig. 1. X-ray diffraction pattern for different glasses xLiF-(50-x)Li$_2$O-20SrO-30Bi$_2$O$_3$ system.
3. RESULTS & DISCUSSIONS

3.1 Physical properties

The amorphous nature of all the samples was confirmed by the absence of Bragg’s peak in X-ray diffraction pattern as shown in figure 1. The variation of measured densities ($\rho$) of the present glasses along with evaluated values of molar volume ($V_m$) as a function of LiF. It is clear that the density of these glasses increases where as molar volume decreases with increase in LiF content. Since the fluorine ion has nearly the same radius (0.136 nm) as that of oxygen ion (0.140 nm), one can expect that the probability of fluorine ions to substitute oxygen is much higher or it may occupy interstitial position.

3.2 Optical absorption

Optical absorption spectra of the pure glasses are presented in figure 2. A distinct cutoff ($\lambda_c$) was observed for each glass sample. It can be seen that $\lambda_c$ decreases with LiF content.

![Optical absorption spectra](image)

Fig. 2 Optical absorption spectra of a typical glass sample.

3.3. EPR and Optical absorption spectra

The EPR spectra of 1 mole% of Cu$^{2+}$ doped samples is shown in figure 3. The spectra closely resembles that of Cu$^{2+}$ in most oxide glasses, which can easily be recognized on the basis of four-line hyperfine splitting due to $^{63}$Cu, $^{65}$Cu (I=3/2), but the isotope splittings were not resolved owing to nearly identical nuclear moments. The hyperfine features were observed on the parallel of the spectrum where as the fourth line must have been overlapped.
on perpendicular features of the spectrum. The spectra were analysed using the spin-Hamiltonian

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

(1)

where the symbols have their usual meaning. The values of \( A_\parallel \) and \( A_\perp \) were calculated using [11] the following equations

\[ H_\parallel (-3/2) - H_\parallel (+3/2) = 3A_\parallel \]  

\[ H_\perp (-3/2) - H_\perp (+3/2) = 3A_\perp \]  

(2)

The spin-Hamiltonian parameters are presented in table 1. From the \( g \) values it is observed that \( g_\parallel > g_\perp > 2.0023 \) (=\( g_\text{e} \)). Therefore it is concluded that \( \text{Cu}^{2+} \) has an octahedral environment along one of the cube axis, and the ground state of \( \text{Cu}^{2+} \) is \( 2 \text{E}_g \text{.} \) 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 \( \text{Cu}^{2+} \) ion as the \( \text{Li}_2\text{O} \) enters the glass network. The optical absorption spectra of 1 mole % \( \text{Cu}^{2+} \) doped samples is shown in figure 4. These spectra show a single optical absorption bands which corresponds to \( \text{Cu}^{2+} \) and are influenced by host structure. The spectra associated with the \( \text{Cu}^{2+} \) ion are \( 3d-d \) transitions which can be described in terms of the ligand field theory [12]. In a regular octahedral field, the \( 3d^9 \) configuration would result in a degenerate ground state \( (2\text{E}_g) \). In glasses it is assumed that due to disordered vitreous state no site is perfectly cubic. Therefore, tetragonal distortions are endemic to the vitreous state which leads to splitting of energy levels. It is observed that the elongated structures are usually more energetically favoured than the compressed ones [13]. But only a
single optical absorption maximum was observed in most of the cases [14, 15]. This single optical band was interpreted as the overlap of all the three transitions. Hence in the present investigation the observed asymmetric band around 13,907 cm$^{-1}$ is due to the overlap of $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transitions. Most of the authors [16, 17] assigned the observed optical peak to the $^2B_{1g} \rightarrow ^2B_{2g}$ transition ($\Delta E_{xy}$) and have used this value in the evaluation of the bond parameters.

![Optical absorption spectra of LiF-Li2O-SrO-Bi2O3 glasses.](image)

**Fig. 4** Optical absorption spectra of LiF-Li2O-SrO-Bi2O3 glasses.

4. Conclusions

The density of these glasses increases whereas molar volume decreases with increase in LiF. With the increase of LiF content the optical band gap energy decreases. From the observed values of $g || > g \perp > ge$ (2.0023) it is concluded that the ground state of Cu$^{2+}$ ions in all the samples under present study is orbital ($2B_{1g}$ state) and the site symmetry around Cu$^{2+}$ ion is tetragonally distorted octahedral sites. The values of $\alpha^2$ and $\beta^2$ indicate that the in-plane sigma bonding is covalent whereas as in-plane and out-of-plane $\pi$ bonding are ionic in nature.
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