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Optical absorption and EPR studies on $(70-x)Bi_2O_3$–xLi_2O–30(ZnO–B_2O_3) $(0 \leqslant x \leqslant 20)$ glasses

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ABSTRACT

Glasses with composition $(70-x)Bi_2O_3$–xLi_2O–30(ZnO–B_2O_3) where $(0 \leqslant x \leqslant 20)$ have been prepared using melt quench technique. DSC studies showed that the glass transition temperature increases with Bi_2O_3 content. Optical absorption spectra of the pure glasses reveled that the cut off wave length increased and optical band gap energy decreased with increase in Bi_2O_3 content. Electron paramagnetic resonance (EPR) and optical absorption studies of zinc-bismuth based glasses were made by introducing Cu^{2+} as a spin probe. It is observed that the spin-Hamiltonian parameters calculated from the EPR spectra are influenced by the glass composition. The Cu^{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^{2+} is $d_{x^2-y^2}$ and the site symmetry around Cu^{2+} ions is tetragonally distorted octahedral. The optical absorption spectra exhibited a broad band corresponding to the *d*–*d* transition bands of Cu^{2+} ion. By correlating EPR and optical absorption data, the bond parameters are evaluated and correlated with the optical basicity of the glasses obtained from various techniques.

1. Introduction

Glasses formed with heavy metal ions have received significant attention because of their interesting optical properties [1–3]. These glasses have a long infrared (IR) cutoff, which makes them ideal candidates for optical transmission [4]. Also, the presence of high third-order non-linear optical susceptibility (χ^3) makes them special candidates for ultra fast optical switches [5,6]. Bismuthate glasses containing alkali oxide act as ionic conductors and possess high conductivity compared to other heavy metal glasses [7,8]. Recently in our previous articles we presented the structural analysis and thermo-dynamical properties of bismuth containing glasses [9–12].

Optical absorption studies on amorphous materials yield important information regarding electronic and vibrational edges plus the contributions from impurities such as transition metal ions. Stevels [13] was the first to suggest that the intrinsic absorption edge of an oxide glass corresponded to the transition of valence electron of an oxygen ion in the glass network to an excited state. Although thermal vibrations are assumed to be responsible for the tail part of the optical absorption edge a number of glasses obeying Urbach rule for the absorption coefficient, whose physical origin is not well understood.

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. The use of copper for doping in the glasses as a colorant has a long history. These glasses exhibit a range of colors from blues to greens to browns depending on composition and melting conditions. 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 [14]. 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 [15,16].

The present study focuses on the optical absorption and EPR studies on $(70-x)Bi_2O_3$–xLi_2O–30(ZnO–B_2O_3) glasses. The influence of Li_2O on the EPR and optical absorption parameters is analyzed. The variation of these parameters is correlated with optical basicity, which is an important parameter of the oxide glasses.

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2. Experimental

Pure and 1 mol% copper doped $(70-x)Bi_2O_3$–xLi_2O–30(ZnO–B_2O_3) glasses, ($0 \leqslant x \leqslant 20$) are prepared by conventional melt quench technique in the temperature range 1100–1200 °C depending on the glass composition. The detailed method of preparation is presented elsewhere [9,10].

The density (ρ) of the glass samples was determined at room temperature by Archimedes method with xylene (ρ = 0.86 g/cc) as the immersion liquid.

The glass transition temperature, T_g, was measured in pure samples using a temperature modulated differential scanning calorimeter (TA Instruments, DSC 2910). All samples were heated at the standard rate of 10 °C min^{-1} in aluminum pans. The accuracy in determining T_g is around ± 1 °C.

The optical absorption spectra of the present glass samples (∼1 mm thickness) 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. The peak-pick option facilitates to determine exact peak position in the absorption spectrum.

The room temperature dielectric constant (ε) was determined at 10 MHz frequency using HP-4192 Impedance Analyzer.

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.

The electrical measurements were made on pure samples by the usual technique of two electrodes method. Silver paste was painted on the polished circular disk surface of the samples with thickness ∼1 mm and ∼10 mm diameter. With painted silver paste, good ohmic contacts were found. The electrical conductivity was measured as a function of temperature from 200 °C up to below glass transition temperature of the respective glass sample. The sample was loaded in a cylindrical furnace using a spring. The dc electrical conductivity measurements were made using a Keithley electrometer model 614. The temperature of the specimen was recorded with a chromel–alumel thermocouple kept in close thermal contact with the specimen surface.

3. Results and discussion

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 Fig. 1. Scanning electron micrograph in Fig. 2 also confirms the amorphous nature. All other samples had similar SEM graphs.

The density and molar volume of the present glasses are presented in Table 1. Both density and molar volume increases with Bi_2O_3 content, which may be due to the higher mass of bismuth when compared to others. Fig. 3 shows the variation of glass transition temperature (T_g) with the bismuth content. It is observed that T_g increases with the increase in the Bi_2O_3 content. This tendency is the same as those of Bi_2O_3–ZnO–10B_2O_3–Na_2O and Bi_2O_3–ZnO–10B_2O_3–K_2O glass systems [17]. It is considered that T_g is dependent on the strength of the chemical bonds in the glass

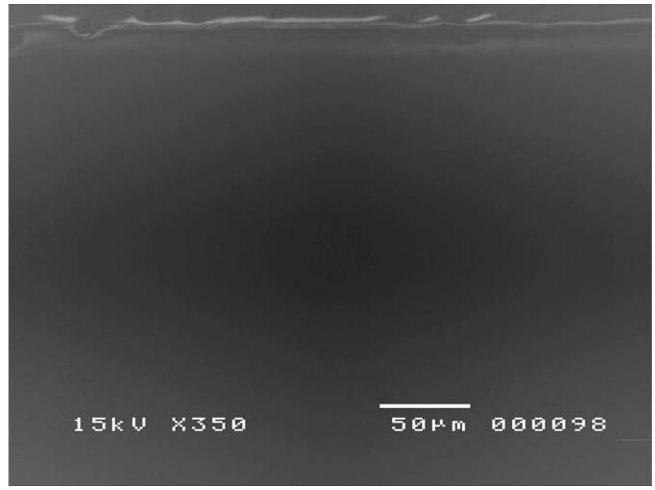

Fig. 2. Scanning electron micrograph of $60Bi_2O_3$–$10Li_2O$–30(ZnO–B_2O_3) glass.

Table 1
Optical parameters of the glass system $(70-x)Bi_2O_3$–xLi_2O–30(ZnO–B_2O_3).

Parameter	x = 20	x = 15	x = 10	x = 5	x = 0
Density (g/cc)	5.452	5.704	5.952	6.152	6.327
Molar volume (cc/mol)	47.98	49.68	51.51	53.15	55.13
λ_c (nm)	413	416	417	418	420
E_g^{opt} (eV)	2.67	2.54	2.45	2.28	2.16
$\alpha_{O^{2-}}\left(E_g^{opt}\right)$	3.89	4.66	5.48	6.27	9.09
$\Lambda\left(E_g^{opt}\right)$ (error ± 0.01)	1.24	1.31	1.29	1.40	1.48
$A\left(E_g^{opt}\right)$ (error ± 0.001)	0.077	0.070	0.062	0.057	0.049
ε	5.565	6.483	6.672	7.368	7.323
n	2.359	2.546	2.583	2.714	2.706
$\alpha_{O^{2-}}(n)$	2.206	2.452	2.558	2.740	2.818
$\Lambda(n)$	0.913	0.988	1.017	1.060	1.077
$A(n)$	0.080	0.070	0.061	0.052	0.036
$g_{\parallel}$	2.314	2.316	2.322	2.314	2.327
$g_{\perp}$	2.068	2.121	2.073	2.073	2.073
$A_{\parallel} \times 10^{-4}$ (cm^{-1})	100	90	99	82	74
$A_{\perp} \times 10^{-4}$ (cm^{-1})	39	63	52	54	49
λ (nm)	718	720	710	744	779
ΔE_{xy} (cm^{-1})	13927	13888	14084	13440	12836
α^2	0.66	0.65	0.66	0.61	0.60
β_1^2	0.99	0.99	1	1	1
β^2	0.84	0.83	0.84	0.91	0.91
Γ_σ (%)	73	74	72	84	85
Γ_π (%)	13	21	0	0	0

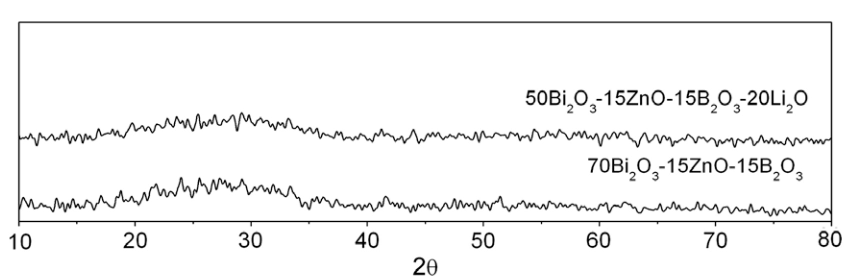

Fig. 1. X-ray diffractograms of the present glasses.