

EPR, Optical Absorption and FTIR Properties of Cobalt Doped Lithium Borophosphate Glass System

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ABSTRACT

Spectroscopic exploration of CoO doped lithium borophosphate glass system has been studied. A systematic investigation on characterization, XRD studies and spectroscopic properties (viz., optical absorption, infrared, and ESR) has been carried out. The X-ray diffraction confirms that the samples prepared were of amorphous nature. The optical absorption spectra of the present glass system exhibited three clearly resolved absorption bands at 530nm, 580nm and 625nm. The bands are attributed due to $^4T_{1g}(^4F) \rightarrow ^2T_{2g}(^2H)$, $^4T_{1g}(^4P) \rightarrow ^4A_{2g}(^4F)$, $^5T_{2g} \rightarrow ^5E_g$. FTIR spectra of CoO doped glasses has indicated stretching symmetry of various bands B – O, P – O, O-H, H-O-H, PO₃ etc. The g-value is found to be minimum at 0.3mol% of CoO. The LBPCo glass doped with 0.3mol% of CoO is found to be ideal candidate for photoluminescence and electrical applications.

Keywords: Borophosphate Glasses, Ti-ions, UV-Vis., FT-IR, EPR.

I. INTRODUCTION

During recent years, there has been an increasing interest in the synthesis and investigation of the structure of B₂O₃-P₂O₅ glasses doped with transition metal ions, due to their high luminescence efficiency, low refractive index and high IR transparency. These glasses find potential applications not only in optical and optoelectronic devices such as ultrafast switches, infrared windows, and optical isolators but also as glass-ceramic-electrolytes. Substitution of B₂O₃ for P₂O₅ results in the increase of room temperature ionic conductivity [1]. Candidature of these materials as solid state LASER devices were studied by many authors [2-5]. Spectral intensities of borophosphate glasses doped with rare earth ions (Sm³⁺ and Dy³⁺) were studied by Aruna et al. and found that the Sm³⁺ and Dy³⁺ glasses containing Li⁺ result in further extension in the UV and the IR wavelength regions[6]. Aim of the present study is to explore the optical properties and local environment of impurity in borophosphate glasses doped with Cobalt metal ions.

II. EXPERIMENTAL DETAILS

Lithium borophosphate glasses with nominal compositions $10Li_2O-(45-x)B_2O_3-(45-x)P_2O_5-xCoO$ (with x=0, 0.1, 0.2, 0.3 and 0.4) were prepared by conventional melt quenching technique in a PID temperature controlled furnace[7-9]. Good quality raw materials Li₂CO₃, NH₄H₂PO₄, H₃BO₃ and CoO with 99% purity were considered as per glass batch calculations for the present investigation. The density of the glasses is determined to an accuracy of (±0.0001 g) by the standard principle of Archimedes' using O-xylene (99.99 % pure) as the buoyant liquid with OHAUS balance (model AR 2140). The physical properties of the glasses were thus calculated from density value and tabulated. The amorphous nature of the glass samples were examined by X-ray diffraction technique by X'pert Pro_PANalytical with Cu K_α radiation. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 400-1600nm (UV region) up to a resolution of 0.2nm using CARY 100 (Varian) spectrophotometer. IR transmission spectra were recorded on a Bruker IFS 66V-IR spectrophotometer in the wave number range of 400-4000 cm⁻¹. The EPR spectra of the glass

samples were recorded using JES-FA200 (JEOL model with X-Band frequency: 8.75 - 9.65 GHz and Sensitivity: 7×10^9 spins/0.1mT) operating in the X-band frequency (≈ 9200 MHz) with a modulation frequency of 100 kHz and width of 0.35mT. The magnetic field was scanned from 50 to 550mT and the microwave power used was 0.998mW. The physical appearance of thus prepared samples was shown in Fig.[1]. For optical studies the glasses were grounded flat shaped to a dimension of about $1 \times 1 \times 0.3$ cm.

III. Results

From the measured values of density and average molecular weight, various physical parameters like Molar volume, Cobalt ion concentration, Inter-ionic distance, Polaron radius and Ionic field strength were evaluated using conventional formulae and tabulated in Table [1]. The X-ray diffraction pattern as shown in Fig [2] confirms that the samples prepared were of amorphous nature. Fig [3] represents the optical absorption spectra of titled glasses recorded at room temperature in the wavelength region of 400 to 1600 nm. The UV-visible spectra of the present glasses exhibit three kinks at about 530, 580 and 625nm except the undoped one in the wavelength region of 400 to 800nm. The half width and peak height of broad band are increase with increase in CoO concentration up to 0.2 mol%, but peak height is found to be maximum at 0.3mol% and decrease in the intensity of this band is observed at 0.4 mol%. The optical band gaps (E_o) of these glasses were obtained by drawing Urbach plot between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ as per equation

$$\alpha(\omega)\hbar\omega = c(\hbar\omega - E_o)^2$$

Fig [4] represents the Tauc's plots of all doped glasses. The values of optical band gap (E_o) were obtained from the extrapolation of the linear portion of these curves are presented in Table [2]. Urbach energy (ΔE) of these glass samples was obtained by taking reciprocal of the slopes of these curves. Fig [5] represents the variation of both Band gap and Urbech energu with mol% of Co concentration. The infrared transmission spectra of the entire glasses exhibited

common variation at high frequency region but show different trend of variation at low frequency or high wave number region as shown in Fig [6]. The details of band positions and their assignments were presented in Table [3]. The EPR spectra of the investigated glass samples were presented in Fig [7]. No EPR signal is obtained with undoped sample LBPCo0. All the doped samples give intense signals at around 160 mT and 410mT; respective g values were hence calculated from field values and presented in Table [4].however LBPCo1 sample show bit higher values than remaining doped samples. The g-value of LBPCo3 sample i.e at 0.3mol% of CoO is found to be lower than remaining samples.

IV. Discussion

A systematic investigation of spectroscopic and Physical properties of Lithium-Boron-Phosphate glasss system doped with CoO is carried out with present study. Boron is found in 3-fold and 4-fold coordination in oxide crystals. B_2O_3 is a well known network former with BO_3 and BO_4 structural units [10]. The connectivity of the glass structure can be increased by the addition of alkali oxide as network modifier. Li_2O convert boron from triangular to tetrahedral coordination and act as a good network modifier. The inter-ionic distance and polaron radius increases but Ionic field strength decreases as expected with increase in dopant concentration in the present study. Least molar volume is observed with LBPCo3 sample, which shows that the packing of the coordination polyhedral in this structural network of borophosphate glasses is better in LBPCo3 i.e with 44.85 mol% of B_2O_3 . Maximum optical energy gap and minimum Urbach energy observed with LBPCo3 sample indicate that there is a remarkable change in the structure of these glasses at 0.3 mol% of Co and respective proportion of other base ingredients with respect to UV-Vis spectra. The rigidity of glass network is supposed to be decreased from 0.3mol% onwards [11]. The intensity of central absorption band (at 580nm) increases and slightly shifts towards longer wavelength side with increase in concentration of Co^{+2} ions. However the dispersion of Co^{+2} and Co^{+3} in the glassy matrix is observed from optical properties [12]. The gradual

transformation of Cobalt ions is also observed from tetrahedral to octahedral positions upto 0.3mol% of CoO. This trend indicates that the LBPCo glass with 0.3mol% of Co is an ideal candidate for practical applications.

V. Acknowledgment

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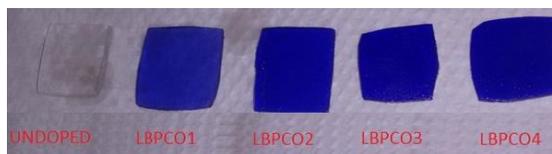


Figure [1] Physical appearance of 1.0 mm thick TiO₂ doped glass samples.

Table [1] : Physical parameters of the LBPCo glass system

Sample code	Mole % of ingredients				Density X10 ³ Kg m ⁻³	Molar volume cm ³ mole ⁻¹	Dopant ion concentration (N _i) x10 ²¹ ions cm ⁻³	Inter ionic distance R _i (Å)	Polaron radius R _p (Å)	Field strength (F) x10 ¹⁵ cm ⁻²
	Li ₂ O	B ₂ O ₃	P ₂ O ₅	CoO						
LBPCo0	10	45	45	0	2.6144	37.9047	-	-	-	-
LBPCo1	10	44.95	44.95	0.1	2.6088	37.9743	1.6076	8.5364	3.4396	1.6905
LBPCo2	10	44.9	44.9	0.2	2.6194	37.8088	3.2152	6.7753	2.7300	2.6835
LBPCo3	10	44.85	44.85	0.3	2.6304	37.6390	4.8227	5.9188	2.3849	3.5163
LBPCo4	10	44.8	44.8	0.4	2.6205	37.7694	6.4303	5.3776	2.1668	4.2598

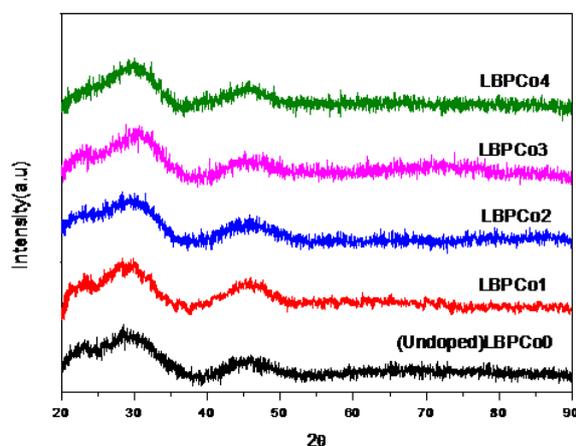


Figure [2]. X-ray Diffraction patterns LBP glass system doped with Co.

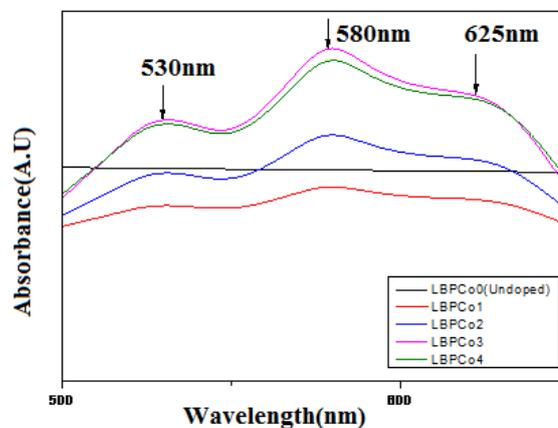


Figure [3]. UV-Visible spectra of the LBP Glass system doped with Co.

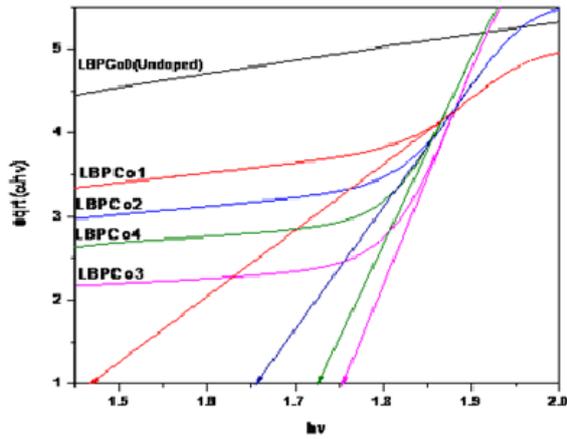


Figure [4]. Tauc's plot of LBP Glasses doped with Co

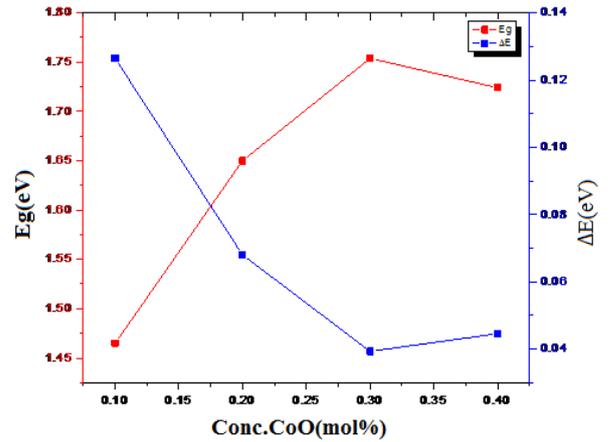


Figure [5]. Variation of Urbach energy (ΔE) and optical band gap (E_g) with CoO concentration.

Table [2]: Energy gap, band position and Urbach energy of LBPCo glasses

Sample code	Energy gap (E_g) eV.	${}^4T_{1g}({}^4F) \rightarrow {}^2T_{2g}({}^2H)$ band position (nm)	${}^4T_{1g}({}^4P) \rightarrow {}^4A_{2g}({}^4F)$ band position (nm)	${}^5T_{2g} - {}^5E_g$ band position (nm)	ΔE (eV)
LBPCo1	1.465	530	580	625	0.1265
LBPCo2	1.650	530	580	625	0.06799
LBPCo3	1.754	530	580	625	0.03931
LBPCo4	1.724	530	580	625	0.04457

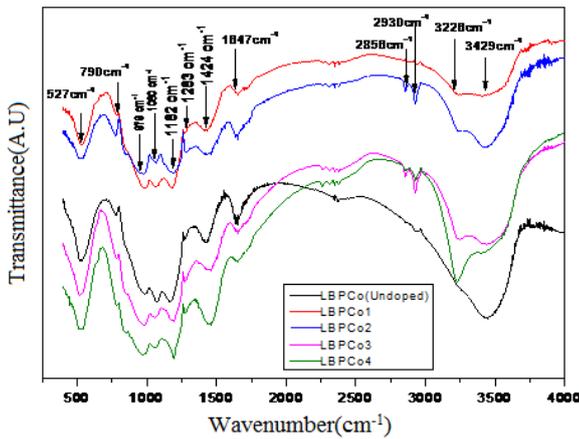


Figure [6]. FT-IR spectra of LBPCo glass system.

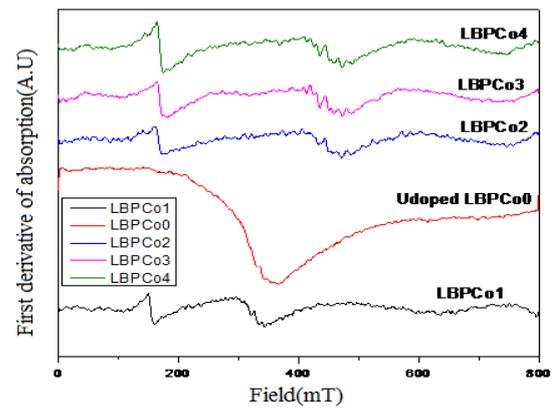


Figure [7] EPR absorption spectra due to Co^{2+} ions in LBPCo glass systems

Table [4]: g-values obtained from EPR spectra

Sample	g ₁	g ₂
LBPCo0	---	---
LBPCo1	4.2623	2.0540
LBPCo2	3.9371	1.5013
LBPCo3	3.8270	1.4741
LBPCo4	3.8628	1.4901

VI. REFERENCES

Table [3]: Position of vibrational bands of LBPCo glasses from FT-IR spectra

Band position (cm ⁻¹)	Assignment	References
527	P-O-P symmetric vibrations	[13]
777	Symmetric stretching of P-O-P groups	[14]
979	PO ₃ symmetric stretching vibrations	[14]
1060	B-O stretch in BO ₄ units from tri, tetra and penta borate groups	[15]
1182	B-O stretch in BO ₃ units from pyro and orthoborate groups	[13]
1283	Asymmetric stretching of O-P-O, $\nu_{as}(O-P-O)$, $\nu_{as}(P=O)$ stretching vibrations of BO ₃ groups	[16]
1424	Vibration modes of BO ₃	[17]
1647	B-O bonds vibration	[16]
3226	Molecular water, O-H groups	[18]
3429	Symmetric stretching of O-H groups, $\nu_s(H-O-H)$	[18]&[19]

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