

# Spectroscopic Exploration of TiO<sub>2</sub> Doped lithium Borophosphate Glass System

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**Abstract-** Spectroscopic exploration of TiO<sub>2</sub> 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 two clearly resolved absorption bands at 531nm and 581nm. The bands are attributed due to <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>B<sub>1g</sub> (531 nm) and <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>A<sub>1g</sub> (581 nm). FTIR spectra of TiO<sub>2</sub> doped glasses has indicated stretching symmetry of various bands B – O, P – O, OH, POH etc. A considerable suppression of the hyperfine structure is clearly evident from the observed ESR spectra of these samples with increase in Ti content. We conclude from this study that tetragonally distorted octahedral positions of Ti<sup>3+</sup> ions existed in the glass system. The glass sample with 1.0 mol% of TiO<sub>2</sub> is a good candidate for the practical applications.

**Keywords-** Borophosphate Glasses, Ti-ions, UV-Vis., FT-IR, ESR.

## I. INTRODUCTION

Borophosphate glasses doped with transition metal ions are of much interest due to their high ultra violet transmission. High transparency and low glass transition temperature of these kinds of glasses was successfully reported by Hashimoto *et al* [1]. Small quantity of TiO<sub>2</sub> can considerably increase GFA and chemical durability of borophosphate glass. The P<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> mixed glasses exhibit distinct properties from those of either pure borate or phosphate networks. The boro-phosphate glasses with Lithium content can find wide range of applications in solid state lasers, solar concentrators, and optical fibres. These glasses are also proved to be suitable for their application in micro batteries, smart card and medical appliance [2, 3]. The addition of small quantities of TiO<sub>2</sub> to boro phosphate glasses can provide ample scope of applicability of this final glass system. Ti ions can cause local field variations and structural modifications due to their valence and variation in coordination.

## II. EXPERIMENTAL DETAILS

The particular composition of glass system according to 10 Li<sub>2</sub>O-(45-x) B<sub>2</sub>O<sub>3</sub>-(45-x) P<sub>2</sub>O<sub>5</sub>:xTiO<sub>2</sub> with 0<x<1.0 mol% (x=0, 0.25, 0.5, 0.75 and 1.0) is chosen for the present study. The present glasses were prepared by using standard melt quenching technique in the normal air atmosphere conditions [4-6]. The raw materials used in this study are AR grade NaH<sub>2</sub>PO<sub>4</sub>(2H<sub>2</sub>O), Li<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub> (99 %pure), TiO<sub>2</sub>. 10 to 15 g of glass batches of the compounds were mechanically homogenized by thoroughly mixing in an agate mortar and melted in a sintered porcelain crucible, which is glazed inner and outer except outside bottom. The furnace used was a programmable temperature controlled furnace (~1600 °C). The glasses were melted at about 1050 to 1100 °C around 30 to 35 minutes till a bubble free liquid was formed. The resultant melt was cast onto a rectangular brass mould held at room temperature. The samples were subsequently annealed at 300 °C in another furnace. 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 1x1x0.2cm

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 amorphous nature of the glass samples were examined by X-ray diffraction technique by X'pert\_Pro\_PANalytical with Cu K<sub>α</sub> radiation with wavelength 1.540598 Å as standard. 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<sup>-1</sup>. 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 x 10<sup>9</sup> 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.

### III. RESULTS

Table[1] shows various physical parameters like Molar volume, Ti ion concentration, Inter-ionic distance, Polaron radius and Ionic field strength for the present glass system, which were calculated from the measured values of density and average molecular weight M using conventional formulae from literature [4, 5]. Fig [2] shows X-ray diffraction pattern of pure and 0.25, 0.5, 0.75, and 1.0 mol% of TiO<sub>2</sub> doped glass samples. The optical absorption spectra of Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>: TiO<sub>2</sub> glasses recorded at room temperature in the wavelength region of 400 to 1400 nm were represented in Fig. [3]. No absorption peaks were found in the spectrum of pure sample. The UV-visible spectra of the present glasses exhibit two kinks at about 531, 581 nm except the undoped one in the wavelength region of 400 to 1400nm. For the doped glasses, the respective peaks were attributed to transitions (<sup>2</sup>B<sub>2g</sub>→<sup>2</sup>B<sub>1g</sub>) and (<sup>2</sup>B<sub>2g</sub>→<sup>2</sup>E<sub>1g</sub>). The wavelengths at peak values, energy gap and Urbach energies were shown in Table [2]. FTIR transmission spectra of the present glass system were shown in Fig.[5]. The spectra exhibited various vibrational bands as illustrated in Table [3]. ESR spectra of Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> glasses doped with different concentrations of TiO<sub>2</sub> recorded at room temperature are presented in Fig. [6]. The ‘g’ values of various glasses were given in Table [4]. The Variation of Urbach energy (ΔE) and optical band gap (E<sub>o</sub>) with TiO<sub>2</sub> concentration is shown in Fig [7].

### IV. DISCUSSION

The X-ray diffraction confirms that the samples prepared were of amorphous nature. There is no indication of any crystalline planes in all the samples. The bands observed in the optical absorption spectra are assigned at 510nm and 600nm respectively from transitions of <sup>2</sup>B<sub>2g</sub>→<sup>2</sup>B<sub>1g</sub> and <sup>2</sup>B<sub>2g</sub>→<sup>2</sup>A<sub>1g</sub> of <sup>3</sup>D<sub>1</sub> electrons of Ti<sup>3+</sup> ions. In the present study the first band was shifted little bit higher wavelength (531nm) side but the second band was shifted towards a lower wavelength (581nm) side. The jumping of the charge carriers (Ti<sup>3+</sup>→Ti<sup>4+</sup>) during the network formation was observed with the present study, which is uniformly changed with TiO<sub>2</sub> content [12]. 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 [13]. From these spectra it is observed that undoped sample exhibit the very high intense IR band at about 3460 cm<sup>-1</sup>. This may be attributed to moist attack on the phosphate glasses. The present IR spectral investigations indicate the Ti<sup>4+</sup> ions exist both in tetrahedral and octahedral positions and they also form B–O–Ti linkages. The presence of part of titanium ions in Ti<sup>3+</sup> state which take modifier

positions if TiO<sub>2</sub> is gradually changed according to optical absorption and EPR spectral studies [14].

No EPR signal is detected in the spectra of un-doped sample. The spectra of LBPTi1 consist of good hyperfine structure centred at g ~ 2. However remaining samples did not exhibit such a distinguishable hyperfine structure. It is diminishing up to LBPTi3 sample. The spectrum of glass LBPTi4 consists of an intense symmetric spectral line centred at g = 2.1391. Signal (1) at higher ‘g’ side is very weak for this sample and also the hyperfine structure which is unable to detect [15]. The intensity of the signal with concentration of TiO<sub>2</sub> gradually changes and this variation is shown in the respective figures. A strong hyperfine interaction is observed at lower concentration of TiO<sub>2</sub> content i.e. at 0.25 mol%. This interaction gradually decreased with increase in TiO<sub>2</sub> content.

### V. CONCLUSIONS

Finally we are able to conclude from this study that the tetragonally distorted octahedral positions of Ti<sup>3+</sup> ions are existed in this glass system. The hyperfine interaction is strong at 1 mol% of TiO<sub>2</sub>. The Ti<sup>4+</sup> ions do exist both in tetrahedral and octahedral positions and they also form B–O–Ti linkages and the glass sample with 1.0 mol% of TiO<sub>2</sub> is a good candidate for the practical applications in non-linear optical devices.

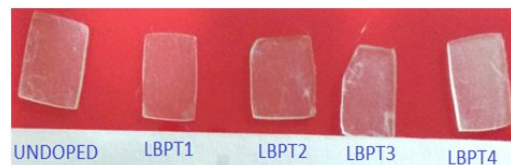


Figure 1. Physical appearance of 1.0 mm thick TiO<sub>2</sub> doped glass samples

Table 1. Physical parameters of the glass samples

Sample code	Density X10 <sup>3</sup> Kg/m <sup>3</sup>	Molar volume cm <sup>3</sup> /mol	Dopant ion concentration (N <sub>i</sub> ) x10 <sup>21</sup> ions/cm <sup>3</sup>	Inter ionic distance R <sub>i</sub> (Å)	Polaron radius R <sub>p</sub> (Å)	Field strength (F) x10 <sup>15</sup> cm <sup>-2</sup>
LBPTi0	2.6144	37.9047	0	-	-	-
LBPTi1	2.6172	37.8394	7.5414	5.0994	2.0547	9.4746
LBPTi2	2.6197	37.7786	15.0828	4.0474	1.6308	15.0404
LBPTi3	2.6166	37.7986	22.6242	3.5357	1.4246	19.7094
LBPTi4	2.6142	37.8085	30.1656	3.2124	1.2944	23.8739

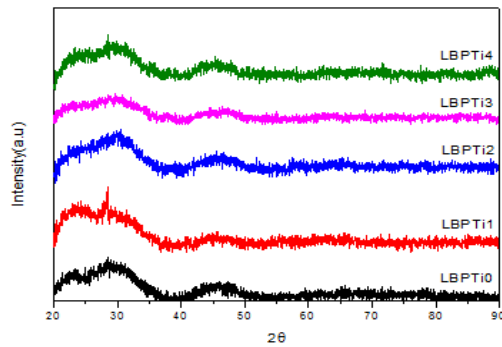


Figure 2. X-ray Diffraction patterns of the LBPTi glass

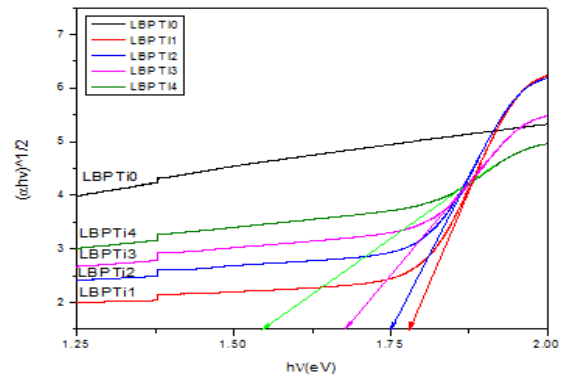


Figure 4. Tauc's plot of LBPTi Glasses

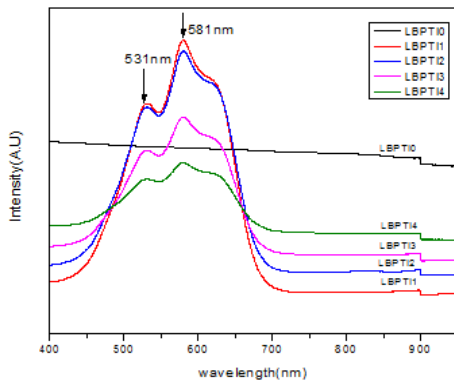


Figure 3. Optical absorption spectra of LBPTi glass system

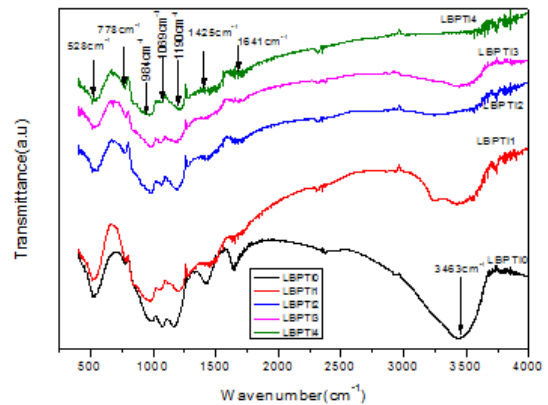


Figure 5. FT-IR spectra of LBP glasses with TiO2

Table 2. The energy gap, wavelengths at peak values and Urbach energy values.

Sample code	Energy gap (E <sub>g</sub> ) eV	Band positions ²B <sub>2g</sub> , ²B <sub>1g</sub> band position(nm)	Band positions ²B <sub>2g</sub> , ²A <sub>1g</sub> band position(nm)	ΔE (eV)
LBPTi1	1.7779	531	581	0.0341
LBPTi2	1.7481	531	581	0.0449
LBPTi3	1.6762	531	581	0.0714
LBPTi4	1.5433	531	581	0.1234

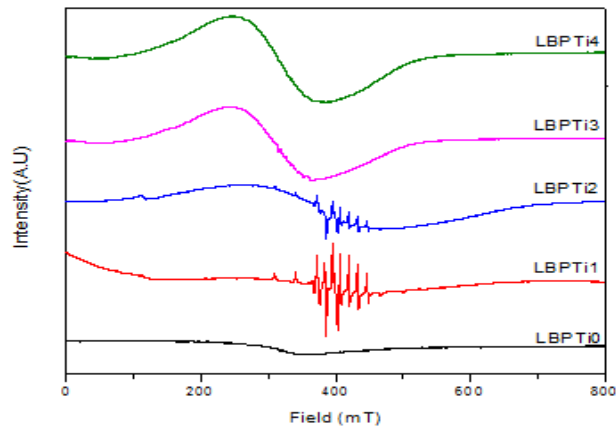
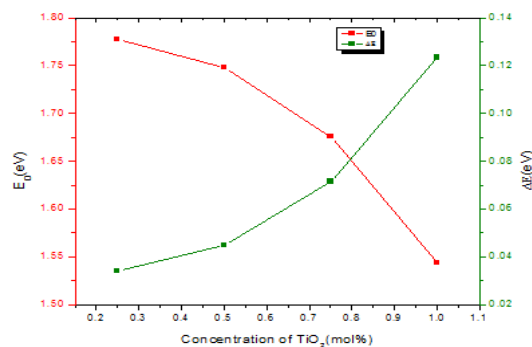
Table 3. Summary of data and assignments of various IR bands of the LBPTi

Glasses doped with TiO2. (With a probable error of ±0.1cm-1)

Ti0 cm <sup>-1</sup>	Ti1 cm <sup>-1</sup>	Ti2 cm <sup>-1</sup>	Ti3 cm <sup>-1</sup>	Ti4 cm <sup>-1</sup>	Assignment	References
528	528	518	518	518	P-O-P symmetric vibrations	[7]
-----	778	777	778	778	P-O-P symmetric stretching vibrations	[8]
984	984	987	987	976	PO <sub>3</sub> symmetric vibrations	[9]
1074	1064	1064	1064	1064	Stretching vibrations of B-O bonds in BO <sub>4</sub> units from tri, tetra and penta borate groups.	[9]
1165	1196	1196	1196	1196	B-O stretch in BO <sub>3</sub> units from pyro and ortho borate groups	[10]
1429	-----	-----	-----	-----	Vibration modes of BO <sub>3</sub>	[10]
1651	-----	-----	-----	-----	Vibration modes of BO <sub>3</sub>	[10]
-----	3240	-----	-----	-----	peak value is assigned to water OH, POH, vibrations originating Mostly for moisture attack on Phosphate glass.	[11]
3450	3428	-----	3491	-----	Symmetric stretching of O-H groups, ν <sub>s</sub> (H-O-H)	[11]

Table 4. Summary of g values from ESR spectra.

Glass Sample	g-Values	
	g1	g2
LBPTi0	---	---
LBPTi1	1.7873	5.9894
LBPTi2	1.8514	5.8428
LBPTi3	2.2095	4.2054
LBPTi4	2.1392	---

Figure 6. EPR absorption spectra due to Ti<sup>3+</sup> ions in LBPTi glass system.Figure 7. Variation of Urbach energy ( $\Delta E$ ) and optical band gap ( $E_g$ ) with TiO<sub>2</sub> concentration.

## VI. ACKNOWLEDGMENT

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