

# Effect of Doping $Ti^{3+}$ Ions on Spectroscopic Behavior of Lead Bismuth Phosphate Glasses

V. Ravi Kumar<sup>1</sup>, G. Naga Raju<sup>2</sup>, S.V.G.V.A.Prasad<sup>2</sup>, P.Raghava Rao<sup>4</sup>, N. Narasimha Rao<sup>5</sup>

<sup>1,2,4,5</sup>Department of Physics, Krishna University, PG Centre, Nuzvid 521 201

**Abstract:** A new Phosphate based glass composition was formulated and used as a host matrix for preparation of glass materials. Titanium oxide doped phosphate glasses were prepared at low melting temperature. The doping of  $TiO_2$  was varied from 0.1 mol % to 1.0 mol% during the glass formation. The effect of  $TiO_2$  content on the optical properties have been investigated. The presence of varying titanium oxide results in spectroscopic changes around  $Ti^{3+}$  ion and is explored to optical absorption, IR and EPR spectra. The EPR spectra exhibit resonance signals characteristic of  $Ti^{3+}$  ions in octahedral sites with tetragonal distribution. The results from IR showed the presence of trigonal and tetrahedral  $PO_4$ ,  $PO_3$  groups within the host network structure. With the introduction of  $TiO_2$  into the glass network, two bands are appeared due to  $TiO_4$  and  $Ti-O-Ti$  symmetric stretching vibrations of  $TiO_6$  structural units. In optical absorption spectra two absorption bands identified due to electronic transitions of  $Ti^{3+}$  ions as  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2E$ .

**Keywords:** Optical absorption,  $PbO-Bi_2O_3-P_2O_5$ , Spectroscopy, Quasi-tetrahedral  $[PO_4]^{2-}$ .

## 1. Introduction

Glass materials are possible alternatives for radiation shielding materials with two advantages brought by their transparency to visible light, and their properties can be modified by using composition and preparation techniques. Phosphorus pent oxide ( $P_2O_5$ ) acts as one of the most important glass former and flux materials. Phosphate glasses are finding ever-increasing applications in many emerging technologies e.g. vitrification of radioactive waste [1], photonics [2], fast ion conductors [3], glass-to-metal seals [4] and biomedical engineering etc. [5]. These glasses possess a series of interesting properties such as low glass transition temperature ( $T_g$ ), lower melting temperature (compared to silicate glass), high thermal expansion coefficient and biocompatibility [6]. In recent years, there has been lot of research on improving the physical properties and the chemical durability of alkali phosphate glasses by adding different metal oxides of high valence cations. Lead bismuth phosphate glasses are found to be suitable candidates for the potential applications in integrated micro batteries, solid electrolytes and low loss optical waveguides. The dopent titanium can, generally, exhibits two vacancies in glasses, namely pure trivalent  $Ti^{3+}$  ions and the colorless to pale yellow  $Ti^{4+}$  ions. Further, the addition of  $Ti^{3+}$  ions into the Lead bismuth phosphate network makes these glasses useful for optically operated devices, since the empty or unfilled d-shells of Ti ions contribute more strongly to the optical properties and posses high value of chemical durability and corrosion resistant. Though, a considerable number of recent studies are available on the phosphate glasses containing titanium ions most of them are focused on structural investigations by means of IR spectroscopic studies [7].

## 2. Materials and Methods

Analar  $PbO$ ,  $Bi_2O_3$ ,  $P_2O_5$  and  $TiO_2$  were used to prepare 7 glass samples with different composition using the conventional method. These reagents were weighed and mixed together with appropriate amounts where as the  $P_2O_5$

and  $PbO$  content ranges are about 60 mol% and 30 mol %. The range of  $Bi_2O_3$  content decreasing from 10 mol % to 9 mol % and the dopent content  $TiO_2$  ranging from 0.1 % 1.0 mol % respectively.

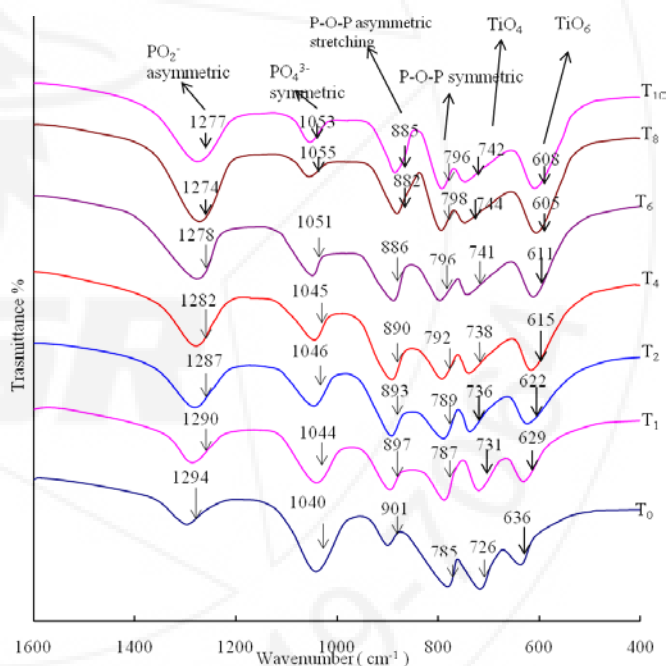


Fig. 2. IR spectra of  $PbO-Bi_2O_3-P_2O_5$  glasses doped with  $TiO_2$ .

## 3. Results

Fig. 1. represents the optical absorption spectra of  $PbO-Bi_2O_3-P_2O_5$  glasses doped with titanium oxide recorded at room temperature in the wavelength region 300-900 nm. The absorption edge observed at 323 nm for glass  $T_0$  is shifted towards slightly higher wavelength side with increase in the concentration of Titanium. The spectrum of glass  $T_4$  exhibited two clearly resolved absorption bands at about 536 and 679 nm due to  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2E$  transitions of  $Ti^{3+}$  ions respectively [8].

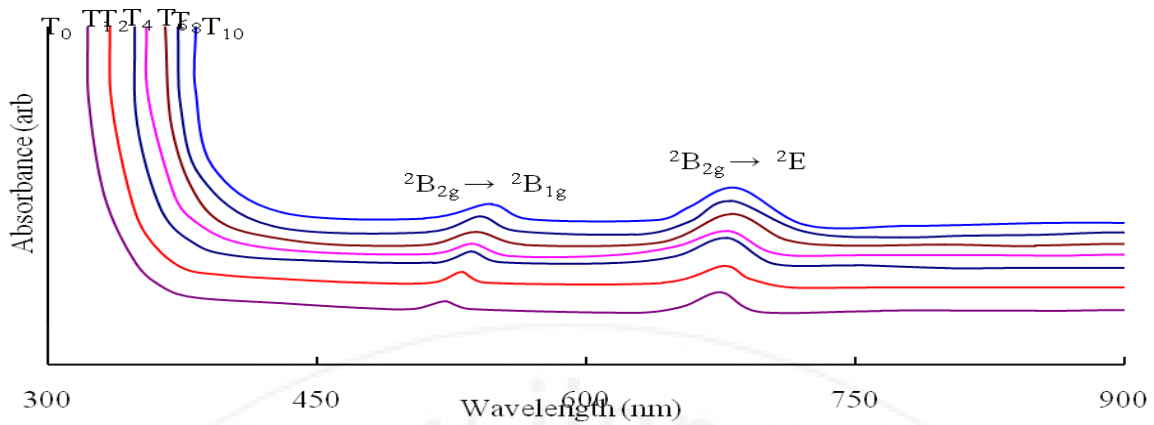


Fig. 1. Optical absorption spectra of PbO-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses doped with different concentrations of TiO<sub>2</sub>.

Fig. 2. represents the infrared transmission spectrum of PbO-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses exhibited conventional vibrational bands (anti-symmetrical vibrations of PO<sub>2</sub><sup>-</sup> groups, PO<sub>4</sub><sup>3-</sup> group, P-O-P asymmetric bending vibrations and P-O-P symmetric stretching vibrations [9]. Additionally, the spectra have exhibited two prominent bands one at 724 cm<sup>-1</sup> due to Ti-O-Ti symmetric stretching vibrations of TiO<sub>4</sub> units and another at 638 cm<sup>-1</sup> due to the vibrations of TiO<sub>6</sub> structural

units [10]. With the introduction of TiO<sub>2</sub>, the intensity of the bands due to PO<sub>4</sub><sup>3-</sup> groups, P-O-P symmetric stretching and TiO<sub>4</sub> units, is observed to decrease with a shift in the band positions towards slightly higher wavenumber; the intensity and the position of P-O-P asymmetric bending vibrational band and the bands due to P=O stretching vibrations and TiO<sub>6</sub> structural units exhibited an increasing trend in this concentration range.

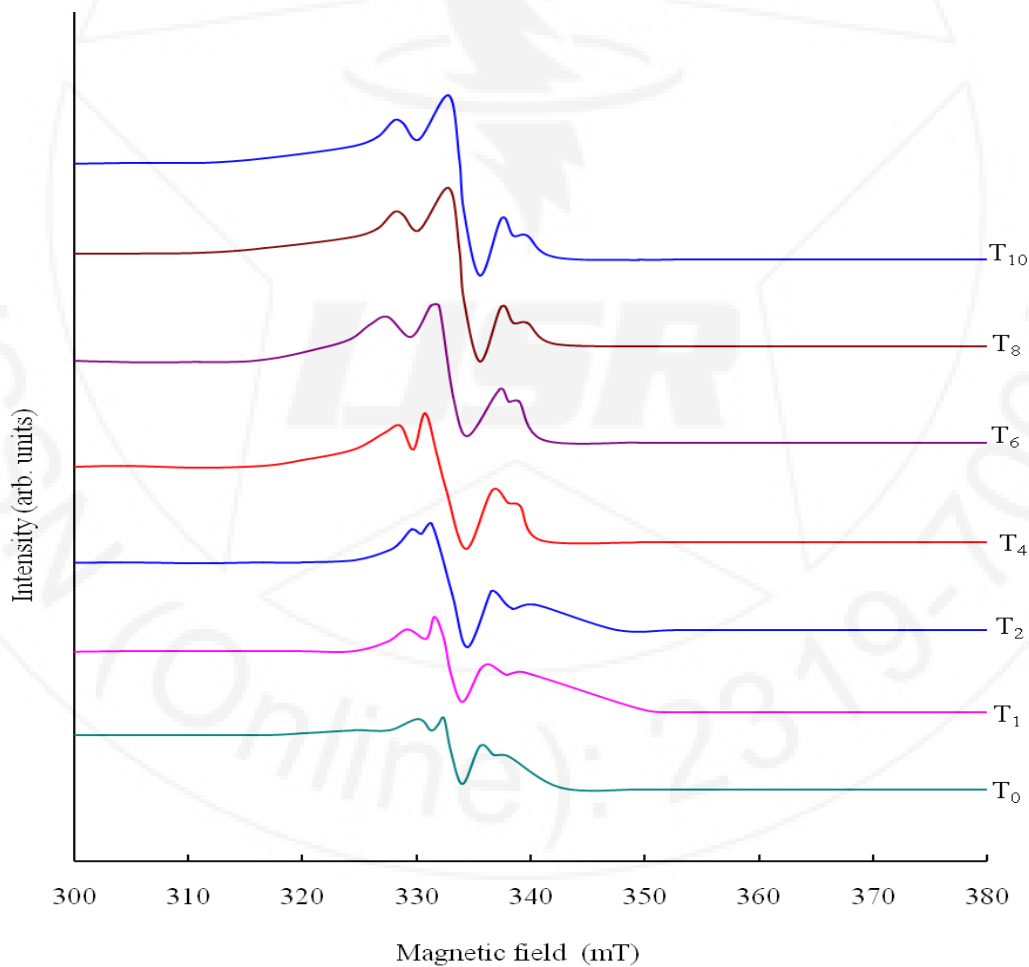


Fig. 3. ESR spectra of PbO-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub> glasses recorded at room temperature.

**Figure 3:** represents the ESR spectra of PbO-Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses doped with titanium oxide recorded at room temperature. The spectrum of each sample consists of a triplet pattern with an intense spectral line centered at about  $g = 1.933$  followed by two small satellites at  $g = 1.964$  and  $1.975$ . The signal of the sample T<sub>10</sub> is observed to be more intense with larger half width.

#### 4. Discussion

In the present glass system is composed of a well known conventional glass former  $P_2O_5$ , an intermediate glass former  $Bi_2O_3$ , modifiers  $PbO$  and dopant  $TiO_2$ . Pure vitreous  $P_2O_5$  forms glass by a continuous random network (polymeric structure) of quasi-tetrahedral  $[PO_{4/2}]^+$  units in which phosphorous is four coordinated and only three of the oxygen atoms of each unit bridge to neighboring units, while the fourth is doubly bonded to the central phosphorous atom.  $Bi_2O_3$  is an incipient glass network former and as such does not readily form glass, but does so in the presence of traditional glass former  $P_2O_5$  and modifier  $PbO$  with triangular  $[BiO_3]$  pyramids. Titanium ions are expected to exist mainly in  $Ti^{4+}$  state in  $PbO-Bi_2O_3-P_2O_5: TiO_2$  glass network. However, the reduction of  $Ti^{4+}$  to  $Ti^{3+}$  appears to be viable during melting, annealing and crystallization processes of the glasses [11]. The  $Ti^{4+}$  ions occupy both tetrahedral and substitutional octahedral sites as corner-sharing  $[TiO_6]^{2-}$  units where as  $Ti^{3+}$  ions occupy only modifying positions in the glass network.  $TiO_4$  and  $TiO_6$  units of  $Ti^{4+}$  ions enter the glass network, may alternate with  $PO_4$  structural units and form linkages of P-O-Ti type. As a consequence a disruption in the  $PO_4$  and  $TiO_4$  tetrahedra with the creation of a number of bonding defects are expected. Using Tanabe-Sugano diagrams for  $d^1$  ions, the bands observed in the optical absorption spectra in the regions 510-550 nm and 670-685 nm are assigned to  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2E$  transitions of  $3d^1$  electron of the  $Ti^{3+}$  ions, respectively. With the gradual increase in the concentration of dopant  $TiO_2$  upto 1.0 mol% in the sample, these bands have exhibited red shift with increasing intensity. So one can conclude that: i) an increase in the concentration of  $Ti^{3+}$  ions or decrease in the concentration of  $Ti^{4+}$  ions and ii) weaker ligand field of existing  $Ti^{3+}$  ions in these samples. In the ESR spectrum the central line at  $g = 1.94$  is due to tetragonally compressed octahedral sites of  $Ti^{3+}$  ions with  $|xy\rangle$  ground state [12] where as the auxiliary components are due to the hyperfine interaction of an unpaired electron with two equivalent  $I = 1/2$  nuclear spins. Based up on the earlier reports [13]. The relatively highest intensity and half-width of the signal observed for the spectrum of the sample  $T_{10}$  suggests a larger concentration of reduced  $Ti^{4+}$  ions in to  $Ti^{3+}$  ions in this sample. The IR spectra of these glasses appears to be dominated by orthophosphate structural units; however, the band due to pyrophosphate structural units lies around  $1100\text{ cm}^{-1}$ , which is not too far from the band position of  $PO_4^{3-}$  units. Hence the observed band at about  $1050\text{ cm}^{-1}$  in the spectra of these glasses may be considered as the superposition of these two bands, especially in the spectrum of more disordered glass. The same is true for metaphosphate groups also, because the band due to these groups is expected at about  $1280\text{ cm}^{-1}$  [14]. If trivalent titanium ions act as modifiers, the  $\pi$ -bond of P=O may be ruptured, creating new non-bridging oxygens. Even if  $Ti^{4+}$  ions enter substitutional positions with octahedral units in the glass network, the  $PO_4$  structural units are subjected to perturbations (like bonding, compression and chemical interactions) due to change in the environment and the incompatibility in ion size. As a result,  $PO_4$  structural units undergo structural distortions involving

changes in bond lengths and angles of P-O bonds. For these reasons we expect decrease in the intensity,  $PO_4^{3-}$  symmetric stretching and a band due to P-O-P symmetric/ Ti-O-P stretching vibrations in the IR spectra. The observed gradual decrease in the intensity of these bands in the spectra of the glasses  $T_0$  to  $T_{10}$  may be ascribed to these reasons, in the networks of these glasses, the titanium ions mostly occupy tetrahedral positions.

#### 5. Conclusions

The present investigation shows the better understanding of the effect of doping  $Ti^{3+}$  ions on spectroscopic behavior of lead bismuth phosphate glasses. From the Optical absorption and ESR spectral studies it indicated that titanium ions in these glasses exist in trivalent state in addition to and tetravalent state. These studies have also revealed that the concentration of  $Ti^{3+}$  ions increases gradually with increases in the concentration of  $TiO_2$ . IR spectral studies indicated that titanium ions exist in tetrahedral and octahedral substitutional positions and form P-O-Ti linkages. This results suggests that the effect of  $Ti^{3+}$  ions in lead bismuth phosphate glasses is dominated by  $Ti^{4+}$  ions.

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