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

V. Ravi Kumar$^1$, G. Naga Raju$^2$, S.V.G.V.A.Prasad$^2$, P.Raghava Rao$^4$, N. Narasimha Rao$^5$

$^{1,2,4,5}$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 $^{2}B_{2g} \rightarrow ^{2}B_{1g}$ and $^{2}B_{2g} \rightarrow ^{2}E$.

Keywords: Optical absorption, PbO$-$Bi$_2$O$_3$-$P_2$O$_5$, Spectroscopy, Quasi–tetrahedral [PO$_4$]$^+[\text{PO}_4]$.

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$_2$O$_5$) 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$_2$O$_3$, P$_2$O$_5$ 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$_2$O$_5$ and PbO content ranges are about 60 mol% and 30 mol %. The range of Bi$_2$O$_3$ content decreasing from 10 mol % to 9 mol % and the dopent content TiO$_2$ ranging from 0.1 % 1.0 mol % respectively.

3. Results

Fig. 1. represents the optical absorption spectra of PbO$-$Bi$_2$O$_3$-$P_2$O$_5$ 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$_2$ exhibited two clearly resolved absorption bands at about 536 and 679 nm due to $^{2}B_{2g} \rightarrow ^{2}B_{1g}$ and $^{2}B_{2g} \rightarrow ^{4}E$ transitions of Ti$^{3+}$ ions respectively [8].
Fig. 2. represents the infrared transmission spectrum of PbO–Bi₂O₃–P₂O₅ glasses exhibited conventional vibrational bands (anti-symmetrical vibrations of $PO_4^3-$ groups, $PO_2^-$ 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$^{-1}$ due to Ti─O─Ti symmetric stretching vibrations of TiO₄ units and another at 638 cm$^{-1}$ due to the vibrations of TiO₆ structural units [10]. With the introduction of TiO₂, the intensity of the bands due to $PO_4^3-$ groups, P─O─P symmetric stretching and TiO₄ 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 TiO₆ structural units exhibited an increasing trend in this concentration range.

![Fig. 2](image_url)

**Figure 3:** represents the ESR spectra of PbO–Bi₂O₃–P₂O₅ 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 $T_{10}$ is observed to be more intense with larger half width.

![Fig. 3](image_url)
4. Discussion

In the present glass system is composed of a well known conventional glass former P2O5, a intermediate glass former Bi2O3, modifiers PbO and dopent TiO2. Pure vitreous P2O5 forms glass by a continuous random network (polymeric structure) of quasi-tetrahedral [PO4]2− units in which phosphorous is four coordinated and only three of the oxygen atoms of each unit bridge to neighboring units, while the forth is doubly bonded to the central phosphorous atom. Bi2O3 is an incipient glass network former and as such does not readily form glass, but does so in the presence of traditional glass former P2O5 and modifier PbO with triangular [BiO3] pyramids. Titanium ions are expected to exist mainly in Ti4+ state as PbO–Bi2O3–P2O5: TiO2 glass network. However, the reduction of Ti4+ to Ti3+ appears to be viable during melting, annealing and crystalization processes of the glasses [11]. The Ti4+ ions occupy both tetrahedral and substitutional octahedral sites as corner-sharing [TiO4]2− units where as Ti3+ ions occupy only modifying positions in the glass network. TiO2 and TiO4 units of Ti4+ ions enter the glass network, may alternate with PO4 tetrahedral units and form linkages of P−O−Ti bonds. As a consequence a disruption in the PO4 and TiO4 tetrahedra with the creation of a number of bonding defects are expected. Using Tanabe-Sugano diagrams for d1 ions, the bands observed in the optical absorption spectra in the regions 510-550 nm and 670-685 nm are assigned to 2B1g → 2B2g and 2B1g → 2B2g transitions of 3d2 electron of the Ti3+ ions, respectively. With the gradual increase in the concentration of dopant TiO2 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 Ti3+ ions and ii) weaker ligand field of non-bridging oxygens. Even if Ti4+ ions enter substitutional positions with octahedral units in the glass network, the PO4 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, PO4 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, PO4 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 T0 to T10 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 Ti3+ 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 Ti3+ ions increases gradually with increases in the concentration of TiO2. 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 Ti3+ ions in lead bismuth phosphate glasses is dominated by Ti4+ ions.

References