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

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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 form 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 aroung Ti^{3+} ion and is explored to optical absorption, IR and EPR spectra. The EPR spectra exhibit resonance signals characterstic 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.

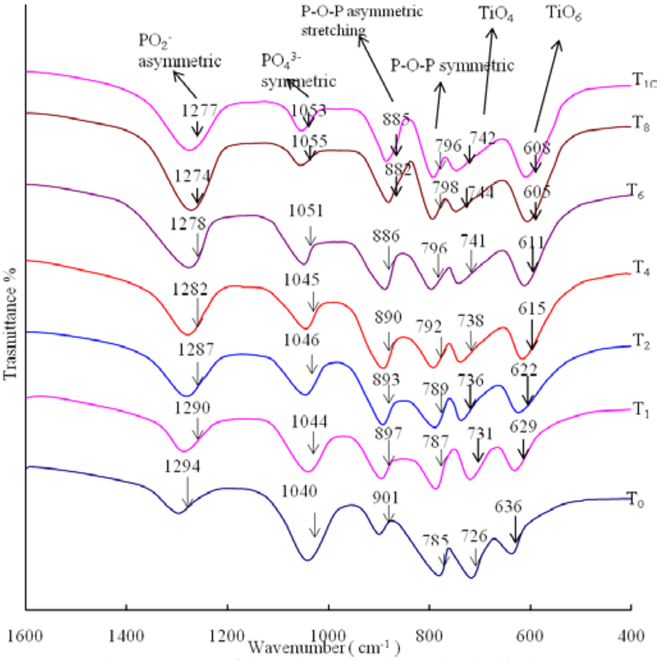

Fig .2. IR spectra of $PbO-Bi_2O_3-P_2O_5$ glasses doped with TiO_2

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].

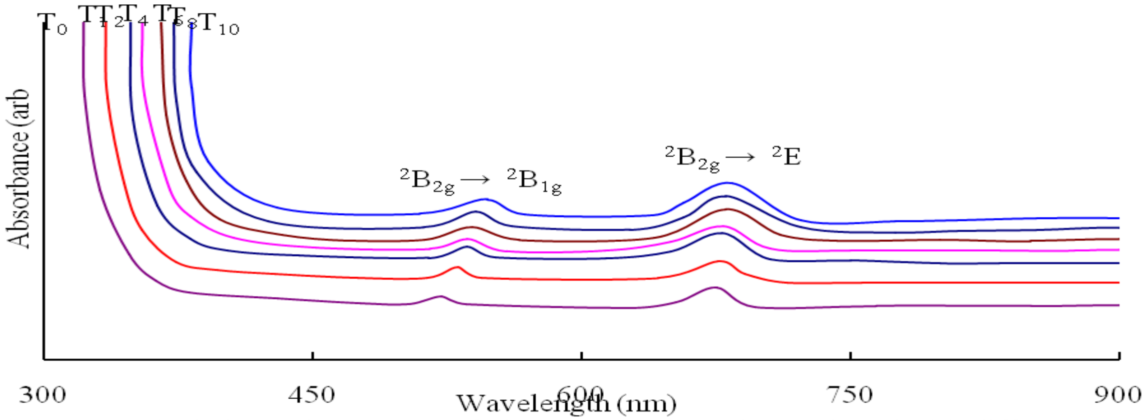

Fig. 1. Optical absorption spectra of $PbO-Bi_2O_3-P_2O_5$ glasses doped with different concentrations of TiO_2.

Fig. 2. represents the infrared transmission spectrum of $PbO-Bi_2O_3-P_2O_5$ glasses exhibited conventional vibrational bands (anti-symmetrical vibrations of PO_2^- groups, PO_4^{3-} 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 TiO_4 units and another at 638 cm^{-1} due to the vibrations of TiO_6 structural units [10]. With the introduction of TiO_2, the intensity of the bands due to PO_4^{3-} groups, P−O−P symmetric stretching and TiO_4 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_6 structural units exhibited an increasing trend in this concentration range.

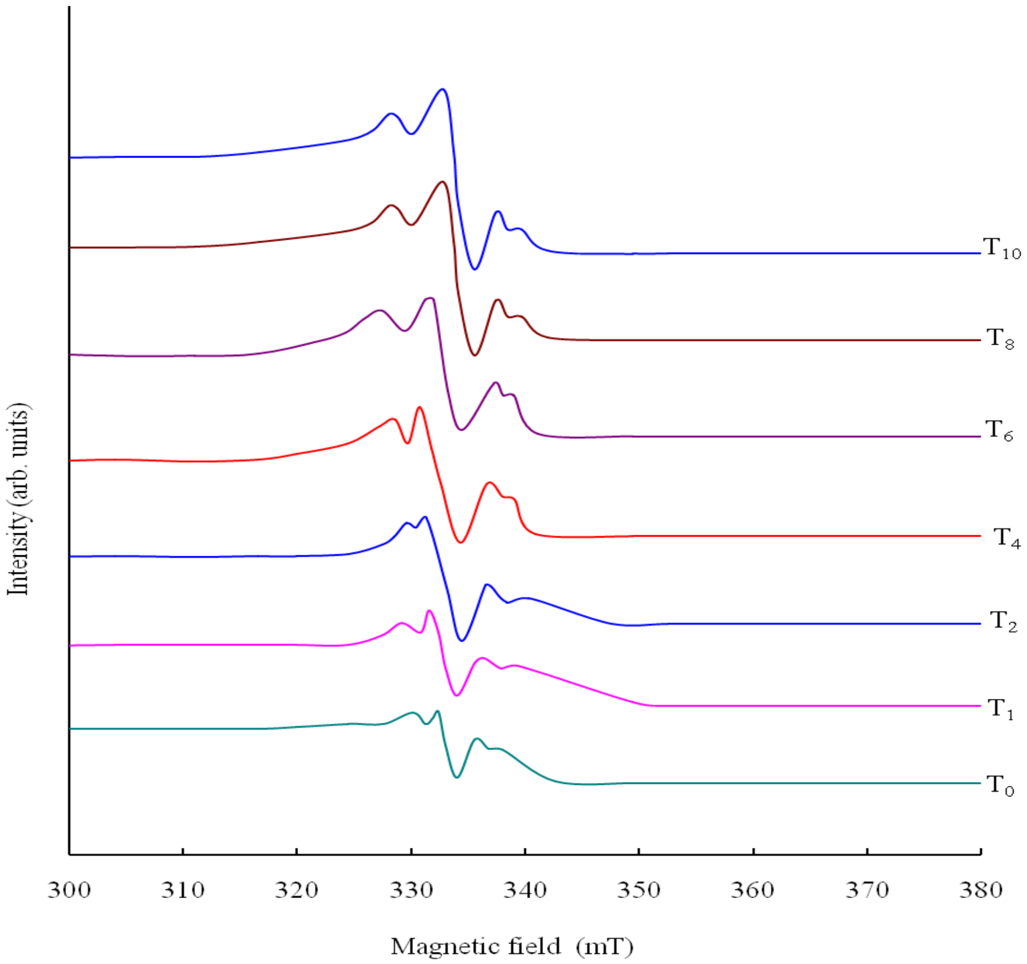

Fig. 3. ESR spectra of $PbO-Bi_2O_3-P_2O_5$: TiO_2 glasses recorded at room temperature.

Figure 3: represents the ESR spectra of $PbO-Bi_2O_3-P_2O_5$ 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.

4. Discussion

In the present glass system is composed of a well known conventional glass former P_2O_5, a intermediate glass former Bi_2O_3, modifiers PbO and dopent 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 forth 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 $\left|xy\right\rangle$ 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 cm^{-1}, which is not too far from the band position of $PO_4{}^{3-}$ units. Hence the observed band at about 1050 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 cm^{-1} [14]. If trivalent titanium ions act as modifiers, the π-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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