



Effect of TiO₂ modifier oxide on a B₂O₃ glass system

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ABSTRACT

The starting material of the glass system $x \text{PbO} - 1/2(1-3x) \text{BaO} - 1/2(1-3x) \text{B}_2\text{O}_3 : 2x \text{TiO}_2$ glasses are prepared by conventional melt quenching technique. The modifiers oxides are varied along with TiO₂ content influence the physical properties and glass formation. The obtained values from the physical parameters such as density and molar volume of glasses were studied. IR spectral studies of the glass network exhibits BO₃, BO₄, B–O–B, Pb–O, PbO₄, TiO₄ and TiO₆ structural units. The analysis of optical and ESR spectral studies Ti³⁺ ions are act as modifiers and these are expected to induce non-bridging oxygen's in the glass network; this observation indicates that there is a decreasing fraction of Ti⁴⁺ ions that have been reduced in to Ti³⁺ ions. The presence of smaller concentration of these donor centers decreases the optical band gap and insulating strength of glass materials.

Keywords: Optical absorption, ESR and IR spectra.

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1. Introduction

The glass forming ability is more for borate and addition of alkali oxides to amorphous boron oxide causes considerable changes on its physical properties [1, 2]. Heavy metal oxide glasses have other applications; in the field of optical fibers, optoelectronic devices; radiation shields and surgical lasers [3]. PbO enter into the glass network as both network former and as network modifier. Normally at higher compositions this oxides acts as modifier and at low concentration it behaves as glass former [4]. High content PbO glasses contain mixture of both PbO₃ and PbO₄ pyramidal structural units with Pb²⁺ at the apex of the pyramid [5]. Borate glasses mixed with PbO, are expected to become highly stable against devitrification and chemically inert [6]. Addition of barium oxide to these glasses further enhanced the applications of these system in the field of solid -state electrolytes for the fabrication of

solid state batteries and various technological applications [7,9].

The addition of titanium oxide to a glass matrix not only improves the chemical durability but also increase its nonlinear refractive index. Therefore it can be used as nonlinear optical devices [10]. The presence of dopant TiO₂ in the standard glass matrices is expected to enhance the glass forming ability and chemical durability of the glasses. Generally titanium, exists in the glass in Ti⁴⁺ state and participates in the glass network with TiO₄, TiO₆ and sometimes with TiO₅ structural units [11]. Further, it is also suggested that these ions may also exist in Ti³⁺ valence state in various glass matrices [12]. The inclusion of Ti⁴⁺ ions into the borate glass network is an added advantage to use these materials for optically operated devices.

2. Experimental Procedure

2.1 Glass Preparation

With the chemical composition of the glasses with sample codes, barium carbonate, lead oxide, boric acid and titanium oxide of Analar grade were obtained from Aldrich Chemical Company. Weighed the chemicals by using electric balance to an accuracy of 0.001 g. The weighed powder formed samples were thoroughly mixed and melted in a Pt

crucible in a temperature range of 800–1000 °C for 30 min until a bubble-free liquid was formed. The melt was then poured into a rectangular brass mould of dimensions 10 × 10 × 1 mm³. The mold was then moved into an annealing furnace at an annealing temperature of 300 °C to avoid cracks and breaking the sample through residual internal strain. The obtained samples were polished with cerium oxide to obtain maximum flatness and transparency.

Table. 1. Various physical parameters of titanium doped BaO–PbO–B₂O₃ glasses

| Glass sample | Avg. Mol. Wt. | Density (g/cm ³) | Mole fraction of TiO ₂ | Molar volume |
|------------------|---------------|------------------------------|-----------------------------------|--------------|
| Ti ₁₀ | 101.125 | 3.829 | 0.482 | 26.273 |
| Ti ₁₅ | 114.867 | 4.414 | 0.336 | 26.025 |
| Ti ₂₀ | 121.176 | 4.731 | 0.251 | 25.612 |
| Ti ₂₅ | 127.484 | 5.046 | 0.176 | 25.264 |
| Ti ₃₀ | 146.17 | 6.016 | 0.098 | 25.123 |

Table. 2. Summary of data on optical absorption spectral data of BaO–PbO–B₂O₃:TiO₂ glasses

| Glass samples | Ti ₁₀ | Ti ₁₅ | Ti ₂₀ | Ti ₂₅ | Ti ₃₀ |
|---|------------------|------------------|------------------|------------------|------------------|
| Ti ³⁺ transitions (nm) | | | | | |
| ² B _{2g} → ² B _{1g} | 529.5 | 534 | 539 | 543.1 | 545.5 |
| Ti ⁴⁺ transition (nm) | | | | | |
| ² B _{2g} → ² A _{1g} | 680.1 | 682.8 | 686.2 | 687.9 | 690 |
| Cut-off wavelength (nm) | 465 | 470 | 474 | 479 | 483 |
| Optical band gap E _g (eV) | 2.39 | 2.33 | 2.27 | 2.21 | 2.16 |

Table. 3. Infrared spectral band positions (in cm⁻¹) of BaO–PbO–B₂O₃:TiO₂ glasses

| Glass | Borate groups (cm ⁻¹) | | | TiO ₄ units (cm ⁻¹) | TiO ₆ units (cm ⁻¹) | Band due to PbO ₄ units (cm ⁻¹) |
|------------------|-----------------------------------|-----------------|-------|--|--|--|
| | BO ₃ | BO ₄ | B–O–B | | | |
| Ti ₁₀ | 1345 | 1120 | 710 | 742 | 641 | 481 |
| Ti ₁₅ | 1339 | 1127 | 710 | 747 | 634 | 479 |
| Ti ₂₀ | 1333 | 1133 | 710 | 755 | 629 | 476 |
| Ti ₂₅ | 1326 | 1138 | 713 | 759 | 625 | 473 |
| Ti ₃₀ | 1321 | 1145 | 715 | 762 | 621 | 470 |

3. Results

The information on short range structured properties of the glasses can be obtained by density and other physical parameters of the glasses. Glass forming oxides possesses lower densities as compared to their corresponding crystalline forms. The density of the glasses influences the geometrical configuration and co-ordination number of cations and changes the structure of the glasses. In borate glasses oxygen coordination number of boron is 3 in the structural unit of BO₃ triangle the boron atom slightly above the plane of the three bridging

oxygens. Three coordinated boron is denoted as B₃ and four coordinated boron as B₄. Hence, boron can have its structure in a triangular or tetrahedral form. Rigidity of the glass cations of tetrahedral groups is more than that of triangular groups of the glass cations. In pure B₂O₃ glasses, most of the borons are involved in [B₃O₆] boroxol rings [13].

From the measured values of density and average molecular weight M of PbO–BaO–B₂O₃:TiO₂ glass and have evaluated various other physical parameters and presented in Table 1. The density of the samples is observed to increase slightly with the

concentration of titanium. It may be noted here Ti_{10} possess more glass forming ability and high insulating strength.

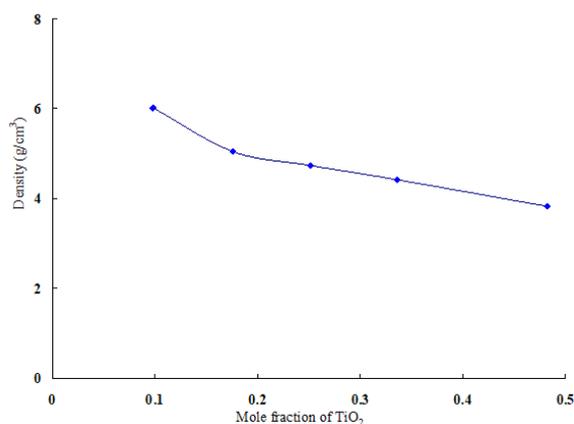


Fig. 1. Variation of density with mole fraction of TiO₂

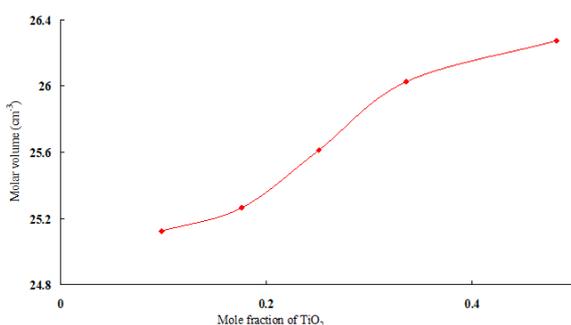


Fig. 2. Variation of molar volume with mole fraction of TiO₂

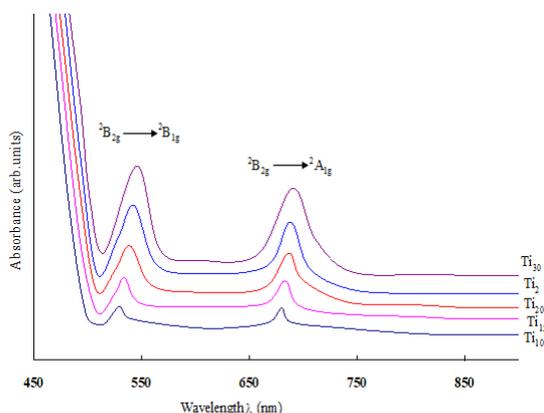


Fig. 3. Optical absorption spectra of PbO-BaO-B₂O₃: TiO₂ glasses

Variation of density with mole fraction and molar volume of the glasses with the concentration of TiO₂ are presented in Figs. 1 and 2. The density of titanium doped glasses increase from 3.829 to 6.016 g/cm³ and corresponding molar volume decreases from 25.123 to 26.273 cm³/mol. It is due to the smaller atomic weight of the titanium as compared to the other chemicals in the system. As the

concentration of titanium increases by the replacement of glass former, molar volume decreases and increases the density is due to shrinkage of the glass network. It means that increasing molecular weight of oxide ions used in the glass, replacing B₂O₃ by titanium might be expected increase the density of these glasses

The optical absorption spectra of PbO-BaO-B₂O₃: TiO₂ glasses recorded at room temperature in the wavelength range 450 to 900 nm are shown in Fig. 3. The spectrum of TiO₂ glasses exhibited two clearly resolved absorption bands at about 525 and 680 nm. These bands are assigned to ²B_{2g} → ²B_{1g} and ²B_{2g} → ²A_{1g} transitions of Ti³⁺ ions. With a gradual increase in the concentration of TiO₂, the half width and intensity of these two bands are observed to increase shifted towards the higher wavelength side. An increase in absorption in the wavelength region from 450 to 900 nm indicates the formation of hole centers (HC) like an OHC (oxygen hole center) or a BOHC (boron oxygen hole center) [14, 15]. Present system of glasses, the possible explanation for the shift of the absorption edge to a higher wavelength with increasing PbO and TiO₂ content is the increase in the oxygen environment, and hence an increase in the formation of bridging oxygen (BO₄ units) is expected. The optical band gap is evaluated from the absorption edges by drawing Tauc plots (Fig. 4) of all glasses. From the extrapolation of the linear portion of these curves, the values of optical band gap (E₀) obtained for PbO-BaO-B₂O₃: TiO₂ glasses along with cut-off wavelengths and band positions are presented in Table 2. The value of E₀ is found to decrease with the increase in concentration of modifier and titanium oxides.

The structure of amorphous solids is determined by infrared spectroscopy. The IR spectra of these glasses were recorded in the wave number range of 400–1600 cm⁻¹ as shown in Fig. 5. The absorption bands lie in the range 1300 to 1400 cm⁻¹, 1000–1200 cm⁻¹, and at about 710 cm⁻¹. These bands are assigned due to stretching relaxations of B–O bonds of the trigonal BO₃ units, vibrations of the BO₄ structural units, and bending vibrations of B–O–B linkages [16]. An absorption band near 470 cm⁻¹ associated with vibrations of PbO₄ structural units in infrared transmission spectra of all the glasses. Pb²⁺

cations play due role in the formation of glass structure. Initially, it acts as a network modifier in the glassy matrix when these cations are ionically bonded, then finally, Pb^{2+} cation will act as glass former [17]. With the introduction of TiO_2 into the glass network, two new bands TiO_4 and Ti-O-Ti symmetric stretching vibrations of TiO_6 structural units have appeared; the intensity of band due to TiO_4 structural units is observed to decrease with increase in the concentration of TiO_2 in the glass matrix, the meta-center shifting of towards slightly higher wavenumber and reversal trend observed in TiO_6 . With increase of the content of modifier oxide and TiO_2 , the intensity of BO_3 and PbO_4 structural units is observed to increase and shifted towards lower wavenumber side and BO_4 structural units is observed to decrease and shifted towards higher wavenumber side. This may be due to the formation of bridging bonds of $Pb-O-B$. Since the stretching force constant of $Pb-O$ bonding is substantially higher than that of the $B-O$. Hence the content of $Pb-O-B$ becomes dominant in the glass network structure. Increasing the concentration of modifier oxide it increases the polarization of Pb^{2+} ions in the glass network and contributes the formation of modified Pb^{2+} -modified boron- oxygen rings and their chains but these chains are influenced by stretching vibrations of TiO_6 octahedral. The summary of the data on various bands observed in the IR spectra of $PbO-BaO-B_2O_3:TiO_2$ glasses are presented in Table 3.

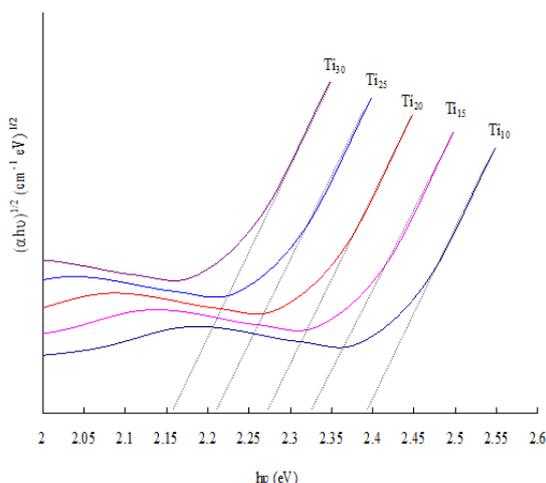


Fig. 4. Tauc plot of $BaO-PbO-B_2O_3:TiO_2$ glasses

The ESR spectra of $PbO-BaO-B_2O_3:TiO_2$ glasses recorded at room temperature as shown in Fig. 6. As the concentration of TiO_2 increases; the intensity and half width of signal increases and it is found to be highest for Ti_{30} , the value of $g=1.948$ is for Ti_{30} . From the insert figure we have studied that as the concentration of TiO_2 increases intensity of ESR signals of all the glass samples were increased.

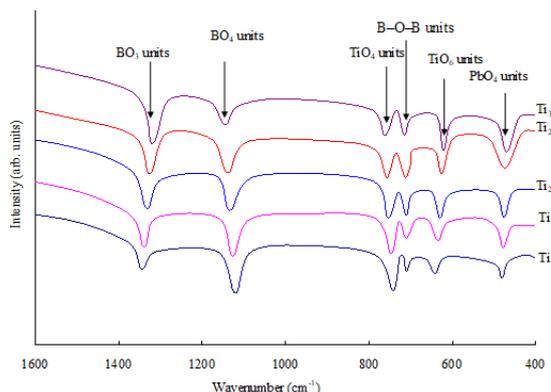


Fig. 5. Infrared transmission spectra of $PbO-BaO-B_2O_3:TiO_2$ glasses

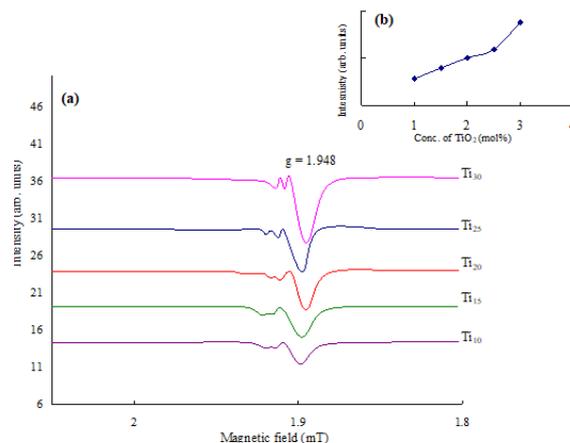


Fig. 6. ESR spectra of $PbO-BaO-B_2O_3:TiO_2$ glasses

4. Discussion

The chemical composition of titanium oxide increases, the molar volume of the samples decreases it indicated that replacement of B_2O_3 by titanium oxides. Decreasing the molar volume also causes the reduction of glass network as result increases the density of the samples. Molecular weight of oxide ions also influences the density of these glasses. In this study observed that molecular weight and density are increases. The rigidity of glasses increases with decreasing density. Density of the glass system explains the different type of structural units present in glass system. It also

illuminates the structure of glass. Molar volume indicates the spatial distribution of the oxygen atoms in the glass network. The decrease in the molar volume can be attributed to closing up of structure of glasses. Increases the modifier and titanium oxide content it leads to the formation of BO_3 structural units in the glass system.

$3d^1$ is the electronic pattern of Ti^{3+} ion. It split into ${}^2\text{E}$ and ${}^2\text{T}_2$ states and ${}^2\text{T}_2$ state again split into three ${}^2\text{B}_2$ states. Octahedral transitions of Ti^{3+} ions exhibits two absorption spectra at about 525 nm and 680 nm these bands are assigned to ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$ transitions.

As the concentration of titanium oxide increases optical band gap is decrease it is due the presence of donor centers in the system and optical absorption edge is shifted gradually toward the higher wavelength side. Increasing the concentration of TiO_2 , titanium ions occupy octahedral positions and also exist in Ti^{3+} state. This leads to formation of NBO's in the glass matrix and there by decreases the degree of localization of electrons thereby decreasing the donor centers in the glass matrix. Hence networking forming Ti^{4+} ions in the glass network is gradually decreased with the generation of donor centers and the presence of Ti^{4+} ions are trapped by Ti^{3+} ions. It causes decreasing of optical band gap [18]. From the results of ESR and optical absorption spectra of $\text{PbO-BaO-B}_2\text{O}_3$ glasses containing different concentrations of titanium oxide indicates that the titanium ions mostly Ti^{3+} ions exist in tetragonal distorted octahedral sites there by stimulate bonding defects. The data on IR spectra, with increase in the concentration of TiO_2 the intensity of the band due to TiO_4 structural units is observed to decrease gradually indicating it influenced by the Ti^{3+} ions and TiO_6 structural units are follows the reversal trend and these ions induces bonding defects in the glass network.

5. Conclusion

As the concentration of modifier oxide and titanium oxide increases; it causes the reduction of BO_4 units into BO_3 units in to B_2O_3 glass system, it decreases the band gap and increase the density of $\text{PbO-BaO-B}_2\text{O}_3\text{:TiO}_2$ glasses. From spectral properties it is concluded that, in borate BO_3 and BO_4 act as network structural units, while the modifier oxides

act as interstitial positions of the glasses. Composition of modifier and titanium oxide increases structural units of BO_3 is observed to increase and BO_4 units is observed to decrease. The density is observed to increase and molar volume, band gap energy is observed to decreases. Modifier oxides are added; it clearly indicated that influence the structure of the glass system was clearly observed. These studies have also revealed that the concentration of Ti^{3+} ions increases gradually with increases in the concentration of TiO_2 . Ti^{3+} ions exist in both tetrahedral and octahedral positions and also form Pb-O-B linkages in the IR spectra. This results suggests that the effect of Ti^{3+} ions in lead borate glasses is dominated by Ti^{4+} ions

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