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# SPECTROSCOPIC PROPERTIES OF $Na_2O$-PbO-$Al_2O_3$-$B_2O_3$-$SiO_2$ GLASSES DOPED WITH $TiO_2$

**K.VIJAYA BABU**
Department of Physics,
Acharya Nagarjuna University,
Nagarjuna Nagar, Guntur.

**Dr. SANDHYA COLE**
Assistant Professor
Department of Physics,
Acharya Nagarjuna University,
Nagarjuna Nagar, Guntur.

## ABSTRACT

*$Na_2O$-PbO-$Al_2O_3$-$B_2O_3$-$SiO_2$(NPABS) glasses mixed with different concentrations of $TiO_2$ (ranging from 0 to 0.9 mol %) are synthesized by melt quenching method. The samples are characterized by x-ray diffraction (XRD), the powder XRD pattern of all the samples confirms amorphous nature of the glass. Optical absorption, Electron paramagnetic resonance (EPR) and Fourier transform infrared (FT-IR) spectroscopic techniques. Glass formation is confirmed by x-ray diffraction spectra. The UV-Vis spectra of these glasses exhibited two clearly resolved bands at about 691 nm and 832 nm due to $^2B_{2g} \rightarrow {}^2A_{1g}$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions of $Ti^{3+}$ ions. From the optical absorption spectral data, optical band gap and Urbach energy are evaluated. From EPR spectra the strength of the signal is increased and hyperfine splitting is resolved with increasing the concentration of $TiO_2$ in the glass matrix. The FT-IR spectral studies have pointed out the existence of conventional and structural units of these glasses. Various physical properties and optical basicity are also evaluated with respect to the concentration of $TiO_2$ ions.*

***Keywords***: *Glass, XRD, Infrared Spectra, EPR, Optical and Physical Properties.*

## 1. INTRODUCTION

Glass is an amorphous material of interest because it is transparent to visible light and is good insulator [1]. These glasses find applications in the different areas of science and technology. Potential applications of borosilicate glasses are based on their extraordinary properties such as good chemical resistance, lower thermal expansion values, good electrical properties, high abrasion resistance, chemical durability, mechanical strength. For these reasons they are used for many applications such as optoelectronics, solar energy technology and astronomical reflecting telescope in micro electromechanical systems, glass ware, industrial piping and bulbs for hot lamps and also they are recently investigated as for immobilization of nuclear wastes [2-10]. NPABS glasses results from the combination of network-forming oxides such as $SiO_2$ and $B_2O_3$ together with the network modifier oxide, $Na_2O$ and intermediate oxide, $Al_2O_3$. $SiO_2$ is transparent in the optical window, $B_2O_3$ increase the glass transparence. $Na_2O$ is common flux, reducing the processing temperature and change the properties of glasses and facilitates the homogenization of the glass system. Lead oxide (PbO) is used as intermediate oxide because it improves the chemical durability and enhances the resistance against diversification. The chemical durability and mechanical properties of borosilicate glass is greatly improved by addition of $Al_2O_3$ because $Al^{3+}$ ions act as an ionic cross-linker between different chains, inhibiting hydration reactions [11, 12]. In general, the titanium plays a dual role in the glass structure, (i) as network former (NWF) in the form of tetrahedral $TiO_4$ or (ii) as network modifier (NWM) in the form of octahedral $TiO_6$ and rarely with a tetragonal pyramid structure of $TiO_5$. The addition of $TiO_2$ contributes to an enhancement in refractive indices of oxide glasses [13].

Titanium dioxide is the most promising photo catalyst because of its low cost, high efficiency, chemical inertness [14-19].

The present study, the environment of titanium ions is investigated in NPABS glasses, using optical absorption and EPR techniques. The FT-IR spectra are also recorded to study the structure of the glasses and the effect of titanium ions on their physical properties.

## 2. EXPERIMENTAL

### 2.1 COMPOSITE PREPARATION

The investigate glasses have been prepared by mixing appropriate quantities from the reagent materials are synthesized. In this study by a melt-quenching method, are summarized in Table 1. The raw materials are $Na_2CO_3$, PbO, $Al_2O_3$, $B_2O_3$, $SiO_2$ and $TiO_2$ were thoroughly mixed in an agate mortar and homogenized mixture was transferred into a silica crucible. The compositions of the materials (10 g) are melting in air in silica crucibles in an electric furnace at temperature $1200^0$C for 20 min until a bubble free liquid is formed. At the end of the melting process in order to obtain homogeneous and the melts are poured on brass mould and subsequently annealed at 400 $^0$C for 3 h and cooled slowly to release the thermal stress with these glasses during the quenching process. The glass matrix is obtained transparent and colorless. The samples are then ground and optically polished. In this procedure, a high melting temperature was employed due the high melting points of the PbO, $B_2O_3$, $SiO_2$, $TiO_2$, and $Al_2O_3$. Additionally, the addition of $Al_2O_3$ to silicate melts increases the viscosity although the addition of alkali oxides ($Na_2O$) promotes the opposite behavior. The decrease from melt temperature to pour temperature permitted adjusting the viscosity, to obtain bubble free transparent glasses with high homogeneity.

**Table 1** Composition of the NPABS glass system doped with different mol% of $TiO_2$

| Glass code | $Na_2O$ (mol%) | PbO (mol%) | $Al_2O_3$ (mol%) | $B_2O_3$ (mol%) | $SiO_2$ (mol%) | $TiO_2$ (mol%) |
|---|---|---|---|---|---|---|
| Pure | 20 | 10 | 5 | 40 | 25 | 0 |
| $T_1$ | 20 | 10 | 4.7 | 40 | 25 | 0.3 |
| $T_2$ | 20 | 10 | 4.4 | 40 | 25 | 0.6 |
| $T_3$ | 20 | 10 | 4.1 | 40 | 25 | 0.9 |

The amorphous nature of the prepared glass was confirmed by X-ray powder diffractometry (XRD) on XRD-6100 SHIMADZU X-Ray diffract meter in the scanning range of 10-80$^0$ (2θ) using Cu $K_\alpha$ radiation having a wavelength of 1.5406 Å at room temperature. Density of the samples was determined to an accuracy of ± 0.001 by standard Archimedes' principle using O-xylene (99.99% pure) as a buoyancy liquid with VIBRA HT density measurement kit. Using the density and average molecular weight the physical parameters such as titanium ion concentration ($N_i$), polar radius ($r_p$), inter titanium ionic distance ($r_i$) in the glass system were evaluated. The optical UV-Visible absorption spectra of prepared glass samples are recorded using JASCO V-670 UV-VIS-Spectrophotomètre in the wavelength region of 200-1200 nm. The Fourier transform infrared transmission spectra of different prepared glasses were measured using KBr

pellet method on SHIMADZU-IR Affinity-1S FT-IR spectrophotometer in the region of 4000-400 $cm^{-1}$ wave number range. The EPR spectra of titanium doped prepared glass samples were recorded on JEOL-FE-IX(X-band) EPR spectrometer operating at 9.125 GHz with field modulation frequency of 100 kHz.

## 3. RESULTS AND DISCUSSION

### *3.1* X-RAY DIFFRACTION SPECTRA

The powdered XRD patterns for the prepared glass samples are presented in Figure. 1. These patterns confirmed the glassy nature of the samples with broad peaks at 2θ values around 20–40° and were free from any detectable crystalline phases as expected [20].

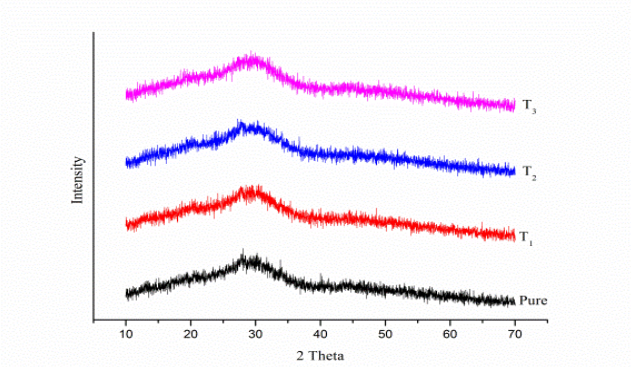


**Fig. 1** XRD Spectra of $TiO_2$ doped NPABS Glasses

### 3.2 Physical properties

Figure 2 shows the variation of density (d) and molar volume ($V_m$) of these glasses as a function of $TiO_2$ content. It is clear from this figure that, with increasing$TiO_2$, density increases and molar volume decreases with $TiO_2$ additions. The sample $T_3$ exhibited higher density 3.022 than the sample $T_2$ of density 2.997g/$cm^3$. This slight decrease in the density of the sample $T_3$ compared to the sample $T_2$ may be attributed to the volume expansion due to the formation of octahedral $TiO_6$ structural unit in the glass network, these values are noted in Table 2. This could further be confirmed through FT-IR measurements of the glasses [21].

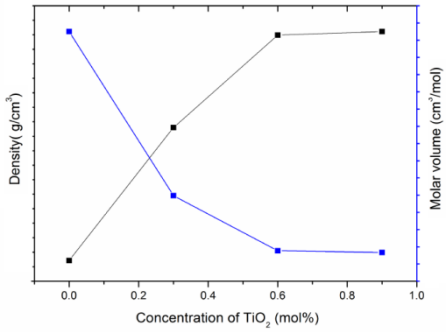


**Fig. 2** Density and molar volume values with a Varied $TiO_2$ content in NPABS glasses

**Table 2** various physical properties of $TiO_2$ doped NPABS glass

| Parameters | Pure | $T_1$ | $T_2$ | $T_3$ |
|---|---|---|---|---|
| Density | 2.960 | 2.987 | 2.997 | 3.022 |
| Molar volume | 29.854 | 29.562 | 29.440 | 29.175 |
| Ion.conc(Ni)x$10^{20}$ | --- | 0.6112 | 1.2277 | 1.858 |
| Interionic distance | --- | 0.2306 | 0.1725 | 0.1510 |
| Refractive index | 1.653 | 1.654 | 1.655 | 1.656 |
| Polaron radius | --- | 0.1043 | 0.0822 | 0.0715 |
| Optical Basicity | 0.4296 | 0.4298 | 0.4299 | 0.4300 |

### 3.3 FT-IR SPECTRA

From Fig. 3, the FT-IR spectra of $TiO_2$ free glass shows four main bands. The band at about 466 $cm^{-1}$ is due to Si-O-Si asymmetric vibration and the small shoulder at 715 $cm^{-1}$ is attributed to bending vibration of B-O-B in $[BO_3]$ triangles [22-24] is observed. The main intense band at 850 -1100 $cm^{-1}$ is due to the combined stretching vibrations of Si-O-Si and B-O-B network of tetrahedral structural units [25]. Here the distinguished feature of glass samples is the shift of the broad band and

intense band from 967 $cm^{-1}$, indicating that $Ti^{3+}$ exists in octahedral coordination. A strong absorption band at 1375 $cm^{-1}$ is attributed to the B-O stretching vibration of $[BO_3]$ triangles (characteristic for $BO_3$ group) [26]. The band at 698 $cm^{-1}$ getting narrow as the $Al_2O_3$ content decreases. On addition of $Al_2O_3$ to the content, the frequency of the band between 850 and 1100 $cm^{-1}$ exhibit a shift to lower wave number and the width becomes wide by decreasing $Al_2O_3$ content. While the frequency of the band at around 1375 cm-1 does not have any changes with the decreasing $Al_2O_3$ content. It may be worth mentioning here that the earlier studies on the IR spectra of various other glasses containing $TiO_2$ indicate the presence of a vibration band at about 769 $cm^{-1}$ due to vibrations $TiO_4$ groups and is observed only for $T_3$**.** Hence, there is a possibility for the formation of single boron-oxygen-titanium frame work in the glass network. In addition the spectrum of $T_3$ glass exhibited single well-resolved band at 710 cm-1 due to B-O-Ti linkages. The summary of the data on the position of various band head in the $TiO_2$ doped NPABS glasses are presented in Table 3.

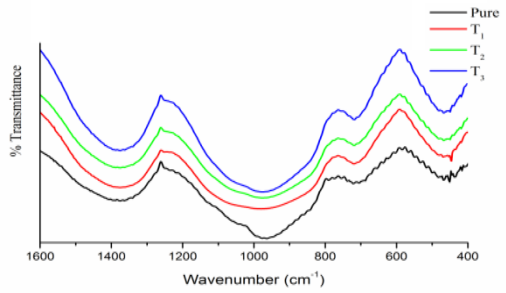


**Fig. 3** FT-IR transmission spectra of NPABS undoped and doped with $TiO_2$

**Table 3** FT-IR spectra f $TiO_2$ doped NPABS glass system

| Pure | $T_1$ | $T_2$ | $T_3$ | Assignment |
|---|---|---|---|---|
| 453 | 454 | 459 | 463 | Asymmetric Vibration of Si-O-Si |
| 714 | 716 | 718 | 720 | Bending Vibration of B-O-Bin $[BO_3]$ triangles |
| - | - | 765 | - | B-O-Ti groups |
| | | | 787 | $TiO_4$ groups |
| 969 | 976 | 981 | 982 | Combined Stretching Vibrations of Si-O-Si and B-O-B |
| 1380 | 1383 | 1385 | 1385 | Stretching Vibrations of $[BO_3]$ |

### 3.4 OPTICAL ABSORPTION SPECTRA

**Fig. 4(a)** Shows the optical absorption spectra of the sodium lead Alumino borosilicate glass samples with different amount of $TiO_2$ are recorded at room temperature in the wavelength region 350-800 nm, the absorption edge observed at 305 nm for the pure glass. It is also observed that the position of the fundamental absorption edge and cut-off wavelength shift towards red as the content of $TiO_2$ increases. It appears that a part of $TiO_2$ is responsible for the increase in the absorption of non-bridging oxygen (NBO) due to which this shift is obtained [27]**.** The spectrum of all the prepared glass samples exhibited two clearly resolved absorption bands at about 691 nm and 832 nm. The bands are attributed due to $^2B_{2g} \rightarrow {}^2A_{1g}$ (691 nm) and $^2B_{2g} \rightarrow {}^2B_{1g}$ (830 nm) transitions of $3d^1$ electron of the $Ti^{3+}$ ions in tetragonal distorted octahedral sites respectively**.** Normally, under ordinary conditions of melting, it is difficult to get $Ti^{3+}$ in glasses as Ti ion tends to achieve its higher valence state ($Ti^{4+}$). The $Ti^{4+}$ ion does not show any absorption in the visible range of the spectrum as it has an electronic configuration $3d^0$. Thus it can be concluded that Ti ions in these glasses are present as $Ti^{4+}$ ions. [28]**.**

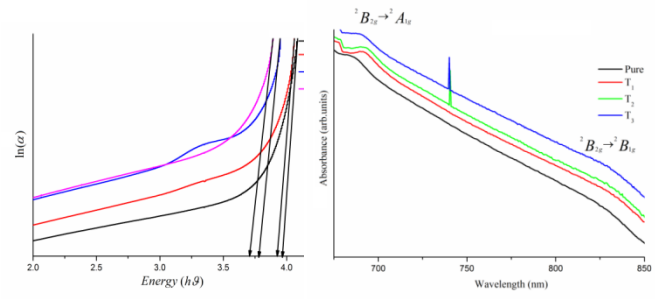


Fig. 4(a) Fig. 4(b)

**Fig. 4(a)** Optical absorption spectra of different Ti-doped NPABS glass system and **Fig. 4(b)** Urbach plots of $TiO_2$ doped NPABS glasses

The fundamental optical band gap of these glasses has been computed based on their optical absorption spectra, for understanding their optically induced transitions. There are two types of transitions, which can occur at the fundamental absorption edge of glass materials. They are direct and indirect transitions. In both cases, electromagnetic waves interact with the electrons in the valence band, which are raise across the fundamental band gap to the conduction band. These photon energies hυ just above the fundamental edge, the absorption α follows the standard relation, $\propto = \frac{A(h\vartheta - Eg)^n}{h\vartheta}$ (1)

where A is a constant and $E_g$ is the optical band gap energy and the exponent 'n' take the values ½ or 2 for allowed direct or indirect transitions, respectively. By plotting $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^2$ as a function of hυ, we can find the optical energy band gap for direct or indirect transitions. As shown in Figs. 5(a), 5(b) and 4(b), the respective values of the band gap energies can be obtained by extrapolating the linear portion of the plot for $(\alpha h\upsilon)^{1/2}=0$ for indirect transition, the optical band for indirect transition values varies from 4.003- 3.764eV and $(\alpha h\upsilon)^2=0$ for direct transitions, whose values vary from 4.005- 3.842eV. The optical band gap energies decrease with the increase of titanium ion concentration. Also Urbach energy values increases from 0.252- 0.269eV with the increase of titanium ion concentration.

**Table 3** Optical band gap energy ($E_{opt}$) for direct and indirect transitions and Urbach energy of Ti-doped NPABS glasses

| Sample code | Cutoff wavelength (nm) | Energy band gap (eV) | | | Urbach energy |
|---|---|---|---|---|---|
| | | Calculated | Direct | indirect | |
| Pure | 305 | 4.073 | 4.005 | 4.003 | 0.252 |
| $T_1$ | 310 | 4.007 | 3.973 | 3.971 | 0.254 |
| $T_2$ | 313 | 3.969 | 3.878 | 3.842 | 0.264 |
| $T_3$ | 317.5 | 3.912 | 3.842 | 3.764 | 0.269 |

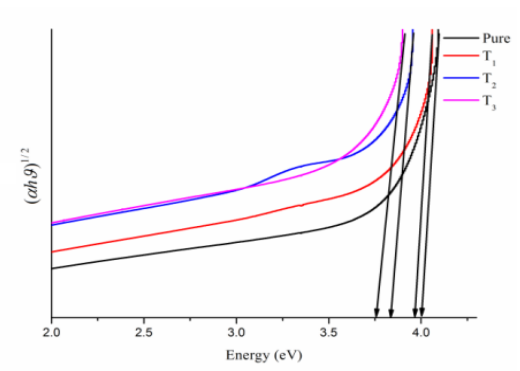


Fig. 5(a)

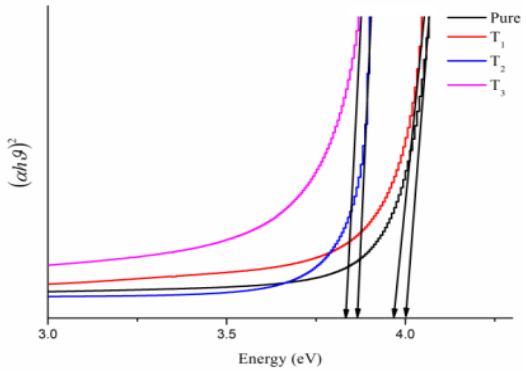


Fig. 5(b)

Fig. 5(a) and 5(b) are Indirect and direct bands of $TiO_2$ doped NPABS glasses

### 3.5 EPR SPECTRA

EPR spectra of $Na_2O$-PbO-$Al_2O_3$-$B_2O_3$-$SiO_2$ glasses with different concentrations of $TiO_2$ recorded at room temperature are shown in Fig. 8. In the undoped glass no EPR signal was detected. When $Ti^{3+}$ ions are introduced into the NPABS glasses, all samples exhibit absorption lines. The EPR spectrum exhibits broad unresolved spectrum is due to $Ti^{3+}$ and its g value is 1.9532**.** The broadness arises due to the dipolar-dipolar interaction of $Ti^{3+}$ ions. The resonance signal observed in EPR spectra with g = 1.9532 is due to distorted octahedral sites of $Ti^{3+}$ ions with |x y |> ground state. The presence of large concentration of such ions may distort the glass network more and induce bonding defects. The near absence of such signal in the spectra of glass $T_3$ clearly indicates the low concentration of such ions in this glass network. The g-value a little less than 2.002 is typically due to $Ti^{3+}$ ions and agrees well with the reported values for $Ti^{3+}$[29-31]**.** Except for the variation in signal intensity no important modifications is observed while increasing the dopant concentrations (Fig. 7). A slight shift in the resonance signals is also observed when modifying the starting glass composition.

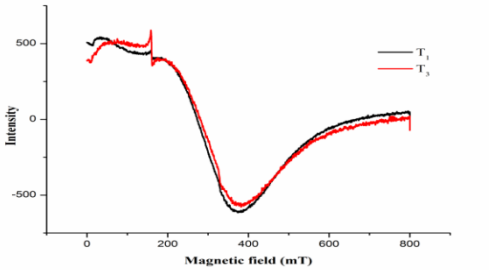


**Fig. 7** EPR spectra of $TiO_2$ doped NPABS glasses

### 4. CONCLUSION

The physical parameters, spectroscopic properties and FT-IR studies on the network structure of $Na_2O_3$-PbO-$Al_2O_3$-$B_2O_3$-$SiO_2$ glasses doped with $TiO_2$ reveals the following conclusions:

The XRD patterns confirm the amorphous structure of the glasses studied. The physical properties like density, average molecular weight (M), titanium ion concentration ($N_i$), molar volume ($V_m$), mean titanium ion separation ($r_i$) and the polaron radius ($r_p$) are evaluated for the glasses studied in the present work varies linearly with x mol% except density values. The optical absorption spectra of the present glass system is attributable to $Ti^{3+}$ ions which contains two broad intense bands are analyzed on the basis of axially elongated octahedral coordination. The band gap of glasses varies from 4.005 to 3.842 eV and 4.003 to 3.764 eV (direct and indirect) and 0.252 to 0.269 eV (Urbach) depending upon

the chemical nature of intermediate oxide. Urbach energy values suggest that defects can be increase due to the increase in Urbach energy with titanium content. The broad unresolved EPR spectrum with g value around 2.002 is attributed to $Ti^{3+}$ ion. The IR spectral investigations indicate the $Ti^{3+}$ ions exist in octahedral positions and they also form B-O-Ti linkages.

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