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Optical Absorption and Emission Spectral Properties of ZnO-Bi_2O_3-B_2O_3:TiO_2 Glasses

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Abstract. A glass composition ZnO-Bi_2O_3-B_2O_3: TiO_2 is selected, and samples were made using melt & quench method. Initial characterization tests like X-ray diffraction and scanning electron microscopy are carried out to assess the solid-state behavior of samples. After fundamental characterization, samples were tested for optical absorption and emission spectral properties. The diffraction patterns and scanning images validate glassy behavior. The experimental density and Ti ion concentrations found to increase with the introduction of TiO_2 while average molecular weight has shown decreasing trend. The absorption spectra have exhibited the two relevant absorption bands of titanium ions in the range about 510 to 550 nm and 680 to 700 nm. Emission spectra of all samples have confirmed that a wide band from 400 to 540 nm is seen and the test sample with low amount of TiO_2 has shown evidence of highest peak intensity in comparison with remaining samples. The reasons for spectral variations by mean of oxidation states and occupational locations of Ti were explored in detail.

KEY WORDS: Cobalt; bismuth; borate glasses; UV-visible absorption; infrared.

1 Introduction

Borate glasses [1–3] are of interest due to their material characteristics like low melting temperature, refractive index, good glass forming ability, highheat resistance, and dielectric constant. Bismuth included borate glasses are specially investigated to explore the second and third order susceptibilities to explore its compatible features for optical devices [4, 5]. Modifier oxide such as zinc oxide addition to the bismuth borate glass network would result in the varying glass network and causes structural modifications with different occupational symmetry. This inclusion makes the borate glass more chemically stable and downs the thermal expansion coefficient value [6, 7]. Further, it enables the glass samples to get transparency due to its characteristic white color.

Titanium oxide is found to be one of the interesting metal oxides which got superior physical and spectral properties even though it included in the small quantities. Titanium ions take two fundamental oxidation states; trivalent and tetravalent those would modify the spectroscopic and general properties of ZnO-Bi_2O_3-B_2O_3 glasses. Most importantly, the properties of glasses are absolutely depending on the structure of the entire glass network, the concentration of titanium ions and its coordination symmetry such as octahedral or tetrahedral. Considering this scenario, lot of research survey is carried out. Literature reports have mainly focused on ternary glass systems and some other studies have discussed the dielectric behavior of titanium, manganese, vanadium, and cobalt ions [8–13]. Spectroscopic investigations on TiO_2 doped zinc-based bismuth borate glasses are limited and compositional impact on physical properties was not assessed. Role of Ti^{3+} and Ti^{4+} ions in ZnO-Bi_2O_3-B_2O_3 has not been studied and fully understood yet. Thus, broad scope is there to explore the behavior of titanium ions in the ZnO-Bi_2O_3-B_2O_3 glass network by systematically investigating the ion concentration, density, compositional acceptance for glass formation ability and mainly optical properties.Therefore, the current work was aimed at synthesizing the ZnO-Bi_2O_3-B_2O_3: TiO_2 glasses after thorough trial and error method of checking the glass composition. Later, study was done to investigate the impact of TiO_2 content on optical and physical properties of ZnO-Bi_2O_3-B_2O_3 glasses.

2 Experimental Procedure

A specific glass composition (25-x ZnO-20Bi_2O_3-55B_2O_3: x TiO_2 (0.5 $\leq$ x $\leq$2.0 mol%) has been identified for the current research investigation. Composition specifications of samples with their nomenclature presented below. The addition of mol% of TiO_2 was limited to 2.0 mol% as transparency of the glass sample has become opaque beyond 2.0 mol%. The samples less than 2.0 mol percentage found to be very clear and transparent

$$\begin{aligned}
&\mathrm{ZBBT_5}: \ 24.5\mathrm{ZnO}-20\mathrm{Bi_2O_3}-55\mathrm{B_2O_3}: \ 0.5\mathrm{TiO_2};\\
&\mathrm{ZBBT_{10}}: 24.0\mathrm{ZnO}-20\mathrm{Bi_2O_3}-55\mathrm{B_2O_3}: \ 1.0\mathrm{TiO_2};\\
&\mathrm{ZBBT_{15}}: 23.5\mathrm{ZnO}-20\mathrm{Bi_2O_3}-55\mathrm{B_2O_3}: \ 1.5\mathrm{TiO_2};\\
&\mathrm{ZBBT_{20}}: 23.0\mathrm{ZnO}-20\mathrm{Bi_2O_3}-55\mathrm{B_2O_3}: \ 2.0\mathrm{TiO_2}.
\end{aligned}$$

Boric acid H_3BO_3, zinc carbonate $ZnCO_3$, bismuth oxide Bi_2O_3, and titanium oxide TiO_2 were taken as starting materials of AR grade. Using agate mortar and piston, calculated quantities of reagents were mixed until smooth powder obtained and then in melted in a porcelain crucibleat around 900 to 980 ^{o}C temperatures for one hour using PID controlled high temperature furnace. After confirming bubble free molten liquid, melts were poured on to desired molds with subsequent annealing at 350°C for one hour. Resultant glass samples were processed to the required transparency and dimensions by making them flat and polished. Rigaku D/Max ULTIMA III X-ray diffractometer with a CuKα radiation source was used to determine the nature and phase compositions of glass powders. With the help of scanning electron microscope, morphological details of glass samples were recorded. In order to evaluate physical parameters, experimental densities were measured by taking *o*-xylene (99.99% pure) as the buoyant liquid with conventional Archimedes' formula. Using UV-3092 model spectrophotometer, absorption spectra covering 300-900 nm with minor value of 0.1 nm were recorded for all the samples. Hitachi make F-2500 FL Spectrophotometer was used to carry out emission spectra of all test specimens under investigation with 2.5 nm separation ability.

3 Results and Discussion

Using the experimental densities of glass samples, molecular weights and densities of constituent metal oxides, the evaluated average molecular weight, distance between internal titanium ions, and polaron radius are found to decrease with the dopant addition [14, 15]. Very slight changes in the density including molecular weight of the samples are observed. When titanium ions enter the borate network, two basic borate structural units are modified because of replacing heavy metal oxide, i.e., Bi_2O_3 by light TiO_2 [14, 15]. Further, bismuth and zinc ions also occupy modifying positions in the glass network that increases disorder the basic borate glass set of connections. The inter links among all the metal ions (B, Zn, Bi, Ti and O) developed would make the glass samples to exhibit more irregular arrangement as the concentration of titanium ions increased. These observations clearly supported by the increasing trend of other physical parameters such as field strength and concentration of titanium ions. Almost three-fold increments in the values of field strength are noted from the sample with low mol% of titanium oxide $ZBBT_5$ to sample with highest conentent of TiO_2, i.e., $ZBBT_{20}$. One interesting observation is that the addition of dopant has resulted four times rise in the concentration of Ti ions; it could be due to the fact that the introduced titanium ions might occupying octahedral positions with two possible oxidation states while other auxialary ions creating interstitial positions, cracks and voids.

The recorded X-ray diffraction patterns exhibited wide peak at around angle of diffraction 22° to 32° in addition to no signs of sharp peaks which clearly

Table 1. Experimental physical features of ZnO-Bi_2O_3-B_2O_3: TiO_2 samples

Glass	Average mol. wt.	Density (g/cm^3)	Concentration of Ti ions N_i (10^{21}/cm^3)	Inter ionic distance of Ti ions r_i (Å)	Polaron radius r_p (Å)	Field strength (V/m)
$ZBBT_5$	151.84	4.526	8.98	0.48	0.19	79.82
$ZBBT_{10}$	151.82	4.521	17.93	0.38	0.15	126.58
$ZBBT_{15}$	151.81	4.512	26.85	0.33	0.13	165.70
$ZBBT_{20}$	151.79	4.505	35.75	0.30	0.12	200.54

suggests amorphous behavior [14–16]. Another observation is appearance of small bump at 2theta 50° in all samples could also be supporting non-crystalline behavior of samples.

In support of recorded XRD scans, scanning electron microscopic (SEM) pictures reveal that there are no clusters, grains with proper boundaries. However, microcrystal grains with irregular shapes in both the samples were seen those might be possible because of annealing process [16]. Thus, both XRD scans and SEM images allow us to conclude that all the prepared glass samples do not show any kind crystalline nature. The SEM images at different magnifications of 20 μm and 1μm for two samples $ZBBT_5$ and $ZBBT_{20}$ are presented in Figure 2.

The sample containing low mol% of titanium oxide, i.e., $ZBBT_5$ has showed the two optical absorption bands; one is at 525 nm representing 2B2g→2B1g transition. This band is seen in the absorption spectra of all the samples and

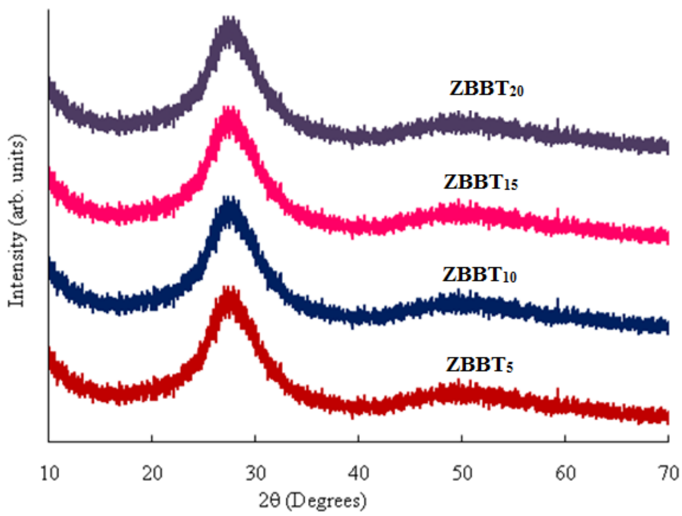

Figure 1. XRD patterns of ZnO-Bi_2O_3-B_2O_3: TiO_2 glasses.

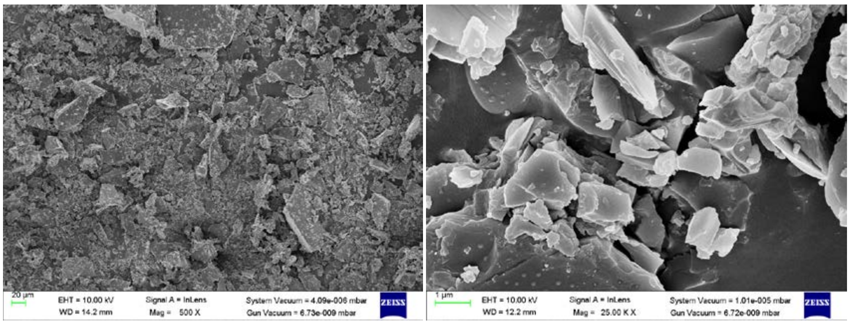

Figure 2. SEM images of $ZBBT_5$ and $ZBBT_{20}$ glasses at different magnifications.

the band intensity is found to increase with the TiO_2 addition. Second band is situated at 684 nm for the aforesaid sample and this transition has been complemented to 2B2g→2A1g [5, 11, 15]. Like first band, band positions and intensity changes have been observed for the remaining samples. Thus, both the bands observed in all the samples are confirming the presence of divalent and trivalent titanium ions. Intensity and peak widths are very low for the $ZBBT_5$ sample due to high percentage of tetravalent Ti ions. $ZBBT_{20}$ has exhibited highest intensity and half-width for both the peaks in comparison with remaining samples. It is associated with the fact that the sample $ZBBT_{20}$ found to have higher concentration of trivalent titanium ions. These ions prefer to take octahedral places thus

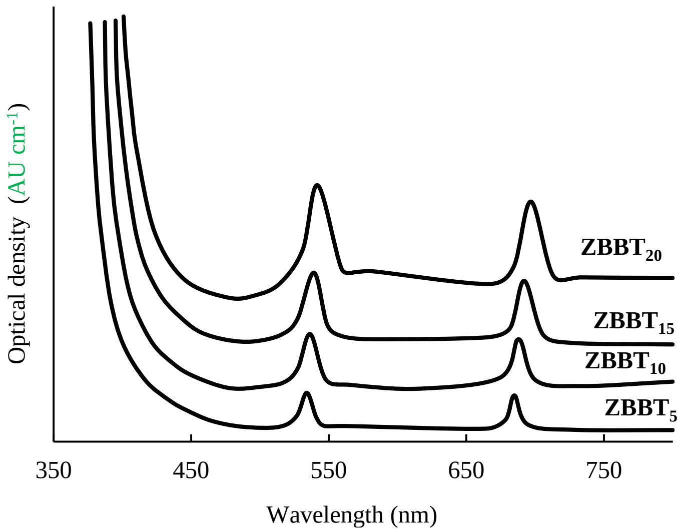

Figure 3. Optical absorption spectra of ZnO-Bi_2O_3-B_2O_3: TiO_2 glasses.

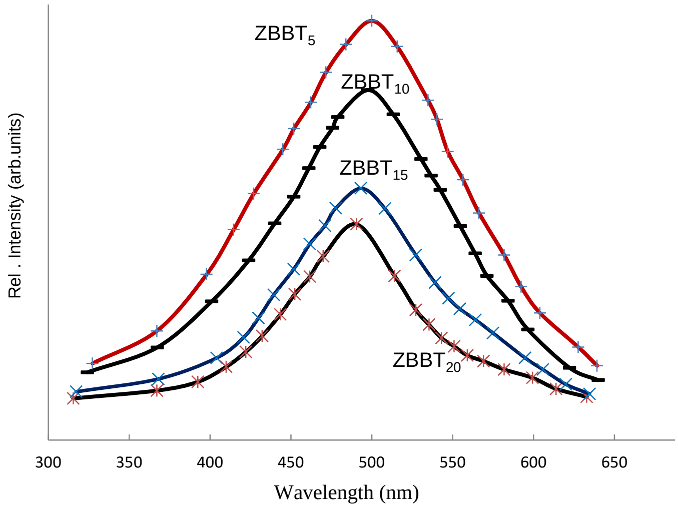

Figure 4. Emission spectra of ZnO-Bi_2O_3-B_2O_3: TiO_2 glasses.

producing significant disorder due to non-bridging oxygens like the behavior of zinc and bismuth ions. It is established fact that increasing disorder among glass network would down the optical gap and cut-off frequencies corresponding to each sample move towards higher wavelength side.

Samples were excited with their corresponding absorption edges to record the emission spectra spanning from 300 to 900 nm and comparison spectra is presented in Figure ‘4. $ZBBT_{20}$ sample displayed the characteristic emission band of titanium ions at around 375 to 560 nm confirming charge transfer nature of titanium ions while intensity and band width found to be small as this sample contains a smaller number of Ti^{4+} ions positioned tetrahedrally [5, 11, 15]. Another fact is that this particular sample has large percentage of dopant that could be the reason to have low concentration of tetravalent titanium ions and subsequent emission behavior.

The sample $ZBBT_5$ also represented the similar emission band at 400 to 600 nm with high intensity and peak breadth compared to all the samples [11, 15]. When the dopant content is low, there might be quite significant Ti^{4+} ions occupying octahedral positions and these ions getting converted into Ti^{3+} ions as content is increased from 0.5 to 2.0 mol%. With the rise in the dopant content, the peak position shifted towards lower wavelength side. Trivalent titanium ions do not contribute to any kind of luminescence while other set of ions are responsible for the emission. TiO6 structural units hosted by the boro-bismuth network in addition to zinc ions would cause the highest intensity of luminescence peaks for $ZBBT_5$. Thus, it facilitates the understanding of gradual transformation of tetravalent Ti ions from octahedral coordination to tetrahedral coordination. Highest luminescence thus exhibited by ZBBT5 due to network positions of titanium ions and relevant coordination symmetry with surrounding other auxiliary ions.

4 Conclusions

XRD scans detail the solid-state natureand SEM imagesdisplayed morphological confirmation of the ZnO-Bi_2O_3-B_2O_3: TiO_2 glass samples. The prepared samples have exhibited absorption bands at about 520 to 545 nm and 675 to 690 nm pertaining to titanium ions confirming the presence of two different oxidation states. $ZBBT_{20}$ sample has shown highest absorption peak-width and intensities for both the optical absorption bands among all samples. Absorption edges displayed red shift with the dopant. The photoluminescence spectra have represented charge transfer broad band of titanium ions at around 480 nm and the sample $ZBBT_5$ shows highest peak intensity and half-width due to larger concentration of tetravalent titanium ions.

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