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Structural studies of mixed glass former ZnO-B₂O₃-P₂O₅:TiO₂ glasses

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Abstract

Study of a series of ZnO-B₂O₃-P₂O₅:TiO₂ glass samples were performed to determine the structural properties. Zinc borophosphate glass samples were prepared by conventional melt quenching technique. The density of the samples was determined in order to study their structure. Inter ionic distance and Polaron radius is studied. The increase in density is due to higher molecular weight of P₂O₅ as compared with B₂O₃. The samples were investigated for structural properties using infrared spectroscopy. The results from infrared transmission spectra showed the presence of trigonal and tetrahedral PO₄, PO₃, BO₄ and BO₃ groups within the host network structure. With the introduction of TiO₂ into the glass network, two bands are appeared due to TiO₄ and Ti-O-Ti symmetric stretching vibrations of TiO₆ structural units.

1. Introduction

In the glasses borate and phosphate are the two fundamental network formers. Both of them were exhibits favorable physical properties for glass forming such as low melting point (T_m) and low glass transition temperature (T_g). These network formers improve the chemical stability of glasses [1]. These materials exhibit good transparency and low melting temperature. The count of B₂O₃ into the phosphate glasses has been to improve the durability of the glasses [2]. The addition of TiO₂ to borophosphate glasses further makes them suitable for applications in optoelectronic devices and integrated circuits. Normally, the ions of titanium, exist in the glass in Ti⁴⁺ state and participate in the glass network forming with TiO₄, TiO₆ and sometimes with TiO₅ structural units [3]. However, there are reports suggesting that these ions may also exist in Ti³⁺ valence state in some of the glass matrices and acts as modifiers [4] such variation in the coordination and valence of titanium ions are expected to cause the structural modifications and expected to influence the spectral properties to a large extent.

2. Experimental Details

The required glass samples are prepared with an increasing concentration TiO_2 into the glass network. The details of the composition of the samples are as follows:

T_0 : 20 ZnO–40 B_2O_3 –40 P_2O_5
 T_5 : 19.5 ZnO–40 B_2O_3 –40 P_2O_5 : 0.5 TiO_2
 T_{10} : 19.0 ZnO–40 B_2O_3 –40 P_2O_5 : 1.0 TiO_2
 T_{15} :18.5 ZnO–40 B_2O_3 –40 P_2O_5 : 1.5 TiO_2

Appropriate amounts of reagent grade ZnO, H_3BO_3 , P_2O_5 and TiO_2 powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 850–900 °C in a PID temperature–controlled furnace for about 1 hour until a bubble–free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 250 °C. The samples used for optical and dielectric studies were prepared by suitable grinding and optical polishing to dimensions of 1.0 cm \times 1.0 cm \times 0.2 cm.

Infrared transmission spectra were recorded on a JASCO–FT/IR–5300 spectrophotometer to an accuracy of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa.

3. Results

The physical parameters such as titanium ion concentration N_i , mean titanium ion separation r_i and polaron radius r_p were evaluated from the measured values of density and calculated average molecular weight \bar{M} using the conventional formulae and were presented in Table 1.

Table 1. Physical parameters of ZnO– B_2O_3 – P_2O_5 : TiO_2 glasses

Sample	Density (g/cm^3)	Ti ion Conc. N_i (10^{21} ions/ cm^3)	Mean Ti ion separation r_i (Å)	Polaron Radius r_p (Å)
T_0	3.041	-	-	-
T_5	3.048	032	34.98	14.26
T_{10}	3.055	0.71	27.24	11.09
T_{15}	3.062	095	24.13	9.820

Infrared transmission spectra of TiO_2 free $\text{ZnO-B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses exhibited conventional vibrational bands due to phosphate groups in the regions 1280 cm^{-1} (anti-symmetrical vibrations of PO_2^- groups / P=O stretching vibrations), 1090 cm^{-1} (a normal vibrational mode of PO_4^{3-} group), 930 cm^{-1} (P-O-P asymmetric bending vibrations) and another band in the region of 760 cm^{-1} due to P-O-P symmetric stretching vibrations [5].

The spectra have also exhibited three usual bands originated from borate groups in the regions 1380 cm^{-1} due to BO_3 units, 950 cm^{-1} due to BO_4 units and 710 cm^{-1} due to bending vibrations of B-O-B linkages (Fig. 1). An additional band in the regions 580 cm^{-1} attributed to the vibrations of TiO_6 structural units is also located [6]. With the gradual increase in the concentration of TiO_2 in the glass network, all the asymmetrical bands are observed to grow at the expense of symmetrical bands. The band due to Ti-O-Ti symmetric stretching vibrations of TiO_4 units.

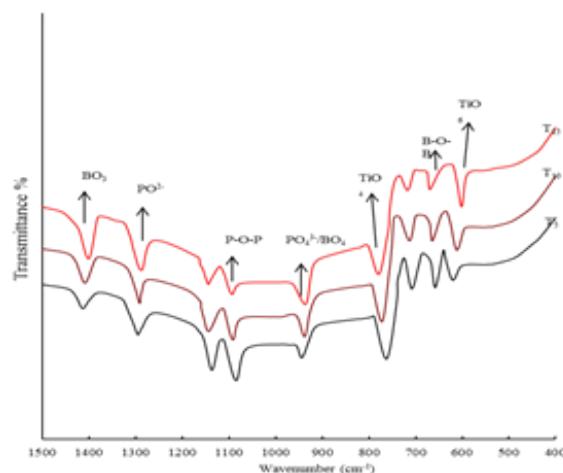


Fig. 1. IR spectra of $\text{ZnO-B}_2\text{O}_3-\text{P}_2\text{O}_5, \text{TiO}_2$ glasses

4. Discussion

P_2O_5 is a strong glass forming oxide, participates in the glass network with PO_4 structural clusters. The PO_4 tetrahedral are linked together with covalent bonding in chains or rings by bridging oxygen's. Neighboring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron. The presence of such PO_4 units in the titled glass samples is evident from the IR spectral studies. B_2O_3 is also a strong glass former, when it is mixed to the phosphate glasses generally, tetrahedral boron entities dominates in the phosphate-rich domain whereas trigonal boron entities prevails in the borate-rich side and form easily B-O-P bridges.

Titanium ions exist mainly in Ti^{4+} state in $\text{ZnO-B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass network. Nevertheless, the reduction of Ti^{4+} to Ti^{3+} is unavoidable during melting at high temperatures and annealing processes of the glasses. Ti^{4+} ions occupy both tetrahedral and substitutional octahedral sites as corner-sharing $[\text{TiO}_6]^{2-}$ units where as Ti^{3+} ions occupy only modifying positions and depolymerize the glass network.

TiO₄ and TiO₆ units of Ti⁴⁺ ions enter the glass network and form linkages of the type P–O–Ti and B–O–Ti.

With the increase in the concentration of TiO₂ the IR spectra revealed the intensity of the bands due to asymmetric vibrations of phosphate groups and also BO₃ groups to grow at the expense of symmetrical bands of phosphate and BO₄ groups. Such variations in the IR spectra suggest an increasing modifying action of titanium ions by creating larger number NBO's. As a result, the phosphate coordination reduces from four fold to three fold, two fold and even to one dimensional and the depolymerization of P–O–P, B–O–B, P–O–B and also P–O–Ti chains takes place and the strength of the glass matrix decreases. Thus the results of IR spectral studies point out that, there is growing degree of disorder in the glass network with the increase in the concentration of TiO₂.

5. Conclusions

The IR spectral studies of these samples have exhibited bands due to TiO₄ and TiO₆ structural units in addition to the conventional bands due to various symmetrical and asymmetrical structural groups. With increase in the concentration of TiO₂, the intensity of symmetrical bands is observed to grow at the expense of asymmetric bands; from these results it is concluded that there is a decreasing degree of disorder in the glass network.

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