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# STUDY OF ZINC-BOROPHOSPHATE GLASSES

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**Abstract:** Zinc-borophosphate glasses having a mole % composition, 30 ZnO - $xB_2O_3$ - (70-x) $P_2O_5$ were prepared by using the melt quench technique. The quantity x had values of 10-40mole %. The mass density of these glasses was found to be in the range of 2.4912 to 3.0142 g $cm^{-3}$. The oxygen packing density and molar volume were estimated to lie in the range 192.385-286.026 g $litre^{-1}$ and 46.78–31.46$cm^3$ respectively. The absorption spectra of these glasses were recorded in the range 190 to 1100nm. No sharp edges were found in the optical spectra, which confirm the amorphous nature of these glasses. The optical band gap energies were found to be in the range 2.40-3.00 eV. It was found that optical band gap energy increases with increasing concentration of $P_2O_5$. The extent of band tailing was worked out from the Urbach plots, which show an exponential dependence of absorption coefficients on photon energies.

**Keywords:** Absorption spectrum, borophosphate glasses, optical band gap energy, Urbach plots.

## INTRODUCTION

To study the nature of materials the absorption spectroscopy is very helpful. A general observation of the absorption versus wavelength spectra can tell whether the material under investigation is amorphous or crystalline in nature. In amorphous materials the absorption edge has a finite slope, but in case of crystalline materials it is very sharp. This technique can also provide information about the optically induced transitions, band gap and band structure of the materials. The band structure of amorphous solids can be described by the CFO Model [Cohen *et al*. 1969], which was further improved by Mott and Davis [1979]. These models provide a picture of the density of states distribution in the energy gap of amorphous semiconducting materials. Various workers [Hogarth and Hosseini 1983, Bausa *et al*. 1991 and Hekmat Shoar *et al*. 1991] have reported experimental results on optical absorption in glassy materials. These measurements of optical absorption coefficients have generally shown an exponential dependence on photon energy. However, the presence of tails at the absorption edges has also been repotted in amorphous materials/glasses [Cohen *et al*. 1969, Hogarth and Ghauri 1979]. These tails are assumed to be due to the inhomogeneties in the glassy materials, structural defects or presence of impurities [Nazar and Ghauri 1982]. The variation of optical band gap of phosphate glasses has been studied as a function of composition [Nazar and Ghauri 1982, Siddiqi *et al*. 1988, Chaudhry *et al*. 1995a,b, Chaudhry *et al*. 1997, Chaudhry and Altaf 1998, and Altaf and Chaudhry 2000], temperature [Bukhari and Nazar 1988] and applied electric field [Ghauri *et al*. 1981, Siddiqi *et al*. 1987].

Most of the published work, or referred above, is concerned with optical properties as well as electrical conduction of these glasses [Ghauri *et al*. 1981, Nazar and Ghauri 1982, Siddiqi *et al*. 1987, Bukhari and Nazar 1988, Siddiqi *et al*. 1988, Chaudhry *et al*. 1995a,b, Chaudhry *et al*. 1997, Chaudhry and Altaf 1998, and Altaf and Chaudhry 2000, Altaf *et al*. 2001]. However, the optical properties of zinc-borophosphate glasses have not gained much attention to the best of our knowledge. The present work is focused on the mass density and optical absorption of these glasses on the bases of addition of second glass former in a glass composition.

## MATERIALS AND METHODS

All zinc-borophosphate glasses were prepared with different compositions as listed in Table 1. These samples were prepared in platinum crucible from analytical grade oxides of zinc, boron and phosphorous. The crucible containing specified proportion of the oxides was placed in a muffle furnace at 1100ºC for three hours. The melt was occasionally stirred to attain homogeneity. The melt was quenched to form disc-shaped samples. These samples were annealed at 200ºC for two hours to eliminate mechanical and thermal stresses.

**Table 1:** Various physical and optical parameters of Zinc-Borophosphate glasses.

| Composition (mole %) | Thickness (cm) | Density (g $cm^{-3}$) | Oxygen Packing density (g-atom $litre^{-1}$) | Molar volume ($cm^3$) | $E_{opt}$ (eV) | ΔE (eV) |
|---|---|---|---|---|---|---|
| $30ZnO\text{-}10B_2O_3\text{-}60P_2O_5$ | 0.160 | 2.4912 | 192.385 | 46.78 | 3.00 | 1.28 |
| $30ZnO\text{-}20B_2O_3\text{-}50P_2O_5$ | 0.179 | 2.6962 | 221.994 | 40.54 | 2.80 | 1.11 |
| $30ZnO\text{-}30B_2O_3\text{-}40P_2O_5$ | 0.124 | 2.8583 | 252.015 | 35.71 | 2.60 | 1.01 |
| $30ZnO\text{-}40B_2O_3\text{-}30P_2O_5$ | 0.176 | 3.0142 | 286.026 | 31.46 | 2.40 | 1.21 |

The densities of these glasses were estimated by using a volumetric method. The optical absorption spectra for these glasses listed in Table 1, were obtained in UV-near infrared region (i.e. 190 to 1100 nm) by using a Hitachi U-2001 double beam spectrophotometer. A representative spectrum is depicted in Fig. 1. The absorption spectra of these glasses show no sharp absorption edge in the UV-visible region. This suggests that the samples are amorphous in nature. The optical absorption coefficient $\alpha(\omega)$ was calculated for each specimen at various photon energies ($\hbar\omega$) by using the Lambert-Bear relation

$$I_t = I_o\, e^{-\alpha(\omega)d} \qquad (1)$$

Where d is the thickness of the sample, $\alpha(\omega)$ is the absorption coefficient, $I_o$, $I_t$ are the intensity of the incident and transmitted photon beams.

## RESULTS AND DISCUSSION

The measured values of density of zinc-borophosphate glasses are listed in Table 1 and depicted in Fig. 2 as a function of $B_2O_3$ concentration. In these glasses, density increases with increasing concentration of $B_2O_3$. Addition of $B_2O_3$ in zinc phosphate glasses, causing an increase in

oxygen packing density as depicted in Fig. 3. The increase in oxygen packing density may squeeze the structure of the sample which in turn causes a decrease in the molar volume as depicted in Fig. 4. The decrease in molar volume of the substance produces an increase in the mass density of the glasses. This may be due to the replacement of an equal amount of low bond strength glass former $P_2O_5$ with $B_2O_3$, which has high bond strength [Kirk Othmer 1963].

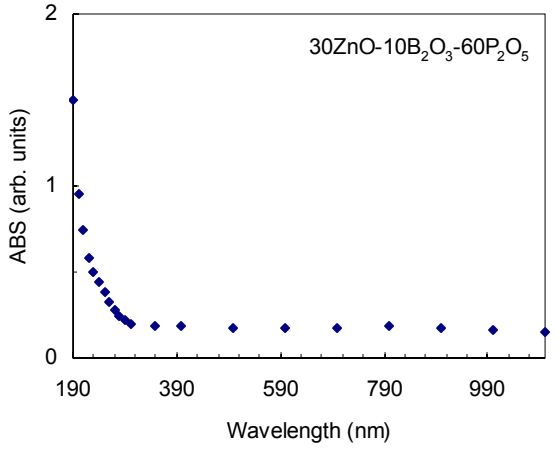


**Fig. 1:** A representative spectrum of absorption versus wave length (nm) for the glass composition $30ZnO\text{-}10B_2O_3\text{-}60P_2O_5$.

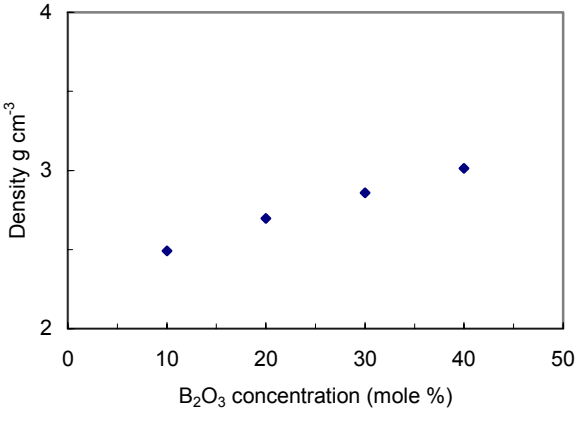


**Fig. 2:** Increase in mass density with the increasing concentration of $B_2O_3$ in zinc-boro phosphate glasses.

The optical absorption coefficients, $\alpha(\omega)$, were calculated at different wavelengths through Eq. (1). This is related to the optical band gap energy, $E_{opt}$, through Mott and Davis [1979] relation:

$$\alpha(\omega) = B\,(\hbar\omega - E_{opt})^n / \hbar\omega \qquad (2)$$

where B is a constant and n is the index which may have different values depending on the mechanism of inter-band transitions.

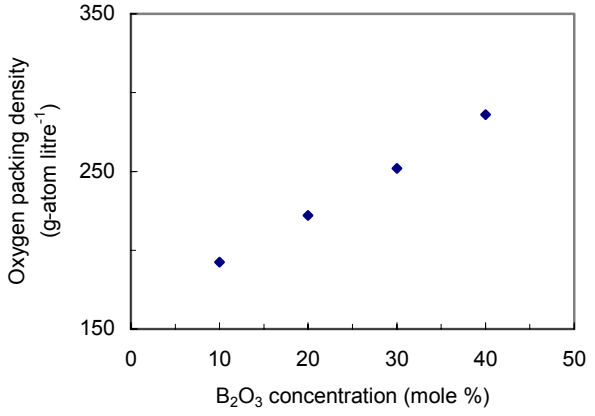


**Fig. 3:** Increase in oxygen packing density with the increasing concentration of $B_2O_3$ in zinc-borophosphate glasses.

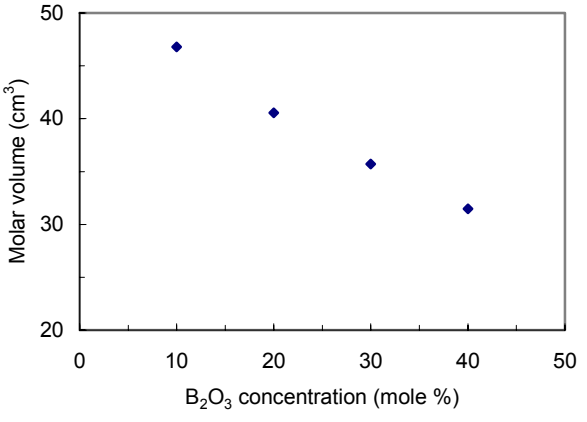


**Fig. 4:** Decrease in molar volume with the increasing concentration of $B_2O_3$ in zinc-boro phosphate glasses.

In most of the glass systems, Eq. (2) presents a straight line response as shown in a representative plot in Fig. 5, for n = 2 and is associated with indirect-like transitions [Mott and Davis 1979]. To estimate the values of band gap energies linear region is extrapolated to meet the $\hbar\omega$ axis at $(\alpha\hbar\omega)^{1/2}=0$. The values of $E_{opt}$ are listed in Table 1 and depicted against the $B_2O_3$ concentration in Fig. 6. It can be observed that the optical band gap energies decrease with increasing amount of $B_2O_3$. This shows that absorption is shifted from UV to visible region and hence the values of $E_{opt}$ shifted from higher energies towards lower ones i.e. 3.00 to 2.40 eV

as $B_2O_3$ concentration increases. These results are similar to the published data [Ahmad and Hogarth 1983, Siddiqi *et al*. 1988, Altaf and Chaudhry 2000]. It is well known that $B_2O_3$ is a high quality glass former, which alters the structure of zinc phosphate. This might have altered the energy states in the forbidden gap causing the optical band gap to decrease with increasing concentration of $B_2O_3$.

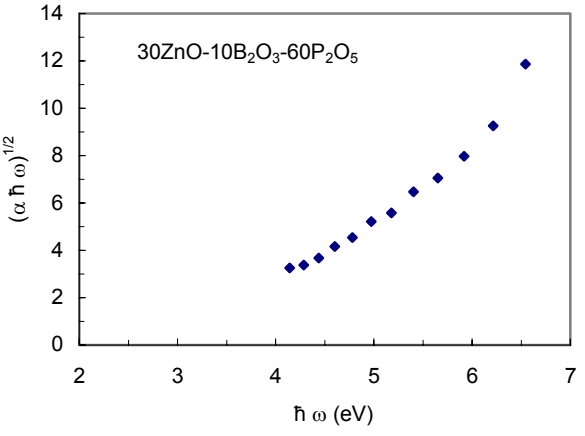


**Fig. 5:** A representative plot of $(\alpha\hbar\omega)^{1/2}$ Vs photon energy ($\hbar\omega$) for the glass composition $30ZnO\text{-}10B_2O_3\text{-}60P_2O_5$.

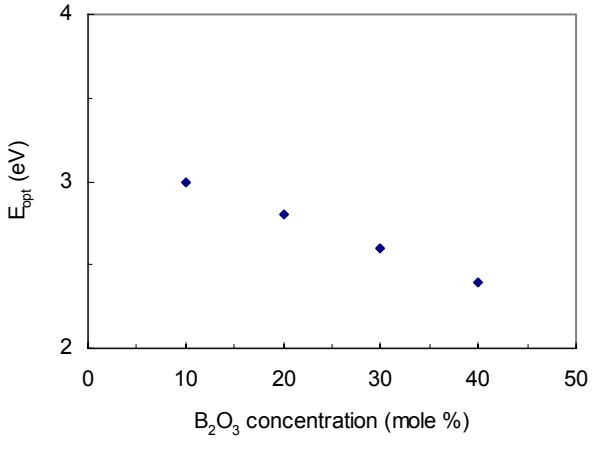


**Fig. 6:** Decrease in optical band gap with increasing concentration $B_2O_3$ in zinc-boro-phosphate glasses.

The fundamental absorption edge usually follows the Urbach rule [Mott and Davis 1979]

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega / \Delta E) \qquad (3)$$

where $\alpha_o$ is a constant, $\Delta E$ is a measure of the band tailing and is known as Urbach energy. A representative plot of log $\alpha(\omega)$ versus $\hbar\omega$ is depicted

in Fig.7 to illustrate the validity of this rule. The results of Urbach energy are plotted against $B_2O_3$ concentration in Fig. 8, which are listed in Table 1.

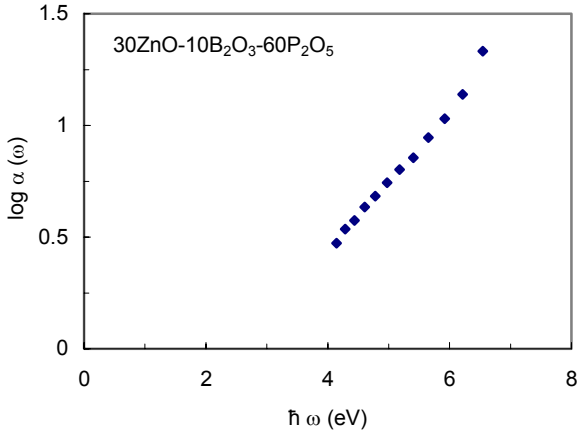


**Fig. 7:** A representative graph of log $\alpha$ vs ($\hbar\omega$) for the glass composition 30ZnO-10$B_2O_3$-60$P_2O_5$.

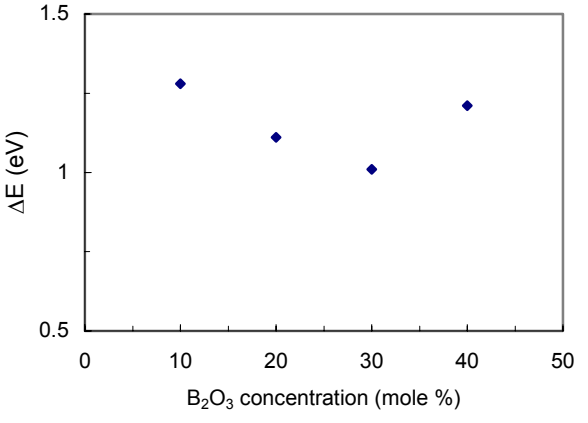


**Fig. 8:** Variation of $\Delta E$ with the change in concentration of $B_2O_3$.

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