

## STUDY OF OPTICAL BAND GAP OF ZINC-BORATE GLASSES

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**Abstract:** The present study deals with binary  $x\text{ZnO}-(100-x)\text{B}_2\text{O}_3$  ( $x=50-60\%$ ) and ternary  $y\text{V}_2\text{O}_5-50\text{ZnO}-(50-y)\text{B}_2\text{O}_3$  ( $y=5-10\%$ ) glass systems. The mass density, oxygen packing density, molar volume and optical energy gap of these glasses were measured at room temperature. The density varies in the range of  $2.92 - 3.57 \text{ g/cm}^3$ . The absorption spectra of these glasses were recorded in the UV-visible range. The optical band gap energies for these glasses were estimated from absorption data using the Mott and Davis relation and found to be in the range of  $1.14\sim 2.92 \text{ eV}$ . These results show that  $E_{\text{opt}}$  decreases with decreasing concentration of ZnO in binary glasses. In ternary glasses  $E_{\text{opt}}$  decreases with increasing concentration of  $\text{V}_2\text{O}_5$  for a fixed amount of ZnO.

**Keywords:** Absorption spectra, borate glasses, optical energy gap, oxygen packing density.

### INTRODUCTION

Optical absorption spectra are a useful tool to study the optically induced transitions, energy gap and band structure of crystalline and non-crystalline materials. Particularly, measurement of the optical absorption coefficient near the fundamental absorption edge is a standard method for the investigation of optically induced electronic transitions in many materials. Two types of optical transitions, i.e. direct and indirect, occur at the absorption edge [Mott and Davis 1979]. These transitions occur when an electromagnetic wave interacts with a valence electron and raises it across the energy gap to the conduction band. However, indirect transitions involve simultaneous interaction with lattice vibrations and the wave vector of the electron.

The fundamental absorption edge in most amorphous materials usually follows the Urbach rule [Urbach 1953]

$$\alpha(\omega) = \alpha_0 \exp [\hbar\omega / \Delta E] \quad (1)$$

where  $\omega$  is the angular frequency of radiations,  $\Delta E$  is a measure of the extent of band tailing and  $\alpha_0$  is a constant. Tauc [1970] suggested that such absorption edges in non-crystalline materials could arise from interband transitions involving tails of the localized states where density of states falls exponentially. The absorption in most of the amorphous materials is believed to be associated with indirect transitions [Hogarth and Ghauri 1979] and is observed to obey the following relation above the exponential tail:

$$E_{\text{opt}} = \hbar\omega - (\alpha \hbar\omega / B)^{1/2} \quad (2)$$

Where  $\alpha$  is the absorption coefficient, B a constant and  $E_{\text{opt}}$  the optical energy gap. Experimental results on optical absorption in various glasses have been reported by Mott and Davis [1979], Bausa *et al.* [1991] and Hekmat Shoar *et al.* [1991]. The measurements of optical absorption

coefficient have generally shown an exponential dependence on photon energy [Hogarth and Hosseni 1983]. However, the presence of tails in the absorption has also been reported in oxide glasses [Hogarth and Ghauri 1979]. These tails are supposed to be due to the existence of structural defects, impurities or other types of inhomogeneities that may be present in these glasses [Siddiqi *et al.* 1987]. 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, Nadeem *et al.* 1993, Bilal *et al.* 1994, Chaudhry *et al.* 1995 and 1997, Chaudhry and Altaf 1998, Altaf and Chaudhry 2000], applied electric field [Ghauri *et al.* 1981, Siddiqi *et al.* 1987] and temperature [Bokhari *et al.* 1988].

### MATERIALS AND METHODS

Binary and ternary borate glasses were prepared with different compositions as listed in Table 1. All the samples were prepared in platinum crucible from analytical grade oxides of boron, zinc and vanadium. The crucible containing requisite proportions of boron oxide, zinc oxide and vanadium oxide was placed in a muffle furnace at 1100 °C for three hours to attain homogeneity in the melt, which was occasionally stirred. Finally, the melt was quenched to form disc-shaped samples. The samples were annealed at 200 °C for two hours to eliminate mechanical and thermal stresses.

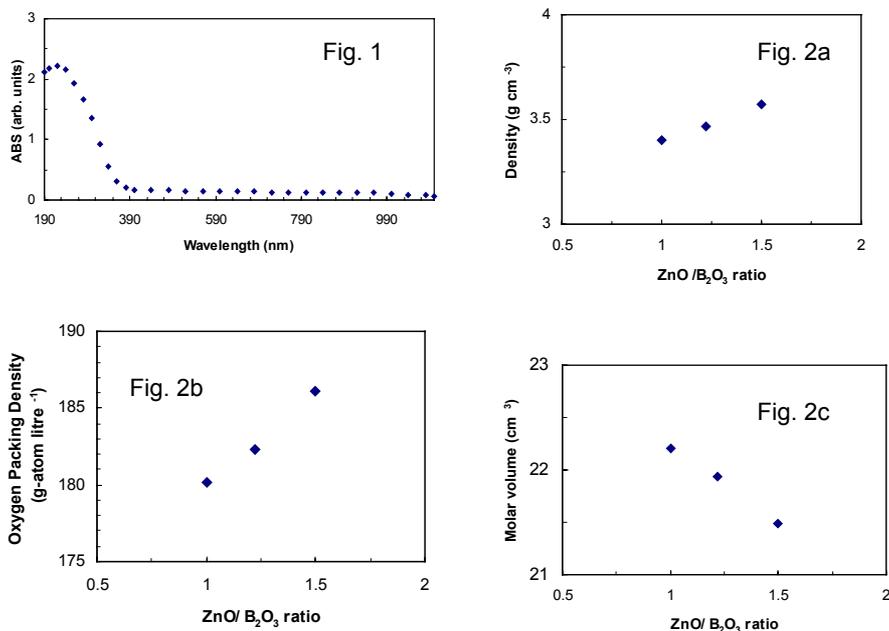
**Table 1:** Various optical and physical parameters of binary and ternary borate glasses.

Composition (mole %)	Thickness (cm)	Density (g cm <sup>-3</sup> )	Oxygen Packing Density (g-atom litre <sup>-1</sup> )	Molar Volume cm <sup>3</sup>	E <sub>opt</sub> (eV)	ΔE (eV)
60ZnO-40B <sub>2</sub> O <sub>3</sub>	0.198	3.57	186.13	21.49	2.92	0.17
55ZnO-45B <sub>2</sub> O <sub>3</sub>	0.186	3.47	182.32	21.94	2.71	0.21
50ZnO-50B <sub>2</sub> O <sub>3</sub>	0.130	3.40	180.17	22.20	2.53	0.23
5V <sub>2</sub> O <sub>5</sub> -50ZnO-45B <sub>2</sub> O <sub>3</sub>	0.199	2.92	323.56	27.82	1.67	1.25
10V <sub>2</sub> O <sub>5</sub> -50ZnO-40B <sub>2</sub> O <sub>3</sub>	0.197	3.13	324.41	27.74	1.14	0.82

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

$$I_t = I_o e^{-\alpha(\omega) d} \quad (3)$$

where  $d$  is the thickness of the sample,  $I_o$  and  $I_t$  are the incident and the transmitted photon intensity respectively.



**Fig. 1:** A representative plot of absorbance vs. photon energy ( $\hbar\omega$ ) for the glass composition 60ZnO-40B<sub>2</sub>O<sub>3</sub>.

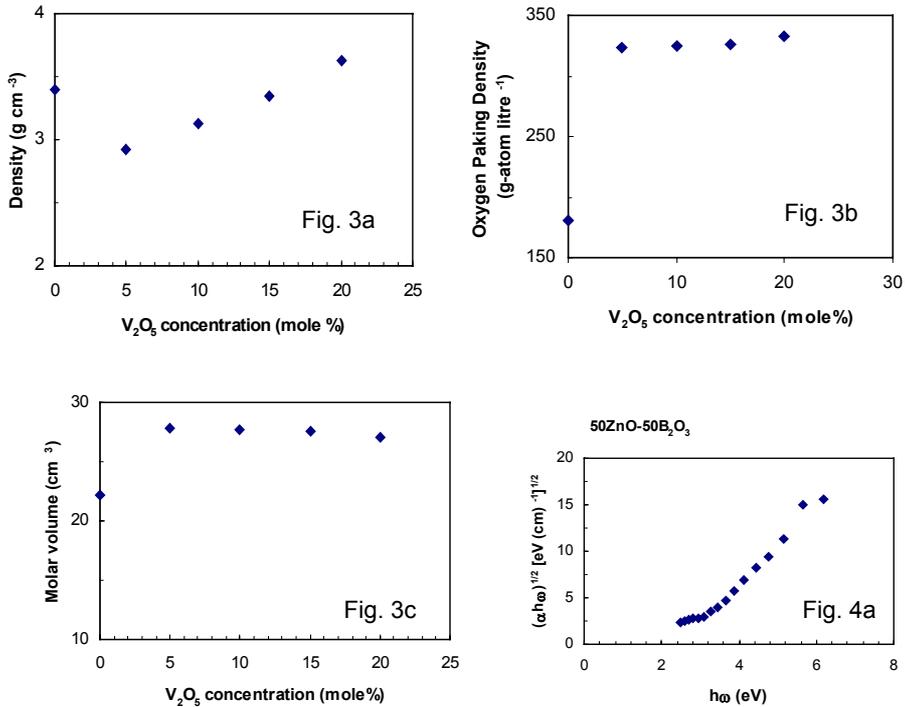
**Fig. 2a:** Increase in density with the increasing ratio of ZnO/B<sub>2</sub>O<sub>3</sub> in zinc-borate glasses.

**Fig. 2b:** Increase in oxygen packing density with the increasing ratio of ZnO/B<sub>2</sub>O<sub>3</sub> in zinc-borate glasses.

**Fig. 2c:** Decrease in molar volume with the increasing ratio of ZnO/B<sub>2</sub>O<sub>3</sub> in zinc-borate glasses.

## RESULTS AND DISCUSSION

The measured densities of the binary zinc-borate and ternary vanadium-zinc-borate glasses are listed in Table 1 and depicted in Figs. 2a and 3a respectively as a function of composition. In binary glass system it can be observed that density decreases with decreasing concentration of ZnO, which act as an intermediate/modifier in a glass system. Addition of ZnO in zinc borate glasses shows an increase in oxygen packing density (Fig. 2b), which squeezes the structure [Morey 1960] of the sample which in turn causes a decrease in the molar volume as depicted in Fig. 2c and hence an increase in the density of the glasses. In ternary vanadium-zinc-borate glasses increasing concentration of V<sub>2</sub>O<sub>5</sub> causes an increase in oxygen packing density and decrease in molar volume as presented in Fig. 3(b, c) respectively. In these glasses increase in packing density may lead to an increase in density of the glass system. This increase in density is also linked with replacement of low density glass former B<sub>2</sub>O<sub>3</sub> with high density former V<sub>2</sub>O<sub>5</sub> [Chaudhry *et al.* 1995, Altaf and Chaudhry 2000].



**Fig. 3a:** Variation of density with the increasing concentration of V<sub>2</sub>O<sub>5</sub> in ternary vanadium-zinc-borate glasses.

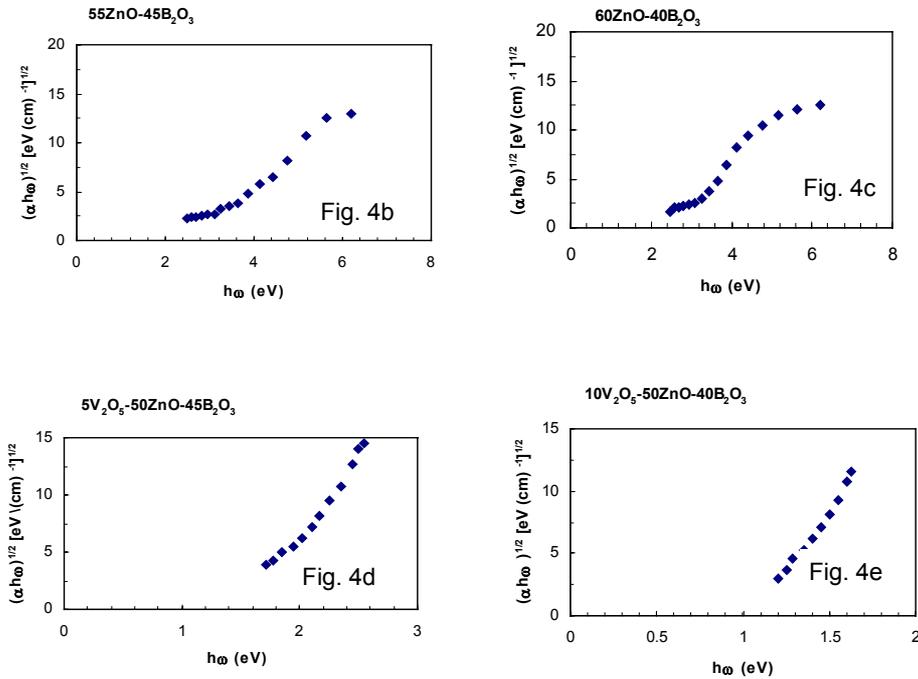
**Fig. 3b:** Variation of oxygen packing density with the increasing concentration of V<sub>2</sub>O<sub>5</sub> in ternary vanadium-zinc-borate glasses.

**Fig. 3c:** Variation of molar volume with the increasing concentration of V<sub>2</sub>O<sub>5</sub> in ternary vanadium-zinc-borate glasses.

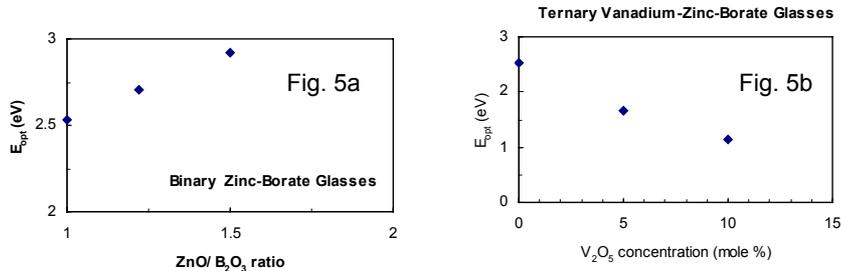
**Fig. 4a:** A plot of  $(\alpha\hbar\omega)^{1/2}$  vs. photon energy ( $\hbar\omega$ ) for the glass composition 50ZnO-50B<sub>2</sub>O<sub>3</sub>.

Usually  $(\alpha\hbar\omega)^{1/2}$  is plotted as a function of photon energy  $\hbar\omega$  to find the optical band gap energy ( $E_{\text{opt}}$ ) using Eq. (2) [Mott and Davis 1979]. This relation holds well above the exponential tail, where it shows linear behavior. The straight region in these curves is extrapolated to meet the  $\hbar\omega$  axis at  $(\alpha\hbar\omega)^{1/2} = 0$ . The value of  $\hbar\omega$  at the meeting point yields a direct measure of optical energy gap. These plots are shown in Figs. 4(a-e) and measured values of  $E_{\text{opt}}$  for these glasses are listed in Table 1. The results are depicted in Figs. 5(a-b) to examine the effect of composition on optical band gap.

In the binary zinc borate glasses the optical band gap energy was found to increase with increasing concentration of ZnO while in ternary vanadium-zinc-borate glass system optical band gap energy was found to decrease with increasing V<sub>2</sub>O<sub>5</sub> content. It is obvious from the above observations that the value of the optical band gap energy is dependent of glass composition.



**Fig. 4:** Plots of  $(\alpha h\nu)^{1/2}$  vs. photon energy ( $h\nu$ ) for borate glasses having compositions:  
 b: 55ZnO-45B<sub>2</sub>O<sub>3</sub>, c: 60ZnO-40B<sub>2</sub>O<sub>3</sub>  
 d: 5V<sub>2</sub>O<sub>5</sub>-50ZnO-45B<sub>2</sub>O<sub>3</sub>, e: 10V<sub>2</sub>O<sub>5</sub>-50ZnO-40B<sub>2</sub>O<sub>3</sub>.



**Fig. 5a:** Increase in optical bandgap with increasing ratio of ZnO/B<sub>2</sub>O<sub>3</sub> in zinc-borate glasses.

**Fig. 5b:** Decrease in optical bandgap with increasing concentration of V<sub>2</sub>O<sub>5</sub> in vanadium-zinc-borate glasses.

Hogarth and Ghauri [1979] measured the optical band gap of cadmium zinc phosphate glasses by absorption measurements and reported an increase in the bandgap with increasing ZnO content. According to their view, addition of divalent oxides like CaO, MgO, PbO, ZnO etc. depolarizes phosphate chain of phosphate glasses. It is generally accepted that absorption edge depends on the oxygen bond strength in

the glass-forming network [McSwain *et al.* 1963]. This process changes the oxygen bonding in the glass-forming network, and any change of oxygen bonding in glass network such as the formation of non-bridging oxygen changes the absorption characteristics. This explains why the absorption edges, and hence  $E_{\text{opt}}$ , move toward the higher energies with increasing concentration of ZnO in zinc borate glasses.

In ternary  $V_2O_5$ -ZnO- $B_2O_3$  glass system the absorption is shifted from UV to visible region and the value of  $E_{\text{opt}}$  moves toward lower energies from 2.53 to 1.14 eV as the vanadium concentration increases. This is in good agreement with the published data [Koffyberg and Koziol 1976, Ahmad and Hogarth 1983].

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