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VARIATION OF BAND GAP WITH COMPOSITION IN ZINC PHOSPHATE GLASSES

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Abstract: Binary zinc-phosphate glasses having mole% composition (x)ZnO-(100-x)P_2O_5 were prepared in Alumina crucible by melt quench technique, where quantity x has values 20-60 mole%. The optical absorbance studies were carried out on these glasses to measure their energy gaps. The absorption spectra of these glasses were recorded in the UV-Visible region. No sharp edges were found in the optical spectra, which verifies the amorphous nature of these glasses. The optical band gap energies for these glasses were found to be in the range 3.39 to 3.68 eV.

Keywords: Absorption spectra, binary zinc-phosphate glasses, optical bandgap.

INTRODUTION

Interest in the study of phosphate glasses arose due to their easy preparation and low melting points compared with borate and silicate glasses, which have been studied extensively. The phosphate glasses are more conductive electrically in comparison to other glass systems and thus are potential candidates for superionic conductors, electrolytes [Rao 1990]. The main problem associated with these glasses is their hygroscopic nature and poor chemical stability, which can be overcome by adding certain modifiers such as lead oxide etc.

The composition of glasses is changed to modify their thermo-chemical stability and to improve their electro-optical characteristics. It has been observed that optical band gap of cadmium phosphate [Ghauri *et al*. 1981] and manganese phosphate [Siddiqi *et al*. 1988] glasses, measured with photoconduction method, changes with their composition. Similarly activation energy is found to decrease monotonically with increasing proportion of CdO in cadmium phosphate binary glass systems [Ghauri and Hogarth 1980]. In zinc phosphate binary glasses density and refractive index are known to increase with increasing ZnO [Morey 1954]. Reports about zinc borate glasses indicate an increase in the optical band gap with increasing proportion of ZnO [Ahmad and Hogarth 1983]. However, no such data is available, to the best of our knowledge, for zinc phosphate binary glass systems. The work in hand is presented to fill this gap and to see how the variation of ZnO affects the band gaps of these glasses.

MATERIALS AND METHODS

The glasses used for the present study were prepared as 20 grams samples by the melt quench technique. The details of glass preparation are reported elsewhere [Chaudhry and Bilal 1995]. For optical absorption measurements all the samples were polished using silicon carbide papers of different grades. The optical absorption spectra for a range of zinc phosphate glass samples were recorded in the UV-Visible spectral range (190-700 nm) at room temperature using a Hitachi U-2000 Spectrophotometer.

RESULTS AND DISCUSSION

The optical absorption spectra recorded as a function of wavelength in the UV-Visible range for various compositions of zinc phosphate binary glasses as listed in Table1 are shown in Fig. 1. This figure points out three features. Firstly, it shows that the absorption edges are not sharp which is an indication of glassy or amorphous nature of our samples. Secondly, it demonstrates that the absorption edges shift towards higher energy with the increasing amount of ZnO. Thirdly, it manifests that there is not any structure in the visible part of the spectrum and a very little amount of radiation is absorbed in this region of wavelengths.

Table 1: Variation of optical band gap of Zinc Phosphate glasses.

Glass Composition mole%		Thickness	Optical Band Gap	Constant	Band Tail Energy
ZnO	P_2O_5	d (cm)	E_{opt} (eV)	B	ΔE (eV)
20	80	3.58	3.5	28.09	0.05
30	70	3.11	3.65	56.85	---
40	60	1.51	3.67	53.29	---
50	50	2.98	3.68	10.1	---
60	40	3.07	3.39	6.05	---

To further illustrate the second observation, the absorption coefficients $\alpha(\omega)$ were determined, near the absorption edge, at different photon energies for all glass samples by using the relation $\alpha(\omega) = 2.303\ A/d$, where A is the absorbency and d is the thickness of the samples. The quantity $\alpha(\omega)$ can be displayed in a number of ways [Mott and Davis 1979] as described by the relation

$$\alpha(\omega) = B\,(\hbar\omega - E_{opt})^n / \hbar\omega \qquad (1)$$

where B is a constant, E_{opt} is the optical band gap energy and the index n can have any value between 1/2 and 3 depending on the nature of the interband electronic transitions [Al-Ani and Higazy 1991]. It has been observed that for indirect allowed transitions the measured absorption data fits well to equation (1) for n = 2 [Mott and Davis 1979, Hogarth and Nadeem 1981]. These results are, therefore, plotted as $(\alpha\hbar\omega)^{1/2}$ versus photon energy ($\hbar\omega$) in Fig. 2, for indirect allowed transitions to find the values of the optical band gap E_{opt}. It can be seen that there exists a linear dependence of $(\alpha\hbar\omega)^{1/2}$ in the photon energy ($\hbar\omega$) except at low photon energies where a band tailing comes into picture. This suggests that at higher photon energies the transitions occurring in the present glass samples are of indirect type. The values of the optical band gaps

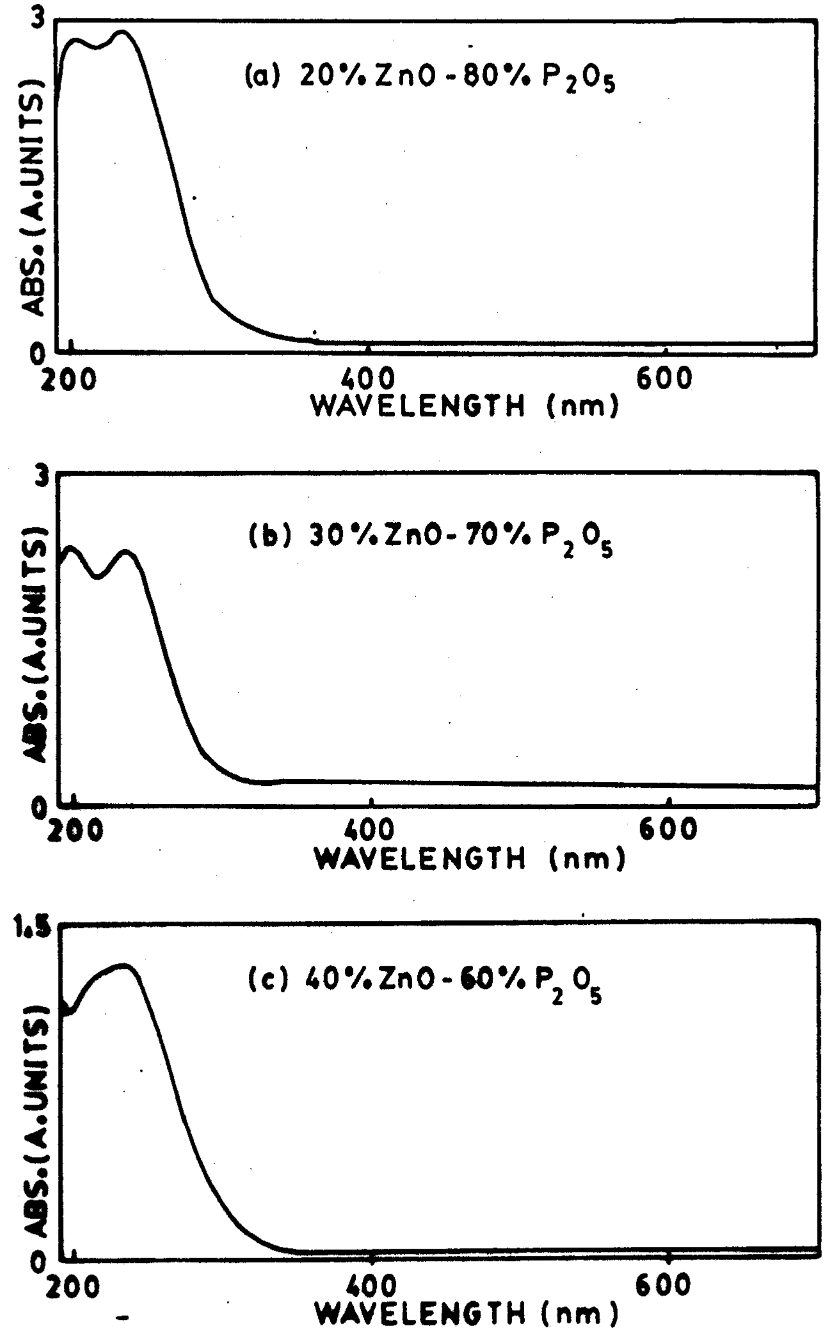
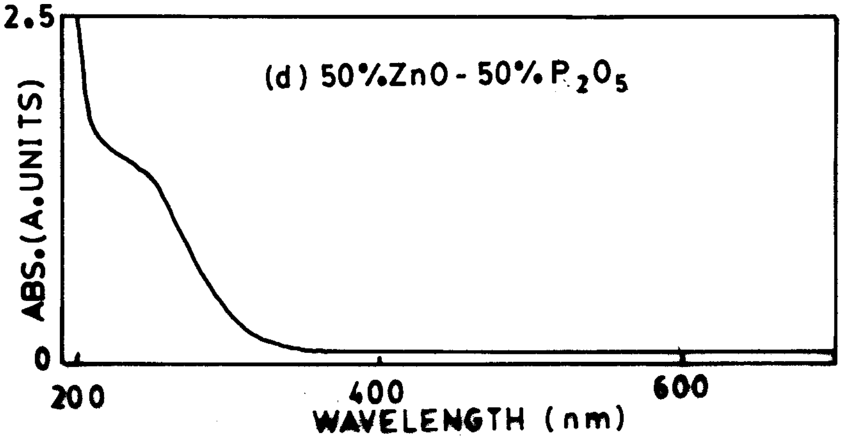


Fig. 1. Continued.

are obtained by the extrapolation of the linear region to meet ($\hbar\,\omega$) axis at $(\alpha\,\hbar\omega)^{1/2} = 0$. These values are listed in Table 1 and are depicted in Fig. 3 as a function of ZnO/P_2O_5 ratio. It can be noticed that the optical band gap slightly increases with increasing amount of ZnO from 20 - 50 mole%



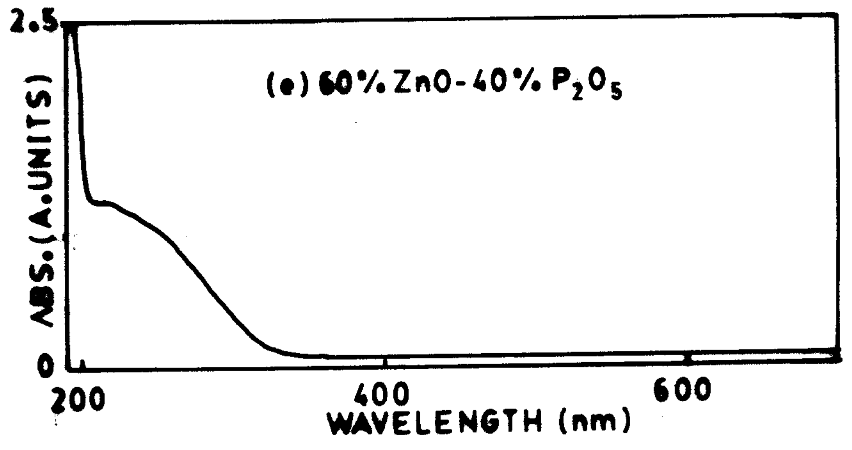


Fig. 1. Optical absorption versus wavelength curves for various compositions of zinc phosphate binary glass system.

and then decreases at 60mole%. This trend of results related to binary phosphate glasses having ZnO concentration of 20-50 mole% is similar to the behavior of density and refractive index of zinc phosphate glasses [Morey 1954]. The decrease in optical band gap of glass prepared with 60mole% of ZnO is due to the presence of the white spots physically observed in the sample. This sort of behavior has also been observed in some other samples such as barium-germinate glass [Asif 2000]. The white spots are related to imperfect mixing of all the components of the given composition due to lack of required temperature as limited by available furnace.

Depolymerization is known to occur [Chakraborty and Paul 1989] in phosphate glasses with the addition of alkali oxides (K_2O, Na_2O etc), alkaline earth oxides (CaO, MgO etc.) and many other divalent metal oxides such as ZnO, PbO etc. Consequently the average chain length is shortened. It also opens up the chain by breaking those oxygen bonds, which form a bridge between the corners of PO_4 tetrahedra. In this way amount of non-bridging oxygen grows high concentration due to a change in the oxygen bonding. The absorption edge depends on the oxygen bond strength in the glass-forming network. This explains why the optical band gap increases in the zinc phosphate binary glasses examined in the present work with increasing ZnO proportion. Similar results have been reported for zinc borate glasses by Ahmad and Hogarth [1983].

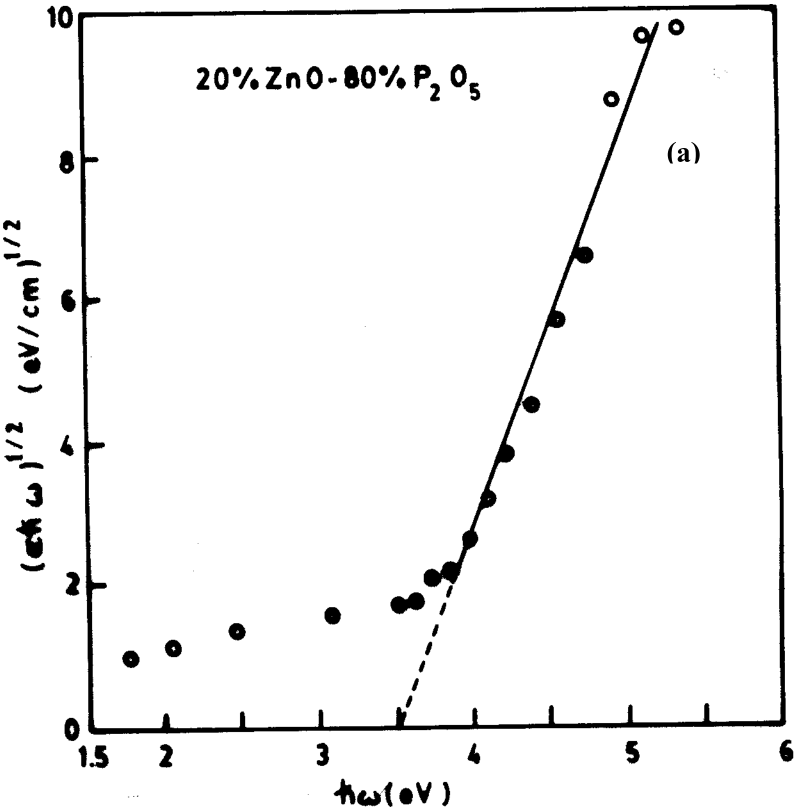
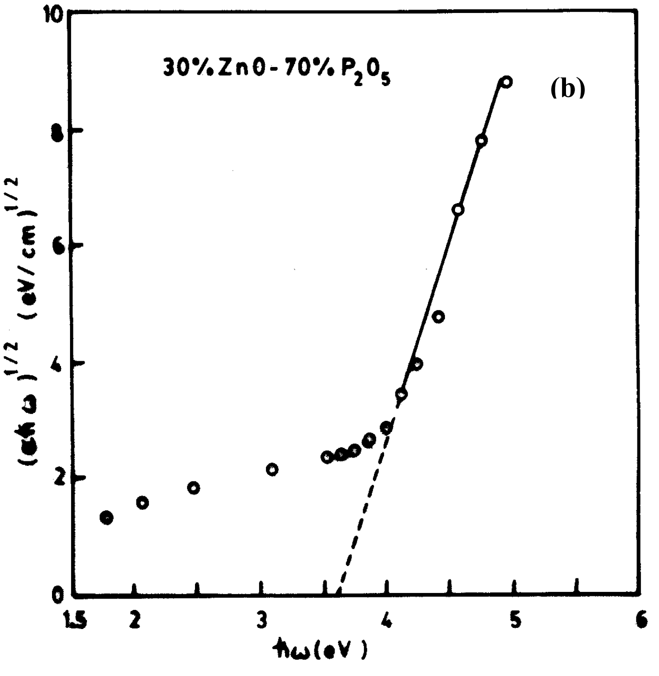


Fig. 2a. (Continued).

The optical absorption coefficient depicts an exponential response with photon energy as represented in Fig. 4 for the present glass system. This behavior of these glass samples is in line with the equation

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega/\Delta E) \qquad (2)$$

where α_o is a constant and ΔE is the width of the tails of localized states. An edge that obeys equation (2) is called Urbach edge and samples that illustrate this edge are said to follow the Urbach rule [Urbach 1953].



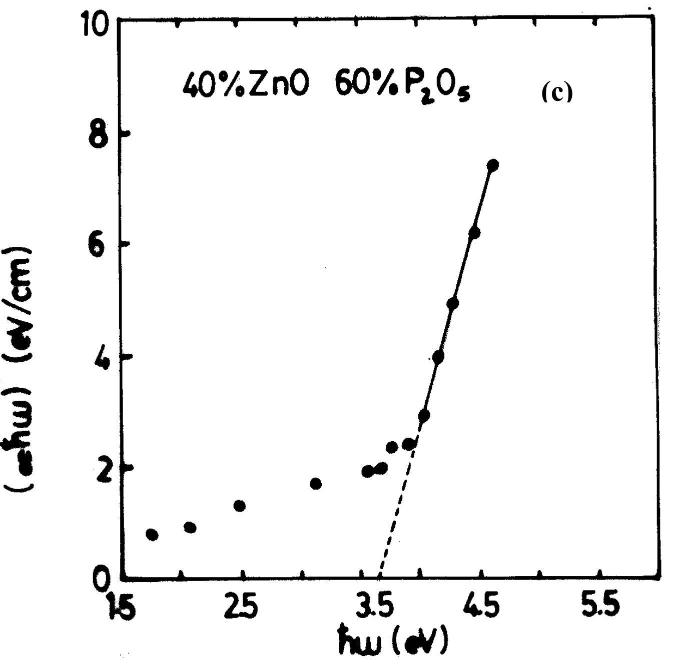


Fig. 2b,c. (Continued).

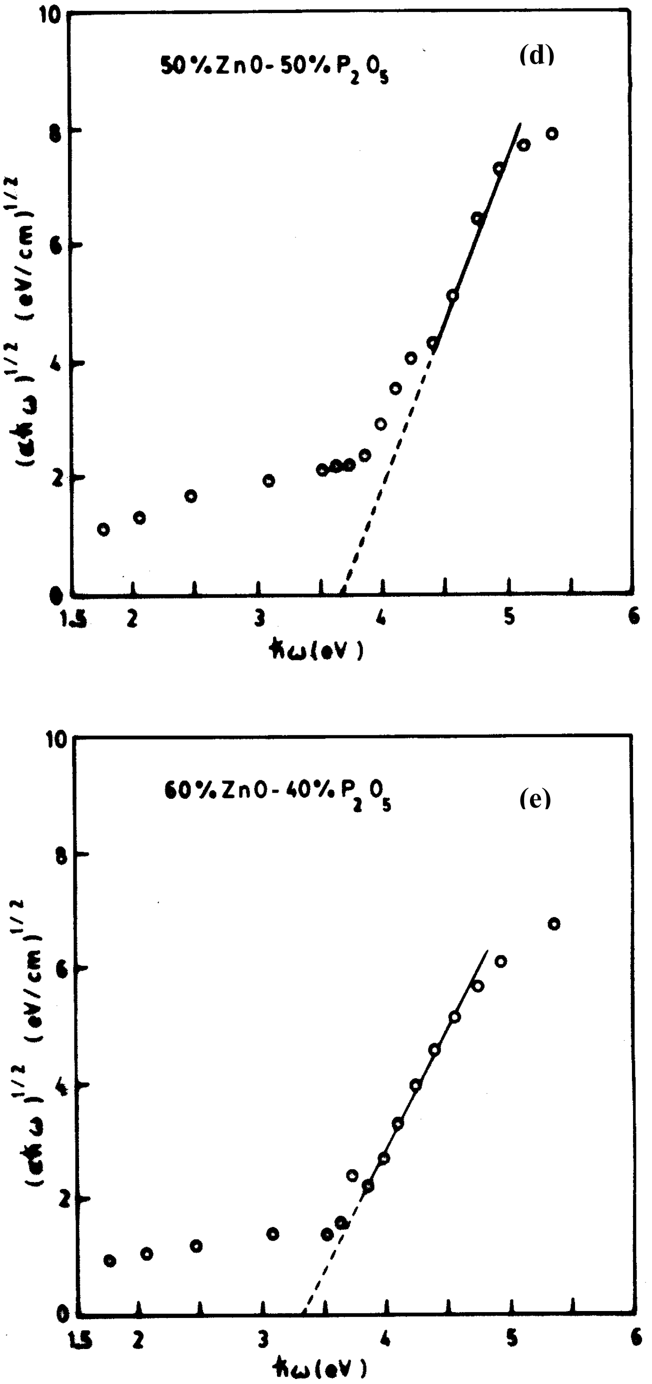


Fig. 2(d, e). Plot of the quantity $(\alpha \hbar\omega)^{1/2}$ versus photon energy ($\hbar\omega$) for zinc phosphate glass compositions to obtain the optical band gaps.

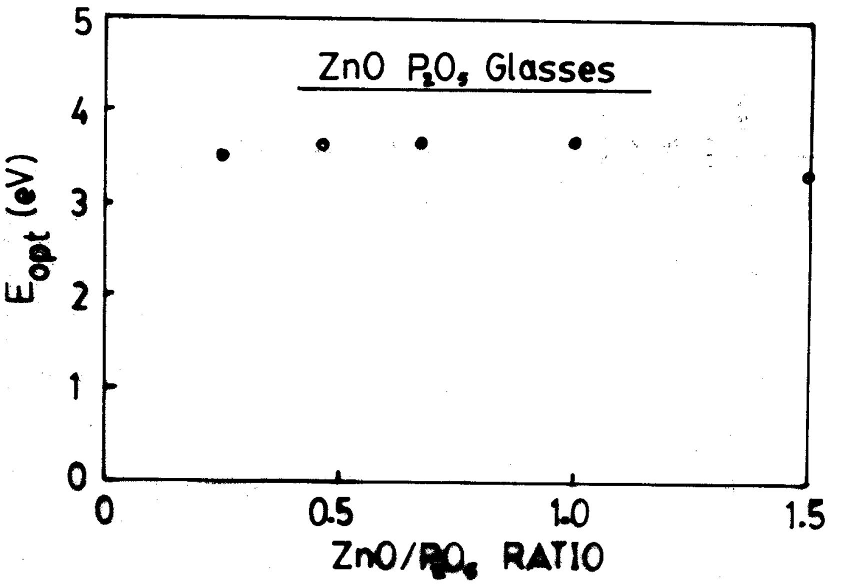


Fig. 3. Variation of optical band gap with ZnO to P_2O_5 ratio in zinc phosphate glass systems.

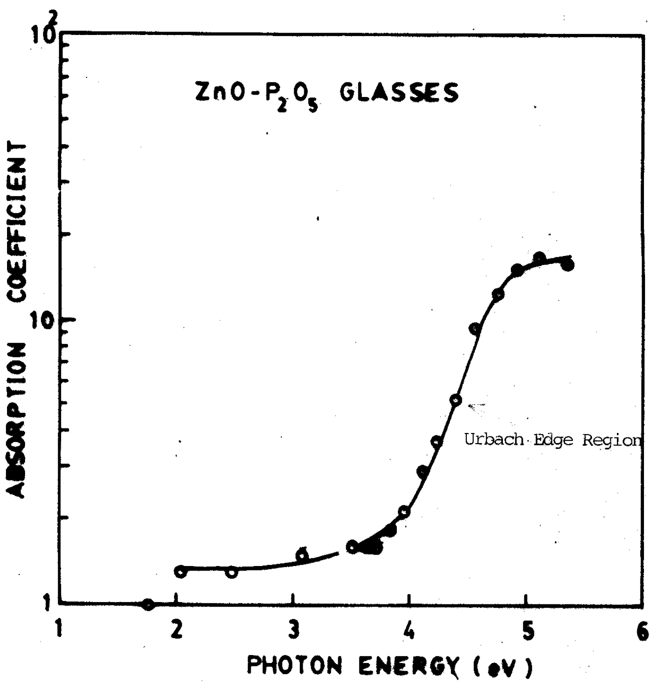


Fig. 4. A representative plot of optical absorption coefficient versus photon energy to show the Urbach edge region for 20 mole% ZnO - 80 mole% P_2O_5 glass.

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