

Optical Characteristics of Some Binary and Ternary Phosphate Glasses

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Abstract

The optical absorption spectra of some binary and ternary phosphate glasses are studied in the UV-visible region by using a spectrophotometer. The observed absorbance versus wavelength curves do not show any sharp edges in these glasses. The optical band gap energies are found to depend significantly on glass composition. The optical band gap energy is found to increase with increasing ZnO content in binary and ternary glass systems.

1. Introduction

The study of optical absorption spectra provides a very useful tool for the investigation of optically induced transitions and an insight into the energy gap and band structure of crystalline and non-crystalline materials. Experimental results on optical absorption in glasses have been reported by various workers (Hogarth and Hosseini 1983; Bausa *et al.* 1991; Hekmat Shoar *et al.* 1991). Most work has been performed on silicate, vanadate and borate glasses. Interest in the study of phosphate glasses arose due to their easy preparation and low melting points compared with borate and silicate glasses. As phosphate glasses are more electrically conductive than other glass systems, they can be used for superionic conductors, electrolytes etc. (Rao *et al.* 1990).

The composition of glasses is changed to modify their thermo-chemical stability and to improve their electro-optical characteristics. For example, the hygroscopic nature and poor chemical stability of phosphate glasses can be overcome by adding modifiers like lead oxide etc. Similarly, the activation energy and the optical band gap are modified by a change in the composition of cadmium phosphate glass systems (Ghauri *et al.* 1981). In binary zinc phosphate glasses, the optical bandgap energy (Chaudhry *et al.* 1994a), density and refractive index are known to increase with increasing ZnO content (Morey 1954). In ternary cadmium-zinc phosphate glasses (with a P_2O_5 content >50 mol%) the optical bandgap is found to increase with an increase in ZnO and to decrease with an increase in CdO (Hogarth and Ghauri 1979). The present study was undertaken to examine the optical absorption behaviour and the variation of optical bandgap in cadmium-zinc phosphate glasses with glass former $P_2O_5 \leq 50$ mol%. This report deals with the optical absorption studies of binary and ternary phosphate glasses and is an extension of recent work (Nadeem *et al.* 1993; Bilal *et al.* 1994; Chaudhry *et al.* 1994a).

2. Experimental

The binary/ternary glass samples used in the present investigations were prepared by the melt-quench technique in the temperature range 1050–1200°C. The details of sample preparation and different measurements are given elsewhere (Bilal 1993). The optical absorption spectra of glass samples were recorded at room temperature in the wavelength range 200–700 nm using a Hitachi U-2000 spectrophotometer.

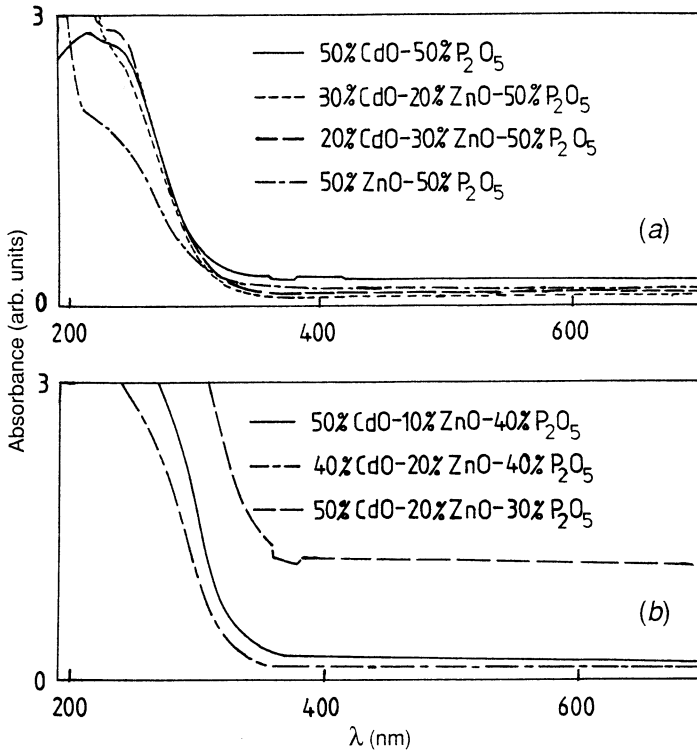


Fig. 1. Optical absorbance versus wavelength curves for various compositions of phosphate glasses: (a) fixed 50 mol% P_2O_5 and (b) fixed 40 and 30 mol% P_2O_5 .

3. Results and Discussion

The optical absorption spectra for various compositions of binary and ternary phosphate glasses with CdO and ZnO contents were recorded in the UV-visible spectral range. The results of these measurements are shown in Fig. 1. It can be seen from these plots that the absorption edges are not sharp which means that present glass samples are of an amorphous nature. This has also been indicated by X-ray diffraction patterns recorded in a separate set of measurements not shown here.

The absorption coefficients $\alpha(\omega)$ for all glass samples were determined, near the absorption edges, at different energies. The quantity $\alpha(\omega)$ is related to the absorbance $A(\omega)$ by the relation $\alpha(\omega) = 2.303 A(\omega)/d$, where d is the sample thickness. In order to find the optical band gaps, the absorption coefficients can

be displayed in a variety of ways (Mott and Davis 1979), as described by the relation

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

where B is a constant, E_{opt} is the optical bandgap energy and the exponent n varies from 0.5 to 3.0 depending on the nature of interband electronic transitions (Al-Ani and Higazy 1991). In the case of non-direct allowed electronic transitions it is observed that the measured optical data fits well to this equation for $n = 2$ (Mott and Davis 1979; Hogarth and Nadeem 1981). The quantity $(\alpha\hbar\omega)^{1/2}$ is, therefore, customarily plotted as a function of photon energy $\hbar\omega$ to determine values of the optical bandgap energy E_{opt} . The optical data from the present measurements are also displayed accordingly and corresponding plots of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ are illustrated in Fig. 2. It can be seen from these graphs that

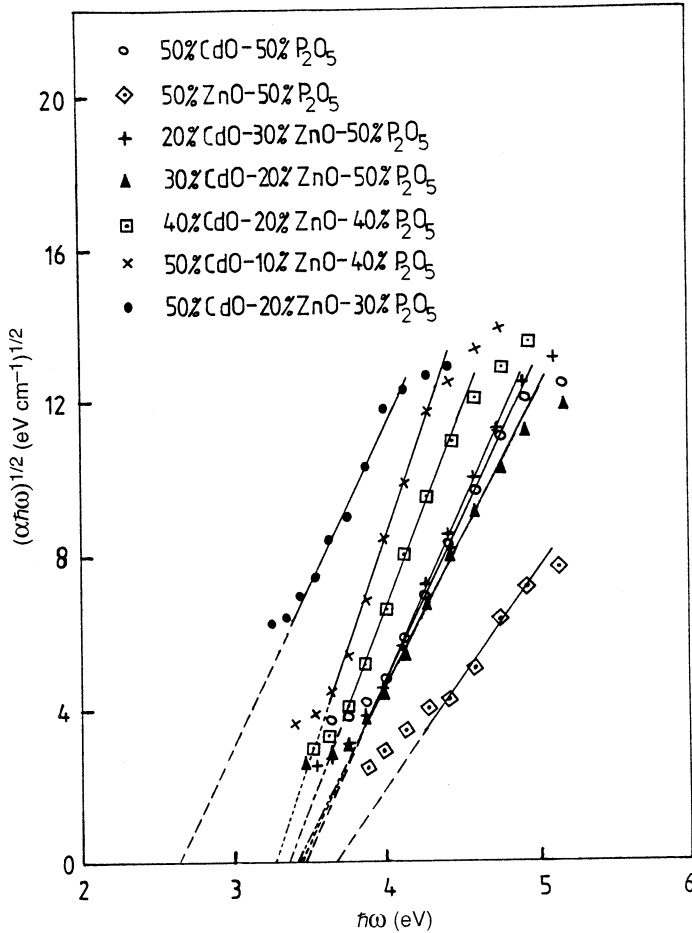


Fig. 2. Plots of $(\alpha\hbar\omega)^{1/2}$ versus photon energy for various compositions of phosphate glasses used to determine the optical band gap energy.

$(\alpha\hbar\omega)^{1/2}$ increases linearly with photon energy near the band edge and deviates from this behaviour where a band tailing occurs. This suggests that the transitions occurring in the present glass samples at higher photon energies are of non-direct type. The linear region of these plots is extrapolated to meet the energy axis at $(\alpha\hbar\omega)^{1/2} = 0$ to obtain the optical band gap value for each glass sample. Values of the optical band gap obtained by this technique are listed in Table 1, which shows that E_{opt} increases slightly with an increase in ZnO content, but declines with an increase in CdO concentration in the present glass samples. Similar observations have already been reported for binary CdO-P₂O₅ (Ghauri *et al.* 1981; Nadeem *et al.* 1993) and ZnO-P₂O₅ glass systems (Chaudhry *et al.* 1994a). In ternary phosphate glass systems containing 70 mol% P₂O₅, E_{opt} has been found to increase with increasing ZnO concentration (Hogarth and Ghauri 1979). The same trend has been observed in the present work related to ternary phosphate glasses where P₂O₅ \leq 50 mol%.

Table 1. Optical band gap energy E_{opt} of phosphate glasses

Sample	Glass composition (mol%)			Thickness (cm)	E_{opt} (eV)
	CdO	ZnO	P ₂ O ₅		
1	50	—	50	0.200	3.45
2	—	50	50	0.298	3.68
3	20	30	50	0.185	3.48
4	30	20	50	0.208	3.43
5	40	20	40	0.169	3.36
6	50	10	40	0.175	3.30
7	50	20	30	0.228	2.67

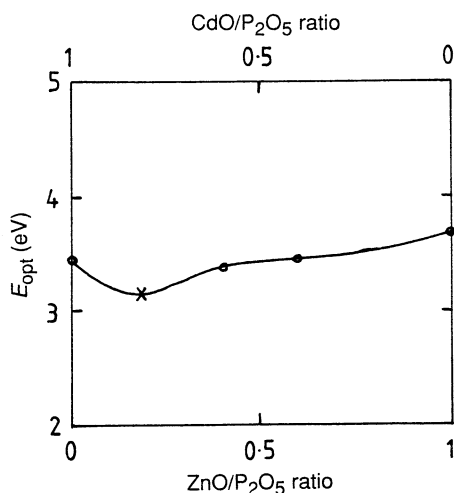


Fig. 3. Plot of the optical band gap energy as a function of two ratios for fixed 50 mol% P₂O₅. The cross represents the value of E_{opt} for 10% ZnO-40% CdO-50% P₂O₅ glass (Chaudhry *et al.* 1994b), indicating an initial decrease in E_{opt} due to the addition of ZnO.

The depolymerisation of phosphate chains is known to occur in phosphate glasses with the addition of alkali oxides (K₂O, Na₂O, etc.), alkaline earth oxides (CaO, MgO, etc.) and many other divalent metal oxides like ZnO, PbO, etc. (Chakraborty and Paul 1989). During this process the individual σ -bonds, which

bridge the phosphate tetrahedra, break due to the addition of divalent metal oxides (ZnO in this case) in the glass forming network and hence increase the number of non-bridging oxygen atoms. In this process the average chain length is also shortened. The optical absorption edges are determined by the oxygen bond strength which in turn depends on the number of non-bridging oxygens (McSwain *et al.* 1963). This explains the increase in the optical band gap of binary or ternary phosphate glasses with increasing ZnO content.

The optical band gap data of these phosphate glasses have also been compared with each other by fixing one component and varying the other two. For example, it is observed that if the glass former P_2O_5 is fixed at 50 mol% in Cd-Zn phosphate glass systems, the E_{opt} falls rapidly for 5–10 mol% of ZnO (Hogarth and Ghauri 1979; Chaudhry *et al.* 1994b). However, if this content rises beyond 10 mol%, E_{opt} is found to rise (see Fig. 3). This may be due to the fact that ZnO acts both as a modifier and as an intermediate. At low values of ZnO it may work as a modifier, while at higher concentrations it acts as an intermediate thereby becoming a part of the glass forming network. If it does not enter into the glass forming network and only acts as an impurity or structural defect it causes the band tailing and hence reduces the band gap energy. However, if it does enter into the network, it increases the band gap as described above. In Fig. 4a the variation of E_{opt} is shown against CdO/ P_2O_5 ratio for a ZnO content

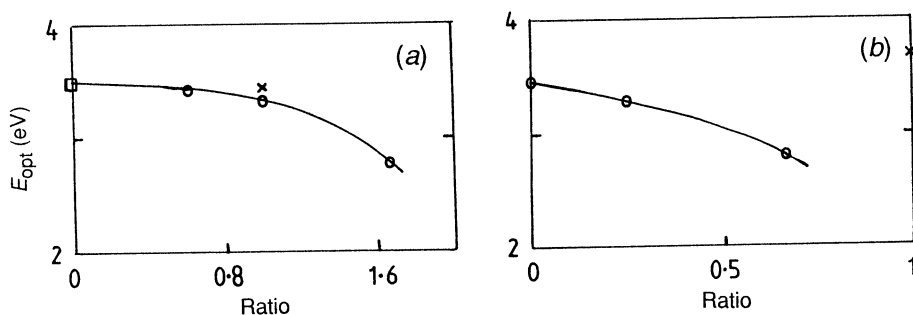


Fig. 4. (a) Variation of E_{opt} with CdO/ P_2O_5 ratio for fixed 20 mol% ZnO. The square represents E_{opt} for 20% ZnO–80% P_2O_5 glass (Chaudhry *et al.* 1994a) and the cross indicates E_{opt} for 50% CdO–50% P_2O_5 for comparison. (b) Variation of E_{opt} with ZnO/ P_2O_5 ratio for fixed 50 mol% CdO. The cross on the right shows E_{opt} for 50% ZnO–50% P_2O_5 .

fixed at 20 mol%. This plot indicates a decrease in E_{opt} with increasing CdO/ P_2O_5 ratio. A rise in the ratio would mean an increase in the amount of CdO, while a decrease in the amount of P_2O_5 . Therefore, a higher value of the CdO/ P_2O_5 ratio would correspond to larger amounts of CdO as compared to the glass forming P_2O_5 . For CdO/ P_2O_5 = 1, the cross in Fig. 4a corresponds to a binary 50% CdO–50% P_2O_5 glass and the middle open circle represents a ternary 20% ZnO–40% CdO–40% P_2O_5 system. It can be seen that, although the CdO/ P_2O_5 ratio is equal to unity for both systems, the value of E_{opt} for the ternary composition is lower than that of the binary cadmium phosphate glass. Obviously, this decrease has been caused by the addition of 20% ZnO. The ternary system seems to behave like a binary CdO– P_2O_5 glass in which E_{opt} decreases

with increasing CdO proportion or it increases with an increasing amount of network former which, in the present case, is P_2O_5 .

On the other hand, if the CdO content is fixed at 50 mol% it can be seen from Fig. 4b that, with the rise of the ZnO/P_2O_5 ratio, E_{opt} decreases. This behaviour contradicts the result that E_{opt} increases with an increase in ZnO content (Hogarth and Ghauri 1979; Chaudhry *et al.* 1994b). To understand this behaviour it should be noted that the CdO content is fixed at 50 mol% and any addition of ZnO would replace a corresponding amount of P_2O_5 to form the ternary system. The lower values of the ZnO/P_2O_5 ratio would represent higher values of P_2O_5 as compared to ZnO. It is probably CdO which, because of its higher concentration, controls the value of the optical band gap. The system now behaves like a binary CdO- P_2O_5 glass in which E_{opt} decreases with an increasing amount of CdO or it increases with an increase in the network former P_2O_5 (Nadeem *et al.* 1993). This explains why E_{opt} falls with increasing ZnO content.

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References

- Al-Ani, S. K. J., and Higazy, A. A. (1991). *J. Mat. Sci.* **26**, 3670.
- Bausa, L. E., Sole, J. G., Duran, A., and Fernandez-Navarro, J. M. (1991). *J. Non-Cryst. Solids* **127**, 267.
- Bilal, M. S. (1993). M. Phil. Dissertation, B. Z. University, Multan.
- Bilal, M. S., Chaudhry, M. A., Altaf, M., and Ahmed, M. A. (1994). *Mod. Phys. Lett. B* **8**, 461.
- Chakraborty, S., and Paul, A. (1989). *J. Mat. Sci. Lett.* **8**, 1358.
- Chaudhry, M. A., Bilal, M. S., Altaf, M., and Ahmed, M. A. (1994a). *Phys. Stat. Sol. a* (submitted).
- Chaudhry, M. A., Bilal, M. S., Altaf, M., Ahmed, M. A., and Rana, A. M. (1994b). *J. Mat. Sci. Lett.* (in press).
- Ghauri, M. A., Bokhari, W. H., and Nazar, F. M. (1981). *Int. J. Elect.* **51**, 201.
- Hekmat Shoar, M. K., Hogarth, C. A., and Moridi, G. R. (1991). *J. Mat. Sci.* **26**, 904.
- Hogarth, C. A., and Ghauri, M. A. (1979). *J. Mat. Sci.* **14**, 1641.
- Hogarth, C. A., and Nadeem, M. Y. (1981). *Phys. Stat. Sol. a* **68**, K181.
- Hogarth, C. A., and Hosseini, A. A. (1983). *J. Mat. Sci.* **18**, 2697.
- McSwain, B. D., Borrel, N. F., and Gongjen, S. U. (1963). *Phys. Chem. Glasses* **4**, 1.
- Morey, G. W. (1954). 'The Properties of Glass', 2nd edn, p. 377 (Reinhold: Germany).
- Mott, N. F., and Davis, E. A. (1979). 'Electronic Processes in Non-Crystalline Materials', 2nd edn (Oxford Univ. Press).
- Nadeem, M. Y., Ali, L., Altaf, M., Chaudhry, M. A., and Rana, A. M. (1993). *BZ Univ. J. Research (Sci.)* **5**, 29.
- Rao, D. S., Karal, P. P., and Parvatti, B. (1990). *J. Mat. Sci. Lett.* **9**, 748.