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THE EFFECT OF GAMMA RAYS ON OPTICAL PROPERTIES OF ZINC PHOSPHATE GLASSES DOPED WITH EUROPIUM OXIDE

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ABSTRACT

A detailed study of the optical absorption spectra as a function of γ-irradiation doses and composition for prepared Eu_2O_3-ZnO-P_2O_5 glass system is presented.

Optical absorption spectra were measured in the wavelength range from 200 to 1100 nm at different γ-doses in the range from 0.25 to 8 Mard. The height of the induced absorption band and the determined values of the optical energy gap (Eopt.) are found to be dependent on γ-doses and **Eu_2O_3 oxide** content

The variation of the position of the fundamental absorption edge (λ_o) with Eu_2O_3 showed two maxima at 1 and 4 wt % Eu_2O_3 oxide contents, however, a systematic increase in (λ_o) with γ-doses is

observed. The optical properties response against the irradiation dose was found to be highly sensitive to low-Doses of γ-ray.

INTRODUCTION

Glasses containing rare-earth ions have considerable potential for applications in optical data, transmission, detection, sensing and laser technologies; for example neodynium phosphate glasses have been widely used in lasers.

The study of optical absorption is a useful method for investigation the optically induced transitions and for providing essential information about the band structure and energy gap in the crystalline and non-crystalline materials [1].

The optical absorption edges in amorphous materials are less abrupt and well defined than for materials having the corresponding crystalline form. Nevertheless those edges have similar shapes in many amorphous materials in spite of the distinct differences of the chemical bonds and coordinations.

For many amorphous materials, the exponential dependence of the absorption coefficient $\alpha(w)$, at angular frequency of radiation, on photon energy $h\,\omega$ takes the form [2].

$$\alpha(\omega) = \alpha_0 \exp.(h\,\omega/\Delta E) \qquad (1)$$

where α_0 is a constant, h the reduced Planck constant and ΔE an energy which is interpreted as the width of tails of localized states in the normally forbidden band gap, which are associated with the amorphous nature. Davis and Mott [3] modified the above relation in a more general form as :

$$\alpha(\omega) = \beta(h\omega - E_{opt.})^n / h\omega \quad \text{.......(2)}$$

where β is a constant, $E_{opt.}$ the optical energy gap and n is an index depending on the nature of the interband electronic transitions. It has been reported [4-10] that a reasonable fit of Equation 2 with n = 2 is achieved for many amorphous materials, particularly at the higher absorption values of the edge and suggests absorption by non-direct transitions.

High-energy radiation, such as Gamma rays change the physical properties of the materials they pass through. The changes are strongly dependent on the internal structure of the absorbed substances and the values of γ-doses. The interaction of γ-rays with solids can cause electronic ionization (or excitation) of the orbital electrons and possibly atomic displacement. The photo-conduction electrons produced will go back and forth and then become freely or loosely bound to trapping centers somewhere in the material's structure. These new electronic configuration in addition to the possible displacement of atoms would cause a change in cross-linking of the molecular structure [11,12]. These new structural changes would cause a change in the optical properties of the substances.

The purpose of present work is to investigate the effect of gamma-rays and the glass compositions on the optical properties of zinc phosphate glasses doped with europium oxide.

EXPERIMENTAL TECHNIQUE

Glass Preparation

The glass samples were prepared from laboratory reagent grades of Analar P_2O_5 , ZnO and Eu_2O_3 oxide, using alumina crucible. The reagents were mixed and heated in an electric furnace for one hour at 350 °C. This allowed the phosphate to decompose and react with other batch constituents before melting would ordinarily occur, the crucible with the mixture was transferred to an electric Furnace kept at between 950 - 1100 °C; the highest temperature being applicable to the mixes richest in Eu_2O_3. After the mixture had melted, it was kept for one hour and stirred by an alumina rod every 20 min. to ensure homogeneity. Each melt was cast into two mild-steel molds to form glass rods of 1cm long and 1.6 cm diameter. After casting each glass was immediately transferred to an annealing furnace, held at 350 °C for one hour. The furnace was then switched off and the glasses were allowed to cool down to room temperature at an initial cooling rate of 3 °C per minute. This procedure was employed to prepare glass sample of the composition 50 mole % ZnO -50 mole % P_2O_5 doped with Eu_2O_3 ranging from 0 to 8 wt %. For optical measurements, samples were cut and polished into the form of cylindrical rods of 1.6 cm diameter and 0.2 cm thickness with parallel faces.

UV Measurements

The UV-160 Shimadzu Spectrophotometer in the wave length range 200-1100 nm, was used for the absorption measurements. The instrument directly provides the optical density (absorption).

Irradiation Facilities

A ^{60}Co γ-cell 220 was used to expose the studied specimens in air to different γ-doses. The exposure dose rate was 1.3 Mrad/h at room temperature.

RESULTS AND DISCUSSION

The experimental data representing the optical absorption spectral distribution for unirridiated and γ-irradiated Eu_2O_3-ZnO-P_2O_5 glass samples of different composition, in the visible and UV range , are shown in Figs 1-6. These figures show that there is no sharp absorption edge indicates glassy state of the studied glass samples. The fundamental absorption edge is located in the UV region from which the values of the optical energy gap ($E_{opt.}$) are obtained.

Fig. 7-a shows the plots of the absorption band edge wavelength (λ_0) against Eu_2O_3 wt %, at different γ-doses. It is clear that, the variation of the position of the fundamental absorption edge (λ_0) with Eu_2O_3 showed two maxima at 1 and 4 wt % Eu_2O_3 oxide

content, for all unirradiated and irradiated glass samples. Such a behavior may be related to structural changes taking place in the studied samples as a result of adding Eu_2O_3 oxide. For all glass samples the variation of the absorption band edge wavelength (λ_0) with γ-doses shows a real shift in the absorption band edge wavelength to a longer wavelength, i.e. to lower energies as shown in Fig. 7.b. The shifts of the absorption band edge to the lower energy regime are a manifestation of a structural rearrangement. They correspond to the transition from the non-bridging anion which bind the electron more loosely than a bridging one [11].

The variation of $(\alpha h \omega)^{1/2}$ with photon energy $h\omega$ for unirradiated and irradiated Eu_2O_3-ZnO-P_2O_5 glasses are shown in Fig. 8 as an examples for glass compositions 0.5 and 5.0 wt % Eu_2O_3 content. The optical data in these figures could be analyzed in terms of indirect transitions in K space according to the Davis and Mott [3] formula (Equation 2). The values of optical energy gap[($E_{opt.}$) are obtained from extrapolation of the linear part of each curve represents the variation of $(\alpha h \omega)^{1/2}$ with $h\omega$ T_6 $(\alpha h \omega)^{1/2} = 0$ for all glass samples. These $E_{opt.}$ values were obtained from our data using the least-squares method. The variation of $E_{opt.}$ with Eu_2O_3 content showed two minima at 1 and 4 wt % Eu_2O_3 oxide content (see Fig. 9), which indicates a structural change in the glass network. According to Reisfeld [12] proposal the Eu ions may enter the glass net network interstitially; hence, some network bonds of P-O-P or Zn-O-P are broken and replaced by ionic bonds between Eu ion and singly bonded oxygen atoms. This effect cause the pronounced change in the compositional dependence range from 1 to 4 wt % Eu_2O_3 content. However beyond 4 wt % Eu_2O_3 content, the addition of Eu_2O_3 showed a slightly change in $E_{opt.}$ values. This may be due to simultaneous filling up of the vacancies amidst the network by the interstitial Eu ions (i.e. increased packing density) and will reduce the averaged interatomic spacing.

The variation of $E_{opt.}$ with γ-doses for all glass samples (Fig. 10a and b) showed a decreases of $E_{opt.}$ with increasing γ-dose, i.e. $E_{opt.}$ was shown to be γ-dose dependent. The decreases in $E_{opt.}$ with γ-dose may be due to the interaction of gamma-radiation with glass samples, which leads to increase the non- bridging oxygen ion content, i.e. this leads electronic ionization in the glass network. This will increase the electronic transitions between localized states in band-edge tails, and as a consequence the values of $E_{opt.}$ are decreased.

In this study a single absorption was observed for irradiated glass samples centered at 535 nm (see Figs 1 to 6). Bishay [13] has reported that, the induced optical absorption of phosphate glasses in the ultraviolet and visible regions consists of a broad spectrum that can be resolved into bands centered at 539, 428, 226 and < 206 mm. Schreurs and Tucker [14] concluded that, the 539 and 428 nm bands were due to hole trapped centers. Beeken Kamp et al [15] have reported that phosphate glasses show hole trap centers at 539 and 350-400 nm. So the observed absorption band in the present work may be due to a hole trap centers in a singly-bonded nonbridging oxygen atom. The height of this observed absorption band if found to be dependent on glass composition (see Fig. 11(a) and γ-dose (see Fig. 11(b)).

REFERENCES

1- C.A. Hogarth and A.A. Hosseini, J. Mater. Sci., 18, 2697 (1983).

2- F. Urbach, Phy. Rev., 92, 1324 (1953).

3- E.A. Davis and N.F. Mott , Phil. Mag., 22, 903 (1970).

4- N,F. Mott and E.A. Davis "Electronic Process in Non-crystalline Materials" (Clarendon, Oxford, 1971).

5- S.K.J. Al-Ani, C.A Hogarth and R.A. El-Malawany, J. Mater. Sci., 20, 661 (1985).

6- A.A. Higazy, A. Hussein, M.A. Ewaida and M. El-Hofy J. Mater. Sci. Lett,7, 453 (1988).

7- A.A. Higazy, A. Husseinm and M.A. Ewaida, J. Mater. Sci; 24, 2203 (1989).

8- A.Abdel-Kader, A.A. Higazy and M.M. El Kholy, J. Mater. Sci. : Mater. in Electronics, 2,204 (1991).

9- S.K.J. Al-Ani and A.A. Higazy, J. Mater. Sci., 26, 3670 (1991).

10- A.A. Higazy and A. Hussein, Radiation Effects and Defects in Solids, 133, 225 (1995).

11- J.M. Stevels "Proceedings of the 11th International Congress on Pure and Applied Chemistry", Vol 5, p. 519, (1953).

12- R. Reisfeld, Structure and Bonding, 13,53 (1973).

13- A. Bishay, J. Amer. Ceram. Soc. 44,545 (1961).

14- J.W.H. Schreurs and R.F. Tucker, Proc. Int. Conf. Phys. Non-Crystalline S olids, Delft, 16 (1964).

15- P. Beekenkamp, H.J.A Van Dyk and J. M Stevels "Proceeding of the International Congress on Glass, Brussels, 1965" (Gordon and Breach 1966).

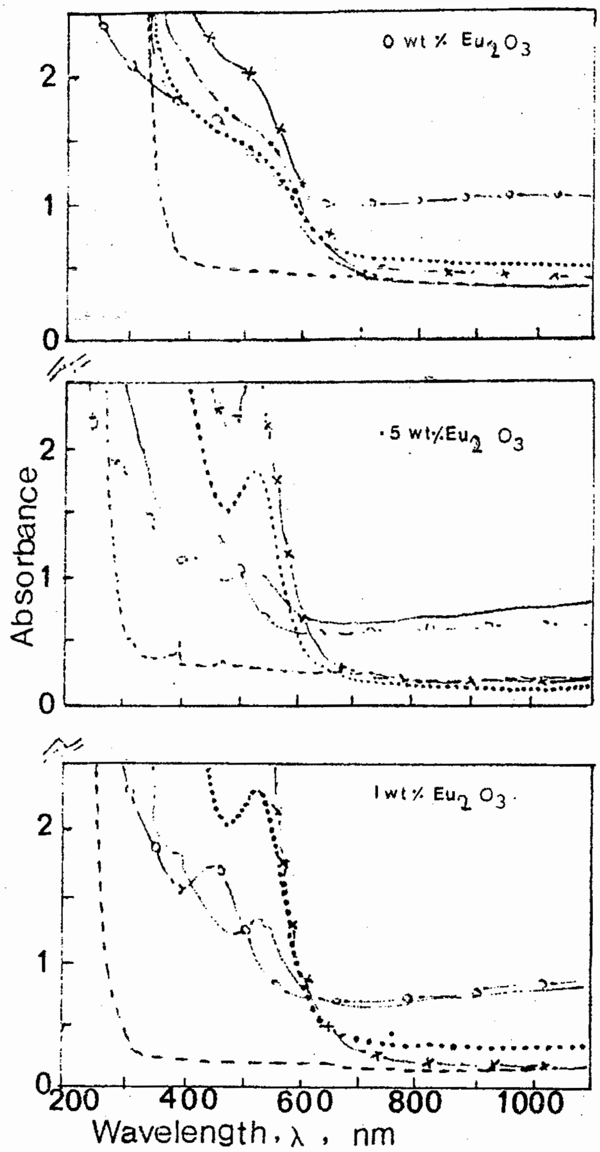

Figure 1 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples (---0, ——.25, –o– .5, –.– 1, ...2, x–x4 Mrad).

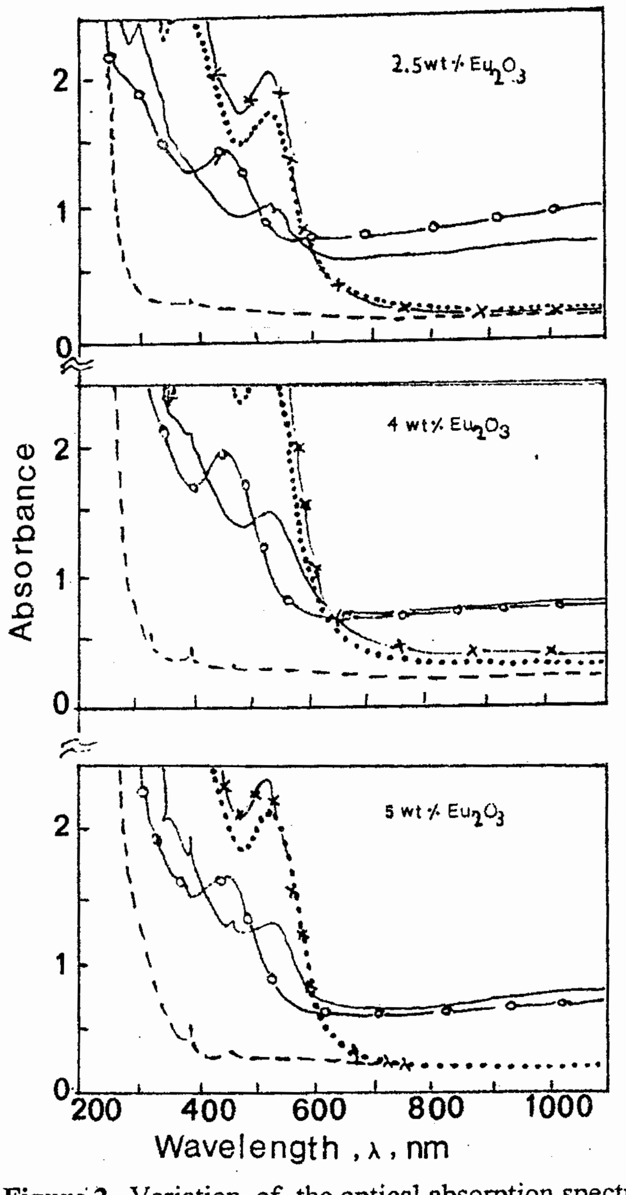

Figure 2 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples

(– – – 0 , ——— .25 , –o– .5 , ... 2 , x–x 4 Mrad)

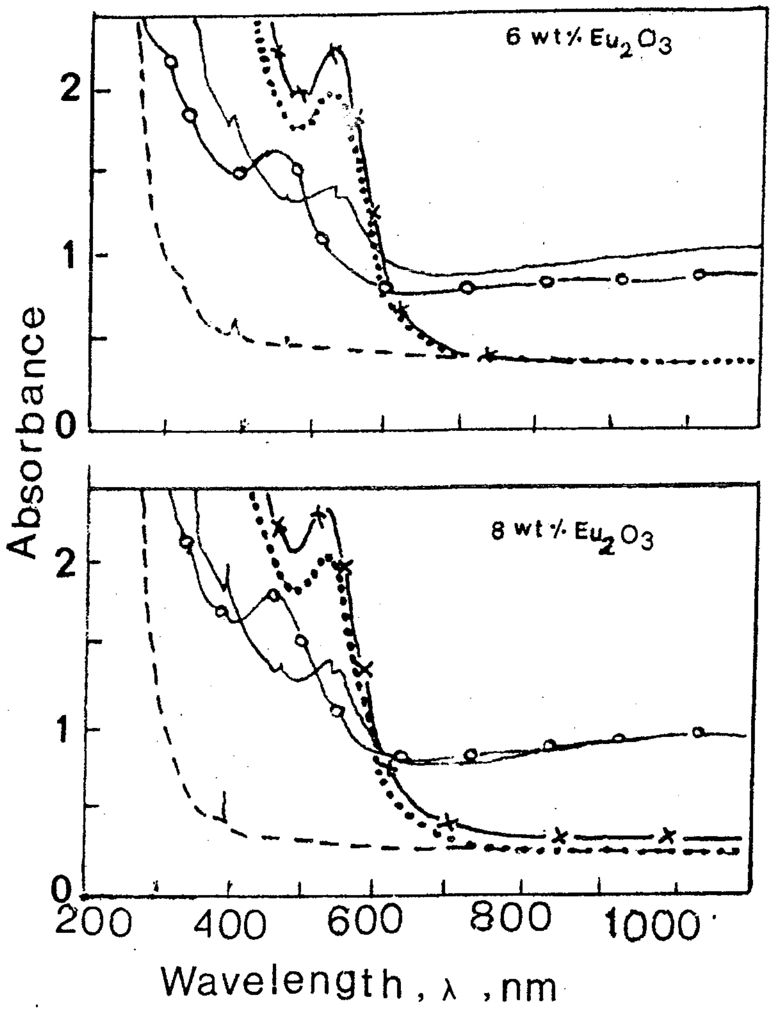

Figure 3 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples

(- - - 0, ——— .25, -o- .5, ... 2, x-x 4 Mrad).

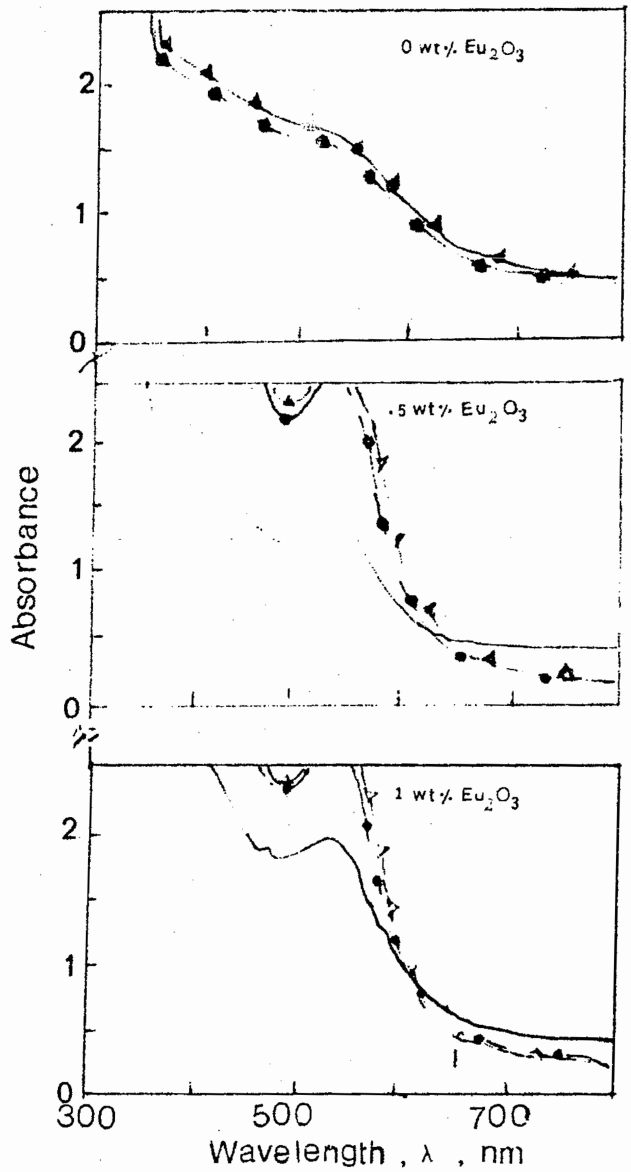

Figure 4 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples

(—— 1 , —•—○— 6 , —▲—△— 8 M rad) .

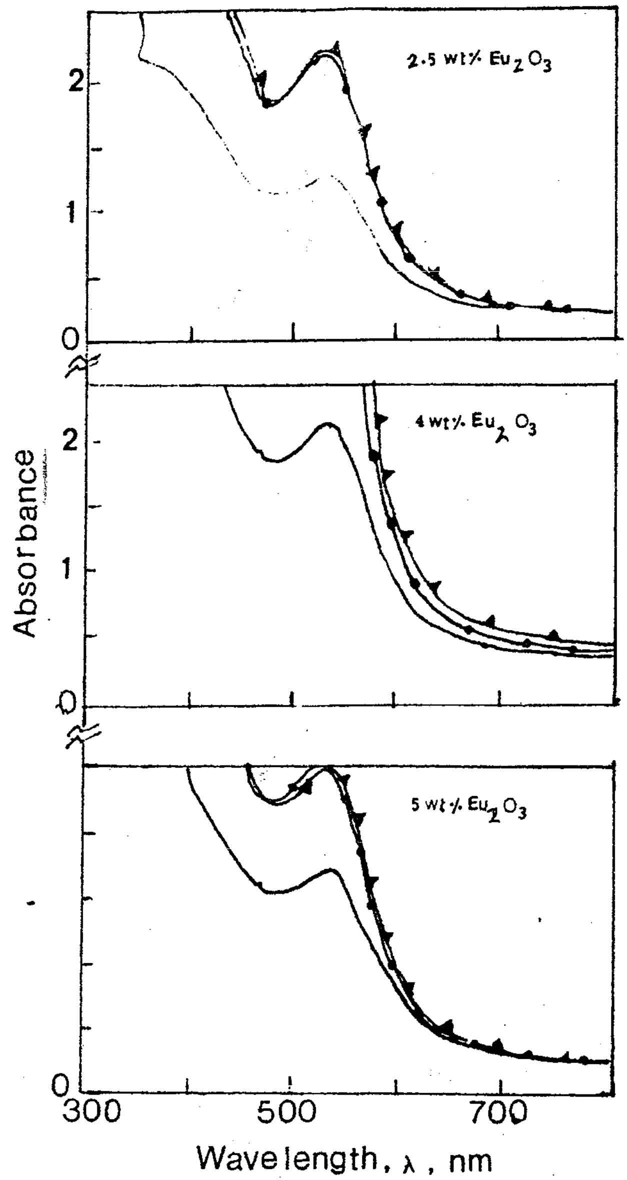

Figure 5 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples (—— 1, -●-●- 6, -▲-▲- 8 Mrad).

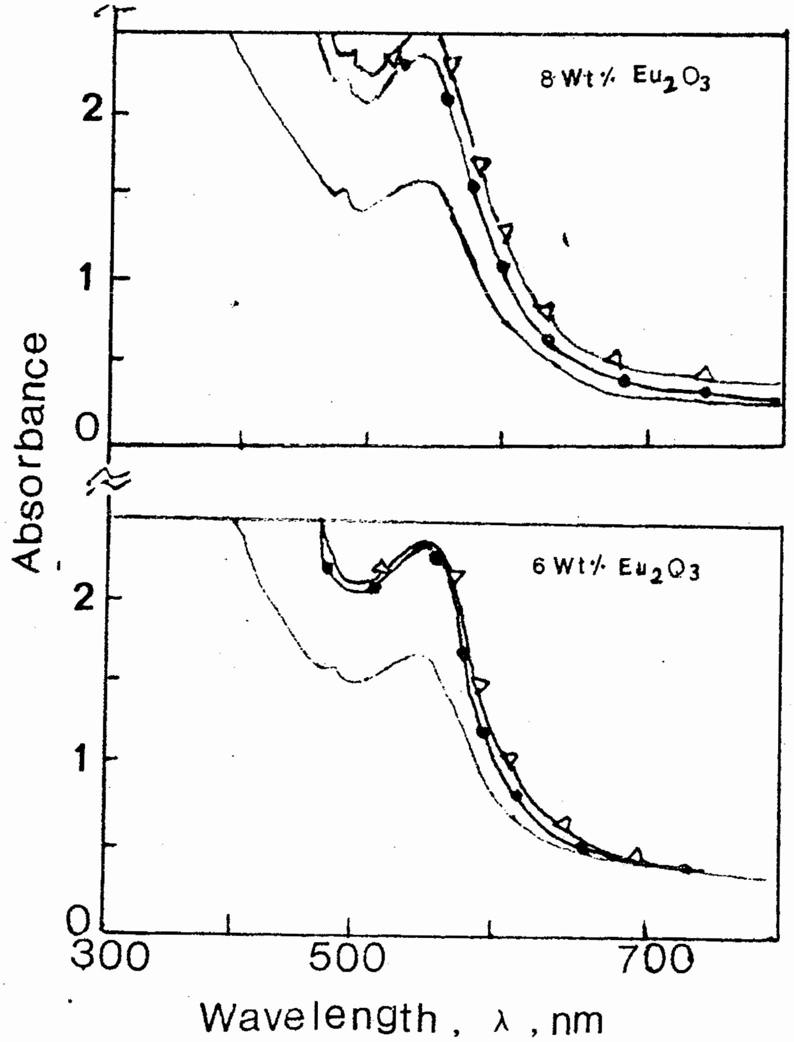

Figure 6 Variation of the optical absorption spectra with wavelength for Eu_2O_3 - ZnO-P_2O_5 glass samples (—— 1 , -o-o- 6 , -▲-▲- 8 M rad) .

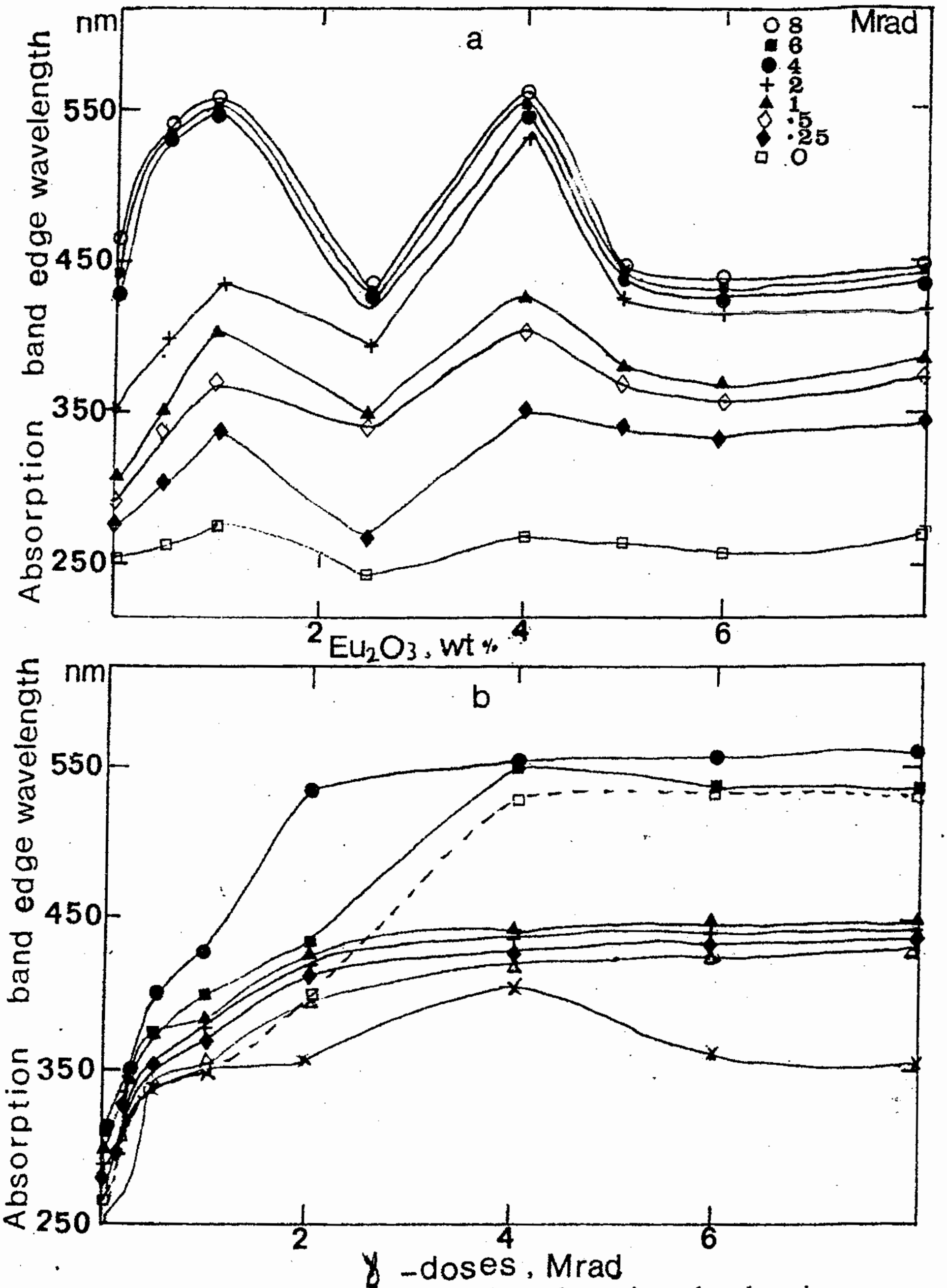

Figure 7 Variation of the absorption band edge wavelength with (a) Eu_2O_3 wt% and (b) γ-dose.

(● 4, ■ 1, □.5 ▲ 8, + 5, ◆ 6, △2.5, × 0 wt% Eu_2O_3)

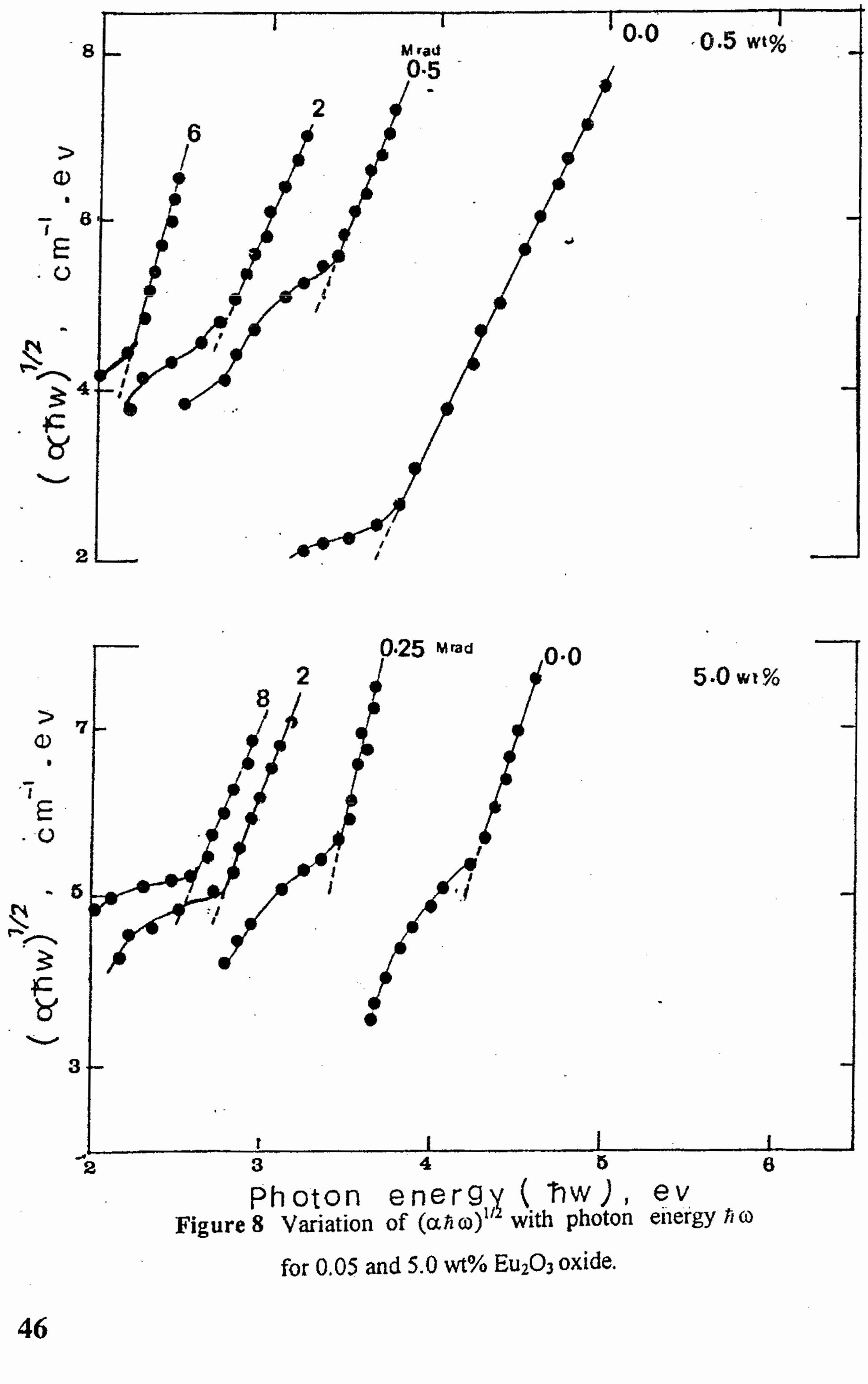

Figure 8 Variation of $(\alpha\hbar\omega)^{1/2}$ with photon energy $\hbar\omega$ for 0.05 and 5.0 wt% Eu_2O_3 oxide.

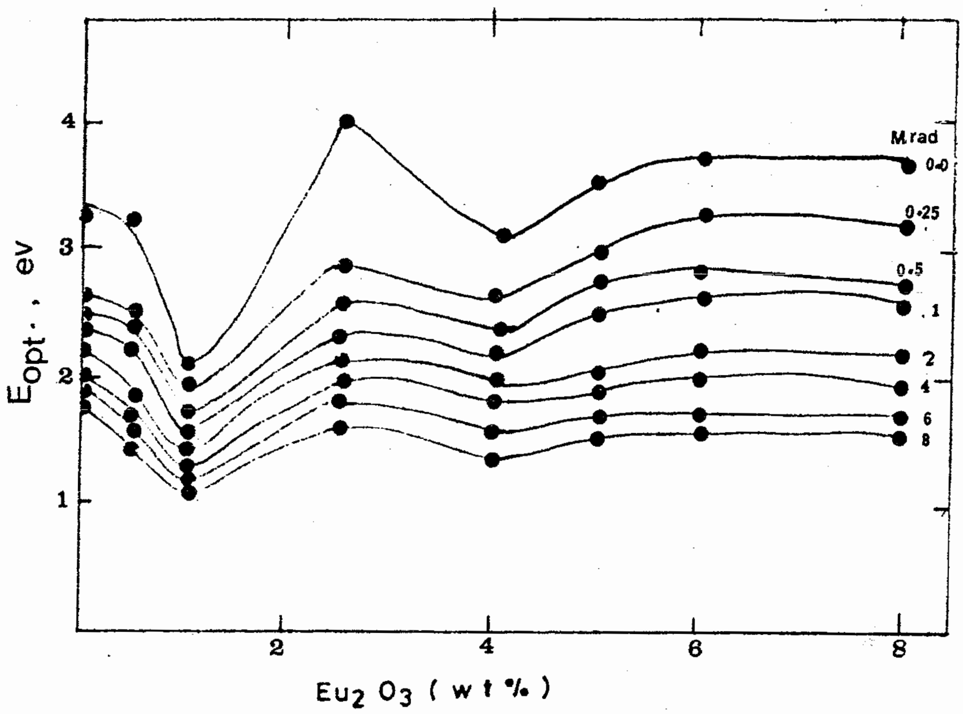

Figure 9 Variation of $E_{opt.}$ with Eu_2O_3 wt%.

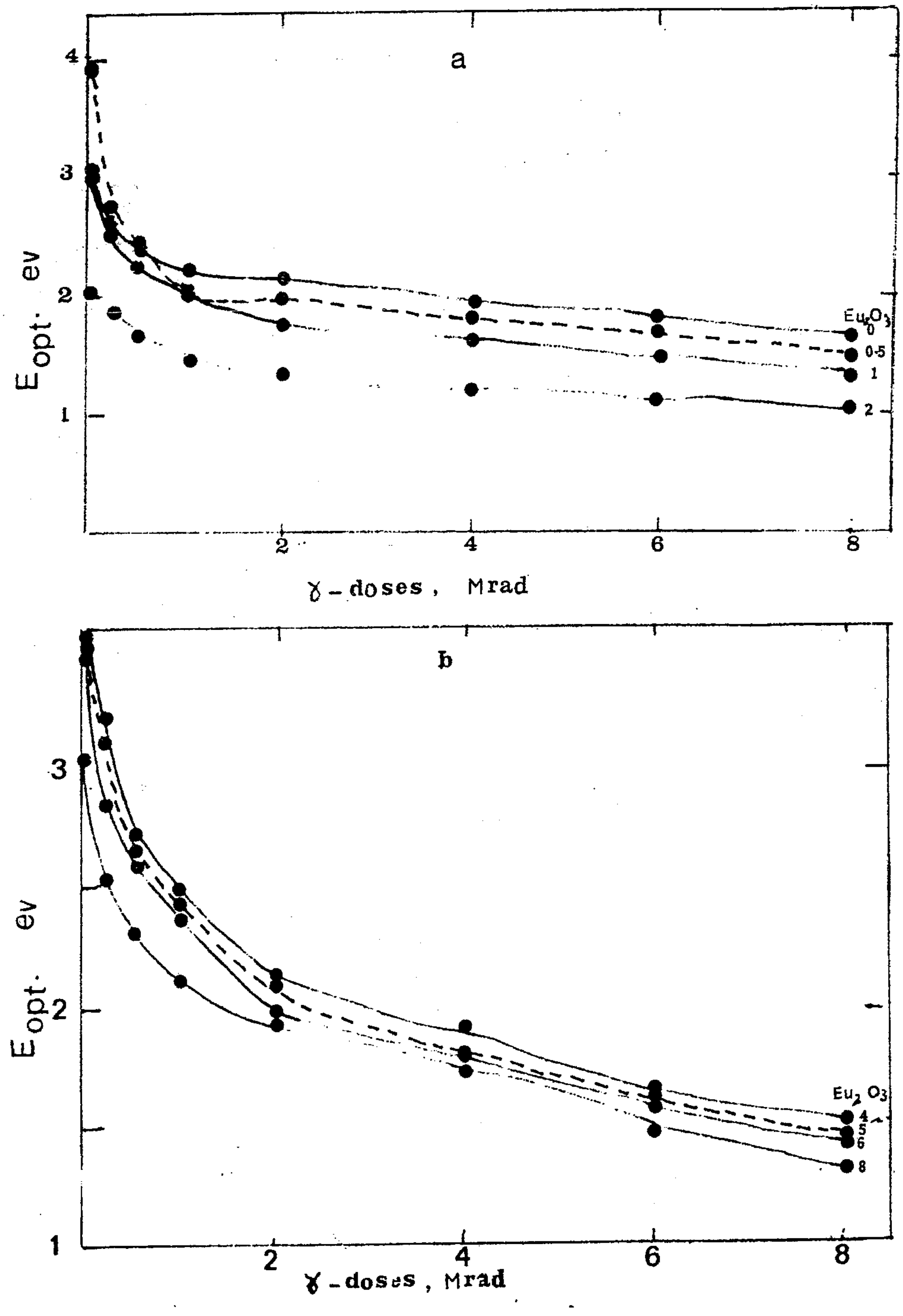

Figure 10 Variation of $E_{opt.}$ with γ-dose.

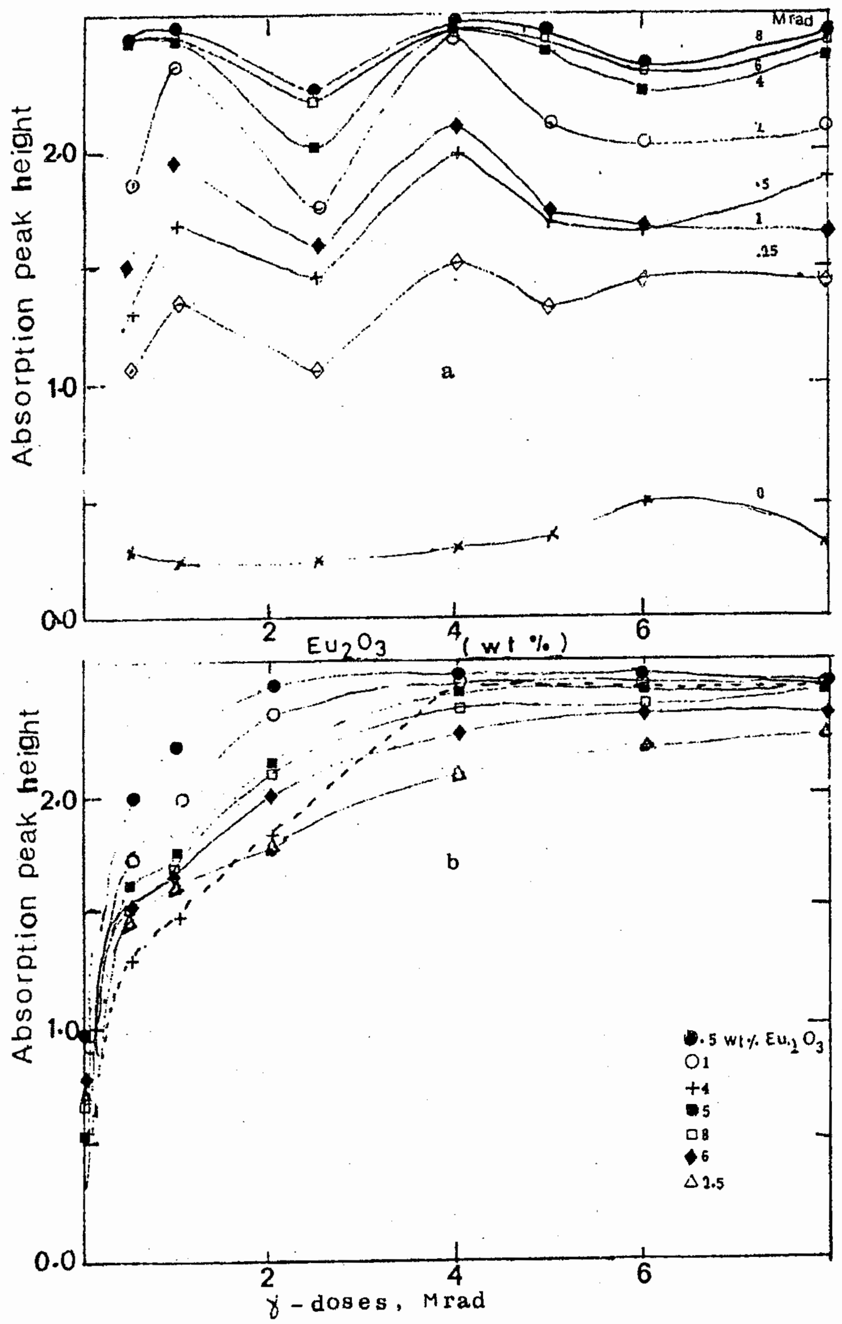

Figure 11 Variation of the peak height of the induced absorption band with Eu_2O_3 wt% and γ-doses