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Electrical conductivity and optical properties of gamma-irradiated niobium phosphate glasses

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A detailed study of the d. c. electrical conductivity and the optical absorption spectra as a function of gamma-irradiation doses for prepared (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass system is presented. The temperature dependence on the d. c. electrical conductivity measurements is studied over the temperature range from room temperature to 573 K. The induced changes in the d. c. electrical conductivity caused by different doses of gamma irradiation (0–16 Mrad) were studied. The electrical conductivity, σ, and the activation energy, E, values were found to be sensitive to the gamma-ray doses. The optical absorption spectra were measured in the wavelength range from 200 to 1100 nm at different γ-doses, in the range from 0 to 28 Mrad. The obtained results are analysed assuming optical absorption by indirect transition. Values of the absorption coefficient, α, the optical energy gap, E_{opt}, and the width of the band tail, ΔE, are found to be γ-irradiation dose dependent. © *2000 Kluwer Academic Publishers*

1. Introduction

Recently phosphate glasses have received a great deal of attention due to their considerable applications in optical data transition, detection, sensing and laser technologies (for e.g. neodymium phosphate glasses have been widely used in lasers). Ever since the descovery of the semiconducting nature of vanadium-phosphate glasses by Denton *et al*. [1], several authors [2–19] have investigated the electrical properties of phosphate glasses containing transition metal oxides. Electrical conduction in these glasses takes place as a result of electrons jumping from metal ions with a low valency state to others with a higher valency, i.e. these transition metal oxide glasses exhibit electronic conduction mechanism. The higher conductivity of these glasses makes them potential candidates for superionic conductors, solid electrolytes, etc. However, this conduction process is difficult to interpret since it is affected by many factors, such as the type and concentration of the transition metal, its proportions in the two valency states, the preparation conditions and the existence of microscopic structures within the glass matrix.

The study of the optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about the atomic vibrations, while the higher energy part of the spectrum gives a knowledge about the electronic state in the atoms.

The absorption coefficient $\alpha(\omega)$ of the optical absorption near the band edge for many amorphous materials shows an exponential dependence on photon energy $\hbar\omega$, given by the formula:

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{\Delta E}\right) \tag{1}$$

where α_0 is a constant, $\hbar = h/2\pi$, h is the Planck constant, ω is the angular frequency of radiation and ΔE is the width of the band tails of the localized states in the normally forbidden band gap that is associated with the amorphous nature of the materials. The above relation was first proposed by Urbach [20] to describe the absorption edge in alkalin halide crystals. Equation 1 has been modified to a more general form by Davis and Mott [21]:

$$\alpha(\omega) = \frac{B(\hbar\omega - E_{opt})^n}{\hbar\omega} \tag{2}$$

where B is a constant, n is an index determined by the nature of the electronic transitions during the absorption process and E_{opt} is the optical energy gap.

It has been found that [22–26], for many amorphous materials, a reasonable fit of Equation 2 with $n = 2$ is achieved. This is the case of indirect transitions, which the interactions with lattice vibrations take place. High-energy radiations, such as γ-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 as a result, a displacement of the orbital electrons and possibly atoms from their sites in the glass lattice will take place. These displaced electrons (photoconduction electrons) will go back and forth and then become freely or loosely

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bound to trapping centres somewhere in the glass matrix. These new electronic configurations in addition to the possible displacement of atoms would cause a change in cross-linking of the molecular structure [27, 28] and possibly a change in the number and nature of bonds [29, 30]. These new structural changes would cause a change in the electrical conductivity and the optical properties of glasses. The changes in properties so produced offer the possibility of using glasses as radiation monitors within appropriate doses ranges. Several authors [31–39] have reported some success in using various glass systems for the detection of γ-rays, neutrons and fissile materials.

The purpose of present work is to investigate the effect of γ-rays on the electrical conductivity and the optical properties of the prepared niobium phosphate glasses.

2. Experimental technique

2.1. Glass preparation

The glass samples were prepared from laboratory reagent grades of analar niobium pentoxide powder (Nb_2O_5, mol. wt. 265.81) and analar phosphorous pentoxide powder (P_2O_5 mol. wt. 141.95), using alumina crucibles open to the atmosphere. The reagents were mixed and initially heated in an electric furnace for 1 h at 400°C; this allowed the phosphate to decompose and react with other batch constituents before melting would ordinarily occur. Then, the mixes were placed for 2 h in a second furnace held at 1450°C. The glass melts were stirred occasionally to ensure homogeneous melts. The melt was cast into two mild-steel split moulds to form glass rods ~0.5 cm long and 1.6 cm in diameter. After casting, each glass was immediately transferred to an annealing furnace, held at 400°C for one hour. After this time, the furnace was switched off and the glasses were allowed to cool to room temperature gradually. This procedure were enployed to prepare niobium phosphate glasses of composition 20 mol. % Nb_2O_3 −80 mol. % P_2O_5.

The glassy structure of our samples was examined by a standard X-ray method. Dry ground glass powders were investigated by using an X-ray Debye Scherrer camera. Photographs of all samples showed the diffuse bands characteristic of the X-ray diffraction patterns of amorphous materials; no sharp line spectra were observed confirming the glass formation.

2.2. The electrical conductivity measurements

For the measurements of d. c. electrical conductivity, electrodes were formed by brush painting silver paste. The d. c. conductivity was measured as a function of temperature, using a spring-loaded sample holder in a wirewound cylindrical furnace. In this work, the current was measured by means of a Keithley electrometer model 616, with a smoothing adjustable power supply (0–1 KV). A fixed voltage of 300 V was applied. The temperature of the specimen was measured by means of a Chromel-alumel thermocouple.

The d. c. electrical conductivity (σ) was then calculated using the formula

$$\sigma = \frac{L}{RA} \tag{3}$$

where L is the thickness of the sample (cm), A is the cross-sectional area of the electrode (cm^2) and R is the resistance (Ω).

2.3. UV measurements

The absorption measurements for the studied glass samples were made using UV-160 Shimadzu spectrophotometer in the wavelength of 200–1100 nm. The instrument directly provides the optical density (absorbance).

2.4. Irradiation facilities

A ^{60}Co γ-cell 220 was used to expose specimens of (20 mole% Nb_2O_5 −80 mole% P_2O_5) glasses in air to different γ-doses. The exposure dose rate was 1.3 Mrad/h at room temperature.

3. Results and discussion

Figs 1 and 2 show the temperature dependence of d. c. conductivity for unirradiated and irradiated (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass samples at different γ-ray doses (0.5 to 16 Mrad). To elucidate the behaviour of conductivity with increasing γ-ray doses (Figs 1 and 2) their trend has been divided into low and high temperature regions. From inspection of these Figures it is

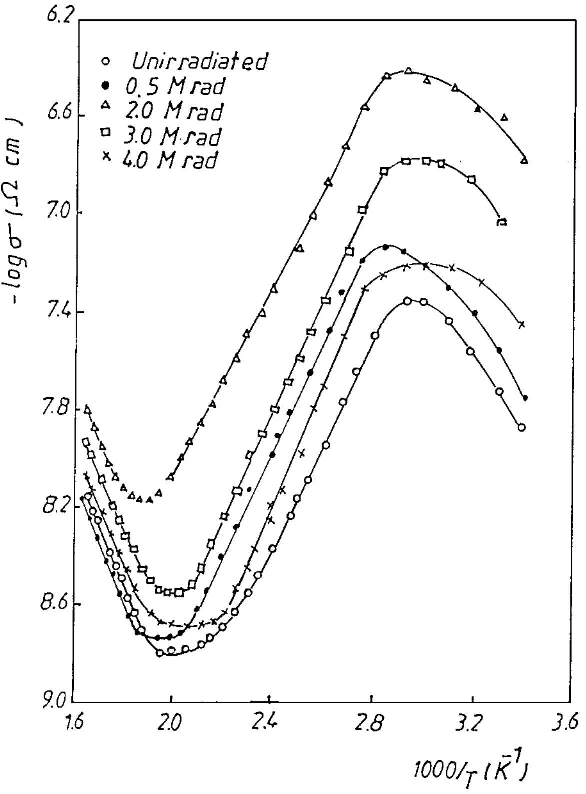

Figure 1 Variation of d. c. electrical conductivity with temperature at different γ-doses (0–4 Mrad) for binary niobium phosphate glasses.

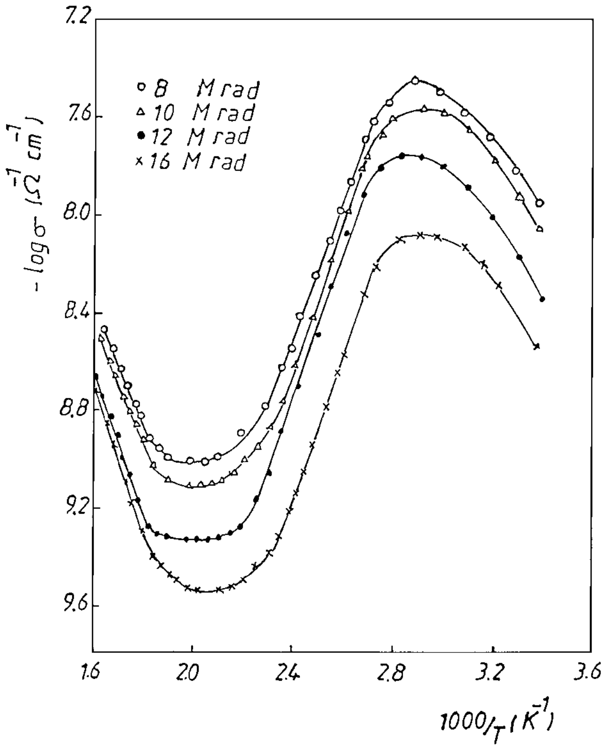

Figure 2 Variation of d. c. electrical conductivity with temperature at different γ-doses (8–16 Mrad) for binary niobium phosphate glasses.

TABLE I Gamma doses and the activation energies for (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass system at different temperature regions

γ-doses M Rad	Activation energy "E_1" (eV) Temp. range (350–500 K)	Activation energy "E_2" (eV) Temp. range (500–623 K)
0.0	0.4498	0.4963
0.5	0.4271	0.4784
1.0	0.4123	0.4665
2.0	0.3590	0.4340
3.0	0.4310	0.5100
4.0	0.4899	0.5760
8.0	0.5360	0.6150
10.0	0.5670	0.6427
12.0	0.5956	0.6603
16.0	0.6420	0.7004

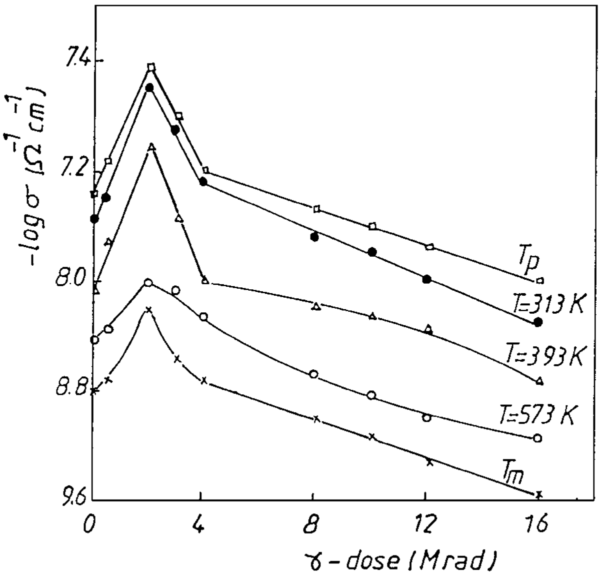

Figure 3 Variation of the induced change in the electrical conductivity with the absorbed γ-dose at different temperatures (where T_m and T_p represent the temperatures at the minimum and maximum values of $\log\sigma$).

observed that, the electrical conductivity for all unirradiated and irradiated glass samples shows that in the low temperature range 345–483 K and also in the high temperature range 483–623 K the plot of $\log \sigma$ against reciprocal temperature gives a good straight lines which reflects the semiconducting behaviour of the specimens under study. This may be taken as evidence that the activation energy in these temperature regions is independent of temperature. However, in the temperature range $T < 345$ K the activation energy showed a pronounced dependence on temperature. Also, from these Figures, it is evident that, the electrical conductivity is a dose dependent. At constant temperature, the electrical conductivity increases with increasing of γ-ray doses up to 2.0 Mrad, then there is a pronounced decrease in the γ-doses range from 2 to 16 Mrad, with inflexion point at 4 Mrad (see Fig. 3). This anomalous behaviour is probably attributable to a change in the conduction mechanism at the inflexion points 2 and 4 Mrad. This dependence of d. c. conductivity on γ-doses might be explained as follows. At the beginning, increasing γ-dose would result in an increase in the number of charge carriers created. This increasing number of charge carriers will continue to take place as γ-dose increases until we approach a situation at which most the possible charge carriers are already created. After this threshold dose-limit (2 Mrad), we might expect a decrease in the d. c. conductivity (see Fig. 3).

The values of the activation energies were calculated from the slopes of the $\log \sigma$ against $1/T$ plots, using a least squares fit, and are represented in Table I. Fig. 4 shows the variation of the activation energies E_1 and E_2 with γ-doses (E_1 is the low temperature activation energy which is less than the high temperature activation energy E_2). The values of E_1 and E_2 are seen to display a decrease with increasing γ-doses up to 2 Mrad. As we increase the γ-doses beyond this value, the E_1 and E_2 values increased with inflexion point at 4 Mrad (see Fig. 4). Figs 3 and 4 show that when the conductivity increases, the activation energy decreases and vice versa, which is consistent with the general formula of Mott [40].

Fig. 5 shows the optical absorption spectra for (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass speciments in the visible and UV range at different γ-doses. It is clear that there is no sharp absorption edge which indicates a glassy state of the studied samples. The optical absorption edge is located in the UV region from which the values of E_{opt} and ΔE are obtained. The values of absorptions coefficient $\alpha(\lambda)$ were calculated from the absorbance, A using the following simple formula

$$\alpha(\lambda) = 2.303\frac{A}{d} \tag{4}$$

where d is the sample thickness.

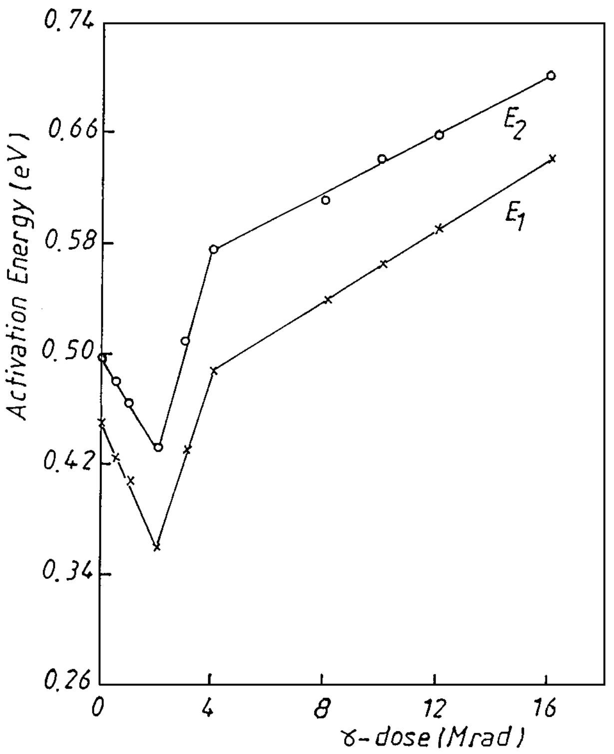

Figure 4 Variation of the activation energies E_1 (low temperature region) and E_2 (high temperature region) with the absorbed γ-dose.

Fig. 6 represents the variation of $\alpha(\lambda)$ with γ-doses at different wavelength, λ. A distinct dependcence of $\alpha(\lambda)$ on γ-doses is observed in the γ-dose ranges (0–4 Mrad) and (16–28 Mrad), however in between these two regions $\alpha(\lambda)$ tends to flatten out.

The variations of $(\alpha\hbar\omega)^{1/2}$ with photon energy $\hbar\omega$ for unirradiated and irradiated (20 mole% Nb_2O_5 -80 mole% P_2O_5) glass samples are shown in Fig. 7 as an examples for different γ-doses. The optical data in this Figure were analyzed in terms of indirect transition in K space according to the Davis and Mott [21] formula (Equation 2). The values of the optical energy gap, $E_{\rm opt}$ are obtained from extrapolation of the linear part of each curve represents the variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ to $(\alpha\hbar\omega)^{1/2} = 0$ for all glass samples. These $E_{\rm opt}$ values were obtained from our data using the least-squares method. According to the Urbach Equation 1, the values of ΔE (the width of the band tails of the localized states) are obtained from the slope of the straight line of the curves, which represented the variation of $\ln\alpha$ with $\hbar\omega$ for all glass samples (Fig. 8).

The variations of $E_{\rm opt}$ and ΔE with γ-dose showed a pronounced discontinuities at 2 and 10 Mrad γ-doses, (Figs 9 and 10, respectively) i.e. $E_{\rm opt}$ and ΔE are shown to be γ-dose dependent. Also this behavior is a manifestation of a structural rearrangement. The decreases in $E_{\rm opt}$ and increases of ΔE values with γ-dose may be due the interaction of γ-radiation with glass samples which leads to electronic excitation and 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 $E_{\rm opt}$ are decreased and the values of ΔE are increased (Figs 9 and 10). However, the increases in $E_{\rm opt}$ and decreases in ΔE values with γ-dose may be related to the increase in the degree of cross-linking as a result of possible displacement of atoms which causes a change in cross-linking of the molecular structure [27, 28] of the studied glass samples.

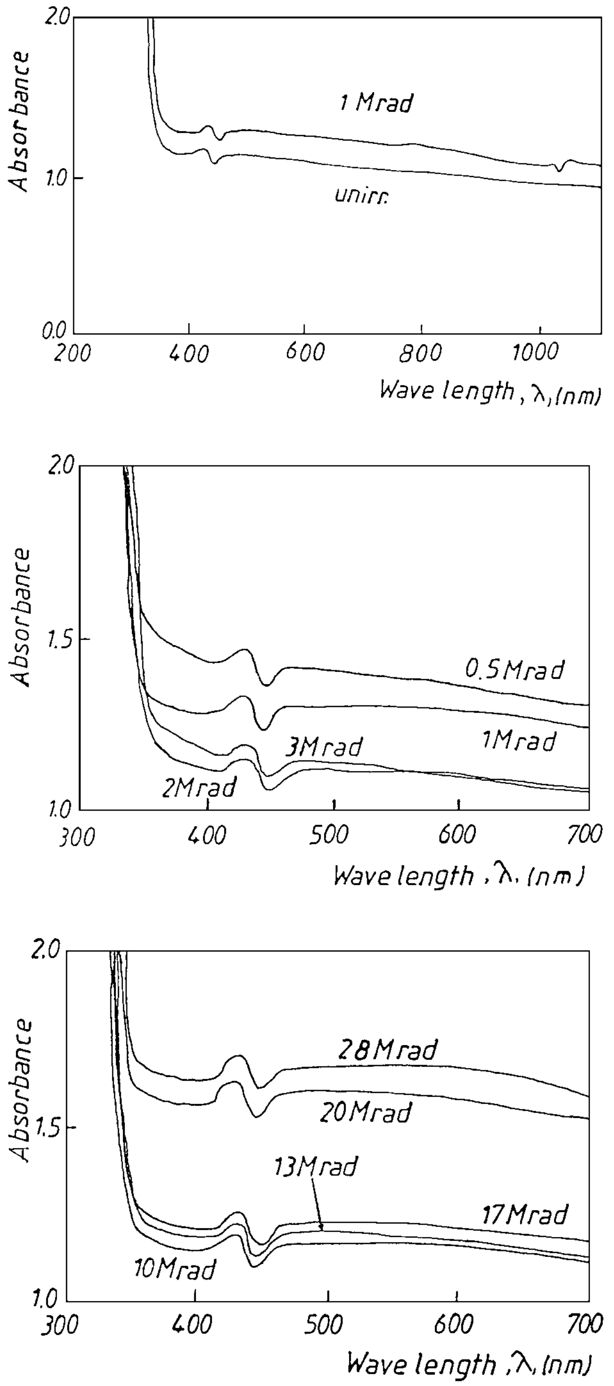

Figure 5 Variation of the optical absorption spectra with wavelength for (20 mole% Nb_2O_5 -80 mole% P_2O_5) glass samples at different γ-doses.

In this work an individual absorption bands were observed for irradiated glass samples centered at 433 nm (Fig. 1). Bishay [41] 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 nm. He also pointed out that the energy of the 539 nm band is dependent on the alkali type, whereas the energy of the 428 nm band increases slightly with increasing ion field strength. Beekenkamp *et al.* [42] have reported that phosphate glasses show hole trap

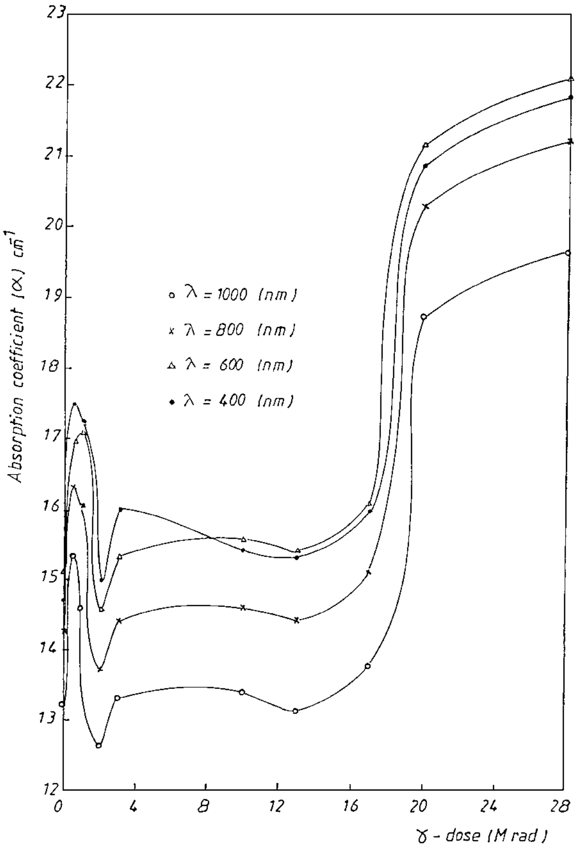

Figure 6 Plot of the absorption coefficient, α, versus γ-dose at different wavelengths, λ.

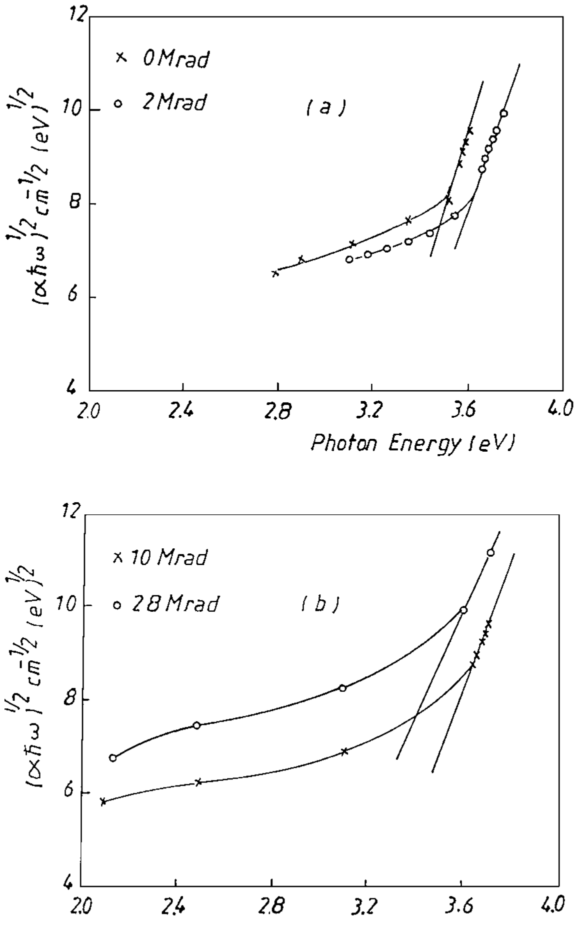

Figure 7 Dependence of $(\alpha\hbar\omega)^{1/2}$ on the photon energy and γ-doses for (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass samples.

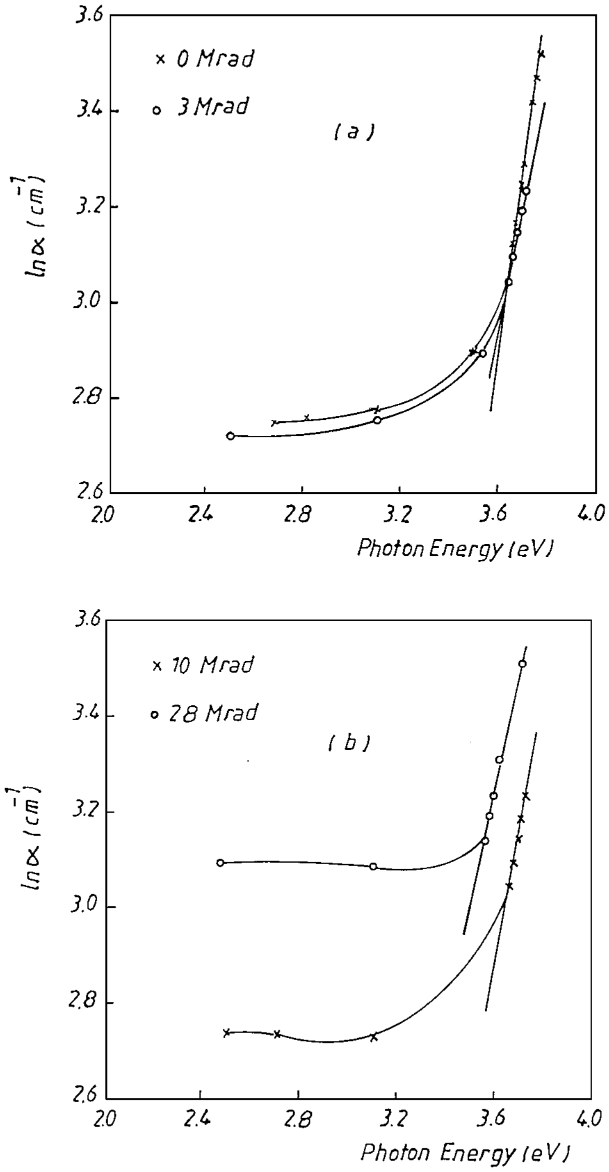

Figure 8 Absorption coefficient ($\ln\alpha$) as a function of photon energy ($\hbar\omega$) at different γ-doses.

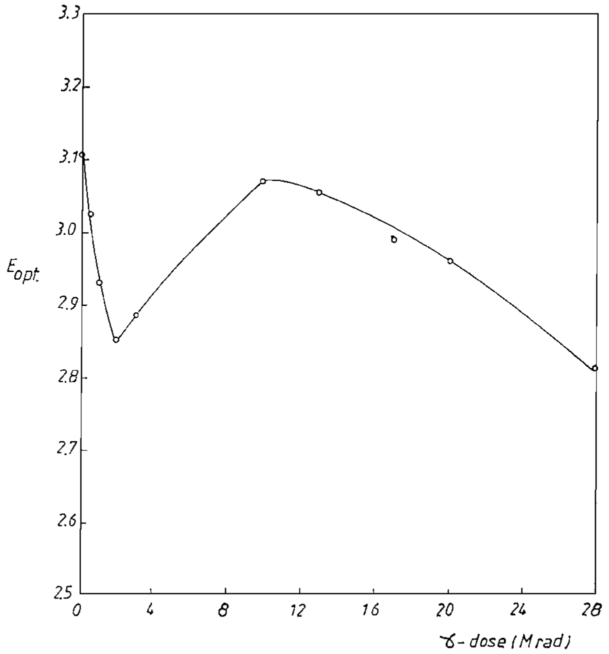

Figure 9 Variation of the optical energy, E_{opt}, with γ-dose for (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass samples.

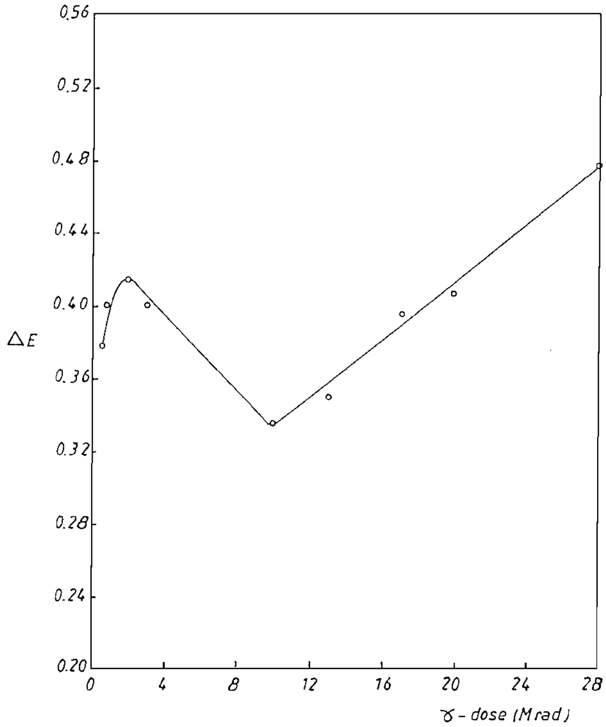

Figure 10 Variation of the width of the band tail, ΔE, with γ-dose for (20 mole% Nb_2O_5 −80 mole% P_2O_5) glass samples.

centres at 539 and 350–400 nm. Then, according to Beekenkamp [42], the observed band in this study may be due to a hole in a singly-bonded nonbridging oxygen distant from a Nb modifier cation.

4. Conclusions

In conclusion, the linear dependence of $\log\sigma$ on the reciprocal temperature reflects the semiconducting behaviour of the present glass samples. The optical absorption data indicated that, the values of E_{opt} were obtained for $n = 2$ i.e. indirect transitions take place, and the values of ΔE were obtained from Urbach edge. The electrical conductivity σ, the activation energy E, E_{opt}, and ΔE values are found to be strongly dependent on γ-dose. This leads us to a study of the possibility of using such a glass system as a gamma dosimeter.

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