DOSIMETRIC GAMMA RADIATION EFFECT ON THE OPTICAL PROPERTIES AND RAMAN SPECTRA OF NOVEL OXYHALIDE PHOSPHATE GLASSES PZLC

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In the present work novel, oxyhalide phosphate glasses with composition $50P_2O_5$ – (45-x)ZnO- 5LiCl- x CuO (where x= 5, 10 and 15 mol%) was prepared. Physical parameters like that the density, ρ, the values of molar volume (V_m), oxygen molar volume (V_O), oxygen packing density (O. P. d) and optical energy gap (E_{opt}) were evaluated. The transmission spectra and the energy gap of these glasses studied under irradiated by gamma rays to the dose 20, 40 and 60 Gy. Herein both, ρ, and O.p.d values are an increase from 3.0273 to 3.1480 $gm{\cdot}cm^{-3}$ and 81.466 to 83.057 respectively, with an increase in CuO from 5 to 15mol%. Otherwise, E_{opt}, V_O, value decrease from 4.17 to 3.42 $gm{\cdot}cm^{-3}$ and 12.275 to 12.019 respectively. Effect of gamma radiation on these glasses leads to a variation of the transmission bandwidth and optical energy gap. These changes are related to the formation of Cu ions through photochemical reactions from electrons or holes during the irradiation process. Also, the structure of this glasses studied by using Raman spectra. The optical properties results indicated that the prepared glasses are promising for optical filter applications invisible, NIR and IR region. The results can be indicated that these glasses are promising for using an ultraviolet radiation dosimeter.

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Keywords: Glasses, Transmission, Energy gap, Gamma

1. Introduction

The glass dosimeters play a considerable role in different applications, such as industrial, medical, and food irradiation purposes. Because of the optical transparency of the glass, the glass dosimeters become of great interest, thus resulting in an overall improvement in the efficiency of the phosphorus.

A large number of studies have been dedicated to the improvement of the luminescence properties of the glass systems [1–8]. The phosphate glasses are often used as biomaterials; because of their chemical composition similarity to that of the natural bones, and it has several advantages over borate and silicate glasses, due to their thermal expansion coefficients, ultraviolet transmission, and melting temperatures. Recently, many studies have focused on the applications of phosphate glasses in medicine and clinical dosimetry (9).

Copper-doped phosphate glasses exhibit interesting electrical and optical properties that make them suitable for use as super-ionic conductors, solid state lasers, and can be doped with high level by metal ions and remain amorphous. However, the poor chemical durability of phosphate glass is one of the main disadvantages of using this type of glass, but limit its use in many applications. Addition transition metal oxide modifier phosphate glass has improved the chemical durability [10] ZnO acts as a good glass modifier because Zn ion acts as anionic cross-linker between different phosphate ions, inhibiting hydration reaction [11]

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Copper phosphate glasses exhibit an optical absorption band in the visible-near infrared region and a fundamental optical absorption edge in the ultraviolet (UV) region [12]. Phosphate glass doped with copper and its structure were studied by many techniques such as XRD, NMR, XPS, EXAFS, FTIR, Raman spectroscopy, hardness, and electrical conductivity

The present work is to investigate the characterization and the effect of Gamma rays irradiated exposure on the optical properties and structure of glass types as a dosimeter. Study of some physical properties such as density, molar volume, transmission, and absorption was carried out to examine the effect of gamma rays and increasing copper oxide in the expense of on zinc oxide phosphate glass for glass dosimeter.

2. Experimental work

The glasses were prepared by the conventional quenching procedure, where the composition is $50P_2O_5$ – 40ZnO- 5 LiCl - 5CuO in mol% (PZLC1), $50P_2O_5$ – 35ZnO- 5 LiCl-10CuO in mol% (PZLC2) and $50P_2O_5$ – 30ZnO- 5 LiCl- 15CuO in mol% (PZLC3) have been melted in alumina crucibles, the temperature was probably between1000 and 1200 °C. Composites were cast in a steel mold at room temperature followed by annealing at 400 °C for 2 h. After annealing, the furnace was turned off and the samples were left to cool down inside. Before testing, the prepared glasses were finely polished. Irradiation tests were performed at the Calliope gamma irradiation plant (Atomic energy authority, Cairo, Egypt), a pool-type irradiation facility equipped with a ^{60}Co gamma source (mean energy of 1.25 MeV) in a high volume (7× 6× 3.9 m^3) shielded cell Absorbed doses of 20, 40 and 60kGy, measured by a Fricke dosimeter, were applied at the dose rate of about 10kGy air/h. The optical absorption spectra of the glass types were measured in the wavelength range 190–1100 nm using UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600).

The vertical (VV) polarized spontaneous Raman spectra of the prepared glass were acquired using a Thermo Scientific DXR Raman Microscope spectroscopy setup with 532 nm excitation [(532 nm Laser type Diode-pumped, solid state (DPSS)] and acquisition time was set to 30 seconds. The incoming signal vertically surface of the bulk sample, and V-polarized Raman scattered signal was collected in the backscattering geometry with a 100x microscope objective.

Table 1. Glasses composition in mol%

Sample Code	Glass composition in mol%
PZLC1	$50P_2O_5$ – 40ZnO- 5 LiCl - 5CuO
PZLC2	$50P_2O_5$ – 35ZnO- 5 LiCl - 10CuO
PZLC3	$50P_2O_5$ – 30ZnO- 5 LiCl - 15CuO

3. Result and discussion

In the present work the density value, ρ, of the prepared glasses at room temperature are determined as follow;

$$\rho(\frac{gm}{cm^3}) = \rho_t \cdot \frac{W_a}{W_a - W_x} \quad (1)$$

where W_a is the weight of the sample in the air, W_x is the weight of the sample in Toluene,ρ_t is the density of Toluene. The density of Toluene at room temperature is 0.865 g cm^{-3}. Density obtained by three repeated measurements showed an estimated error was±0.002 g· cm^{-1}. The density, ρ, of prepared glass samples has been increased from 3.0273 to 3.148 in g· cm^{-3} with CuO concentration increased from 5 to 20 mol%, this increasing attributed to the higher molecular weight, creation nonbridging oxygen NBO or bridging oxygen (BO) and coordination number of constituent atoms in the glasses matrix. The molar volume of the prepared glasses calculated by using formula as follow;

$$V_m = \frac{\sum M_T}{\rho} \quad (2)$$

where M_T is the total molecular weight of the multi-component glass system given as; $M_T=x_iZ_i$, where x_i and Z_i are the mole fraction and the molecular weight of the oxides respectively. The value of Vm of prepared glasses is in the range 35.66 to 36.21 cm^3. The results of V_m indicate that firstly at CuO content up to 5mol% bridging oxygen (BO) was created in the glasses network so molar volume increase otherwise at CuO content equal 10 mol% nonbridging oxygen created leads to decrease in Vm (see Table 1). Moreover the oxygen molar volume, V_o, is evaluated by;

$$V_O = \frac{\sum M x_i}{\rho \cdot \sum x_i n_i} \quad (3)$$

where, n_i, is the number of oxygen atoms in each oxide and x_i is the molar fraction of each component, i, The oxygen packing density, Opd, determined by this equation;

$$O.p.d = \frac{100\rho O_i}{M_i}, \quad (4)$$

where O_i is a number of oxygen atoms in the oxide formula, the results of V_m, V_O, and Opd can give good information about the structure of the network of prepared glasses. Here the values of V_O decrease from 12.28 to 12.02 increasing CuO content in mol% from 5 to 20 mol%. Otherwise, the value of Opd increases from 81.47 to 83.06 in g atom lit^{-3} with increasing CuO concentration from 5 to 20 mol% (these results obtained in Table 2).

Table 2. Density (ρ), molar volume (V_m), oxygen packing density (O. P. d), oxygen molar volume, an optical energy gap (E_{opt}), and glass transition temperature.

Sample code	Density, ρ (g/cm^{-3})	Molar volume V_m (cm^3)	Oxygen molar volume, V_o (cm^3)	O. P. d $g.atom.l^{-1}$
PZCL1	3.0273	36.21	12.28	81.47
PZCL2	3.0718	35.66	12.09	82.73
PZCL3	3.148	36.06	12.02	83.06

The variation of optical transmittance spectra at room temperature of the glasses sample PZCL1, PZCL2 and PZCL3 were reported is shown in Fig. (1). It was found that for CuO equal 5 mol% showed a strong wide visible transmission band extending from 376 to 638 nm with peak 540 nm. these glasses exhibit bandpass filters behaviour in the visible range. The wide of this band and the height of optical band intensity decreases with increasing CuO concentration (see Fig. 1). Otherwise the transmission cutoff wavelength, λ_o, towards to higher wavelength with increasing Cu^{2+} ions in the glasses matrix. The obtained results reveal that this decrease is related to structural changes which Cu^{+2} ions occupation as interstitial in the glasses network.

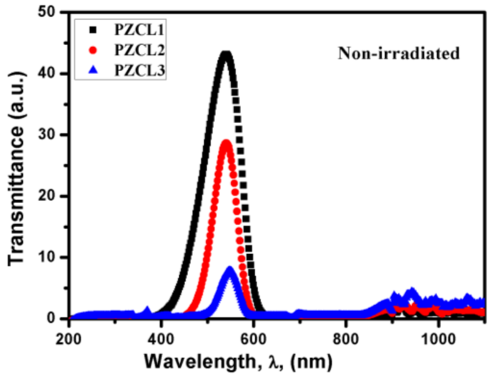

Fig. 1. Optical transmittance spectra of the prepared glasses PZCL1, PZCL2 and PZCL3 before the dose of gamma irradiation.

The optical absorption coefficient $\alpha(\nu)$ can be determined at various wavelengths according to the relation [13];

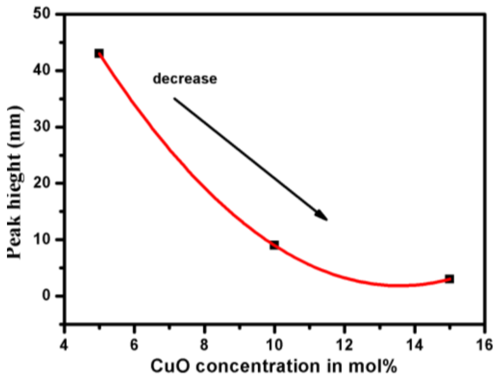

Fig. 2. The relation between the height transmittance spectra of the prepared glasses PZCL1, PZCL2 and PZCL3 before the dose of gamma irradiation.

The present glasses PZCL1, PZCL2 and PZCL3 are irradiated to a dose of 20, 40 and 60 KGy, the UV-Vis transmission spectrum intensity decrease with increasing the dose of gamma radiation. The intensity of transmittance of PZCL1 highly decreases from 43 to 22% increasing gamma dose from 20 to 60 KGy, and very low decreasing for PZCL2 and PZCL3 glasses, this is shown Fig. 3, 4 and 5.

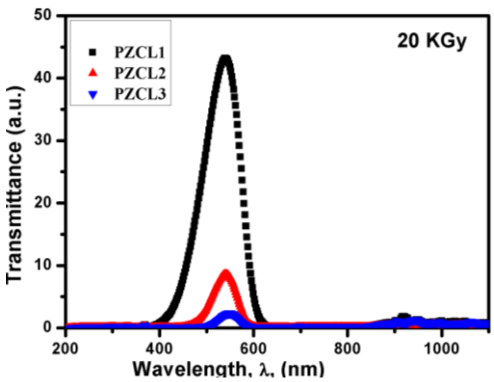

Fig. 3: Optical transmittance of PZCL1, PZCL2 and PZCL3 glasses after gamma radiation dose =20 KGy

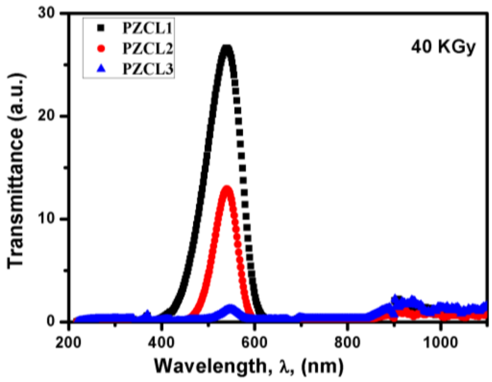

Fig. 4: Optical transmittance of PZCL1, PZCL2 and PZCL3 glasses after gamma radiation dose =40 KGy

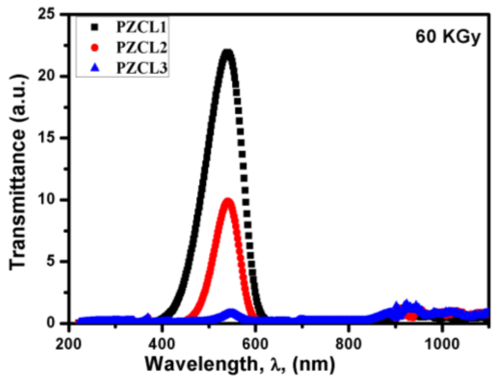

Fig. 5. Optical transmittance of PZCL1, PZCL2, and PZCL3 glasses after gamma radiation dose = 60 KGy

We determine the optical absorption coefficient as a function of frequency $\alpha(\nu)$ at a various frequency according to the relation; $\alpha(\nu) = \frac{1}{L}\ln\left(\frac{I_0}{I}\right) = 2.303(\frac{A}{L})$, where, ν, is the frequency of radiation, I_0 and I_t stands for intensities of the incident and transmitted light rays, respectively and , L, is the thickness of the glass samples. The factor ln(I_0/I) corresponds to absorbance. In amorphous materials the absorption coefficient increases with the photon energy attributed to nearest the energy gap, also the absorption edge of amorphous materials increases exponential with photon energy. When the energy of the incident light is less than the band gap leads to exponential decay of density of the localized state into the gap [13- 16]. We note that the band energy (Urbach and optical gap) are depends on different factors such as: (1) thermal vibrations in the glasses lattice; (2) static disorder; (3) induced disorder; (4) average photon energies; (5) strong ionic bonds.

Davis and Mott [14] estimated an formula for the, α(ν) with relation the photon energy ($h\nu$) for two different cases as follow: direct and indirect transitions mechanism through the following expression; $[\alpha(\nu)\cdot h\nu]=B(h\nu-E_{opt})^{n}$, where, h = 8.28π·10^{-15} (eV·s), n = 1/2 for direct transition, but when n = 2 this for indirect transition, *B* is a constant related to the extent of the band tailing, and E_{opt} is optical band gap energy.

Fig.6, obtain of a diagram of $(\alpha h\nu)^{1/2}$ *vis.* (hν) for the prepared glasses PZCL1, PZCL2, and PZCL3 before the irradiated gamma-ray dose. Where E_{opt} calculated utilizing from the linear part of a plot by extrapolating it to intercept the hν axis at $(\alpha h\nu)^{1/2} = 0$. It is clear that E_{opt} has been decreased from 4.17 to 3.42 eV with CuO concentration increased from 5 to 20 mol%. Many authors [15- 17] have been suggested that the changing of the absorption band to lower energy attributed to converting the non-bridging oxygen NBO, which has a less-tightly bound electron than bridging oxygen BO. Hence the decreasing in the energy gap of PZCL3 is caused by increases in the number of NBO.

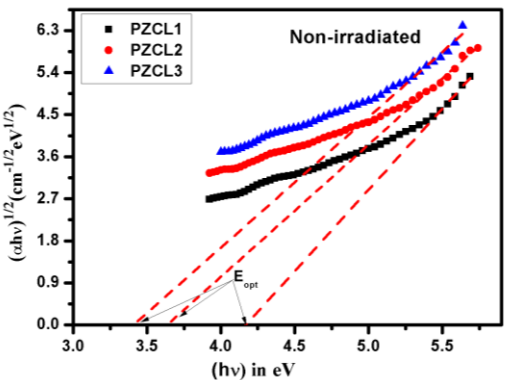

Fig. 6. $(\alpha h\nu)^{1/2}$ *vis.* $h\nu$ *of the PZCL1, PZCL2 and PZCL3 glasses before irradiated by gamma dose.*

When the prepared glasses were irradiated to different doses of gamma irradiation 20, 40 and 60 KGy, the optical band gap value, Eopt, is obtained to decrease as the gamma dose increase, this shown in Fig. 7, 8 and 9. Also, all these results of Eopt for prepared glasses before and after irradiation with gamma radiation are summarized in Table 3.

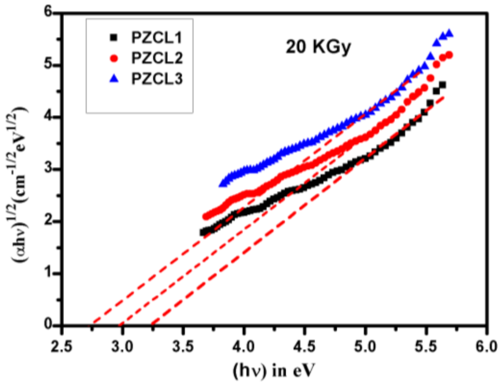

Fig. 7. $(\alpha h\nu)^{1/2}$ *vis.* $h\nu$ *of the PZCL1, PZCL2 and PZCL3 glasses after irradiated by gamma dose equal to 20 KGy.*

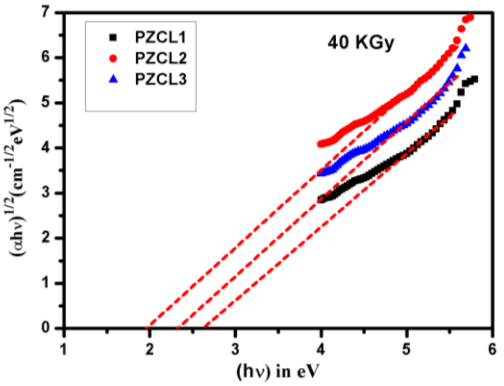

Fig. 8. $(\alpha h\nu)^{1/2}$ *vis.* $h\nu$ *of the PZCL1, PZCL2 and PZCL3 glasses after irradiated by gamma dose equal to 40 KGy.*

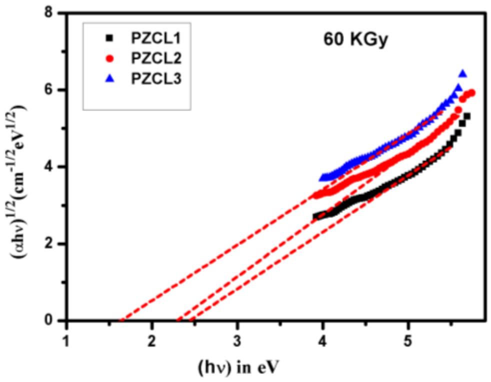

Fig. 9. $(\alpha h\nu)^{1/2}$ *vis.* $h\nu$ *of the PZCL1, PZCL2 and PZCL3 glasses after irradiated by gamma dose equal to 60 KGy.*

Table 3. Optical band gap value, Eopt, of prepared glasses PZCL1, PZCL2 and PZCL3 before and after gamma irradiation dose 20, 40 and 60 KGy.

Glasses code	E_{opt}, in eV before irradiated	E_{opt}, in eV after 20 KGy	E_{opt}, in eV after 40 KGy	E_{opt}, in eV after 60 KGy
PZCL1	4.17	3.23	2.62	2.44
PZCL1	3.65	2.97	2.32	2.28
PZCL1	3.42	2.72	1.96	1.62

When incorporating transition metal oxide like that CuO to phosphate glasses leads that largest chance for changing their valences by photochemical reactions from holes (h^+) and electron generated during the irradiation exposure such as follow.

(1)- Defect +hν → free hole+ trapped electron
(2)- Cu^{2+} + free electron → Cu^+
(3) Cu^+ + free hole → Cu^{2+}
(4) Cu^+ + free electron → Cu^0

Generally, the electron generated faster than a hole in the glasses matrix and hence the accumulation velocity of Cu^0 is higher than that of Cu^{++}. We can suggest that the decreasing values of E_g with increasing gamma dose from 20 to 60 KGy due to increasing the number of the unpaired electrons per unit volume with increasing the spin density in unfilled bands this leads to decrease the band gap between valence band and conduction band in the network structure of prepared glasses. Besides that, with irradiation by gamma dose, this leads to the defects centers formed from charge trapping of the electrons/ holes which often have electronic states in the gap between the valence and the conduction bands. Therefore optical photons can induce a transition from the valence band to the defects level or from the defect level to the conduction band.

Fig. 10 shows the Raman spectra of prepared glasses PZCL1, PZCL2, and PZCL3. From this figure we can analyze the structure of present network as follow; the band around at 357 cm^{-1}can be contributed to P- O- Zn linkages. The band at 550 cm^{-1} refer to the PO_4^{3-} related to P-O- Cu^{2+} bonds [18,19] and a band at 700 cm^{-1} assigned to the symmetric bridging stretching vibration (ν_s) of the –P-O-P- units along the chains [18- 20]. A band at 731 cm^{-1} can be due to the second symmetric stretching mode of P-O-P bridging bonds in short phosphate units. The band around 1200 cm^{-1} can be attributed to the terminal P-O stretching vibrations of the PO_2 units [21]. Finally the band around 1250 cm^{-1} related to the P= O, the double bond in the polyphosphate chain.

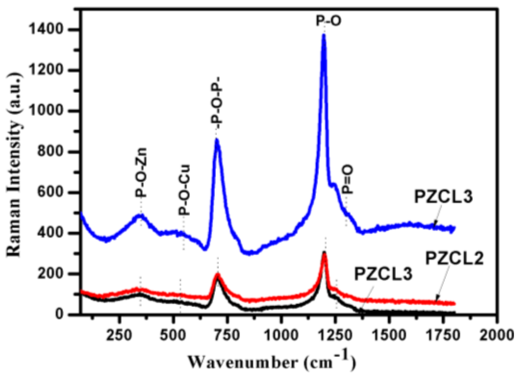

Fig. 10 Raman spectra of prepared glasses PZCL1, PZCL2 and PZCL3.

4. Conclusions

Novel quaternary glasses P_2O_5- ZnO- LiCl- CuO were prepared. The density value increase with the increase of CuO ions otherwise optical energy gap decrease with increasing Cu ions. These glasses have strong transmittance band at center 540 nm with intensity decrease with increasing CuO concentration.

Gamma irradiation causes effects by photochemical reaction with distortion the phase of Cu^{2+} leads to decreasing the optical band gap and intensity of transmittance. The optical transmission reveals that of these glasses acts as abroad bandpass filter in the UV- Vis region.

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