

## Research Article

# Dosimetric UV Exposure Effect on the Optical Properties of Ag<sub>2</sub>O Doped P<sub>2</sub>O<sub>5</sub>-ZnO-CuO Glass

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Silver phosphate glass types within composition 60P<sub>2</sub>O<sub>5</sub>-30ZnO-10CuO-100000 ppm Ag<sub>2</sub>O were prepared by melt-quenching technique. The optical properties of these glass types were studied under UV exposure at different times, 0, 20, 80, 105, and 115 minutes. The optical absorbance spectra were measured in the range of wavelength from 190 to 3200 nm. The absorbance bandwidth decreases with increasing the time of UV exposure. The optical energy gap,  $E_g$ , linear refractive index,  $n$ , ratio between molar refraction,  $R_m$ , and molar volume,  $V_m$ , and metallization criterion ( $M$ ) were estimated. The value of  $E_g$  decreases from 2.132 to 1.91 eV with increasing the time of UV exposure from 0 to 115 min. Otherwise  $n$  value and metallization increase with increase in the time of UV exposure. The results indicated that these glass types are promising for using an ultraviolet radiation dosimeter.

## 1. Introduction

Phosphate glass types are attractive hosts and also considered to be promising for optical amplifier, fibres, laser, and dosimetry [1]. Otherwise, the disadvantage of phosphate glass is the poor chemical durability, so adding modifier like transition metals oxides leads to increasing the benefits of the glass types with decreasing their chemical durability [2, 3]. The advantage of phosphate glass types is having low melting temperature, small viscosity, and high solubility of rare earth ions [4]. Many studies on the characterization of phosphate glass types proved that, by adding cation with high value of electrostatic field strength like Zn<sup>2+</sup> and Pb<sup>2+</sup>, the covalence of P-O-M bonds increases [5, 6]. The doping by transition metal ions like Ag leads to capturing the electron and causing positive hole and it can undergo photochemical reaction which can modify their valences [7]. What is more important is that phosphate glass types contain Ag<sup>+</sup> and Cu<sup>+</sup> ions which can be used as potential antimicrobial properties [8, 9]. Moreover Ag<sup>+</sup> was found to have the highest potent antimicrobial effect against different microorganisms compared to Cu<sup>+</sup> ions [10]. Some oxide of glass types irradiated

by ionizing radiation and excited by UV light obtained emission of visible photons; this phenomenon is called the radio photoluminescence (RPL). It is a phenomenon observed in phosphate glass types doped with silver. When UV with ionized X-ray or gamma irradiation incident on the glass types contains CuO as transition metal with binary glass types, P<sub>2</sub>O<sub>5</sub>-ZnO affected in and induced defects were showed through the positive holes or generated electrons during the irradiation process [11, 12]. Hence we add Ag<sub>2</sub>O and CuO to phosphate glass types with composition 60P<sub>2</sub>O<sub>5</sub>-30ZnO-10CuO that can be used as a dosimeter. The present work is to investigate the characterization and the effect of UV irradiated exposure on the optical properties of glass types with composition 60P<sub>2</sub>O<sub>5</sub>-30ZnO-10CuO-100000 ppm Ag<sub>2</sub>O with different times of exposure to UV light at 20, 80, and 105 to 115 minutes.

## 2. Experimental Work

Herein the phosphate glass types within composition 60P<sub>2</sub>O<sub>5</sub>-30ZnO-10CuO doped with 100000 ppm Ag<sub>2</sub>O were melted by quenching technique in alumina crucibles at

TABLE 1: Time of UV irradiated exposure, optical energy gap,  $E_g$ , band width,  $\delta\lambda$ , refractive index,  $n$ , ratio of molar refraction over molar volume, and metallization,  $M$ , of prepared glass types  $60\text{P}_2\text{O}_5\text{-}30\text{ZnO-}10\text{CuO}$  doped with 100000 ppm  $\text{Ag}_2\text{O}$ .

Time of UV irradiated exposure in minutes	Optical energy gap, $E_g$ , in eV	Band width, $\delta\lambda$ , in nm	Refractive index	$R_m/V_m$ in $\text{mol}^{-1}$	Metallization, $M$ ,
0	2.13	1800	2.681	0.674	0.326
20	2.11	1590	2.69	0.675	0.325
80	1.98	1465	2.747	0.685	0.315
105	1.93	1455	2.767	0.689	0.311
115	1.91	1385	2.776	0.691	0.309

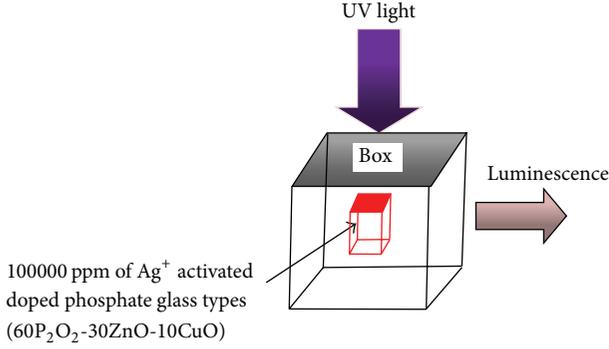


FIGURE 1: Setup of UV irradiated exposure.

temperature of  $1200^\circ\text{C}$ . The prepared sample was transferred to an annealing furnace and kept at  $400^\circ\text{C}$  for 2 h. Herein the prepared glass types contained  $\text{Cu}^{2+}$  ions which leads to bluish colors. The optical absorption spectra of the glass types were measured in the wavelength range 190–3200 nm using UV-VIS-NIR spectrophotometer (Schimadzu, UV-3600). Irradiation was performed at room temperature with a UV light which is emitted mainly in the spectra at 254 nm wavelength radiation and provides evaluated light beam irradiance of  $7.2 \text{ mW/cm}^2$  at a distance of 30 cm from the sample. No external filter was used during irradiation (this setup is shown in Figure 1). The optical properties of prepared glass types were investigated under UV irradiation exposure at different times, 0, 20, 80, 105, and 115 min.

Scanning electron microscopy (SEM) was performed using JEOL™ Model JSM-T330 operating at 25 kV. To determine the elements in a crystalline phase by using EDx (Energy Dispersive Spectrum) X-ray detector can measure the intensity of the X-rays versus the energy.

### 3. Result and Discussion

Studying the optical absorption edge in UV-region is a very useful method for characterizations of both the optical transitions and electronic band structure of the amorphous material [13–15]. Two mechanisms are possible to determine direct and indirect transition that can be occurring in band gap by UV absorption spectra at the fundamental absorption edge of the amorphous material. Figures 2(a)–2(e) show UV, VIS, and NIR absorbance spectra of prepared glass types  $60\text{P}_2\text{O}_5\text{-}30\text{ZnO-}10\text{CuO-}100000 \text{ ppm } \text{Ag}_2\text{O}$  irradiated

by UV with time of 0, 20, 80, 105, and 115 min, respectively. The absorbance value of prepared glass types decreased by increasing the time of UV light exposure. The broad absorbance band from  $\lambda_1 = 1390$  to  $\lambda_2 = 3190$  nm (where  $\delta\lambda = \lambda_2 - \lambda_1 = 1800$  nm) in prepared glass types with no irradiation by UV was obtained (see Figure 2(a)). When the prepared glass is exposed to UV light at different times from 20 to 105 to 115 min, this leads to the absorbance band pass decreasing from 1590 to 1465 to 1455 to 1385 nm; consequently, this is shown in Figures 2(a)–2(e). This means that the time of UV exposure increase leads to the absorbance band pass being decreased. In two cases, the electromagnetic waves interact with the electrons in the valence band and hence were excited to the conduction band. In glassy materials, the absorption coefficient  $[\alpha(\omega)]$  increases with the photon energy nearest to the energy gap. Davis and Mott [16] gave a formula for  $[\alpha(\omega)]$  as a function of photon energy ( $\hbar\omega$ ) for two different cases: firstly direct and secondly indirect transitions through the following expression:  $\alpha(\omega) = A (\hbar\omega - E_g)^n / \hbar\omega$ , where  $\hbar = 4.14 \cdot 10^{-15} \text{ (eV}\cdot\text{s)}$ ,  $n = 1/2$  for direct transition but  $n = 2$  for indirect transition,  $A$  is a constant related to the extent of the band tailing, and  $E_g$  is optical band gap energy. Moreover the absorption edge of glassy materials increases exponentially with photon energy. The energy of the incident light is less than the band gap due to the increase in absorption coefficient and leads to exponential decay of density of the localized state into the gap [13, 14] in which the absorption edge denotes Urbach edge, where  $\alpha(\omega)$  value is in the range from 10 to  $10^3 \text{ cm}^{-1}$ . Urbach energy strongly depends on many factors as follows: (1) temperature; (2) thermal vibrations in the glass types lattice; (3) induced disorder; (4) static disorder; (5) strong ionic bonds; and (6) average photon energies. Figures 3(a)–3(e) showed the plot  $(\alpha\hbar\omega)^{1/2}$  versus  $(\hbar\omega)$  of the studied prepared glass types, where the energy,  $E_{\text{opt}}$ , has been estimated from the linear regions of the curves by extrapolating them to meet the  $x$ -axis at  $(\alpha\hbar\omega)^{1/2} = 0$  [17–19] and the values are listed in Table 1 for both samples. The optical energy gap values decrease from 2.131 to 1.91 eV with increasing the UV irradiate exposure time from 0 to 115 min; this is shown in Figure 4. When incorporating  $\text{CuO}$  and  $\text{Ag}_2\text{O}$ , largest chance for Ag and Cu ions leads to changing their valences by photochemical reactions from holes ( $\text{h}^+$ ) and electron generated during the irradiation exposure. Hence the following reactions happened:  $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}^0$ ,  $\text{Cu}^+ + \text{h}^+ \rightarrow \text{Cu}^{++}$ ,  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$ , and  $\text{Ag}^+ + \text{h}^+ \rightarrow \text{Ag}^{++}$  [20]. The electron is generated faster than  $\text{h}^+$  in

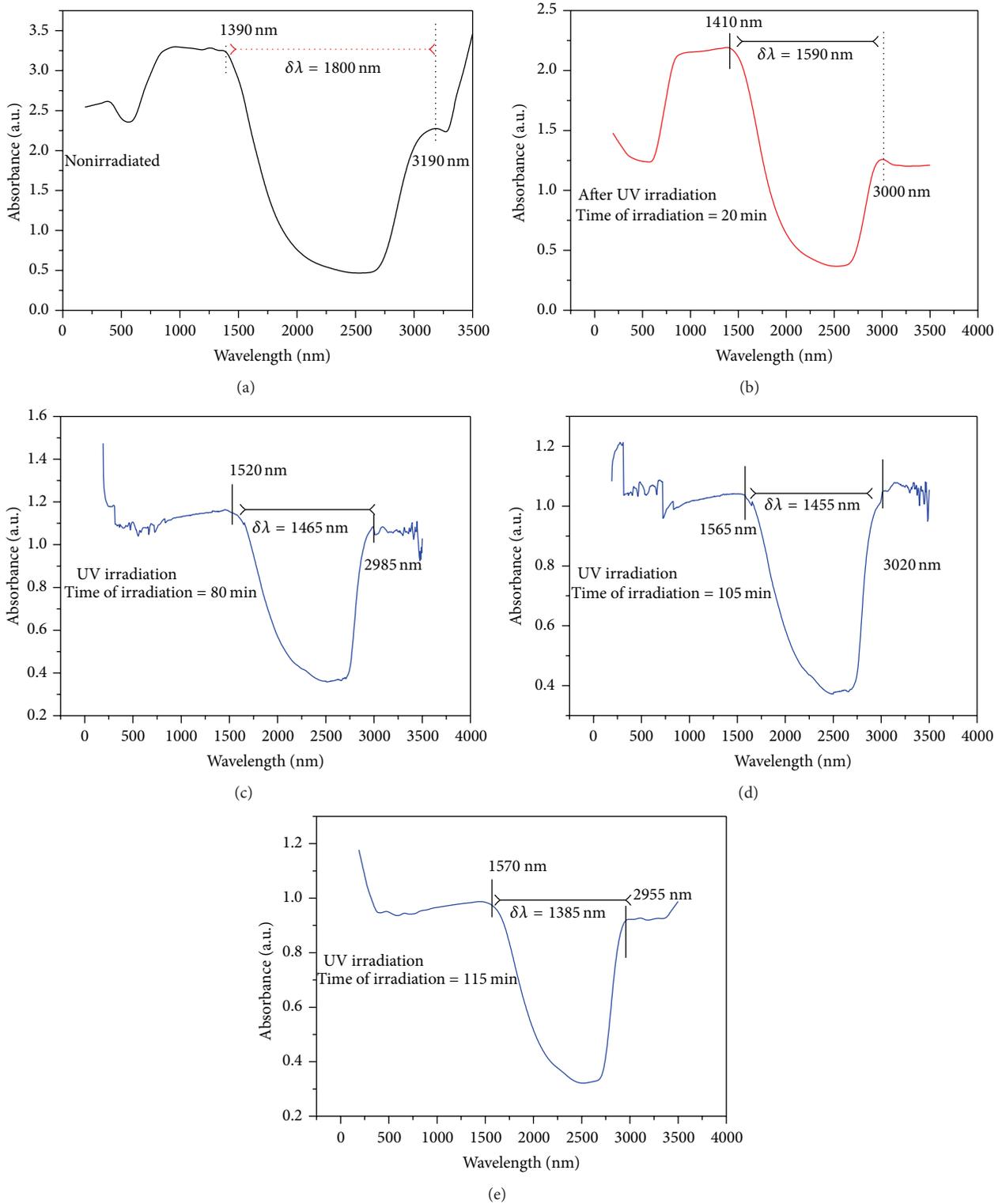


FIGURE 2: (a) Absorbance spectra of prepared glass types before UV irradiation. (b) Absorbance spectra of prepared glass types after UV irradiation exposure time = 20 min. (c) Absorbance spectra of prepared glass types after UV irradiation exposure time = 80 min. (d) Absorbance spectra of prepared glass types after UV irradiation exposure time = 105 min. (e) Absorbance spectra of prepared glass types after UV irradiation exposure time = 115 min.

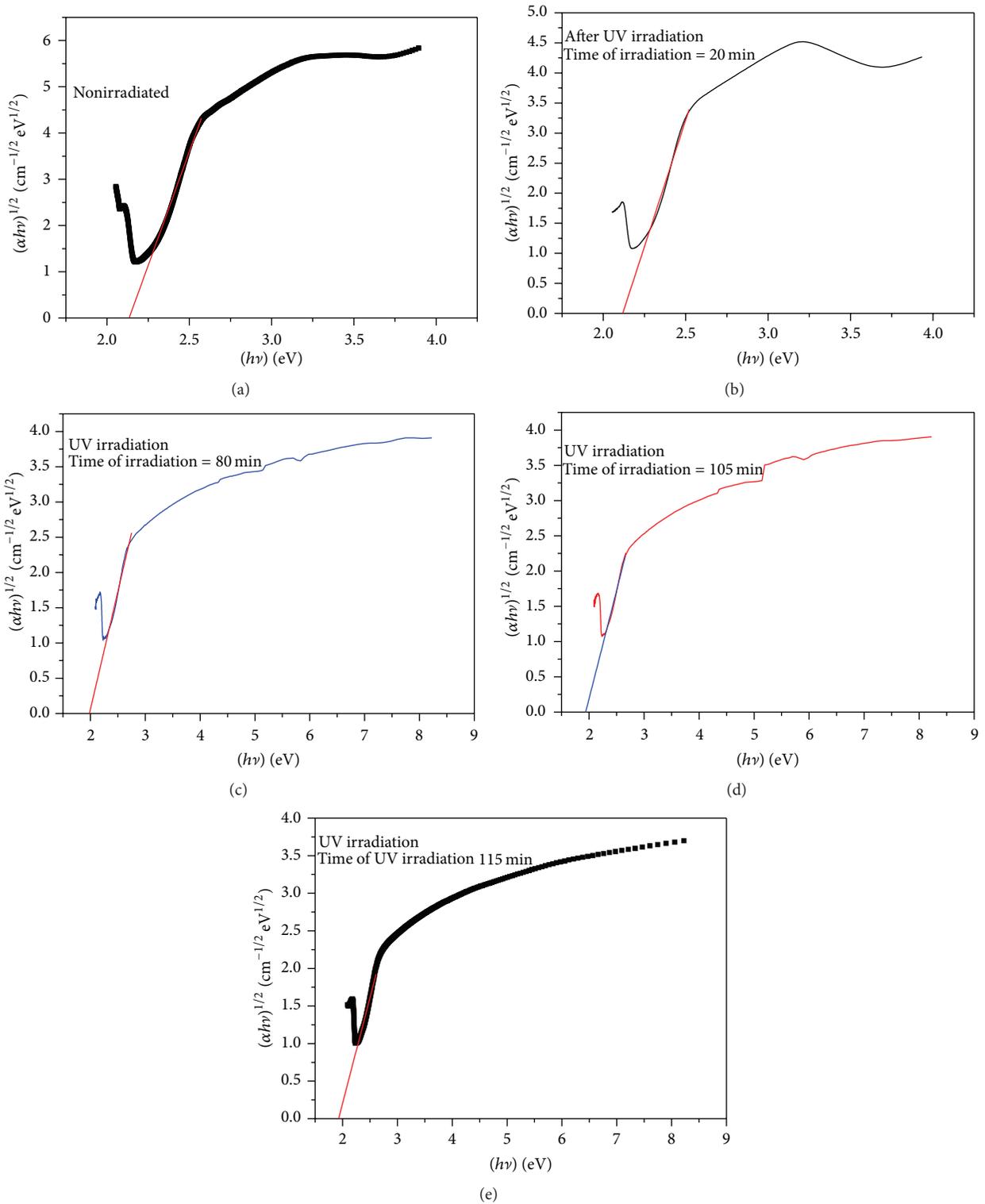


FIGURE 3: (a) The dependence of  $(\alpha h\nu)^{1/2}$  on  $(\alpha h)$  for prepared glass types before UV irradiation. (b) The dependence of  $(\alpha h\nu)^{1/2}$  on  $(\alpha h)$  for prepared glass types after UV irradiation time = 20 min. (c) The dependence of  $(\alpha h\nu)^{1/2}$  on  $(\alpha h)$  for prepared glass types after UV irradiation time = 80 min. (d) The dependence of  $(\alpha h\nu)^{1/2}$  on  $(\alpha h)$  for prepared glass types after UV irradiation time = 105 min. (e) The dependence of  $(\alpha h\nu)^{1/2}$  on  $(\alpha h)$  for prepared glass types after UV irradiation time = 115 min.

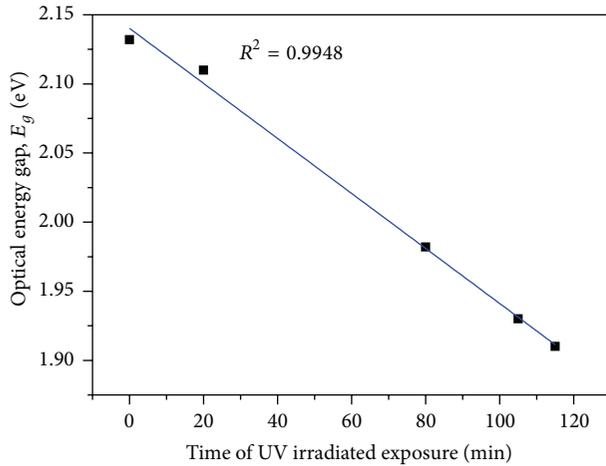


FIGURE 4: Optical energy gap with UV irradiation exposure time at different times of prepared glass types.

the glass types matrix and hence the accumulation velocity of  $\text{Ag}^0$  and  $\text{Cu}^0$  is higher than that of  $\text{Ag}^{++}$  and  $\text{Cu}^{++}$ . We can explain the observed decreasing values of  $E_g$  from 2.131 to 1.91 eV with increasing the UV irradiate exposure time from 0 to 115 min due to increasing the number of the unpaired electrons per unit volume with increasing the spin density in unfilled bands. In addition to irradiation of UV, the defects centers formed from charge trapping of the electrons or holes which often have electronic states in the gap between the valence and the conduction bands. Hence optical photons can induce transition from the valence band to the defects level or from the defect level to the conduction band.

The refractive index ( $n$ ) at different wavelength can be determined by  $R_m/V_m = [((n^2 - 1)/(n^2 + 2))]$ , where molar refraction  $R_m$  is in  $\text{cm}^3 \cdot \text{mol}^{-1}$  and  $V_m$  is the molar volume in  $\text{cm}^3$ . Duffy and Ingram [21] have obtained an empirical formula that relates the energy gap,  $E_g$ , to the molar refraction  $R_m$  as follows:  $E_g = 20(1 - R_m/V_m)^2$ ; the metallization criterion,  $M$ , can be determined by expression  $M = 1 - R_m/V_m$ . If  $R_m/V_m = 1$  this means that the linear refractive index becomes infinite; moreover, when ( $R_m/V_m < 1$ ) and ( $R_m/V_m > 1$ ) this indicated the nonmetallic and metallic character of material, respectively. Herein the refractive index increases from 2.681 to 2.776 when the time of UV exposure of prepared sample increases from 0 to 115 min; this is shown in Figure 5. Also the ratio of  $R_m/V_m$  value increases from 0.674 to 0.691 in  $\text{mol}^{-1}$  when the time of UV exposure increases from 0 to 115 min. Otherwise the metallization value of prepared glass types decreases from 0.326 to 0.309 when the time of UV exposure increases from 0 to 115 min. Tošić et al. [22] estimated that the phosphate glass types containing ZnO have shorter phosphate anions length as bond of nonbridge oxygen replaces bond of bridging oxygen on the P-tetrahedra change in the polarizability of  $\text{O}_2^-$  surrounding the copper ions due to increasing the distortion which strongly depends on the field strengths of network modifier former ion. So the increasing of polarizability with time of

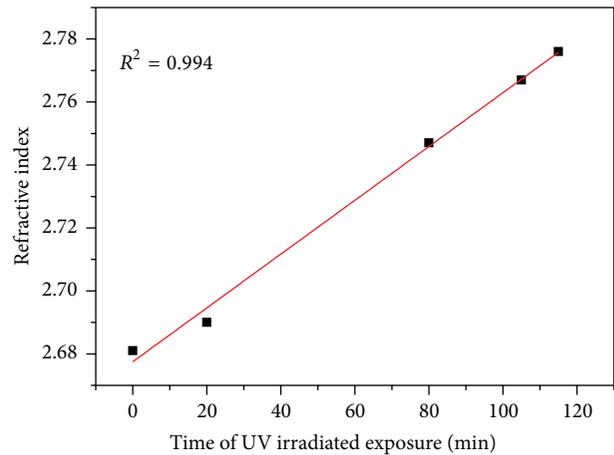


FIGURE 5: Refractive index with UV irradiation exposure time at different times of prepared glass types.

UV exposure increasing from 0 to 115 min leads to increase in refractive index. Measurement of a dosimeter character is the process of finding at least one physical property that can be used for designing radiation dosimeter which can be possible calibration. Here we found that the relation between optical energy gap and UV irradiated exposure time is good linear fitting with regression value ( $R^2 = 0.9948$ ) (see Figure 4); this indicates the increase in the nonbridge oxygen due to increase in the number of free electrons. Also the relation between the value of refractive index and the time of UV irradiated exposure is in good agreement with high regression ( $R^2 = 0.994$ ) (see Figure 5). Hence we can estimate that the prepared glass types with composition  $60\text{P}_2\text{O}_5\text{-}30\text{ZnO}\text{-}10\text{CuO}\text{-}100000$  ppm  $\text{Ag}_2\text{O}$  may be used in the instrument of UV dosimeter. Finally we investigated the prepared glass types by using SEM at room temperature; this is shown in Figure 6(a); no crystalline was obtained in this figure. After the prepared glass types annealed at  $600^\circ\text{C}$ , the crystalline silver as shape sheets appeared, and it was analyzed by using EDX (see Figures 6(b) and 6(c)).

#### 4. Conclusion

The incorporation of  $\text{Ag}_2\text{O}$  into the ternary glass in the system  $60\text{P}_2\text{O}_5\text{-}30\text{ZnO}\text{-}10\text{CuO}$  leads to preparing activated phosphate glass types under UV irradiation. The band width decreases with increasing the time of UV irradiated exposure of prepared glass types. The value of optical energy gap decreases linearly with increasing the time of UV exposure. Otherwise the refractive index increases with increasing the time of UV exposure and polarizability of nonbridging oxygen.

#### Competing Interests

The authors declare that they have no competing interests.

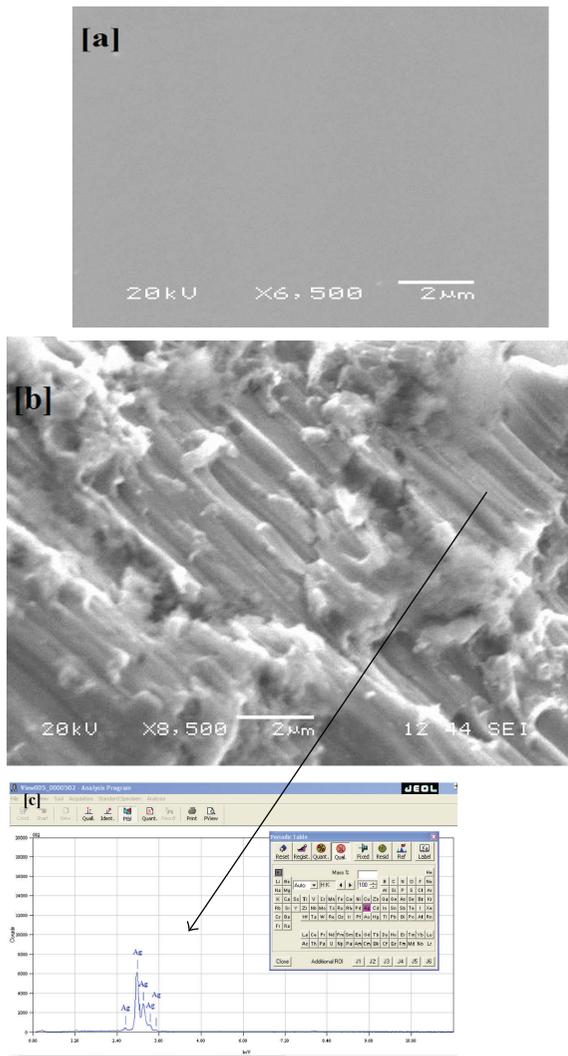


FIGURE 6: (a) SEM of prepared glass types at room temperature. (b) SEM of prepared glass types at 600°C. (c) EDX of prepared glass types at 600°C.

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