

## Studying the Structural and Optical properties of PVA doped with CuO and FeCl<sub>3</sub> composites films

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### ABSTRACT

In this research, we are studying structural and optical properties of film (PVA doped with CuO and FeCl<sub>3</sub>). The (CuO) with concentration (7%), and (FeCl<sub>3</sub>) with different concentrations of FeCl<sub>3</sub> (3, 7, and 9) %, preparing by casting method with thickness (25±5) μm, the structure characterized by using (XRD). The investigation of (XRD) indicates that the pure (PVA) and doping films are polycrystalline structure. The results of the measuring size, micro grain strain, dislocation density and number of crystals of each sample show that the grain size increases with increasing concentration from (3.676-11.57) nm. The absorbance and transmittance spectra have been recorded in the wavelength range (200-1100) nm in order to study the optical properties. The optical band gap of (PVA) decreases with increasing concentration of FeCl<sub>3</sub> from (4.3- 1.6) eV, and extinction coefficient, refraction index, the optical conductivity are varies with increasing concentration.

**Keywords:** (PVA) films, doping, CuO and FeCl<sub>3</sub>.

### دراسة الخواص التركيبية والبصرية لاغشية بوليمر فينال الكحول المشوبة باوكسيد النحاس وكلوريد الحديد

الخلاصة:

في هذا البحث تم دراسة الخواص التركيبية والبصرية لاغشية بوليمر فينال الكحول المشوبة (باوكسيد النحاس وكلوريد الحديد) كلوريد النحاس بنسبة (7%) وكلوريد الحديد بنسب مختلفة (3, 7, 9) % المحضرة بطريقة الصب وبسمك (25±5) μm, وباستخدام تقنية حيود الاشعة السينية. وجد ان الاغشية النقية المشوبة ذات تركيب متعدد التبلور وتم حساب كل من الحجم الحبيبي وكثافة الانخلاعات وتشوه البلورة وعدد الطبقات لكل نموذج وقد وجد أن الحجم الحبيبي يزداد من (3.676-11.57) nm مع زيادة التركيز للشوائب. اما طيف الامتصاصية والنفاذية سجل ضمن مدى الطول الموجي (200-1100) nm وقد وجد ان فجوة الطاقة تقل بزيادة نسبة كلوريد الحديد من (4.3- 1.6) eV اما معامل الخمود ومعامل الانكسار والتوصيلية البصرية تتغير بعد زيادة نسبة التشويب.

الكلمات المفتاحية: اغشية PVA، تشويب، CuO and FeCl<sub>3</sub>.

### INTRODUCTION

Polymer materials have been widely used because their easy of processing, relatively low cost and mass production compared to silica based optical materials [1]. The properties of a polymer may be improved and controlled substantially by adding suitable dopant [2]. Some metallic salts with Polyvinyl Alcohol (PVA) presents important variations in the optical absorption and the

refractive index. The optical parameters of doped polymers are strongly dependent on the electronic configuration inside the electrolytes. In order to obtain materials with improved optical properties, it is necessary to understand and control of electronic mechanisms involved in the process[3]. Polyvinyl alcohol (PVA) is molecular formula is (C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>, and density is between (1.19 - 1.31) g/cm<sup>3</sup>. PVA has a melting point of 230°C. It decomposes rapidly above 200°C, as it can undergo pyrolysis at high temperatures [4]. Different additives such as polymer, salts, nanocomposites and ions are usually added to PVA in order to modify and improved its properties [5]. Generally the polymer behavior and as a rule of composite materials, new properties, different of both matrix and filler ones, could be evidenced [6]. Studied many of researchers them from: Tawansi et al [7] studied the (PVA) films filled with various mass fractions of FeCl<sub>3</sub> and prepared by using a casting method. The structural, electrical and magnetic properties were clarified. The filling level (FL) dependence of certain IR absorption peaks was correlated with the obtained physical parameter characterizing the other properties. Kumar et al [8] studied PVA and doped PVA films were prepared by solution casting. The Change in electrical conductivity of pure PVA and transition elements FeCl<sub>3</sub> and NiCl<sub>2</sub>·6H<sub>2</sub>O doped PVA films with and without  $\gamma$ -irradiation in the temperature range (50–130) °C they were found that Fe<sup>+3</sup> doped PVA films shows higher conductivity than Ni<sup>+2</sup>

Khalifa et al [5] studied pure and Fe<sup>+3</sup> doped polyvinyl alcohol (PVA) films, by using FeCl<sub>3</sub>, and prepared by a solution casting method. The effect of Fe<sup>+3</sup> doping on the photoluminescence (PL) behavior of PVA is investigated in the temperature range from (10 -300) K. Meena et al [9] studied madean attempt to disperse CuO nanoparticles in the polyvinyl alcohol (PVA) and to understand the change in structural, optical and electrical properties of the polymer film. CuO nanoparticles were added in four concentrations (2.55.0, 7.5 and 10) %.

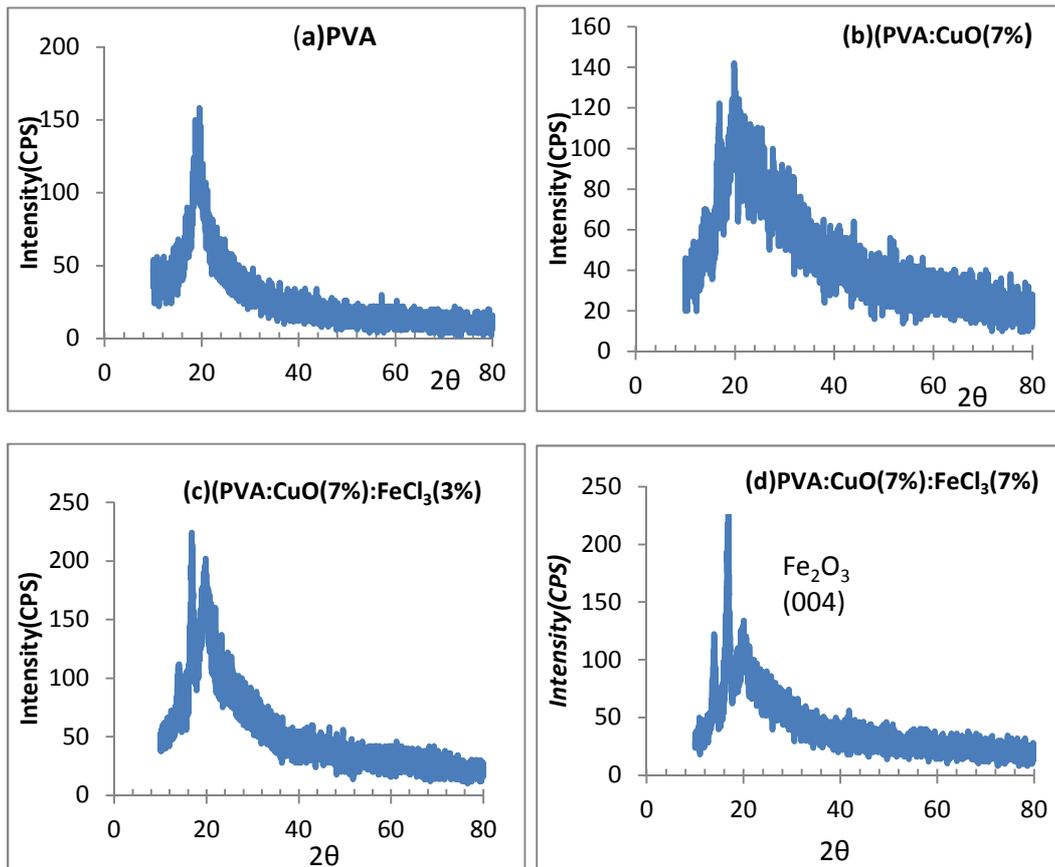
In the present work is to investigate the structural and optical properties of polyvinyl alcohol (PVA) doped with copper oxide (CuO) and (FeCl<sub>3</sub>).

### **Experimental**

Films of Polyvinyl alcohol (PVA) with Copper Chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O) and Iron Chloride (FeCl<sub>3</sub>) were prepared by casting method. The aqueous solution of this polymer was prepared by dissolving 4gm of pure PVA at (70000 molecular weight) in 50ml of distilled water. To obtain the complete dissolution a magnetic stirrer for two hour at 40°C until PVA was completely soluble, and dissolved (CuCl<sub>2</sub>·2H<sub>2</sub>O) at (170. 48molecular weight) of distilled water with concentration (7%) for (15) min at 40°C and dissolved (FeCl<sub>3</sub>) at (162.2 molecular weight) of distilled water with different concentration of FeCl<sub>3</sub> (3, 7, and 9)% for (30) min at 40°C. and added to the polymer solution, heated for (20) min at 20°C until completely dissolved. These homogenous solutions were casted in a glass dish (diameter of 5 cm) and left to dry for 72 hour to remove any residual solvent.. The thickness of the films was (25±5)  $\mu$ m. It was determined by using micrometer at different places in each film. The films were ready which cut into pieces for characterization .To investigate the structure of the polymer by using X- ray diffraction type (SHIMADZU Japan) XRD600, wave length 1.5418 Å°. Absorbance and transmittance measurement were carried out by using (UV-visible 1800 spectra photometer) in the wavelength range (200 – 1100) nm.

**Results and discussion:**

XRD spectrum of PVA films shown in figures (1). As showing in Fig. (1)a and the diffraction pattern of PVA indicates a diffraction band at  $2\theta = 19.348^\circ, 20.66^\circ$  and  $16.9707^\circ$ . Figure (1)b the diffraction pattern of PVA:CuO(7%) indicates that a diffraction band at  $2\theta = 16.9152^\circ, 20.0227^\circ$  and  $19.3448^\circ$ . Figure (1)c the diffraction pattern of PVA:CuO (7%):FeCl<sub>3</sub>(3%) indicates that a diffraction band at  $2\theta = 16.8703^\circ, 19.6838^\circ$  and  $20.8205^\circ$ . Figures (1)d the diffraction pattern of PVA:CuO(7%):FeCl<sub>3</sub>(7%) indicates that a diffraction band at  $2\theta = 16.803^\circ, 13.9583^\circ$  and  $19.9829^\circ$ . Figure (1) e the diffraction pattern of PVA:CuO(7%):FeCl<sub>3</sub>(9%) indicates that a diffraction band at  $2\theta = 17.0682^\circ, 14.1942^\circ$  and  $19.6040^\circ$ . It is well known that the peaks at  $2\theta < 20^\circ$  are due to crystalline nature of PVA polymer molecular. The intensity from films has been increases after the doping process and became sharper due to crystallinity. The doping FeCl<sub>3</sub> is effect at 7% percentage where a new peak at  $2\theta = 13.9583^\circ$  corresponds to ( 004) and at 9% percentage where a new peak at  $2\theta = 14.1942^\circ$  corresponds to ( 103) by using the (Jcpds) cards- Fe<sub>2</sub>O<sub>3</sub>- 00-015-0615 (Fixed Slit Intensity).



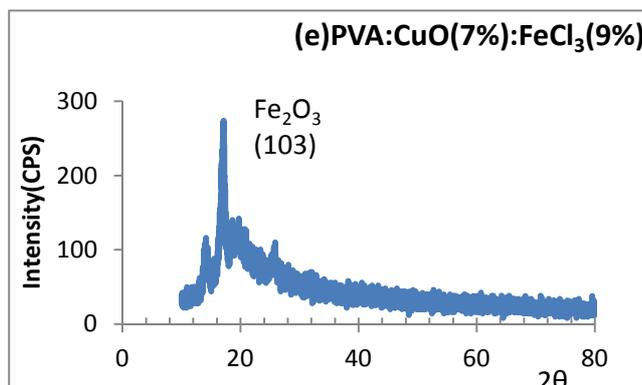


Figure (1) X-ray diffraction (XRD) for the polymer before and after doping.

The calculated value of the structural parameters, grain size, strain and number of crystals determined by using of the following formulas:

1-The strain ( $\epsilon$ ) [10, 11]:

$$\epsilon = \beta \cos\theta / 4 \quad \dots(1)$$

Where  $2\theta$  is the Bragg angle,  $\beta$  the full width at half maximum.

2-Dislocation density ( $\eta$ )[10,12]:

$$\eta = 1 / (G.s)^2 \quad \dots(2)$$

Where g.s.is crystallites size of the grains in the films is estimated by using the Sherer formula [10, 13,14] :

$$G.s = K \lambda / \beta \cos\theta \quad \dots(3)$$

Where K is a constant taken to be 0.94,  $\lambda$  the wavelength of X-Ray ( $\lambda = 1.54 \text{ \AA}$ ).

3-Number of Crystals ( $N_0$ )[15]:

$$N_0 = t / (G.s)^3 \quad \dots(4)$$

t is the film thickness.

Table (1) Shows structural parameters grain size, strain, dislocation density and number of crystals as a function of concentrations.

Samp.	G.s (nm)	$\eta * 10^{-3} \text{ (nm)}^{-2}$	$N_0 \text{ (nm)}^{-2}$	$\epsilon * 10^{-3}$
PVA	3.676	73.999	503.28	9.844
PVA:CuO(7%)	10.44	9.1748	21.974	3.466
PVA:CuO(7%):FeCl <sub>3</sub> (3%)	11.04	8.205	18.5895	3.278
PVA:CuO(7%):FeCl <sub>3</sub> (7%)	11.57	7.47	16.1413	3.127
PVA:CuO(7%):FeCl <sub>3</sub> (9%)	9.72	10.584	27.223	3.723

The increases of grain size with increasing concentration of FeCl<sub>3</sub> may be attributed to the improvement of growth crystalline that leads to crystallinity and decreases of strain and dislocation density with increasing concentration of FeCl<sub>3</sub> that leads to decreases structural defect, these results agreement with results [5],[7],[8] [9]. Fig. (2) shows the relation between absorbance and transmittance with the wavelength, we found that the behavior of curves is the same. The rapid increases of the a absorption in the low energy and sudden decrease in special energy , and the absorbance increases with increasing the concentration FeCl<sub>3</sub> that its related to

changes in films structure, transmittance increases with the wavelength and decreases with increasing the concentration of FeCl<sub>3</sub>.

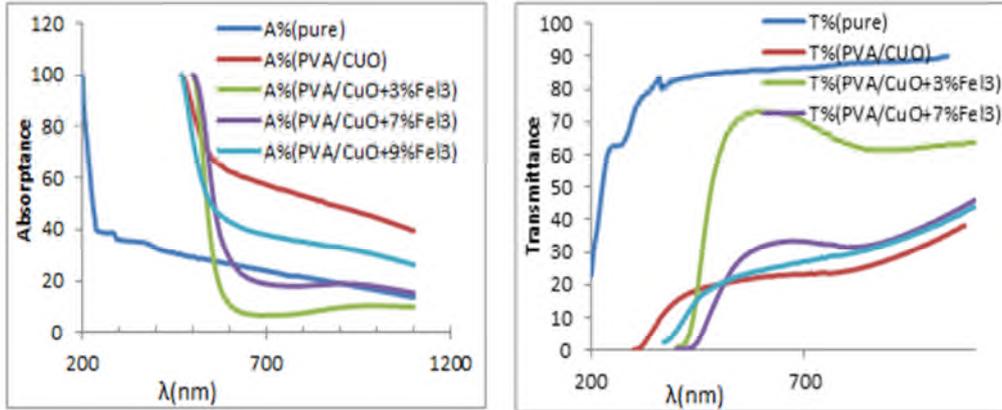


Figure ( 2) shows the relation between absorbance and transmittance with the wavelength.

We determined the absorption coefficient ( $\alpha$ ) by using the following equation [16]:

$$\alpha = \frac{2.303 A}{t} \quad \dots(5)$$

Where A is the absorbance. The optical absorption coefficient ( $\alpha$ ) of PVA films is very important to determine kind of electronic transition if ( $\alpha > 10^4$ ) the transition is direct and if ( $\alpha \leq 10^4$ ) the transition is indirect [15,16]. Fig (3) shows the dependence of the absorption coefficient on the photon energy for samples before and after doping.

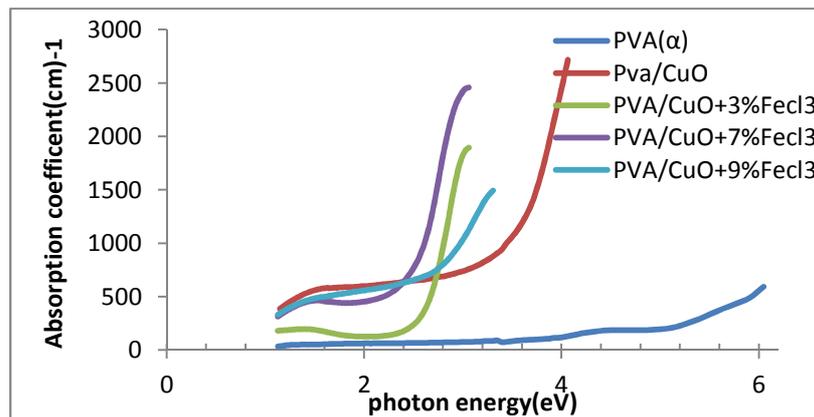


Figure (3) shows the dependence of the absorption coefficient on the photon energy

The optical energy band gap is determined by the following equation [17]:

$$\alpha E = B(E - E_g)^r \quad \dots(6)$$

Where B is a constant and the exponent (r) is an empirical index, which is equal to 2, 3, 1/2 and 3/2 depending on the nature of electronic transition responsible for the absorption. The plot of the product of absorption coefficient and photon energy  $(\alpha h\nu)^{1/2}$  versus the photon energy  $h\nu$  at room temperature, extrapolation of the linear portion of this curve to a point  $(\alpha h\nu)^{(1/2)}=0$  gives the optical energy band gap  $E_g$  for the PVA pure films and PVA doping which can be considered as an evidence for indirect transition .The value of energy gap are listed in table (2).

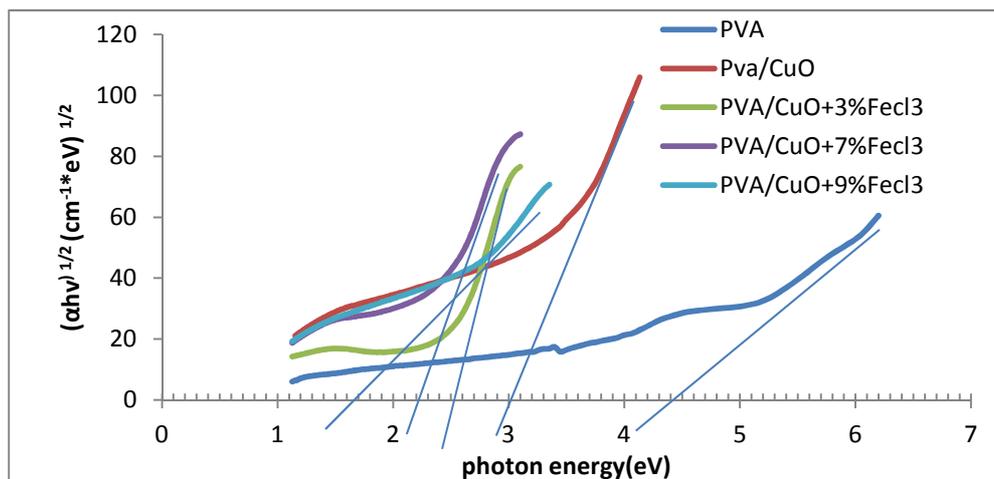


Figure (4) shows the relation between  $(\alpha h\nu)^{(1/2)}$  and photon energy.

Table (2) Show the energy gap for PVA before and after doping.

Sam.	$E_g$ (eV)
PVA	4.3
PVA:CuO(7%)	3
PVA:CuO(7%):FeCl <sub>3</sub> (3%)	2.5
PVA:CuO(7%):FeCl <sub>3</sub> (7%)	2.2
PVA:CuO(7%):(FeCl <sub>3</sub> )(9%)	1.6

The Fe<sup>+3</sup> doping is found to affect strongly on the optical energy gap of the polymer films, a decreases in the energy band gap with increasing of FeCl<sub>3</sub> concentration may be due to an increases in structural disorder of the polymer films and increases of the density of localized states in the band gap, which causes a shift optical energy gap to lower values of photon energy this results agreement with results of [5],[7],[8] [9][25].

The extinction coefficient and absorption coefficient can be related by[18].

$$k = \frac{\alpha \lambda}{4\pi} \quad \dots(7)$$

The extinction coefficient (k) behaves just like the absorption coefficient ( $\alpha$ ) because they are joined by previous relation(7). From Fig.(5) we observe that the increases in absorption coefficient causes increasing in extinction coefficient values.

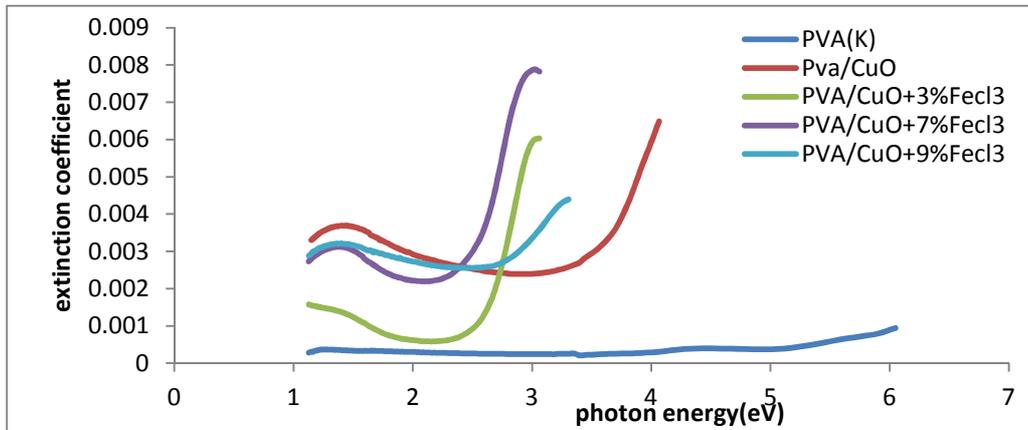


Figure (5) shows the dependence of the extinction coefficient on the photon energy.

The refraction index  $n$  value provides the optical properties of the films and it is related by the following equation [19].

$$n = \left[ \frac{4R}{(R-1)^2} k^2 \right]^{1/2} \frac{(R+1)}{(R-1)} \quad \dots (8)$$

Where  $R$  is the reflectance were calculated by using the relation: [19, 20]

$$R + T + A = 1 \quad \dots (9)$$

Fig.(6) show that an increasing in the refractive index after doping, resulting from the intermolecular hydrogen bonding between  $Fe^{3+}$  ions with the adjacent OH group of PVA.

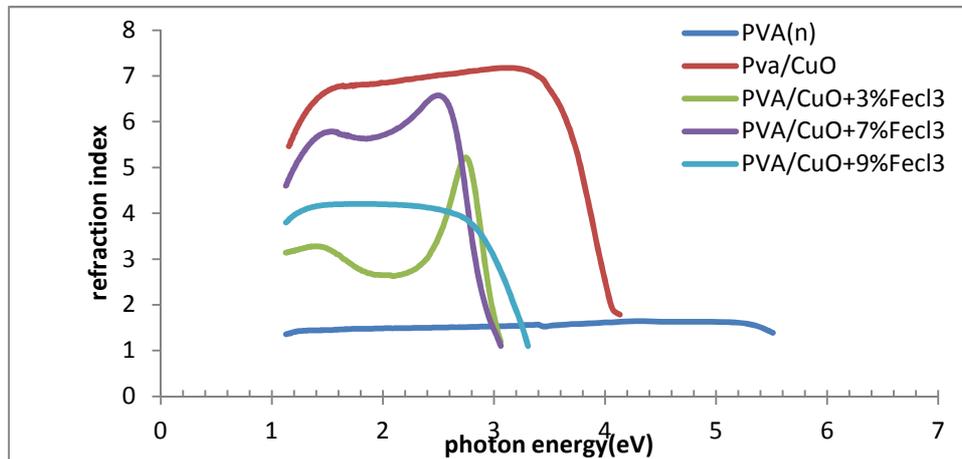


Figure (6) shows the relation between refractive index and photon energy.

The real ( $\epsilon_r$ ) and imaginary ( $\epsilon_i$ ) parts of dielectric constant can be expressed by the following equations[21]:

$$\epsilon_r = n^2 - k^2 \quad \dots (10)$$

$$\epsilon_i = 2 n k \quad \dots (11)$$

The real and imaginary parts dependences on photon energy of samples are shown in Fig. (7). It can be concluded that  $\epsilon_r$  is larger than  $\epsilon_i$  because it mainly depends on  $n^2$  according to equation (10) because the extinction coefficient effect is very small and could be neglected. It is clear from this figure that the imaginary part depends on extinction coefficient according to equation (11) because the refractive index value is very small [22]. The real and imaginary parts in Fig.(7) show that an increasing after doping. Which indicates that the samples have no same structure. Hence, the change in the doping concentration gave change in the chemical composition of the polymer [23].

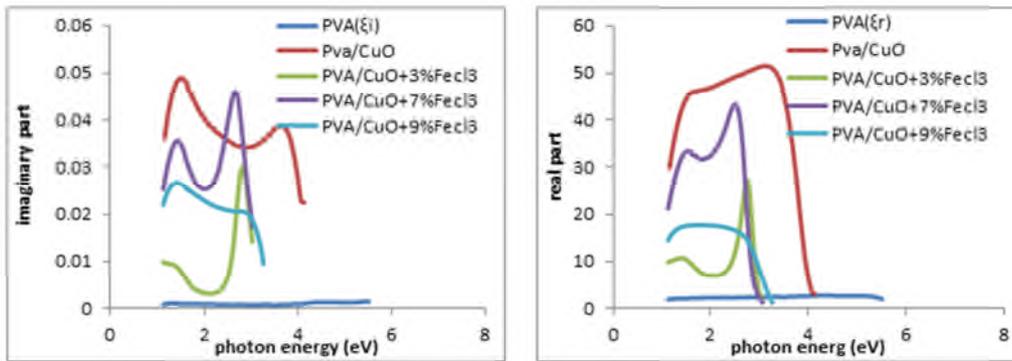


Figure (7) shows the relation between imaginary and real part of dielectric constant with photon energy.

And the Fig. (8) Shows the relation between optical conductivity and photon energy, The behavior of pure sample is different from the doped samples. The optical conductivity increases in low photon energies and then at higher photon energies it decreases, this behavior is resemble absorption coefficient because the depending on it according to equation [24,25].

$$\sigma = \frac{\alpha n c}{4\pi} \quad \dots (12)$$

Where

c:the velocity of light.

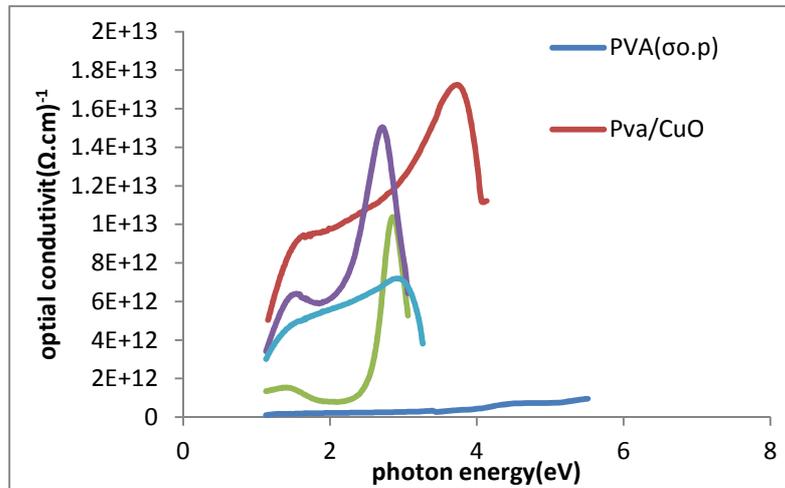


Figure (8) shows the relation between optical conductivity and photon energy.

Table (3) Properties of PVA thin films for different concentrations at photon energy (2.95 eV).

Sam.	$\alpha(\text{cm}^{-1})$	n	$K*10^{-3}$	$\xi_r$	$\xi_i$	$\sigma (\Omega.\text{cm})^{-1} * 10^{12}$
PVA	72.77	1.52	0.241	2.36	0.0007	0.265
PVA:CuO(7%)	714.85	7.14	2.412	51.1	0.0341	12.2
PVA:CuO(7%):FeCl <sub>3</sub> (3%)	1539.32	2.37	5.1	5.63	0.0210	8.73
PVA:CuO(7%):FeCl <sub>3</sub> (7%)	2266.15	1.7	7.5	3.05	0.023	9.64
PVA:CuO(7%):(FeCl <sub>3</sub> )(9%)	921	3.27	3.0	9.96	0.0198	7.17

### CONCLUSIONS

- The concentrations of FeCl<sub>3</sub>(9%) increases the structural disorder
- PVA before doping is insulator and PVA after doping became semiconductor.
- The optical constants of polyvinyl alcohol (absorption coefficient, refractive index extinction coefficient, real and imaginary dielectric constant) are changing with the increasing of concentrations of FeCl<sub>3</sub>.
- The energy band gap of polyvinyl alcohol decreases with the increasing of concentrations of FeCl<sub>3</sub>.
- Energy gap(1.6) eV of shows to use the polymer as Photodetectors in visible region.

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