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Optical constants of cobalt chloride doped poly (vinyl alcohol) thin films

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Abstract:
The investigation on variation of the optical band energy gap Eg of a polymer doped with colored mineral salt has been receiving increasing attention. In recent study, Eg and other optical properties of poly vinyl alcohol PVA doped with cobalt chloride CoCl2 were studied in wavelength range of (400-900) nm. thin films (PVA-CoCl2) were prepared through the blending solution method routine. Allowed direct transition results Eg showed that decreasing in its value with increasing the concentration of CoCl2.

***Keywords**: Thin Films, Optical Properties, Coblt Chloride, Energy Gap, Cast Method*

INTRODUCTION

Thin films are currently under investigation as a technique for achieving better chemo-physical properties of semiconductors, which were difficult to obtain in their natural form [1], depending on easily changing of these properties that attracted the interest of scientists and researchers to use it in wide applications, specifically the manufacture of conventional and high reflectivity mirrors, electromagnetic radiation detectors, integrated circuit manufacturing, resistors, capacitors, switches and thin connectors. They also contributed to the current development of digital computing and space research [3,4], Because of its importance, it became necessary to find methods to preparation them based on some factors, including the use of membrane and the type of materials used in preparation and the cost of preparation, and these methods method of thermal chemical deposition, method of thermal evaporation in the vacuum and casting method and others [5]. The effect of doping on thin films is to obtain a clear idea on the changes caused by impurities on the physical properties of thin films, producing new improved properties that differ from the properties of its original components where greater absorption and a lower energy gap are obtained [6]. One of the important materials used to preparation of thin films

are polymers because it is ease of processing and low cost [7], their properties can be greatly improved and controlled by adding mineral salts to it [8]. Abdallhet. al were reported that the increment amount of cupper chloride $CuCl_2$ causing significantly decreasing in Eg for allowed direct transition [9].pure and doped Polyvinyl alcohol (PVA) polymer were chosen in this research as a cheap polymers for studying the effect of doping with cobalt chloride salt (CoCl2).

Experimental part:

Doped PVA thin films have been prepared via the blending solution method. Firstly, 0.67 g of PVA was dissolved in 20 mL of distilled water under constant stirrer and heated gently to prevent thermal degradation of polymer (sol.A). 0.14 g of CoCl2 was dissolved in 10 mL of distilled water under vigorous stirrer for 10 min (sol.B). Then, the two solutions were mixed in volumetric ratio (0.1, 0.2, 0.3, 0.4) V/V (Sol.B/Sol.A) and thin films were made by casting onto glass substrate (2.5x7) cm2 and allowing to evaporation residual solvent overnight.
Thin films thickness was measured using the optical interferometer method employing He-Ne laser 0.632

nm, and it was about (400-430) nm. 80T, PG Instrument UV-Visible spectrophotometer was recorded PVA-CoCl2 Thin films spectra in range of 400-900 nm. The absorption coefficient (α) is calculate using the following equation [10]:

$$\alpha = 2.303\frac{A}{t} \quad (1)$$

The energy gaps of prepared thin films is calculate by equation [11]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^m \quad (2)$$

Where E_g energy gap between direct transitions, B is proportionality constant, and m is exponential constant, m =1/2 for the allowed direct transition. Extinction coefficient calculated using the formula [12]

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

Also one can calculate the refractive index using the relation [13]:

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

Dielectric constants represent the ability of material to the polarization and the different frequencies with complex deportment.

Dielectric constant can be calculated by using the refractive index, where at the optical waves (visible region) frequencies of the electronic polarizing is the predominant on the other polarization types, and the degree of polarization depends on the molecular properties of material which make this material isolated in addition to the electric filed.

The following equations were used to determine the real and imaginary dialectic constants, where the real dialectic constant is given by [14]:

$$\varepsilon_r = n^2 - k^2 \quad (5)$$

$$\varepsilon_i = 2nk \quad (6)$$

The optical conductivity of thin films was calculated using the equation [15]:

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

Results and discussion:

Figure (1) shows the absorption spectra of doped PVA samples at different concentrations under investigation the range 400-900 nm which is the convenient spectral region. It is note that, in the UV-region, the absorption increased as the wavelength increasing for all samples. Moreover, the two absorption bands shown clearly in the visible region due to the sample is semitransparent. In addition, the absorption edge has slightly changed (increased) with increasing concentration.

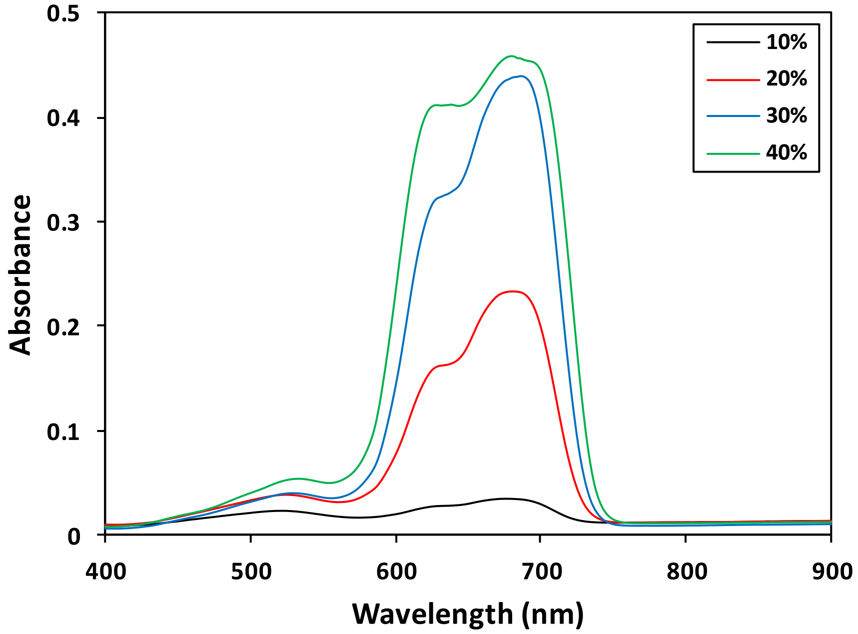

Figure (1): The spectra of absorbance versus wavelength

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The reflectance values are shown in figure (2).

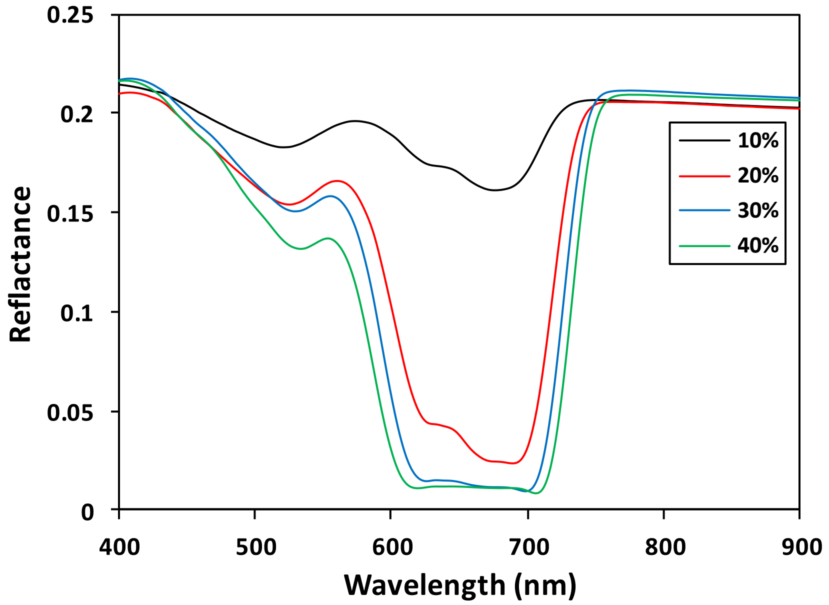

Figure (2): The spectra of reflectance against wavelength.

The values of reflectance decreased as raising the amount of ($CoCl_2$), that suggested the process of bonding between molecules resulting in a decrease in the amount of radiation reflected by polymer particles because dissolved ($CoCl_2$) molecules in the solution and the decrease of these values with increased concentration of ($CoCl_2$) this is due to a decrease of polymer particles in the solution and thus a decrease in solution density as the reflectance is entirely dependent on the density.

Coefficient α $(cm)^{-1}$ of the light absorption was calculated by using equation (1). Figure (3) illustrates α of (PVA) films with serious concentrations of mineral salt as a function of the energy of photon. It observed that the absorption was smallest at low energy and that may be due to the possibility of lower electron transition which simply indexed to the energy of the incident photon is not sufficient to move of an electron present in its valence band (VB) to the excited state in the conduction band.

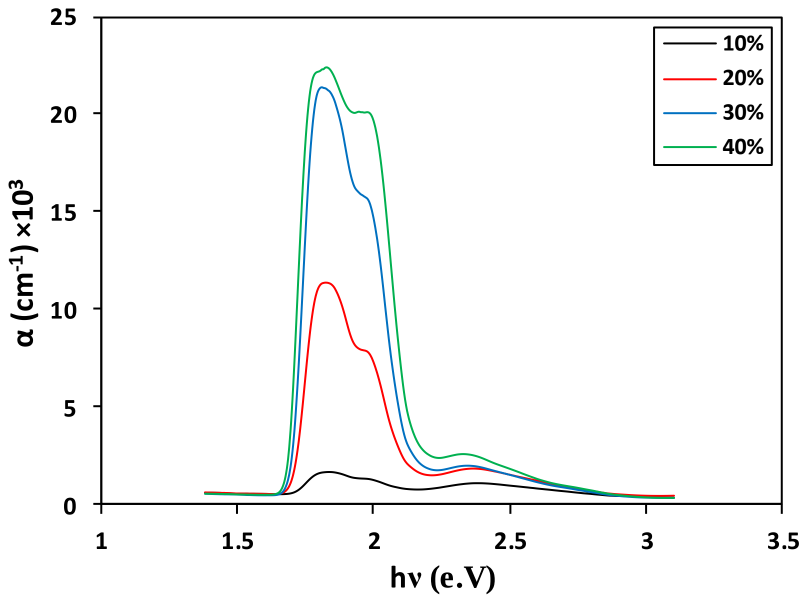

Figure (3): The coefficient α of absorption versus the photon energy (hυ)

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The values of optical energy gap (Eg) of pure and doped PVA with series ratio of $CoCl_2$ thin films were determined by Tauc's plot [16] via extrapolating the absorbance edge and as shown in figure (4).

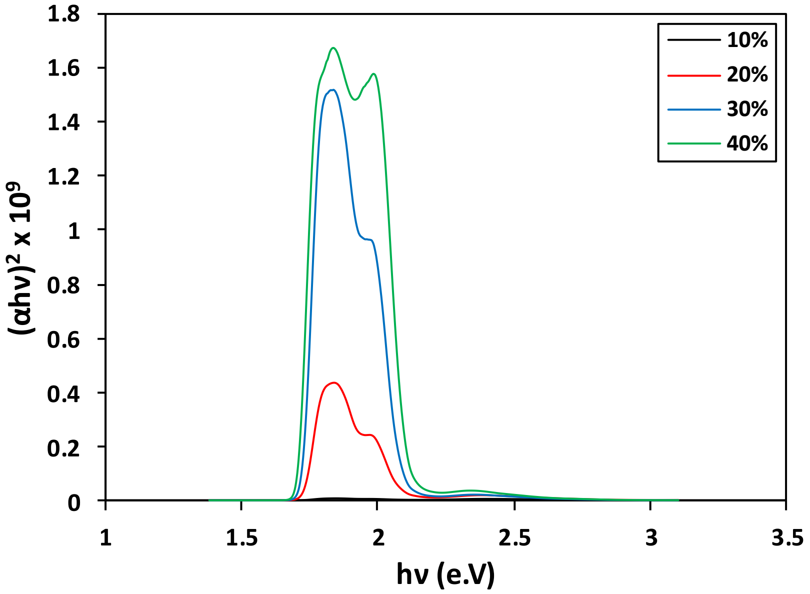

Figure (4) The variation of $(\alpha h\upsilon)^2$ versus the photon energy (hυ)

In general, the values of direct E_g was reduced with increasing the concentration of ($CoCl_2$) for all prepared samples. The direct Eg decreases from 3.7 eV for pure PVA to 2.3 eV as rising of ($CoCl_2$) ratio was shown in the figure (3).

Extinction coefficient (k) was estimated by using equation (3). The change of extinction coefficient for (PVA-($CoCl_2$) films with series ratio of ($CoCl_2$) salts in response to energy of the photon was shown in figure (5).

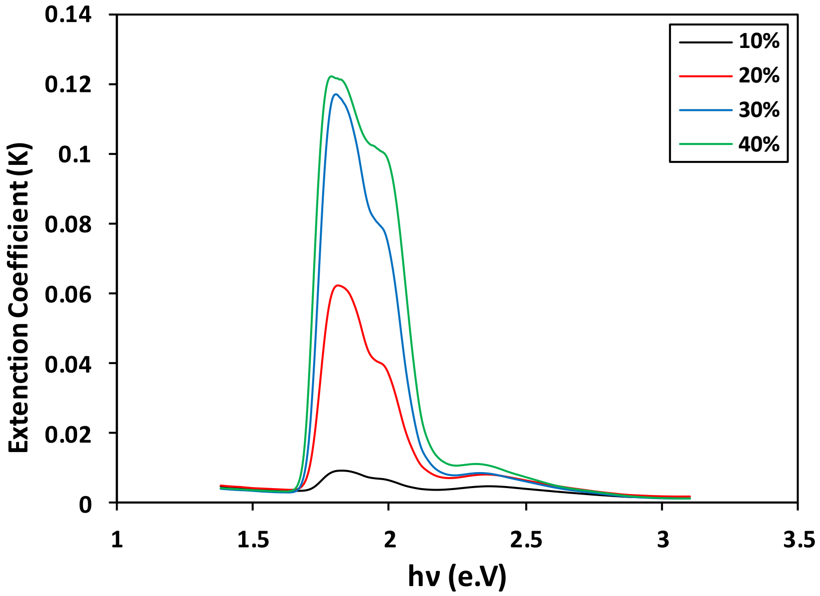

Figure (5) The variation of extinction coefficient versus the photon energy (hυ)

It can be noted that extinction coefficient is of lowering values at low concentrations, but it increases with increasing the weight percentage of the added $CoCl_2$. This is attributed to increased absorption coefficient with ratio added from $CoCl_2$.

The refractive index (n) is calculated from equation (4). Figure (6) show the various of refractive index for (PVA-($CoCl_2$)) and films with different ratio of ($CoCl_2$) salts as a function of the photon energy.

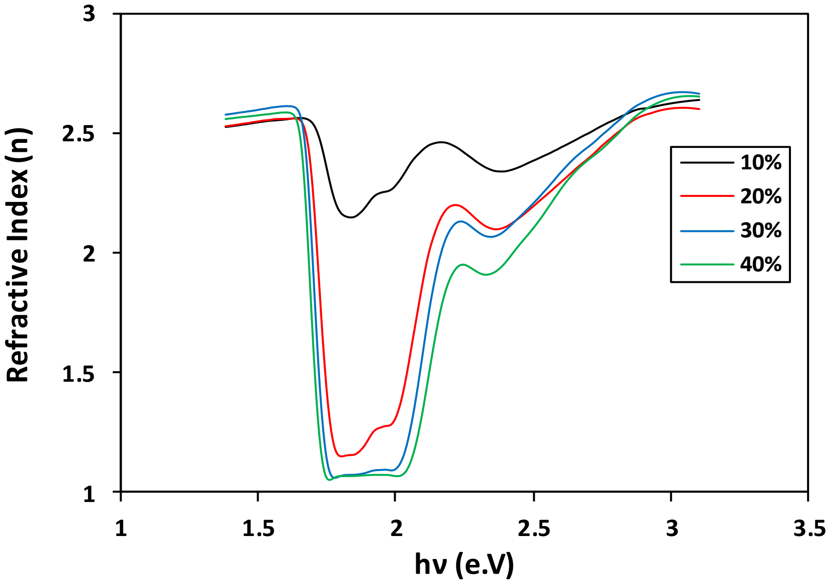

Figure (6) The variation of refractive index of PVA-($CoCl_2$) versus the photon energy (hυ)

From the figure (6), it seen that less the refractive index with higher ratio added (Cobalt chloride) due to significantly increasing of the free electrons number. The real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) for (PVA-($CoCl_2$)) thin films have been estimated by usingequations (5) and (6), respectively. Figures (7, 8) show the change of (ε_r, ε_i) in response of the photon energy.

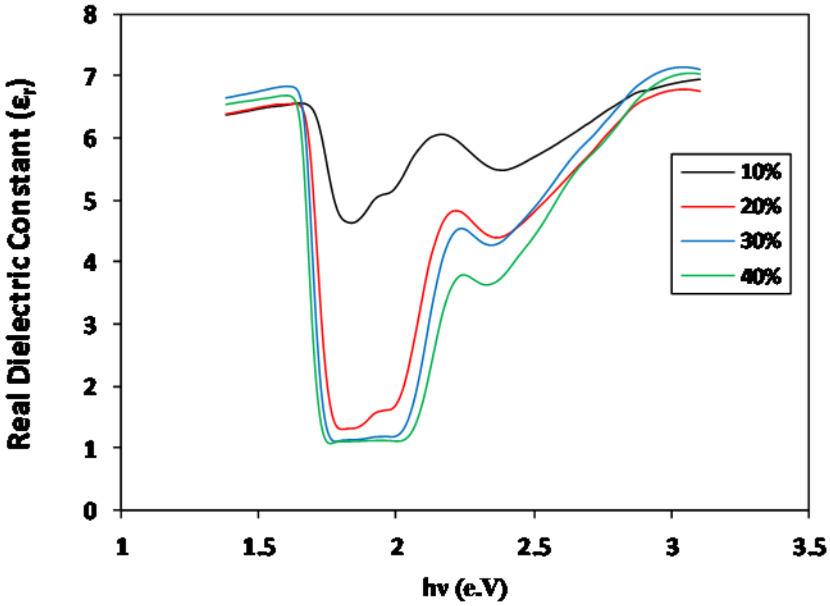

Figure (7) The variation of real part dielectric constants (σr) versus the photon energy (hυ)

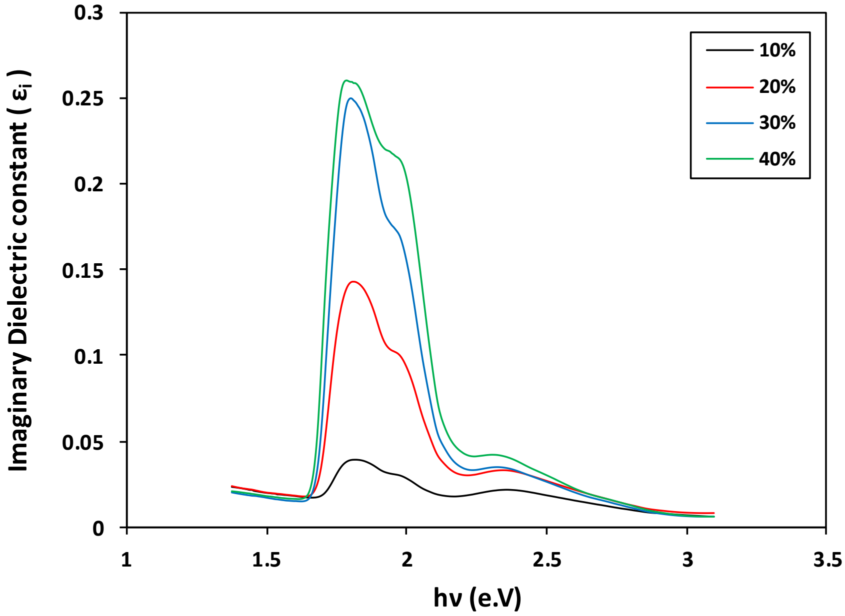

Figure (8) The effect of $CoCl_2$ concentration on the imaginary part dielectric constants (ε_i)

It can be recognized that (ε_r) decrease and increase (ε_i) with increasing the weight percentage of the added (Cobalt chloride), and this behavior is similar to (n) and (k) because (ε_r) depends on (n^2) due to low value of (k^2), while (ε_i) is dependent on (k) value that change with the variation of the absorption coefficient can attributed to the relation between (α) and (k).

Figure (9) shows the dependence of the optical conductivity for PVA thin films on the concentrations of ($CoCl_2$) thin films. It is clear that the optical conductivity increase with increase concentration of ($CoCl_2$) for all samples.

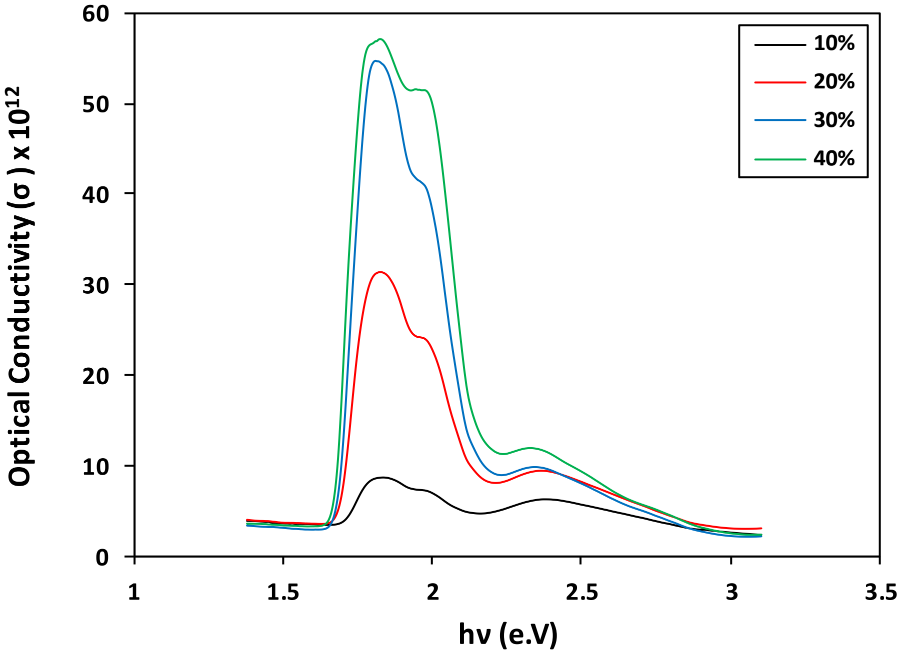

Figure (9) The influence of $CoCl_2$ concentrations on optical conductivity (σ) of PVA thin films

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Conclusions

Poly(vinyl alcohol) doped with mineral cobalt chloride thin films were produced via blending solution method.The experimental results of absorption spectra observed that the direct band gap energy of pure PVA was 3.7 eV and PVA doped with $CoCl_2$ was 2.3 eV. These properties give the possibility to use the film made in the manufacture of infrared detectors and selective surface equipment. Because of its high absorption of sunlight, it capable to collect solar energy and opened the way for the formation for photovoltaic devices from basic materials.

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