

Effect of cobalt chloride (CoCl₂) on the electrical and optical Properties of (PVA-PVP-CoCl₂) films

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Abstract

In this research, many samples have been prepared by adding CoCl₂ to the poly vinyl alcohol and poly vinyl pyrrolidon with different weight percentages (0, 3, 6 and 9) wt%. The effect of cobalt chloride concentration on the D.C electrical properties have been investigated. Results showed that the D.C electrical conductivity of such composites increased with increasing of weight percentages of CoCl₂, and the activation energy changed with increasing of filler concentration, as well as the effect of addition cobalt chloride on optical properties of poly vinyl alcohol and poly vinyl pyrrolidon have been studied. The absorbance has been recorded in the wavelength (200-1100) nm, also the absorption coefficient, real and imaginary dielectric constant, energy gap, extinction coefficient and refractive index have been determined.

Keywords: electrical properties, optical properties, (PVA-PVP) composites, cobalt chloride.

Introduction

Although many people probably do not realize it, everyone is familiar with polymers. They are all around us in everyday use, in rubber, plastics, resins and in adhesives and adhesive tapes, and their common structural feature is the presence of long covalently bonded chains of atoms. They are an extraordinarily versatile class of materials, with properties of a given type often having enormously different values for different polymers and even sometimes for the same polymer in different physical states. An even greater range of values is available for the electrical conductivity of polymers: the best insulating polymer may have a conductivity as low as $10^{18} \Omega^{-1} \text{ m}^{-1}$, whereas a sample of poly acetylene doped with a few percent of a suitable donor may have a conductivity of $10^4 \Omega^{-1} \text{ m}^{-1}$, a factor of 10^{22} higher. [1] Poly (vinyl alcohol) (PVA), a polyhydroxy polymer, is the largest, synthetic, water-soluble polymer produced in the world based on volume. It is produced commercially by the hydrolysis of poly (vinyl acetate) (PVAC) [2]. Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. PVA is odorless and nontoxic, as well as has high oxygen and aroma barrier properties [3] PVP is a white, hygroscopic powder with a weak characteristic order. In contrast to most polymers, it is readily soluble in water and a large number of organic solvents, such as alcohols, amines, acids, chlorinated hydrocarbons, amides and lactase. [4]

Experimental work

The samples have been prepared by casting method. The materials used in this work are polyvinyl alcohol and poly vinyl pyrrolidon with CoCl₂. The weight percentages of CoCl₂ are (3, 6 and 9) wt%. The resistivity was recorded by temperature from (50 to 90)^oC by using Keithley electrometer type (616 C). The volume electrical conductivity σ_V defined by: [5]

$$\sigma_V = 1/\rho = 1/RA \quad \dots\dots\dots(1)$$

A=guard electrode effective area.

R=volume resistance

L=average thickness

The activation energy was calculated using equation:[6]

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad \dots\dots\dots(2)$$

σ = electrical conductivity at T temperature

σ_0 = electrical conductivity at absolute zero of temperature.

K_B = Boltzmann constant and $E_{act.}$ = Activation Energy

The absorption spectra of (PVA-PVP-CoCl₂) composites have been recording in the length range (200-1100)nm by using UV spectrophotometer (UV-1800), the absorption coefficient(α) was calculated from the following equation: [7]

$$\alpha = 2.303 A/d \quad \dots\dots\dots(3)$$

Where A is absorption and d is the sample thickness

The optical energy gap has been calculated by using this equation [8]

$$\alpha h\nu = B (h\nu - E_g)^r \quad \dots\dots\dots(4)$$

Where hf is the energy of photon, B is proportionality constant and E_g is optical energy gap.
 The extinction coefficient (k) is directly proportional to the absorption coefficient (α): [9]

$$k = \alpha\lambda / 4\pi \quad \dots\dots\dots(5)$$

Where λ is the wavelength of light.

The refractive index has been calculated by using this equation [10]

$$n = [4R / (R-1)^2 - (R+1/R-1)]^{1/2} \quad \dots\dots\dots(6)$$

The real and imaginary part of dielectric constants have been determined from this equation:[11]

$$\epsilon_1 = n^2 - k^2 \quad \dots\dots\dots(7)$$

$$\epsilon_2 = 2nk \quad \dots\dots\dots(8)$$

Results and Discussion

Figure (1) shows the volume electrical conductivity for (PVA-PVP-CoCl₂) composites as a function of cobalt chloride concentration. From this figure we can see that the electrical conductivity is increased with the increasing of the concentration of cobalt chloride composites. This behavior attributed to the increase of the ions charge carriers [12,13]. Figure (2) shows the variation of electrical conductivity of (PVA-PVP-CoCl₂) with temperature. The volume electrical conductivity increases with increasing of temperature this is means that these materials have resistance of negative thermal coefficient (i.e. that resistance decrease with temperature increased). The explanation of this behavior is the polymeric chains and impurity ions act as traps to make charge carriers moving by hopping process. The conductivity of all samples will increase because of the increasing charge carriers and its movement. [14], these results are similar to the results reached by the researchers in this behavior [15]

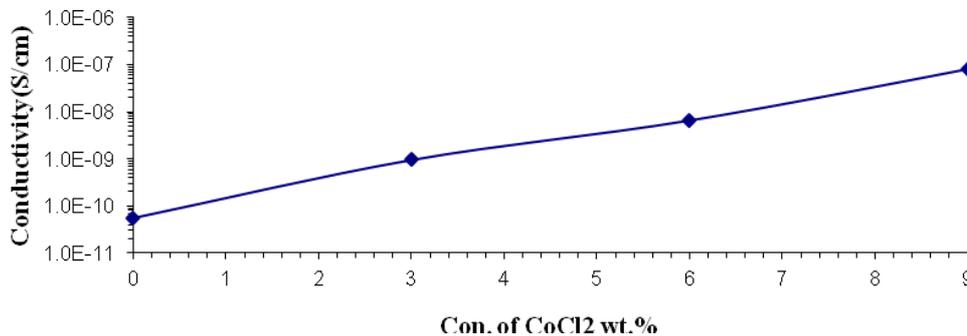


Figure (1): Variation of D.C electrical conductivity with CoCl₂ wt% concentration.

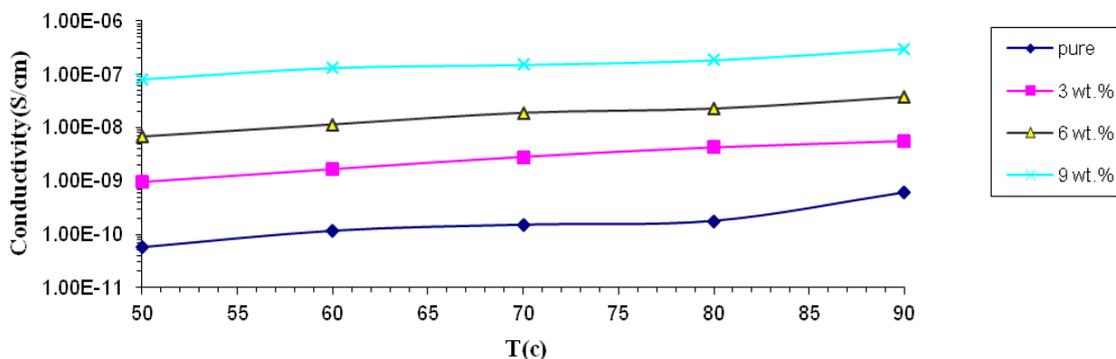


Figure (2): Variation of D.C electrical conductivity with temperature.

Figure (3) show that the variation of Ln D.C electrical conductivity with inverted absolute temperature of composites, the activation energy was determined from equation (2). The activation energy has high values at low

concentration while at high concentration it has low values, these due to increase the local levels in the distance between conduction band and valence band ,this is consistent with the findings of the researchers [16].The decrease in activation energy with increasing (CoCl₂) concentration shown in figure (4).

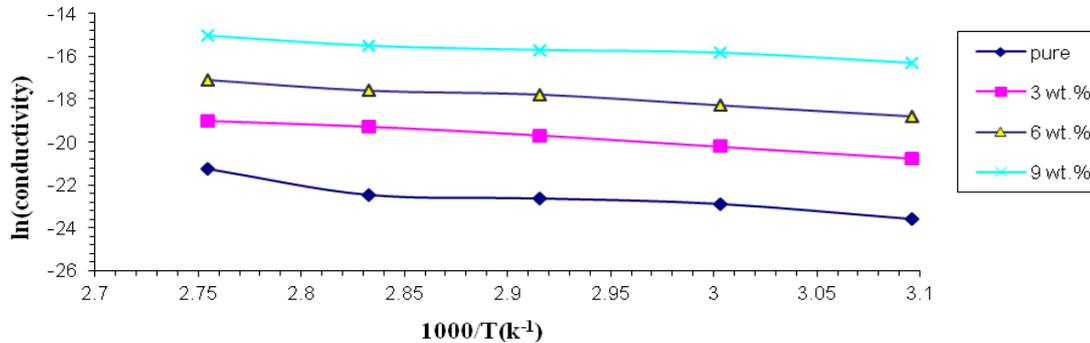


Figure (3): Variation of D.C electrical conductivity with reciprocal absolute temperature of composites.

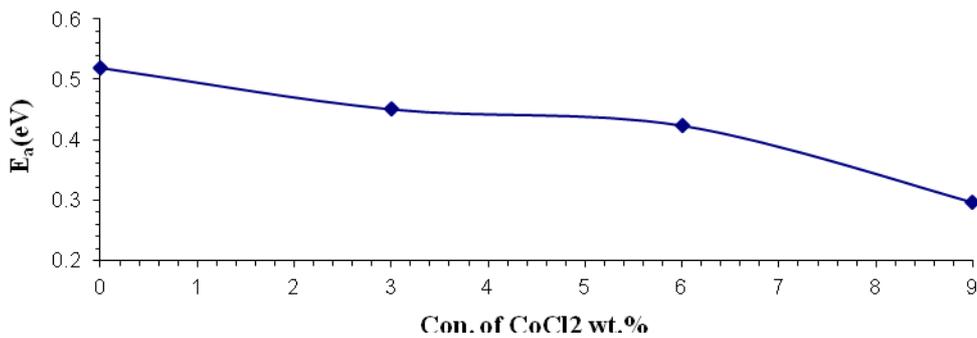


Figure (4): Variation activation energy with CoCl₂ concentration.

The relationship between the absorbance and wavelength of the incident light for (PVA-PVP-CoCl₂) composites at room temperature shown in figure (5). From this figure note that intensity of the peak increases as a result of increasing concentration of CoCl₂ and no shift in the peak position. The increase of absorbance with the increase of weight percentage of the CoCl₂, this is due to absorb the incident light by free electrons [17].

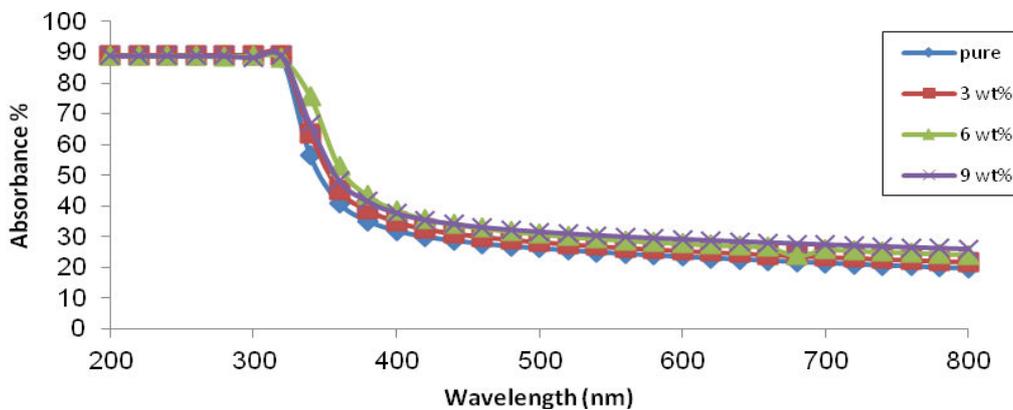


Figure (5): Variation between Absorbance and wavelength of composites.

Figure (6) shows the relation between the absorption coefficient and photon energy of the (PVA-PVP-CoCl₂) composites. From this figure it note that the absorption coefficient dependent on the photon energy, where the absorption is little at low energy this is means that the possibility of electron transition is little because the energy of the incident photon is notice sufficient to move the electron from the valance band to the conduction band. At high energies the absorption coefficient assists in figuring out the nature of electron transition when the values of the absorption coefficient is high ($\alpha > 10^4$) cm⁻¹ it is expected that direct transition of electron occur on the other hand when the values of absorption coefficient is low ($\alpha < 10^4$) cm⁻¹ it is expected that indirect transition of electron occur [18].

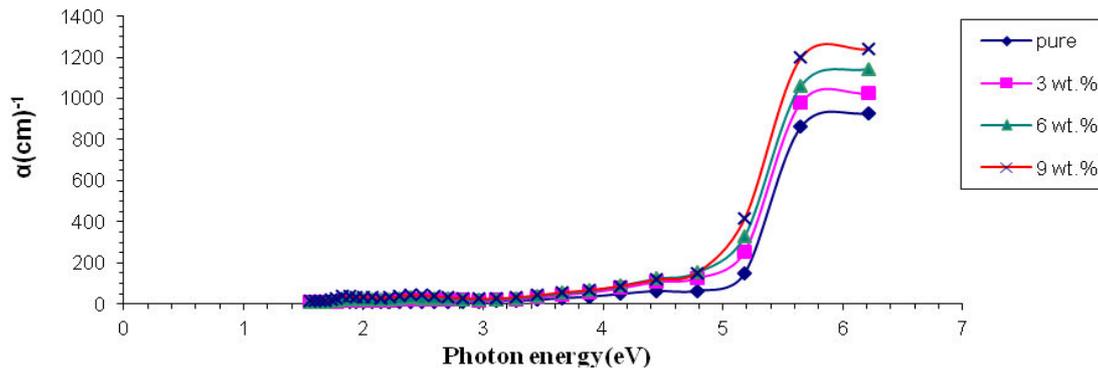


Figure (6): The absorption coefficient with various photon energy of composites.

The relation between $(\alpha hf)^{1/2}$ (cm⁻¹ .eV)^{1/2} and photon energy of composites **shown in figure (7) from this figure we note that** the value of optical energy gap decrease by increasing of weight percentage of coCl₂,also the transition which occurs in the samples is allowed indirect transition as shown in table (1).This behavior attributed to the fact that composites are of heterogeneous type (i.e. the electronic conduction depends on added impurities), the increase of the added rate provides paths in the polymer which facilitate the crossing of electron from the valance band to the conduction band, this explains the decrease of energy gap with the increase of the added salt [19].

Table (1) Show values of energy gap for indirect transition (allowed, forbidden) of (PVA –PVP-CoCl₂) composites

Sample	The values of energy gap for the indirect transition (eV)	
	allowed	forbidden
pure	4.85	4.6
3wt%	4.7	4.4
6wt%	4.55	4.2
9wt%	4.5	4.1

Figure (8) shows the relationship between $(\alpha hf)^{1/3}$ (cm⁻¹ .eV)^{1/3} and photon energy of composites ,we can see from this figure the value of forbidden energy gap decreases by increasing weight percentage of CoCl₂ as well as this value of forbidden indirect transition is less than the one value which is represent allowed indirect transition.[20]

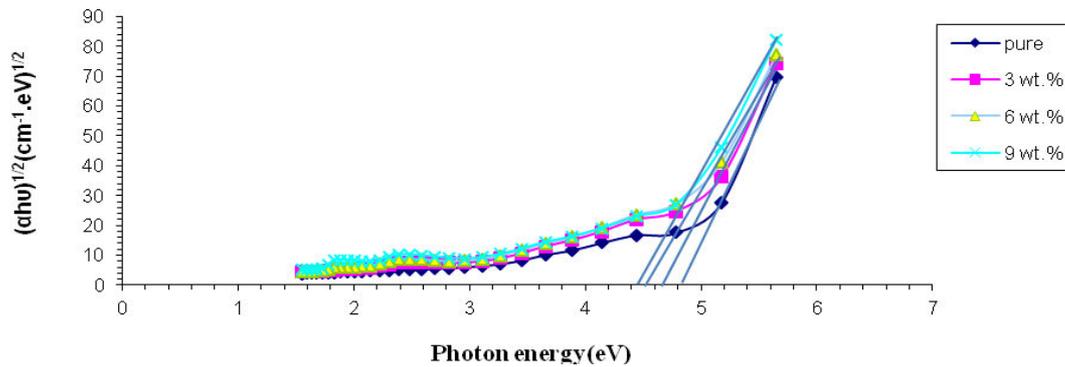


Figure (7): The relationship between $(\alpha h\nu)^{1/2}(\text{eV}\cdot\text{cm}^{-1})^{1/2}$ and photon energy of composites.

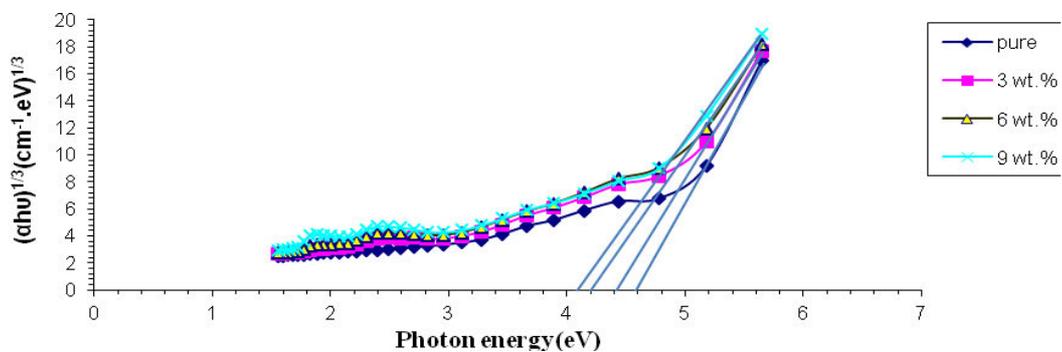


Figure (8): The relationship between $(\alpha h\nu)^{1/3}(\text{eV}\cdot\text{cm}^{-1})^{1/3}$ and photon energy.

Figure (9) show the relation between refractive index and photon energy for PVA-PVP- CoCl_2 composites. From this figure we find out the refractive index increase with increasing CoCl_2 concentration because of increasing in density composites. In the ultraviolet region we note that a high values of the refractive index because of the little transmittance in this region, but in the visible region note that low values because of the high transmittance in this region[21].The variation between extinction coefficient of (PVA-PVP- CoCl_2) composites with various photon energy as shown in figure (10). This figure shows that the extinction coefficient has low values at (UV-region) and with little concentration as well as it is increased with increasing additive concentrations of CoCl_2 because of increasing in absorption coefficient, but at visible region we note that the extinction coefficient is very low because of the low absorption at this region [22].

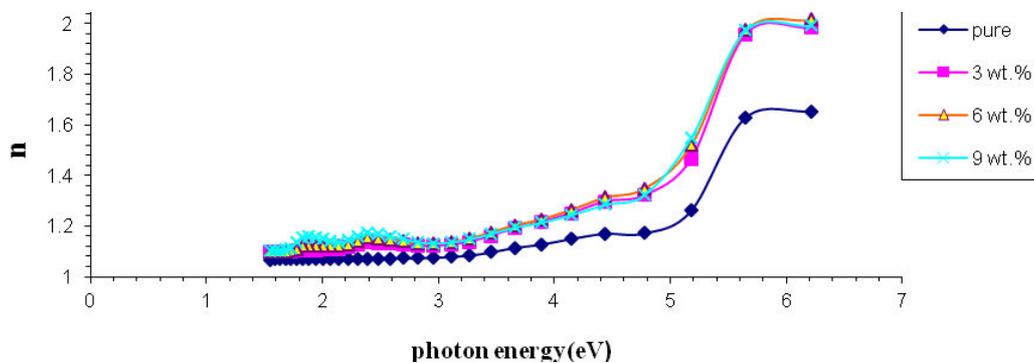


Figure (9): The variation between refractive index and photon energy of composites.

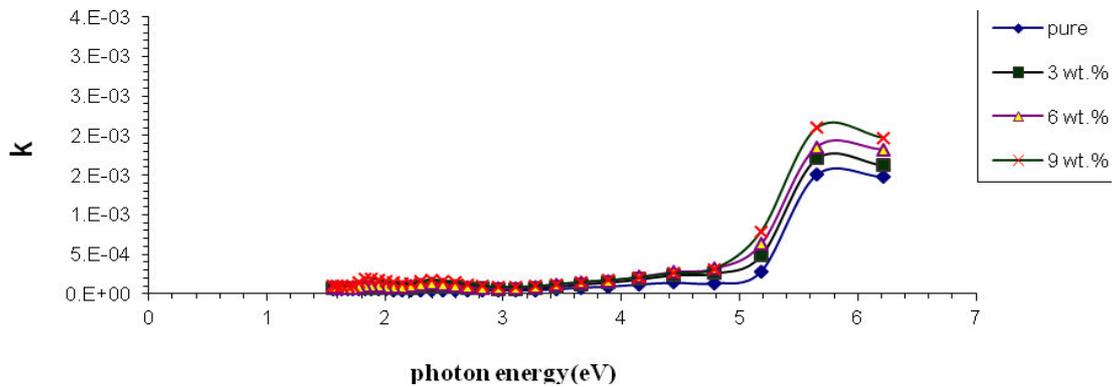


Figure (10): The relationship between extinction coefficient and photon energy of composites.

The figures (11,12) show that variation between (real and imaginary) parts of dielectric constants. It is concluded that the variation of ϵ_1 mainly depends on (n^2) because of small values of (K^2), while ϵ_2 mainly depends on the (K) values which are related to the variation of absorption coefficients.

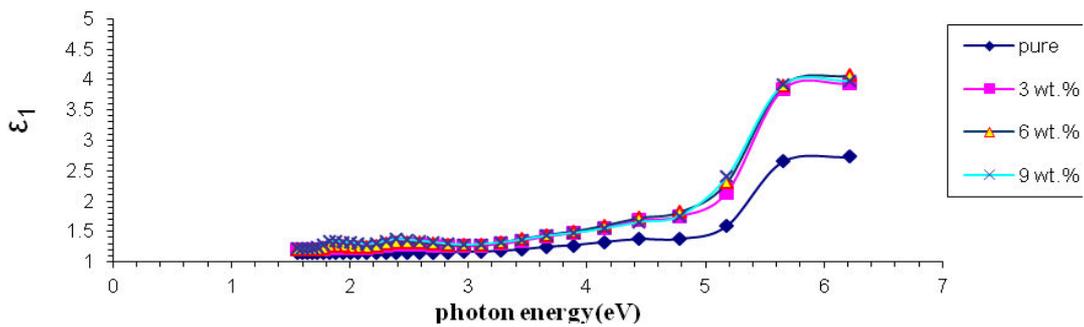


Figure (11): The variation of real part of dielectric constant with photon energy of composites.

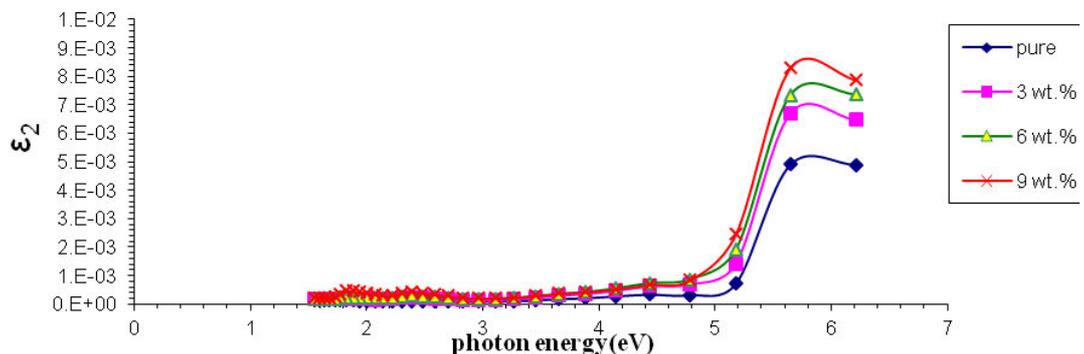


Figure (12): The variation of imaginary part of dielectric constant with photon energy of composites.

Conclusions

- 1- D.C electrical conductivity for (PVA-PVP-CoCl₂) composites increased with increasing of temperature and CoCl₂ wt.% concentration.
- 2- Activation energy of PVA-PVP-CoCl₂ composites decreases with increasing of the CoCl₂ concentration.
- 3- The absorption coefficient for all PVA-PVP-CoCl₂ samples increases with increasing of CoCl₂ wt.% concentration.

- 4- The energy gap of indirect transition decreases with increasing of CoCl_2 wt.% concentration.
- 5- Extinction coefficient, refractive index and dielectric constant (real and imaginary) increased with increasing of concentration.

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