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Studying the Influence of Cobalt Chloride on the Optical Properties of Poly (vinyl alcohol) Films

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Abstract

The change in the optical band gap and optical activation energy have been investigated for pure and doped Poly (vinyl alcohol) with different cobalt chloride concentrations have been prepared to study their optical properties from the absorption spectra. The absorption spectra were measured in the wave range from (200-800) nm at room temperature. The optical band gap (E_g) for allowed direct transition decrease with increase the concentration of Cobalt Chloride. The optical activation energy for allowed direct transition band gap was evaluated using Urbach- edges method.

Keyword: poly(vinyl alcohol), optical energy gap.

Introduction

Conductive polymers are organic compounds that conduct electricity. Such compounds may be true metallic conductors or semiconductors. It is generally accepted that metals conduct electricity well and that organic compounds are insulating, but this class of materials combines the properties of both. The biggest advantage of conductive polymers is their processibility. Conductive polymers are also plastics (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the exquisite methods of organic synthesis [1]. Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal salts have considerable effect on the optical and electrical properties of PVA (polyvinyl alcohol) polymer [2,3].

A vinyl polymer, namely polyvinyl alcohol (PVA) has several interesting physical properties, which are very useful in material science and technical applications. PVA, as semi crystalline water soluble material exhibits. Certain physical properties resulting from crystal-amorphous interfacial effects [4].

Poly (vinyl alcohol) (is a polymer with carbon chain backbone with hydroxyl groups attached to methane carbons. These OH-groups can be a source of hydrogen bonding and hence assist in the formation of polymer [5].

In general the absorption spectra in UV region increase with increasing dose. In principle , photon with energy greater than the band gap energy will be absorbed. Electromagnetic wave packet interact with electron in the Valence Band (VB), which is then raised across the band gap on the Conduction Band (CB) via two possible types of electronic transition, i.e. direct transition and indirect transition. In the direct transition the wave vector for the electron remains unchanged, while in the indirect transition the lattice vibration or phonons assist the transition so that the minimum of the CB lies in the different part of k-space from the maximum of the VB.[6]

Materials and Methods

The materials used in this work was a powder of commercial PVA doped by Cobalt Chloride films were prepared at room temperature by solution casting method. The PVA was dissolved in distilled water and heated gently in water bath to prevent thermal decomposition of polymer. The polymer was stirred by magnetic stirrer for completely dissolved. The cobalt chloride with different ratios (0.5,1,2,4,6,8,and 10%)were dissolved in distilled water and added to the polymer solution, heated for awhile for completely dissolved. The solution poured on to a glass plate and left to dry for 24 hr to remove any residual solvent. The thickness of the films were ranging from (55 – 60) µm. Thickness measurements were made using micrometer.

The optical absorbance (A) of the samples were measured as function of wavelength (λ) at the range from (200-800) nm by using computerized Shimadzu UV-VIS 160 A-Ultraviolet- spectrophotometer full scale absorbance up to (2.5). The light sources are halogen lamp and socket-deuterium lamp.

Optical Measurement

The absorption peak at UV region, were used to study the shifting in the optical energy gap for PVA and PVA-$CoCl_2$ films at 25 ^{0}C . The best definition of the energy gap is the minimum energy difference between the lowest minimum of conduction band and the highest maximum of the valance band [7].

The value and shape of the mobility gap in PVA depend on the preparation conditions such as substrate temperature, degree of impurity and defect of the material. Any variation in such parameters leads to a shift in the absorption edge towards higher or lower energy. The absorption coefficient which can be determined from the normal incidence transmission through plane-parallel plate of thickness (d) interference and multiple reflections are neglected. The reflectance (R) and transmittance (T) are related by the equation (1)

$$T = B(1-R)^2 e^{-\alpha d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where B is a constant and α is the absorption coefficient.

This equation can be rewritten as follows:

$$\alpha d = 2.303\,A + \ln[B(1-R)^2] \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

A is the optical absorbance, ($A = -\log T$).

So the absorption coefficient α (ω) in term of absorbance become:-

$$\alpha(\omega) = 2.303\,(A/d) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

For direct band-to-band transition, the energy dependence of absorption coefficient is of the form:

$$\alpha = (\alpha_o (h\nu - E_g)^r)/h\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where (hν) is the photon energy and (Eg) is the energy gap, r is a constant depending on the type of the electronic transitions. It takes the value (1/2) for allowed direct transition and (3/2) for forbidden direct transition and the absorption coefficient ($\alpha \geq 10^4$ cm^{-1}). The energy dependence absorption coefficient is of the from:

$$\alpha = \alpha_o (h\nu - E_g \pm E_p)^r / h\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where (Eg) is the minimum energy gap, (Ep) is the phonon energy, (+) absorbed (-) emitted, (r) takes the value (2) for allowed indirect transition and (3) for forbidden indirect transition and the absorption coefficient ($\alpha < 10^4$ cm^{-1}). By plotting $(\alpha h\nu)^{1/r}$ versus (hν) for fixed (r)value, the extrapolation of the liner part could be used to define Eg .[7,8]

Result and Discussion

The direct optical band gap for allowed direct transition can be evaluated from extrapolating of linear region of the curve to a point of $(\alpha h\nu)^{1/2}$ versus hν for pure PVA and PVA doped with cobalt chloride at different concentration at room temperature (25)°C. As shown in Figs. (1 to 8).

The effect of doping with $CoCl_2$ on the values of photon energies are shown in Table (1) .Table 1 shows that Eg decreases in the trend pure PVA, PVA+0.5% $CoCl_2$, PVA+1% $CoCl_2$, PVA+2% $CoCl_2$, PVA+4% $CoCl_2$, PVA+6% $CoCl_2$, PVA+8% $CoCl_2$, and PVA+10% $CoCl_2$.

The shift in the energy gap could be attributed to the formation of polarons in the doped film[7].

The polymer-salt composites are characterized by interaction of the salt with the polar group of the polymer, which gives rise to complex formation. This complex formation is mainly dominated by the cations (Co^{2+}) with the OH groups in the polymer. That is, the cations bound to several OH groups in a polymer chain may induce a stiffening of the chain (intrachain effect) and bounding with other chains may act as temporary cross-links (interchain effect). PVA-$(Cl)^-$ also shows a similar effect. The evidence of polaron formation made the reaction in band - to- band transition due to shifting of band density of state toward the energy gap (9).

Table (1)
The energy band gap according to the direct allowed transition for PVA and PVA doped with $CoCl_2$ at room temperature.

Films type	*E g (eV)*
Pure PVA	5.65
PVA+ 0.5%	5.58
PVA+1%	5.55
PVA+2%	5.50
PVA+4%	5.45
PVA+6%	5.4
PVA+8%	5.37
PVA+10%	5.26

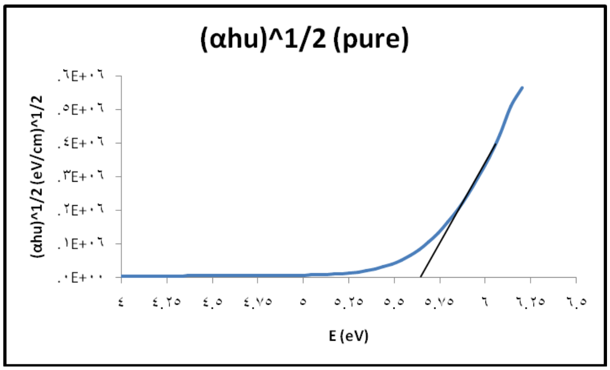

Fig. (1) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for pure PVA at room temperature.

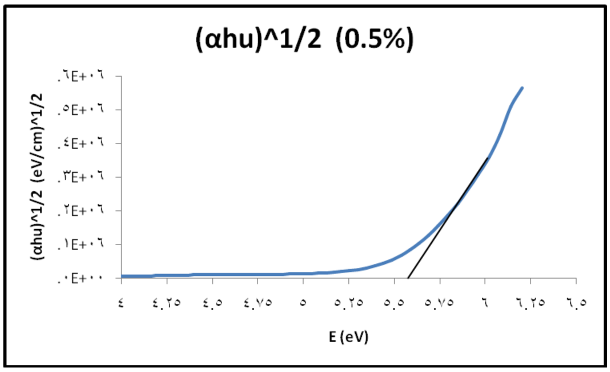

Fig.(2) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+0.5% ($CoCl_2$) at room temperature.

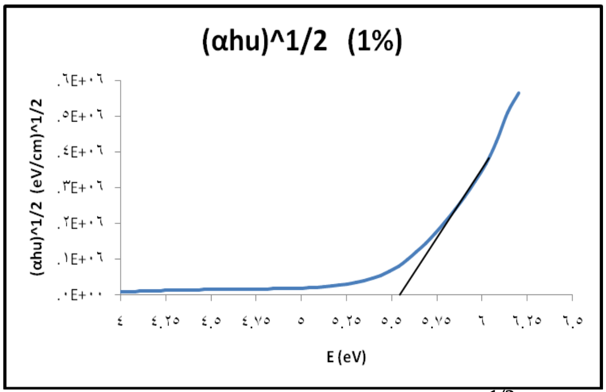

Fig.(3) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+1.0%($CoCl_2$) at room temperature.

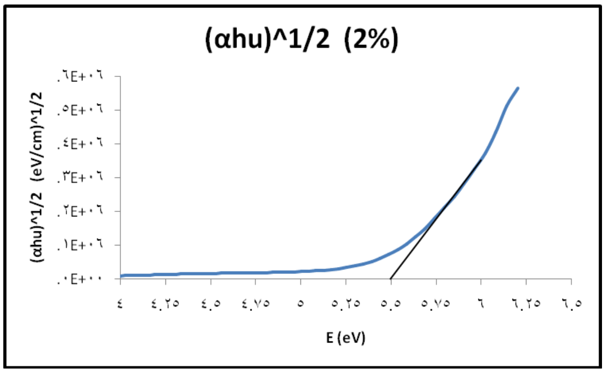

Fig. (4) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+2.0% ($CoCl_2$) at room temperature.

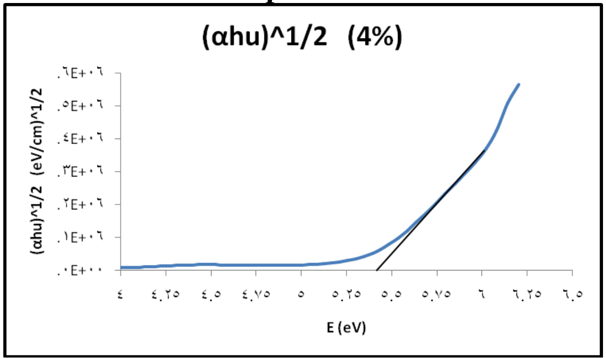

Fig.(5) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+4.0% ($CoCl_2$) at room temperature.

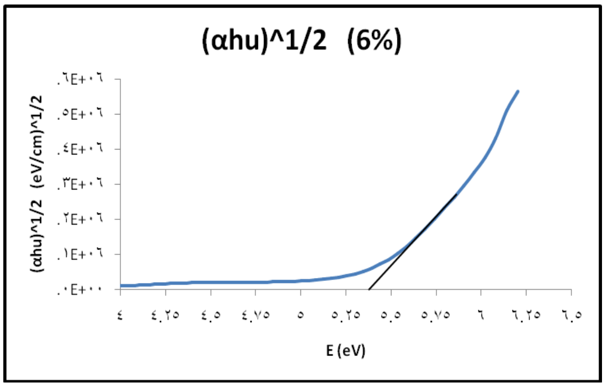

Fig.(6) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+6.0% ($CoCl_2$) at room temperature.

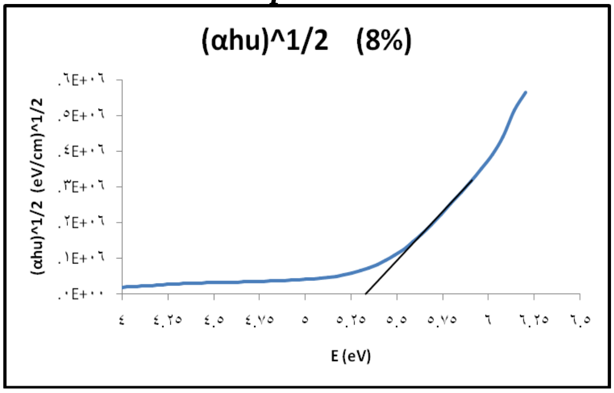

Fig.(7) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+8.0% ($CoCl_2$) at room temperature.

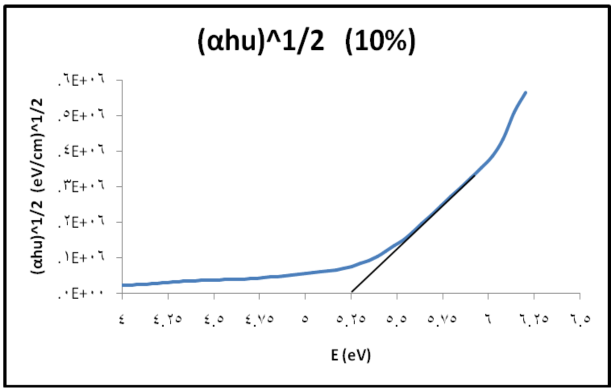

Fig.(8) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for PVA+10.0% ($CoCl_2$) at room temperature.

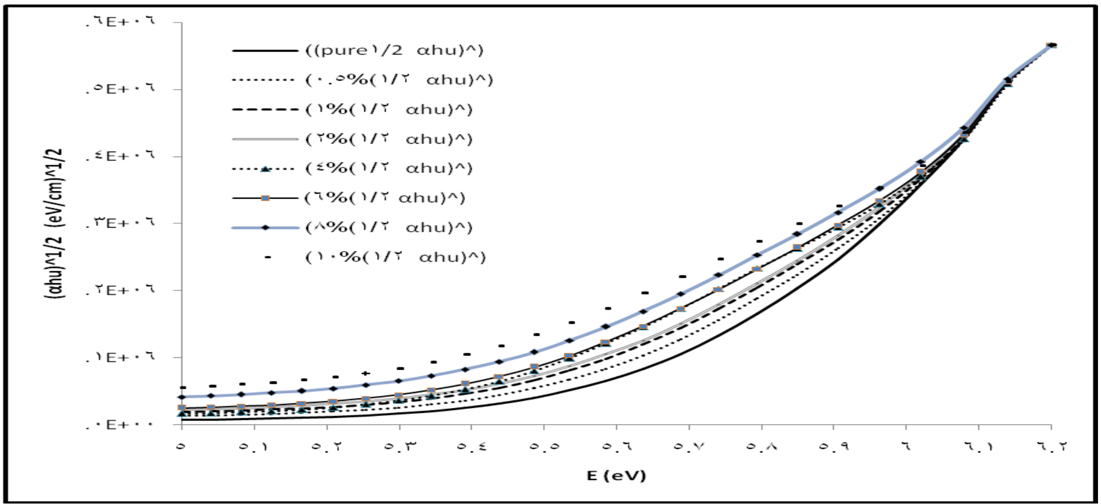

Fig.(9) The direct transition $(\alpha h\upsilon)^{1/2}$ Vs. energy for pure PVA and the doped PVA ($CoCl_2$) at room temperature.

Conductivity measurement of PVA with and without cobalt chloride can be obtain by adopting data of energy gap, (Table (1) and Figs.(1 to 8)).

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach. The absorption edge of non-metallic materials gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, ln(α), on photon energy, hv , is found to hold over several decades for a polymeric material and takes the following form:

$$\alpha = \alpha_{\circ}\, e^{\left(\frac{hv}{E_t}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where α_0 is a constant and Et is interpreted as the width of the tails of localized states in the gap region. To evaluate the values of α_o and Et, it was α in logarithmic scale as a function of photon energy hv as shown in Fig.(1). The reciprocal of the slope of each line yields the magnitude of *Et* and its values for different $CoCl_2$ content of films. It is clear that dopant increases the width of the tail of localized states and decreases the energy gap of PVA thin films. Using Eq. (6) at a constant temperature a graph representing $\ln(\alpha)$ on the y-axis and energy (E (eV)) on the x-axis (Fig.(10)) in the range of the Urbach tail would yield a straight line.

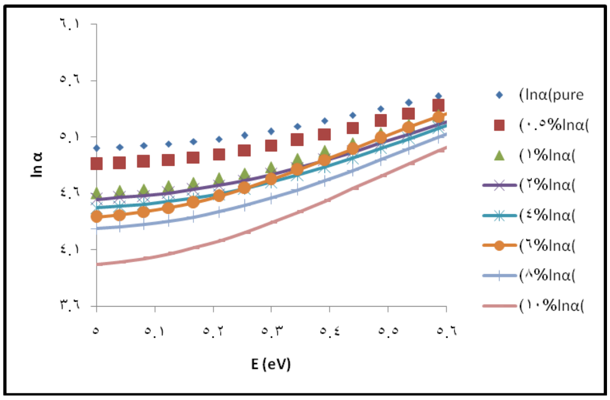

Fig.(10) Plots of ln α vs. E of the pure and doped PVA with different concentrations of $CoCl_2$.

The optical absorption measurements were carried out in the UV/VIS region (300-900 nm) for films of pure PVA and doped PVA. The absorption spectra at about 300 nm of pure and doped PVA films may be attributed to n-π * transition of the hydroxyl group in the polymeric macromolecule. It is clear from this figure that transmittance spectra for all films increased with increasing wavelength while reflectance decreased. Increasing the $CoCl_2$ content of the films decreases transmittance and increases reflectance for a lower wavelength range. This means that there is some absorption in that wavelength range. For each composition typical spectral behavior of transmittance and reflectance are given for pure and doped PVA films.

The refractive index, $n(\lambda)$, was determined from the absolute values of the transmittance and reflectance of the investigated films using the following formula:

$$n = \left[\frac{1+R}{1-R}\right] + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2} \qquad \text{.........................} (7)$$

where k is the extinction coefficient and R is the optical reflectance. The extinction coefficient can be obtained from the relation where $k = \alpha\lambda/4\pi$. Plots in Fig.(11) represent the dispersion in the refractive index for pure and doped PVA thin films in the investigated range of wavelengths. Inspection of Fig.(11) indicates for all compositions that the refractive index decreases with increasing wavelength.

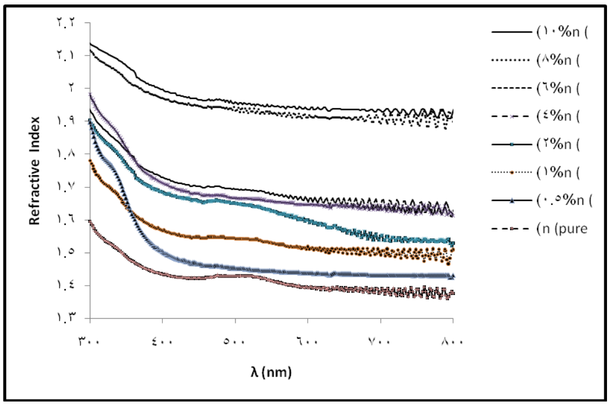

Fig.(11) The refractive index dispersion curves of pure and doped PVA with $CoCl_2$ percents.

Conclusions

The optical absorption measurements were carried out in the UV/IV region (200-800 nm) for films of pure and doped PVA with different concentrations of $CoCl_2$.

The refractive index decreased with increasing wavelength and it increased as $CoCl_2$ content increased from 0% to 10%.

The optical energy gap decreased from 5.65 to 5.26 eV as the $CoCl_2$ content increased from 0% to 10%.

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الخلاصة

تم فحص التغيير في فجوة الطاقه المحضورة وطاقة التنشيط قد تم فحصها لشرائح مركب PVA النقي والمشوب من خلال الامتصاص البصري للاطوال الموجية من (200−800) نانوميتر في درجة حرارة الغرفة. ان فجوة الطاقة المحضورة تقل بزيادة تركيز ملح الكوبالت كلورايد. وان طاقة التنشيط للانتقال المباشر تم حسابها باستخدام طريقة Urbach-edges ووجد انها تزداد بزيادة تركيز ملح الكوبالت كلورايد.