

Studying of the optical properties of poly (vinyl alcohol) films using Aluminum sulphate as additive by measuring allowed direct transition energy gap

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Abstract:

The change in the optical band gap and optical activation energy have been investigated for pure Poly (vinyl alcohol) and Poly (vinyl alcohol) doped with Aluminum sulphate to proper films from their optical absorption spectra. The absorption spectra were measured in the wave range from (200-700) nm at temperature range (25-140) °C. The optical band gap (E_g) for allowed direct transition decrease with increase the concentration of Aluminum sulphate. The optical activation energy for allowed direct transition band gap was evaluated using Urbach-edges method. It was found that ΔE increases with increasing the concentration of $Al_2(SO_4)_3$ and decreases when temperature increases.

Key word: poly(vinyl alcohol), optical energy gap, activation energy

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 polymer [2].

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 [3].

Poly (vinyl alcohol) (PVA) 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 [4].

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

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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.[5]

Materials and Methods:

The materials used in this work was a powder of commercial PVA and Aluminium sulphate, 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 Aluminium sulphate with different ratios (0.5, 1, 3, 5, 7, 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 (0.14 – 0.2) mm. Thickness measurements were made using micrometer.

The optical absorbance (A) of the samples were measured as function of wavelength (λ) at the range from (200-700) 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, which increases with increasing concentration were used to study the shifting in the optical energy gap for

PVA and PVA- $\text{Al}_2(\text{SO}_4)_3$ films at different doses from temperature range (25 – 140) °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 [6].

The value and shape of the mobility gap in PVA depend on the proportion 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)

$$T=B(1-R)^2 \exp(-\alpha d) \text{ ---- (1)}$$

Where B is a constant. This equation can be rewritten as follows :

$$\alpha d = 2.303 A + \text{Ln} [B(1-R)^2] \text{ -----(2)}$$

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

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

$$\alpha(\omega) = 2.303 (A/d) \text{ -----(3)}$$

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

$$\alpha = \alpha_0(h\nu - E_g)^r / h\nu \text{ -----(4)}$$

Where (h ν) is the photon energy and (E $_g$) 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 ($\alpha \geq 10^4 \text{ cm}^{-1}$). The energy dependence absorption coefficient is of the from:-

$$\alpha = \alpha_0(h\nu - E_g \pm E_p)^r / h\nu \text{ -----(5)}$$

Where (E_g) is the minimum energy gap, (E_p) is the phonon, (+) absorbed (-) emitted, (r) take the value of It takes the value (2) for allowed indirect transition and (3) for forbidden indirect transition and the absorption coefficient ($\alpha < 10^4 \text{ cm}^{-1}$). By plotting $(\alpha h\nu)^{1/r}$ versus $(h\nu)$ for fixed (r) value, the extrapolation of the liner part could be used to define E_g [6].

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 $(\alpha h\nu)^2$ versus $h\nu$ for pure PVA and PVA doped with Aluminum sulphate at different concentration with temperature rang from (25 – 140) °C. As shown in Figs. (1 to 6)

The effect addition of $\text{Al}_2(\text{SO}_4)_3$ on the values of photon energies are shown in Table (1). They shows that E_g decreases with increasing the concentration of Aluminum sulphate up to 7% concentration at temperature range from (25 – 140) °C. The shift in the energy gap could be attributed to the formation of polorans in the doped film[6].

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 (Al^{3+}) with the OH groups in the polymer. That is, the cations (Al^{3+}) 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). $\text{PVA}-(\text{SO}_4)^-$ also shows a similar effect. The evidence of poloran formation made the reaction in band - to- band transition due to shifting of band density of state toward the energy gap.

There are two polaron bands in the energy gap. The first one represents the transition from valance band to bonding polaron band. The second band represents the transition from valance band to anti-bonding polaron band.

For temperature above 100 °C the optical energy gap of PVA and PVA- $\text{Al}_2(\text{SO}_4)_3$ were increased with increasing in temperature at constant film concentration as shown in Table 1 and Figs. (4 to 6) this may be due to the change in the properties of the polymer at high temperatures. The films color's at concentration (3 -10) % convert to dark at 140 °C (Thermal stability of PVA turned to darkness above 150 °C and rapidly decomposed above 200 °C).

Table (1): The energy band gap according to the direct allowed transition for PVA and PVA doped with $\text{Al}_2(\text{SO}_4)_3$ at temperature range (25 – 140) °C .

Film Concentration	E_g (eV)				
	25 °C	70 °C	100 °C	120 °C	140 °C
Pure PVA	5.45	5.39	5.35	5.41	5.5
PVA+ 0.5% $\text{Al}_2(\text{SO}_4)_3$	4.95	4.88	4.82	5.05	5.1
PVA+ 1% $\text{Al}_2(\text{SO}_4)_3$	4.85	4.8	4.77	4.85	5.05
PVA+ 3% $\text{Al}_2(\text{SO}_4)_3$	4.75	4.72	4.7	4.75	-
PVA+ 5% $\text{Al}_2(\text{SO}_4)_3$	4.7	4.68	4.6	4.7	-
PVA+ 7% $\text{Al}_2(\text{SO}_4)_3$	4.75	4.7	4.69	4.72	-
PVA+ 10% $\text{Al}_2(\text{SO}_4)_3$	4.75	4.72	4.7	4.73	-

At concentration of (7-10) % the energy gap increased with increasing the concentration of $\text{Al}_2(\text{SO}_4)_3$ at a temperature of (25 – 120) °C as shown in Table (1) and Figures.(7-8) but the increase is slowly because as the salt concentration increases, the free ions become closer with an increase in columbic attraction between them. This result in the formation of neutral ion pairs, and hence, the increase in the number of free ions occurs with a decreasing rate [7].

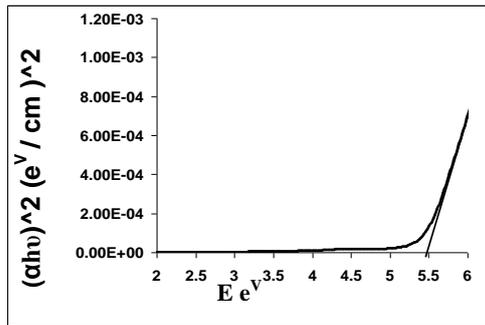


Fig. (1) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA at 25 °C

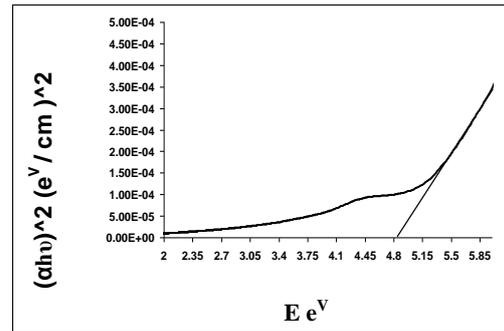


Fig.(5):The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA-1 % $Al_2(SO_4)_3$ at 120 °C

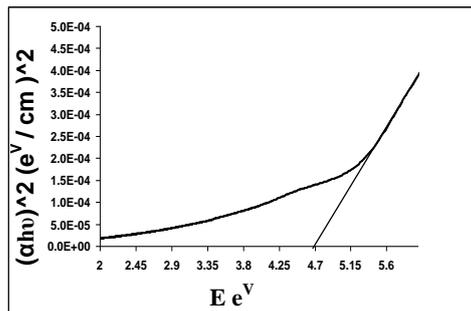


Fig.(2) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA -3% $Al_2(SO_4)_3$ at 25 °C

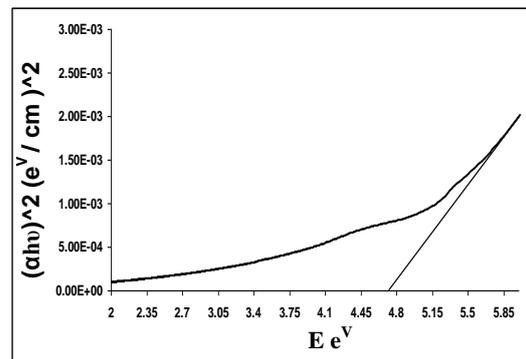


Fig.(6) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA -5% $Al_2(SO_4)_3$ at 120 °C

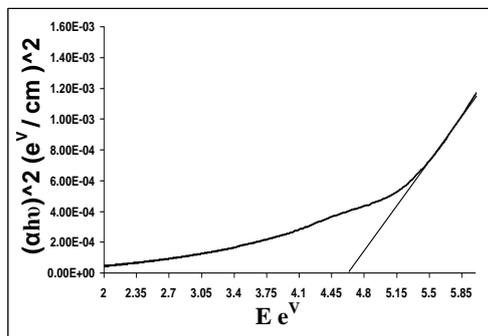


Fig.(3) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA -5% $Al_2(SO_4)_3$ at 70 °C

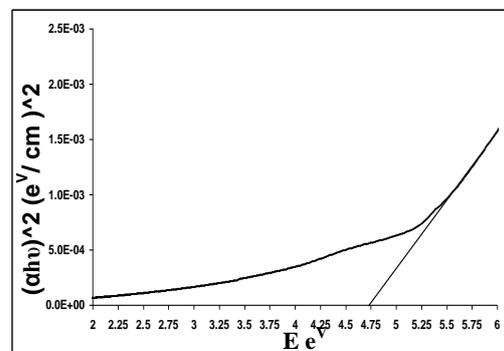


Fig.(7) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA-7% $Al_2(SO_4)_3$ at 25 °C

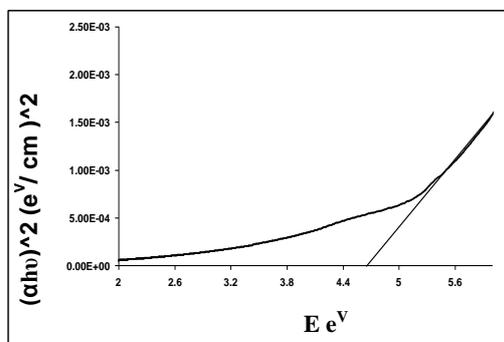


Fig.(4) :The direct transition $(\alpha h\nu)^2$ Vs. energy for PVA -5% $Al_2(SO_4)_3$ at 100 °C

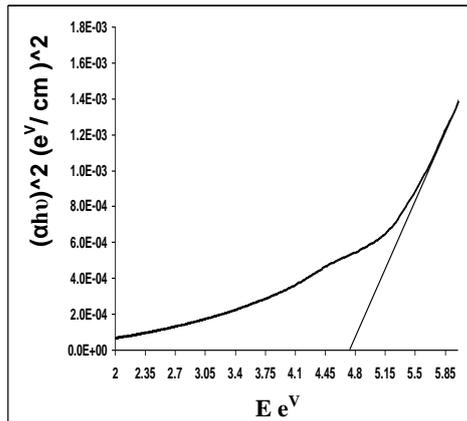


Fig.(8) :The direct transition($\alpha h\nu$)² Vs. energy for PVA- 10%Al₂(SO₄)₃ at 70 °C

Conductivity measurement of PVA with and without Aluminum sulphate can be obtain by adopting data of energy gap, (Table 1 and Figs.(1to 6)).

The conductivity measurement for PVA in the presence of Al₂(SO₄)₃ for different concentration up to 7% Al₂(SO₄)₃ increase with temperature increase up to 120 °C .When the temperature is increased, the mobility of the polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the transitional motion of ions[8].

At concentration of (7-10) % the optical energy gap increase with increase the concentration of Al₂(SO₄)₃ from temperature range (25 – 120) °C as shown in Table (1) and Figures.(7-8) and the conductivity will decrease, this may be due to the aggregation of ions leading the formation of ion clusters, thus decreasing the number of mobile charge carriers.[9]

The optical activation energy, ΔE is the energy width of the tail of localized states in the band gap was evaluated using the Urbach-edges method given by the formula [5]

$$\alpha(\omega) = \alpha_0 \exp(h\nu/\Delta E) \text{ ----- (6)}$$

Where α_0 is a constant and $\omega = 2\pi \nu$. The activation energy ΔE of pure PVA

and PVA doped with Al₂(SO₄)₃ were determined from the slope of the straight lines of $\ln(\alpha)$ versus photon energy $h\nu$ of figs. (9 to 13)

The results of ΔE values at different ratio and different temperatures are shown in Figs.(9 to 13) . and Table (2)

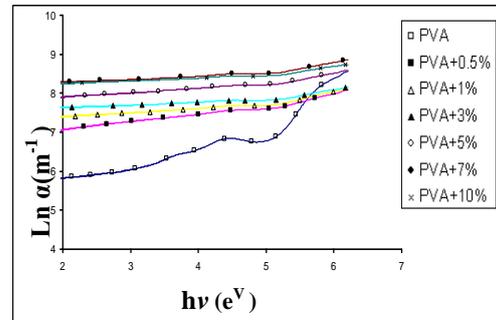


Fig. (9): The optical activation energy ΔE at 25 °C for PVA and PVA-Al₂(SO₄)₃ at different concentrations.

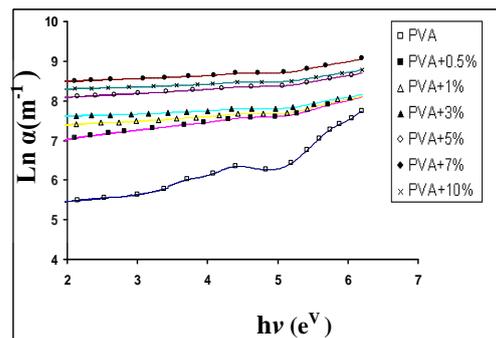


Fig. (10): The optical activation energy ΔE at 70 °C for PVA and PVA-Al₂(SO₄)₃ at different concentrations.

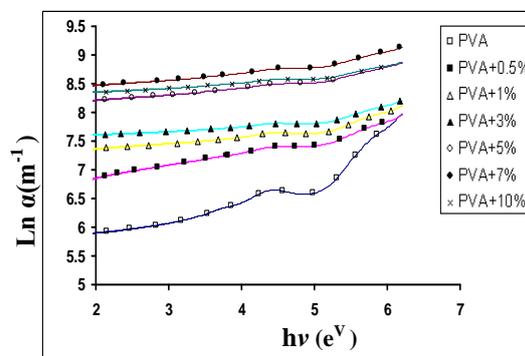


Fig. (11): The optical activation energy ΔE at 100 °C of PVA and PVA-Al₂(SO₄)₃ at different concentrations.

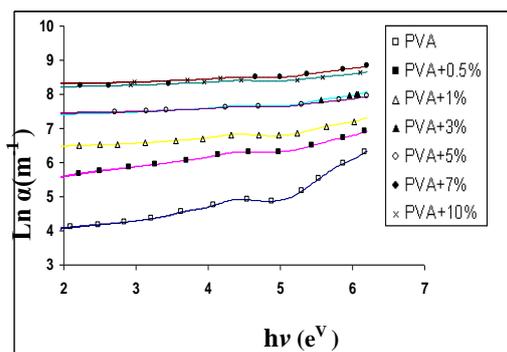


Fig. (12): The optical activation energy ΔE at 120°C of PVA and PVA- $\text{Al}_2(\text{SO}_4)_3$ at different concentrations.

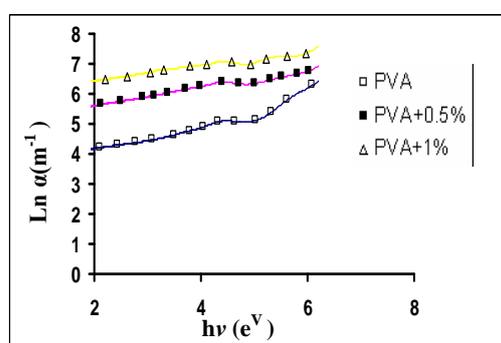


Fig.(13) : The optical activation energy ΔE at 140°C of PVA and PVA- $\text{Al}_2(\text{SO}_4)_3$ at different concentrations.

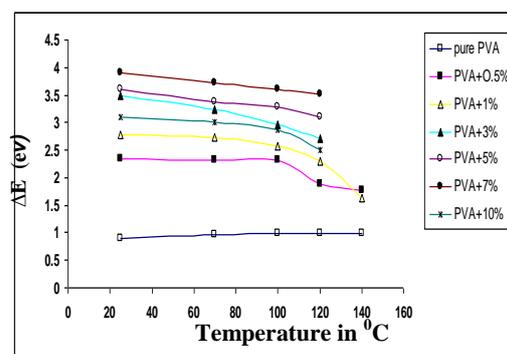


Fig.(14) : The optical activation energy of PVA and PVA- $\text{Al}_2(\text{SO}_4)_3$ at different concentrations.

Table 2: The optical activation energy of pure PVA and PVA - $\text{Al}_2(\text{SO}_4)_3$ at different concentration and different temperatures.

Film Concentration	ΔE (eV)				
	25 ^o C	70 ^o C	100 ^o C	120 ^o C	140 ^o C
Pure PVA	0.95	0.96	0.98	0.98	0.99
PVA+0.5%	2.35	2.33	2.31	1.89	1.77
PVA+1%	2.78	2.73	2.58	2.30	1.63
PVA+3%	3.5	3.23	2.96	2.7	-
PVA+5%	3.61	3.38	3.29	3.1	-
PVA+7%	3.9	3.71	3.6	3.52	-
PVA+10%	3.09	3.16	2.86	-	-

The results of ΔE values versus different temperatures are shown in fig.14 and Table 2. It can be seen that the activation energy is strongly effected by concentration of Aluminium sulfate more than the effect of temperature, ΔE increased with increasing the concentration of $\text{Al}_2(\text{SO}_4)_3$ up to 10% concentration and decrease with temperature as shown in Table 2 .

From fig. (14) and Table 2 it can be seen that PVA doped with 7% $\text{Al}_2(\text{SO}_4)_3$ have the higher activation energy.

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دراسة الخصائص البصريه لشرائح افلام بولي فينيل الكحول باستخدام مضافات كبريتات الالمنيوم عن طريق قياس فجوة الطاقه للانتقال المباشر

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الخلاصة:

تم فحص التغيير في فجوة الطاقه المحضورة وطاقه التنشيط قد تم فحصها لشرائح مركب PVA النقي والمشوب من خلال الامتصاص البصري للاطوال الموجية من (200-700) نانوميتر وبدرجة حرارة تتغير بمعدل (25-140) م⁰. ان فجوة الطاقه المحضورة تقل بزيادة تركيز ملح سلفات الالمنيوم وان طاقه التنشيط للانتقال المباشر تم حسابها باستخدام طريقة Urbach-edges ووجد انها تزداد بزيادة تركيز ملح سلفات الالمنيوم وتقل بزيادة درجة الحرارة.