Studying of the optical properties of poly (vinyl alcohol) films using different Metalssulphate as additivesby measuring allowed direct transition energy gap

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Abstract

The change in the optical band energy gap have been investigatedfor pure Poly (vinyl alcohol)and Poly (vinyl alcohol) doped with different metalssulphate to proper films from their optical absorption spectra. The absorption spectra were measured in the wave rangefrom (200-800) nm at room temperature. The width of the tail of localized states in the band gap (E_g) was evaluated using the Urbach-edges method.

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

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].

Avinyl 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) (is a polymer with carbon chain backbone with hydroxylgroups attached to methane carbons. These OH- groups can be a source of hydrogenbonding 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 gapenergy 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.[5].

Materials and Methods

The materials used in this work was a powder of commercial PVA doped by Coppe rsulphate, Nickel sulphate, Ferrous sulphate, Manganese sulphate and Zincsulphate a 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 metals sulphate with fixed ratios (0.5%) 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 24hr to remove any residual solvent. The thickness of the films were ranging from (40 – 45) 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 (200-700)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, were used to study the shifting in the optical energy gap for PVA and PVA-M-SO_4 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 [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)

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

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

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

A is the optical absorbance, (A= - log T).
So the absorption coefficient α (ω) in term of absorbance become:-

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

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

$$\alpha = \alpha_o(h\upsilon\text{-}Eg)^r\ /\ h\upsilon \ \text{------(4)}$$

Where (hʋ) 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:-

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

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 ($\alpha < 10^4\ cm^{-1}$). By plotting $(\alpha h\upsilon)^{1/r}$ versus (hʋ) 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 $(\alpha h\upsilon)^2$ versus hʋ for pure PVA and PVA doped with metals sulphate ^{0}C. As shown in Figs.(1 to 6)

The effect addition of MSO_4 on the values of photon energies are shown in Table (1).Table 1 shows that Eg decreases in the trend
PVA+ 0.5% $CuSO_4$, PVA+0.5% $FeSO_4$, PVA+ 0.5% $NiSO_4$, PVA+ 0.5% $ZnSO_4$ and PVA + 0.5% $MnSO_4$
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 (M^{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-$(SO_4)^-$ 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.

Table (1): The energy band gap according to the direct allowed transition for PVA and PVA doped with Metal-SO_4 at25^{o}C.

Films type	E_g(eV) at 25 ^{o}C
Pure PVA	5.48
PVA+ 0.5% $CuSO_4$	6.25
PVA+ 0.5% $NiSO_4$	6.27
PVA+ 0.5% $FeSO_4$	6.28
PVA+ 0.5% $MnSO_4$	6.3
PVA+ 0.5% $ZnSO_4$	6.32

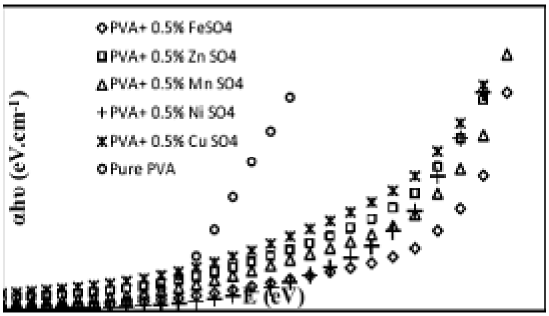


Figure (1): The direct transition $(\alpha h\upsilon)^2$ *Vs*. energy For pure PVA and doped films

Energy gap measurement of PVA with and without metals sulphate can be obtain by adopting data of energy gap, (Table 1 and Fig.(1)).

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, $h\nu$, is found to hold over several decades for a polymeric material and takes the following form:

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

where α_0 is a constant and E_t is interpreted as the width of the tails of localized states in the gap region. T_o evaluate the values of α_0 and E_t, it was α in logarithmic scale as a function of photon energy $h\nu$ as shown table (2) and the graphs in Figure (2). The reciprocal of the slope of each line yields the magnitude of *Et* and its values for different MSO_4 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 graph representing ln (α) on the y-axis and $h\nu$ on the x-axis in the range of the Urbach tail would yield a straight.

Table (2) The E_t and σ for pure and doped PVA with Metal-SO_4 at 25^{o}C.

Films type	Et
Pure PVA	1.666
PVA+ 0.5% $CuSO_4$	1.369
PVA+ 0.5% $NiSO_4$	1.282
PVA+ 0.5% $FeSO_4$	1
PVA+ 0.5% $MnSO_4$	0.833
PVA+ 0.5% $ZnSO_4$	0.625

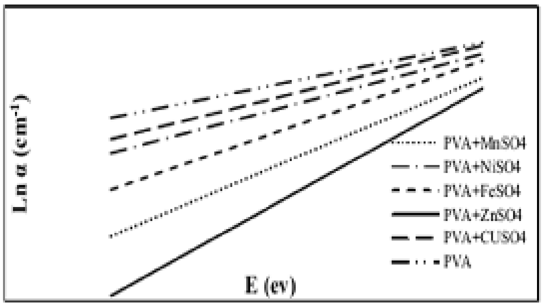


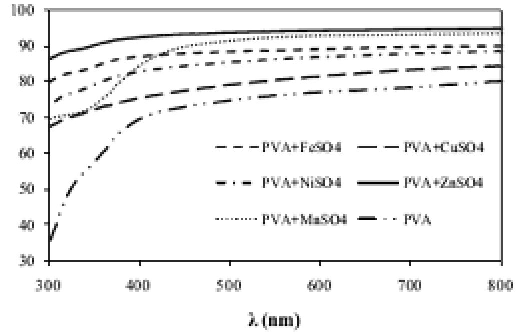
Figure (7): Ln α Vs E(eV) for pure and doped PVA

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. The transmittance and reflectance of pure and doped PVA polymer films recorded in the applied wavelength range are shown in Figures (8) and (9) respectively . It is clear from this figures that transmittance spectra for all films increased with increasing wavelength while reflectance decreased. 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:

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

Where k is the extinction coefficient and R is the optical reflectance. Figure (10) indicates for all compositions the refractive index decreases with increasing wavelength.



.Figure (8): The transmittance*Vs*. wavelength for pure and doped PVA

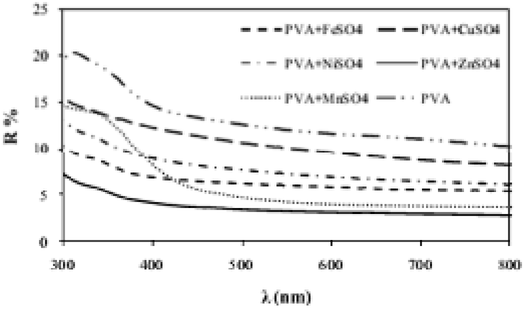


Figure (9): The reflectance *Vs*. wavelength for pure and doped PVA.

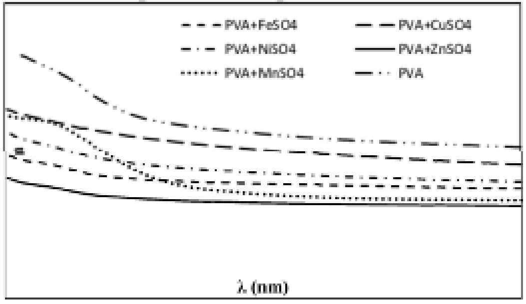


Figure (10)The refractive index dispersion curve for pure and doped PVA

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دراسة الخصائص البصرية لشرائح البولي فينل الكحول باستخدام املاح الكبريتات كمضافات من خلال قياس الانتقال المباشر المسموح لفجوة الطاقة

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الملخص:

تم فحص التغيير في فجوة الطاقه لشرائح مركب PVA النقي والمشوب باملاح الكبريتات من خلال الامتصاص البصري للاطوال الموجية من (200–800) نانوميتر في درجة حرارة الغرفة . وان طاقة التنشيط للانتقال المباشر تم حسابها باستخدام طريقة Urbach-edges