Study the Optical properties of Poly (vinyl alcohol) Doped Cupper Chloride

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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) films with different cupper chloride concentrations. The optical properties were measured in the wave length range from (200-800) nm at room temperature. The optical band gap (E_g) for allowed direct transition decrease with increase the concentration of cupper chloride. The optical activation energy for allowed direct transition band gap was evaluated using Urbach- edges method.

Keywords: optical band gap, optical activation energy, PVA.

Introduction

In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarisation properties [1-3]. Various composite materials have been recently synthesized by starting from different polymers and a wide variety of dopants like metals, oxides, inorganic salts, and other particles [4,5].The incorporation of the dopants into polar organic polymers can induce pronounced changes in various properties of polymers in order to modify and improve its properties[6-8].

This article discloses the investigation of the effect of doping with different concentrations of $CuCl_2$ on the optical properties of poly(vinyl alcohol) films. 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 interacts 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 [9].

Experimental

1. Films preparation

PVA films doped with Cupper Chloride 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 copper chloride with different ratios (1, 3, 5, 7, 9, and 10%) were dissolved in distilled water and added to the polymer solution, heated for a while 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 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.

2. Optical measurement

The absorption peak at UV region, were used to study the shifting in the optical energy gap for PVA and PVA-$CuCl_2$ films at 25 $^{\circ}$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 [10].

The value and shape of the mobility gap in PVA depends 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)

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

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

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

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

$$\alpha\,(\omega) = 2.303\,(A/d) \quad \text{....................................(3)}$$

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

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

Where ($h\nu$) 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:

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

Where (Eg) is the minimum energy gap, (Ep) is the phonon, (+) 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 ($h\nu$) for fixed (r)value, the extrapolation of the liner part could be used to define Eg [11].

Result and Discussion

The relationships between $(\alpha h\nu)^2$ versus photon energy for the polyvinyl alcohol samples are shown in Fig.(1 to 7) for allowed transition. It can be evaluated from extrapolating of linear region of the curve to a point of $(\alpha h\nu)^2$ versus hν for pure and doped PVA with cupper chloride at different concentrations at room temperature (25)°C.

The effect of CuCl$_2$ addition on the values of photon energies are shown in Table (1). Eg decreases in the trend pure PVA, PVA+1% CuCl$_2$, PVA+3% CuCl$_2$, PVA+5% CuCl$_2$, PVA+7% CuCl$_2$, PVA+9% CuCl$_2$ and PVA+10% CuCl$_2$.

The shift in the energy gap could be attributed to the formation of polorans in the doped film [9].

The polymer-salt composites may be characterized by interaction of the salt with the polar group of the polymer, which gives rise to complex formation. The complex formation may be mainly dominated by the cations (Cu^{2+}) with the OH groups in the polymer. 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$_2$)$^-$ 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 CuCl$_2$ at room temperature.

Films type	E g (eV)
Pure PVA	5.9
PVA+ 1%	5.86
PVA+3%	5.81
PVA+5%	5.79
PVA+7%	5.76
PVA+9%	5.74
PVA+10%	5.7
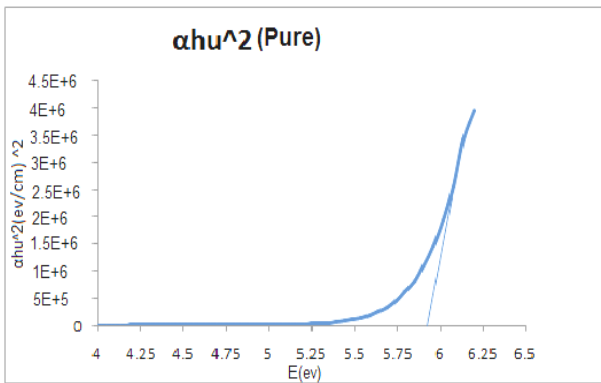
Fig.(1) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for pure PVA at room temperature.
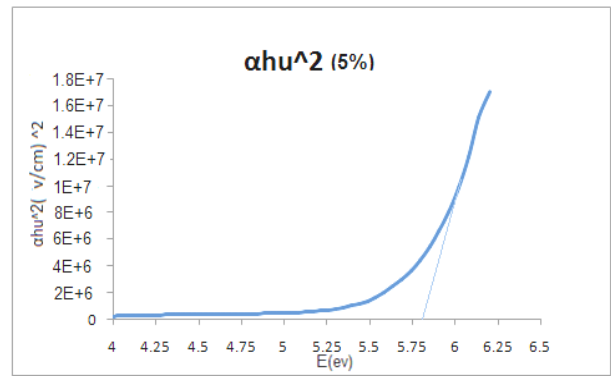
Fig.(4) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+5 %($CuCl_2$) at room temperature.
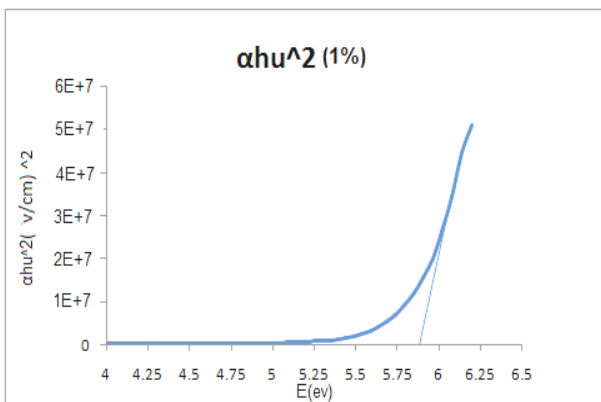
Fig.(2) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+1% ($CuCl_2$) at room temperature.
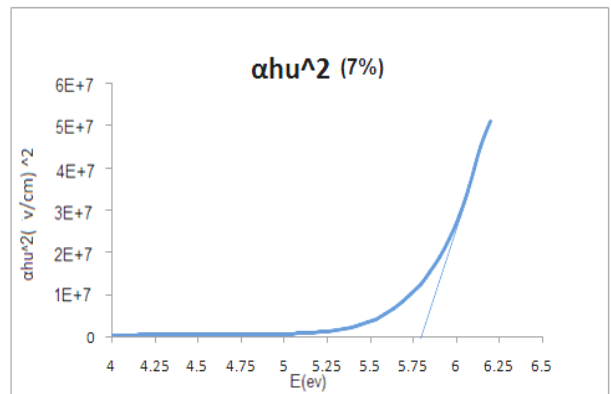
Fig.(5) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+7% ($CuCl_2$) at room temperature.
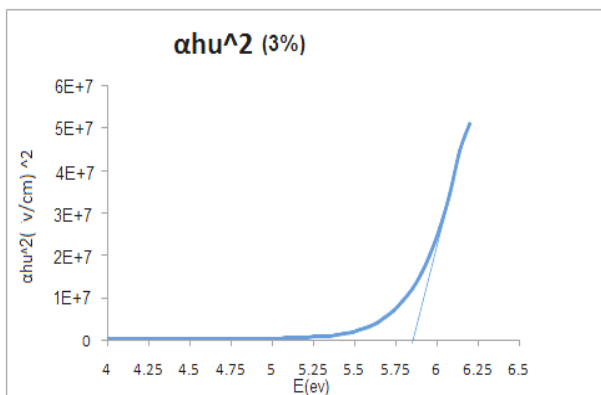
Fig.(3) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+3% ($CuCl_2$) at room temperature.
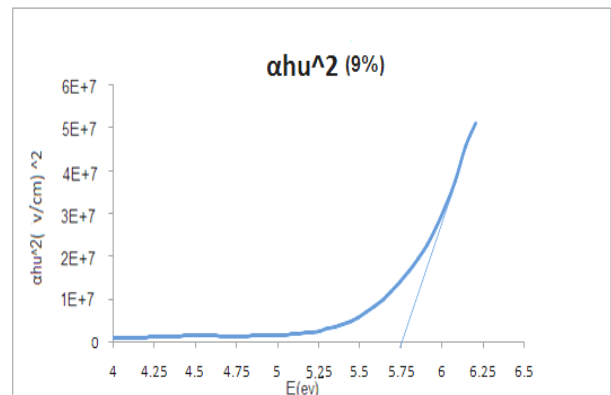
Fig.(6) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+9% ($CuCl_2$) at room temperature.
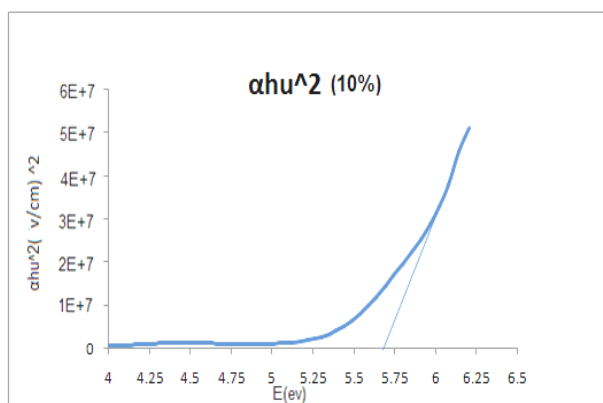
Fig.(7) The direct transition $(\alpha h\upsilon)^2$ Vs. energy for PVA+10% (CuCl$_2$) at room temperature.

Conclusion

The optical absorption in the UV-visible region for pure and doped filmes were studied. it is found that the Eg for allowed direct transtion decreases with increasing the concentration of CuCl$_2$.

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الخلاصة

تم فحص التغيير في فجوة الطاقه المحضورة وطاقة التنشيط لشرائح مركب PVA النقي والمشوب من خلال الامتصاص البصري للاطوال الموجية من (٢٠٠-٨٠٠) نانوميتر. ان فجوة الطاقة المحضورة تقل بزيادة تركيز ملح كلوريد النحاس. وان طاقة التنشيط للانتقال المباشر تم حسابها باستخدام طريقة -Urbach edges.