Doping Effect (($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$))(2%)w/v on Optical Energy gap of (GA/PVA) composite films

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Abstract

In this research we fabricated new Thin films of of pure(50:50)%GA/PVA& (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$).Were prepared using cast method .Optical absorption spectra of these thin films have been recorded in the wave length range(200-800)nm using UVspectrophotometer Optical band gap of the films has been calculated by using Taucs relation and variations in the values of optical band gap of pure(50:50)%GA/PVA (3.94 ev)& (50:50)%GA/PVA doping By($CoCl_2.6H_2O$)(3.8 ev) &($CuCl_2.6H_2O$) (3.62ev)

Keywords: Gum acacia , optical band gap , optical conductivity , a doping

1.Introduction

The optical behavior of materials is important to determine its usage in optoelectronic devices[1]. Knowledge of optical constants of a material such as optical band gap, refractive index and extinction coefficient is quite essential to examine materials potential opto-electronic applications. Further the optical properties may also be closely related to the materials atomic structure , electronic band structure and electric properties[2].Poly(vinyl alcohol) (PVA) is one of the most important polymeric materials as it has many applications in industry, It is a potential material having avery high dielectric strength, good change storage capacity and dopant dependent electrical and optical properties and of course it is relativity low cost. Natural polymer such as Gum Acacia (GA).Gum acacia is a natural polysaccharide formed by alkaline deactivation of the second most abundant naturally occurring chitin of crab and shrimp shells. Due to the amino groups that (GA) possesses in its chain, it can be dissolved in dilute aqueous acid solutions, such as hydrochloric acid and prop ionic acid. Since it is inexpensive, non-toxic and possesses potentially reactive amino functional groups, gum acacia has been evaluated for numerous applications, including medicine, food, cosmetics and wastewater treatment [3]. Polymer blending is one of the useful ways to have new material with required properties and there have been great scientific and commercial progress in the area of polymer blends [4]. In this paper an attempt was introduced to obtain the effect of $CoCl_2.6H_2O$ and $CuCl_2.6H_2O$ additive on the optical properties of (50:50)% (GA/PVA).

2.Theoritical part

The UV absorption mainly corresponds to the electron transition from the top of the valence band to the bottom of the conduction band. In general, the direct transition occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector $\Delta k=0$ for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the conduction band when the wave vector is equal to zero as shown in Fig. (1-a)

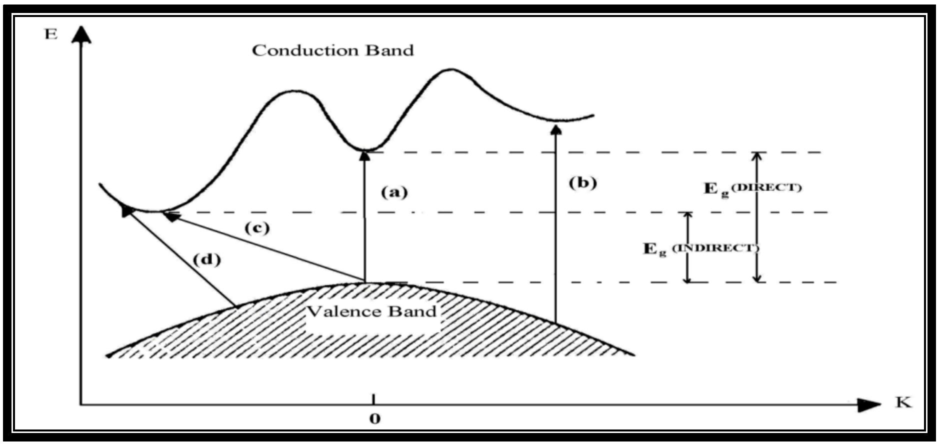

Figure1.The optical transitions(a)Allowed direct,(b)Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect [5]

This transition is described by the following relation [5].

$$\alpha h\nu = Ɓ(h\nu - Eg)^{1/2} \quad \text{----(1)}$$

Where α is absorption coefficient, Ɓ is inversely proportional to amorphousity, ($h\upsilon$) is the photon energy and (Eg) is the energy gap.

If the transition occurs between states of the same wave vector, (but the wave vector does not equal to zero), the transition is called forbidden direct transition as shown in Fig. (1-b). It obeys the following relation[5].

$$\alpha h\nu = \text{Ɓ}(h\nu - Eg)^{3/2} \text{ -----(2)}$$

In indirect transition there is a large momentum difference between the points to which the transition takes place in valence and conduction bands. This means that the conduction band minima are not at the same value of k as the valence band maxima, then, assistance of a phonon is necessary to conserve the momentum, therefore :

$$h\nu = Eg \pm Ep \text{--------(3)}$$

Where Ep is the energy of an absorbed or emitted phonon [6]. For an allowed indirect transition, the transition occurs from the top of the valence band to the bottom of the conduction band as shown in Fig.(1-c) so that [6].

$$\alpha h\nu = \text{Ɓ}(h\nu - Eg)^{2} \text{----(4)}$$

While, the forbidden indirect transitions occur from any point near the top of valence band to any point other than the bottom of the conduction band ,as shown in Fig. (1-d), then we have [6].

$$\alpha h\nu = \text{Ɓ}(h\nu - Eg)^{3} \text{-----(5)}$$

Experimentally, it is possible to differentiate between direct and indirect processes by the level of the absorption coefficient (α); α takes values from (10^4 to 10^5) cm^{-1} for direct transitions and (10 to 10^3) cm^{-1} for indirect transitions at the absorption edge[7]. From the equation related to the absorption of ray, the relation between the incident light intensity (Io) and the penetrating light intensity (I) is described in the following equation [7]:

$$I = Io\, e^{-\alpha t} \text{ -------(6)}$$

where (t) is the thickness of the matter and (α) is the absorption coefficient, it is
measured by cm^{-1} [6].

$$\alpha t = 2.303 \log I/ Io \text{ ------(7)}$$

here the amount of (log I/Io) represents the absorbance (A). The absorption coefficient can be calculated as follows:

$$\alpha = 2.303(A/t) \text{ -------(8)}$$

The absorbance (A) and transmittance (T) can also be calculated as in the following equation[6]:

$$R + A + T = 1 \text{ ------(9)}$$

The fast increase in absorption of the ray energy is proportional to the energy gap of the absorbing material. The fundamental absorption edge represents the lowest difference in energy between the highest point in the valence band and lowest point in the conduction band [8].

The extinction coefficient (k) was calculated using the following equation: [5]

$$K = \alpha\lambda/4\pi \text{ ------(10)}$$

The relation between reflectance and refractive index is given in the following equation[9]:

$$R = (n-1)^2 + k^2/(n+1)^2 + k^2 \text{ ------(11)}$$

Where (n) is the refractive index, (k) is the Extinction Coefficient. R is the reflectance.

Refractive index can be expressed by the following equation [9]:

$$n = [4R/(R-1)^2 - k^2]^{1/2} - (R+1)/(R-1) \text{ ------(12)}$$

The values of optical band gap (E_{opt}) Eg can be correlated to the number of carbon atoms per molecule through the expression given by eq10[10].

$$E_{opt} = 34.3/M^{1/2} \text{ -------(13)}$$

Where M is the number of carbon atoms in carbonaceous cluster.

The absorption coefficient α, and the refractive index n from eq(12), were used to obtain the optical conductivity (σ), using the relation[10].

$$\sigma = \alpha n c/4\pi \text{ -------(14)}$$

where c is the velocity of light in the space.

3. Experimental work

Polyvinyl alcohol PVA of molecular weight 10000 g/mol as a matrix element supplied by (BDH chemicals) with GA polymer supplied by (Aldrich) were used in this study with high purity were used as basic polymeric materials ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$). The weight percentages of ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) are (2 wt/v%). The polymers were dissolved in HCL by using magnetic stirrer in mixing process to get homogeneous solution at 75 ^{0}C for about 2 hour, the solution was cooled at room temperature of (50:50)% ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$), powder ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) were dissolved in HCL .Appropriate mixtures of (50:50)% GA/PVA solution into flat glass then put in another Petri dish mixtures of the same ratio of (GA:PVA)with 2%weight of ($COCl_2.6H_2O$) solution & ($CuCl_2.6H_2O$) solution in third flat glass. Homogenous films were obtained after drying the solution in an oven for 24 hours. The thickness of the prepared films was measured by a compound microscope (Nikon) in conjunction with an acculometer which gives least count 10 and 2μm at the magnification 1:10 and 1:200,respectively was used. small section of the sample was taken and mounted vertically to get a clear section view of the thickness. the film used for the present study is of the thickness 10μm. Absorbance and transmittance measurements were carried out using single beam UV/VIS spectrophotometer (Jenway 7315) in the wavelength range (200-800) nm.

4.Results & Discussions

4.1. The absorbance of composite

The UV-vis absorption of blend (50:50)% (GA/PVA) pure & (50:50)%(GA/PVA)/$CoCl_2.6H_2O$& (50:50)% (GA/PVA)/ $CuCl_2.6H_2O$ films are recorded at room temperature in the wavelength range (200-800) nm shows the relationship between absorbance of (50:50)% (GA/PVA) pure and (50:50)% (GA/PVA) doped $CoCl_2.6H_2O$and (50:50)%(GA/PVA)A doped $CuCl_2.6H_2O$ composite and wave length, from the figure (2), it was appeared that the absorbance tends to decrease with increasing the wavelength in UV region (10-400)nm , this behavior attributed to the absorbance of polymer in high energies. The optical absorption of the polymer films in the UV region is high, and this aspect highlights the possibilities of uses of these films in the fields related to the UV protecting. It was found that the absorption shifts towards higher wavelength due to doping by $CuCl_2.6H_2O$ and shifts towards lower wavelength due to doping by $COCl_2.6H_2O$.

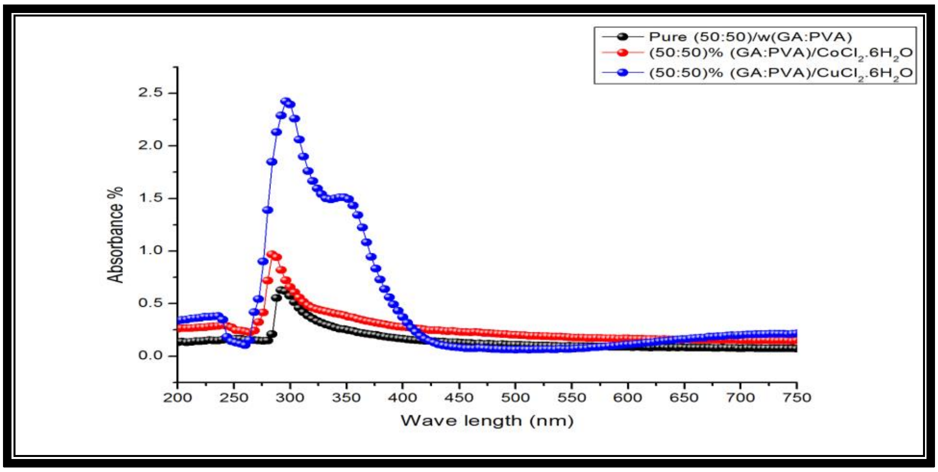

Figure2.The relationship between absorbance and the wave length of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer

3.2.The absorption coefficient

Fig.(3) shows the dependency of the absorption coefficient (α) on the wavelength for the samples. At short wavelength, (α) takes higher value then increases with decreasing (λ) (increasing photon energy), and the marked increase of the absorption coefficient at higher energies may be attributed to extra transition from the bonding molecular orbit to nonbonding[11].

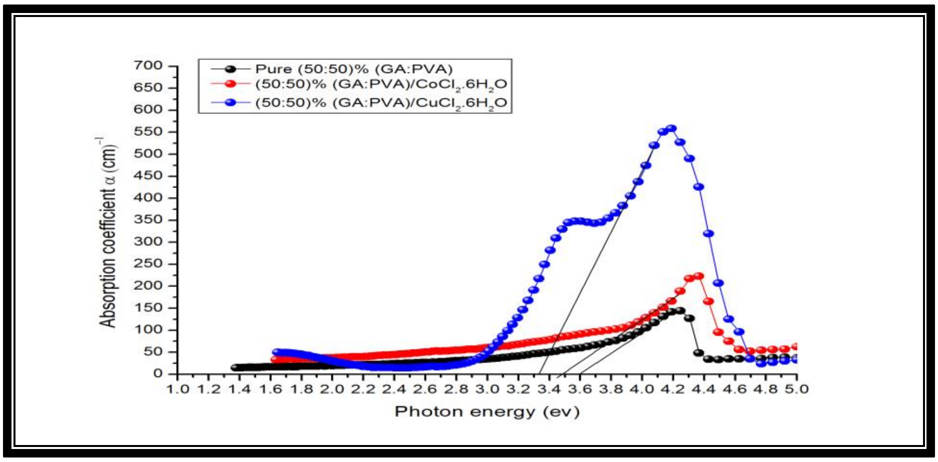

Figure 3. Relation between absorbance coefficient (α) versus ($h\nu$) of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer

3.3.The direct allowed &forbidden energy gap and indirect transitions

Fig. (4)& Fig.(5) and Fig. (6) represented the direct allowed & forbidden energy and indirect transition were calculated by using eq.1,eq4, the energy gap values dependence in general on the crystal structure of the composites and the arrangement and distribution way of atoms in the crystal lattice. From these figures we can see that the energy band gap is decreased by a doping ($CuCl_2.6H_2O$) then ($COCl_2.6H_2O$)[12].

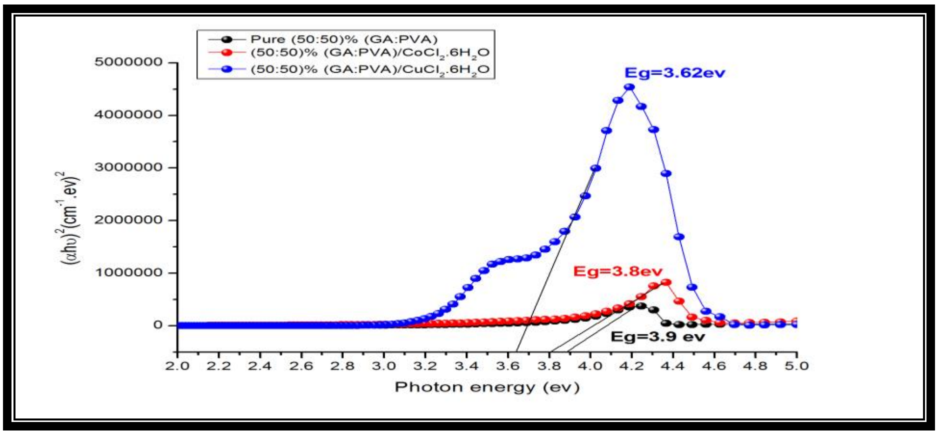

Figure 4. Relation between $(\alpha h\nu)^2$ versus $(h\nu)$ of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer

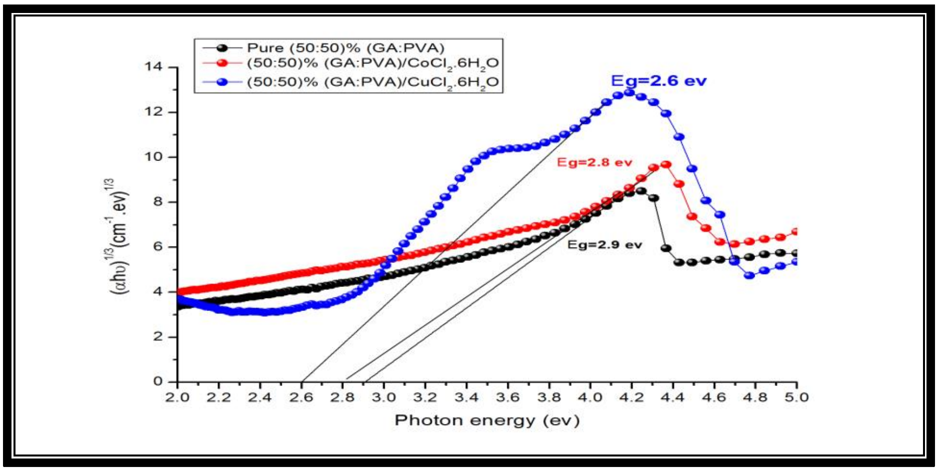

Figure 5. Relation between $(\alpha h\nu)^{1/3}$ versus $(h\nu)$ of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer.(direct forbidden energy)

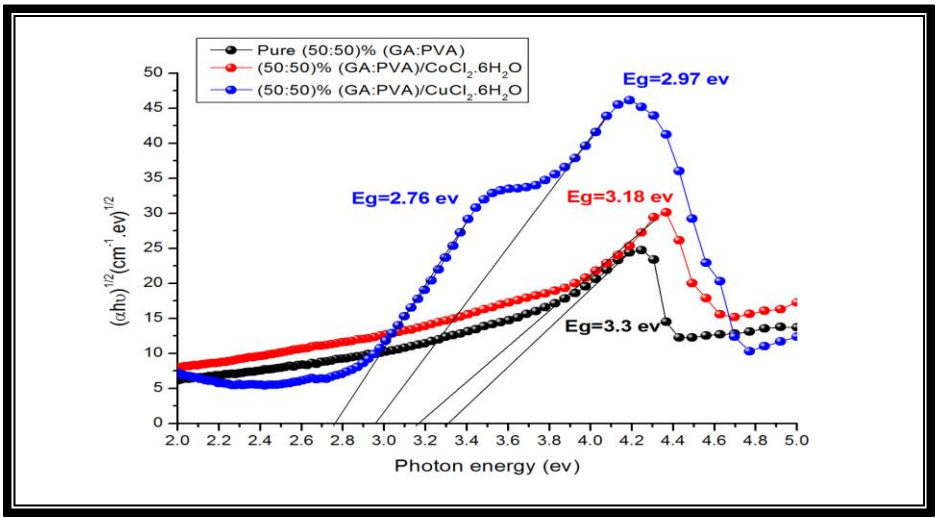

Figure 6. Relation between $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer.(indirect transitions)

3.4.The number of carbon atoms per molecule.

The values of optical band gap (E_{opt}) Eg can be correlated to the number of carbon atoms per molecule through the expression given by eq(13) [10]

The calculated values of M for (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer are presented in table (1)

Table 1. Optical data of (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$) composite polymer

Composition	Absorption edge (ev)	Direct allowed band gap (ev) (E_{opt})	Direct forbidden band gap (ev)	Indirect band gap (ev)	M
Pure (50:50)%(GA:PVA)	3.6	3.9	2.9	3.3	77
(50:50)%(GA:PVA)/ ($CoCl_2.6H_2O$)	3.5	3.8	2.8	3.18	81
(50:50)%(GA:PVA)/ ($CuCl_2.6H_2O$)	3.32	3.62	2.6	2.76,2.97	90

3.5.The Optical conductivity

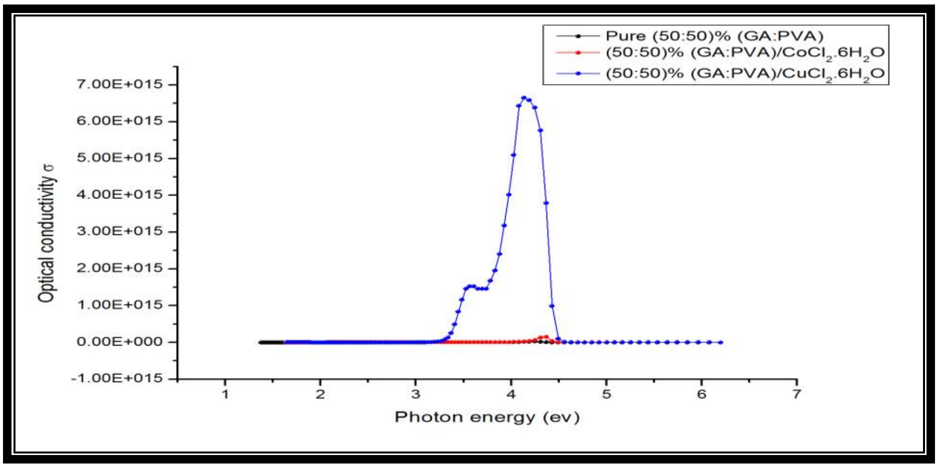

Figure 7. Optical conductivity of (50:50)%GA/PVA doping By ($CoCl_2.6H_2O$) & ($CuCl_2.6H_2O$).

Fig.7 shows the variation of optical conductivity σ with the incident photon energy $h\nu$. The optical conductivity increases of (50:50)%GA/PVA doping By ($CuCl_2.6H_2O$) polymer in same concentration with a doping ($COCl_2.6H_2O$). The conductivity enhancement in polymer attributed to the reducing the crystalline phase which provide the conducting pathways for the mobility of ions as well as polymer segments. Thus the observed effect of pure (50:50)%GA/PVA & (50:50)%GA/PVA doping By ($COCl_2.6H_2O$) & ($CuCl_2.6H_2O$). On the optical conductivity and the conduction behavior of blend polymer films can be explained on the basis of charge transfer complex formation [12].

5. Conclusions

The absorbance of GA/PVA is increased of doping By ($CuCl_2.6H_2O$) in concentration (2%)

- The composites have indirect energy band gap which decrease with increasing of (50:50)%GA/PVA doping By ($CuCl_2.6H_2O$) polymer.
- The optical constants(absorption coefficient, direct (allowed &forbidden) and indirect transitions' energy, Optical conductivity)are changed with GA/PVA doping By ($CuCl_2.6H_2O$) composite films

6. References

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تاثير التشويب ب(كلوريد النحاس المائي وكلوريد الكوبلت المائي) بتركيز(2%)على فجوة الطاقة البصرية لأغشية المتراكب البوليمر GA/PVA

مهند قادر كريم ، سوزان عبد الله حسن ، معد محمد امين

قسم الفيزياء ، كلية العلوم ، جامعة كركوك ، كركوك ، العراق

الملخص

تم في هذا البحث تحضير أغشية جديدة من البوليمر المتراكب(GA/PVA)%(50:50) النقي ثم تم دراسة تأثير التشويب بكلوريد النحاس والكوبلت المائي بتركيز (2%) بطريقة الصب . طيف الامتصاصية الضوئية لهذه الأغشية الرقيقة تم تسجيلها بين مدى الطيف (200–800) نانوميتر بواسطة جهاز مطياف الأشعة فوق البنفسجية.فجوة الطاقة البصرية للأغشية تم حسابها بواسطة علاقة Tauc وقد وجد اختلاف في فجوة الطاقة البصرية للأغشية المختلفة التراكيز, بالنسبة ل(GA/PVA)%(50:50) النقي كانت فجوة الطاقة البصرية (3.94 الكترون فولت) اما في حالة التشويب بكلوريد الكوبلت المائي بتركيز 2% فكانت (3.8 إلكترون فولت) وبكلوريد النحاس بنفس التركيز فكانت (3.62 إلكترون فولت).

كلمات مفتاحية: كم اكاسيه, فجوة الطاقة البصرية , التوصيلية البصرية , التشويب