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RESEARCHARTICLE

EFFECT OF CHROMIUM OXIDE CONCENTRATION ON OPTICAL PROPERTIES OF PVA FILMS

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ABSTRACT

Pure and Cr_2O_3 –doped polyvinyl alcohol (Cr_2O_3 –PVA) composite films with different Cr_2O_3 concentrations were prepared by solution cast technique. FTIR spectra comparison shows that the Cr_2O_3 molecules are interstitially distributed among polyvinyl alcohol chains, i.e., there is no chemical bonding between the Cr_2O_3 and polymer at the specified conditions of the research. The optical properties (absorption, transmission, refraction index, extinction coefficient, real and imaginary parts of the dielectric constant) for the samples are investigated at room temperature in wave length range of (190- 1100) nm. The optical band gap (E_g) for allowed direct transition decrease with increase the concentration of Cr_2O_3 from 5.53 eV for pure PVA to 4.72,2.62 and 2.38 eV for 5%,10%,and 15% respectively.

INTRODUCTION

The poly vinyl alcohol (PVA) is an important material regarding to its large scale of applications .It is used in surgical devices, sutures, hybrid islet transplantation, implantation, blend membrane (Osiribilis W. Guirguis and Manal T.H. Moselhey, 2011), and in synthetic cartilage in reconstructive joint surgery. Anew type of soft contact lens was developed from (PVA) hydrogel prepared by low temperature crystallization technique (Eaga*et al*., 2009).(PVA) also used in sheets to make bags for premeasured soap, for washing machines, or to make longer bags used in hospitals.(PVA)was selected as the hydrogel component based on able water soluble, desirable physiochemical properties and its biocompatibility. Furthermore, chemically cross linked PVA hydrogel has been gaining increasing attention in the field of bio medics (Kim *et al*., 2003). In recent years,studies on the electric and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarization properties (AL-Ramadin, 2000; Reddy *et al*., 2006 and Tauc, 1974).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 (Asogwa *et al*., 2010 and Vandervorst *et al*., 2003).(Rabee, 2011) showed that the absorption coefficient increases and energy gap of the indirect allowed and forbidden decreases with increase the weight percentage of silver carbonate content. Found that, the compositions such as PVA-ZnO-$Pb(CH_3COO)_2$ can be used as the reversal photographic materials with a direct blackening besides he showed another interesting property of lead nanoparticles in a PVA-ZnO composition is their ability to activate excitonic luminescence of Zinc oxide. Mustafa *et al*. (2013) found the optical band gap (E_g) for allowed direct transition decrease with increase the concentration of cupper chloride with PVA. Also was found that the optical absorption is due to direct transition, and the optical energy gaps values shifted to lower energies on kaolin light concentration from 5.53 for pure PVA to 5 eV for 20% kaolin addition (Omed Gh.Abdullah *et al*., 2011). The study effect of thickness on optical properties of PVA doped $Ni(CH_3COO)_2$ films has shown that all optical properties such as transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, and the real and imaginary parts of dielectric constant have been affected by increasing the thickness. The optical energy gap increased and the Urbach energy decreased when the thickness of films was increased (Tahseen H. Mubark, 2013). The aim of the present paper is to investigate the optical properties of poly vinyl alcohol (PVA) films doped with varying concentration of chromium oxide (Cr_2O_3).

Experimental details

Films of PVA-Cr_2O_3 composite were prepared by solution casting; 2gm of pure polyvinyl alcohol PVA supplied from Sigma-Aldrich company has been dissolved in 30 ml of distilled water to obtain a pure PVA film; the doping to (5,10

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and 15wt%) were prepared by mixing amount of (0.1,0.2 and 0.3 gm of into Cr_2O_3 pure PVA solution, the complete dissolution was obtained using a magnetic stirrer at temperature 60 ºC for 2 hr, these homogeneous solutions were spread on a glass plate.The whole assembly was placed in a dust free chamber and allowed to evaporate the solvent slowly in air at room temperature for 48 hr. The thickness of the films was 28±4 µm, it was determined using micrometer Ultraviolet-Visible absorption spectra.Wave length190-1100nm using of the carried out at a room temperature in the Shimadzu UV/VIS -160A a double beam spectrophotometer. The infrared spectrophotometer (perkin Elmer 65) was used for recording the FTIR spectra in the wave number range 500-4000 cm^{-1}.

RESULTS AND DISCUSSION

The infrared (IR) absorption spectra for the pure PVA films with different Cr_2O_3 concentration shows the absorption peak at 3368 cm^{-1} which refers to the intermolecular hydrogen bonding and – OH stretch vibration. The vibrational band observed at 2941 cm^{-1} is associated with C - H stretching from alkyl groups. The absorption corresponding to the –C- O stretching occurs at 1096 cm^{-1}(EI-Hefian *et al*., 2010).These main PVA characterizing peaks are observed in all doped samples which indicates that the Cr_2O_3 molecules are interstitially distributed among polyvinyl alcohol chains without forming any chemical bonding between them at the specified conditions of the research. The spectrophotometer method was used to determine the optical constants of the samples. The variation of the optical absorption with wavelength (190-1100)nm for all prepared films is shown in Fig (1).The spectrum of pure PVA is characterized by an absorption peak at wavelength 283 nm as well as a shoulder near 330 nm. No absorption peaks are noticed at higher wavelengths. The absorption peak can be attributed for the absorption by simple carbonyl groups along the polymer chain. On other hand, the shoulder can be assigned to the appearance of the –CO-$(CH{=}CH)_3$- groups (OmedGh.Abdullah *et al.*, 2011 and El-Khodary, 2009). The absorption peak was shifted to higher wavelength and the absorption increased as Cr_2O_3 concentration increased as show in Fig 1.

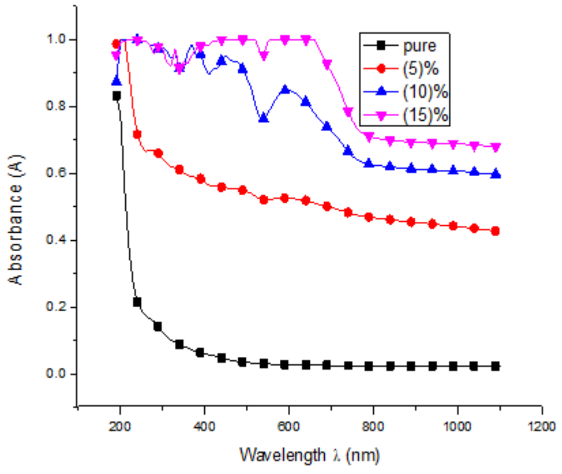

Fig. 1. Absorbance of PVA/Cr_2O_3 films with different concentrations

The optical transmission spectra as a function wavelength is shown in Fig.2. We can see from this figure that the transmittance decreases with increasing the concentration of Cr_2O_3.This may be attributed to the creation of levels at the energy band by increasing concentration and this leads to the shift of peak to smaller energies (Tahseen H. Mubark, 2013).

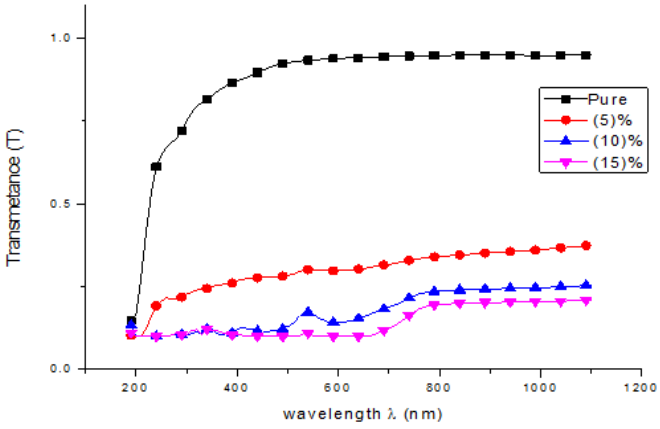

Fig. 2. Transmission spectra for PVA/Cr_2O_3 films with different concentrations

The Reflectance (R) calculated from the spectrum of absorption (A) and transmission (T) according to the law of energy conversation (Chopra, 1969 and Khodair *et al.*, 2012).

$$R + T + A = 1 \qquad (1)$$

The extinction coefficient (k) is the absorption energy in the thin film and it also represent the imaginary part of refraction index according to the relation (Mahaboob *et al.*, 2012).

$$n = c/v = n_0 - k \qquad (2)$$

Where:
(v) is the velocity of light in the thin films,(c) is the velocity of the light in the vacuum and (n_0) is the real part of refractions index .Also the extinction coefficient is related to absorption coefficient (α) by the relation (Sze, 1981).

$$K = \alpha \lambda / 4\pi \qquad (3)$$

Where λ is the incident photon wave length. Absorption coefficient (α) represents the relation of decreasing in intensity of radiation through the material i.e it can be estimated from the optical absorption spectrum owing to the following relation (OmedGh.Abdullah *et al.*, 2011; Haidar and Simon, 2009 and Baiiatoand Foulger, 2003).

$$\alpha = (1/t).\ (1n\ 1/T) = 2.303A / t \qquad (4)$$

Where (t) is the thickness of the thin film in cm, and (T) is the transmittance and A is defined by log (l_o / l) where l_0 and l are the intensities of the incident and transmitted beams respectively. Refractive index (n) associated with the reflectance of thin film by the relation (Heavens, 1973).

$$n = \{(1+R)/1-R)^2 - (k2+1)\}^{1/2} + (1+R/1-R) \qquad (5)$$

The reaction between the light and the charges of the medium occur by presses of the absorption of energy in material and that lead to polarized of the medium's charges, this polarization decrypted by the complex dielectric constant for the medium by the relation (Kraus, 1984 and Osama Z. Abed *et al.*, 2013).

$$\varepsilon = \varepsilon_r - \varepsilon_i \qquad (6)$$

Where; (ε_r) is the real part of the dielectric constant,(ε_i) is the imaginary part of the dielectric constant.

From the last relation the real and imaginary parts of the dielectric constant are calculated as following:

$\varepsilon_r - \varepsilon_i = (n - k)^2$ (7)
$\varepsilon_r = n^2 - k^2$ (8)
$\varepsilon_i = 2nk$(9)

As direct band gap semiconductors, the incident photon energy (hν),absorption coefficient(α),and optical energy gap (E_g) are related by the following relation (Mahaboob *et al.*, 2012):

$$h\nu\alpha = \bar{A}(h\nu - E_g)^r \quad (10)$$

where r is the power that characterizes the transition process. Specifically, r, can take the values 1/2, 3/2, 2 and 3 for transitions designated as direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively (El-Khodary, 2010). It was found that r = ½ is the best fit for our results (allowed direct transition)get:

$$(\alpha h\nu)^2 = \bar{A}(h\nu - E_g) \qquad (11)$$

Where ($\bar{A}$) is a constant, ν is the frequency, h is planck's constant and E_g is the

The optical properties (absorbance, transmittance, reflectance, refractive index as a function of wavelength in the range (1900-1100 nm) are shown in figures (1-7) respectively. We can observe from fig (3) the reflectance increased by decrease the concentration of Cr_2O_3 and refractive index similar to the reflectance as shown in Fig (4).

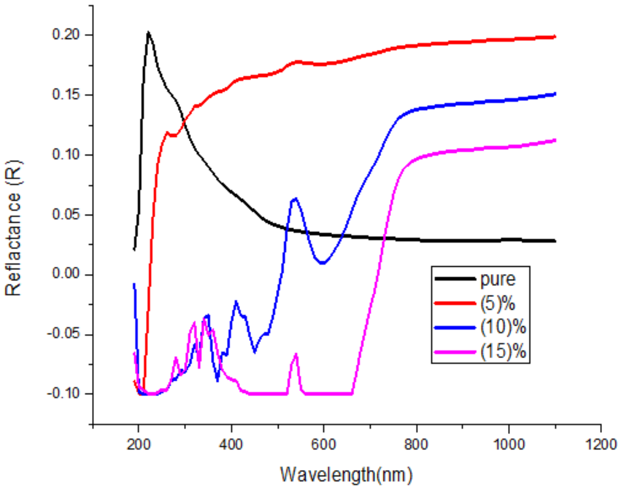

Fig. 3. The Reflectance of PVA/Cr_2O_3 films with different concentrations

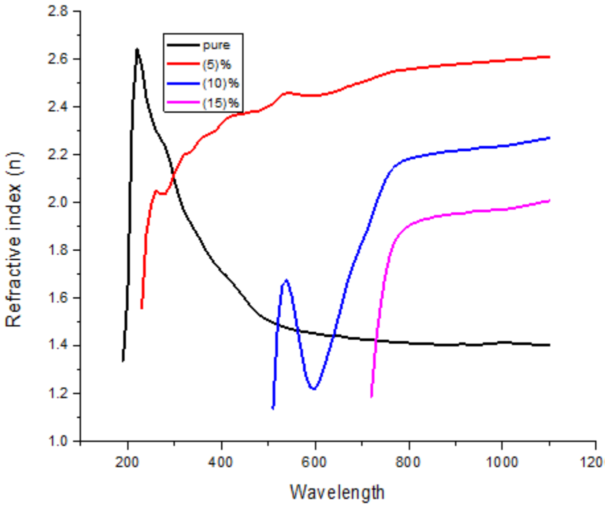

Fig. 4. The refractive index PVA/Cr_2O_3 films with different concentrations

From Fig.(5) the extinction coefficient(k) increased with increases of concentration at lower photon energy (k) takes higher value, which is a result of increasing the number of atomic refractions due to the increase of the linear polarizability.

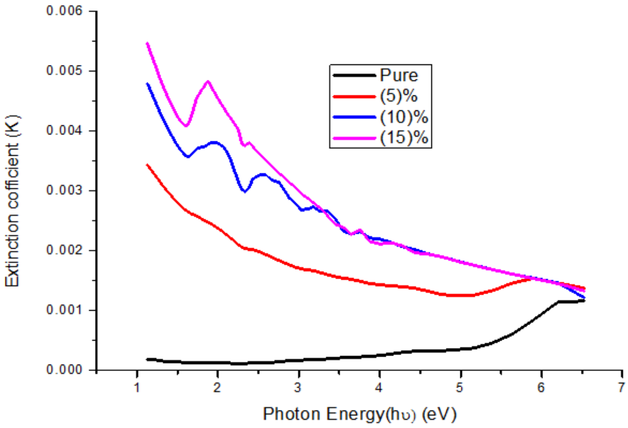

Fig. 5. The extinction coefficient against photon energy for PVA/Cr_2O_3 films with different concentrations

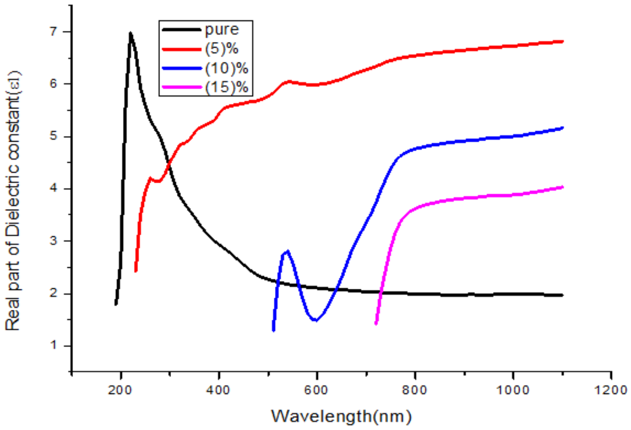

Fig. 6. Real part of dielectric constant against wavelength for PVA/Cr_2O_3 films with different concentrations

Real part and imaginary part of dielectric constant of the films increased with increases of wavelength, real part increased by decrease the concentration but the imaginary part of dielectric constant of the films increased with increases the concentration of Cr_2O_3 a shown in Figs (3) and(4) respectively. The variation of $(\alpha h\nu)^2$ versus photon energy for Cr_2O_3films at different concentration are plotted in figs (8-11). Optical band gap (E_g) can be evaluated by extrapolation of the liner part to the abscissa yields the optical energy band gaps to be 5.53 eV for pure PVA to 4.72, 2.62 and 2.38 eV for 5%,10%, and 15% respectively.

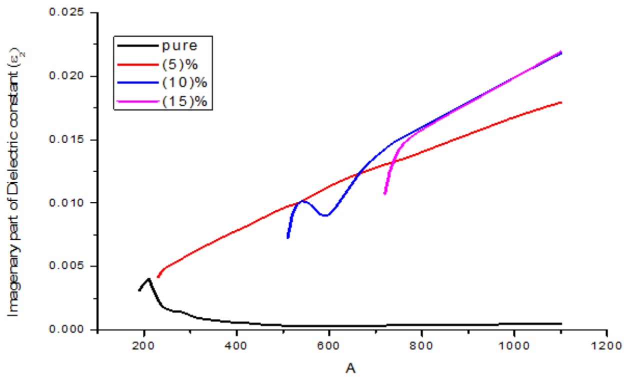

Fig. 7. The imaginary part of dielectric constant against wavelength for PVA/Cr_2O_3 films with different concentrations

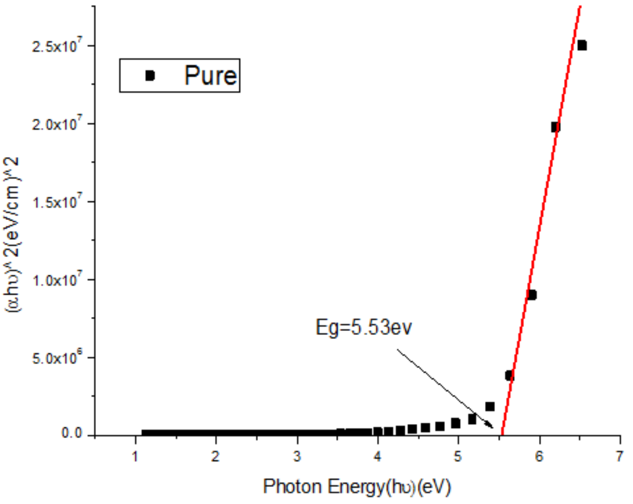

Fig. 8. $(\alpha h\nu)^2$ against photon energy for pure PVA film

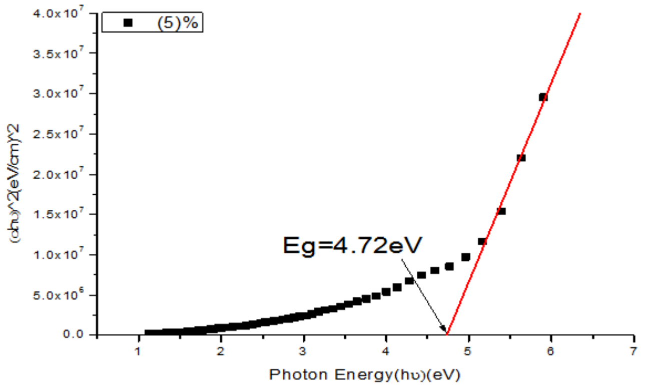

Fig. 9. $(\alpha h\nu)^2$ against photon energy for PVA+ 5 w% Cr_2O_3 film

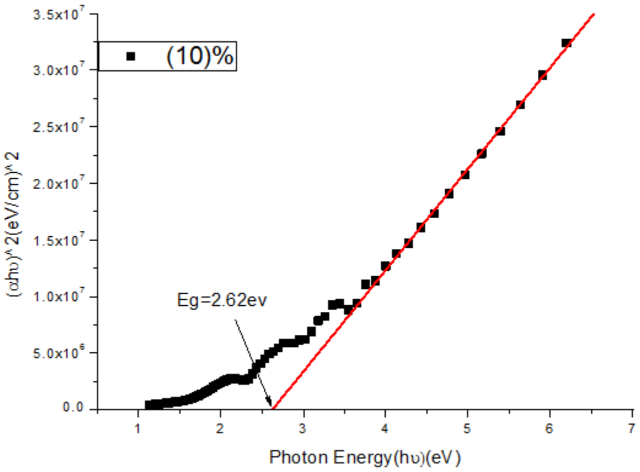

Fig.10. $(\alpha h\nu)^2$ against photon energy for PVA+ 10 w% Cr_2O_3 film

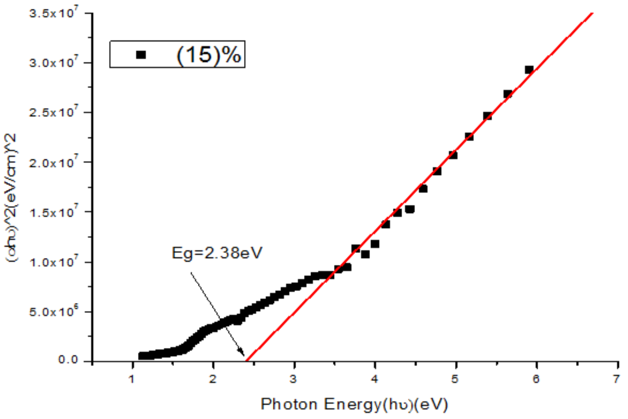

Fig. 11. $(\alpha h\nu)^2$ against photon energy for PVA+ 15w% Cr_2O_3 film

It is observed that the E_g decreased with increasing Cr_2O_3 concentration. May reflect the role of Cr_2O_3in modifying the electronic structure of the PVA matrix due to appearance of various polaronic and defect levels (Omed Gh.Abdullah *et al.*, 2011 and El-Khodary, 2009).The decrease in the optical energy gap with filling may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix (OmedGh.Abdullah *et al.*, 2011).These charge transfer complexes increase the electrical conductivity by providing additional charges, this cause a decrease of the optical energy gap. As the doptant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized state (OmedGh.Abdullah *et al.*, 2011 and Sangawar *et al.*, 2007).

Conclusions

The study of effect concentration Cr_2O_3 on optical properties for PVA doped Cr_2O_3 films has shown that all the optical properties such as transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, and the real and imaginary parts of dielectric constant have been affected by increasing the concentration. The optical energy gap decreased when the concentration of Cr_2O_3 was increased.

REFERENCES

AL-Ramadin, Y. 2000. Optical properties of poly (vinylchloride)/ poly(ethylene oxide) blend. *Optical Materials,* 14:287-290.

Asogwa, P., Ezugwu, S., Ezema, E. 2010. Variation of optical and solid state properties with post deposition annealing in PVA-Capped MnO_2thin films. *Superficies* y 23,18-22.

Baiiato, J. and S. Foulger 2003. "Optical Properties of Perfluorocyclobutyl polymer", *Journal of Optical Society of America* B, 20(9),1838-1843.

Chopra, K. 1969. "Thin films phenomena" Mc Graw-Hill, New York.

Eaga CM., Kandukuri JM., Allenki V., Yamsani MR. 2009. "In-sity gels- a novel approach for ocular drug delivery der Pharmacia letter" *Der Pharm Lett1,* 21,21-33.

EI-Hefian, E.A., M. M. Nasef and A. H. Yahaya, 2010. 'The prepation and characterization of chitosan poly (vinyl alcohol) blended films", *E-Journal of Chemistry* 7 (4),1212-1219.

El-Khodary, A. 2009. "Vibrational, thermal, optical and magnetic investigations of PVA with $FeCI_3$ and $CoCI_2$", *Physica, B*404,1287-1294.

El-Khodary, A. 2010. "Evolution of the optical magnetic and morphological properties of PVA films filled with $CuSO_4$", physica B: Condensed Matter 405(16),4301-4308.

Haidar, A. and G. Simon, 2009. "Effect of kaolin light concentration on optical characteristic of PVA films *"Eng.Teach.Journal*, 27(14) pp2653-2665.

Heavens, O. S. 1973. Thin films physics" Halasted press, Jon Wily and sons,New York.

Khodair, Z.T. *et al.* 2012. *Iraqi Journal of Physics*, Vol 10(14), pp83-89.

Kim SJ., Lee YM., Km Kim, S. 2003. "Synthesis and characteristics of inter pen treating polymer network hydro gels composed of poly vinyl alcohol and poly (N-isopropyl acryl amide". I, *React Funct Polym*, pp61-6755.

Kraus, J.D. 1984. "Electromagnetic", Mc Graw-Hill, New York 3ed.

Mahaboob, M. *et al.* 2012.*Chemical Engineering and Applications*, 1 pp124-133.

Mustafa Abdallh, Osama Hamood and Emad Yousif 2013. Study the optical properties of poly (vinyl alcohol) doped cupper chloride; *Journal of AL-Nahrain University,* Vol.16(1), pp-17-20.

Omed Gh. Abdullah, Bakhtyar K. Aziz. 2011. "Effect of thickness on the optical parameters of NiO prepared by spray pyrolysis technique". *Asian Transactions on Science and Technology,*Vol.1(4), pp-12-15.

Osama. Z. Abed, *et al.* 2013. "Optical and structure properties of MgxZn1-x O. Thin films by pulsed laser". *Diyala Journal for Pure Sciences,* vol9(3),p 44-50.

Osiribilis W. Guirguis, Manal T. H. Moselhey, 2011. "Optical study of poly (vinyl alcohol) /hydroxyl propyl methyl cellulose blends" *J Mater Sci.*,46,5775-5789.

Prosanov, I.Y. Photochemical Formation of Metal Lead in a polymeric Matrix, Far Eastern Transport University, Department of physics.680021, Khabarovsk, Seryshev str.47, Russia.

Rabee, B.H. *European Journal of Scientific Research* ISSN1450-216x57, 4, 2011, p583. *Euro Journals publishing,* Inc.2011.http://www.eurojournals.com/ejsr.htm.

Reddy, V., Zhu, Q., Mail, L., Chen, W. 2006. Optical, electrical and discharge profiles for (PVA+NaIO4) polymer electrolytes. *Journal of Applied Electrochemistry*, 36(9):1051-1056.

Sangawar, V.S., R.J. Dhokne, A. U. Ubale, P.S. Chikhlikar, and S.D. Meshram, 2007. "Structural characterization and thermally stimulated discharge conductivity (TSDC) study in polymer thin films," *Bull. Mater.Sci*., 30 (2),163-166.

Sze, S.M. 1981. "Physics of Semiconductor Devices", Jon Wily and sons, New York. 2 ed .

Tahseen, H. Mubark. 2013. Effect of thickness variation on the optical properties of PVA: $Ni(CH_3COO)_2$ films, Diyala *Journal for Pure Sciences*, Vol 9(3),pp-1-13.

Tauc, J. 1974. Amorphous and Liquid Semiconductor. Plenum Press, London, NewYork.

Vandervorst, P., Lei, C., Lin, Y., Dulton, A., Sun, Y., Keddie, J. 2003. The fine dispersion of functionalized carbon nanotube in acrylic latex coatings. *Pro.Org.Coat.*, 153,163-205.

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