

## Structural and optical properties of thermally evaporated zinc phthalocyanine thin films

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**ABSTRACT.** Thermally evaporated zinc phthalocyanine (ZnPc) films in the as deposited condition were identified to be as-amorphous. It undergoes structural transformation upon annealing up to 613 K. The optical properties and spectral behavior of as deposited and annealed thin films of ZnPc were studied using spectrophotometric measurements of the transmissivity and reflectivity at normal incidence of light in the wavelength range 200-2500 nm. The refractive index,  $n$ , and absorption index,  $k$ , were calculated and it was found that they are independent of film thickness in the thickness range 205-530 nm. Annealing at 613 K increases absorbance of films by 5-6 times in comparison with absorbance of as deposited ones and shifts peak positions of all bands towards low energy side of spectra except the peak position of N-band is shifted towards high energy side of spectra. The absorption spectra in the UV-VIS. region has been analyzed in terms of both molecular orbital and band theories. Indirect allowed transitions near the onset and fundamental absorption edges were observed. The energy at the onset was obtained and equals to 1.45 and 1.51 eV for as deposited and annealed films, respectively. The fundamental energy gap was obtained and equals to 2.94 and 2.88 eV for as deposited and annealed films, respectively. The absorption spectra shows four absorption bands. The oscillator strength,  $f$ , the electric dipole strength,  $q^2$ , the molar extinction coefficient,  $\zeta_{\text{molar}}$ , were calculated for as deposited and annealed ZnPc thin films.

### 1. Introduction

Phthalocyanines, Pcs, are P-type semiconductors characterized by high thermal and chemical stability. Pcs also show interesting photophysical properties and both photo and dark semi-conductivity, which make them particularly interesting for use in more advanced technological applications such as optical recording (Gu *et al.*, 1995), nonlinear optics (Yamashita *et al.*, 1998), light emitting diodes (Blochwitz *et al.*, 1998), basis for the optical sensing (Vukusic & Sambles, 1992), photodynamic therapy (Cubeddu *et al.*, 2001) and as gas sensors (Huo *et al.*, 2000). The application of Pcs in any one of technological devices will certainly be provided as thin films. The optical constants of thin films provide us with information concerning microscopic characteristics of the material and its determination is very important for using it in any one of such devices. (Davidson, 1982) investigated the effect of the central metal atom on the absorption spectra of phthalocyanine films. The

visible and near ultraviolet spectra have been measured for thin films of H<sub>2</sub>Pc, MgPc, FePc, CoPc and ZnPc (Davidson, 1982), other optical properties such as transmissivity and reflectivity of films leading to determination of spectral response of refractive index and absorption index were not investigated. Absorption coefficient,  $\alpha$ , of thin films of free base, copper and zinc phthalocyanines, chlorinated copper phthalocyanine and free base protoporphyrin were reported for photon energies between 0.5 and 11.8 eV (Schechtman, & Spicer, 1970), the data for ZnPc was obtained from a single sample of thickness 530 Å in as deposited condition of unknown structure. There is approximation in calculation of  $\alpha$ , this approximation may have introduced as much as a 25% error into scale of  $\alpha$  for ZnPc (Schechtman, & Spicer, 1970). There is disagreement in literature as to the role of the influence of annealing temperature on absorption spectra of some phthalocyanine derivatives such as FePc (El-Nahass *et al.*, 2001), CuPc (El-Nahass *et al.*, 2001), CoPc (El-Nahass *et al.*, 2003) and MgPc (Krishnakumar & Menon, 1997). There was no significant influence of annealing temperature on absorption coefficient of investigated metal Pcs (El-Nahass *et al.*, 2001, a; El-Nahass *et al.*, 2001, b; El-Nahass *et al.*, 2003). Krishnakumar and Menon (Krishnakumar & Menon, 1997) studied the influence of annealing temperature of 398 K with soaking time of 24 hrs on absorption spectra of MgPc in spectral range 200-1100 nm. Annealing temperature (398 K) shifted the maximum absorption from 365 nm to 333 nm and resulted in considerable broadening of Q and B bands

To our knowledge, there are no enough efforts concerning determination and characterization of optical constants, spectral and structural features of ZnPc. The aim of the present work is to study the influence of some environmental conditions such as film thickness and annealing temperatures on structure formation, spectral behavior and optical constants of thermally evaporated ZnPc thin films, utilizing improvements introduced on methods used in determination of optical constants from the experimental transmissivity,  $T$ , and reflectivity,  $R$ , measurements (Soliman *et al.*, 1988; Laaziz *et al.*, 2000).

## 2. Experimental details

### 2.1. Samples preparation:

Zinc phthalocyanine powder used in the present study was obtained from Kodak, UK. ZnPc thin films of different thickness ranging from 205-530 nm were prepared by conventional thermal evaporation technique using a high vacuum coating unit (Edwards type E306A, England). The pressure during deposition was  $10^{-3}$  Pa. ZnPc thin films were sublimated from quartz crucible heated by tungsten filament onto a clean optical flat fused quartz substrates for optical measurements and onto clean flat glass and KBr substrates for structural investigations. The substrates were kept at room temperature during deposition. The film thickness and rate of deposition were controlled and monitored during deposition by film thickness monitor (model, TM-350 MAXTEK, Inc.). The deposition rate was controlled at 0.5 nm/sec. Thickness was determined accurately after deposition interferometrically (Tolausky, 1970). The structural analysis of ZnPc films with thickness of 530 nm were performed by X-ray diffraction (XRD), infrared spectroscopy (IR) and differential scanning calorimeters (DSC) techniques. Philips X-ray diffraction system (model X'pert Pro) equipped with Cu anode. A filtered Cu  $k_{\alpha}$  radiation ( $\lambda = 1.5418$  Å) was used. The X-ray tube voltage and current were 40 kV and 30 mA, respectively. IR spectroscopy on ZnPc was performed using ATI Mattson (infinity series FTIR) infrared spectrophotometer in the spectral range 4000-400  $\text{cm}^{-1}$ . For this study, 1mg of ZnPc

powder was mixed with 50 mg of vacuum dried IR-grade KBr. The DSC of as deposited and annealed ZnPc thin films collected in powder form has been studied using a (PERKIN-ELMER7 series) thermal analysis system with heating rate 10°C/min. The measurements of transmissivity,  $T(\lambda)$ , and reflectivity,  $R(\lambda)$ , as well as absorbance,  $A(\lambda)$ , were carried out using a double beam spectrophotometer model (Shimadzu, type UV-3101 PC) at normal incidence of light in the wavelength range 200-2500 nm. All the measurements were carried out at room temperature.

## 2.2. Method of calculating optical constants:

The methods (Bennett & Booty, 1966; Nilson, 1968; Abélcs & Théyé, 1966 ; Bennett & Booty, 1967) used for determining optical constants comprise computer software intended to solve equations relating those constants to spectrophotometric measurements of the transmissivity,  $T$ , and reflectivity,  $R$ , at normal incidence of light. These equations allow for coherent multiple reflections inside the thin film and incoherent multiple reflections inside the substrate. In principle,  $n$  and  $k$ , can be obtained from equations of the form (Bringans, 1977)

$$R(\lambda) = f_R(n, k, n_s, \lambda), \quad (1)$$

$$T(\lambda) = f_T(n, k, n_s, \lambda) \quad (2)$$

where  $n$  and  $n_s$  are refractive index of film and substrate, respectively,  $k$  is extinction index and  $\lambda$  is wavelength of incident light. The absolute values of total measured transmissivity,  $T$ , reflectivity,  $R$ , back reflectivity,  $R'$ , after introducing corrections resulting from the absorbency and reflectance of the substrate are given by (Agiev & Shklyarevskii, 1978; Shklyarevskii *et al.*, 1969):

$$T = \frac{I_{ft}}{I_q} (I - R_q) \quad (3)$$

where  $I_{ft}$ ,  $I_q$  are the intensities of light passing through film-substrate system and reference quartz, respectively and  $R_q$  is the reflectance of reference quartz substrate.

$$R(\lambda) = \left( \frac{I_{fr}}{I_m} \right) R_m \quad (4)$$

where  $I_{fr}$ ,  $I_m$  are the intensities of light reflected from the sample and the reference mirror, respectively, and  $R_m$  is the mirror reflectance.

$$R' = \left( \frac{I'_{ft}}{I_m} \right) R_m \quad (5)$$

where  $I'_{ft}$  is the intensity of incident light on substrate only.

The film transmissivity,  $T_f$ , film reflectivity,  $R_f$ , and film back reflection,  $R'_f$  for a system consisting of deposited film onto semi-infinite transparent substrate are expressed as (Laaziz *et al.*, 2000):

$$T_f = \frac{T(1 - R_s R'_f)}{1 - R_s} \quad (6)$$

$$R_f = R - \frac{T_f^2 R_s}{1 - R_s R'_f} \quad (7)$$

$$R'_f = \frac{R' - R_3}{1 - R_3(R' - 2)} \quad (8)$$

where  $R_f$  and  $T_f$  are the reflectivity and transmissivity of the air-film interface in the direction of incident beam,  $T_f R_3$  is the first internal reflection in the substrate-air interface,  $T_f R_3 R'_f$  is the second internal transmittance of film air-interface. Substituting (8) in (6) and (7), simple formulae for calculating film transmittance,  $T_f$ , and film reflectance,  $R_f$ , are obtained as:

$$T_f = T \frac{[(1 + R_q)^2 - 2R_q R']}{1 + R_q(1 - R') + R_q^2(R' - 2)} \quad (9)$$

$$R_f = R - \left( \frac{T_f^2 R_q [1 - R_q(R' - 2)]}{(1 + R_q)^2 - 2R_q R'} \right) \quad (10)$$

To calculate the refractive index,  $n$ , and absorption index,  $k$ , of films, a new modification bidifference search technique of Bennett and Booty (Bennett & Booty, 1966) has been introduced by us. A computer program for the search was used to minimize simultaneously the difference between the calculated and experimental values of both transmissivity and reflectivity as:

$$|T_{cal} - T_{exp}| = 0 \quad (11)$$

$$|R_{cal} - R_{exp}| = 0 \quad (12)$$

where  $T_{exp}$  and  $R_{exp}$  are the experimentally determined values of  $T_f$  and  $R_f$  calculated from (9) and (10), respectively.  $T_{cal}$  and  $R_{cal}$  are the calculated values of T and R using Murmann's exact equations (Heavens, 1964; Liddeli, 1981). The experimental errors were taken into account as follows:  $\pm 2.2\%$  for film thickness measurements,  $\pm 0.1\%$  for  $T_f$  and  $R_f$  calculations,  $\pm 3\%$  for refractive index and  $\pm 2.5\%$  for absorption index measurements (Konstantinov *et al.*, 1998).

The absorption coefficient,  $\alpha$ , is related to the absorption index,  $k$ , as:  $\alpha = \frac{4\pi k}{\lambda}$  and to the molar extinction coefficient,  $\zeta_{molar}(\nu)$  ( $\zeta_{molar}(\nu)$  is the molar extinction coefficient, that is often used to describe the absorption of light by nonsolid molecular media) by the relation (Schechtman, & Spicer, 1970):

$$\alpha = \frac{N}{N_{av}} 10^3 \ln(10) \zeta_{molar} = \frac{\rho}{MW} 10^3 \ln(10) \zeta_{molar} = G \zeta_{molar} \quad (13)$$

where  $N$  is the concentration of the material (molecule per unit volume),  $\rho$  is the material density,  $MW$  is the molecular weight,  $N_{av}$  is the Avogadro's number and  $G$  is a constant that depends on the material.

The oscillator strength,  $f$ , and the electric dipole strength,  $q^2$ , are given by (Kumar, 2000):

$$f = 2.2 \times 10^{-15} \frac{m_e}{e} \frac{MW}{\rho t} \frac{9n_x}{(n_r^2 + 2)^2} \int_0^\infty A(\lambda) d\lambda \quad (14)$$

$$q^2 = \frac{1}{2500} \zeta_{molar}(\nu) \frac{\Delta\lambda}{\lambda_0} = \frac{1}{2500} \zeta_{molar}(\nu) \frac{\nu_0}{\Delta\nu} \quad (15)$$

where,  $\Delta\nu$  is the absorption half band width and  $\nu_0$  is the resonance frequency,  $t$  is the film thickness and  $n_\infty$  is the refractive index at infinite frequency.

The optical energy gap,  $E_g$ , and the type of transition was determined from the analysis of  $\alpha$  near the onset and the fundamental absorption edges using the equation by Davis *et al* ( in Fox, 2001) for amorphous semiconductors as :

$$nah\nu = B(h\nu - E_g \pm \eta_{ph})^x \quad (16)$$

where B is a constant related to electrical conductivity and energy level separation,  $x = 2$  or  $3$  for indirect allowed and forbidden transitions, respectively, and  $x = 1/2$  or  $3/2$  for direct allowed and forbidden transitions, respectively and  $\eta_{ph}$  is phonon energy.

### 3. Results and discussion

The differential scanning calorimetry (DSC) thermograph of as deposited and annealed ZnPc (613 K) thin films collected in powder form is depicted in Fig.1(a, b). Fig.1(a) shows two main endothermic peaks at 365 and 656 K, crystallization of amorphous phase proceeds in between those two peaks. Fig.1(b) indicates that the process is irreversible.

An X-ray diffraction (XRD) pattern derived from as received powder zinc phthalocyanine is depicted in Fig.2(a). The X-ray traces of powder ZnPc were identified to be  $\beta$ -form. The  $\beta$ -form of ZnPc has monoclinic unit cell with parameters  $a=14.567 \text{ \AA}$ ,  $b=4.874 \text{ \AA}$ ,  $c=17.27 \text{ \AA}$ ,  $\beta=106.15^\circ$  and space group  $P2_1/n(14)$  (ICCD card No. 39-1882).

XRD results obtained from films, in as deposited condition, are plotted in Fig.2(b). The films in as deposited condition were identified to be amorphous phase with halo around  $2\theta \approx 25^\circ$  in addition to presence of a peak at  $2\theta = 6.94^\circ$ . Annealing at 573K transforms the as deposited amorphous phase of ZnPc into crystalline  $\beta$ -form. Increasing annealing temperature to 613 K increases volume fraction of  $\beta$ -form as shown in Fig.2 (c and d).

Deposition conditions, processing variables and type of central atom in the molecule of Pc influence the structure of thermally evaporated thin films. Amar (Amar *et al.*, 2002) performed XRD structural study of thermally evaporated metal-free Pc thin films with various film thicknesses. All samples studied have polycrystalline structure and the unit cell was found to be  $\alpha$ - form. Variation of deposition rate from  $0.5\text{-}1 \text{ nms}^{-1}$  had little effect on the structure. El-Nahass (El-Nahass *et al.*, 2003) studied the structure of thermally evaporated CoPc thin films, the as - deposited samples showed amorphous structure in addition to one significant intense peak at  $2\theta=6.92^\circ$ . Scanning electron microscope image of the as-deposited CoPc showed microcrystallites in the amorphous structure. The same phenomenon is also occurring in other metal substituted Pcs (Hassan & Gould, 1992; Resel *et al.*, 2000; Brinkmann *et al.* 1996) and metal-free phthalocyanine (Amar *et al.*, 2002). The presence of significant peak at  $2\theta = 6.94^\circ$  in as-deposited ZnPc thin films suggests the existence of a small proportion of a crystalline polymorph.

The infrared absorption technique may also be used in confirming the existence of polymorphs identified by XRD technique. Fig.3 shows infrared transmission spectra of ZnPc in a powder as well as in thin film forms (as deposited and annealed at 613K). The main spectral features, which distinguish between the different crystalline forms of metal

substituted family (Hassan & Gould, 2000; Soliman, 2003) were found to lie in the region  $800 - 700 \text{ cm}^{-1}$ . The typical behavior in the spectra especially at  $723-726 \text{ cm}^{-1}$  in the three cases indicates a  $\beta$ -form of ZnPc.

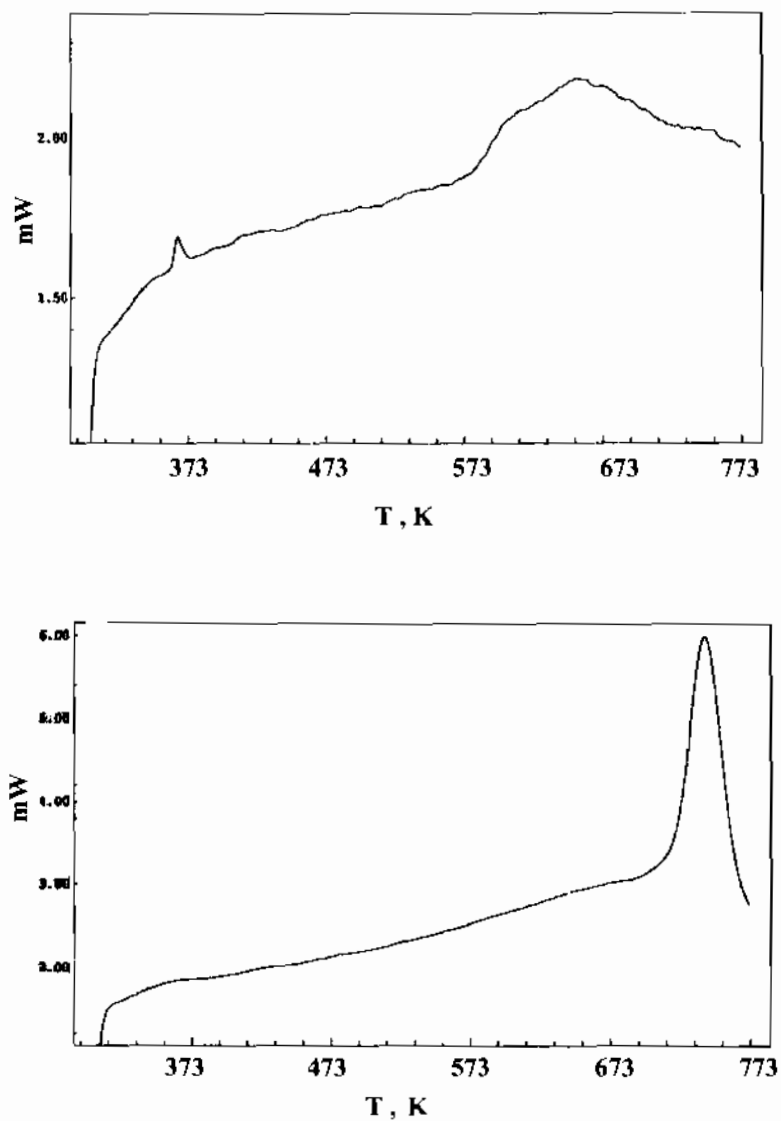


Fig.1. DSC thermograph :(a) for as deposited ZnPc thin films collected in powder form, (b) annealed (613 K) ZnPc thin films collected in powder form.

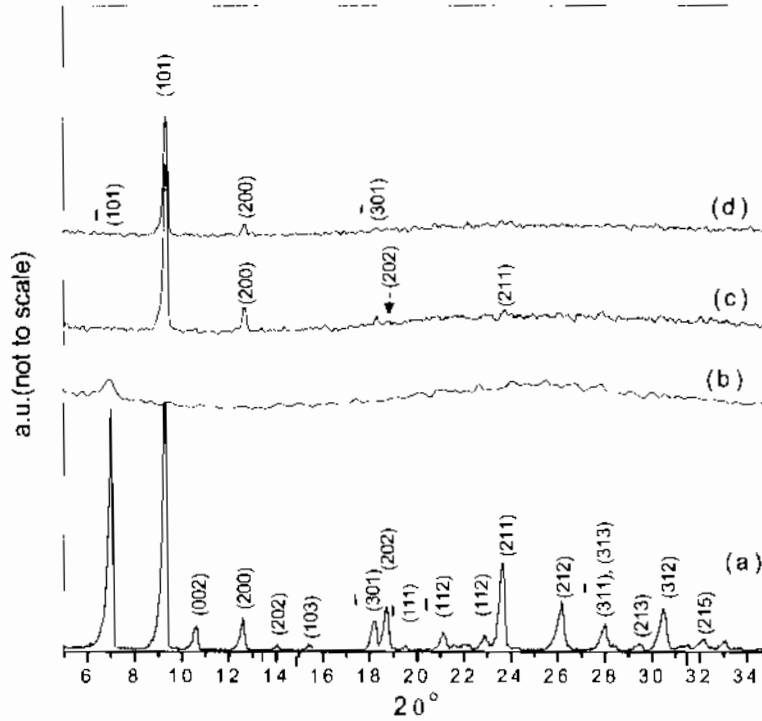


Fig. 2. X-ray diffraction patterns for ZnPc: (a) powder, (b) as deposited thin film, (c) thin film annealed at 573 K and (d) thin film annealed at 613 K.

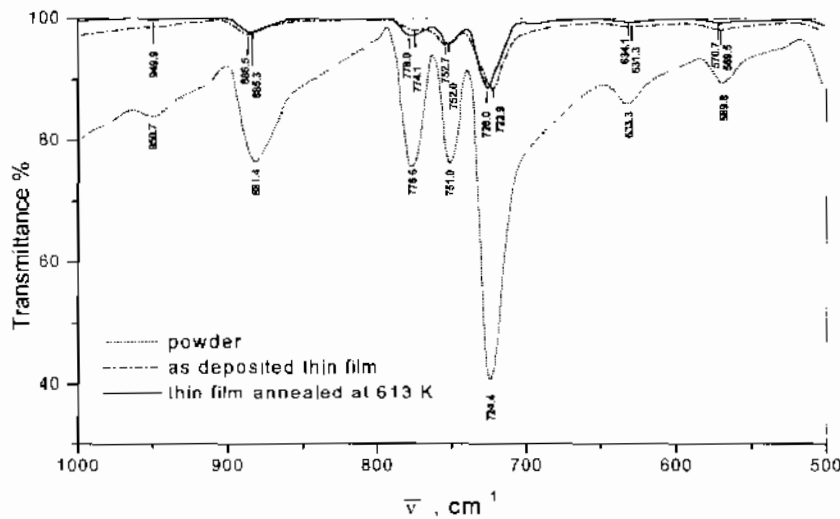


Fig. 3. Infrared transmission spectra of ZnPc: (a) powder form, (b) as deposited film and (c) films annealed 613 K.

The absorbency spectra in the UV-VIS. region of spectra for as deposited and annealed (613 K for 2hrs) ZnPc thin films of different thickness is depicted in Fig. 4(a, b). Inspection of Fig.4(a, b) shows that absorbance of films increases with increasing film thickness without changing peak position. Annealing at 613 K increases the absorbance of films by 5-6 times in comparison with absorbance of films of as deposited condition. In both conditions, four absorption bands take notations Q, B (Soret), N and C (Edwards & Gouterman, 1970). The Q band exists in the visible region of spectra while others (B, N and C) exist in the UV region of spectra. Annealing at 613 K shifts the peak position of all bands towards low energy side of spectra, results in resolving the peak of Soret band into two peaks at energies of 3.4 and 3.68 eV and transforms the shoulder at 4.25 eV of N-band

to a peak at 4.4eV. It is also noted that the bands B, N and C appear with intensities that are comparatively higher than of Q-band.

In the Q-band region, it is noticed from Fig.4(a, b) that the doublets are the only features in absorbance spectra of as deposited and annealed ZnPc films. The higher energy peak of Q-band has been assigned to first  $\pi-\pi^*$  transition on the phthalocyanine macrocycle (Mack & Stillman, 1997). The lower energy peak has been explained as an exciton peak (Laurs & Heiland, 1987).

The Soret band, have a peak at 3.7 eV for as deposited films. The asymmetry in low energy side of Soret band, suggests presence of other peak at 3.51 eV. (Davidson, 1982) observed the same peak (3.51 eV) for ZnPc and for some other members of phthalocyanines family such as  $H_2Pc$  and  $CuPc$ . Annealing at 613 K splits Soret band into two peaks at 3.4 and 3.68eV. The splitting of Soret band is Davydov splitting (Edwards & Gouterman, 1970). The energy separation in the Q and B bands is tabulated in Table 1. The structural information that can be gathered from analysis of shape of Q and B-bands is that molecules of ZnPc are in tilted arrangement.

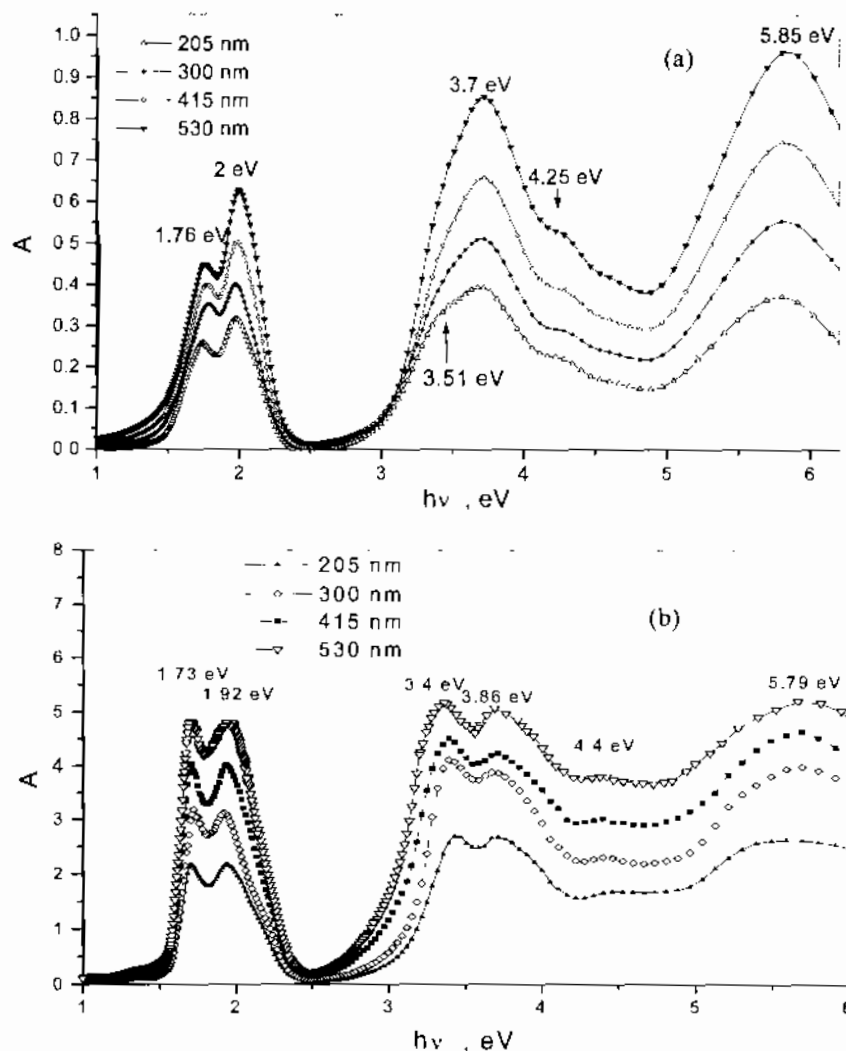


Fig. 4. Spectral behavior of absorbance,  $A$ , (a) for as deposited ZnPc thin films and (b) for annealed ZnPc thin films.



A shoulder at 4.25 and a peak at 4.4 eV in N-band were resolved for as deposited and annealed ZnPc thin films, respectively. The shoulder was also reported near 4.3 eV for other members of phthalocyanine family such as H<sub>2</sub>Pc, ZnPc (Davidson, 1982; Schechtman & Spicer, 1970), FePc (Davidson, 1982; El-Nahass, 2001), CoPc (Nilson, 1986) and NiPc (Edwards & Gouterman, 1970). It is thought that  $\pi \rightarrow d$  transitions are involved in FePc and CoPc and  $d \rightarrow \pi^*$  in NiPc. This is because FePc, CoPc and NiPc have partially occupied d-bands due to existence of Fe, Co and Ni atoms as a central atom in their molecular structures. The shoulder at 4.25eV and the peak at 4.4eV of as deposited and annealed films of ZnPc, respectively, can be attributed to charge transfer from a sp<sub>z</sub> mixing orbital to the  $\pi$  electron system of the macrocyclic ring of the phthalocyanine.

A strong absorption peak is resolved at 5.85 eV in the C-band. Such a peak was reported by (Davidson, 1982) for ZnPc and CuPc and by (Schechtman & Spicer, 1970) for CuPc, H<sub>2</sub>Pc, ZnPc and CuPc-Cl. Annealing shifts this peak towards low energy side of spectra to be at 5.79 eV

The oscillator strength,  $f$ , the electric dipole strength,  $q^2$ , and molar extinction coefficient,  $\zeta_{\text{molar}}$ , corresponding to each peak in absorption spectra are tabulated in Table 2(a, b) for as deposited and annealed films. Annealing at 613 K for 2 hrs increases  $f$ ,  $q^2$  and  $\zeta_{\text{molar}}$  by about one order. The increase in oscillator strength as a result of annealing reflects the increase of extent of interaction between the central Zn ions and Pc ring.

Observations of Figs.5 and 6, show that there is fundamental absorption edge in the wavelength range 380-450 nm. The sharpness of this edge is higher in annealed films than in as deposited ones. At wavelength < 800 nm, the values of transmissivity,  $T_f(\lambda)$ , and reflectivity,  $R_f(\lambda)$ , decreases with increasing film thickness. There are four transmission bands whose sharpness is greater in annealed films than in as deposited ones. The presence of such bands recommends these films as good band pass or as good band stop optical filter material depending on wavelength. At wavelength > 800 nm,  $T_f(\lambda) \gg R_f(\lambda)$  and their total sum is equal to unity, the films are transparent.

Table 1. The peak energy separation (Davydov splitting) in the visible (Q) and Soret (B) bands.

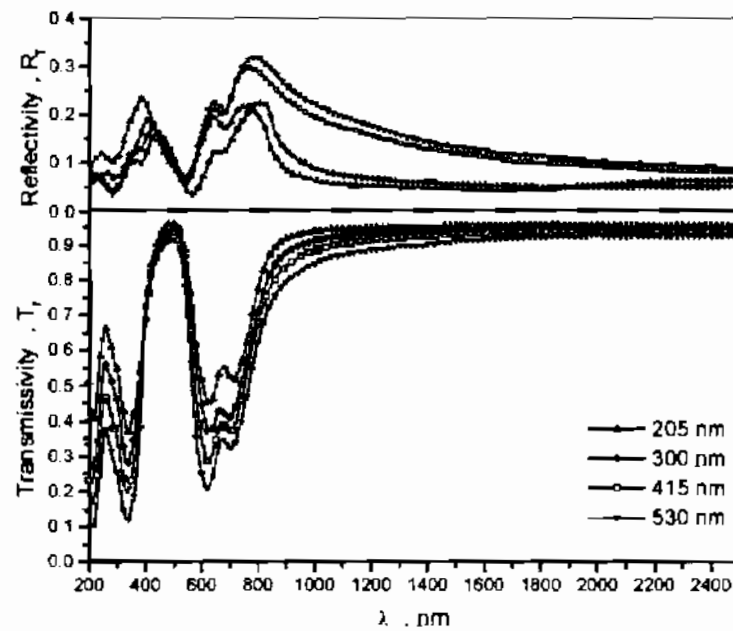
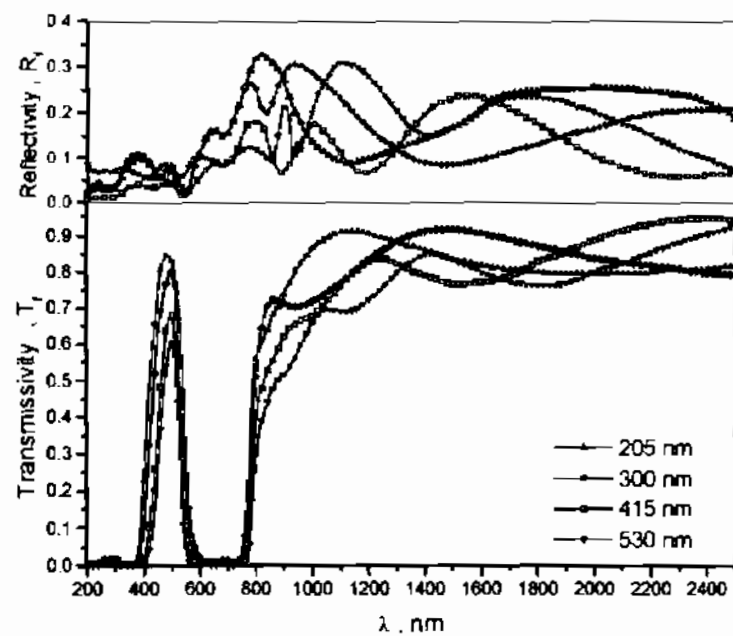
Film condition	$\Delta Q$ , eV	$\Delta B$ , eV
As deposited	0.24	0.19
Annealed	0.19	0.28

Table 2(a). Calculated values of molar extinction coefficient,  $\zeta_{\text{mol}}$ , oscillator strength,  $f$ , and electric dipole strength,  $q^2$ , for as deposited ZnPc thin films

Band	Peak energy, eV	$\zeta_{\text{mol}}$ , Liters.mol <sup>-1</sup> .cm <sup>-1</sup>	$f \times 10^{-1}$ mole <sup>-1</sup>	$q^2$ , Liters.mol <sup>-1</sup> .cm <sup>-1</sup>
Visible	1.76	3538	1.15	7.9
Q	2	4513	1.89	9.48
Soret	3.51	--	--	--
B	3.7	5945	5.87	10.246
Variable -N	4.25	--	1.88	--
C	5.85	5641	1.11	12.4

Table 2(b). Calculated values of molar extinction coefficient,  $\zeta_{mol}$ , oscillator strength,  $f$ , and electric dipole strength,  $q^2$ , for annealed ZnPc thin films.

Band	Peak energy . eV	$\zeta_{mol}$ , Liters.mol <sup>-1</sup> .cm <sup>-1</sup>	$f \times 10^{-2}$ mole <sup>-1</sup>	$q^2$ , Liters.mol <sup>-1</sup> .cm <sup>-1</sup>
Visible	1.73	26565	1.12	86.71
Q	1.92	28931	1.64	50.88
Soret	3.4	35761	2.72	132.9
B	3.68	35008	6.32	110.7
Variable -N	4.4	--	1.21	--
C	5.79	49018	0.32	105.37

Fig. 5. Spectral behavior of transmissivity,  $T_t$ , and reflectivity,  $R_r$ , for as deposited ZnPc thin films.Fig. 6. Spectral behavior of transmissivity,  $T_t$ , and reflectivity,  $R_r$ , for annealed ZnPc thin films.

The calculations of  $n$  and  $k$  were performed for films with different film thickness ranging from 205–530 nm. The results of calculations showed that  $n$  and  $k$  are independent of films thickness for ZnPc, therefore each value of  $n$  and  $k$  depicted in Figs.7 and 8 represents the average value of  $n$  and  $k$  for different thickness at a given wavelength. The dispersion curve depicted in Fig.7 shows normal dispersion at  $\lambda > 1000$  nm, in which a single oscillator model can be applied (El-Nahass & El Den, 2001) while at  $\lambda < 1000$  nm, the anomalous dispersion and the appearance of many peaks in  $k$  spectrum (Fig.8) may be attributed to multioscillator model (Stendal et al., 1996). Two absorption bands are observed in the wavelength range 200–450 nm and other two absorption bands in the wavelength range 550–800 nm. The amplitude of these bands increases upon annealing. The peak in the wavelength range 300–400 nm (Soret band) has been split into two peaks upon annealing.

The spectral distributions of absorption coefficient,  $\alpha$ , for as deposited and annealed ZnPc thin films are shown in Fig.9. Annealing process increases the absorption coefficient of films in comparison with that of as deposited ones. The absorption coefficient curve confirmed the splitting of Soret band and the existence of 3.51 eV peak in spectra of ZnPc films.

To determine the energy gap,  $E_g$ , and the type of interband transitions responsible for optical absorption, a plot of  $(\alpha h\nu)^{1/2}$  versus photon energy (near the absorption edge of the Q and Soret bands) was found to be the best fit for our calculations and is shown in Figs.10 and 11 for as deposited and annealed ZnPc films, respectively. These figures indicate that indirect allowed transitions are occurring in such films. The fundamental energy gap is 2.94 and 2.88 eV for as deposited and annealed films, respectively. The interband transitions at the fundamental edge are accompanied with phonon emission in as deposited and annealed films. The phonon energy is 0.1 and 0.22 eV for as deposited and annealed films, respectively.

The type of electronic transition and energy gap of some substituted metal Pcs are listed in Table 3. It shows that the band gap varies considerably with metal substitution and does not depend on type of crystal structure. This result is in disagreement with that obtained by (Kumar *et al.*, 2000) for rare earth phthalocyanine (RePc) doped borate glasses and metal compound phthalocyanine doped borate glasses. They (Kumar *et al.*, 2000) showed that the band gap have a nearly steady value  $\approx 2.1$  eV throughout the glass samples which pointed out the fact that it is unaltered by the nature of central metal ion of Pc ring. They showed that the type of electronic transition is indirect allowed transition, the result which agrees with ours.

## Conclusions

Crystalline powder of ZnPc transforms to as- amorphous phase in as deposited films. Increasing annealing temperature to 613 K resulted in formation of stable  $\beta$ -form. Increasing film thickness leads to increasing absorbance of ZnPc films without changing peak position. Annealing at 613 K for 2 hrs increases the absorbance of ZnPc films by about 5–6 times in comparison with that of as deposited ones. Four absorption bands are resolved for deposited films. Annealing shifts these bands towards low energy side of spectra, transforms the shoulder into a peak and splits the Soret band. Annealing increases the oscillator strength, electric dipole strength and molar extinction coefficient, noticeably. The transmissivity spectra recommends these films as a good band pass or as a good band

stop optical filter material depending on incident wavelength. The refractive index and absorption index are independent of film thickness. The type of electronic transition responsible for optical absorption is indirect allowed transition. The fundamental and onset energy gap slightly depend on crystal structure of the film. The fundamental energy gap is 2.94 and 2.88 eV for as deposited and annealed films, respectively.

Table 3. Values of energy gap for Pc films with different metal base.

Compound	Film treatment	Resulting structure	$E_g^{ind. allowed}, eV$	$E_g^{dir. allowed}, eV$	Reference
ZnPc	As deposited	As-amorphous	2.94	---	Present work
ZnPc	Annealed at 613 K	$\beta$ -form (monoclinic)	2.88	---	Present work
RePc	Doped borate glass	Not determined	2.1	---	Kumar <i>et al.</i> , (2000)
CIAIPc	Low substrate temperature	Crystalline (monoclinic)	---	3.05	Araghi & Krier, (1997)
CIAIPc	High substrate temperature	Crystalline (triclinic)	---	3.05	Araghi & Krier, (1997)
FePc	annealed	Not determined	---	2.63	El-Nahass <i>et al.</i> , (2001)
CuPc	As deposited + annealed at 473 K	Not determined	---	2.74	El-Nahass <i>et al.</i> , (2001)
MgPc	As deposited	Not determined	---	2.6	Krishnakumar & Menon, (1997)
CuPc	As deposited	Not determined	---	2.71	Ambly & Menon, (1995)
PbPc	Low substrate temperature	Crystalline (monoclinic)	---	2.42	Collins <i>et al.</i> , (1993)
PbPc	High substrate temperature	Crystalline (triclinic)	---	2.42	Collins <i>et al.</i> , (1993)

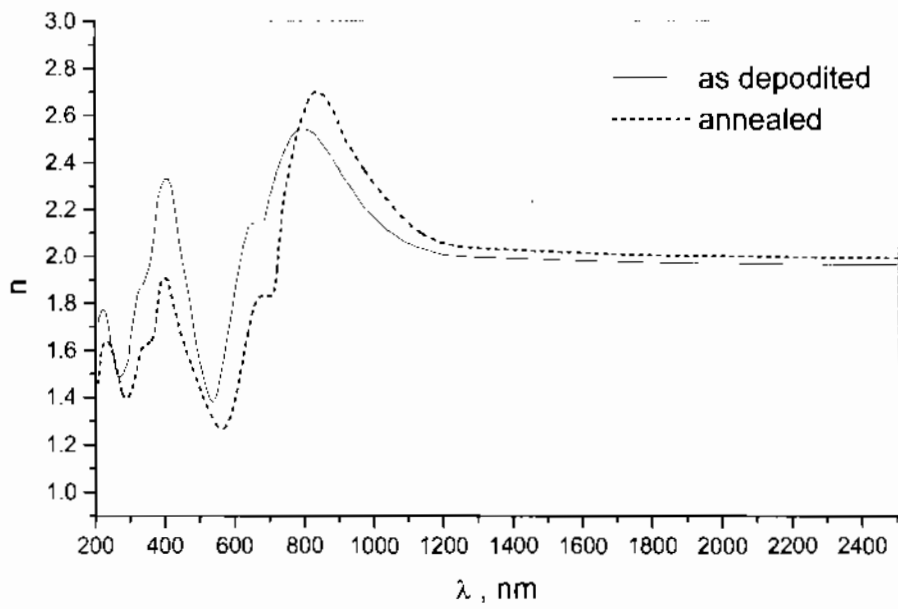


Fig. 7: Spectral behavior of refractive index,  $n$ , for ZnPc thin films.

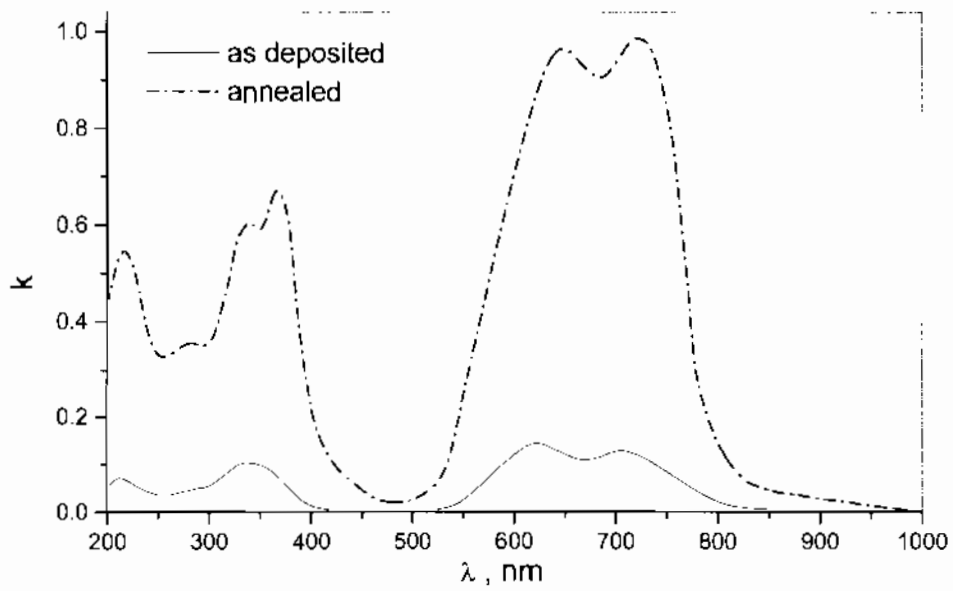


Fig. 8: Spectral behavior of absorption index,  $k$ , for ZnPc thin films.

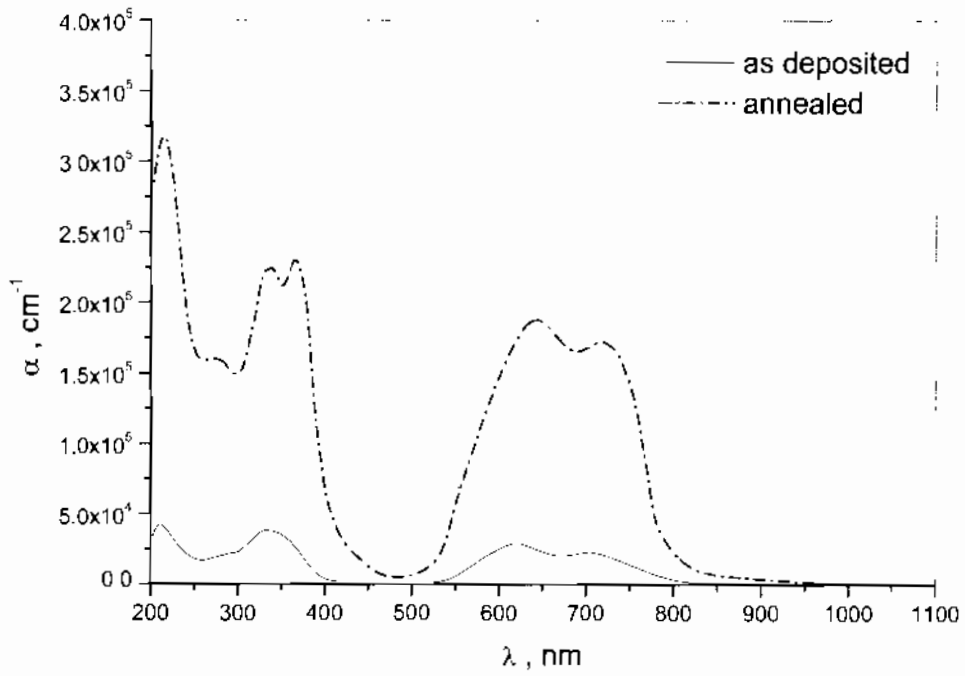


Fig.9: Spectral behavior of absorption coefficient,  $\alpha$ , for ZnPc thin films.

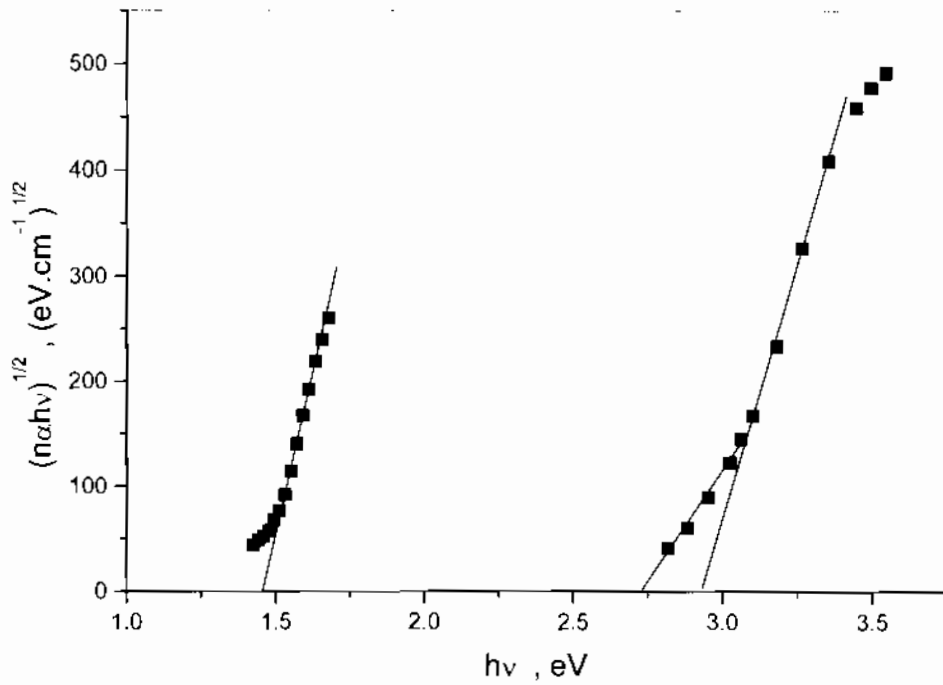


Fig. 10: Plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  for as deposited ZnPc thin films.

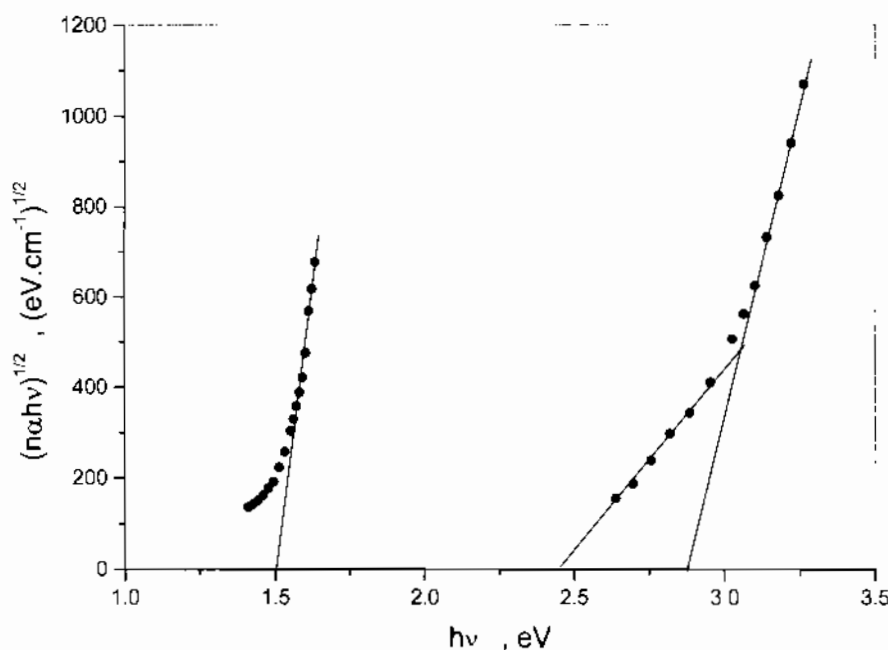


Fig. 11: Plot of  $(\alpha chv)^{1/2}$  versus  $h\nu$  for annealed ZnPc thin films.

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## الخواص التركيبية والضوئية لأغشية زنك فتالوثيانين الرقيقة والمبخرة حراريا

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المستخلص. تم تصنيف أغشية زنك فتالوثيانين المبخرة حراريا على أنها جزئيا أمورفية التركيب، يحدث لها تغيير في التركيب التكويني نتيجة لإجراء عملية التخمير وحتى درجة حرارة ٦١٣ كلفن. تم دراسة الخواص الضوئية والسلوك الطيفي للأغشية من زنك فتالوثيانين باستخدام جهاز المطياف الضوئي وذلك بتعيين النفاذية والانعكاسية للضوء الساقط عموديا عليها وفي المدى الموجي ٢٠٥-٥٣٠ نانومتر. وجد أن معامل الانكسار (n) ومعامل الامتصاص (k) لا يعتمدان على سمك الغشاء وذلك في المدى من سمك الغشاء الذي فحصناه والذي يتراوح بين ٢٠٥-٥٣٠ نانومتر. يزداد امتصاص الأغشية للضوء بمقدار يتراوح من ٥-٦ مرات نتيجة لتخمير الأغشية عند درجة حرارة ٦١٣ كلفن وذلك بمقارنتها بامتصاص الأغشية المبخرة فقط. تزداد عملية التخمير مواقع قمم شرائط الامتصاص تجاه الجانب الأقل في الطاقة من الطيف فيما عدا قمة شريط الطاقة (N) فقد زحزحت تجاه الجانب الأعلى في الطاقة من الطيف. بين تحليل الطيف في مدى الموجات فوق البنفسجية والطيف المرئي مستخدمين نظرية المدارات للجزئيات ونظرية النطاق للجامد الآتي: وجود انتقالات غير مباشرة مسموح بها وبالقرب من حواف التدفق والأساسية، تكون فجوة الطاقة عند حافة التدفق ١,٤٥ و ١,٥١ إلكترون فولت للأغشية المبخرة والمخمرة على الترتيب. تكون فجوة الطاقة عند الحافة الأساسية ٢,٩٤ و ٢,٨٨ إلكترون فولت للأغشية المبخرة والمخمرة على الترتيب. بين طيف الامتصاص وجود أربع شرائط امتصاص. تم حساب الثوابت الطيفية لأغشية زنك فتالوثيانين في الحالة التي رسب عليها وفي حالة إجراء عملية التخمير.

