



# Optical properties of thermally evaporated tin-phthalocyanine dichloride thin films, $\text{SnPcCl}_2$

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Received 17 December 2002; received in revised form 26 September 2003; accepted 20 October 2003

## Abstract

The optical properties of tin-phthalocyanine dichloride thin films have been studied. The films used in the characterisation studies were thermally evaporated. The spectral and optical parameters have been investigated using spectrophotometric measurements of transmittance and reflectance in the wavelength range 200–2100 nm. The absorption spectra recorded in UV–VIS region for the as-deposited and annealed samples showed two absorption bands, namely the Q- and Soret band. No remarkable effect was observed after annealing. A structure with energy separation of magnitude 0.2 eV is seen on the Q- and Soret bands. A transition involving d-electrons of the central metal atom was indicated in the high photon energy region. The dispersion curve of the refractive index showed an anomalous dispersion in the absorption region and a normal one in the transparent region. The band-model theory was applied to determine the optical parameters. The fundamental and the onset of the indirect energy gaps were determined to be 2.79 and 1.51 eV respectively.

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PACS: 78.20.Ci

Keywords: Optical; Phthalocyanine; Thin film

## 1. Introduction

In recent years, organic materials have become increasingly important in the field of optoelectronics due to their various applications. Among these materials, a series of phthalocyanines represent a large family of heterocyclic conjugated

molecules with high chemical stability. Phthalocyanines as a class of organic materials are generally thermally stable and can easily be deposited as thin films with high quality by thermal evaporation without dissociation. Metal phthalocyanines (MPc's) have gained considerable attention in recent years because they have been successfully applied in many applications such as dyes, pigments, photocopying agents [1], gas sensors [2,3], solar cells [4–6] and light emitting diodes [7,8]. Optical absorption studies of MPc's thin films have attracted the researchers over the

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last decade [9–15]. Relatively few studies have focused on the halogenated MPC's although there is evidence that they may exhibit properties suitable for gas sensing applications [16]. It has also been shown that the halogenated Pc's exhibit remarkable morphological and thermal stability over a larger temperature range compared to unhalogenated Pc's [17].

In the present work, the study is aimed at characterizing the optical properties of thermally evaporated tin-phthalocyanine dichloride ( $\text{SnPcCl}_2$ ) thin films onto a quartz substrate. The absorption spectra were measured in the wavelength range 200–900 nm and the optical constants were determined. The fundamental and the onset energy gaps were also estimated.

## 2. Experimental details

A dark blue coloured  $\text{SnPcCl}_2$  powder was obtained from ACROS organic company, USA, with purity of 98.85%. The powder was not further purified by suitable purification methods as the facility was not available. Thin  $\text{SnPcCl}_2$  films of different thicknesses, ranging from 180 to 835 nm, were prepared by thermal evaporation technique using a high vacuum coating unit (Edwards, E306A). The films were deposited onto rectangular optically flat quartz substrates at room temperature (300 K). The quartz substrates were carefully cleaned by putting them in chromic acid for 10 min and then rinsed by deionized water. The material was sublimated from a quartz crucible source heated by a tungsten coil in a vacuum of  $10^{-4}$  Pa during the deposition. The rate of deposition was controlled at  $3.5 \text{ nm s}^{-1}$  by using a quartz crystal thickness monitor (Edwards, Model FTM6). The thickness was also monitored by using the same thickness monitor and subsequently calibrated interferometrically by Tolansky method [18]. A shutter, fixed near to the substrate, was used at the initial and final stages of evaporation to be sure that the films are deposited at the same rate. The shutter could also be useful for obtaining films purer than the powder where it prevents the impurities, which have vapour pres-

ures different from phthalocyanine, from reaching the substrates.

The transmittance,  $T(\lambda)$ , and reflectance,  $R(\lambda)$  spectra of films were measured at normal incidence at room temperature in the spectral range of 200–2500 nm by using a computer-aided double-beam spectrophotometer (Shumadzu 3010 UV-VIS-NIR). An uncertainty of 1% was given by the manufacturer for the measurements obtained by this spectrophotometer. A blank quartz identical substrate to the one used for the thin film deposition was used as a reference for the transmission scan. However, the reflection scan was taken at an incident angle of  $5^\circ$ . The other films were prepared on potassium bromide (KBr) single crystals for IR measurements to identify the crystalline nature and also to check the chemical and thermal stabilities of the material under study.

## 3. Method of calculations

The spectral data obtained directly from the spectrophotometer were transformed to absolute values after corrections of the absorbance and reflectance of the substrate. The absolute values of transmittance and reflectance are given by [19]

$$T = \left[ \frac{I_{ft}}{I_{fq}} \right] (1 - R_q), \quad (1)$$

where  $I_{ft}$  is the intensity of light passing through the film–substrate system and  $R_q$  the reflectance of quartz substrate, and

$$R = \left[ \frac{I_{fr}}{I_{fm}} \right] R_m - T^2 R_q, \quad (2)$$

where  $I_{fm}$  is the intensity of light reflected from the reference mirror,  $I_{fr}$  the intensity of light reflected from the sample reaching the detector and  $R_m$  is the mirror reflectance.

In order to determine the optical constants, refractive index  $n$ , and, absorption index  $k$ , of the absorbing thin film deposited onto a non-absorbing substrate, at least two measured quantities are required. These quantities can be  $T$  and  $R$ , where  $T$  is the transmittance of the film and  $R$  is the reflectance when light is incident normally on the film through air. According to the well known

Murmann's equations [20],  $T$  and  $R$  are functions of the refractive index,  $n$ , the absorption index,  $k$ , the refractive index of air,  $n_o$ , the refractive index of the substrate,  $n_s$ , the film thickness,  $d$ , and the wavelength,  $\lambda$ . These variables are computed for calculations. A modified search method [19] was used to calculate the refractive index ( $n$ ) and absorption index ( $k$ ). In this technique, the absolute values  $T(\lambda)$  and  $R(\lambda)$  were used by a constructed computer program which is based on minimizing  $(\Delta R)^2$  and  $(\Delta T)^2$ , simultaneously, where

$$(\Delta R)^2 = |R_{(n,k)} - R_{\text{exp}}|^2, \quad (3)$$

$$(\Delta T)^2 = |T_{(n,k)} - T_{\text{exp}}|^2, \quad (4)$$

where  $T_{\text{exp}}$  and  $R_{\text{exp}}$  are the experimentally determined values of  $T$  and  $R$  respectively, and  $T_{(n,k)}$  and  $R_{(n,k)}$  are the calculated values of  $T$  and  $R$ , using Murmann's equations. The search in this method is carried out in two operations, the bivariate search operation and step-length optimization operation. In the first one, ranges of  $n_1 \rightarrow n_2$  and  $k_1 \rightarrow k_2$  are entered to calculate  $T_{(n,k)}$  and  $R_{(n,k)}$  throughout the ranges. In each step, the variance  $(\Delta R)^2$  and  $(\Delta T)^2$  are calculated to obtain the minimum variances which converge to unique points and hence gives the optimum values of  $n$  and  $k$  simultaneously.

The second one is developed to speed up convergence i.e. increase the run-time to improve the accuracy. The values  $n$  and  $k$  obtained at the minimum variances are noted as  $n_m$  and  $k_m$ . The values  $[n_m - (n_2 - n_1)/10]$  and  $[k_m - (k_2 - k_1)/10]$  are then compared to specific tolerance values ( $t_n = 0.01$ ) and ( $t_k = 0.001$ ). If these values are smaller than the tolerance values, then  $n = n_m$  and  $k = k_m$  and the program will be ended. If not, the calculation is repeated to obtain the equivalence.

## 4. Result and discussion

### 4.1. Infrared spectral study

The infrared (IR) absorption technique may be used to identify the crystalline nature of MPC thin

film, as the IR spectrum is markedly dependent on the chemical composition, as well as on its crystalline form [21]. PC's are known to have different polyforms that can strongly be identified by IR absorption technique [21,22]. It was also reported that the  $\alpha$ -form of MPC can be characterized by a band around  $720 \text{ cm}^{-1}$ , while  $\beta$ -form can be characterized by a band at a greater wave number ( $\sim 778 \text{ cm}^{-1}$ ) [23]. In our study, we have used IR absorption to identify the phase of the material and to check its chemical and thermal stability after evaporation and after annealing at  $250^\circ\text{C}$  for 3 h.

Fig. 1 shows the infrared absorption spectra of powder, as-deposited film and annealed film. The three spectra are nearly identical reflecting the chemical and thermal stability of the material by either thermal evaporation or annealing at  $250^\circ\text{C}$  for 3 h. This also indicates that they have polycrystalline forms. It is shown that the band which characterizes the  $\alpha$ -form appeared at  $718 \text{ cm}^{-1}$ , while the one which characterizes the  $\beta$ -form appeared at  $773 \text{ cm}^{-1}$  but with much less intensity. This indicates that the material is rich in  $\alpha$ -form. No remarkable change in the bands by annealing the film indicates that the annealing at  $250^\circ\text{C}$  for 3 h is not enough to make the  $\alpha$ -form disappear. Due to the unavailability of the annealing equipment it was not possible to anneal the samples at higher temperatures, and therefore a transition to the higher temperature  $\beta$ -form could not be observed.

### 4.2. Optical properties

The UV and visible spectra for PC's originates from the molecular orbitals within the  $18-\pi$  electrons system and from the overlapping orbitals on the central metal atom [24]. The optical absorption spectra of SnPcCl<sub>2</sub> films with different thicknesses are shown in Fig. 2(a). The direct electronic transitions between orbitals in the energy range 600–800 nm is called Q-band, while an intense band that appeared in the energy range 200–400 nm is called Soret band [13]. It is shown that there is an increase in the absorption peaks with the increase in film thickness. An invariance of the wavelength corresponding to the peaks as a

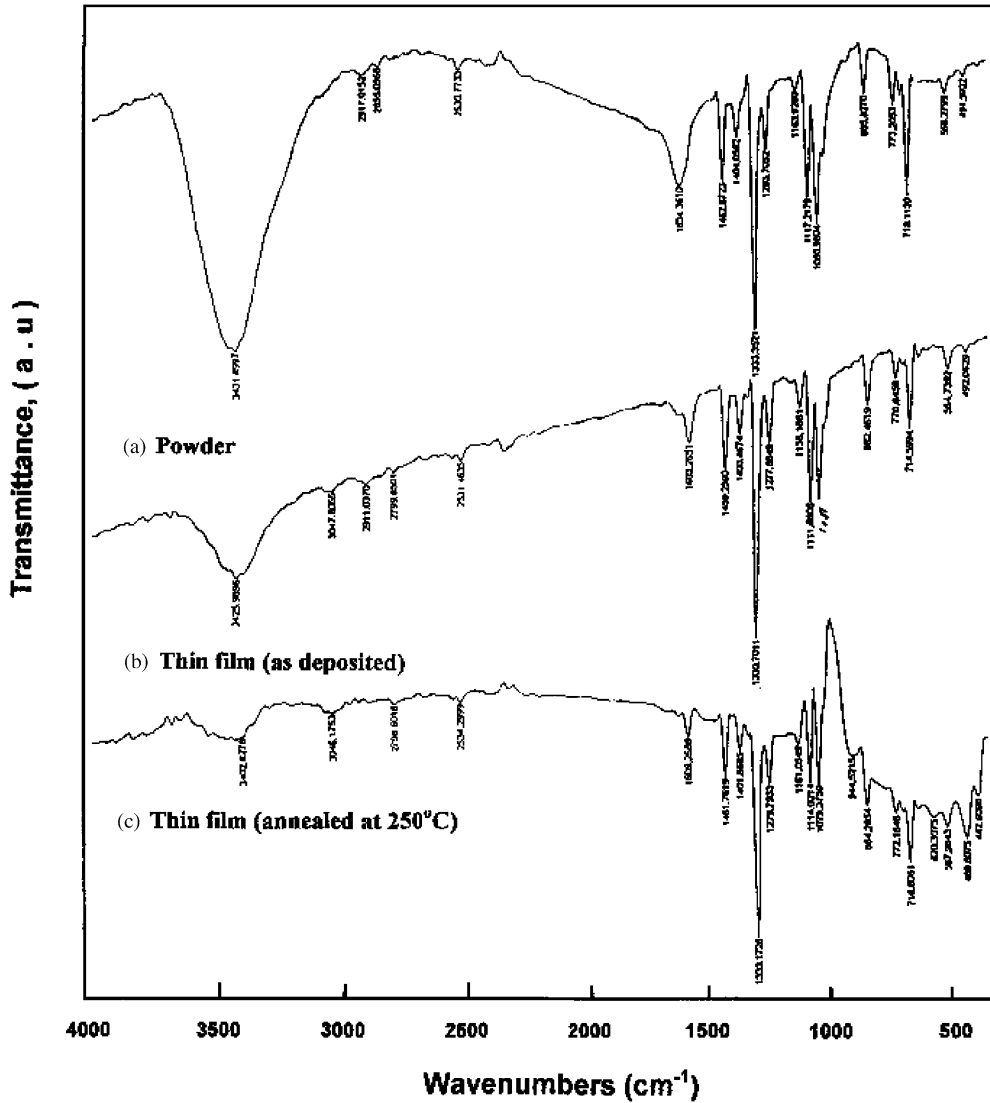


Fig. 1. Infrared spectra of SnPcCl<sub>2</sub> for (a) powder form; (b) thin film, as-deposited and (c) thin films, annealed at 250°C for 3 h.

function of the film thicknesses is also shown. This gives evidence of a unique structure of the films. Fig. 2(b) shows the absorption spectra for the as-deposited sample and for the same one after annealing at 250°C for 3 h in vacuum. The two spectra are nearly identical and a very slight effect was observed after annealing at this temperature.

The spectral distribution of  $T(\lambda)$  and  $R(\lambda)$  measured at normal incidence in the wavelength range of 200–2500 nm for as-deposited films with

different thicknesses ranging from 180 to 835 nm are shown in Fig. 3(a and b). It is quite clear that at a longer wavelength ( $\lambda > 900$  nm), the films become transparent and no light is scattered or absorbed, i.e. non-absorbing region ( $T + R = 1$ ). The inequality  $R + T < 1$  at a shorter wavelength ( $\lambda < 900$  nm) implies the existence of absorption i.e. absorbing region. It is also observed that the intensity of transmittance peaks within the absorption region decreases with an increase in the film thickness.

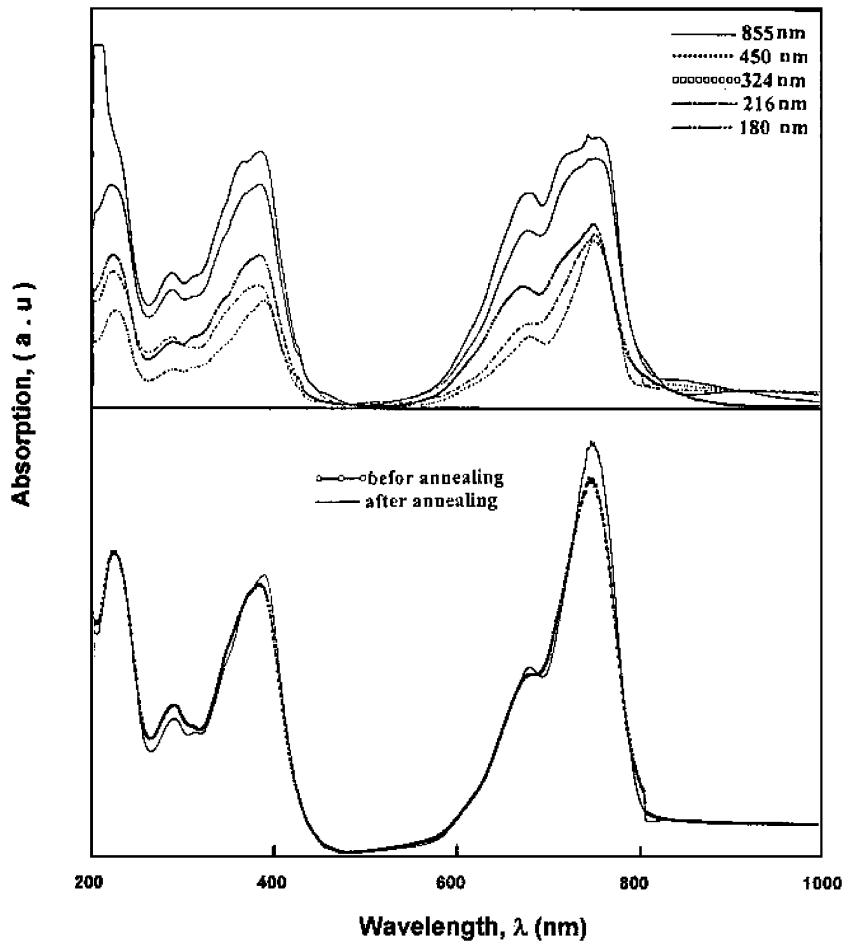


Fig. 2. Optical absorption spectra for (a) SnPcCl<sub>2</sub> thin films with different thicknesses; (b) as-deposited and annealed films.

Calculation of the real and the imaginary parts of complex refractive index from the absolute values of transmittance and reflectance has been performed by taking into account the experimental error in measuring the film thickness of  $\pm 3\%$  and in both  $T$  and  $R \pm 1\%$ . The errors in the calculated values of the refractive index,  $n$ , and absorption index,  $k$ , were estimated to be  $\pm 2.5\%$  and  $\pm 2.3\%$ , respectively. The calculated optical constants were found to be independent of the film thickness in the wavelength range used for measurements and within the estimated experimental errors. The dispersion curve of refractive index  $n(\lambda)$  for SnPcCl<sub>2</sub>, plotted from the mean values of various film thicknesses in the range of 200–2100 nm, is

presented in Fig. 4. It shows an anomalous dispersion in the range from 200 to 800 nm exhibiting various peaks. However, it shows a normal dispersion in the region of wavelength from 800 to 2100 nm, where the refractive index decreases rapidly and then the rate of decrease becomes very low, reaching a nearly constant value at around 2100 nm. The single oscillator model is applied in the region of normal dispersion and the data are used to obtain the oscillator parameters. It was found that the values of the lattice dielectric constant ( $\epsilon_L$ ), dielectric constant at high frequencies ( $\epsilon_\infty$ ), oscillator energy ( $E_o$ ) and dispersion energy ( $E_d$ ) are 4, 3.63, 1.99 and 5.2 eV, respectively.

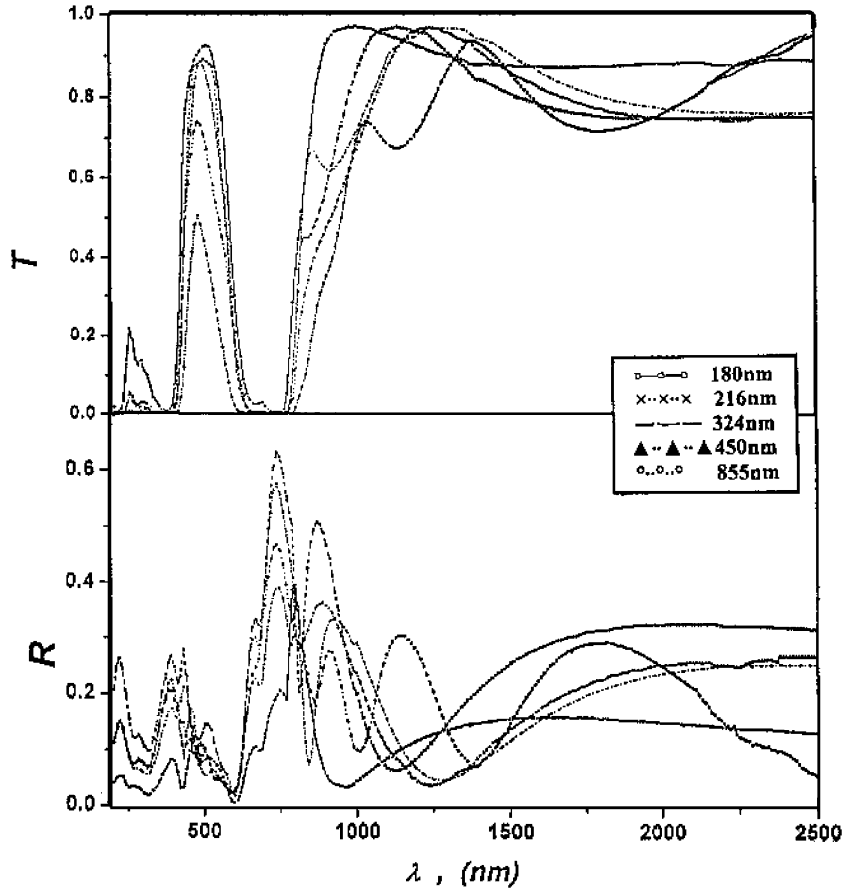


Fig. 3. The spectral distribution of (a)  $T(\lambda)$  and (b)  $R(\lambda)$  for  $\text{SnPcCl}_2$  thin films with different thicknesses.

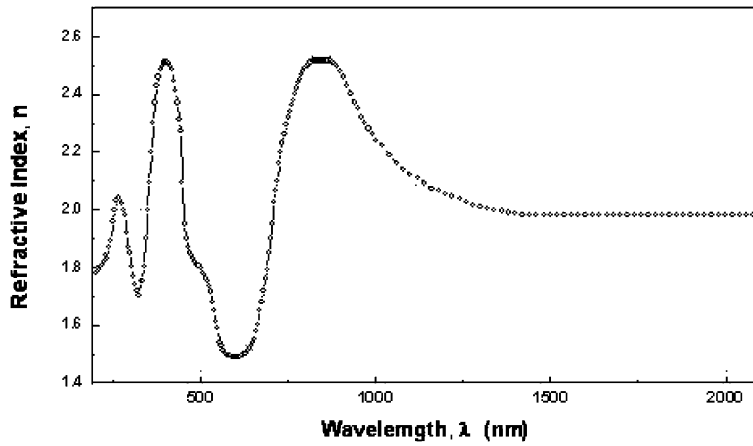


Fig. 4. The dispersion curve of the refractive index  $n(\lambda)$  for  $\text{SnPcCl}_2$  thin films.

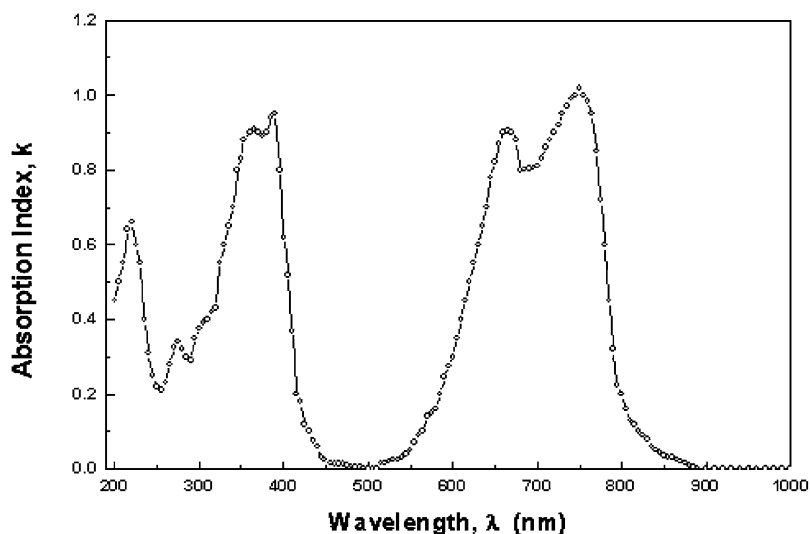


Fig. 5. The spectra distribution of the absorption index  $k(\lambda)$  for SnPcCl<sub>2</sub> thin films.

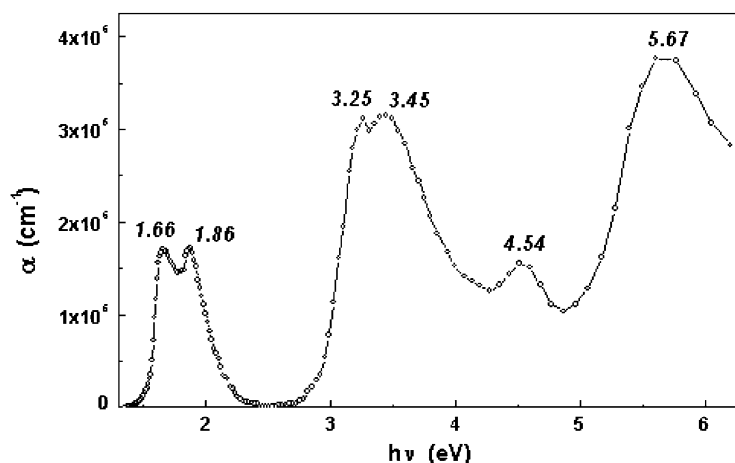


Fig. 6. The spectral behaviour of the absorption coefficient  $\alpha$  for SnPcCl<sub>2</sub> thin films.

Fig. 5 shows the spectral distribution of the absorption index  $k(\lambda)$  for the films. The resolved peaks in this distribution coincide with the peaks obtained by the experimentally measured absorption spectrum. The absorption coefficient was calculated from  $k(\lambda)$  data using the formula ( $\alpha = 4\pi k/\lambda$ ) and its spectral behaviour is presented in Fig. 6. The visible and near ultraviolet transitions in phthalocyanine molecules have generally been interpreted in terms of  $\pi$  to  $\pi^*$  excitation between

bonding and antibonding molecular orbitals. However, calculations on phthalocyanine indicated that  $\pi$ – $\pi^*$  transitions alone cannot account for the observed strong continuum at high photon energies [25].

The high-energy peak of Q-band that appeared at 1.86 eV has been assigned to the first  $\pi$ – $\pi^*$  transitions on the phthalocyanine macrocycle and the low energy peak appeared at 1.66 eV with an energy separation of 0.2 eV [26,27]. This peak has

been explained differently as a second  $\pi$ - $\pi^*$  transition, as an exciton peak [28], as a vibrational interval [29] and as a surface state [30].

Looking next at the Soret band, we find that some structure is present. A doublet peak at 3.25 and 3.45 eV with an energy separation of 0.2 eV, shoulder and peak at the energy range of 4.0–4.7 eV and high-energy strong absorption peak at 5.67 eV. In agreement with the result obtained by Davidson [31], the energy separation in Soret band, which was attributed to a vibrational quantum of the Pc ring, is 0.2 eV and similar to that of the peaks in the visible region. The similarity of structure observed on both the Q-band and the Soret band is taken as a supporting evidence for an explanation of the structure in terms of a molecular vibration [31]. As mentioned previously, the presence of peaks at high photon energy indicates these transitions involving the d-electrons of the central metal.

To obtain information about direct or indirect interband transitions, the fundamental absorption edge data could be analysed within the framework of the one-electron theory of Bardeen et al. [32]. This theory has been successfully applied to analyse the absorption edge of different phthalocyanines [9,10,13]. The absorption ( $\alpha < 10^4 \text{ cm}^{-1}$ ) is related to indirect interband transitions. The variation in absorption coefficient,  $\alpha$ , is related to the photon energy  $h\nu$  for the indirect interband

transition by the relation

$$\alpha = \alpha_0(h\nu - E_g \pm E_{\text{phonon}})^2,$$

where  $\alpha_0$  is a constant,  $E_g$  is the optical energy gap and  $E_{\text{phonon}}$  is phonon energy assisting the indirect transition.

The indirect band gap was determined by plotting  $\alpha^{1/2}$  as a function of photon energy as shown in Fig. 7. The extrapolation of the straight line graphs  $\alpha^{1/2} = 0$  will give the values of the optical band gaps. The values of the fundamental energy gap and onset gap were determined to be 2.79 and 1.51 eV, respectively. Both the fundamental and onset energy gaps were photon assisted with energies of 80 and 65 meV, respectively.

## 5. Conclusions

The optical properties of thermally evaporated SnPcCl<sub>2</sub> thin films have been studied using the spectrophotometric measurements of transmittance and reflectance in the spectral range of 200–2500 nm. The optical constants,  $n$  and  $k$ , were found to be practically independent of the film thickness. IR spectral analysis confirmed that SnPcCl<sub>2</sub> is rich in  $\alpha$ -form and chemically and thermally stable up to 250°C. The absorption spectra showed evidence for the existence of two absorption regions identified as the Q-band and

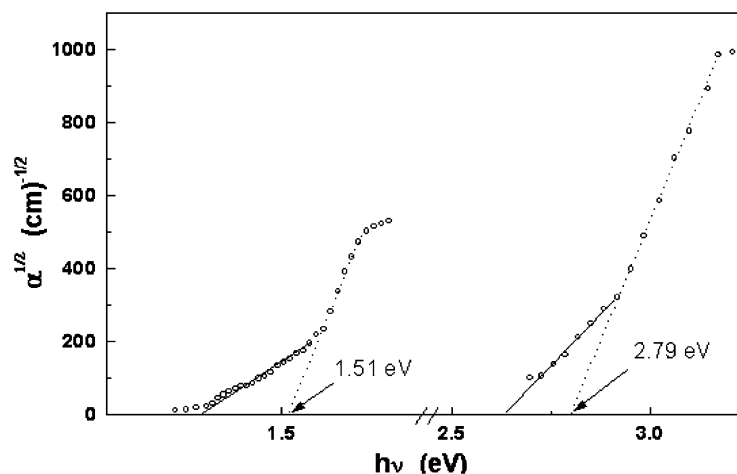


Fig. 7. The photon energy dependence of  $\alpha^{1/2}$  for SnPcCl<sub>2</sub> thin films.



the Soret band. The stability in the peak positions for different thicknesses gave an evidence of a stable structure of the films. The effect of annealing has no significant change in the absorption spectra. The peaks that appeared in visible and near-infrared region are referred to the  $\pi$ - $\pi^*$  transition. The presence of peaks at high photon energy indicates these transitions involving the d-electrons of the central metal. Indirect fundamental and onset energy gaps were estimated to be 2.79 and 1.51 eV, respectively. Both the fundamental and onset energy gaps were photon assisted with energies of 80 and 65 meV, respectively.

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