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STRUCTURAL PROPERTIES AND UV TO NIR ABSORPTION SPECTRA OF METAL-FREE PHTHALOCYANINE (H_2PC) THIN FILMS

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The structural properties and absorption spectra of H_2Pc thin films have been studied. The films used in these studies were thermally evaporated on glass/quartz substrates with thickness ranging from 60 to 460 nm. The XRD studies of H_2Pc thin films showed that the as-deposited films have α-form with monoclinic system. The mean crystallite size (L), the dislocation density (δ) and the strain (ξ) were evaluated. The molecular structure of H_2Pc thin films is confirmed by analysis of (FTIR) spectra. The surface morphology of H_2Pc thin films was examined by scanning electron microscope. The absorption spectra of H_2Pc recorded in the UV – VIS – IR region for the as-deposited and the annealed thin films of different thickness have been analyzed. The spectra showed two absorption bands namely the Q-band and the Soret (B)-band. The Q-band shows its characteristic splitting (Davydove splitting) with $\Delta Q = 0.21$ eV. Values of some important optical parameters, namely optical absorption coefficient (α'), molar extinction coefficient ($\varepsilon_{\mathrm{molar}}$), half-band-width ($\Delta\lambda$), electronic dipole strength (q^2) and oscillator strength (f) were calculated. The fundamental and the onset of the indirect energy gaps were also determined as 2.47 and 1.4 eV, respectively.

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1. Introduction

Phthalocyanine (Pc) compounds have received attention over the last decade, primarily because of their potential as surface-conductivity based gas sensors [1]. Pc's have also the advantages of being very stable against thermal and chemical decomposition and present very intense optical absorption in the visible region. Due to these properties, Pc's have great applications in solar energy conversion. They also have the potential to serve as an active material for molecular electronic devices such as, electrochromic displays [2] and optical data storage [3]. Metal–free phthalocyanine (H_2Pc) has been reported to exist in at least three polymorphic forms (α, β and γ) [4]. The two common polymorphic forms are α and β forms. Assour [5] has presented experimental evidence that α and β forms differ only in particle size. Sidorov and Kotlyar [6] have found that α-form is completely converted to the β-form when heat-treated above 300° C.

In the present work, the structural properties of metal-free phthalocyanine (H_2Pc) were studied. Also, the absorption spectra in the UV – VIS – NIR region have been studied and some of optical parameters have been determined.

2. *Experimental*

The powder of H_2Pc was obtained from Kodak Company, UK. Thin films of H_2Pc of different thickness, ranging from 60 to 460 nm, were prepared by thermal vacuum evaporation technique using coating unit (Edwards, 306A). The films were deposited onto pre-cleaned glass substrates for structure measurements and onto optically flat quartz substrates kept at room temperature for optical measurements. H_2Pc films were vacuum deposited by using quartz crucible source heated by a tungsten coil in a vacuum (10^{-4} Pa) during deposition. The thickness was monitored using the thickness monitors (model FTM4, Edwards Co. England). The thin films were annealed at 350° C for one hour to enable identifying the form transformations within the films.

The structural properties of H_2Pc were investigated using X-ray diffraction (XRD), Fourier transform infrared absorption spectra (FTIR) and electron microscope techniques. XRD measurements were made using filtered CuK_α radiation in a Philips (model X′Pert) diffractometer. Infrared spectroscopy of H_2Pc was performed using Bruker, Vector 22 infrared spectrophotometer in the range from 400 to 2000 cm^{-1}. For this study, 1 mg of H_2Pc powder was mixed with vacuum dried IR-grad KBr and then deposited onto KBr optically flat substrate kept at room temperature. The morphology of H_2Pc thin films was studied using (JEOL JEM-100S electron microscope). Films of H_2Pc have been thermally evaporated onto copper grid coated with a thin layer of carbon. The films were imaged by scanning electron microscope as well as by diffraction electron microscope.

The absorbance spectra (A) of as-deposited films and for one hour annealed films at 350° C of H_2Pc were measured at normal incidence in the spectral range 200 – 800 nm by using double-beam spectrophotometer (JASCO, V-570 UV-VIS-NIR).

3. *Results and discussion*

3.1. *Structural investigation*

3.1.1. **X-Ray diffraction**

X-ray diffraction pattern (XRD) derived from the metal-free phthalocyanine (H_2Pc) in the powder form is shown in Fig. 1. It shows a distinct similarity to those reported

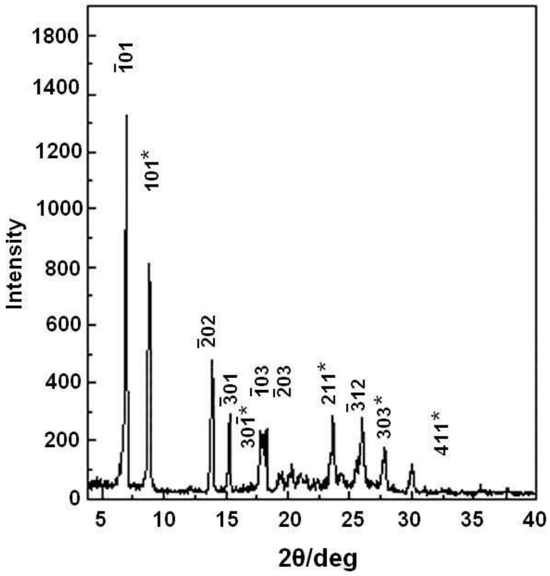

Fig. 1. XRD patterns of H_2Pc in the powder form.

TABLE 1. The calculated values of the lattice parameters.

lattice parameters	a [Å]	b [Å]	c [Å]	β_0
H_2Pc (investigated sample)	17.31	4.72	14.8	104.1
H_2Pc (single crystal) [9]	21.00	4.91	23.1	–

for β-CuPc [7,8]. The powder of H_2Pc was identified as a mixture of α-form and β-form. Lattice spacings, d_{hkl}, were calculated using Bragg's equation and Miller indices. They are compared with the corresponding data given in the Card No. 02-0312 of α-H_2Pc and No. 37-1844 of β-H_2Pc. The calculated lattice parameters are collected in Table 1 which indicate that H_2Pc has a monoclinic unit cell.

XRD patterns of H_2Pc thin films of different thickness ranging from 300 to 460 nm, together with the powder form sample, are shown in Fig. 2. It can be seen that XRD patterns of H_2Pc films show similar characteristics to those of CuPc, CoPc, and H_2Pc films [7,10−12]. All of these samples were identified to be of α-form and had a monoclinic unit cell. Other workers have identified the α-form of metal phthalocyanines as tetragonal or orthorhombic [13]. Shihub and Gould [12] did not succeed to distinguish between the two alternate structures the tetragonal and orthorhombic structures of CoPc films. As observed from the Fig. 2, there is only a single peak around $2\theta = 6.85°$, indicating a preferred orientation of the $(\bar{1}01)$ plane. A similar observation was attained in the structure study of α-form of cobalt phthalocyanine (CoPc) [12] thin films, deposited onto glass substrates held

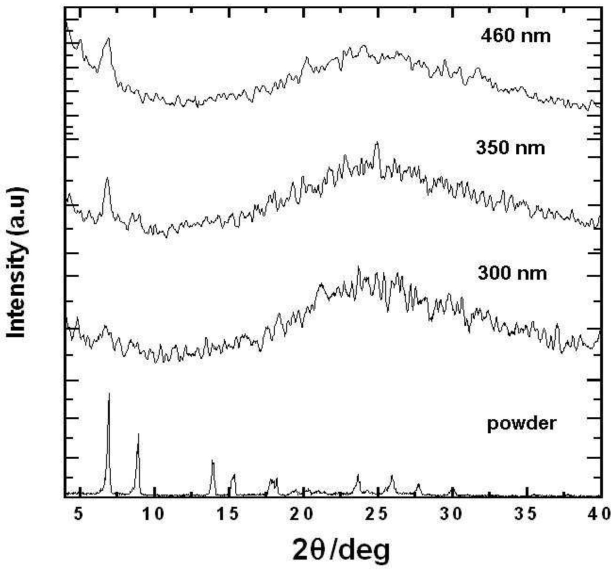

Fig. 2. XRD patterns of H_2Pc in the powder form and as-deposited thin films of different thickness.

at room temperature. A strong preferred orientation was observed, which was in either (001), or the (200) plane, depending on whether the structure is tetragonal or orthorhombic, respectively.

An X-ray structural study as a function of film thickness showed that as the film thickness increases, the intensity of the single peak at $2\theta = 6.85^\circ$ increases. This is in agreement with observations made by Amar et al. [13], although the peaks observed in their work in the range $2\theta = 25^\circ - 30^\circ$ did not appear in the present patterns. This may be attributed to the difference in the thickness of the used samples, which is not so great to affect the film morphology. The increasing value of the intensity of the $(\bar{1}01)$ peak is most probably related to the greater volume of the material, giving rise to the X-ray reflections. Karasek and Decius [10] observed similar behaviour in H_2Pc films.

Figure. 3 shows the XRD patterns of H_2Pc of the powder and of thin film of thickness 460 nm as a representative example for a sample deposited at room temperature and annealed at 350° C for one hour. It can be seen from the figure that the degree of crystallinity increased by the annealing process at 350° C for one hour. Also, there is only one significant peak, its intensity increases with the annealing process, while there is no change in the preferred orientation by annealing, which still with the $(\bar{1}01)$ plane. This result does not agree with that obtained for CoPc thin films [12], where the annealing process made the material undergo form transformation from α-form to the stable β-form. This indicaties that annealing at 350° C for one hour in the present work is not enough to transform the material from α- to β-form. Figure 4 shows XRD patterns of H_2Pc of the powder and the

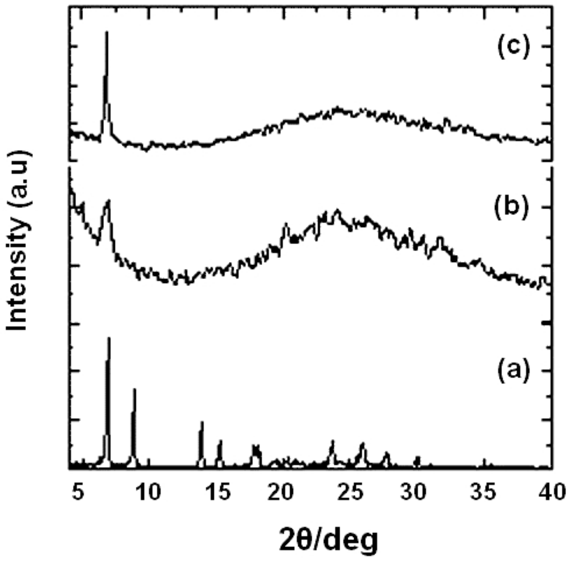

Fig. 3. XRD patterns of the H_2Pc in (a) the powder form, (b) as-deposited thin film of thickness 460 nm *and (c) thin film of thickness 460* nm *annealed at* 350° C *for one hour.*

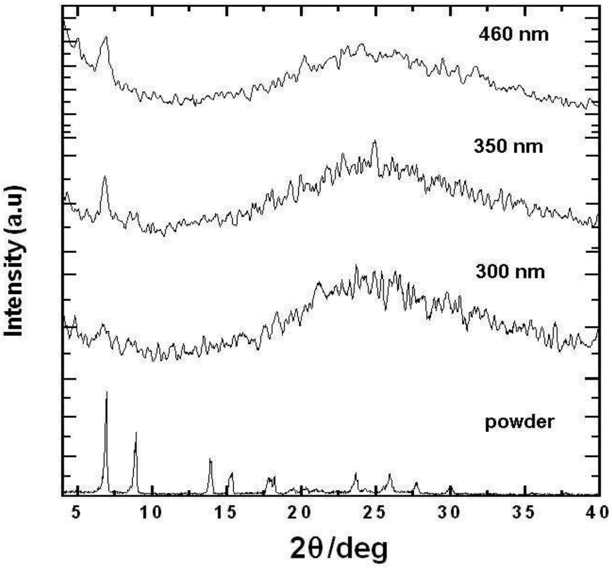

Fig. 4. XRD patterns of H_2Pc in the powder form and thin films after annealing at 350° C *for one hour.*

annealed thin films of different thickness. It is observed from the figure that heat treatment process increases the degree of crystallinity in the H_2Pc thin films of different thickness.

The mean crystallite size (L) of the films is estimated by using the Scherrer's expression [14]

$$L = \frac{K_S \lambda}{\beta' \cos\theta}, \tag{1}$$

where λ is the X-ray wavelength of CuKα (0.15418 nm), $\beta' = \sqrt{\beta_s^2 - \beta_r^2}$ (where β_s is the width of the strong peak at half maximum intensity for the thin film and β_r is the width of the strong peak at half maximum intensity for the powder) [15], and θ is the corresponding Bragg's angle. The Scherrer's constant K_S is of the order of unity, ≈ 0.9 for phthalocyanines [10]. The strain relation is [16]

$$\beta' = \frac{\lambda}{L \cos\theta} - \xi \tan\theta . \tag{2}$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula [17]

$$\delta = \frac{1}{L^2} . \tag{3}$$

Table 2 shows a comparison of the mean crystallite size (L), dislocation density (δ) and strain (ξ) for H_2Pc thin films of different thickness, before and after annealing at 350° C for one hour. The mean crystallite size (L) of H_2Pc thin films has a value ranging from 14.42 nm for thickness 350 nm (as-deposited) to 66.68 nm for thickness 460 nm (annealed). These values lie within the range reported by other workers. Hassan and Gould [7] observed a mean crystallite size value of 28.8 nm for α-CuPc films. Moreover, other authors [14,18−20] have reported the values of crystallite size in the order of 10 to 150 nm for various phthalocyanines. The mean crystallite size, for the films of different thickness, increases after annealing at 350° C for one hour. Similar observations for mean crystallite size were reported [21] for α-CuPc films. The dislocation density (δ) and the strain (ξ) decrease by annealing

TABLE 2. The values of the mean crystallite size (L), dislocation density (δ) and strain (ξ) for H_2Pc thin films of different thickness (before and after annealing at 350° C *for one hour; as-dep. = as-deposited and ann. = annealed).*

d [nm]	L [nm]		$10^{-4} \times \delta$ [nm^{-2}]		$10^{-3} \times \xi$	
	as-dep.	ann.	as-dep.	ann.	as-dep.	ann.
300	–	34.43	–	8.44	–	3.75
350	14.42	38.29	48.09	6.82	8.97	3.36
460	14.89	66.68	45.11	2.25	8.71	1.94

at 350° C for one hour. Since the dislocation density and strain are manifestation of the dislocation network in the films, the decrease in the dislocation density and strain indicates the formation of high-quality films with annealing process.

3.1.2. **Infrared spectra**

Figure 5 shows the IR spectra of the powder, of the as-deposited film and of the annealed H_2Pc film at 350° C for one hour. A comparison between the spectra of H_2Pc powder and thin film forms shows the thermal stability of H_2Pc by obtained thermal evaporation as well as after annealing at 350° C. This indicates that the thermal evaporation technique is a good method for the preparation of H_2Pc thin films. The relevant absorption data along with the possible vibrational modes [22] are presented in Table 3. The powder showed the absorption peak at 713.1 cm^{-1}, which is a characteristic of the α-form, and also the absorption peak at 740.5 cm^{-1}, which is a characteristic of the β-form. The peak around 732.5 cm^{-1} is seen in the as-deposited and in the annealed thin film. The peak at 769.6 cm^{-1}, which is a characteristic of the α-form, appeared in the as-deposited thin film and it is shifted to 771.6 cm^{-1} by the annealing process of the thin film at 350° C for one hour.

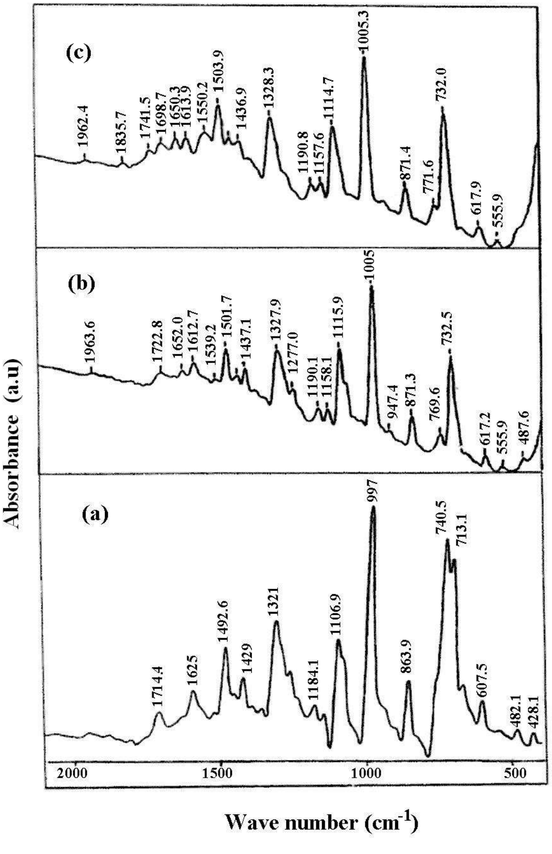

Fig. 5. Infrared spectra of H_2Pc for (a) powder form, (b) as-deposited thin film and (c) thin film annealed at 350° C *for one hour.*

TABLE 3. IR spectral data for the powder, as-deposited and annealed thin film of phthalocyanine (H_2Pc).

Powder	Thin film as-deposited	Thin film after annealing	Assignment
607.5	617.2	617.8	Out-of-plane deformation perphyrin
685.7	683.6	682.7	Out-of-plane deformation phenyl
713.1	–	–	C–H deformation
740.5	732.5	732.0	Out-of-plane bending of C–H bond of phenyl
800.0	769.6	771.6	C–H out-of-plane in prophyrine
863.9	871.3	871.4	C–H out-of-plane in prophyrin
944.4	947.2	947.3	Monosubstituted vinyl
997.0	1005.2	1005.3	Monosubstituted vinyl
1106.9	1115.9	1114.7	C–H bending complex
1150.0	1158.1	1157.8	Stretch in phenyl
1184.1	1190.1	1190.8	C–H bending in phenyl
1257.5	1277.0	–	C-H bending in prophyrin
1321.0	1327.9	1328.3	C–H bending in phenyl
1429.0	1437.1	1436.5	C–H bending in phenyl
1462.5	1464.3	1467	C=C stretch in prophyrin
1492.6	1501.7	1503.9	Stretch in phenyl
1525.0	1539.2	1550.2	N–H bending vibration
1598.7	1612.7	1613.9	C=C stretch in phenyl
1625.0	–	–	CH, CH_2 stretch
–	1652.0	1650.3	C=N stretching vibration
–	–	1698.7	C=N stretching vibration
1714.4	1722.8	–	Stretch in phenyl

This result is in a good agreement with the result obtained by Sharp and Lardon [23]. The peak around 1257.5 – 1277 cm^{-1} appeared in the powder and in the as-deposited thin film of H_2Pc, while the absorption peak at 1625 cm^{-1} appeared only in the powder form. The annealed thin film of H_2Pc showed absorption peaks at 1698.7 cm^{-1} and 1741.3 cm^{-1}, while the absorption peak at 1650 cm^{-1} is seen in the as-deposited thin film and in the annealed film. The powder and annealed film showed absorption peak at 1827.7 – 1835.7 cm^{-1}. The peak at 1539 cm^{-1} is due to the N–H vibration in metal-free phthalocyanine (H_2Pc), as reported by Stymne et al. [24].

Kobayashi et al. [25] found intense bands in the range from 888 to 919 cm^{-1} what appears to be consistent with the metal ligands M–N, for Fe, Co, Ni, Cu, Zn, Pd and Pt series of phthalocyanines. In the present spectrum, the absence of such bands suggest that the sample under test does not contain any metal derivatives of phthalocyanines (M-Pc). The bands in the spectrum at 487.6 and 1227 cm^{-1}

disappeared after annealing the films, indicating that these bands are related to the α-form. The band of small intensity at 1835.7 cm^{-1} appeared after annealing. The other absorption peaks, shown in Table 3, appeared in the powder, in the as-deposited and in the annealed thin films.

From the analysis of the absorption peaks in the IR spectra, the powder of phthalocyanine (H_2Pc) has a mixture of α- and β-forms, as confirmed by X-ray diffraction analysis for the powder of H_2Pc. The thin films are identified as α-form which partially changed to β-form by the annealing process. These results indicate that the annealed thin films are rich in β-form, and to change completely from α-form into β-form one needs more successive sublimations.

3.1.3. **Electron microscope investigations**

Figure 6 shows the scanning electron micrographs (SEM) of thin films of thickness 350 and 460 nm. The figure reveals a granular structure with microcrystallite sizes consistent with the mean crystallite size (L), which was estimated from the half-width of the ($\bar{1}01$) reflection for the same samples shown in Fig. 2. These crystallites shown in Fig. 6 are nearly spherical in nature. Also, Fig. 6 indicates that the degree of cyrstallinity is improved with the increase in film thickness, which is in agreement with results obtained by X-ray analysis.

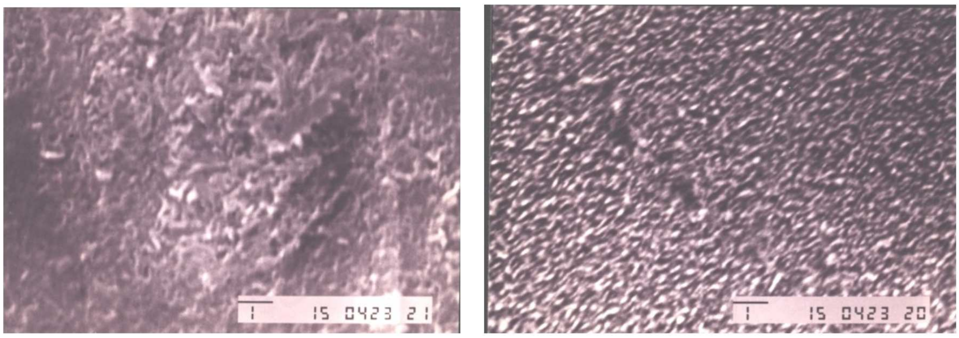

Fig. 6. Scanning electron micrograph of H_2Pc thin films (magnification, $\times 1000$) (a) for a film of 350 nm *(b) for a film 460* nm*.*

To investigate the crystalline state of the H_2Pc films, very thin film of thickness 60 nm, suitable for electron-diffraction study, was prepared. The electron diffraction pattern of the as-deposited film consists of halos (Fig. 7a) confirming the amorphous nature for H_2Pc. For H_2Pc film annealed at 350° C for one hour, the electron diffraction showed that the film is characterized by the appearance of rings (Fig. 7b), indicating that the annealed H_2Pc film has a polycrystalline structure. The analysis of such electron-diffraction pattern is listed in Table 4. The data of electron-diffraction microscope revealed that the annealing process of thin film at 350° C leads to partial transformation of the forms. The rings which have the

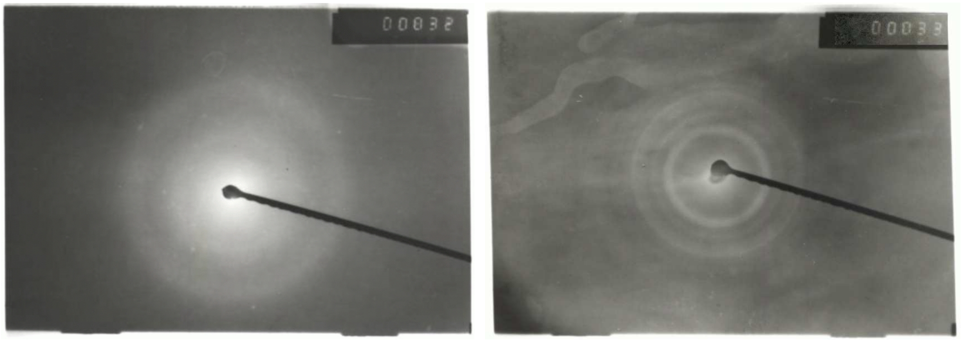

Fig. 7. Electron diffraction pattern of H_2Pc thin film of 60 nm *(a) as-deposited film (b) annealed film at* 350° C *for one hour.*

TABLE 4. Electron diffraction data of H_2Pc films.

hkl	Standard d [Å]	Calculated d [Å]
$\bar{2}02$	6.35	6.40
$\bar{1}03$	4.95	4.98
211	3.76	3.8

reflections ($\bar{2}02$) and ($\bar{1}03$) are related to the α-form, the ring which has the line (211) is related to the β-form.

3.2. Absorption spectra

The UV and visible spectra of phthalocyanines originate from the molecular orbitals within the 18π electron system and from the overlapping orbitals on the central metal atom [26]. The optical absorption spectra of H_2Pc films of different thickness, ranging from 60 to 312 nm (as-deposited and after annealing at 350° C for one hour), are shown in Fig. 8. As seen in this figure, the absorption spectra of the as-deposited and the annealed films are nearly identical, with a very slight difference observed in the region about 500 nm. Also, there is an increase in the absorption peaks with increasing film thickness. Absorption spectra of H_2Pc in Fig. 8 show the existence of two characteristic absorption regions, namely the Q-band and B-band (Soret band). The Q-band lies in the range from 536.2 to 783.2 nm in the visible region and the Soret band lies in the range from 254.2 to 408.5 nm in the UV region.

The absorption bands are due to electronic transitions from the ground state to an excited state. During such a transition in a molecule, electrons are promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Fig. 9a). In a semiconductor bulk solid, the transitions

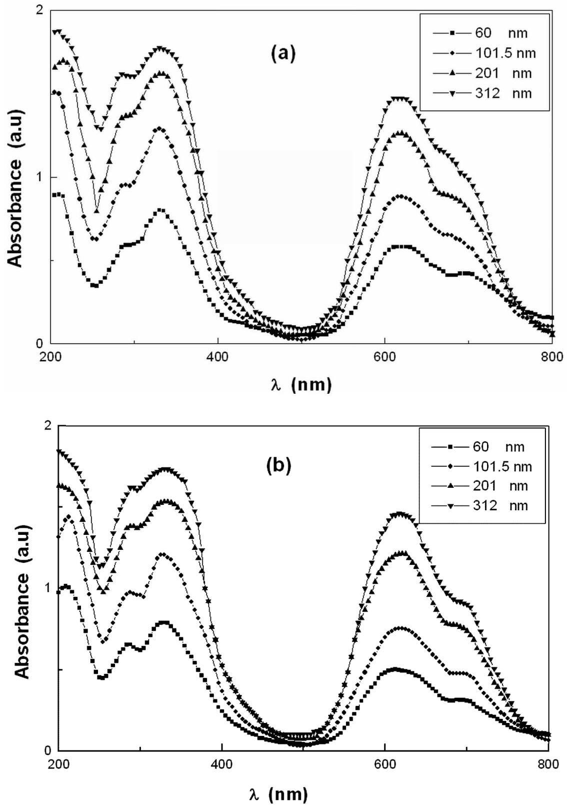

Fig. 8. Optical absorption spectra of H_2Pc for (a) as-deposited thin film and (b) thin film annealed at 350° C for one hour.

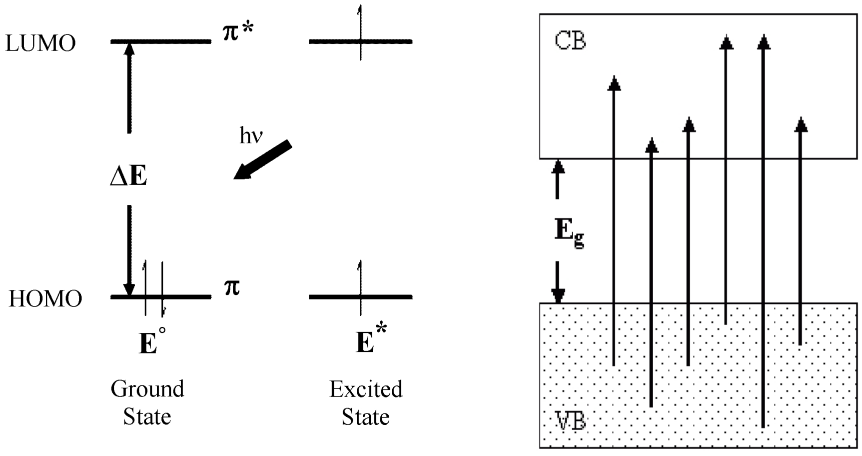

Fig. 9. Energy diagram and electronic transitions in (left) a molecule and (right) a bulk solid.

occur between the valence band (VB) and the conduction band (CB), as shown in Fig. 9b. The VB and CB are the solid state analogue of the HOMO and LUMO of a molecule. E_g is the band gap or difference between the valence and the conduction bands [27].

The optical absorption coefficient (α') of a solid describes the exponential decay of light intensity with the path within solid. It is described using the expression [28]

$$I = I_0 \exp\{-\alpha' d\}\,, \tag{4}$$

where I is the intensity transmitted through the sample at a particular wavelength, I_0 is the incident light intensity at the same wavelength and d is the film thickness.

The absorption of an optical medium can be sometimes quantified in terms of the optical density (OD). This is sometimes called absorbance, and is defined as [29]

$$\text{Absorbance (Abs.)} = OD = \log(1/T_m), \tag{5}$$

where $T_m = I/I_0$ is the transmittance. It is apparent from Eq. (4) that the optical density is directly related to the absorption coefficient (α') through

$$O.D = (\alpha' d/2.303). \tag{6}$$

The variation of the absorption coefficient (α') as a function of the incident energy ($h\nu$) for H_2Pc thin film of thickness 60 nm is shown in Fig. 10. In the visible region, there are two absorption peaks, which show absorption maxima at 1.79 and 2.00 eV in the Q-band. In the next band B (Soret band) in the UV region, the maximum absorption lies at 3.72 eV and a shoulder is seen near 4.31 eV on the high energy side of the Soret peak. These results are in good agreement with those obtained for CoPc, ZnPc and FePc [28].

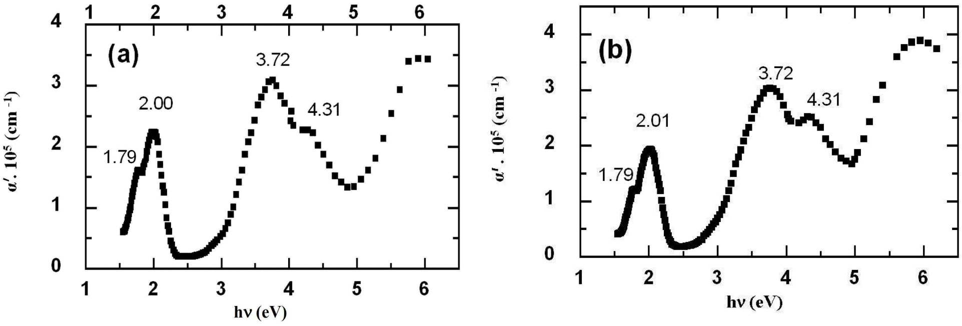

Fig. 10. The absorption coefficient α', for (a) as-deposited H_2Pc thin films and (b) after annealing (thickness 60 nm*).*

Table 5 lists the energies of the absorption maxima present in the spectra. In the H_2Pc film, the Q band consists of a high-energy peak at 2.00 eV and a

TABLE 5. The absorption maximum in (eV) of H_2Pc films as-deposited and annealed at 350° C for one hour.

Compound	Visible(Q)		ΔQ	Soret (B)	Variable (N)
	Q_x	Q_y			
H_2Pc as-deposited	1.79	2.00	0.21	3.72	4.31
H_2Pc annealed	1.79	2.01	0.22	3.72	4.31
Davison [28]	1.79	2.00	0.21	3.33 3.53 3.74	4.29
Schechtman [35]	1.75	2.00	0.25	3.7	4.3

low-energy peak at 1.79 eV, which are labeled by Q_y and Q_x, respectively. The high-energy peak of the Q band has been assigned to the first $\pi - \pi^*$ transition of Pc macrocycle [30–32]. The low energy peak of the Q band has been variously explained as a second $\pi - \pi^*$ transition [33] and as a vibrational interval [34]. The difference between Q_y and Q_x is defined as the Davydov splitting (ΔQ) which equal 0.21 eV in the present spectrum. The annealing process has no marked effect on the energy values for the different bands.

It is useful to relate the absorption coefficient (α') to the molar extinction coefficient ($\varepsilon_{\mathrm{molar}}$), corresponding to the transition at frequency (ν), which is used to describe the absorption of light by nonsolid molecular media [35,36]. If the solid has a concentration of N' molecules per unit volume, the absorption coefficient (α') and the molar extinction coefficient ($\varepsilon_{\mathrm{molar}}$), they are related by the expression [35]

$$\alpha' = \frac{N'}{N_{\mathrm{Avo}}} \times 10^3 \ln(10)\, \varepsilon_{\mathrm{molar}} = \frac{\rho}{M} \times 10^3 \ln(10)\, \varepsilon_{\mathrm{molar}} = \mathrm{const}\, \varepsilon_{\mathrm{molar}} \,. \qquad (7)$$

Here N_{Avo} is the Avogadro's number, M is the molecular weight of H_2Pc, ρ its density and $\varepsilon_{\mathrm{molar}}$ is in units of liters per mole-cm. The important spectral parameters are namely: the absorption coefficient (α'), the oscillator strength (f), the electric dipole strength (q^2) and the absorption half-band-width ($\Delta\lambda$). These optical parameters for the thickness of 60 nm of H_2Pc, as-deposited and after annealing, are evaluated using the expressions [37]

$$f = 4.32 \times 10^{-9} \int \varepsilon_{\mathrm{molar}}(\nu) \mathrm{d}\nu, \qquad (8)$$

$$q^2 = \frac{1}{2500} \varepsilon_{\mathrm{molar}} (\Delta\lambda/\lambda). \qquad (9)$$

The calculated parameters are collected in Table 6. A comparison of these results shows that all parameters vary in the band regions, and have slight change by annealing process.

TABLE 6. The spectral parameters of H_2Pc film of thickness 60 nm (a) as-deposited, (b) annealed at 350° C *for one hour.*

Band		$\Delta\lambda$ [nm]	$10^5 \times \alpha'$ [cm^{-1}]	$10^5 \times \varepsilon_{\mathrm{molar}}$ [mol^{-1} l cm^{-1}]	q^2 [$Å^2$]	f
N	a	81.03	2.42	0.37	4.18	1.79
	b	89.87	2.51	0.386	4.82	1.66
B	a	81.2	3.14	0.48	4.71	2.27
	b	123.77	3.05	0.467	6.95	1.88
Q_y	a	141.9	2.24	0.34	3.14	0.47
	b	127.78	1.89	0.291	2.41	0.42
Q_x	a	113.04	1.62	0.25	1.62	0.28
	b	86.28	1.21	0.186	0.93	0.22

3.3. Determination of the energy gap

To obtain information about the direct and indirect interband transitions, the fundamental absorption edge data could be analyzed within the framework of one-electron theory of Bardeen et al. [38]. This theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine derivatives [39].

The variation in absorption coefficient (α') with photon energy for band to band transitions is obtained as

$$\alpha' = \alpha_0 (h\nu - E)^r, \tag{10}$$

where E is the energy gap and r determines the type of transition. The value of r can be 1/2 or 2 for allowed direct and allowed indirect optical transition, or 3/2 and 3 in the case of forbidden direct and indirect optical transition, respectively. The dependence of the absorption coefficient (α') on photon energy ($h\nu$) was plotted for different values of r. The best fit was obtained for $r = 2$. This is the characteristic behaviour of allowed indirect transitions which is in good agreement with the result obtained by Kumar et al. [36] for rare earth (RePc) phthalocyanine doped borate glasses. Figure 11 shows the functional dependence of $(\alpha' h\nu)^{1/2}$ on $h\nu$ for the film (of thickness equal 60 nm) as-deposited and after annealing. The energy gap at the fundamental intense band was found to be 2.47 eV for both H_2Pc thin films before and after annealing, respectively. This gap can be interpreted as a maximum in the refractive index, because the extinction at that photon energy is quite small [40]. The other energy gap (onset) was found to be 1.4 and 1.41 eV for H_2Pc before and after annealing the thin film, respectively. The values of energy gap and phonon energies for the film as-deposited and after annealing are listed in Table 7.

As observed from the table, the band gap of the as-deposited H_2Pc film does not change remarkably after annealing.

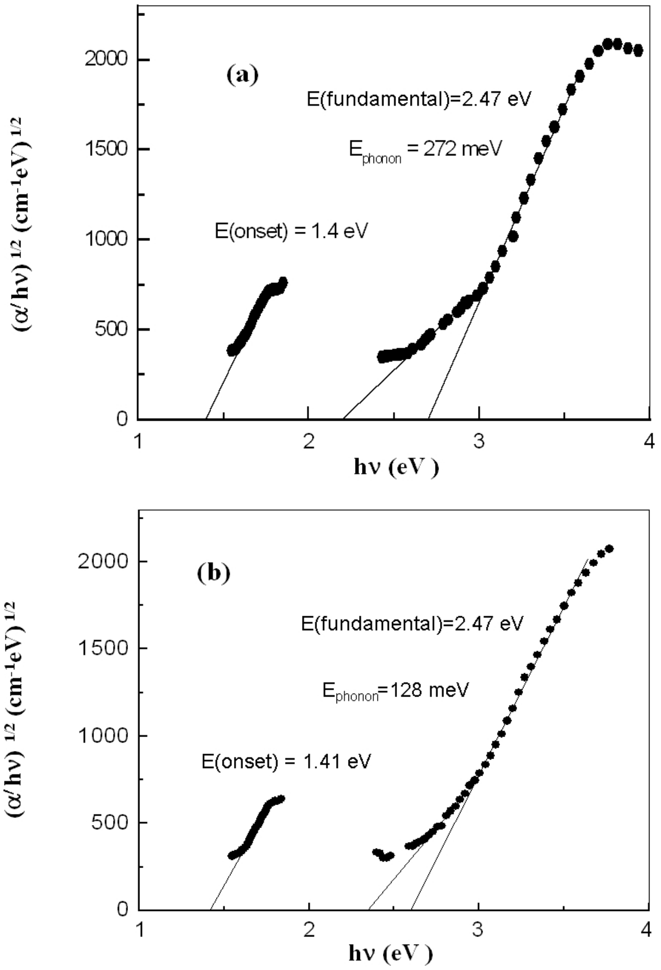

Fig. 11. The variation of absorption coefficient with incident photon energy (a) as-deposited thin film, (b) thin film annealed at 350° C for one hour.

TABLE 7. The values of energy gap.

	Fundamental energy gap		Onset energy gap
	E_f [eV]	E_{phonon} [eV]	E_0 [eV]
H_2Pc (as-deposited)	2.47	272	1.4
H_2Pc (annealed)	2.47	128	1.41
H_2Pc (single crystal) [41]	–	–	1.4

4. *Conclusions*

X-ray diffraction patterns of the H_2Pc show that the powder of H_2Pc is a mixture of the α- and β-form with monoclinic system. Films of different thickness show a X-ray diffraction peak that implies a preferential orientation in the $(\bar{1}01)$ direction with structure of the monoclinic α-form. The crystallite size increases with annealing and the dislocation density and the strain decrease with annealing. The FTIR spectra show characteristic peaks of H_2Pc. The analysis of IR spectra confirmed that H_2Pc thin film is rich in the α-form. The SEM data show that the degree of crystallinity improved with increasing film thickness. The absorption spectra showed two distinct bands, the Soret B-band and the Q-band, with the characteristic splitting to Q_x and Q_y (referred to the $\pi - \pi^*$ transition). Some of the important spectral parameters, namely the optical absorption coefficient (α'), the molar extinction coefficient ($\varepsilon_{\mathrm{molar}}$), the half-band-width ($\Delta\lambda$), the electronic dipole strength (q^2) and the oscillator strength (f) have been evaluated. The indirect fundamental and the onset energy gaps were determined to be 2.47 and 1.4 eV, respectively. The results show a small effect of annealing on the optical parameters.

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STRUKTURNA SVOJSTVA I UV – NIR APSORPCIJSKI SPEKTRI BEZMETALNIH TANKIH SLOJEVA FTALOCIJANINA

Proučavali smo strukturna svojstva i apsorpcijske spektre tankih slojeva H_2Pc. Te tanke slojeve, debljine 60 do 460 nm, naparavali smo na staklene i kremene ploče. Proučavanje rendgenograma je pokazalo da su neobrađeni tanki slojevi monokliničke α-strukture. Odredili smo srednju veličinu kristalita (L), gustoću dislokacija (δ) i naprezanje (ξ). Potvrdili smo molekulsku strukturu tankih slojeva H_2Pc analizama FTIR spektara. Površine slojeva ispitivali smo pretražnim elektronskim mikroskopom. Analizirali smo apsorpcijske spektre neobrađenih i opuštenih tankih slojeva različite debljine u UV – VIS – IR području. Ti spektri pokazuju dvije apsorpcijske vrpce, Q-vrpcu i Soretovu B-vrpcu. Q-vrpca pokazuje svoju značajku (Davydovog) cijepanja sa $\Delta Q = 0.21$ eV. Izveli smo vrijednosti važnih optičkih parametara: optičkog apsorpcijskog koeficijenta (α'), molarnog koeficijenta gašenja ($\varepsilon_{\mathrm{molar}}$), poluširine pojasa ($\Delta\lambda$), elektronskih dipolnih jakosti (q^2) i oscilatornih jakosti (f). Odredili smo osnovne energijske procijepe i početke neizravnih energijskih procijepa od 2.47 odnosno 1.4 eV.