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Linear and Non-Linear Optical Properties for Organic Semiconductor (CuPc) Thin Films

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Abstract

Thin films of Copper Phthalocyanine CuPc of various thicknesses (150, 300 and 450) nm have been deposited using pulsed laser deposition technique using Q – Switched Nd:YAG laser pulse at 1.64 µm wavelength, 6 Hz frequency, 9 ns width, and 240 mJ energy at room temperature. The study showed that the spectra of the optical absorption of the thin films of the CuPc are two bands of absorption one in the visible region at about 635 nm, referred to as Q-band, and the second in ultra-violet region where B-band is located at 330 nm. CuPc thin films were found to have direct band gap with values around (1.81 and 3.14) eV respectively. The vibrational studies were carried out using Fourier transform infrared spectroscopy (FT-IR). Finally, From open and closed aperture Z-scan data non-linear absorption coefficient and non-linear refractive index have been calculated respectively using He-Ne laser which have beam waist of (24.2 µm), wave-length of (632.8 nm) and Rayleigh thickness was 2.9 mm.

Key words

Copper Phthalocyanine, thin film, PLD, optical properties and non-linear properties.

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الخصائص البصرية الخطية وغير الخطية للأغشية الرقيقة من أشباه الموصلات العضوية (CuPc)

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الخلاصة

تم ترسيب أغشية رقيقة من CuPc بأسماك مختلفة (150، 300، 450) نانومتر باستخدام تقنية الترسيب بالليزر النبضي في درجة حرارة الغرفة. أظهرت الدراسة أن أطياف الامتصاص البصري للأغشية الرقيقة لـ CuPc تحتوي على منطقتين للامتصاص، أحدهما في المنطقة المرئية عند حوالي 635 نانومتر، يشار إليه بـ Q-band، والثاني في منطقة الأشعة فوق البنفسجية يدعى ب B-band عند 330 نانومتر. وفجوة الطاقة للأغشية الرقيقة من CuPc ذات فجوة نطاق مباشرة بقيم حوالي (1.81 و 3.14) eV على التوالي. أجريت الدراسات الاهتزازية باستخدام مطيافية الأشعة تحت الحمراء لتحويل فورييه (FT-IR). - أخيرا من خلال تقنية z-scan تم حساب معامل الامتصاص اللاخطي ومعامل الانكسار اللاخطي على التوالي باستخدام ليزر He-Ne الذي يبلغ محيط شعاعه (24.2 مايكرومتر) وطول الموجة (632.8 نانومتر) وكانت سماكة رايلي 2.9 مم.

Introduction

In recent years, significant research efforts have been devoted to the characterization and fabrication of various organic semiconductor thin films. The mineral phthalocyanine is one of the most important organic compounds that can be applied in electro-optic devices, photoconduction agents [1], photovoltaic cell elements [2], nonlinear optics [3], electro catalysis [4], and other photo-electronic devices [4]. Many researchers have studied various metal-substituted Phthalocyanine [5-9]. Among the metal substituted phthalocyanine is copper II phthalocyanine (Cu-Pc) which was found to have superior properties [10]. Copper-phthalocyanine (Cu-Pc) is an organic semiconductor [11]. They are thermally and chemically highly stable [12]; most of them can synthesised easily from ordered thin films. In addition to that, large non-linear optic response for copper Phthalocyanine, which arises from its 2-D conjugated π electron system, lends CuPc as a possibility in an expected that metal Phthalocyanine MPc can be causing strong reverse saturable absorption RSA behaviors [13]. Throughout this work of investigation, the Z-Scan method was used for measuring both non-linear coefficients of absorption β and the index of the non-linear material refraction n_2. The method has been shown by Sheik Bahae et al. [14]. The research explores the spectral and nonlinear characterization setup of thin films of different thicknesses (150,300 and 450 nm) of CuPc.

Experimental work

1-Sample preparation

The blue pigment powder supplied by Sigma – Aldrich of 99% purity, molecular formula of $C_{32}H_{16}N_8Cu$ was used in this work as the source material of different thickness (150,300 and 450) nm films obtained by Q – Switched Nd: YAG laser pulsed laser deposition (PLD) technique under vacuum mode with 10^{-3} torr on glass substrate at room temperature. It can be control the thickness of the film by the number of pulses. Slides were cleaned using detergent to remove dust on the surface and rub it gently for 10 minutes. The slides were placed in a clean flask containing distilled water. Treatment was replaced by a solution of distilled water with a pure alcohol solution and the slides were cleaned with smooth paper. The substrate was placed 3 cm from the CuPc target. The diameter of the CuPc target billet is 10 mm and 2 mm thickness and weight of 0.25 g with 6 tons pressure.

2- Z-Scan measurement

Nonlinear optical (NLO) characteristics of CuPc was investigated with the utilization of the Z-scan method for determining non-linear coefficient of absorption (β) and the non-linear refractive index (n_2) [14]. He–Ne laser (4.80 mW) of wavelength at 632.80nm and beam diameter of 2.50 mm was utilized as a source. The beam was focused utilizing positive lens of (f =150) mm at the focus point of the sample. Pinhole used to locate the laser has a diameter (1 mm). In addition, the laser beam intensity I_0 was 2261685 mW/cm^2. The sample was moved along the Z-axis. The transmittance through the sample was recorded as a function of its location. The beam waist (w_0) was measured at focus point to be equal to 24.20µm and the Rayleigh Z_0 was (2.9 mm) according to the equation below [14]:

$$\boldsymbol{Z_0 = \frac{\pi w_0{}^2}{\lambda}} \qquad \textbf{(1)}$$

The representation of the Z-Scan set-up has been depicted in Fig.1.

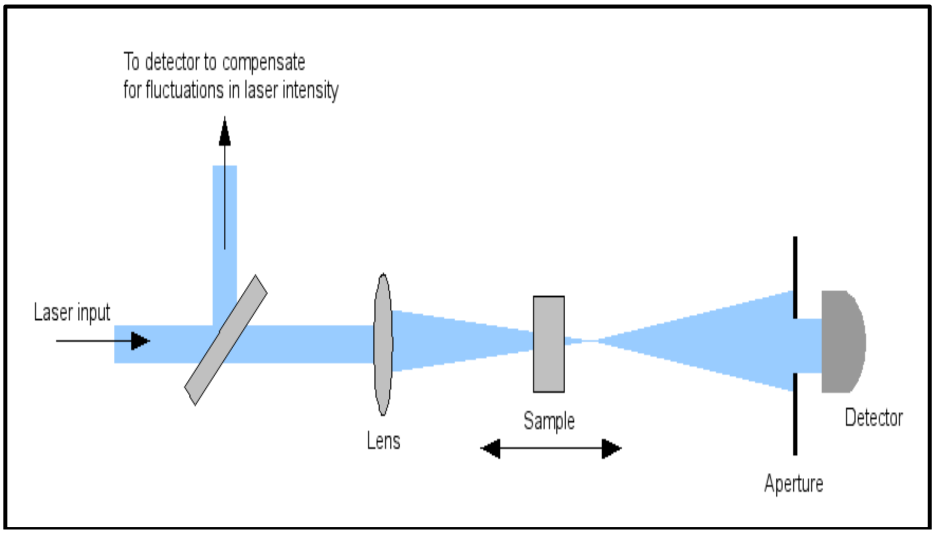


Fig.1: Device of the Z-scan approach [14].

Results and discussion

1 Optical properties

1-1 Absorption and measurements

Fig.2 exhibits the UV-Vis. absorbance spectrum of the prepared CuPc films of different thickness (150, 300 and 450) nm, asssesed utilizing double beam (SHIMADZU UV-1800) UV spectrophotometer, is plotted as a function of the wavelength in the 300 – 1100 nm range. From this spectrum, it can be noted that two bands were obtained. The first one is in the UV phase, and named the B-band (Soret) at 330 nm, while the other is in the visible region, 605 – 670 nm wavelength range, namely the Q band. This indicates that the range of the spectrum is from π to π* orbital's transition. A flat area was found in the phase at 390 – 530 nm region. The band became prominent with the increasing thickness obeying Beer – Lambert law. This result is in good agreement with that of N. Touka et al. [15]. Table 1 shows the values of maximum absorption peaks for CuPc thin films with various thicknesses.

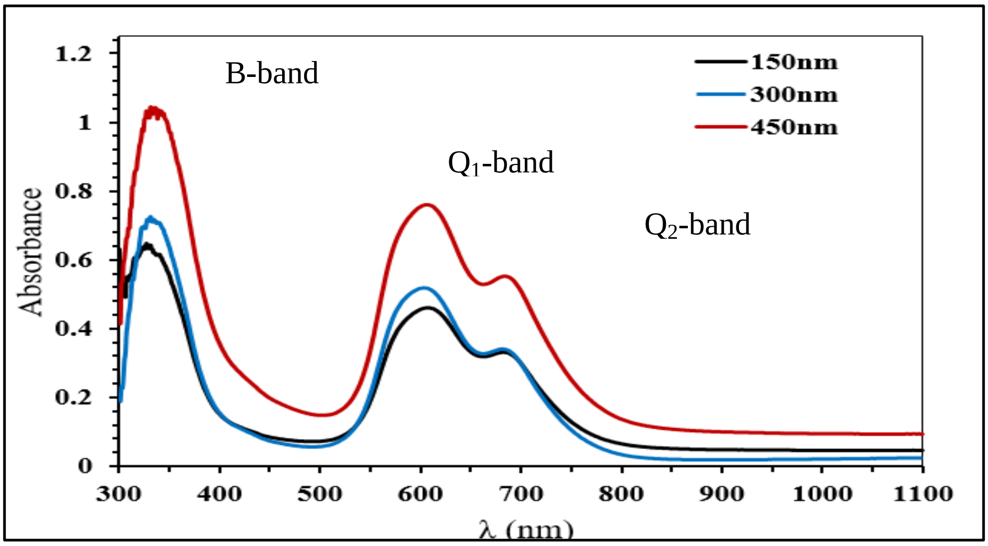


Fig.2: Absorbance as function of wavelength regarding CuPc thin films having various thicknesses at room temperature.

Table 1: Values of maximum absorption peaks for CuPc thin films with various thicknesses.

Thickness (nm)	**B band**	**Q-band**	
	peak position (nm)	**Q_1 peak position (nm)**	**Q_2 peak position (nm)**
150	333	617	694
300	343	618	695
450	346	619	695

1.2 The transmission spectrum

The transmission spectra for CuPc thin films deposited through the technique of PLD at various thickness were indicated in Fig.3. It may be indicated that all films are transparent and no scattering and absorbance of light occur at long wavelengths (λ more than 900) nm. While at short wavelengths (λ less than 900) nm, the presence of absorption can be seen. The figure illustrates that the maximum transmission value is at the range (400-550) nm and small transmission variations have been seen with thin film thickness variation in the same range. The transmittance decreases strongly when thin film thickness increases for both B and Q band.

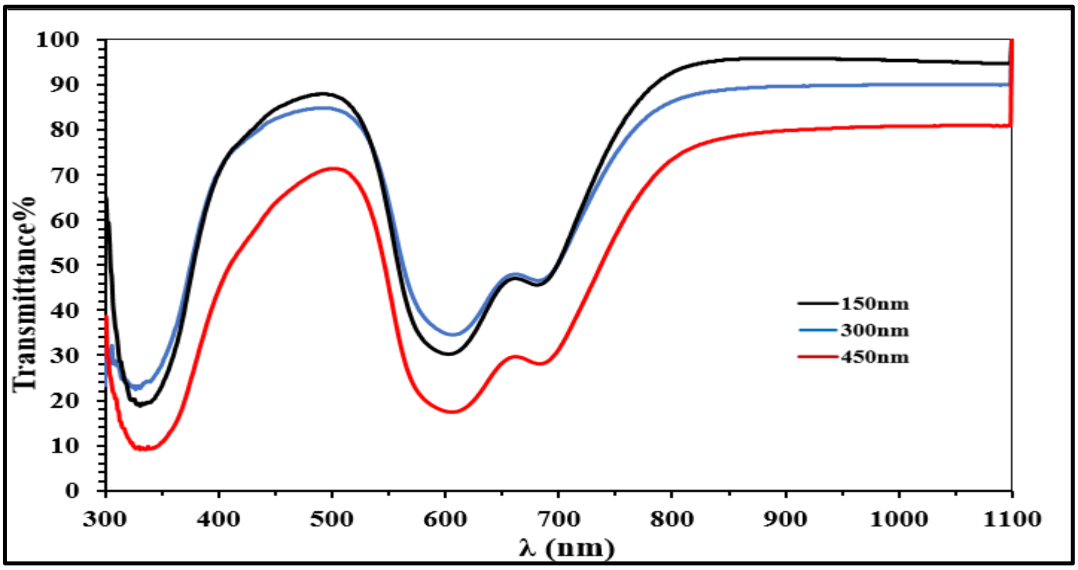


Fig.3: Transmission spectra for CuPc thin films that are prepared through the technique of PLD at different thickness.

1.3 The reflectance spectrum

The reflectance spectra for different thickness regarding the thin films of CuPc deposited via PLD technique are shown in Fig.4. It simply shows maximum variation in Q and B bands and minimum variation in wavelength range (400-580) nm. The reflectance spectra are increasing with increasing thickness for both B and Q bands.

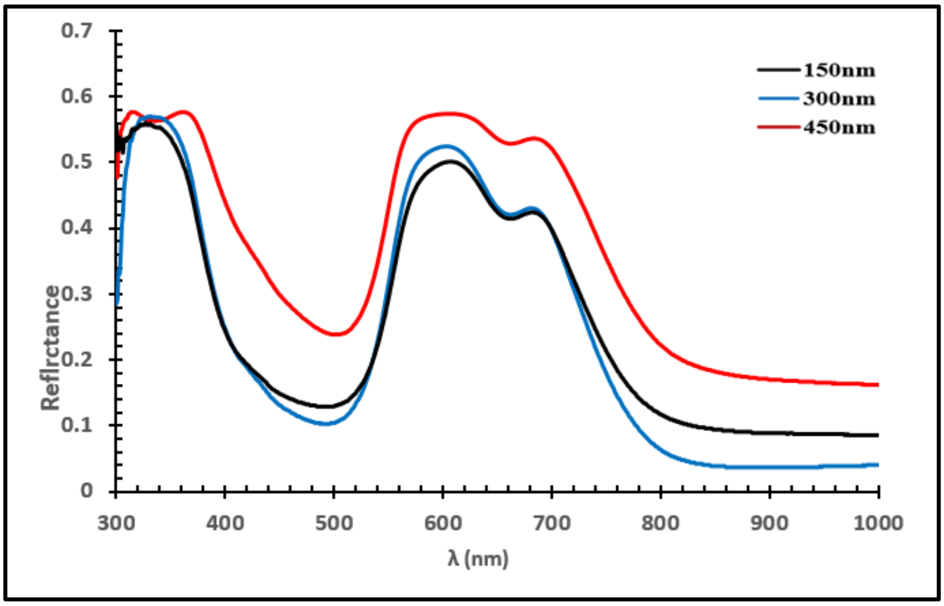


Fig.4: Reflectance spectra for thin films of CuPc prepared via PLD technique at different thickness.

1.4 The absorption coefficient

This measure depends on wavelength for the deposited CuPc films having different thicknesses substrate; as shown in Fig.5, this figure demonstrates that the CuPc thin films absorption coefficient is featured through strong absorptions in Q and B bands at wavelength region that is between (600 and 661)nm for Q band and between (318 and 375) nm for the B with a sharp edge on the long side of wavelength from (690 to 800) nm for Q band and from (350 to 375) nm for the B band. With regard to Q and B bands, high α values (α more than $10^4\ cm^{-1}$) are shown via absorption coefficient, indicating that there were larger probabilities regarding allowed direct transitions and after that there was a decrease in α as the wavelength is increased. Furthermore, there is a decrease in absorption coefficient as the thickness thin films of CuPc are increased.

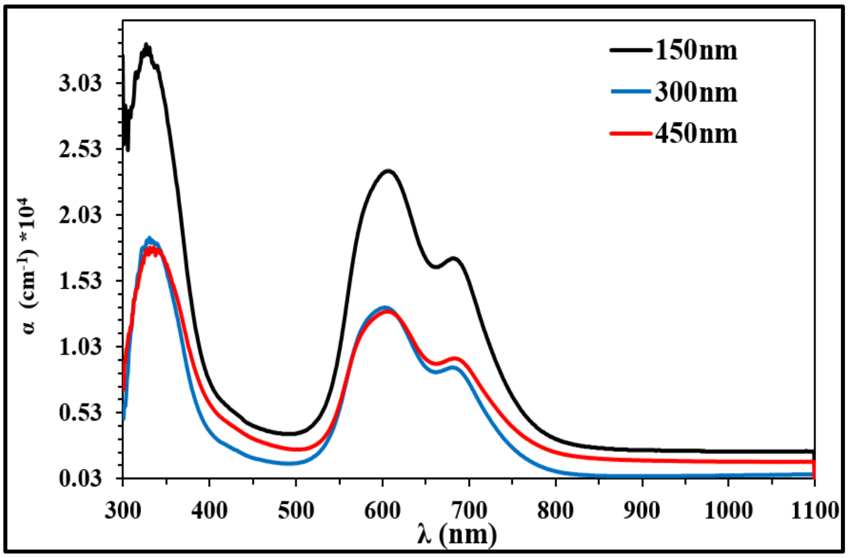


Fig.5: The coefficient of the absorption as function of wavelength for thin film of CuPc considering a variety of the thickness values.

1-5 Optical energy band gap

From Tauce equation was determined optical energy gap values for CuPc for different thickness thin films with regard to B-band edge as well as the Q-band edge. This equation is applied to obtain the optical transitions through plotting relations of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) as well as determining optimum linear part. In addition, it was indicated that there is a yield linear dependence for r =1/2 relation. The portion extrapolation (Eg) at [$(\alpha h\nu)$ 2 = 0] is shown in Fig.6 and 7 respectively for different thicknesses. Ultraviolet-Visible Spectrum provides absorption edge which is related to intense band referred to as Soret band (B-band) that is resulting from direct electronic transition from π to π* orbitals in range of (350nm-500nm) Furthermore, the other band is referred to as Q-band appearing in visible region in range of (600-700 nm). Q-band edge appearing in 2 trapping levels has been associated to the procedure of charge transfer from highest occupied molecular orbit (HOMO) to lowest unoccupied molecular orbit (LUMO). When the thicknesses increases, there will be a slight increase in optical energy gap as shown in Table 2.

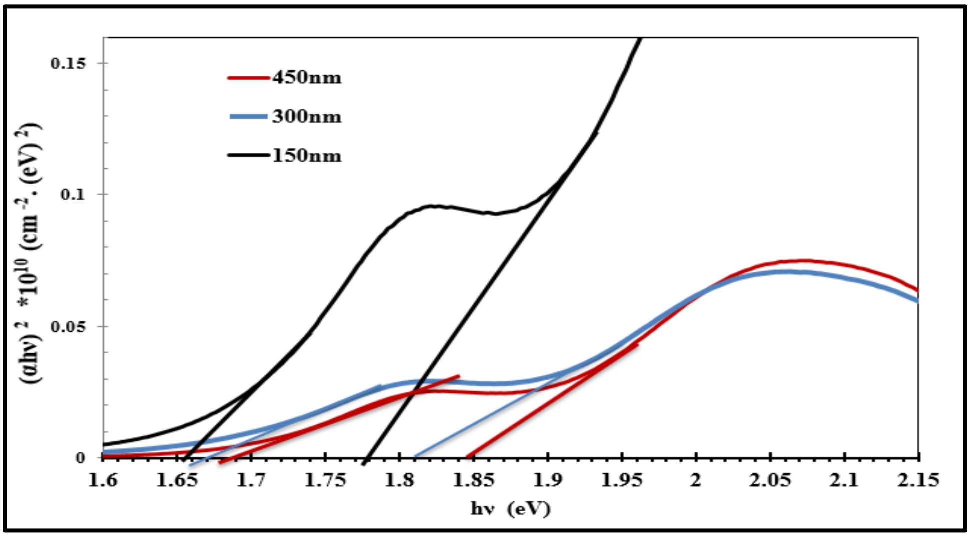


Fig.6: Graph shows $(\alpha h\nu)^2$ vs. the energy of the photon for CuPc at different thicknesses at Q-band.

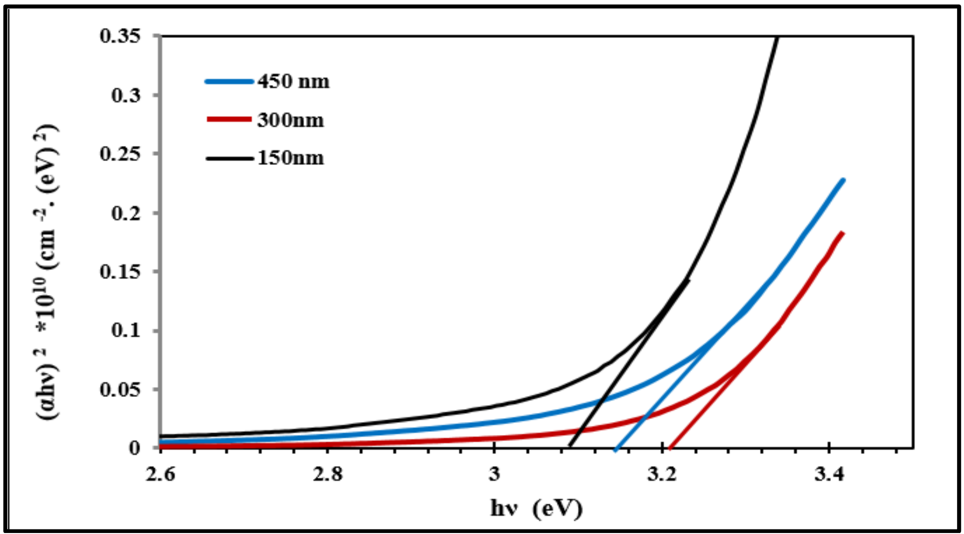


Fig.7: Graph shows $(\alpha h\nu)^2$ vs. the energy of the photon for CuPc at different thicknesses at B-band.

Table 2: Thin film thickness effect on optical energy gap for CuPc thin films.

Thickness (nm)	Energy gap (eV) B- band	Energy gap (1) eV Q_1- band Traping	Energy gap (2) eV Q_2- band Traping
150	3.06	1.65	1.78
300	3.14	1.66	1.81
450	3.2	1.67	1.84

1.6 Fourier transform infra-Red (FTIR) analyses of CuPc)

The FTIR spectrum of β – CuPc was measured and compared with the non-metal Phthalocyanine spectrum (H_2Pc) expressed in Fig.8. FTIR spectrum for CuPc powder shows that the region 400 – 800 cm^{-1} demonstrates an absorption band distinguishes from molecule β–CuPc, and to observe the strong absorption band at (729.02) cm$^{\mathbf{-1}}$ for copper metal, while for metal-free Phthalocyanine (H_2Pc) shows broadband of N-H in the region around 3435.97 cm^{-1}, while is absent in the CuPc spectrum and absorption band at 2853.23 – 2924.09 cm^{-1} is due to the stretching band of C-H that is coincidence with the results obtained by different workers [16].

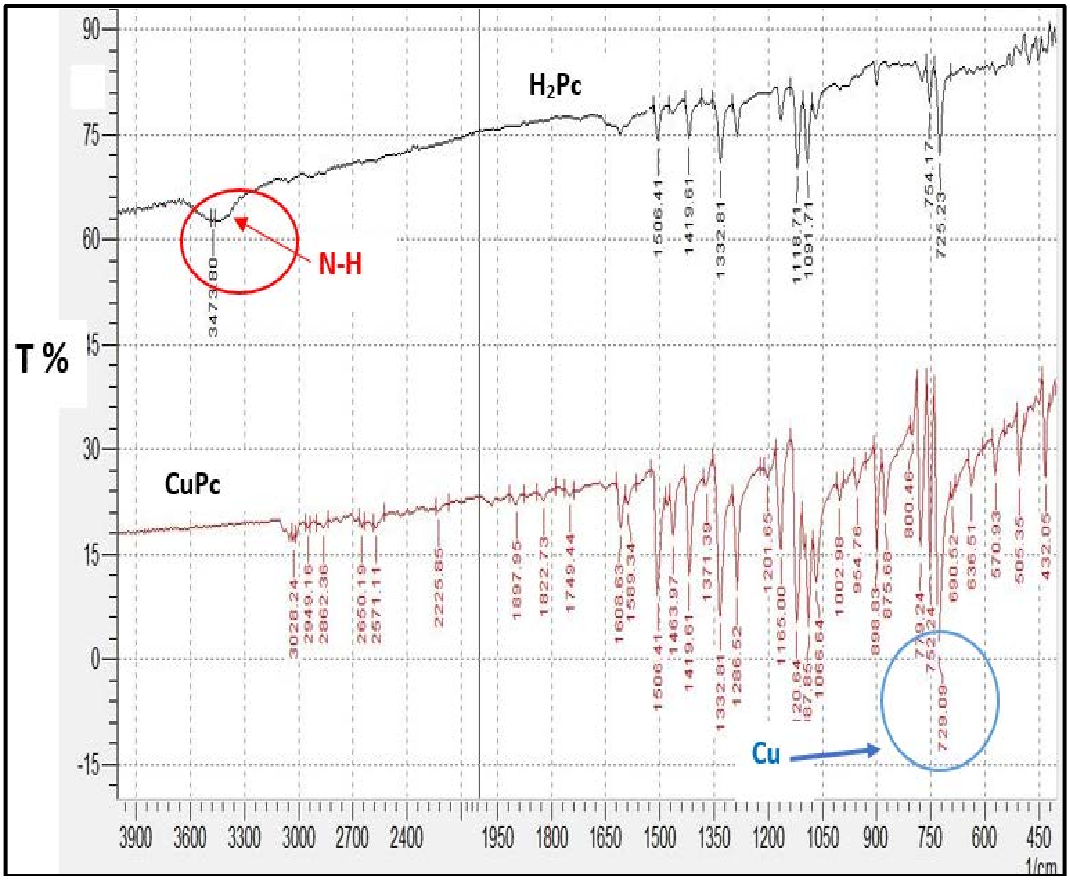


Fig.8: The FTIR spectrum of CuPc and metal Phthalocyanine spectrum (H_2Pc).

2. Z-Scan measurements

The Z-scan curves were been obtained for CuPc thin films have been illustrated in Fig. 9 and 10 respectively. The closed aperture for CuPc thin films show self-defocusing which indicated the negative non-linear refraction as seen as in Fig.9, while Fig.10 describe open aperture for CuPc thin films which show Reverse saturable absorber behavior.

For estimating the non-linear refractive index (n_2) the standard equations below [14] have been used:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \left|\Delta\varphi\right| \qquad (2)$$

$$n_2 = \frac{\Delta\phi_0 \lambda}{2\pi L_{eff} I_o} \qquad (3)$$

Where the ΔT_{p-v} the difference between valley and peak values of output power, $\left|\Delta\varphi\right|$-the phase-shift and s represents the transmittance of linear aperture which is calculated with $S = 1 - exp^{-r_a{}^2/w_a{}^2}$ where ra represents the aperture radius and wa represents the radius of the beam at aperture in the linear regime in the case where it is maintained in far field. In addition to that, λ represents the wavelength of the source (632.80nm), $I_o = 2P_0/\pi w_o{}^2$ is the peak intensity in the sample and $\{L_{eff} = 1\text{-}exp^{(-\alpha_0 L)})/\alpha_0\}$ represents the efficient length of the α_0 represent the sample's linear coefficient of the absorption.

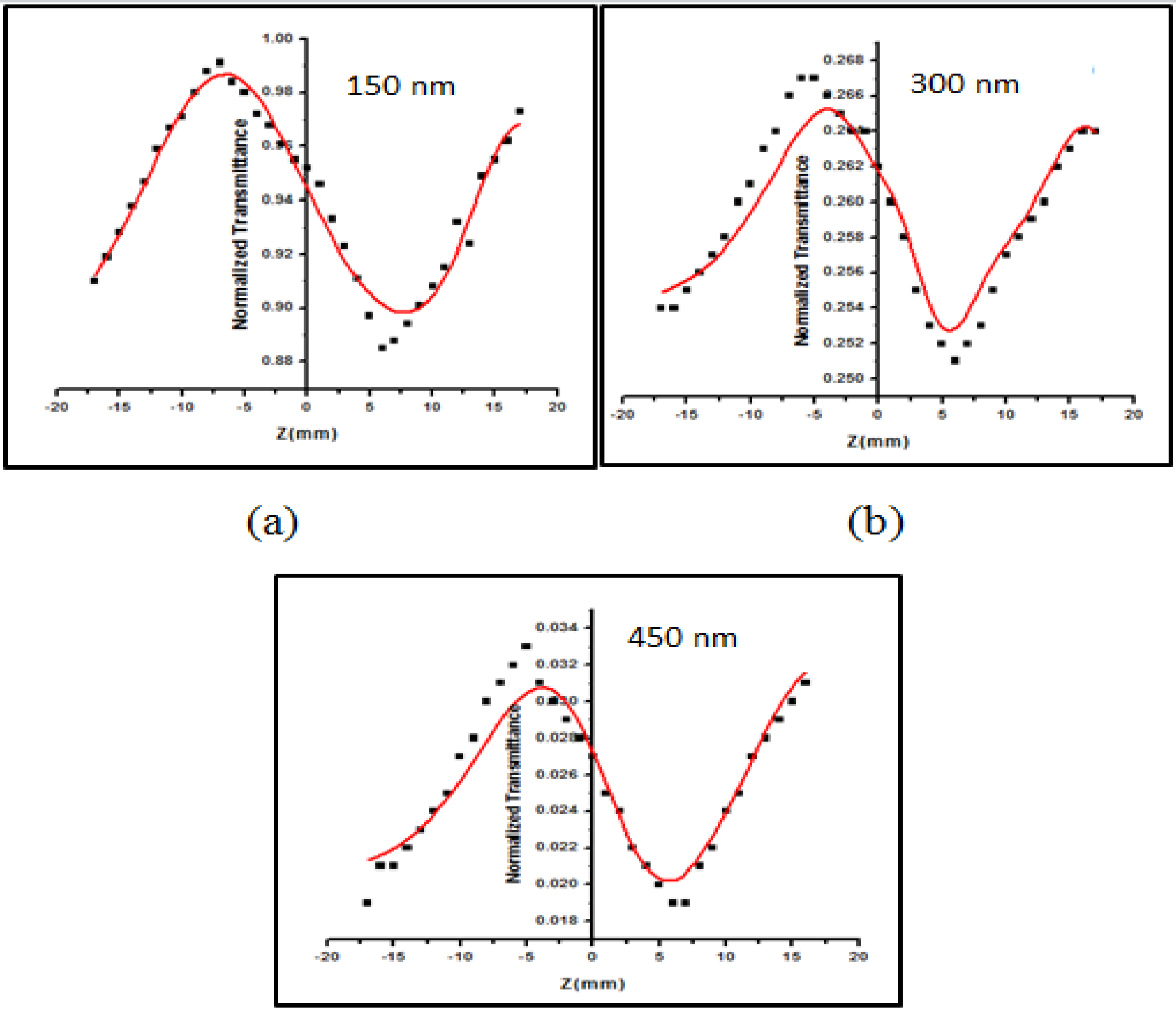
In case of open aperture z-scan, can obtain the coefficient of non-linear absorption. Fig.10 illustrates the case where the sample is translated in the direction of focus, there is a decrease in the transmittance, and that indicates the reverse saturable absorption (RSA) behavior of CuPc.

RSA can be considered as the foremost non-linear method of absorption to take place in the organic dyes [17, 18]. The β non-linear coefficient of the absorption could be specified with regard to equation [19]:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \qquad (4)$$

where ΔT is the peak (or valley) power value of laser beam transition at the open aperture of sample. The observed values of the non-linear refractive index and non-linear coefficient of the absorption have been given in Table 3.

Table 3 shows the refractive index and non-linear absorption coefficient related to Copper Phthalocyanine thin films at various thicknesses decrease with increasing thickness.



(a) (b)

(c)

Fig.9: a, b, and c; the curve (closed-aperture Z- scan) of CuPc thin films at different thickness.

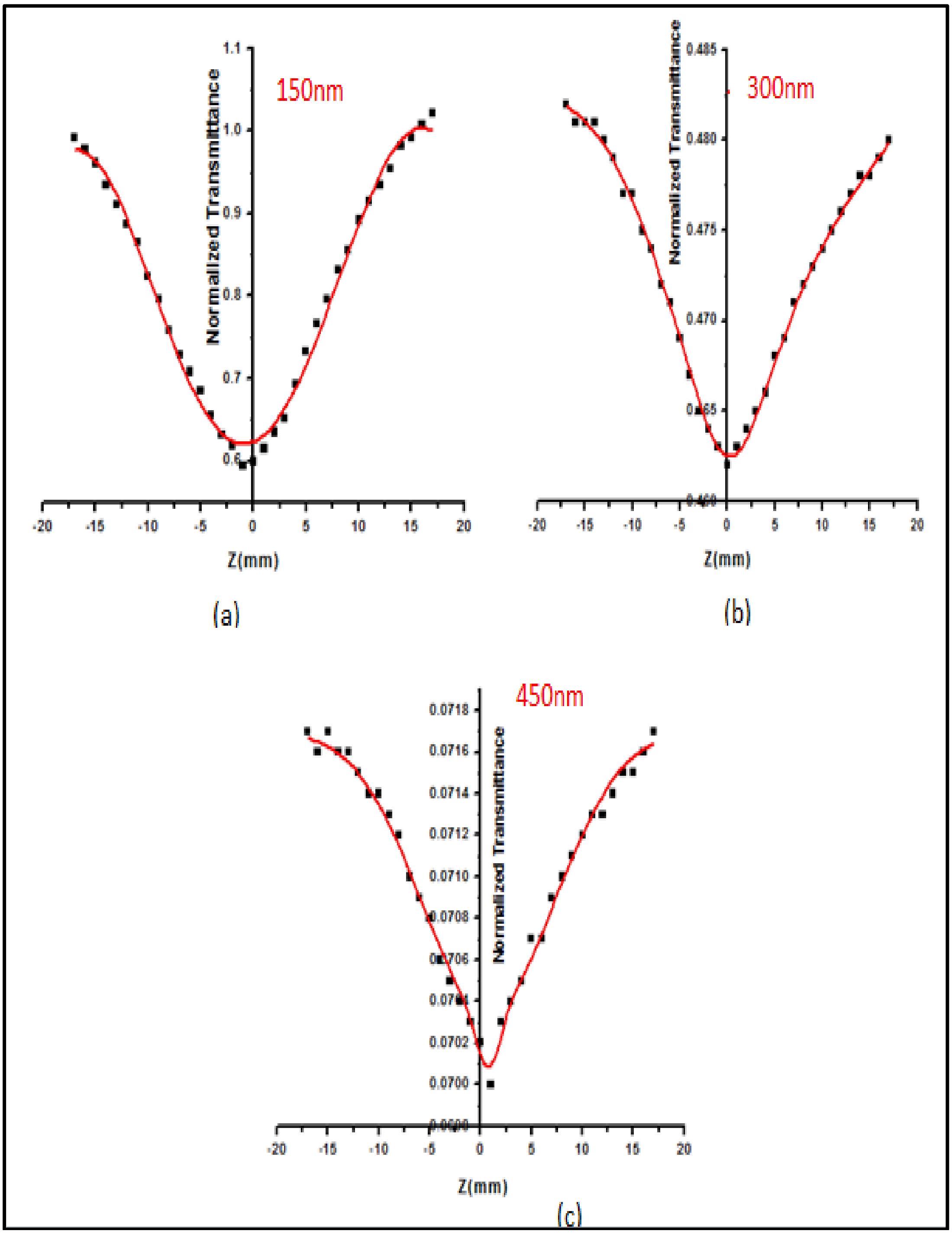


Fig.10: a, b, and c; the curves (open-aperture Z- scan) of the CuPc thin films at different thickness.

Table 3: Illustrate measured values of effective length, non-linear refractive index and non-linear absorption coefficient for different thicknesses thin films of CuPc.

Thickness(nm)	**Leff * 10^{-6} (cm)**	**n_2*10^{-8} (m^2/W)**	**β (m/W)**
150	1.67	-7.21	4.9
300	3.335	-0.465	1.73
450	5.04	-0.258	0.17

Conclusions

Thin films were manufactured from CuPc by pulsed laser deposition on substrates with different thicknesses; it has found that there are B and Q bands observations in the UV-Vis. absorption spectra of films prepared with different thickness. CuPc thin films have direct band gap and it increase with the increasing thicknesses. FTIR analysis of spectra in the range of molecular vibration represents of CuPc powder measured at normal room temperature it can be observed that a line which refers to Cu metal. The non-linear refractive index and non-linear absorption coefficient were measured for thin films at different thicknesses using the Z-scan technique with He-Ne laser. The non-linear refractive is a negative sign at a different thickness and the non-linear absorption coefficient is a positive.

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