Pump-Probe Technique to Study of the All-Optical Switching Properties of Copper Phthalocyanine Thin Film prepared via Pulsed laser deposition

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Abstract Z-scan has been utilized for studying the non-linear properties and optical limiting behaviors of the dye Copper Phthalocyanine thin films. The refractive index is negative, which indicates a self-defocusing behavior and non-linear absorption coefficient ($\beta$) of CuPc is a positive sign is a result of RSA. The optical switching behaviors of dye have been researched with the use of the method of the pump-probe with 9ns Q-Switched Nd: YAG laser at pump beam equal to 532 nm and a probe beam equal to 630nm Diode laser. The thin films of copper Phthalocyanine also reflect a significant limiting of the optical power of CW laser with an adequate threshold of the optical limiting. The dye’s switching behavior is a result of the probe beam’s excited-state absorption (ESA) with the molecules of the dye. The modulation of the probe beam with the increase of intensity of the pump has been researched as well.

Keywords: Copper Phthalocyanine; thin film; PLD; NLO materials; All optical switching; excited-state absorption (ESA).

Introduction

The metal-Phthalocyanines (MPC) were researched extensively for decades. Lately, a great deal of interest was driven to triplet excited states’ dynamics in the Phthalocyanines due to their aromatic 18$\pi$ electron system and the capability to contain over 70 types of the metallic as well as the nonmetallic ions in the cavity of the ring [1-3]. In addition to that, MPC’s large non-linear optic response such as copper Phthalocyanine, which arises from its 2-D conjugated $\pi$ electron system, lends CuPc as a possibility in a variety of the photonic devices, like the power limiting, all optic switching, optics stability [4-6] and so on. It was assumed that for all-optic switching behaviors, the cross-section of the absorption of the excited state require being higher in comparison with ground state absorption.
cross-section. It is expected that MPc can be causing strong RSA behaviors [7]. Throughout this course of investigations, the Z-Scan method was used for measuring both non-linear coefficients of absorption $\beta$ and the index of the non-linear material refraction $n_2$. The method has been shown by S. Bahae et al. [8] in their study that was proven simple and of high sensitivity. Additional material’s optic switching behavior was researched as well with the use of the method of the pump-probe [9].

**Experimental work**

**Sample preparation**

The blue pigment powder supplied by Sigma – Aldrich of 99% purity, was used in this work as the main source. The thin film of CuPc prepared by pulsed laser deposited (PLD) [10]. Optical glass is utilized in the form of the substrate which is cleaned by acetone using the ultrasonic approach for 10 minutes. Film thickness was measured by the optical interferometer method [11] and was found to be 0.5 μm.

**Z-Scan measurement**

Non-linear optical (NLO) characteristics of CuPc was investigated with the utilization of the Z-scan method for determination of non-linear coefficient of absorption ($\beta$) and the nonlinear refractive index ($n_2$)[8]. He–Ne laser (4.80mW) of wavelength 632.80nm has been utilized as a source and the diameter of the beam = 2.50mm and the beam has been focused utilizing positive lens of ($f$=150mm) at the focus point of the sample. Pinhole used to locate the laser has a diameter (1 mm). It was moved along the Z-axis. The transmittance through the sample has been seen as a function of its location. The beam waist ($w_0$) is measured at focus length to be equal to 24.20μm and the Rayleigh length $Z_0$ was found to be (2.9mm). The representation of the Z-Scan setup has been depicted in Fig. (1).

![Figure (1): Device of the Z-scan approach](image-url)
Pump-probe experimentation for the research of the optical switching

CuPc sample’s optical switching behavior has been examined with the method of the pump-probe where the linearly polarized, frequency doubled Q-SwitchingNd:YAG with a rate of repetition equal to 10Hz at 532nm is utilized for the excitation of the sample of dye. The weak laser of Diode at 630 nm is utilized for the probe beam to scan sample for the non-linear optic switching properties. The probe beam’s intensity is maintained constant whereas intensity of the pump has been differed with the ND filters. The signal of beam of the probe has been left to focus on photo detector of Si (“Thorlabs, DET-10A”) with the use of converging lens and the result has been captured with the oscilloscope (“Tektronix TDS2022C”). The experimental set-up has been depicted in Figure(2).

![Figure (2): Representation of pump-probe experimentation for the optical switching, p-polarizer, L-lens, A-Aperture, PD-photo diode.](image)

Results and discussions

The spectrum of the linear absorption of typical CuPc thin film and value of energy band gap are reported elsewhere [12]. These molecules show high energy B (Soret) band and low energy Q – band/bands. This material has a window, between those 2 bands of absorption, with high linear transmittance, which makes them appealing as optical limiters for visible spectra at 390 – 530nm regions. The band gap value of the thin film of CuPc is 3.14 eV. Figure3 (a) illustrates the usual copper Phthalocyanines spectrum of emission, which indicates a peak of emission, which is approximate to 338nm and a peak of excitation of approximately 315nm, and a peak of emission, which is approximate to 700nm when excitation by 630nm as shown in Figure 3 (b), which is good agreement with the reported results [13]
Figure(3): The spectrum of the emission of the (blue, right) and the spectrum of the absorption (red, left) of copper Phthalocyanine (a) excited by 315nm (b) excited by 630nm

**Z-scan measurements**

The Z-scan curves for CuPc thin film samples have been illustrated in Figure(4). The closed scan of aperture for CuPc Figure4 (a) shows a pre-focal peak which is followed with a post-focal signature of the valley which indicated the negative non-linear refraction and open aperture as in Figure4 (b) shows Reverse saturable absorber behavior type. For estimating the non-linear refractive index \( n_2 \) the standard equations below \[8\] have been used:

\[
\Delta T_{p-v} = 0.406(1 - S)^{0.250} \left| \Delta \phi \right| \\
\]

\[
n_2 = \frac{\Delta T_{p-v} \lambda}{2 \pi L_{eff} I_0} \\
\]

Where the \( \Delta T_{p-v} \) the difference between valley and peak values of output power, \( \left| \Delta \phi \right| \) the phase-shift and \( S \) represents transmittance of linear aperture which is calculated with \( S = 1 - \exp^{-r_a^2/w_a^2} \) where \( r_a \) denotes the radius of aperture and \( w_a \) denotes radius of the beam at aperture in the linear regime in a case where it is maintained in far field. In addition to that, \( \lambda \) represents the wavelength of the source (632.80nm), \( I_0 = 2P_0/\pi w_0^2 \) is the peak intensity in the sample and \( \{L_{eff} = 1-\exp(-a_0 L)/a_0 \} \) represents the efficient length of the \( a_0 \) represent the sample’s linear coefficient of the absorption.

The separation between the peak and the valley in the closed aperture scan (\( \Delta Z_{p-v} \sim 7Z_0 \)) this does not satisfy the electronic refractive non-linearity condition \[14\] thus the non-linear refraction in this material due to the fact that it is thermal in nature \[15\].

In case of open aperture z-scan, can obtain the nonlinear absorption coefficient. Figure4 (b) 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 may be considered as the foremost non-linear method of absorption to take place in the organic dyes \[16, 17\]. The \( \beta \) non-linear coefficient of the absorption could be specified with regard to equation \[18\]: 
\[ \beta = \frac{2\sqrt{2} \Delta T}{l_0 \Delta \phi} \]

(3)

Where, \( \Delta T \) is the peak (or valley) power value of laser beam transition at the open aperture of sample.

The RSA might be a result of the NLO method, which includes ESA, two-photon absorption (TPA), non-linear scattering (NS), free carrier absorption (FCA), or with combining all those [18, 19]. In the organic materials of the NLO, in the case where the band gap of the energy \( E_g \) is larger than \( 2 \times \) photon energy \( E_{photon} \) of the wavelength of excitation (\( E_g > 2E_{photon} \)), TPA is a predominant method [20]. In present work, \( E_{photon} \) of the beam of laser = 2.33eV, which is smaller compared to the energy of the band gap (\( E_g = 3.14eV \)). Which is why, TPA’s role in non-linear optical impact is not significant. Which is why, RSA is a predominant approach would be ESA’s evidence at 632.8nm operating wavelength. The observed values of the non-linear refractive index and nonlinear coefficient of absorption have been given in Table 1.

![Figure 4](image)

**Figure 4:** (a) closed aperture z-scan (b) Open aperture z-scan of CuPc thin film.

| Thickness(μm) | \( \Delta \phi \) | \( \Delta \phi \) | \( \Delta \phi \) | \( \Delta \phi \) | \( \Delta \phi \) | \( \Delta \phi \) | \( \Delta \phi \) |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.5            | 5.04            | 0.029           | 0.17            | -0.258          |

**Table 1: Non-linear optical coefficients of CuPc thin film.**

**Optical limiting measurements**

Optical limiting may be described as a nonlinear optical procedure where transmitted material’s intensity is increased in case of the low incident intensities and at a particular value of the threshold
intensity, the transmission stays unchanged. In this paper, the optic limiting has been based on non-linear absorption. In this case, no aperture or pinhole is used. Based on this mechanism, the all-optical limiting may be referred to as the power-absorbing configuration of the optical limiters [21].

From Figure 5, it can be observed the threshold of optical limiting is significant in the case where this material will be utilized to protect the human eyes [22]. The value of the optical limiting threshold has been discovered to be 6.2mW, which rather coincides with results that have been reported in the literature for other types of material [23]. From limiting threshold, (P th) and optical damage (PD) can be given the dynamic range (DR) which equals to 1.25. Generally, a variety of physical methods plays a role in the optic limiting of material that was proposed [14, 24]. Those mechanisms may be a result of RSA, TPA, FCA, non-linear refraction, photo-refraction, and induced scattering. The optical limiting behavior, which has been viewed in CuPc thin films, is a result of the self-defocusing (which is induced with the non-linear refraction). Which is why, self-defocusing is a result of thermal non-linearity, which holds more responsibility for any observed responses throughout the optic limiting.

Pump-probe experiment

The recorded probe beam output with different pump intensities has been illustrated in Figure 6 (a). which indicates that we have (RSA) process it means that the absorption cross-section of excited state is greater compared to lower state while Figure 6(b) illustrates the actual traces of probe beam switching in the impact of the pump pulses. A large probe beam modulation is noticed with the increase of the intensity of the pump beam, and this is a result consistent with [25].
Figure (6): (a) the modulation of probe beam with varying intensities of the pump beam in the thin film of the CuPc (b) the traces of the optical switching in the experiment of the pump probe

The absorption behavior and the optical switching of dyes of the Phthalocyanine group are explained in general with 5 level diagrams of energy [26] as depicted in Figure(7). The interaction of laser pulse (532nm, 9ns) with the molecule of the dye could excite it from the ground state $S_0$ to vibration $S_1$ state levels. In a case where the molecule experiences a vibration relaxation in the $S_1$ and afterward reaches $S_n$ with additional absorption, it is referred to as the singlet ESA, instead, in the case where a molecule from the $S_1$ state relaxes to 1st state of the triplet $T_1$ via inter-system crossing and after that is excited to $T_2$ with additional absorption, it is known as the triplet ESA. Singlet ESA has a higher possibility of happening in the case where the duration of excitation pulse $\leq$ pico-seconds. For nano-second pulses, $S_n$ and $T_n$ levels’ relaxation times are considerably shorter compared to pulse duration (typically of $\leq$ ps order). In addition, Nano-second pulses have been utilized in this experiment, triplet ESA possibly makes considerable contributions to observed non-linear absorptions. The physical approach of all of the optical switching is the fact that pump pulse undergoes excitation of molecules, the triplet state $T_1$ population witnesses an increase through the inter-system crossing that performs strong absorption of the beam of the probe, and transmission is decreased.

Figure (7): Diagram of the 5 level energy of CuPc dye [26]
In the case where there is not any pump pulse, the triplet state population is decreased and it again begins to transmit the beam of the probe. This observed switching in the CuPc shows that there is a possibility of fabricating an optical switching ON-off gate through the design of a proper device. It should be mentioned that the triplet state relaxation to the ground state is not allowed, which will result in a slower switching from the Off to the On states [4].

Conclusions

Nonlinear refractive index, non-linear absorption coefficients, optical limiting properties, and optical switching behavior of the CuPc thin film prepared via PLD technique have been researched. The observed non-linear refractive index is a result of the thermal non-linearity owing to the CW excitation. The nonlinear absorption is a result of the reverse saturation absorption of a thin film, which is fundamentally a result of the absorption of the excited state of CuPc molecules. Optical limiting measurements have confirmed that CuPc thin film shows sufficient optical limiting threshold at a wave-length of 532nm. This notable switch in CuPc demonstrates that one can manufacture an ON-off optical gate through the design of a proper device.

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