



Structural, linear and nonlinear optical study of zinc tetra-*tert*-butyl phthalocyanine thin film



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ABSTRACT

Zinc tetra-*tert*-butyl phthalocyanine (ZnTTBPC) thin films were deposited on cleaned glass substrates by thermal evaporation technique. The ZnTTBPC films undergo phase transformation from unstable amorphous into stable crystalline form when annealed at 473 K as evidenced from the X-ray diffraction study. The UV–vis absorption spectral study revealed an increase in the optical band gap from 3.03 eV for amorphous α -phase to 3.12 eV for the crystalline β -phase of the film. The AFM topographic images display a significant change in the surface morphology of film due to thermal annealing. Nonlinear optical studies of stable β -phase were performed with picosecond (ps) laser pulses operating at a wavelength of 800 nm. The present work is, the first such attempt to measure the third order nonlinear optical (NLO) coefficients of thermally evaporated β -phase ZnTTBPC thin films using ps laser pulses. The strong nonlinear absorption (NLA) and nonlinear refraction (NLR) coefficients (β and n_2) i.e. 2×10^{-7} cm/W and -7×10^{-11} cm²/W, respectively, indicates thermally evaporated ZnTTBPC films could be a promising material for nonlinear optical device applications.

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1. Introduction

Phthalocyanines (Pc), metallated phthalocyanines and their substituted derivatives have attained research importance due to their applicability in nonlinear optics [1], gas sensing [2], solar cell [3,4], photodynamic therapy [5] etc. The physical properties of Pc molecules may be modified by introducing a metal atom inside their empty core by the replacement of two protons or by attaching an axial/peripheral substitution outside or by temperature treatment. Inclusion of metal in general can increase the symmetry of the Pc molecule, whereas the peripheral substitution can account for the solubility to an extent. The Pc derivatives gained particular attention in the field of non-linear optics compared to other organic counterparts because of their versatile properties such as higher values of non-linear absorption and refraction coefficient, which can be exploited for suitable device fabrications based on these parameters. From the application point of view, deposition of Pc molecules on suitable substrate in the form of thin film enables to investigate the physical properties in a better way rather than in the free molecular state due to the weak van der Waals interaction between the Pc molecules in solid state [6–8].

Most of the reports on Pc based NLO studies were performed on either in solution or molecules doped into polymer matrix form. But the lesser solubility of Pc always poses obstacles in finding optical device applications. The restriction on solubility and advantage of higher thermal stability of Pc molecule suggests the thermal evaporation technique to be advantageous for preparing Pc film. α and β are the two main polymorphic phases that thermally evaporated Pc thin films form on glass substrate [9]. The physical properties of Pc based thin films are influenced by the presence of meta stable pseudomorphic layer present on the glass substrate surface at room temperature [10,11]. Presence of such a layer and thermal instability of α -phase at higher substrate temperature made us to focus on the NLO studies of thermally stable β -phase. To the best of our knowledge, third order NLO study of thermally evaporated β -phase of ZnTTBPC films still remains unexplored. The objective of the present work is to investigate the structural, linear and nonlinear optical properties of ZnTTBPC films deposited on glass substrate.

2. Materials and methods

2.1. Thin film deposition

Zinc tetra-*tert*-butyl phthalocyanine powder (Sigma-Aldrich) was used as a material for the preparation of the film. Thin films

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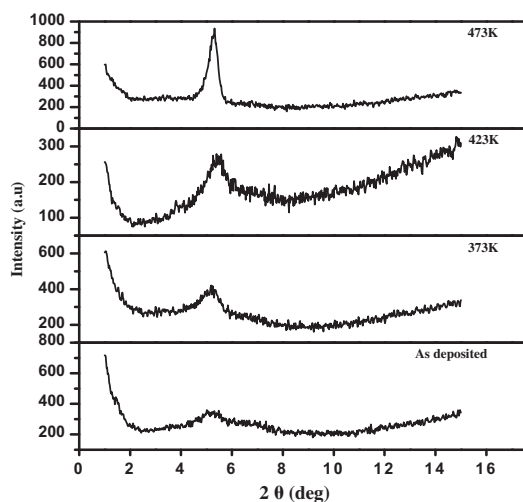


Fig. 1. Powder XRD pattern of as-deposited and annealed ZnTTBPC films.

of ZnTTBPC were deposited on an ultrasonically cleaned corning glass substrate through vacuum thermal evaporation technique using Hind Hi Vac vacuum coating unit. ZnTTBPC powder was kept inside a molybdenum boat, which was used as heating element. The film deposition speed was kept at 2.5 nm/s. Thin films were coated on the substrate of dimension $37 \times 12 \times 1$ mm, at room temperature under a pressure of 10^{-5} Torr. As-deposited thin films were annealed for 90 min at four different temperatures i.e. 303 K, 373 K, 423 K and 473 K, using a muffle furnace.

2.2. Measurements and devices used

The thicknesses of the prepared thin films were recorded using the thickness monitor attached to the coating unit. Further, the thickness of the prepared film was cross checked through ellipsometry. Structural properties of the films were recorded using Rigaku Miniflex 600 powder X-Ray diffractometer with $\text{Cu K}\alpha 1/40$ kV/15 mA radiation source ($\lambda = 1.54056 \text{ \AA}$), with Ni $\text{K}\beta$ filter at a scanning speed of $2^\circ/\text{min}$. Linear optical absorption spectra of the film was recorded using Shimadzu 1800 UV–vis spectrophotometer in the wavelength range of 300–1000 nm. Atomic force microscope (AFM), Agilent 5500 was employed to measure the surface roughness of the film through non-contact mode. The third order NLO study of stable β - phase of the film was performed with Z-scan set up using ps laser pulses operating at 800 nm. The ps pulses were generated by Ti: sapphire laser (Coherent) operating at a repetition rate of 1 kHz with pulse duration of ~ 2 ps at 800 nm wavelength.

3. Results and discussion

3.1. Powder XRD characterisation

Fig. 1 displays the powder XRD patterns recorded for as deposited and thermally annealed ZnTTBPC thin films. The single intense characteristic peak observed at $2\theta = 5.3^\circ$ in the XRD pattern accounts for the crystallinity of ZnTTBPC film. The crystallinity of the film increases with increase in annealing temperature, attaining a maximum at 473 K. Thermal annealing modifies the structural features of ZnTTBPC molecule. More specifically, annealing of the film at different temperatures reveals the existence of two main phases (α and β) present in ZnTTBPC. The ZnTTBPC film annealed at 303 K is in meta stable α -phase. Transformation from the meta stable α -polymorphic form to stable β -form occurs when the film is thermally annealed at 473 K.

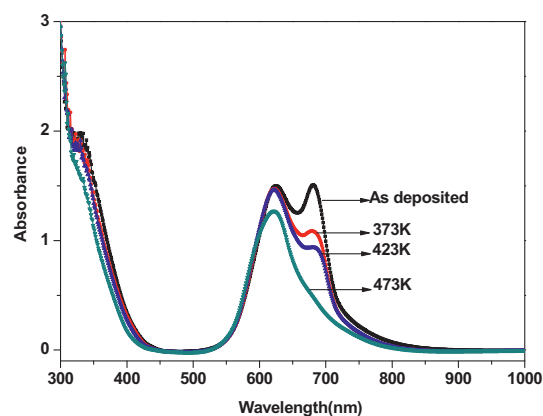


Fig. 2. Effect of annealing on absorption spectra of ZnTTBPC film.

3.2. Linear optical absorption study

Fig. 2 displays the UV–vis absorption spectra recorded for ZnTTBPC thin films coated on glass substrate. The spectra consists of B (Soret) and Q band in the wavelength range 300–400 nm and 550–700 nm, respectively. Presence of B band is due to the direct electronic transition between highest occupied molecular orbital (π) to lowest unoccupied molecular orbital (π^*) of the Pc ring. B band encloses only single peak positioned at 331 nm. The absorption edge of the peak in the B band can be related to fundamental absorption from which the energy band gap was obtained. Q band in the absorption spectrum observed for ZnTTBPC film consists of two peaks, Q_x and Q_y (absorption doublet). The first peak is located at 625 nm (Q_x) and that of shoulder peak (Q_y) at 681 nm. The absorption doublet in Q band is due to the so called Davydov splitting, associated with the Pc molecule which arises due to the presence of more than one structurally similar interacting molecules inside the unit cell. Optical absorption spectra of Pc thin films can be affected either by temperature treatment or by the incorporation of the various metal atoms inside the central cavity [12,13]. The extensive coupling mechanism existing between the Pc ring and the central metal ion is responsible for the origin of electronic spectra in ZnTTBPC molecules. As the annealing temperature increases, the shoulder peak (Q_y) at higher wavelength goes on suppressing and when the temperature reaches 473 K, only the higher energy peak of Q band found to exist without any change in its peak position. The Davydov splitting observed for as deposited film indicates that unit cell of ZnTTBPC contain chemically identical molecules which are oriented at different angles. In case of β -polymorph absence of such splitting implies uniformity in the orientation of the molecules. The possible reason for this may be due to the fact that, as deposited film is a mixture of both α and β - phases and the percentage of α -phase in it is very high compared to β . Results of structural study agrees well with this observation.

Optical band gap of the ZnTTBPC film can be found by analysing the absorption spectra of the film near the absorption edge using the following equation,

$$\alpha = \alpha_0 (h\nu - E_g)^n$$

where α represents the absorption coefficient, α_0 , a constant and E_g which gives the band gap. The value of n determines the given transition is of allowed ($n = 1/2$) or forbidden ($n = 3/2$) type. From α^2 versus photon energy ($h\nu$) graph one can elucidate band gap values by extrapolating $\alpha^2 = 0$, since ZnTTBPC is a direct band gap material.

The optical energy band gap calculated from Tauc's plot (Fig. 3) varies from 3.03 eV to 3.12 eV, when the annealing temperature increases from 303 K to 473 K. The increase in the band gap is attributed to the removal of pseudomorphic layer present on the

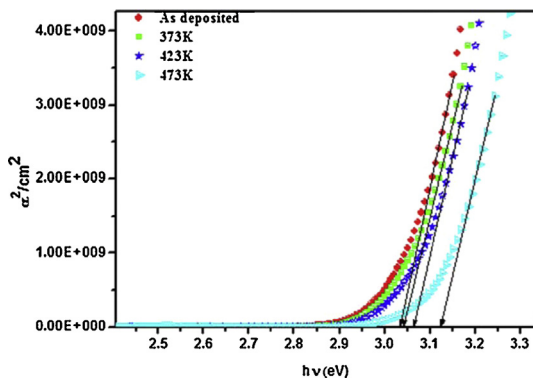


Fig. 3. Band gap calculation using Tauc's plot for as deposited and annealed film.

glass with increased annealing temperatures, which in turn will increase the interaction between molecules and substrate by reducing the distortions in the electronic spectra. The results of optical study reported in this paper is in good agreement with the observations of other researchers [14]. Due to higher chemical and thermal stability of the molecules, degradation of the film is not observed up to 473 K. This suggests that no defects or compositional changes of material introduced during thermal annealing of the film.

3.3. AFM analysis

Fig. 4 represents the three dimensional image of as deposited and phthalocyanine films annealed at 473 K. The film surface was scanned over an area of $6 \times 6 \mu\text{m}^2$. As-deposited film contains irregular shaped objects, as shown in Fig. 4(a). The film annealed at 473 K consist of (Fig. 4(b)) regularly shaped objects with proper orientation. The AFM observations on ZnTTBPC films were on par with the results of powder XRD pattern collected. The orientation of objects along a particular direction observed in Fig. 4(b) may account for increased crystallinity of stable β -phase. The surface of as deposited film consists of coalesced grains which form the larger sized particles compared to the surface structure of the annealed film. The larger sized particles observed on the surface of as deposited film may be arising from the agglomeration of randomly oriented objects which may determine the particle size on the pseudomorphic layer [15] or amorphous polycrystalline aggregates of meta stable α -phase. The surface roughness of the as-deposited and annealed film was estimated from the height parameter measurements. The AFM image observation revealed that as deposited film has a higher RMS roughness value of 17.34 nm compared to 15.49 nm for the annealed film. The high value of roughness for as deposited is attributed to the mixture of both phases which gives rise to non-uniform distribution of grains in the as deposited film or due to the nucleating behaviour of the molecules at lower substrate temperature. After annealing, single

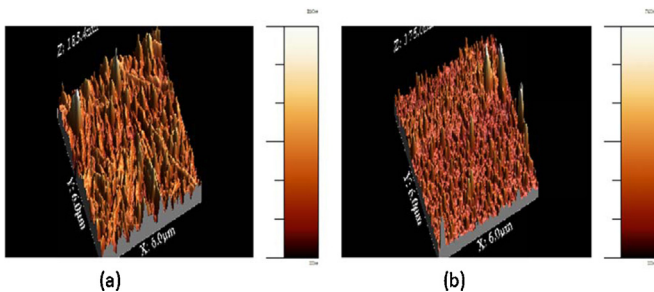


Fig. 4. AFM 3D image of ZnTTBPC (a) as deposited thin film and (b) thin film annealed at 473 K.

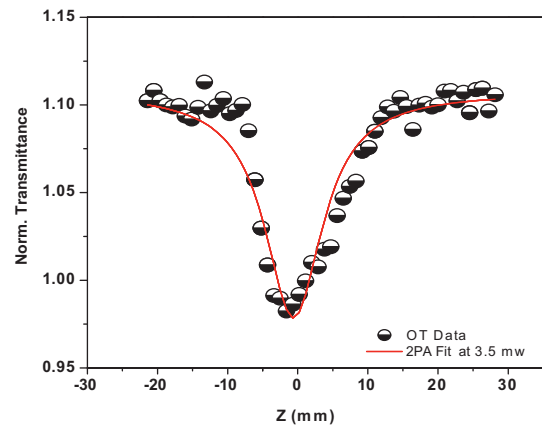


Fig. 5. Open aperture normalised transmittance curve of β -polymorphic ZnTTBPC film.

stable phase with large and uniform grain size is attained. The decrease in average height (56.74 to 40.67 nm) value observed after annealing may be due to the removal of the pseudomorphic layer at higher temperature.

3.4. Third order NLO studies of stable β -polymorph ZnTTBPC film

Standard Z-scan technique was employed to probe third order NLO properties of stable and well oriented β -polymorphic ZnTTBPC film, which has the advantage of simultaneous determination of sign and magnitude of NLA and NLR coefficient over other similar techniques like THG and DFWM. The ps studies were performed on thin films having thickness ~ 250 nm providing $\sim 72\%$ linear transmittance under non-resonant excitation wavelength of 800 nm (the single photon absorption of the ZnTTBPC film at this wavelength is negligibly small). Zero contribution to either of nonlinear coefficients from the substrate glass plate was confirmed at the probing laser wavelength. Open aperture studies have been performed at an average power of ~ 3.5 mW with a respective peak intensity of ~ 96 GW/cm².

Fig. 5 shows the open aperture Z-scan result of ZnTTBPC film on glass substrate. In the above graph, initially the normalised transmittance data gradually decreases when sample moves from left to right resulting a valley and reaching a minimum at $z=0$ (focus) then starts to increase with increase in z values giving a peak. This shows the observed nonlinear absorption is due to reverse saturable absorption (RSA) and the coefficient of nonlinear absorption can be obtained by fitting the normalized transmittance data of the open aperture results with the theoretical equation given by Sheik-Bahae [16].

The open aperture data points are found to be best fitted with the two photon absorption (2PA) equation:

$$T(z) = \frac{1}{\pi^{0.5} q_0(z)} \int_{-\infty}^{\infty} \ln \left[1 + q_0(z) e^{-x^2} \right] dx$$

with

$$q_0(z) = \beta L_{\text{eff}} I_0 \quad \& \quad L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$$

here $T(z)$ represents the normalised energy transmittance values with respect to the sample thin film distance, z from the focus and x is the time. L_{eff} and I_0 denotes the effective sample thickness and peak irradiance at focus, respectively. The linear absorption coefficient, α_0 indicates the fraction of radiation absorbed per unit thickness of the thin film sample. NLA coefficient, β value calculated for

Table 1
Comparison between NLA coefficients of ZnTTBPC in different forms.

ZnTTBPC sample form	Excitation wavelength (nm)	Laser pulse type	NLA coefficient (cm ² /W)
Solution (acetone) [17]	532	Nanosecond	4.9×10^{-10}
Nanoparticles [17]	532	Nanosecond	1.6×10^{-9}
Film (polymer doped) [18]	800	Picosecond	1.5×10^{-8}
Present study	800	Picosecond	2.0×10^{-7}

ZnTTBPC film with average power of ~ 3.5 mW using the above relation was 200 cm/GW, suggesting 2PA was the mechanism behind the observed nonlinear absorption in ZnTTBPC films. The observed mechanism, 2PA is supported by (a) negligible linear absorption at 800 nm, not allowing any 1 + 1 kind of nonlinear absorption (b) use of ~ 2 ps pulses. Nitschke et al. studied the third order NLA of ZnTTBPC in solution and nanoparticle dispersed in water under nanosecond laser pulses at an exciting laser wavelength of 532 nm [17]. Rao et al. investigated NLA study on ZnTTBPC film doped in PMMA polymer matrix with ps laser pulse using 800 nm excitation [20]. The results of their study and present study are presented in Table 1.

The results in the above table indicate NLA coefficient of thermally evaporated film is 3 orders larger than ZnTTBPC solution, 2 orders higher than ZnTTBPC nanoparticles and an order more than ZnTTBPC doped PMMA film. The reason for this may be attributed either to the probing excitation wavelength or the nature of the ZnTTBPC sample. In thermally evaporated film, there is no other chance of external contribution to the NLA as the substrate glass has not shown any sign of nonlinearity at the probing wavelength. In other cases contribution from the solvent, size of nanoparticle or the polymer matrix may also matter. To obtain NLR coefficient n_2 , closed aperture scans were performed by keeping an aperture in front of the detector and measured the energy transmitted through the aperture in the far-field as a function of sample position in Z-direction. The measured values of closed aperture scan data may contain the traces of both nonlinear refraction and nonlinear absorption since the closed aperture transmittance is influenced by both the processes. In order to extract the nonlinear refraction part alone or to remove the contributions of nonlinear absorption, closed aperture transmittance data should be divided by the respective open aperture values. The result achieved through this way reflects effects of pure nonlinear refraction only [19]. The n_2 value can be obtained by fitting the normalised transmittance versus sample position graph with the theoretical equation given by,

$$T_{CA} = 1 + \frac{4\Delta\Phi(z/z_0)}{\left[\left(\frac{z}{z_0}\right)^2 + 9\right] \times \left[\left(\frac{z}{z_0}\right)^2 + 1\right]}$$

where $\Delta\Phi = kn_2 I_0 L_{\text{eff}}$ is the on-axis phase shift at focus, k is the wave number, z_0 is the Rayleigh range ($=\pi\omega_0^2/\lambda$) and ω_0 is the beam spot radius at focus. Closed aperture scans were performed at lower intensities where the contribution from the higher order nonlinear effects are negligible (the value of $\Delta\Phi$ estimated in all the cases was $< \pi$). The scan was performed at lower peak intensity of 26 GW/cm² corresponding to an average power of 0.95 mW compared to nonlinear absorption experiments to make it free from other higher order nonlinear optical effects [20].

Fig. 6 shows the result of closed aperture Z-scan. The presence of a peak before the focal point (left side of Z=0) followed by a

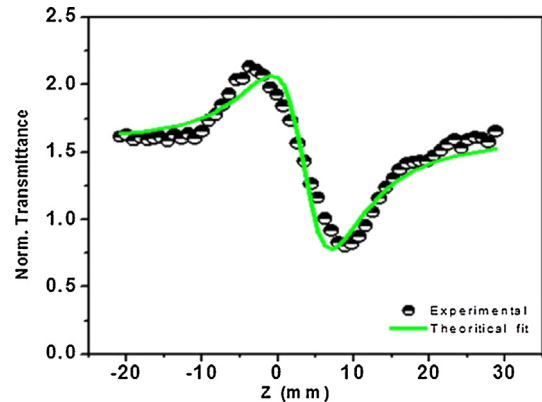


Fig. 6. Closed aperture normalised transmittance curve of β -polymorphic ZnTTBPC film.

valley after the focus in the graph implies that the observed nonlinear refraction is of negative type. In this case, sample acted like a thin lens and due to negative nonlinear refractive index, convergence of the incoming beam occurs at pre-focal positions and then starts to diverge after focus. Appearance of such nature in NLR is due to the self-defocusing nature of the ZnTTBPC sample. From the fitted data the n_2 value obtained was -7×10^{-11} cm²/W. A closed observation of Fig. 6 reveals that the peak is positioned at -3.42 mm on $-z$ side and valley at $+8.82$ mm in $+z$ side of the normalised closed aperture curve showing peak–valley position is not symmetric about the focus ($z=0$). Possible reason for this behaviour may be arising due to the extent of surface uniformity of the film that contributes to nonlinear scattering [21,22] and errors in the calibration of translating stage.

Table 2 clearly indicates that the magnitude of NLR coefficient is better for thermally evaporated ZnTTBPC except for the nanosecond scan result, which has comparable value with our result. The main difference between NLR coefficient of other ZnTTBPC forms and thermally evaporated one is in the negative sign, indicating the self-defocusing nature as discussed above. The reason for this large NLR coefficient of ZnTTBPC film may be attributed to higher thermal stability of β -polymorphic ZnTTBPC film with the input laser energy. In positive NLR coefficient self-focussing cases, sample itself acts like a lens that focus the incoming laser pulse and the intensity of the self-focussed region increases thereby causing damage to the system. Self focussing is mainly due to the thermally induced changes on nonlinear refractive index. For thermally evaporated β -polymorphic ZnTTBPC samples, no such problems of thermal instability or the structural damage through the self focussing effects because of its thermally stable nature and negative n_2 values.

Table 2
Comparison between NLR coefficients of ZnTTBPC in different forms.

ZnTTBPC sample form	Excitation wavelength (nm)	Laser pulse type	NLR coefficient (cm ² /W)
Solution (CHCl ₃) [23]	532	Nanosecond	0.86×10^{-11}
Solution (CHCl ₃) [23]	800	Femtosecond	1.14×10^{-15}
Film (polymer doped) [18]	800	Picosecond	2.3×10^{-13}
Present study	800	Picosecond	-7.0×10^{-11}

4. Conclusions

In summary, we have investigated the structural and optical properties of thermally evaporated phthalocyanine thin films as a function of annealing temperature. From the XRD data an increase in crystallinity of ZnTTBPC film for β -polymorphic phase is observed. Annealing at elevated temperature decreases the defects and increased the quality of the film formed. Linear optical studies indicate that the thermal annealing increases the optical energy band gap of ZnTTBPC film. Decrease in the RMS roughness value is observed for annealed ZnTTBPC film. Third order NLO studies on stable, defect less and well oriented β -polymorphic form of film was carried out with ps laser pulses. The Z-scan measurements revealed the presence of RSA type of non-linear absorption and self defocusing type nonlinear refraction in thermally evaporated ZnTTBPC. Our result shows the value of 2PA coefficient obtained for thermally evaporated film stands superior to that obtained for ZnTTBPC in other forms. The nonlinear refractive index shows negative value, indicating self-defocusing nature of the film and hence protecting the sample from any damage. Present study on thermally evaporated β -ZnTTBPC film indicates that the sample is a promising material for NLA and NLR based device fabrication even for comparatively higher temperature applications.

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