Intensity Dependent Third Order Optical Nonlinearity of Zinc-Tetraphenyl Porphyrin Ultrathin film in Nano-Second Regime

Abstract. The third order nonlinear optical properties of 5,10,15,20 Tetraphenyl 21H,23H-porphine zinc (II) (ZnTPP) thin films have been investigated by using single beam Z-scan technique with 6 ns laser pulse operating at 532 nm. The ultrathin films of ZnTPP with the thickness of the order of 120 nm were fabricated by means thermal vacuum coating technique. The UV-Visible spectrum depicts signature absorption curve identifying the enhancement in the symmetry of the molecule from D_{2h} symmetry to D_{4h}, due to the presence of central Zn metal ion. The ZnTPP thin film is exhibiting reverse saturation absorption (RSA) and strong self-defocusing effect. The effective two photon nonlinear absorption coefficients (β_{eff}) and nonlinear refractive index (n_2) obtained at different input on-axis peak intensities (I_0) are of the order of 10^{-6} to 10^{-5} m/W and 10^{-13} to 10^{-11} m^2/W. The decrease in β_{eff} with the increase in intensity indicates that the observed RSA is due to the excited state absorption (ESA) from T_1 triplet state to higher triplet state (T_n).

INTRODUCTION

The increased utilization of high intensity laser beam has rendered great challenges for designing efficient nonlinear optical (NLO) materials for the protection from human exposure and modern day optoelectronic device fabrication[1]. Therefore it is highly essential to explore and evaluate innovative NLO materials for the practical applications. Numerous studies show that, organic-inorganic nano-composites have been found to offer optimum NLO performances for quantum optical applications[2]. Among these, ultrathin films of porphyrins and metalloporphyrins have emerged as promising candidates of NLO materials[3]. Porphyrins are versatile, planar, highly conjugated group of aromatic molecules with the flexibility of engineering its photo-physical properties to the required framework[4]. The ability to fabricate larger assembly of material with well-defined optical nonlinearity is an essential premise for future applications. Taking this into account, in the present work we have fabricated ultrathin film of ZnTPP and evaluated for its NLO characteristics using standard Z-scan technique at different input peak fluencies.

EXPERIMENTAL

5,10,15,20 Tetraphenyl 21H,23H-porphine zinc (ZnTPP) powder procured from Sigma-Aldrich was used without further purification for the fabrication of thin films. The ZnTPP powder was deposited on an ultrasonically cleaned glass substrate using Hindi Hi vacuum thermal coating unit. The ZnTPP powder was sublimated from a molybdenum boat, which was also used as a heating element. The rate of film deposition was maintained at 2.5 nm/s using quartz film thickness monitor, incorporated in the coating unit. Thin films with thickness of the order of 120

nm were developed on the substrate of dimension 37 x 12 x 1 mm, at room temperature under a pressure of 10^{-5} Torr. The UV-Visible absorption spectrum was studied using shimadzu-1800 spectrophotometer. Z-scan studies were carried out using nano-sec Q-switched Nd-YAG laser operating at 532 nm with average power of 1.94 mW.

RESULTS AND DISCUSSIONS

UV-Visible Absorption Spectroscopy

The linear absorption spectrum of the fabricated ZnTPP thin film is depicted in Fig.1. The observed characteristic B and Q absorption bands are ascribed to π-π* singlet transitions between bonding and anti-bonding molecular orbital of the porphyrin ring. The obtained UV-Visible absorption spectrum is in accordance with the earlier reported studies[5].

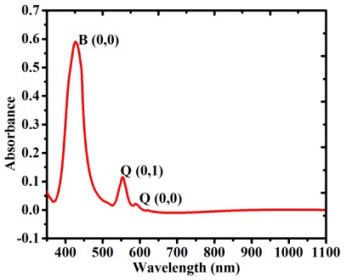

FIGURE 1. UV-Visible absorption spectra of fabricated ZnTPP thin film

Third Order Nonlinear Optical Properties

The third order nonlinear optical properties of the developed ZnTPP thin films were probed by means of single beam Z-scan technique proposed by shiek bahae et al.[6]. Figure 2 depicts the nonlinear transmittance curve of ZnTPP thin film obtained using open aperture Z-Scan experiment.

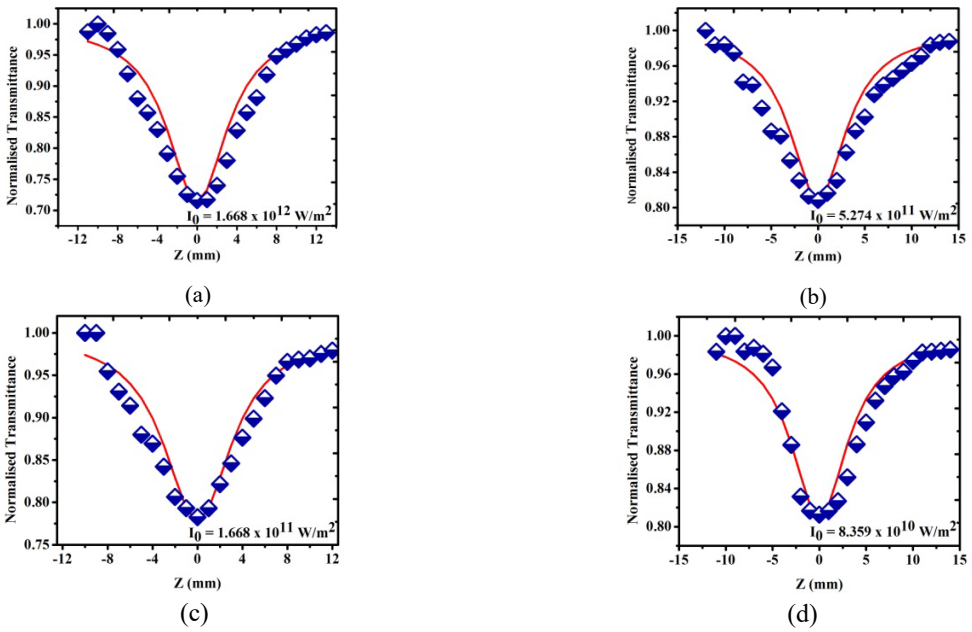

FIGURE 2. Open aperture Z-Scan transmittance curve of ZnTPP film with variable input peak intensities

From the Fig. 2 we observe that due to the strong reverse saturation absorption (RSA) process, the transmittance of the film decreases at focal plane and are close to unity far away from the focal point. The observed nonlinear absorption behavior is attributed to the excited state absorption (ESA) process from the triplet state T_1 to the higher triplet state T_n[7]. The inclusion of the Z_n metal ion into the core of tetraphenyl porphyrin molecule enhances the inter-system crossing from singlet state S_1 to the triplet state T_1 electronic state[8]. Hence the excited-state absorption cross section (σ_{ex}) in the ZnTPP thin film is larger when compared to ground-state absorption cross section (σ_{gr}) at the focal plane (z = 0), which is the characteristic feature observed in RSA materials. The linear transmittance of the film at 532 nm is 94.95 % indicating that the observed NLO phenomenon is due to non-resonance effect. The Rayleigh range (z_0), pulse width, beam waste (ω_0), repetition rate of the z-scan set up were 3.641 mm, 6 ns, 2.484 x 10^{-5} m and 10 Hz respectively.

Figure 3 depicts the nonlinear transmittance signal of ZnTPP thin film obtained for closed aperture Z-scan study. The Z-scan transmittance signal comprising of pre-focal peak followed by the post-focal valley indicates the negative nonlinearity due to the self-defocusing nature of the film[6]. The observed nonlinear refraction behavior of the ZnTPP thin film is attributed to both the thermal and electronic kerr effect[9].

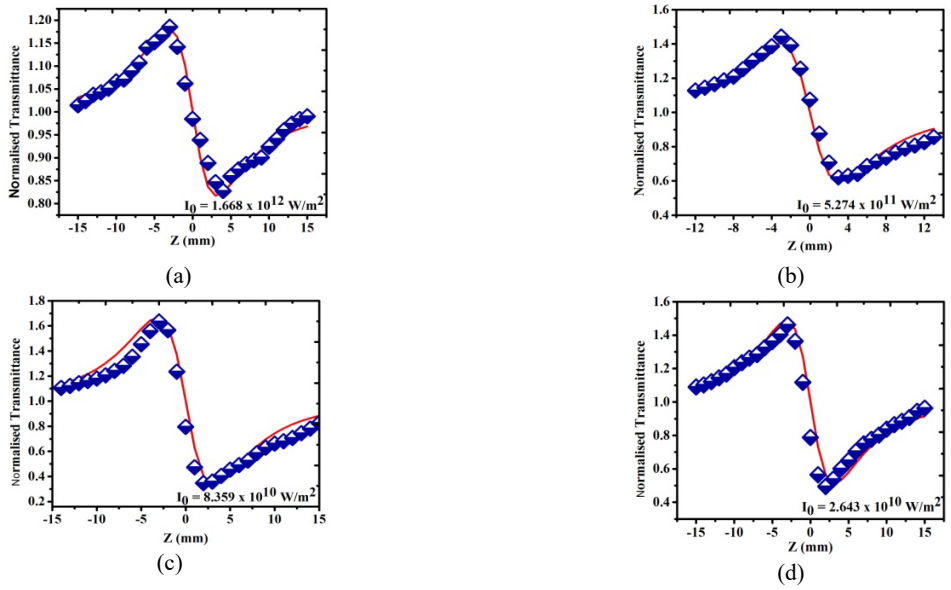

FIGURE 3. Closed aperture Z-Scan transmittance curve of ZnTPP film with variable input peak intensities.

The effective two photon absorption coefficients (β_{eff}) and nonlinear refaractive index (n_2) obtained using open aperture and closed aperture Z-scan measurements at different input peak intensities (I_0) are summarized in table 1. From the table 1, it can be seen that the maximum effective two photon absorption coefficient (β_{eff}) is obtained at an input peak intensity of 8.359 x 10^{10} W/m^2 and at higher intensities the value of β_{eff} reduces. This indicates that the ESA is the dominant process contributing towards the observed RSA. ESA is a sequential two photon absorption process involving real intermediate states, whereas in the two photon absorption (TPA) processes simultaneous absorption of two photons occurs by a material system and is considered to be a weak process due to the presence of virtual intermediate level[10].

TABLE 1. Third order nonlinear optical coefficients of ZnTPP thin film at different input peak intensities

On axis peak input intensity I_0 (W/m^2)	**Effective two absorption coefficient β_{eff} (m/W)**	**On axis peak input intensity I_0 (W/m^2)**	**Nonlinear refractive index n_2 (m^2/W)**
1.668 x 10^{12}	4.9 x 10^{-6}	1.668 x 10^{12}	-4.649 x 10^{-13}
5.274 x 10^{11}	1.03 x 10^{-5}	5.274 x 10^{11}	-3.268 x 10^{-12}
1.668 x 10^{11}	3.8 x 10^{-5}	8.359 x 10^{10}	-3.402 x 10^{-11}
8.359 x 10^{10}	6.5 x10^{-5}	2.643 x 10^{10}	-7.824 x 10^{-11}

CONCLUSION

We have investigated the third order nonlinear optical properties of the ZnTPP ultrathin film fabricated using thermal vacuum coating technique. The ZnTPP thin film demonstrates strong reverse saturation absorption and self-defocusing effect at nano-second regime. The nonlinear optical coefficients (β_{eff} and n_2) were obtained at different input on-axis peak intensities. The decrease in the βeff value with the corresponding increase in the input peak intensity indicates that the observed RSA is due to the sequential excited state absorption process. The obtained results suggest that the fabricated ZnTPP thin film is a promising material for nonlinear optical device fabrication.

REFERENCES

1. M.O. Senge, M. Fazekas, E.G.A. Notaras, W.J. Blau, M. Zawadzka, O.B. Locos, and E.M. Ni Mhuircheartaigh, Adv. Mater. **19**, 2737 (2007).
2. A. Wang, W. Zhao, X. Chen, Y. Yang, W. Zhu, and D. Shang, Dye. Pigment. **157**, 20 (2018).
3. L. Jiang, F. Lu, Y. Gao, Y. Song, H. Liu, H. Gan, T. Jiu, Y. Li, Y. Li, S. Wang, and D. Zhu, Thin Solid Films **496**, 311 (2006).
4. G. de la Torre, P. Vaquez, F. Agullo-Lopez, and T. Torres, Chem. Rev. **104**, 3723 (2004).
5. M. Gouterman, J. Mol. Spectrosc. **6**, 138 (1961).
6. M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, and E.W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).
7. M. Chniti, C. Cassagne, J.L. Godet, and G. Boudebs, J. Nonlinear Opt. Phys. Mater. **24**, 1550030 (2015).
8. K. Tanimura, T. Kawai, and T. Sakata, J. Phys. Chem. **84**, 751 (1980).
9. G. Ao, Z. Xiao, X. Qian, Z. Li, Y. Wang, X. Zhang, and Y. Song, Molecules **20**, 5554 (2015).
10. M. V. Vijisha, V. V. Sini, N.K. Siji Narendran, and K. Chandrasekharan, Phys. Chem. Chem. Phys. **19**, 29641 (2017).