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THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF MAGNESIUM PHTHALOCYANINE THIN FILM BY He-Ne LASER

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ABSTRACT

In the present work, The third order optical nonlinearity and optical limiting properties of Magnesium phthalocyanine (MgPc) thin film have been investigated. Third order optical nonlinearity of MgPc thin film has been studied by z–scan method using a cw He-Ne laser at ~633nm wavelength as an exciting source. The normalized transmission for both open and closed aperture z scan are measured and it is found that the nonlinear absorption in MgPc is mainly due to reverse saturable absorption (RSA) process. The nonlinear refraction studies exhibit the self defocusing behavior of the MgPc thin film and the origin of nonlinear refraction is of thermal nature. The optical limiting study revealed that MgPc thin film shows lower limiting threshold that is very useful for eyes and sensor protection.

Keywords: *Nonlinear Absorption Coefficient, Nonlinear Refraction, Optical Limiting, RSA, Z- Scan*

I. INTRODUCTION

In the last few years, phthalocyanines are being intensively studied as targets for optical switching and optical limiting devices, sensors, light emitting devices, photosensitizers and nonlinear optical materials. These are highly stable and versatile compounds capable of bonding more than 70 different metallic and non-metallic ions in the ring cavity [1, 2]. Another peculiar feature of these compounds is their ability to form different kinds of condensed phases. It is possible to develop thin films of phthalocyanines by several techniques such as spin coating, molecular beam epitaxy and thermal evaporation technique that allow fabrication of practical devices. There are various mechanisms for optical nonlinearity, such as nonlinear refraction, nonlinear absorption (NLA) and induced scattering bur the origin of these nonlinearities vary widely and includes reverse saturable absorption (RSA), two photon absorption (TPA), optically induced molecular re-orientation in liquid crystals and the electronic Kerr Effect [3]. Nonlinear optical properties of ZnPc thin films in PMMA as a substrate at 633nm wavelength has been reported and found to have high 3rd order nonlinear susceptibility value with excellent optical limiting properties [4].

Various experimental techniques namely degenerate four wave mixing [5], nonlinear imaging techniques [6], nonlinear interferometry [7], nonlinear ellipse rotation [8], three wave mixing [9], beam distortion measurement [10] and classical z-scan [11-13] are efficiently used to investigate the nonlinear behavior of materials. Interferometery, DFWM and ellipse rotation are highly sensitive techniques but requires complex experimental setup. Beam distortion measurement requires precise beam scans followed by detailed wave propagation analysis. Single beam z-scan method is a standard tool for determining nonlinear parameters of nonlinear materials because of its simplicity, sensitivity, accuracy and the ease of separation between nonlinear refraction and nonlinear absorption. Z-scan technique involves motion of the sample across the focal plane of laser beam along the direction of propagation of the laser beam. Assuming Gaussian beam optics, this experiment allows an intensity scan of the irradiated sample, and provides information about the nonlinearity in the sample. This results in changing the spot size of the incident beam on the sample to a minimum at the focus and then increasing again on crossing the focus.

MgPc thin films have extensively been studied using femto-second and nano-second pulses for their nonlinear parameters [14]. The purpose of the experiment in the present course of investigation is to determine the variation in transmission as the incident intensity changes by translation along the z-axis. The change in the transmittance of the focusing Gaussian beam in a medium is recorded as a function of position of medium. We have estimated the various nonlinear optical coefficients of MgPc thin film alongwith the optical limiting behavior at low input power.

II. EXPERIMENTAL

The MgPc thin films have been synthesized by standard thermal evaporation technique [15]. Polished borosilicate (BK7) optical glass was used as a substrate, that was cleaned with supersonic method in acetone. A molybdenum boat was used as a heat transfer source. Thin film was deposited at 2.5×10^{-5} mBar pressure and 200^oC substrate temperature. The deposition rate was maintained at 0.3nm/s. Heat treatment was given at 350^oC for 2 hours. Film thickness was measured by stylus profiler (Taylor Hobson) and was found to be 1.2 micron. The absorption spectrum was carried out by using UV-visible spectrophotometer model no. 18-1885-01-0151 with spectral bandwidth of 2nm.

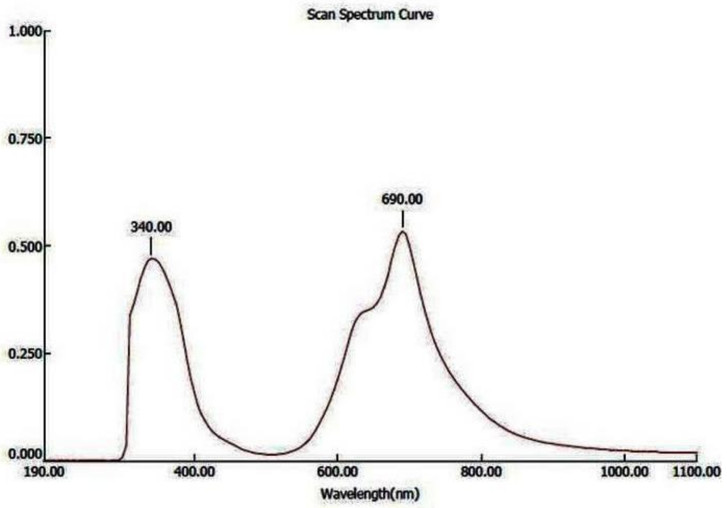

Fig. 1. Linear absorption spectra (UV-VIS) of the MgPc thin film

For the present study, a low power (~30mW) He-Ne laser at ~633nm wavelength was used as the source of optical energy. The beam diameter of the Gaussian output from the laser head was measured to be 2mm. The beam was focused by a combination of convex lenses of equivalent focal length 77mm to a spot size of 32.386 µm with Rayleigh range of 2.45mm. For closed aperture scan, the distance between the focusing lens and the aperture size was adjusted so as to get the optimum value of the linear aperture transmittance ($s = 0.4$), which averages out possible beam non-uniformities, thus reducing background signals and loss in sensitivity. For open aperture (s=1), all the transmitted power was collected and focused on the power detector (OPHIR, 3A-FS-SH).

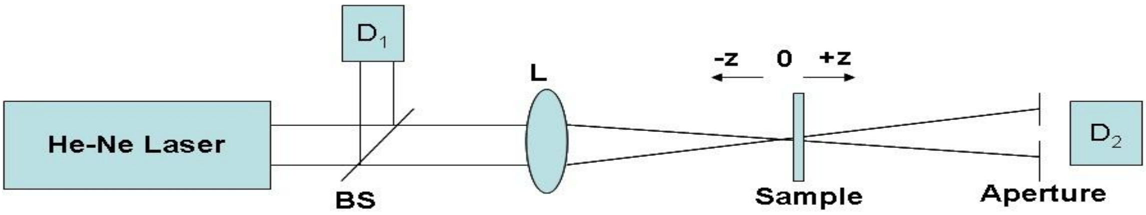

Fig. 3. Schematic diagram of Z- scan experiment (aperture will be removed in open aperture Z scan Experiment)

III. RESULTS AND DISCUSSION

3.1 UV-Visible Characterization

The UV-vis spectrum (Fig. 1) is carried out by spectrophotometer from 190nm to 1100nm wavelength which shows two strong bands, attributed to the π- π* electronic transitions in MgPc, a broad Q band between 600-800nm and a Soret or B-band in the UV region. . The Q- band is much broader and splits in to two components with peak at 690 and 620 nm. It is showing that the periphery of the complex is asymmetrically substituted. This splitting of Q band is attributed to the aggregation of the molecules or molecular disorder which is in agreement with the previously reported in literature [14]. The linear absorbance was found to be $0.351 cm^{-1}$ at a wavelength ~633 nm. Also the transmittance is measured to be 44% at 633nm.

3.2 Z-Scan Measurements

The nonlinear refractive index is measured using the closed aperture z-scan configuration. Fig 4 shows the measured normalized transmittance as a function of Z-position. The closed aperture Z-scan curve exhibit a pre-focal transmittance maximum (peak) followed by a post-focal transmittance maximum (valley) signatures. The peak- valley signature signifies the self defocusing character of the dye molecule, indicating a negative nonlinear refractive index [11]. The theoretical relation of $T - z$ for the closed aperture case is given by [16]

$$T = 1 + \frac{4\Delta\Phi_0 (z/z_0)}{[(z/z_0)^2 + 9][(z/z_0)^2 + 1]} \quad (1)$$

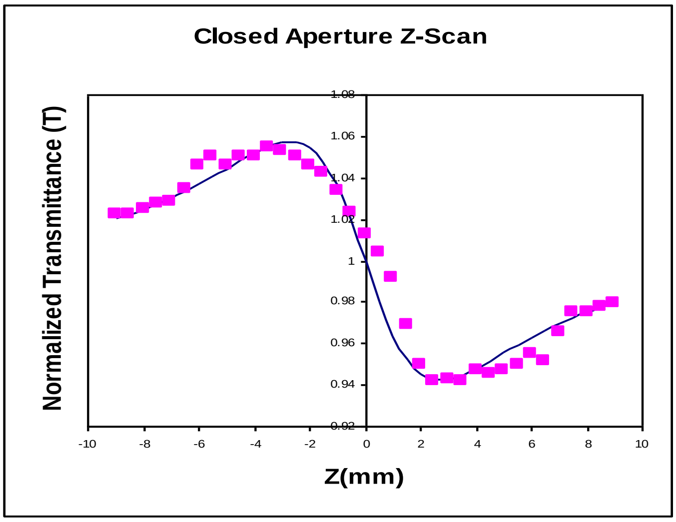

Fig. 4. Closed aperture Z- scan, solid line is showing theoretical fit

The solid curve in fig. 4 is showing the theoretical value of T at corresponding z. Following standard relations are utilized in calculation of nonlinear refractive index [17],

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\Delta\Phi_0 \qquad (2)$$

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff} \qquad (3)$$

Where ΔT_{p-v} is the peak to valley transmittance difference from the closed aperture scan, $\Delta\Phi_0$ is the on-axis nonlinear phase shift and S is the linear aperture transmittance given by $S = 1-\exp\left(-2r_a^2 / \omega_a^2\right)$, where r_a is the aperture radius and ω_a is the beam radius at the aperture in linear regime when kept in far field. $I = 2P / \pi\omega_0^2$ is the peak intensity of the laser beam at focus $(z=0)$ and $L_{eff} = \left(1-e^{-\alpha L}\right) / \alpha$ is the effective length of the sample with α as the linear absorption coefficient and L as sample thickness. λ is the wavelength of interacting laser beam at ~633nm. The origin of nonlinear refraction can be attributed as electronic, molecular, electrostrictive or thermal in nature [18]. The closed aperture Z-scan of MgPc thin film shows a peak to valley separation of ~ 2.5 z_0 and a peak- valley separation of more than 1.7 times the Rayleigh range z_0 is an indication of thermal nonlinearity and hence the observed nonlinear effect is a third order process [19].

From the best fit of equation 1 to the experimental data in fig. 4, the value of $\Delta\Phi_0$ is obtained as 0.285. The estimated value of n_2 for MgPc thin film is ~0.943 × 10^{-5} cm^2/W.

Open aperture z-scan is used for calculating nonlinear absorption coefficient β. Fig. 5 shows the normalized transmission T as a function of the distance z-along the lens axis in the far field. It is worth noting the bleaching effect in cyanine group of dyes is quite high and this bleaching of ground singlet level leads to an overall increase in absorption coefficient due to incident optical energy. Metal phthalocyanines (MPc's) are widely researched because the spin orbit coupling enhances the population of the triplet state due to the metal atom effect. Due to metal atom at the center, there is an increase in intersystem crossing and hence the populations at triplet state increases, that further enhances the possibility of reverse saturable absorption (RSA) effect, improving the nonlinear response [20-21].The theoretical relation between T and z for the open aperture configuration is given by[22],

$$T = 1 - \frac{q_0}{2\sqrt{2}(1 + z^2 / z_0^2)} \tag{4}$$

Where $q_0 = \beta I_0 L_{eff}$ with z_0 as the Rayleigh range.

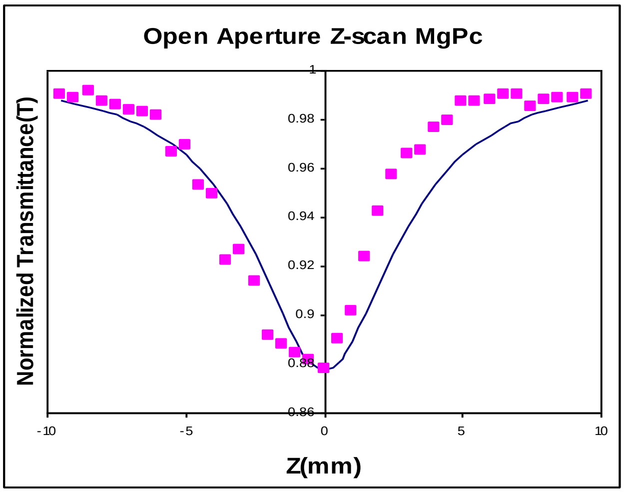

Fig. 5. Open aperture z-scan, solid line is showing theoretical fit

From the best fit of equation 4 to the experimental data in fig. 5, the value of q_0 is obtained as 0.346. Hence by using all known parameters we have calculated the nonlinear absorption coefficient β of MgPc and is found to be 1.135 cm/W.

The real and imaginary part of third order nonlinear optical susceptibility $\chi^{(3)}$ has been calculated from the estimated values of n_2 (closed aperture scan) and β (open aperture scan) using following relations [11],

$$\mathrm{Re}[\chi^{(3)}] = 10^{-4} \frac{\varepsilon_0 n_0^2 c^2}{\pi} n_2 \tag{5}$$

$$\mathrm{Im}[\chi^{(3)}] = 10^{-2} \frac{\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \beta \tag{6}$$

$$\chi^{(3)} = \sqrt{(\mathrm{Re}\,\chi^{(3)})^2} + \sqrt{(\mathrm{Im}\,\chi^{(3)})^2} \tag{7}$$

Where ε_0 is the permitivity of free space, c is speed of light in vacuum and n_0 is the linear refractive index of the sample. The third order nonlinear susceptibility calculated for MgPc thin films using above relations is ~1.22×10^{-6}esu.

3.3 Optical Limiting

Optical limiting properties of magnesium phthalocyanine have been studied using He Ne laser at ~633nm (Fig. 8). With low input optical energy, the output energy was showing linear relationship by obeying Beer- Lamberts rule. As the input incident energy reaches a threshold value, input output energy relationship becomes nonlinear.

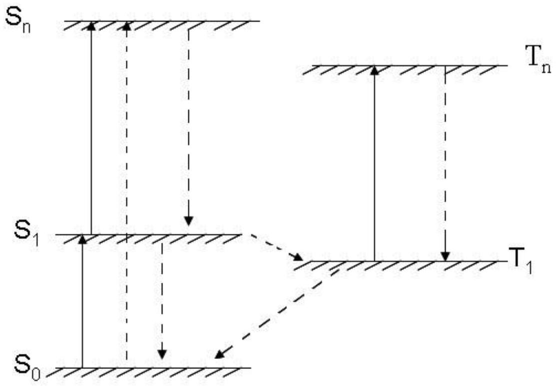

Fig. 6 The five level energy diagram of a typical dye molecule, radiative and noradiative transitions are indicated by solid and dotted lines respectively

On the basis of the energy level diagram, the optical limiting effect of phthalocyanine molecule is explained as follows: initial photons excitation populates S_1 that can go to the 2^{nd} excited singlet level S_n. The life time of this singlet upper energy level is very short these relax back to the S_1 state via non-radiative transition. From S_1, the first triplet state T_1 is populated via intersystem crossing with a time constant τ_{ST}. Successively a 2^{nd} photon excites the molecule from T_1 to the excited state T_n. Because of the introduced metal ion in the ring cavity, the increasing strength of spin orbit coupling enhances intersystem crossing rate, excited state absorption and triplet population number. If the absorption cross section of the excited state is larger than that of the ground state, it is called RSA process. Under CW excitation, the thermal effect will increase the excited state absorption, inferring that ESA assisted RSA is the nonlinear mechanism responsible for the optical limiting behavior of the magnesium phthalocyanine [23].

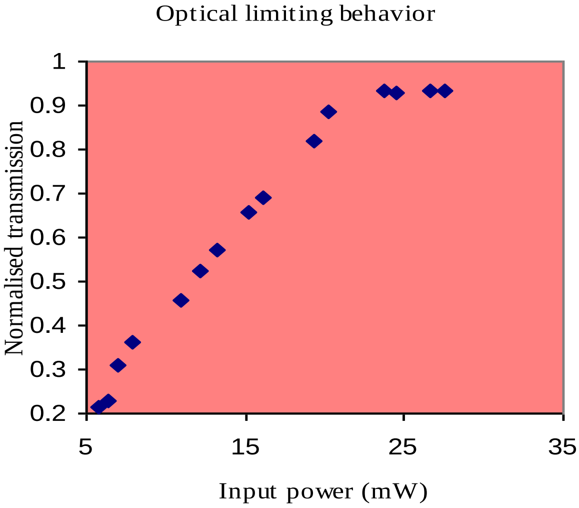

Fig. 8 Optical limiting characteristics of MgPc at 633 nm wavelength of He-Ne laser

IV. CONCLUSION

We have investigated the nonlinear optical coefficients of MgPc thin film with low power He-Ne laser at ~633 nm wavelength. Nonlinear refractive index n_2 is calculated and found to be 0.943 × 10^{-5} cm^2/W. Third order nonlinear susceptibility $\chi^{(3)}$ has also been calculated and found to be 1.22×10^{-6}esu. β is calculated to be 1.135cm/W. It is observed that there is high nonlinear absorption effect (Im $\chi^{(3)}$ >> Re $\chi^{(3)}$). The overall high nonlinearity of these MgPc molecules results due to strong absorption at ~633nm combined with a high thermo optic coefficient. It is worth noting that the value of $\chi^{(3)}$ for magnesium phthalocyanine thin film is larger than those of some representative 3rd order nonlinear materials such as organic polymers and organic metals [24-25]. Optical limiting behavior of MgPc was studied by transmission measurement technique at low input optical power of He-Ne laser. Limiting threshold for MgPc is estimated to be around 20mW. It inferred that MgPc is a potential candidate for the optical limiting applications at low optical powers.

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REFERENCES

[1] M.C. Larciprete, R. Ostuni, A. Belardini, M. Alonzo, Nonlinear optical absorption of zinc-phthalocyanines in polymeric matrix, Photon, Nanostructures,2007, 5(2-3), 73-78

[2] R.S.S. Kumar, S. Venugopal Rao, L. Giribabu, D. Narayana Rao, Femtosecond and nanosecond nonlinear optical properties of alkylphthalocyanines studied using Z-scan technique, Chem. Phys. Lett., 447 (2007) 274-278

[3] Dan T. Nguyen,, Chuanxiang Sheng, Jayan Thomas, Robert Norwood, Brian Kimball, Diane M. Steeves, Nasser Peyghambarian, Observation of nonlinear transmission enhancement in cavities filled with nonlinear organic materials, Applied optics, 47, 2008, 5777-5783

[4] S. J .Mathews, S. Chaitanya Kumar, L. Giribabu, Nonlinear optical and optical limiting properties of phthalocyanines in solution and thin films of PMMA at 633 nm studied using a cw laser, Materials Letters, 61, (2007) 4426-4431

[5] R. Sai Santosh Kumar, S. Venugopal Rao, L. Giribabu, D. Narayana Rao, Ultrafast nonlinear optical properties of alkyl phthalocyanines investigated using degenerate four-wave mixing technique, Optical Materials, 31 (2009) 1042–1047

[6] G. Boudebs, M. Chis, J P Bourdin, Third-order susceptibility measurements by nonlinear image processing, Journal of Optical Society of America B, 13, (1996) 1450-1456

[7] Parinda Vasaa, B.P. Singh, Praveen Tanejaa, Pushan Ayyub, Antiresonant ring interferometry as a sensitive technique for measuring nonlinear optical properties of thin films, Optics Communications, 233 (2004) 297–304

[8] Zhi-Bo Liu, Xiao-Qing Yan, Jian-Guo Tian, Wen-Yuan Zhou, Wei-Ping Zang, Nonlinear ellipse rotation modified Z-scan measurements of third-order nonlinear susceptibility tensor, Optics Express, 15 (2007) 13351-13359

[9] R. Adair, L. L. Chase, S. A. Payne, Nonlinear refractive-index measurements of glasses using three-wave frequency mixing, Journal of Optical Society of America B, 4 (1987) 875–881

[10] W. E. Williams, M. J. Soileau, E. W. Van Stryland, Optical switching and n_2 measurements in CS_2, Optics Communication, 50 (1984) 256–260

[11] Sheik- Bahae M, said A A, wei T H, Hagan D J, Van Stryland E W, Sensitive measurement of optical nonlinearities using a single beam, IEEE Journal of Quantum Electronics, 26 (1990) 760-769

[12] S.J. Mathews , S. Chaitanya Kumar , L. Giribabu, S. Venugopal Rao, Large third order nonlinear optical and optical limiting properties of symmetric and unsymmetrical phthalocyanines studied using Z-scan, Optics Communications, 280 (2007) 206–212

[13] S. Venugopal Rao, N. Venkatram, L. Giribabu, and D. Narayana Rao, Ultrafast nonlinear optical properties of alkyl-phthalocyanine nanoparticles investigated using Z-scan technique, Journal of Applied Physics, 105 (2009) 053109(1) - 053109(6)

[14] Jun Mi,Lijun Guo, Ye Liu, Weimin Liu, Excited-state dynamics of magnesium phthalocyanine thin film, Physics Letters A,2003, 310 486-492

[15] Mohammed T. Hussein, Eman M. Nasir, Addnan H. Al-Aarajiy, Structural and surface morphology analysis of nickel phthalocyanine thin films, Advances in Materials Physics and Chemistry 3, 2013,113-119

[16] R. de Nalda, R del Coso, J. Requejo-Isidro, Limits to the determination of the nonlinear refractive index by the Z-scan method , J. opt. Soc. Am. B , 2002, Vol. 19, No.2

[17] Sheik-Bahae M, Said A A, Stryland E W V, High-sensitivity, single-beam n_2 measurements, Opt. Lett.,1989, 14 955

[18] Nagaraja K K, Pramodini S, Nagaraja H S and Poornesh P, Effect of annealing on the structural and nonlinear optical properties of ZnO thin films under cw regime, J. Phys. D Applied Phys., 2013, 46 055106

[19] Pramodini S, Poornesh P, Sudhakar Y N and Selva Kumar M, $\chi(3)$ and optical power limiting measurements of Polyaniline and its derivative Poly (o-toluidine) under CW regime, Opt. Commun.,2013, 293 125

[20] B. Derkowska, M. Wojdyla, R. Czaplicki, Influence of the central metal atom on the nonlinear optical properties of MPcs solutions and thin films, Optics Communications, 274 (2007) 206-212

[21] Shirk J.S., Lindle J.R., Bartoli F.J., Kafafi Z.H., Snow A.W. and Boyle M.E., Third-Order Nonlinear Optical Properties of Metallo-Phthalocyanines, Journal of Nonlinear Optical Physics & Materials, 1 (1992) 699-726

[22] Eric W. Van Stryland, Mansoor Sheik- Bahae (M. G. Kuzyk and C. W. Dirk, Eds., Marcel Dekker, Inc.), Characterization techniques and tabulations for organic nonlinear materials 1998, 655-692

[23] Pramodini S, Poornesh P, Third-order nonlinear optical studies of anthraquinone dyes using a CW He–Ne laser, Laser Phys. 2014, 24 055402

[24] A. Clementi, N. Chiodini, A. Paleari, Cubic optical nonlinearity in nanostructured SnO_2:SiO_2 , Applied Physics Letters, 84 (2004) 960-962

[25] Kumar, G. Ravindra**,** Rajgara F.A.**,** Z-scan studies and optical limiting in a mode-locking dye, Applied Physics Letters, 67 (1995) 3871-3873