Study of spatial rings in TPPOH₄ doped in boric acid glass

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Abstract. Single beam optical nonlinearity is studied in TPPOH₄ doped in boric acid sandwiched films between two microscope glass slides at three different molar concentrations (4x10⁻⁴ M, 1x10⁻⁴ M, 5x10⁻⁵ M). It shows absorption peak at 700nm with bandwidth of 70nm. We have used diode laser output at 671nm to probe resonant optical nonlinearities. We have observed interesting phenomena of formation of spatial concentric rings centered on the z-axis of the sample. To our knowledge this is first such observation of spatial rings in these systems. We have carried out studies to separate the contribution to the ring formation due to absorptive/refractive optical nonlinearity and the thermal nonlinearity.

1. Introduction
The phenomenon of spatial ring as nonlinear optical phenomenon has been long since a subject of study in different media like gases and solids [1-7]. The rings were observed as the incident intensity increases beyond certain threshold value. Various explanations have been put forward to understand the phenomena in respective media. The spatial concentric rings of same wavelength can occur because of thermal/absorptive optical nonlinearity or due to both. When medium interacts with the optical field in the non-resonant case, the rings pattern observed is primarily due to thermal in origin. In the case of resonant irradiation we could observe the rings pattern only beyond the threshold intensity which could be attributed to the changes in the intensity dependent nonlinear optical complex refractive index as well as due to thermo-optic coefficient.

S. D. Durbin et al (1981) [1,2] observed rings pattern in the transmitted laser beam, when the irradiation intensity of linearly polarized cw Argon ion laser was above 130 W/cm² on the thin film 4-cyno-4'-phenyl-biphenyl (5CB) nematic liquid crystal. They observed that the rings are formed beyond the threshold intensity which coincides with threshold intensity of Fredericksz transition. They further observed that the width of the rings decreases as we move towards the center of the ring pattern. R. Sohrab and N. M. Lawandy [3] theoretically predicted central dark zone formation in pink ruby rod when excited with laser lines from with Argon-ion and dye lasers. Martine Le Berre et al [4] theoretically explained spatial ring formation in cw lasers due to dense absorbing gaseous media. Dense gaseous medium gives conical emission for nearly resonant high intensity laser beams [5-7]. S.J. Mathews et al also observed spatial rings in Phthalocyanines[8].

2. Sample preparation and characterization

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Organic dye doped in an inorganic host like boric acid glass have been well studied for quite some
now. The idea of using organic dyes like porphyrin molecules, (which has large absorption cross-
section in the visible band) doped in boric acid glass films helps lower the saturation intensities. This
helps us to investigate numerous nonlinear optical phenomena at lower power level. For our study we
have chosen TPPOH$_4$ doped in boric acid glass sandwiched between two glass slides at three different
molar concentrations ($4 \times 10^{-4}$M, $1 \times 10^{-4}$M, and $5 \times 10^{-5}$M) with corresponding thickness of
$176 \pm 5 \times 10^{-6}$ m, $242 \pm 18 \times 10^{-6}$ m, $153 \pm 5 \times 10^{-6}$ m as our nonlinear medium. Samples were prepared by melt
quenching method. The absorption spectra of all the sandwiched films were recorded using (HR 4000)
ocean optics UV-visible spectrometer with resolution of 0.23 nm in the range 200-1100. The dye free
boric acid film was taken as the reference. We observed two absorption peaks at near at 445 nm and
700 nm with bandwidth of 72.5nm and 66nm respectively for $4 \times 10^{-4}$M concentration as seen in figure
1. It shows emission peak at 752nm with Stokes shift of 52nm. We have used diode laser output at
671nm to probe resonant optical nonlinearities

![Absorption spectrum of TPPOH$_4$ doped in boric acid](image)

3. Experimental procedure

The experimental setup is in single beam z-scan geometry where the sample is translated along the z-axis for varying intensity as function of position on the axis beyond the focusing lens. It is set in the
tight focusing geometry by using lens of focal length 10cm with completely filled aperture with expanded laser beam of 1.5in to achieve the smallest spot-size of 3.8µm and peak intensity of $8.4 \times 10^8$
W/m$^2$. Laser power of 150mW at 671nm from Diode Laser (Model SDL-671-120T) having a Gaussian TEM$_{00}$ mode is used. Z scan measurements for both open and closed aperture case are carried out for
all the samples studied. Z scan plots were obtained after correcting for fluctuations in the laser power by
way normalizing (D2) with that of the power monitored through the reference arm of the setup
(D1). Reverse saturable absorption is clearly seen in case of the open aperture data wherein the
transmission decreases as the intensity increases as it approached the beam waist. The change in
transmission is more for higher concentrations. Closed aperture data shows the typical signature of
negative optical nonlinearity with peak followed by valley. The asymmetry in the peak height as
compared to valley depth is due to the presence of reverse saturable absorption which enhances the
valley depth and reduces the peak height.

3.1 Data analysis

Open aperture data collected the z-scan open and closed aperture data of TPPOH$_4$ at three different
concentrations are as shown in figure 2. From open aperture data we confirm that our sample has
reverse saturable absorption behavior at all three concentrations of interest and this property is
increasing with increasing concentration. Closed aperture data tells that sample has negative nonlinear refractive index because of peak followed by valley. The nonlinear refractive index ($n_2$) of samples because of thermal and optical nonlinearity at three different concentrations were estimated as $5.07\pm0.13\times10^{-5}$ cm$^2$/W, $1.84\pm0.04\times10^{-6}$ cm$^2$/W, $9.13\pm0.11\times10^{-6}$ cm$^2$/W and corresponding third order susceptibilities ($\chi^{(3)}$) estimated to be $3.27\pm0.19\times10^{-7}$ cm$^2$/V$^2$, $1.18\pm0.05\times10^{-8}$ cm$^2$/V$^2$, $5.89\pm0.07\times10^{-7}$ cm$^2$/V$^2$. These nonlinear refractive indices, which we measured through above process originated from optical and thermal nonlinear process. The thickness of these sandwiched films is by estimated by finding the first zeroes of the degenerate four wave mixing signal [9].

Figure 2. Normalized transmittance of Z Scan data in (a) Open aperture mode and (b) Closed aperture mode of TPPOH$_4$ doped in boric acid glass with different molar concentrations viz (○)$9.7\times10^{-5}$M (□)$3.9\times10^{-4}$M (Δ)$4.8\times10^{-5}$M.

3.2 Analysis of rings
During the Z scan experiment in these samples we observed spatial rings, of alternate dark and bright intensity, which seems to depend upon the position of the sample on the z-axis and hence the intensity. We performed the same z-scan with dye free boric acid films and did not observe any rings in the transmitted beam profile. From this we conclude that TPPOH$_4$ is only responsible for the rings formation. The rings thickness is decreasing from first ring to nth ring as we move radially outwards. Size of the rings & number of rings are only dependents on the beam spot size. Once the rings are formed at a given spot size it seems that changing the intensity levels, while keeping the spot size same does not changes the ring pattern in terms of number and size of rings formed. Possibly we can say that once the rings are formed it is kind of semi permanent in nature. The onset of ring formation at the threshold intensity of the TPPOH$_4$ sample for all three different concentrations samples were measured to be $1.35\times10^5$ W/m$^2$, $2.89\times10^5$ W/m$^2$ and $2.25\times10^5$ W/m$^2$. Further we observe that the rings so formed would take about 10 hours to disappear after the laser irradiation is stopped. Figure 3 shows the rings pattern pictures in the transmitted intensity of TPPOH$_4$ at molar ratio $3.9\pm0.02\times10^{-4}$M.
Figure 3. Observed rings in the transmitted intensity of TPPOH$_4$ (3.9±0.02×10$^{-4}$M) doped in boric acid glass at intensity of (a) 1.63×10$^{10}$W/m$^2$ (b) 1.21×10$^{8}$W/m$^2$ (c) 1.22×10$^{6}$W/m$^2$

We modulated the input intensity by help of mechanical chopper and observed no rings as the chopping frequency is increased beyond 1600 Hz, 1300Hz and 1400 Hz for the 4 x 10$^{-4}$M, 1 x 10$^{-4}$M, 5 x 10$^{-5}$M samples respectively. As seen in the figure 4 at 60 Hz chopper frequency we could see the thermal decay and at 850 Hz there was no thermal decay in the transmitted pulse. Rings were observed at both these frequencies in the sample with 4x10$^{-4}$M of TPPOH$_4$ doped in boric acid glass.

Figure 4. Temporal variation of thermal nonlinearity with modulating frequency at (a) 60Hz (b) 850Hz in the sample with 4x10$^{-4}$M of TPPOH$_4$ doped in boric acid glass.

We have done the z-scan closed aperture for rings pattern. We maintained the aperture size in such a way that the central spot of rings passes through the aperture. The z-scan has been carried out different chopping frequencies when the rings were formed. Figure 4 is the snapshot for two chopping frequencies, both at low and high frequency. In figure 5 the low frequency curve is due to combined thermal and optical nonlinearity [T$_1$] and high frequency curve [T$_2$] gives the estimate of optical nonlinearity. T$_1$-T$_2$ transmittance curve gives the effect of thermal nonlinearity. We have measured optical nonlinear refractive indices ($n_2$) from the graphs as 2.29±0.06×10$^{-7}$ cm$^2$/W, 4.42±0.06×10$^{-7}$ cm$^2$/W, 1.04±0.01×10$^{-6}$ cm$^2$/W and corresponding susceptibilities are 1.82±0.52×10$^{-9}$ cm$^2$/V$^2$, 3.52±0.05×10$^{-9}$ cm$^2$/V$^2$, and 8.30±0.15 × 10$^{-9}$ cm$^2$/V$^2$. Thereby we have succeeded in estimating the contribution of thermal and optical nonlinearity in the formation of the rings. More study are underway to understand the exact mechanism of these phenomena.
Figure 5. Closed aperture Z-Scan of TPPOH$_4$ at three different concentrations of for low (54Hz) and high (1300 Hz) chopping frequencies.

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