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Enhanced Third Order Nonlinear Optical Properties of Methyl Orange Dye Doped Potassium Penta Borate Octa Hydrate (MOPPB) Single Crystals Using CW Diode Laser for Optical Limiting Applications

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Abstract

Single crystals of pure (PPB) and methyl orange dye doped Potassium Penta Borate octa hydrate (MOPPB) are grown by slow evaporation technique at ambient conditions. Single crystal X-Ray Diffraction study verifies the orthorhombic family of both pure and MO doped PPB crystals. FTIR assures the incorporation of MO dye into PPB crystals. The Reverse Indentation Size Effect (RISE) behavior and soft nature of both pure and MO doped PPB crystals are verified by the Micro Hardness Study. Absorbance studies shows PPB possess lower cut-off wavelength at 190 nm due to π - π^* transitions whereas MOPPB crystals have two peaks, one at 278.60 nm due to π - π^* transitions and the second one at 464.65 nm due to n - π^* transitions. The inclusion of MO dye molecules alters the band structure resulting in reduction of bandgap to 5.7 eV (MOPPB) from 5.91 eV (PPB). Kurtz powder test shows green emission in both pure PPB and MOPPB with relative SHG efficiency of 0.45 times and 0.40 times that of SHG output of KDP. Z-scan studies performed with 785 nm laser excitation exposes that both pristine and MO doped PPB crystal exhibit reverse saturable nonlinear absorption and self-focusing nonlinear refraction which is thermo-optic in origin. Two photon absorption induced optical limiting action is demonstrated in both PPB and MOPPB crystals. Increase in NLO coefficient due to MO dye confirms the superiority of MOPPB than PPB for optical limiting applications.

Key Words: Single crystal study, FTIR, Micro Hardness study, Z-scan study and optical limiting behavior.

1. Introduction

Nowadays, nonlinear optical (NLO) materials are overwhelmingly explored because of their dynamic and vibrant applications in telecommunications, optical switching, optical modulation, 3-D optical memory devices, optical limiters etc., [1]. For the past three decades, these NLO materials are attracting the scientific community for the generation of short wavelength lasers using second and third harmonic generation phenomenon [2-4]. With horizon of laser wavelength expanding very rapidly, one alarming fact of laser is that they can easily damage photosensitive components including human eyes [5]. So in recent years, utilization of organic NLO materials are no longer limited to production of laser through harmonic generation, but also in addressing the solution for laser accidents [6-8]. Laser safety devices that functions on NLO phenomenon are generally called as optical limiters which exhibits transparency at low powers and turns opaque at high incident intensities. Regardless of the input power magnitude, these optical limiters are designed to maintain irradiance, power, fluence or energy transmitted by an optical system below some specified maximum value. Fabrication and testing the performance of optical limiters made of organic, inorganic and semiorganic materials are under recent limelight. Among them, organic azo dyes are interesting as they possess broad spectral response and high nonlinear absorption coefficients. Azo dyes contain organic compounds which contain the colouring agent (N=N) possessing the functional group R-N=N-R' where R' and R are aryl groups. When these dyes are doped into the host materials, they show improved nonlinear optical absorption phenomena such as Saturable Absorption (SA), Reverse Saturable Absorption (RSA), etc., [9-10]. In the choice of host material, inorganic borates such as Potassium Penta Borate octa hydrate (PPB) are potential candidate as they possess high mechanical and thermal stability along with high NLO coefficients [11-14]. PPB is basically a transparent material and is highly transparent to visible region. Hence addition of organic dyes like Methyl orange (MO) can avail interesting visible absorption to the host and these change in band structure can influence the nonlinear absorption behavior of the system [15-20]. Methyl Orange dyes find wide applications in light emitting diodes, organic semiconductors, photo voltaic devices, thermal printing, biology, medical fields as wound healing, photo dynamic therapy, pharmaceutical chemistry, etc., [21]. Also the chromophore of MO shows excellent nonlinear optical behavior especially Reverse Saturable Absorption [9-10]. The molecular structure of Methyl Orange is shown in Fig. (1). This article reports the preparation and characterization of pure (PPB) and methyl orange doped potassium penta borate (MOPPB) for the

optical limiting applications for the first time. Under CW Diode laser of 785 nm wavelength excitation, both the materials exhibit optical limiting action exposing their suitability for laser safety devices.

2. Crystal Growth and Structural Confirmation

Commercially available Potassium Penta borate octa hydrate ($B_{10}H_{16}K_2O_{24}$) and Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) were taken for the reaction. Saturation point at room temperature was noted to grow the pure PPB single crystals. For MOPBB the doping concentration was taken in the ratio of 1:0.05M. pH of both pure PPB and MOPBB solutions were maintained at 7 and 5, respectively. After 4 hours of vigorous stirring both the solutions were filtered and sealed with perforated sheet and left undisturbed for slow evaporation at ambient condition. Fig.2 (a) & (b) shows the harvested pure and MO doped PPB single crystals after a period of 35 and 45 days, respectively. The pristine crystals and doped PPB were subjected to single Crystal X-ray Diffraction (XRD) studies using an ENRAF NONIUS CAD4 X-Ray Diffractometer with a MoK_{α} radiation ($\lambda=0.71073\text{\AA}$). The unit cell parameters for pure PPB and MO doped PPB are tabulated in Table 1. The obtained results were in good agreement with reported literature [22]. It was also clear from the changes seen in the unit cell parameter and volume that MO entered successfully into the crystal lattice of the parent material without any change in the crystal structure.

Molecular structure and the functional group associated with grown crystals were identified by Perkin–Elmer Fourier Transform Infrared (FTIR) spectrometer. The recorded FTIR spectra of pure and MO doped PPB crystals are shown in Fig. 3 and it gives the necessary information about the molecular arrangements of the crystals. The strong and broad band associated with the stretching vibrations of the hydroxyl group with strong hydrogen bonding appears at 3444 cm^{-1} [23]. Also, the peak at 3378 cm^{-1} is due to the O-H stretching vibrations [24]. The C-H stretching vibration is characterized at 3062 cm^{-1} [25]. The C-H stretching mode vibrations due to MO appear at 2669 cm^{-1} [18]. The peak at 1844 cm^{-1} is due to the stretching vibrations of CO band [26]. NH_2 in plane deformations are characterized at 1653 cm^{-1} and 1434 cm^{-1} [27]. The peak at 1358 cm^{-1} is due to C-CH in-plane deformations [28]. The B-O stretching vibrations of BO_3 is confirmed by the peak at 920 cm^{-1} . Moreover the wagging of N-H vibrations are confirmed from the peaks at 782 cm^{-1} , 765 cm^{-1} and 734 cm^{-1} [29]. OBO terminal bending and ring bending vibrations are

assured by the peaks at 590 cm^{-1} and 508 cm^{-1} . The spectral band assignments of MO doped PPB crystals are shown in Table 2.

3. Mechanical Stability

Mechanical stability of the crystals was tested under Vickers Microhardness Tester (Shimadzu HMV-2). Both PPB and MOPPB crystals were subjected to three loads 25, 50 and 100 g and the corresponding hardness value were plotted. Also, the direct variation of stress and strain relating to the stiffness constant can be calculated from the Wooster's relation [30-32]. The Vicker's Hardness number can be calculated using the formula $H_V = \frac{1.8544P}{d_2} \text{ kg/mm}^2$. Measure of Hardness value could easily say the measure of resistance to the permanent deformation or damage. This mechanical stability of the grown bulk material depends on structure, lattice energy, binding energy, interatomic spacing and Debye temperature. Also, it is closely related to the elastic constants, yield strength and stiffness constant [22]. From Fig. 4, it can be observed that the hardness number gradually increases with the applied load. Both pure PPB and MOPPB show the increase of hardness number with applied load thereby proving the Reverse Indentation Size Effect (RISE) [30]. On doping PPB with MO there was a clear improvement in the hardness number. This is because, MO dye being a large molecule gets filled up in the voids of the PPB crystal structure resulting in a compact lattice. The deforming capacity of both the crystals was observed to decrease on increasing loads above 100g which resulted in crack formation. Heavier load dislocates the lattice and cracks are developed on the crystal surface. The Meyer's index for Pure PPB is 1.6 and that of MOPPB is 2. Hence, both the crystals belong to the soft nature and can be utilized for laser safety devices.

4. Linear optical study

The absorption and the transmission spectra of PPB and MOPPB were studied between wavelengths 200-1200 nm using Perkin-Elmer UV-visible spectrometer. The optical bandgap of both pure PPB and MOPPB crystals can be calculated by the following formula $E_g = \frac{1.243 \times 10^3}{\lambda_{max}}$. The inter and intra molecular hydrogen bonding between the Methyl Orange dye and the OH groups in the host molecule PPB could be easily identified by the UV-Vis absorption spectroscopic studies. The recorded transmission spectra of pure PPB and MOPPB crystals are shown in Fig. 5. From the figure, the lower cut-off wavelength of pure PPB was found at 190 nm [22] due to π - π^*

transitions whereas MOPPB crystals have two peaks, one at 278.60 nm due to π - π^* transitions and the second one at 464.65 nm due to n - π^* transitions [33]. This confirms the addition of host molecule in the parent material. It is known that the MO dye contains one azo group and two phenyl rings. This azo group acts as a bridge between two phenyl rings and the OH-BO groups of the borate molecule [20]. This modifies the optical properties of the PPB crystals. Hence the inclusion of MO dye molecules introduces the additional energy levels between the valence band and conduction bands [20-21]. Because of this the bandgap of MOPPB crystals is decreased to 5.7 eV from 5.91 eV which is for pure PPB. Hence, alteration in band structure along with change in visible absorption is observed in MOPPB crystals.

5. Nonlinear Optical Behavior

5.1 SHG Study

Kurtz-Perry Technique was equipped to study the second harmonic generation employing the Q-Switched Nd:YAG laser of wavelength 1064 nm. In the SHG Study, Potassium Dihydrogen Phosphate (KDP) was taken as a reference whose SHG signal output was 70 mV. The recorded output of pure and MO doped PPB crystals were found to be about 32 mV and 28 mV respectively. Thus, Pure PPB is 0.45 times and MO doped PPB is 0.40 times that of SHG output of KDP. The decrease in output of MO doped from that of pure PPB might be due to the self-absorption of the input 532 nm wavelength by the doped material itself [24]. This can be well correlated readily by the absorption peak at 532 nm wavelength from the Fig. 5. Hence we could clearly observe that doping of MO in PPB shows some serious changes in the SHG efficiency.

5.2 Z-Scan and Optical Limiting Study

The nonlinear absorption (NLA) and nonlinear refraction (NLR) along with third order NLO susceptibility of pure PPB and MO doped PPB were determined from open aperture (OA) and closed aperture (CA) Z-scan experiment respectively. The continuous wave laser beam with 785 nm wavelength having peak power of 50 mW was focused and passed through the grown material. The sample was moved on the sample stage from the source to the detector along the direction of beam propagation. The transmittance of the beam was recorded at far-field for various positions of the sample with and without aperture in front of the detector. Then the graph was drawn between the transmittance and position of the sample. In general, nonlinear absorption arises due to various phenomenon like saturable absorption (SA), reverse saturable absorption (RSA) that originates

from two photon absorption (2PA), multiphoton absorption (MPA), excited state absorption (ESA) or free carrier absorption (FCA)[36]. Here, valley-like OA curve (Fig. 7) of pure and MO doped PPB exposes the existence of reverse saturable absorption (RSA). To validate the observed nonlinearity and identify the mechanism responsible for nonlinear absorption, the experimental data were fitted with the theoretical equations given in Sheik-bahae formalism for an open aperture,

$$T_{nPA} = 1 / \left[1 + (n - 1) \beta_n L \left(\frac{I_0}{1 + \left(\frac{z}{z_0}\right)^2} \right)^{n-1} \right]^{\frac{1}{n-1}},$$

where, β_n is the nonlinear absorption coefficient, n is order of the nonlinear absorption ($n = 1, 2, 3, \dots$), L is the effective thickness of the sample, I_0 is the incident intensity of the laser beam at the focal point and $\left(z_0 = \frac{\pi \omega_0^2}{\lambda}\right)$ is the Rayleigh length[37]. The theoretical plots (solid line) matched very well with the experimental fits (solid circle) for two photon absorption equation. Thus both pure and MO doped PPB crystals exhibit two-photon absorption. Here as the mode of excitation is CW, observed nonlinearity is mostly thermo-optic in origin. And the presence of near-resonant energy states close to excitation wavelength have created sequential 2PA involving thermally induced excited state absorption. And, the closed aperture (CA) technique reveals about the negative or positive lens resulting in self-defocusing or self-focusing behaviour of the sample. Here, the prepared sample shows the self-focusing behaviour i.e. pre-focal valley followed by post-focal peak indicating the nonlinearity of the sample to be a positive lensing effect due to thermal effect. Theoretical validation of experimental data was made by fitting the theoretical normalized transmittance using the relation for closed aperture, $T_{CA} = 1 \pm 4\Delta\phi \left(\frac{z}{z_0}\right) / \left[1 + \left(\frac{z}{z_0}\right)^2 \right] \left[9 + \left(\frac{z}{z_0}\right)^2 \right]$ where, $\Delta\phi$ is the phase distortion of the transmitted laser beam due to refraction. Estimated nonlinear absorption coefficient (β), nonlinear refractive index (n_2), third-order NLO susceptibility of pure PPB and MO doped PPB are summarized in Table 4. 2PA coefficient, nonlinear refractive index and third-order NLO susceptibility of MOPPB is higher than PPB which assured the superiority of azo dye incorporation in PPB crystals.

By optical limiting measurement, the critical power of the laser beam at which the nonlinearity starts to affect the transmission can be measured. Optical Limiting (OL) curves illustrated in Fig. 8 were extracted from the corresponding open aperture (OA) Z-scan data. The position-dependent fluence was calculated from the equation $F(z) = (4\sqrt{\ln 2} E_{in} / \pi^{3/2} \omega(z)^2)$,

where $F(z)$ is the fluence, E_{in} is the incident laser energy, ω_0 is the beam waist of the laser beam at the focus. The observed reverse saturable absorption and self-focusing could be attributed to the optical limiting behaviour of the pure PPB and MOPPB crystals. The onset optical limiting threshold of PPB and MOPPB is $0.843 \times 10^{-6} \text{ J/m}^2$ and $0.832 \times 10^{-6} \text{ J/m}^2$ respectively. Thus MOPPB stands superior than pure PPB for optical limiting applications which includes the safeguard of optical components from laser damages.

Conclusions

Good quality crystals of Pure and MO dye doped PPB crystals were grown by slow evaporation technique. Both crystals exhibited the orthorhombic nature and small change in lattice parameters confirms the inclusion of MO dye into PPB crystal structure. PPB and MOPPB show the increase of hardness number with applied load (RISE) and soft nature of the material. On doping PPB with MO there was a clear improvement in the hardness number because, larger MO dye the voids of the PPB crystal structure resulting in a compact lattice. Red shift in cut-off wavelength shifts from UV region (190 nm) to visible region (465 nm) in MOPPB crystal ascertains the inclusion of MO dye in PPB. Decrease in bandgap of PPB (5.91 eV) due to MO incorporation in MOPPB (5.7 eV) crystals is because azo group acts as a bridge between two phenyl rings and the OH-BO groups of the borate molecule. Relative SHG efficiency of pure PPB and MOPPB is 0.45 times and 0.40 times that of SHG output of KDP. OA Z-scan studies performed with 785 nm laser excitation exposed that crystals exhibit reverse saturable absorption due to two-photon absorption. Here the presence of near-resonant energy states close to excitation wavelength created sequential 2PA involving thermally induced excited state absorption. CA Z-scan studies exposed that the prepared sample possess self-focusing behavior due to thermos-optic origin. 2PA coefficient, nonlinear refractive index and third-order NLO susceptibility of MOPPB is higher than PPB which assured the superiority of azo dye incorporation in PPB crystals. The observed two-photon absorption and self-focusing could be attributed to the optical limiting behaviour of the pure PPB and MOPPB crystals with onset optical limiting threshold of $0.84 \times 10^{-6} \text{ J/m}^2$ and $0.83 \times 10^{-6} \text{ J/m}^2$ respectively. Thus MOPPB stands superior than PPB for optical limiting applications which includes the safeguard of optical components from laser damages.

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Figures

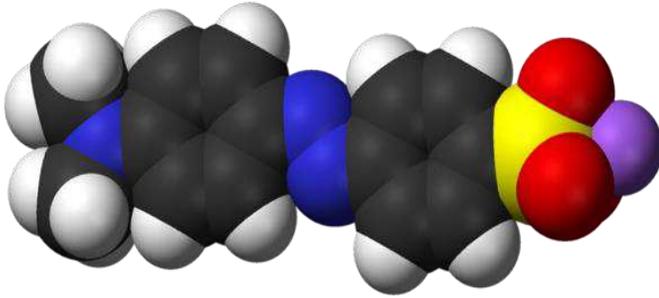


Fig.1 Molecular Structure of Methyl Orange

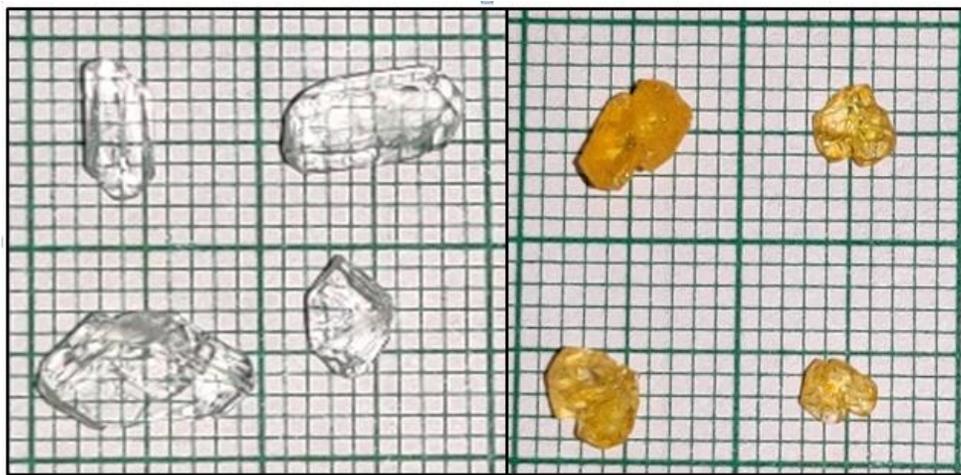
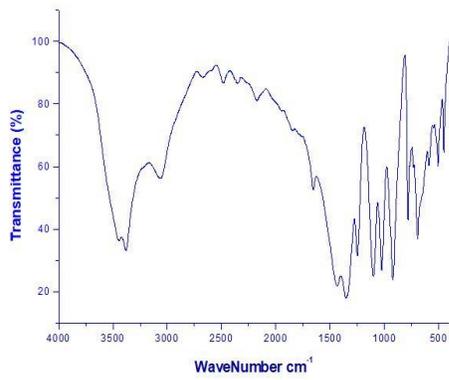
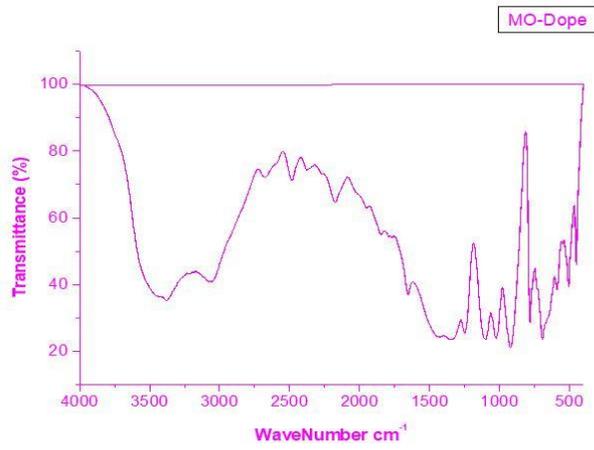


Fig.2 (a) Pure (b) MO doped PPB crystals

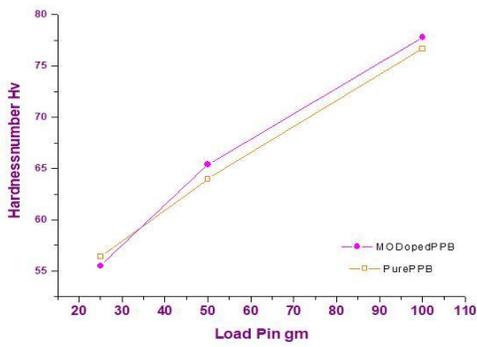


(a)

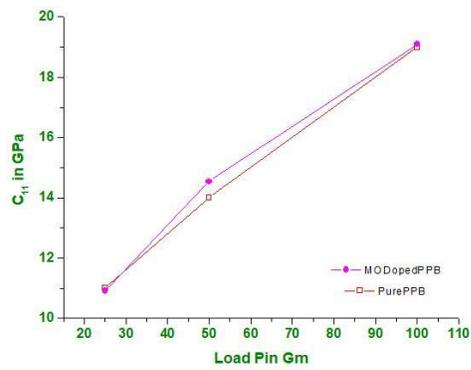


(b)

Fig. 3 FTIR Spectra of (a) pure and (b) MO Doped PPB



(a)



(b)

Fig. 4 (a) Hardness Number and (b) Stiffness constant plots for pure PPB and MOPPB

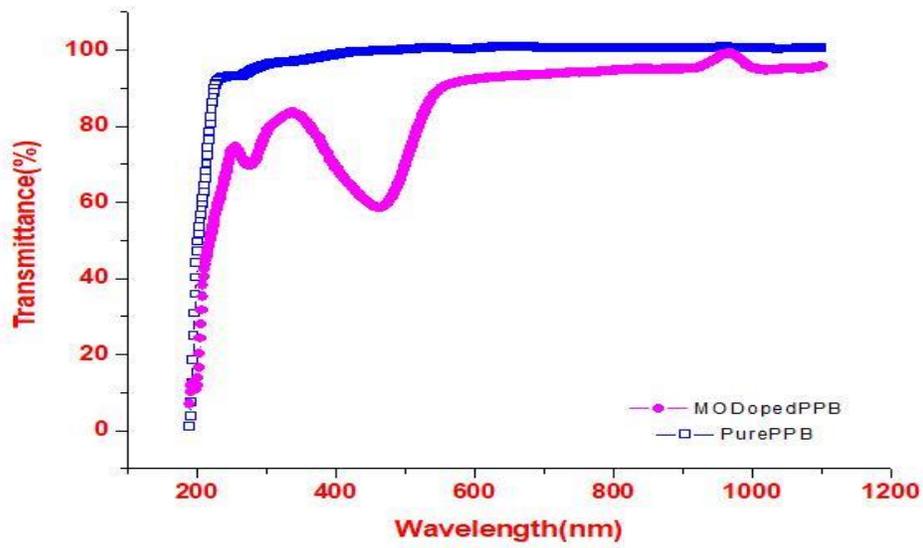


Fig. 5 Optical Transmission spectrum of pure and MO doped PPB

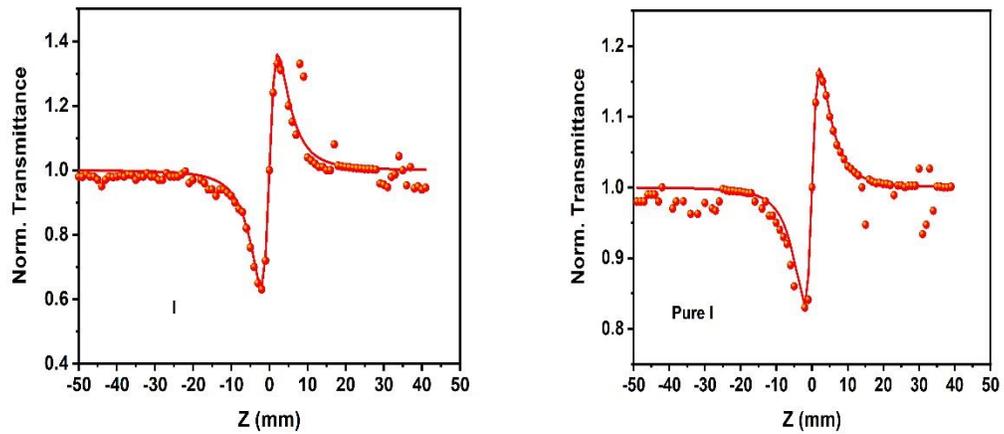


Fig.6 Closed Aperture Mode of MOPPB and Pure PPB

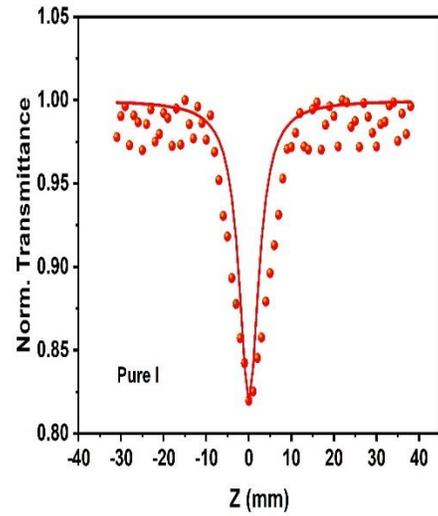
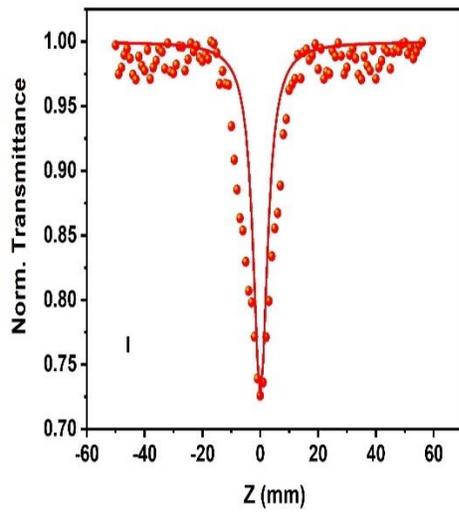


Fig.7. Open Aperture Mode of MOPPB and Pure PPB

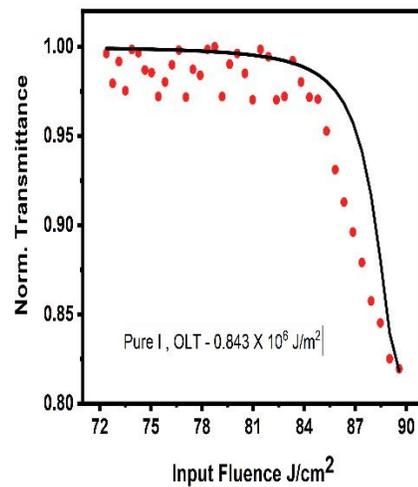
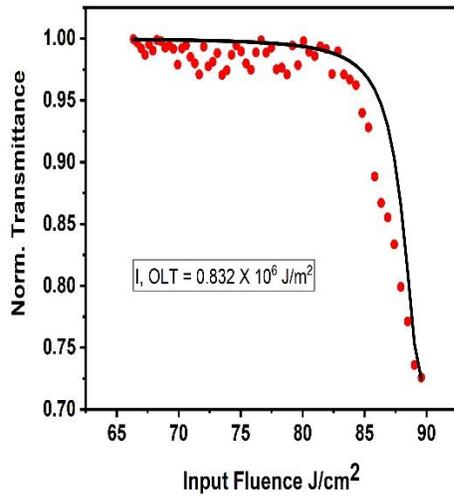


Fig.8 Optical Limiting Behaviour of MOPPB and pure PPB

Tables

Table 1: Single crystal XRD Data

	Pure PPB	MOPPB
Unit cell paramaters	a=9.05Å,b=11.17Å,c=11.06Å	a=9.09Å,b=11.20Å,c=11.12Å
Crystal Structure	orthorhombic	Orthorhombic
Volume	1120Å ³	1132Å ³

Table 2: Spectral band assignments of MO doped PPB crystals

Wavenumber (cm⁻¹)	Spectral band assignments
3444	Asymmetric N-H stretching
3378	O-H stretching vibrations
2669	C-H stretching vibrations
1844	CO band stretching vibrations
1434	Symmetric stretching vibrations of C-H
1358	C-N in plane deformation
1250	Deformation mode of CH ₃
1102	C-C stretching vibrations
924	B-O stretching mode
782	N-H wagging
508	O-B-O ring bending

Table 3 Input laser parameters

Various Input Parameters	Values
Laser Type	CW Laser
Wavelength of the laser (λ)	785nm
Peak power	50mW
Focal length of the lens (f)	10 cm
Diameter of the laser beam (d)	0.1 cm
Thickness of the sample (L)	0.1 cm
Beam Waist (ω_0)	2.498×10^{-3} cm
Intensity of the laser beam (I_0)	2.155KW/cm^2
Aperture Radius (r_0)	3mm
Spot Size at the aperture (ω_0)	0.5 cm

Table 4: Calculated Third order NLO Parameters for pure PPB and MOPPB

Third Order NLO Coefficient	Pure PPB	MOPPB
Nonlinear absorption coefficient (β)	0.98×10^{-5} m/W	1.68×10^{-5} m/W
Nonlinear refractive index(n_2)	4.62×10^{-12} m ² /W	10.2×10^{-12} m ² /W
Real part NLO susceptibility, $\text{Re}(\chi^{(3)})$	5.9×10^{-10} m ² /V ²	13.2×10^{-10} m ² /V ²
Imaginary part NLO susceptibility, $\text{Im}(\chi^{(3)})$	3.4×10^{-9} m ² /V ²	5.9×10^{-9} m ² /V ²
Susceptibility($\chi^{(3)}$)	3.5×10^{-9} m ² /V ²	6.1×10^{-9} m ² /V ²
OL Threshold	0.843×10^{-6} J/m ²	0.832×10^{-6} J/m ²

Figures

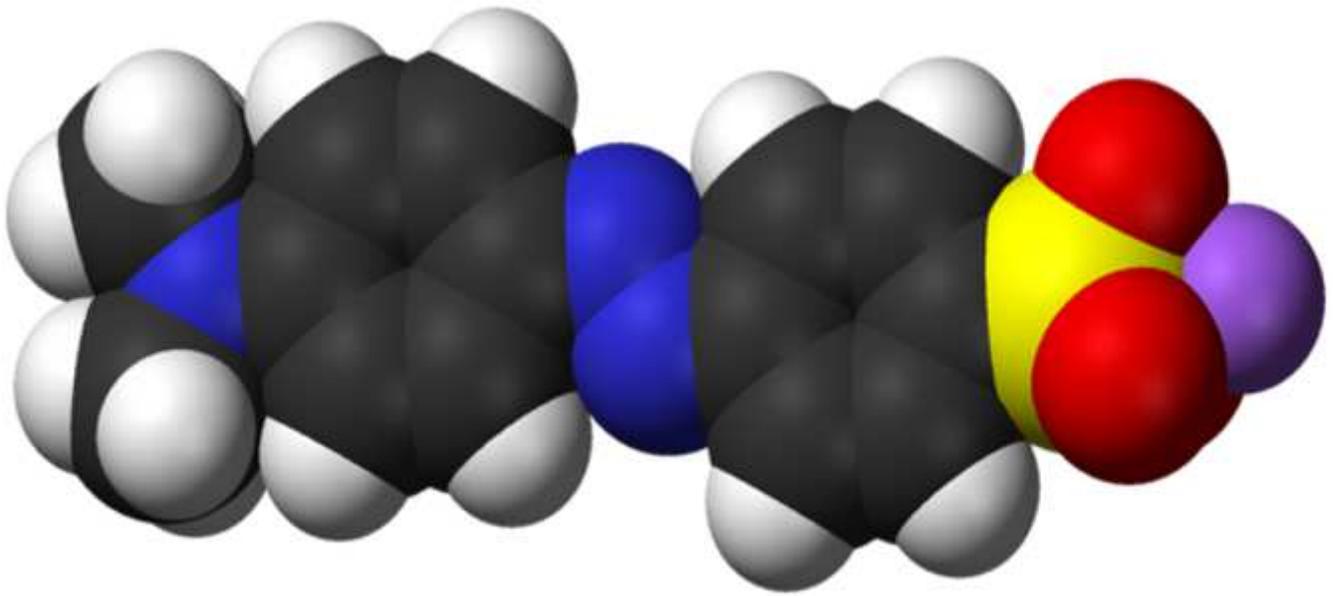


Figure 1

Molecular Structure of Methyl Orange

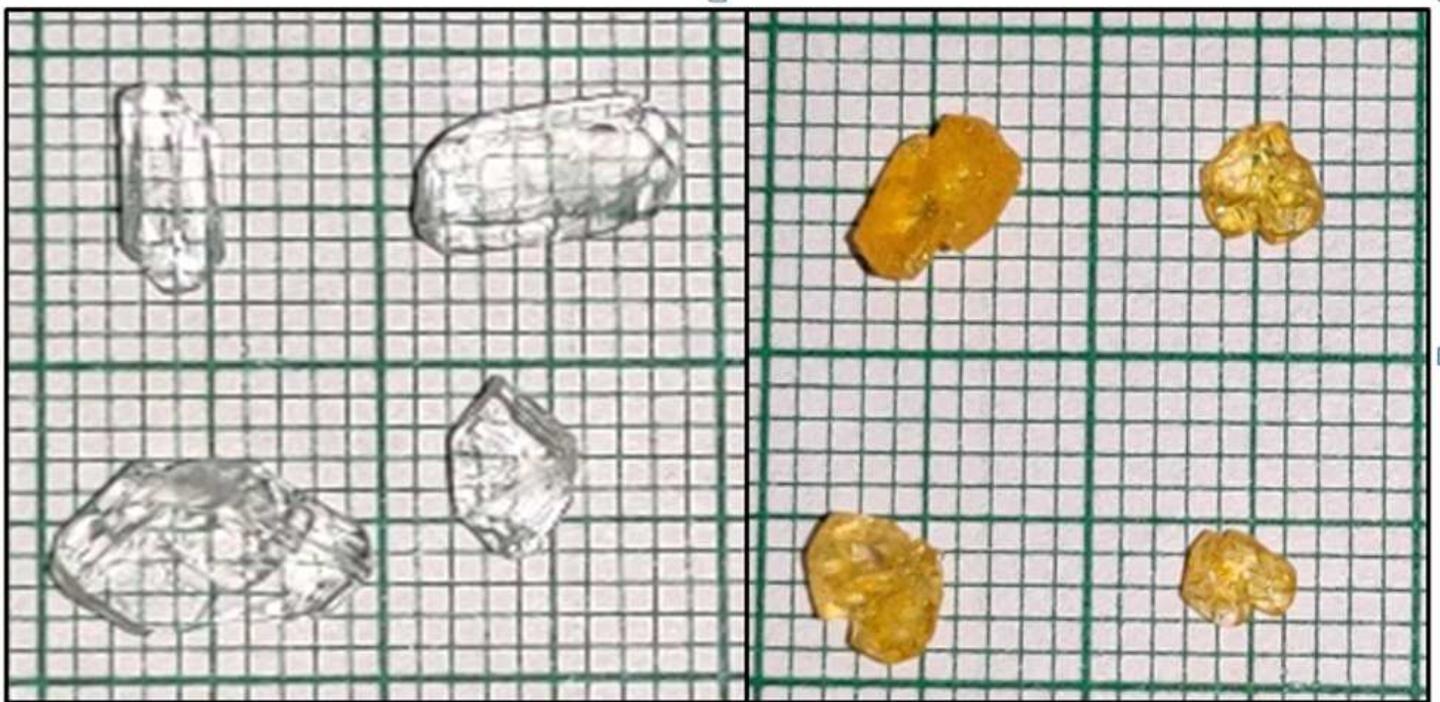
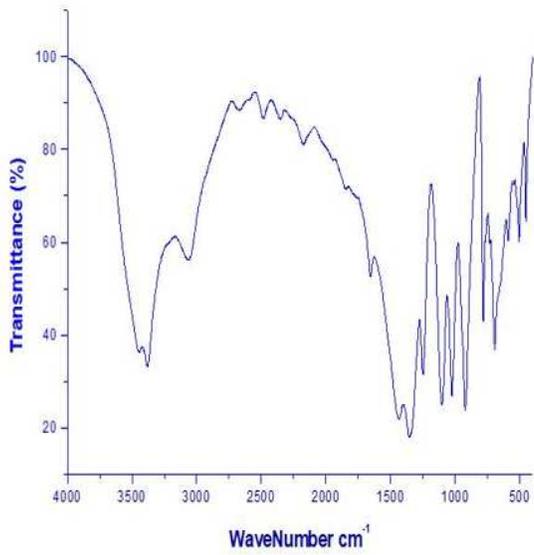
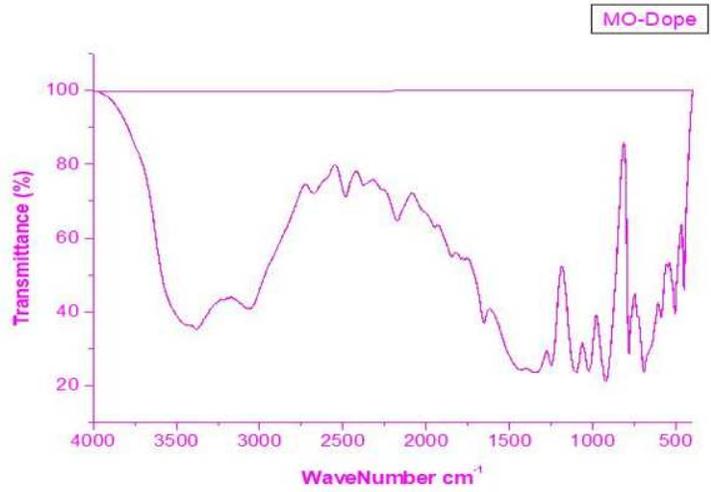


Figure 2

(a) Pure (b) MO doped PPB crystals



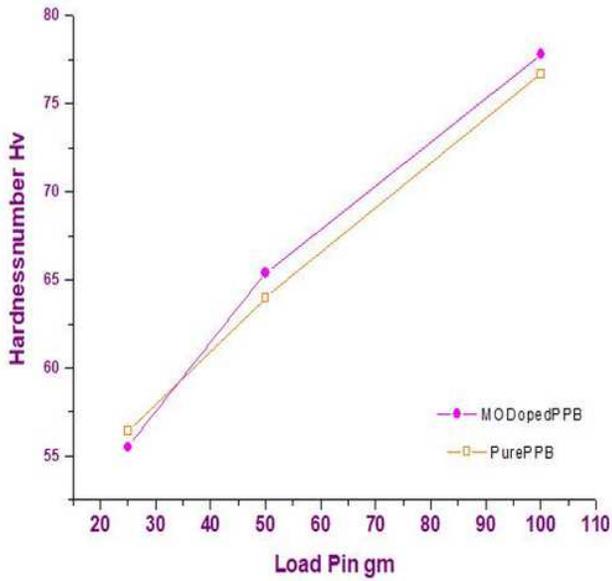
(a)



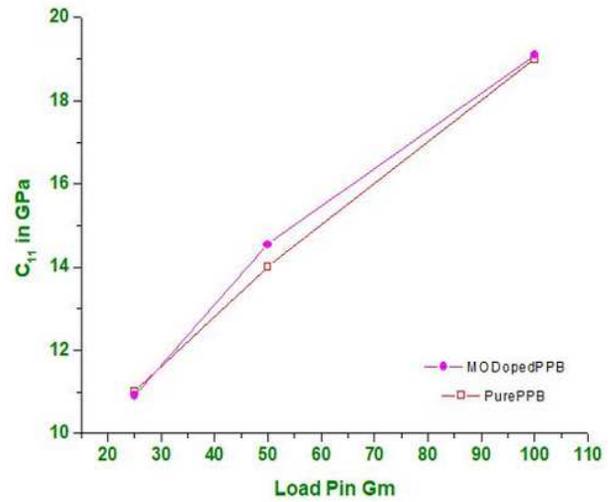
(b)

Figure 3

FTIR Spectra of (a) pure and (b) MO Doped PPB



(a)



(b)

Figure 4

(a) Hardness Number and (b) Stiffness constant plots for pure PPB and MOPPB

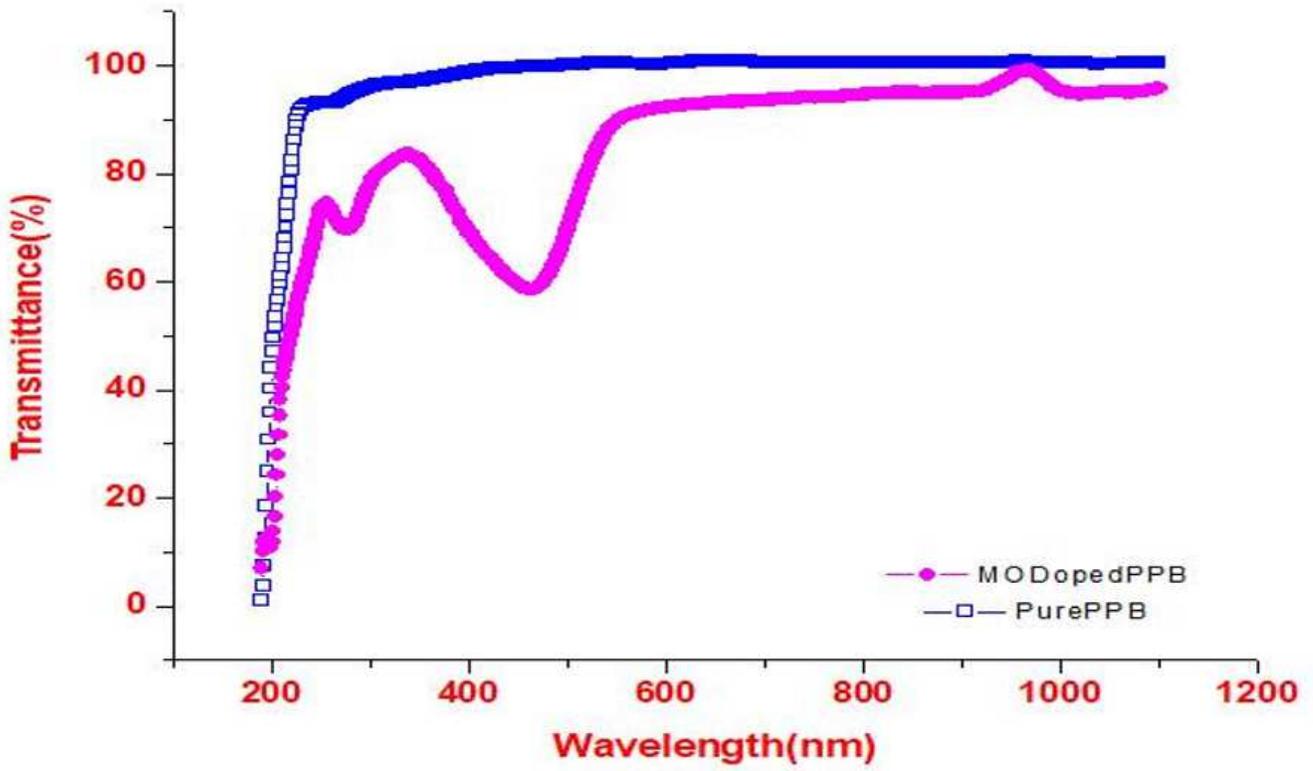
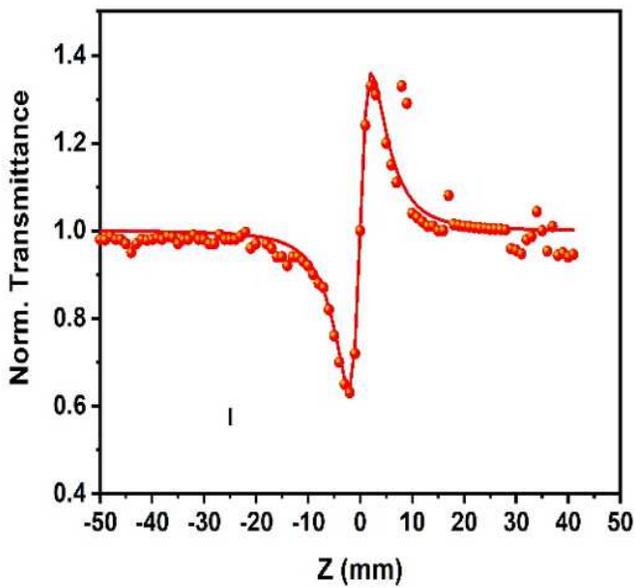
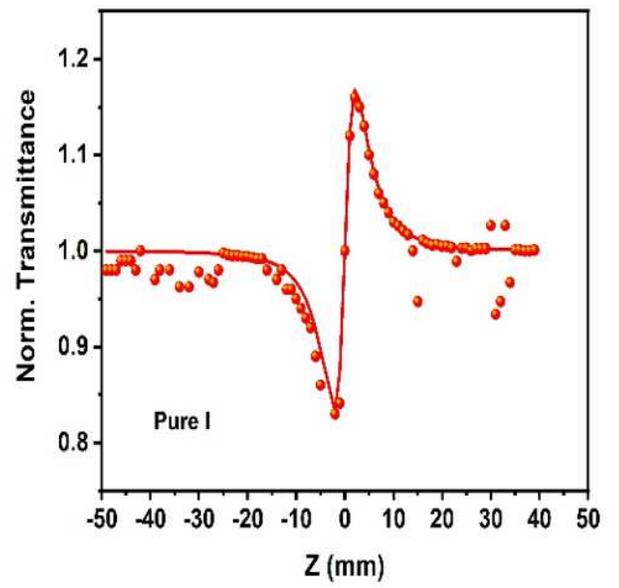


Figure 5

Optical Transmission spectrum of pure and MO doped PPB



(a)



(b)

Figure 6

Closed Aperture Mode of MOPPB and Pure PPB

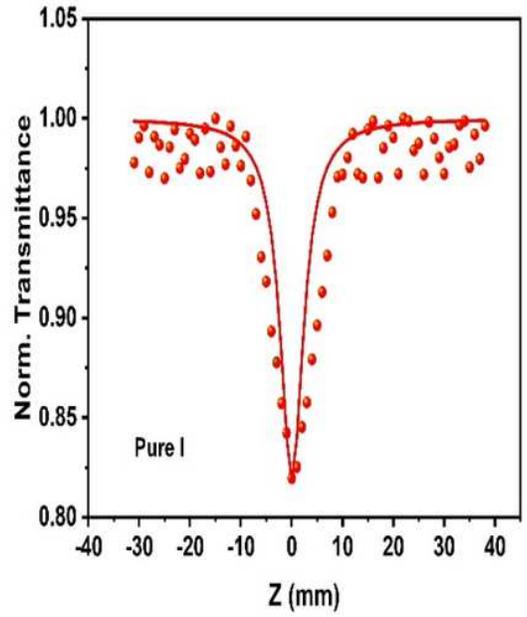
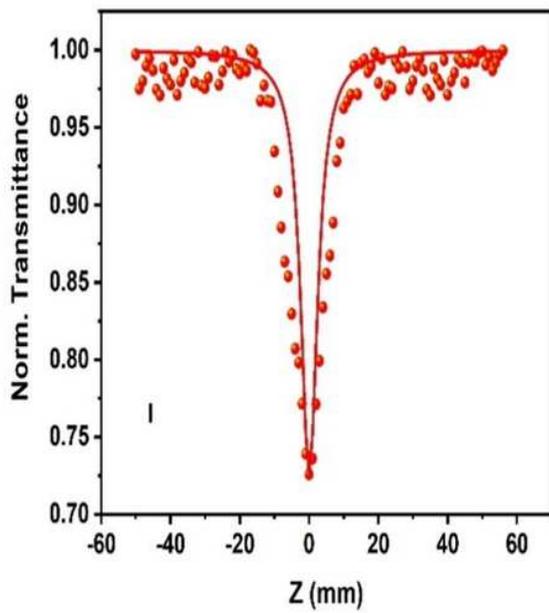


Figure 7

Open Aperture Mode of MOPPB and Pure PPB

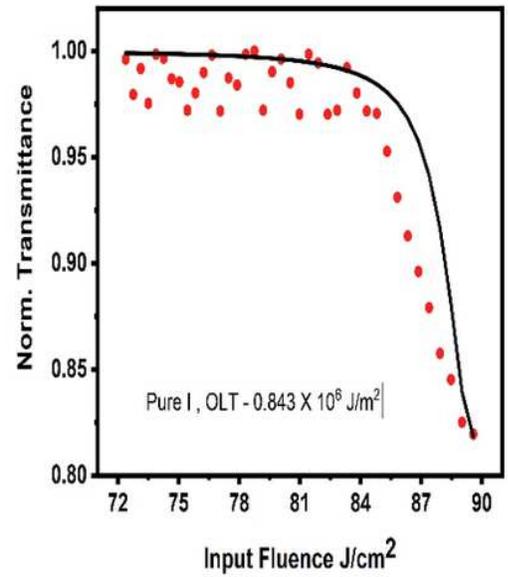
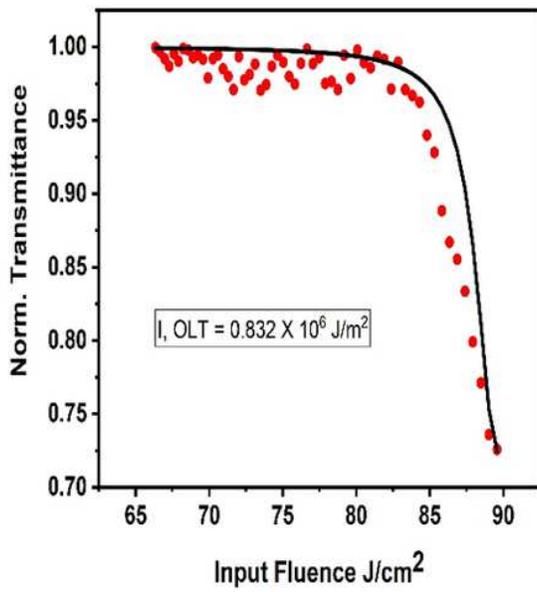


Figure 8

Optical Limiting Behaviour of MOPPB and pure PPB