

# Investigation of third order nonlinear optical properties of meta-Nitroaniline single crystal

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A nonlinear optical crystal of meta-Nitroaniline (m-NA) was grown by slow evaporation solution growth technique at room temperature using methanol as solvent. In this work, the structure, FTIR spectrum, transmittance spectrum, optical band gap, second harmonic generation efficiency were discussed and analysed in detail. Third order nonlinear optical studies were performed by using single beam Z-scan technique with continuous wave Nd: YAG laser. Closed aperture Z-scan studies reveal the negative nonlinearity in the crystals and open aperture Z-scan reveals the saturation absorption. The nonlinear parameters such as nonlinear refractive index  $n_2$ , absorption coefficient  $\beta$  and nonlinear optical susceptibility  $\chi^{(3)}$  were evaluated for the m-Nitroaniline crystal.

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## 1. Introduction

Organic crystals with large second-order nonlinear susceptibilities are of great interest because of their potential use in optical parametric amplifier and oscillator in the infrared region [1-3]. Meta-nitroaniline (m-NA) is an important material in the research field of nonlinear optics, which exhibits enhanced nonlinear and electro-optic effects [4,5]. Meta-Nitroaniline (m-NA) with chemical formula  $C_6H_6N_2O_2$ , is a well-known organic nonlinear optical material which has been examined by several researchers in the recent past on its crystal growth and properties [6-10]. The Z-scan technique is a popular method for the measurement of optical nonlinearity of the material. It has the advantage of high sensitivity and simplicity and is used to measure the third order nonlinear optical properties [11,12]. One can simultaneously measure the magnitude and sign of the nonlinear refraction and nonlinear absorption, which are associated with the real part  $Re\chi^{(3)}$  and imaginary part  $Im\chi^{(3)}$  of the third order nonlinear susceptibilities. This research work is aimed towards the growth of m-Nitroaniline (m-NA), and to investigate third order nonlinear optical properties of the grown crystal.

## 2. Experimental procedure

### Synthesis

In the present work, m-Nitroaniline (m-NA) crystals were grown by using slow evaporation solution growth technique. AR grade m-Nitroaniline was dissolved in methanol and stirred well for 7 hours at room temperature.

The purity of the salt was further increased by repeated recrystallization. The supersaturated solution was filtered by Whatmann filter paper after it was closed with a perforated cover and kept in a dust free atmosphere. Then the seed crystals were harvested to attain an optimal size and shape in a time period of 20 days. The grown crystals were optically transparent and defect free having dimensions  $15 \times 6 \times 3 \text{ mm}^3$ . The photograph of the grown crystal is shown in Fig. 1.



Fig. 1. As grown single crystal of m-NA.

## 3. Results and discussion

### 3.1. Single crystal XRD

Good quality of seed crystal was selected and it was subjected to single crystal XRD analysis at room temperature. Single crystal X-ray diffraction data for m-

Nitroaniline (m-NA) were recorded by using BRUKER AXS KAPPA APEX (II) CCD diffractometer with Mo  $K\alpha$  ( $\lambda = 0.710693 \text{ \AA}$ ) radiation. It was observed that m-NA crystal belonged to orthorhombic crystal system with space group  $Pbc2_1$  and the unit cell parameters were,  $a = 5.086 \text{ \AA}$ ,  $b = 6.509 \text{ \AA}$ ,  $c = 19.21 \text{ \AA}$  and volume =  $654.48 \text{ \AA}^3$ . The observed values are in good agreement with the reported values [13]

### 3.2. Powder XRD

Powder X-ray diffraction analysis was achieved with the powdered sample of m-NA crystal and the pattern recorded using Rich Seifert diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) was shown in Fig. 2. The sample was scanned from  $10^\circ$ -  $60^\circ$  at scan rate of  $2^\circ \text{ min}^{-1}$ . All the observed reflections were indexed for orthorhombic structure and the unit cell parameters were calculated using PROSZKI ver. 2.4 program. The calculated lattice parameters are,  $a = 5.087 \text{ \AA}$ ,  $b = 6.485 \text{ \AA}$ ,  $c = 19.306 \text{ \AA}$  and volume of the unit cell,  $V = 636.88 \text{ \AA}^3$ . Sharp and strong peaks confirmed the good crystallinity of the grown crystal. The cell parameters were matched to the single crystal XRD values.

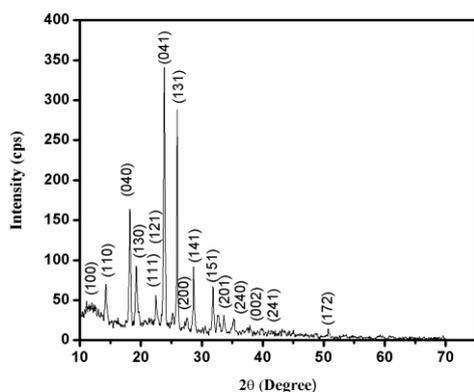


Fig. 2. Indexed powder XRD patterns of m-NA crystals.

### 3.3. Fourier transforms infrared analysis (FTIR)

Infrared spectroscopy is used to identify the functional groups and modes of vibration of the grown crystal. The FTIR spectrum was recorded using a Perkin Elmer FTIR spectrometer using potassium bromide pellet technique in the range of  $400$ – $4000 \text{ cm}^{-1}$ . The FTIR spectrum of the m-NA is shown in Fig.3. The sharp peak found at  $3414.70 \text{ cm}^{-1}$  is due to N-H stretching [14]. The peak at  $2982.06 \text{ cm}^{-1}$  is due to very weakly bonded N-H stretching. The aromatic C-H stretching band is found at  $3082.03 \text{ cm}^{-1}$  [15]. The N-H plane bending mode is observed at  $1608.74 \text{ cm}^{-1}$ . The  $\text{NO}_2$  aromatic stretching mode is observed by the peaks at  $1502.45 \text{ cm}^{-1}$ ,  $1320.75 \text{ cm}^{-1}$ . The C-H in plane and out of plane bending vibrations generally lie in the region  $1320.75$ – $1087.84 \text{ cm}^{-1}$  and  $641 \text{ cm}^{-1}$  respectively.

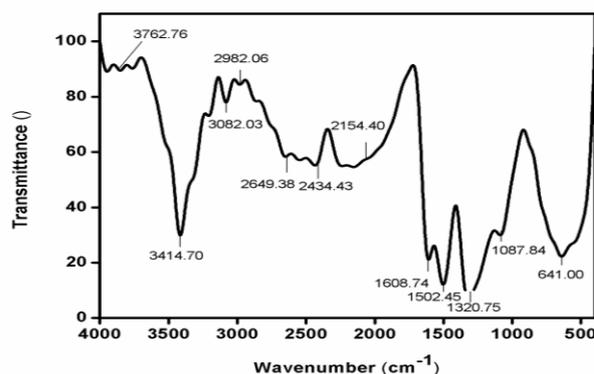


Fig. 3. FTIR Spectrum of mNA crystal.

### 3.4. UV studies

UV-Vis-NIR absorption and transmittance studies were carried out for the grown m-NA crystal between the wavelength range of  $200 \text{ nm}$  and  $1100 \text{ nm}$  using Perkin-Elmer lambda 35 UV-Spectrometer. The resultant transmittance is shown in Fig. 4. The crystals are transparent in the entire visible region and the UV cut off wavelength of the crystals is found to occur at  $362 \text{ nm}$ . suitable for the fabrication of nonlinear optical devices.

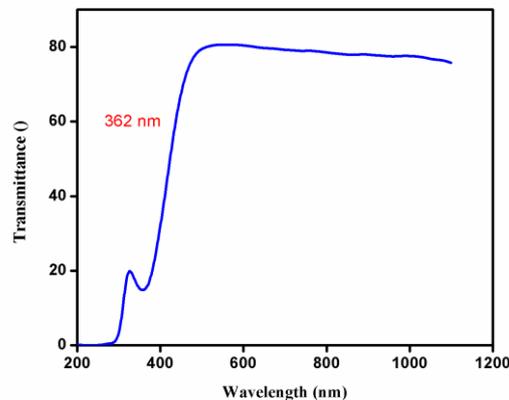


Fig. 4. Transmission spectra of pure m-NA single crystals.

### 3.5. Determination of optical band gap

The optical transmittance and reflectance spectra are analyzed to determine the optical constants, such as absorption coefficient ( $\alpha$ ) and refractive index ( $n$ ). The optical absorption coefficient ( $\alpha$ ) is calculated from the transmittance and absorbance data using the following relation [16],

$$\alpha = \frac{2.303 \log(1/T)}{t} \quad (1)$$

where  $T$  is the transmittance and  $t$  is the thickness of the crystal.

The optical band gap ( $E_g$ ) is calculated from the transmission spectrum using the formula [17]

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

where  $A$  is a constant,  $E_g$  is the band gap,  $h$  is the Planck's constant and  $\nu$  is the frequency of the incident photons. The tauc's graph is plotted between the square of the product of absorption coefficient and the incident photon energy  $(\alpha h\nu)^2$  with the photon of energy  $(h\nu)$  at room temperature, given in Fig.5. This shows a linear behavior that can be considered as evidence of the direct transition. The band gap energy of the m-NA crystal was found to be 3.91 eV.

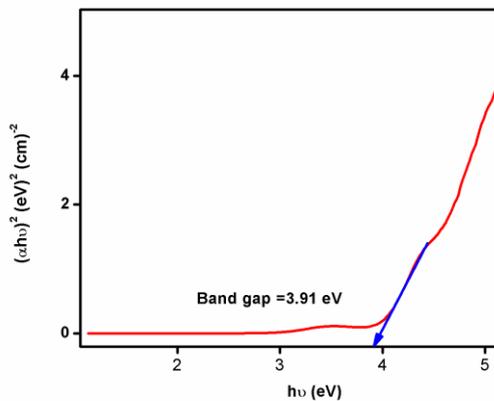


Fig. 5. The variation of  $(\alpha h\nu)^2$  Vs  $h\nu$  (eV).

### 3.6. Second harmonic generation (SHG) study

The SHG efficiency of mNA has been measured by Kurtz and Perry powder technique [18]. A Q-switched Nd:YAG laser ( $\lambda=1064$  nm, Quanta Ray, USA) with a pulse duration of 6 ns and at a repetition rate of 10 Hz was used to excite the powder samples. The grown single crystals of mNA were ground into fine powder with uniform particle size and then filled into the micro capillary tube. The emission of bright green radiation ( $\lambda = 532$  nm) from the crystals confirm the generation of second harmonics. The second harmonic signal of 11.2 mJ was obtained for an input energy of 0.68 joule measured using dual channel energy meter (Coherent Molelectron, USA). The SHG value of potassium di hydrogen phosphate (KDP) crystal gives a signal of 8.8 mJ for the same input energy. Thus it is observed that the SHG efficiency of the m-NA is 3 times more than that of the standard KDP crystal.

### 3.7 Experiment setup of Z-scan

The Z-scan experiments were performed using a 532 nm diode pumped Nd:YAG laser beam (Coherent Compass TM 215M- 50), which was focused by 3.5 cm

focal length lens. The laser beam waist  $\omega_0$  at the focus is measured to be 15.84  $\mu\text{m}$  and the Rayleigh length to be 1.48 mm. The schematic of the experimental setup used is shown in Fig. 6. A 1mm wide optical cell containing the sample in solvent is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter (Field master Gs- coherent). For an open aperture Z-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture.

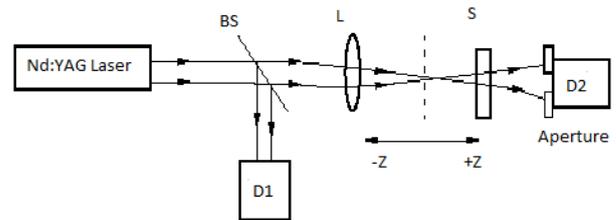


Fig. 6. Experimental setup for Z-scan Instrument.

#### 3.7.1 Non linear optical parameter

Z-scan technique [19,20] based on the spatial distortion of a laser beam, passed through a nonlinear optical material, is widely used in material characterization because of their simplicity, high sensitivity and well-elaborated theory.

The measurable quantity  $\Delta T_{p-v}$  can be defined as the difference between the normalized peak and valley transmittances,  $T_p - T_v$ . The variation of this quantity as a function of  $|\Delta\phi_0|$  is given by

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} |\Delta\phi_0|, \quad (3)$$

Where  $S=1-\exp(-r_a^2/\omega_a^2)$  is the aperture linear transmittance (0.01),  $\Delta\phi_0$  is the on-axis phase shift. The on-axis phase shift is related to the third-order nonlinear refractive index by

$$|\Delta\phi_0| = kn_2 L_{eff} I_0, \quad (4)$$

where  $k = 2\pi / \lambda$ ,  $L_{eff} = [1 - \exp(-\alpha L)] / \alpha$  is the effective thickness of the sample,  $\alpha$  is the linear absorption coefficient,  $L$  the thickness of the sample,  $I_0$  the on-axis irradiance at focus and  $n_2$  the third-order nonlinear refractive index.

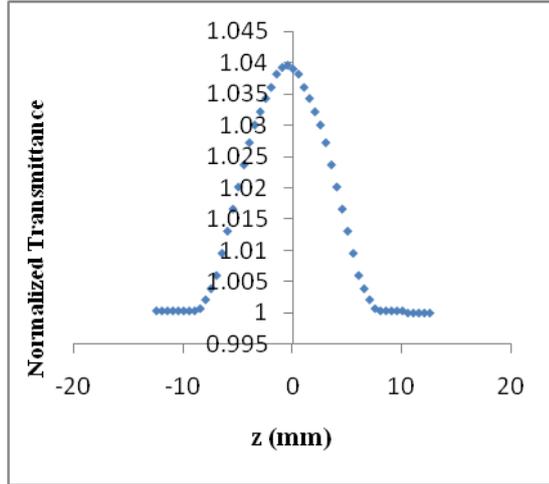


Fig. 7. Open aperture curve for mNA crystal.

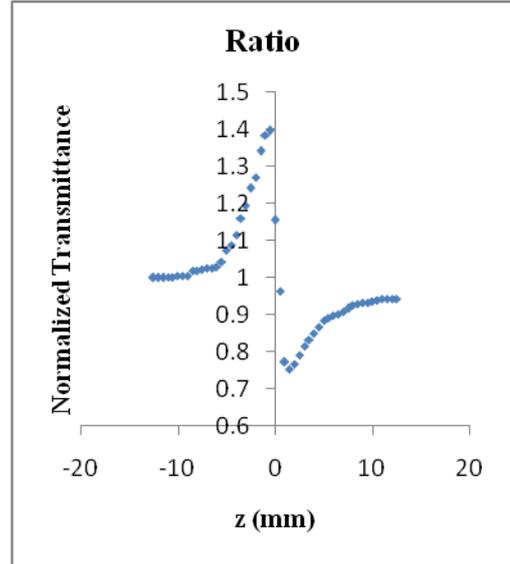


Fig. 9. Ratio Curve for m-NA crystal.

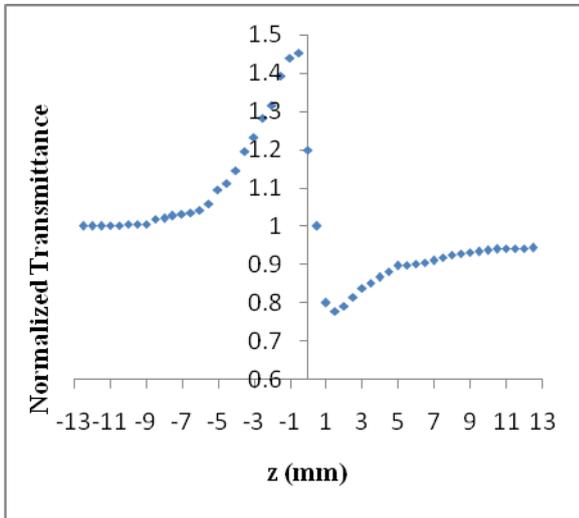


Fig. 8. Closed aperture Z-scan curve of mNA crystal.

Generally the measurements of the normalized transmittance versus sample position, for the cases of closed and open aperture, allow determination of  $n_2$  the nonlinear refractive index and the saturation absorption coefficient  $\beta$ . Here, since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of  $n_2$  is less straightforward from the closed aperture scans. Therefore, it is necessary to separate the effect of nonlinear refraction from that of nonlinear absorption. A simple and approximate method to obtain purely effective  $n_2$  is to divide the closed aperture transmittance by the corresponding open and closed aperture as shown in Figs. 7, 8 and this represents such plots obtained for the samples, i.e., the ratio of closed aperture and the open aperture Z-scans as shown Fig. 9. The data obtained in this way reflects purely the effects of nonlinear refraction.

The nonlinear absorption coefficient  $\beta$  can be estimated from the open aperture Z-scan data. The normalized transmittance for the open aperture condition is given by

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \quad (5)$$

For  $q_0(0) < 1$ , where  $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2/z_R^2)$ ,  $z_R = k\omega_0^2/2$  is the diffraction length of the beam and  $\omega_0$  is the beam waist radius at the focal point and  $k = 2\pi/\lambda$  is the wave vector.

The experimental measurements of  $n_2$  and  $\beta$  allow one to determine the real and imaginary parts of the third-order nonlinear optical susceptibility  $\chi^{(3)}$  according to the following relations

$$\text{Re } \chi^{(3)}(\text{esu}) = 10^{-4} \frac{\epsilon_0 c^2 n_0^2}{\pi} n_2 \left( \frac{\text{cm}^2}{W} \right) \quad (6)$$

where  $\epsilon_0$  is the vacuum permittivity, and  $c$  the light velocity in vacuum:

$$\text{Im } \chi^{(3)}(\text{esu}) = 10^{-2} \frac{\epsilon_0 c^2 n_0^2 \lambda}{4\pi^2} \beta \left( \frac{\text{cm}^2}{W} \right) \quad (7)$$

The absolute value of  $\chi^{(3)}$  is calculated from

$$|\chi^{(3)}| = [(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2]^{1/2} \quad (8)$$

The nonlinear parameters such as nonlinear refractive index  $n_2$ , nonlinear absorption coefficient  $\beta$ , and nonlinear susceptibility  $\chi$ , has been evaluated and tabulated in Table 1.

Table 1. Non-linear optical parameter.

| Compound       | $n_2 \times 10^{-8}$ (cm <sup>2</sup> /W) | $\beta \times 10^{-4}$ (cm/W) | $\chi^{(3)} \times 10^{-6}$ esu |
|----------------|---|-------------------------------|---------------------------------|
| m-Nitroaniline | 1.43                                      | 2.82                          | 1.53                            |

#### 4. Conclusion

The single crystal of meta-Nitroaniline (m-NA) was successfully grown by slow evaporation solution growth technique at room temperature using methanol as solvent. The single crystal X-ray and Powder X-ray diffraction studies confirm the orthorhombic structure with space group Pbc2<sub>1</sub>. The Fourier transform infrared (FTIR) study was used to reveal the functional groups present in the grown crystal. The optical transmission studies reveal that the crystal has UV cut-off wavelength around 362 nm. The SHG efficiency of the m-NA is 3 times more than that of the standard KDP crystal. The Z-scan measurements further confirm that the material exhibits large third order nonlinear optical properties for the grown m-Nitroaniline crystal. Closed aperture Z-scan studies reveal the negative nonlinearity in the crystals and open aperture Z-scan the saturation absorption.

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