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OPTICAL AND TRANSPORT PROPERTIES OF NLO META NITROANILINE SINGLE CRYSTALS

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Abstract. Single crystals of Meta nitroaniline (mNA) were grown successfully by slow evaporation technique. The as-grown crystal was clear, transparent and the size of the crystal attained was 8 x 4 x 3 mm^3 within a period of 3 weeks. The grown crystals were subjected to single crystal X-ray diffraction analysis to confirm their orthorhombic system. An attempt was made to calculate polarizability by Penn analysis and compare with the traditional method and results are tabulated. The optical properties of the grown crystal were calculated from UV-transmission spectrum analysis. Dielectric constant studies were carried out at different temperatures and frequencies. The second harmonic generation efficiency of the grown crystal was confirmed by Kurtz and Perry powder technique.

1. Introduction

Nonlinear optics (NLO) deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in frequency, phase, or other physical properties. NLO is one of the few modern scientific frontiers where the interest is not only for understanding of new physical phenomena, but also to realize the technological applications. The newly emerging technology of photonics utilizes photons instead of electrons to acquire, store, transmit and process information. Technologies such as optical communication, optical computing and image analysis have been developed by using NLO processes to perform functions of frequency conversion, light modulation, optical switching and optical memory storage. Progress in these areas would be greatly enhanced by the availability of materials compatible with various device embodiments and having sufficiently large NLO response [1-3]. In the present investigation we report bulk growth, fundamental properties, optical, dielectric, and second harmonic generation (SHG) properties of Meta nitroaniline single crystals.

2. Experimental

2.1 Crystal growth. The starting material was commercially available as Meta nitroaniline salt and its purity has been improved by recrystallizing in acetone for several times. The solvent evaporation technique was used to grow the single crystal of Meta nitroaniline. A recrystallized salt was dissolved in acetone, a saturated solution was prepared and the solution was filtered using a borozil filter paper. The filtered solution was taken in a beaker, which was hermetically sealed to avoid the evaporation of the solvent. A good yellow-colored single crystals having dimension 8 x 4 x 3 mm^3 with perfect external morphology is harvested within a period of 20 days and is shown in Fig. 1.

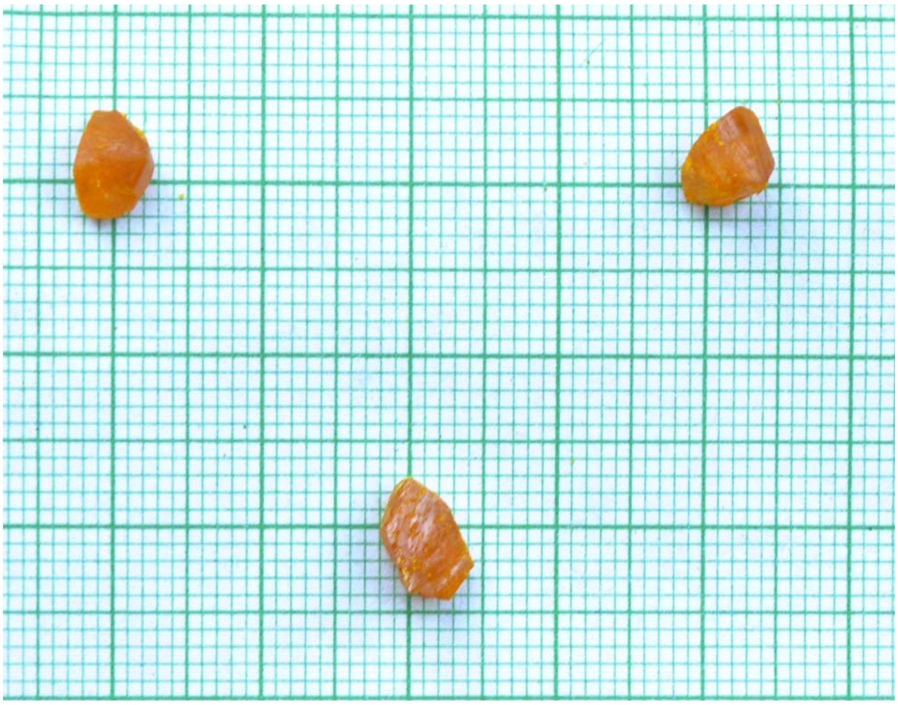

Fig. 1. As grown Meta nitroaniline crystals from acetone.

3. Results and Discussion

3.1. Density measurements. The density of Meta nitroaniline crystal was calculated by the equation shown below [4]:

$$\rho = MZ/(N_A V), \quad (1)$$

where M is molecular weight of Meta nitroaniline; molecular unit cell $Z = 4$; N_A is Avogadro's number; V is volume and a, b and c are the lattice parameters of Meta nitroaniline crystal. The theoretical density is found to be 1.4162 g/cm^3. The density of Meta nitroaniline crystal was measured experimentally by the floatation method at room temperature (32 ºC), and the measured density can be obtained by the following equation:

$$\rho = m\rho_{solvent}/(m - m'), \quad (2)$$

where m is the mass of Meta nitroaniline crystal sample in the air, m' is the mass when the Meta nitroaniline single crystal sample was immersed in CCl_4 and $\rho_{solvent}$ is the density of solvent (CCl_4) used at measured temperature. The density was measured by floatation technique. From this measurement, the density of the crystal is found to be 1.4190 g/cm^3. The experimentally measured density is in good agreement with the theoretically found value.

3.2. Single-crystal X-ray diffraction. Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using ENRAF NONIUS CAD-4 automatic X-ray diffractometer.The calculated lattice parameters are a = 6.50 Å, b = 19.32 Å, c = 5.07 Å, the volume of the system V = 647.7 Å^3, and the crystal belongs to orthorhombic system, which was very well agreed with that of reported values [5].

3.3. Crystal structure of Meta nitroaniline. The molecular formula of Meta nitroaniline has $C_6H_6N_2O_2$ and crystallizes in an orthorhombic unit cell of space group $Pbc2_1$ and point group mm2. Crystal structure of the grown crystal is shown in Fig. 2 [6].

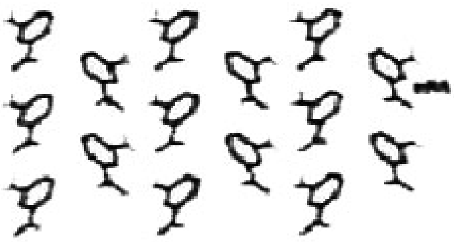

Fig. 2. Crystal structure of Meta nitroaniline.

3.4. Determination of some characteristic data. The molecular weight of the grown crystal is M = 138.14 g/mol, and total number of valance electron Z=52. The density of the grown crystal was found to be ρ = 1.42 g·cm^{-3} and dielectric constant at 1 MHz is ε_∞ = 37.6. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}}, \tag{3}$$

where Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the Meta nitroaniline single crystal. The Plasma energy is terms of Penn gap and Fermi energy [7] is given as

$$E_P = \frac{\hbar\omega_P}{\left(\varepsilon_\infty - 1\right)^{1/2}} \tag{4}$$

and

$$E_{\mathrm{F}} = 0.2948\left(\hbar\omega_P\right)^{4/3}. \tag{5}$$

Polarizability, α is obtained using the relation:

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3, \tag{6}$$

where S_0 is a constant for a particular material, and is given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{7}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by

$$\alpha = \frac{3M}{4\pi N_A \rho}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right), \tag{8}$$

where the symbols have their usual significance. N_A is Avagadro number and the calculated fundamental data on the grown crystal of Meta nitroaniline are listed in Table 1.

Table 1. Some theoretical data for Meta nitroaniline single crystal.

Parameters	Values
Plasma energy (eV)	21.06
Penn gap(eV)	3.48
Fermi gap (eV)	16.97
Polarizability (cm^3) Penn analysis	5.02×10^{-23}
Clausius-Mossotti Equation	5.06×10^{-23}

3.5. Optical transmission studies. The optical transmission spectrum (Fig. 3) was recorded in the range 300–1100 nm using VARIAN CARY 5E spectrophotometer. The transparency is around 70 % within the range of 450-1100 nm. The lower cutoff wavelength of Meta nitroaniline is 410 nm. The crystal has good optical transmission in the visible region. The transparency in the visible region for this crystal suggests its suitability for second harmonic generation.

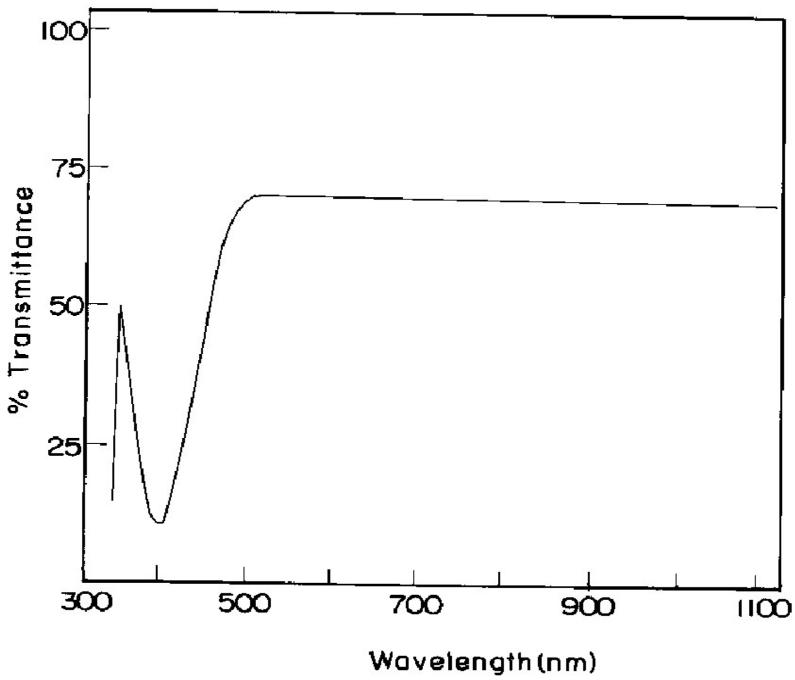

Fig. 3. Optical transmittance spectrum.

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula:

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t}, \tag{9}$$

where t is the thickness of the sample. Optical band gap (E_g) was evaluated from the transmission spectrum and optical absorption coefficient (α) near the absorption edge is given by [8]:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}, \tag{10}$$

where A is a constant, E_g the optical band gap, h the Planck constant and ν the frequency of the incident photons. The variation of $(\alpha h\nu)^2$ with $h\nu$ in the fundamental absorption region is plotted in Fig. 4. The band gap of the crystal can be evaluated by extrapolation of the linear part, which is found to be 3.35 eV.

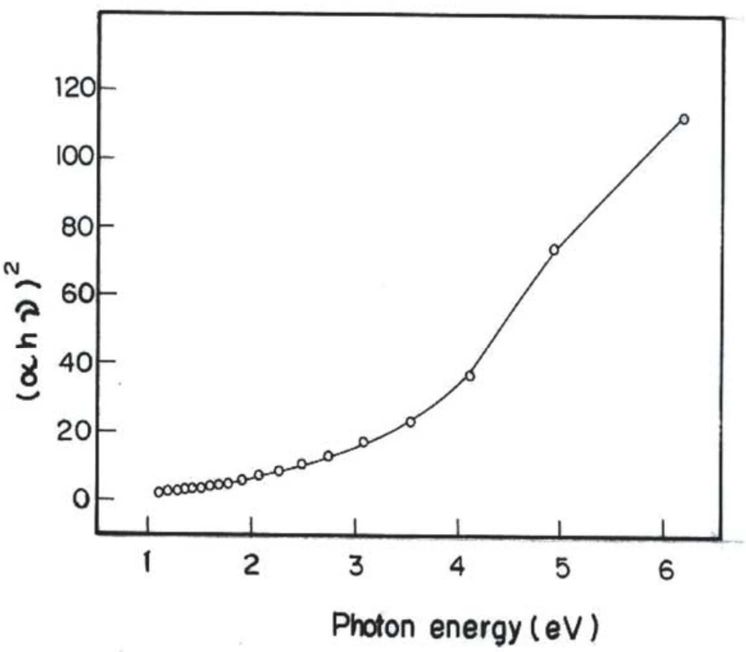

Fig. 4. $(\alpha h\nu)^2$ versus $h\nu$.

Extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda\alpha}{4\pi}. \tag{11}$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}. \tag{12}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T}. \tag{13}$$

Refractive index (n) can be determined from reflectance data using the following equation:

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)}. \tag{14}$$

The refractive index (n) is 1.33 at λ = 1100 nm.

From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [9]:

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2. \tag{15}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi}, \tag{16}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electric susceptibility χ_C is 0.162 at λ = 1100 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [10]:

$$\varepsilon_r = n^2 - k^2, \quad \varepsilon_i = 2nk. \tag{17}$$

The value of real ε_r and ε_i imaginary dielectric constants at λ=1100 nm are 1.252 and $8.643 \times 10^{-5,}$ respectively.

3.6. Dielectric constant studies. The dielectric constant of the Meta nitroaniline crystals were studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. Figure 5 shows the plot of dielectric constant (ε_r) versus log frequency.

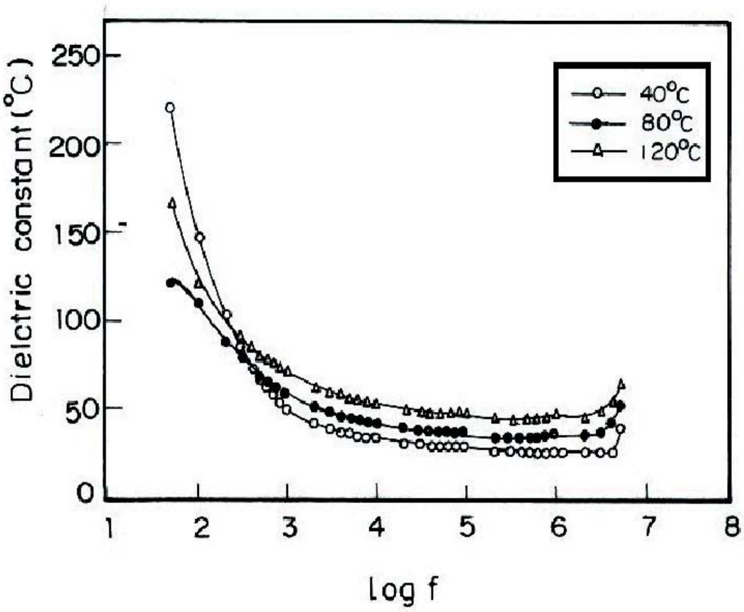

Fig. 5. Dielectric constant versus log f.

The dielectric constant has high values in the lower frequency region and then decreases with the applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely; space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. From the plot, it is also observed that dielectric constant decreases with increasing frequency and temperature, attributed to space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample [11].

3.7. NLO studies. The second harmonic generation property in Meta nitroaniline was confirmed using a Q-switched Nd: YAG laser by Kurtz powder technique. The sample was ground into very fine powder and tightly packed in a micro capillary tube. Then it was mounted in the path of Nd: YAG laser beam of energy 6.18mJ/sec and pulse width about 10 ns were used. When KDP crystal was used as a reference material, it produced 91.60 mW as output beam voltage. But it was about 118.20 mW for the grown sample and hence it is confirmed that the material has NLO efficiency of Meta nitroaniline higher than KDP crystal. The output could be seen as a bright green flash emission from the sample. The green emission confirmed the second harmonic generation in the grown Meta nitroaniline crystal. Thus the SHG efficiency of Meta nitroaniline is higher than KDP.

4. Conclusion

Single crystals of Meta nitroaniline were grown by slow evaporation technique. The grown crystals were characterized by single crystal XRD analysis and confirmed that the crystals belong to orthorhombic system. The physical parameters such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability have been determined for the grown crystals. The band gap energy for the grown crystal was found to be 3.5 eV. The optical constants such as extinction coefficient (K), refractive index (n), electric susceptibility (χ_c) and dielectric constants were calculated as a function of wavelength. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures. The second harmonic generation of the grown crystal was measured.

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