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Synthesis, Growth and Optical Studies of o-Phenylenediaminium 4-Nitrobenzoate Single Crystal

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Abstract - *o-Phenylenediamine 4-Nitrobenzoate (PD4NB) single crystal was synthesized from o-Phenylenediamine as donor and 4-Nitrobenzoic acid as acceptor. PD4NB crystal was grown by solution growth technique using methanol as solvent. The cell parameters and crystalline perfection of the grown crystal were studied by single crystal and high resolution X-ray diffraction analyses. The title compound was classified into orthorhombic crystal system with non-centrosymmetric $P2_12_12_1$ space group. FTIR spectral analysis revealed the existence of functional groups and their corresponding vibrational modes have been assigned. The optical transmission properties of the crystal were studied by UV–Vis spectral analysis. PL spectral study revealed the transition mechanism of ions. Laser induced damage threshold of the grown crystal was estimated using Nd:YAG laser source. The second harmonic generation efficiency of the grown crystal was studied by Kurtz-Perry test.*

***Key Words*: Nonlinear optics; Crystal growth; Optical property; Laser damage threshold;**

1. INTRODUCTION

Developing and designing the organic molecular NLO crystals have been precisely overlooked since they exhibit a degree of high nonlinearity and are studied in theoretical and experimental levels by both engineering and scientific communities. They possess enormous advantages like light weight, low fabrication cost, large area bendy displays etc which gives them edge over their inorganic counterparts. They have evidenced excellent upswing in almost all the scientific arenas due to their striking optical device applications such as optical switches, optical modulators, optical communications, optical data storage etc [1-3]. The complexation of o-phenylenediamine and its derivatives has shown interesting properties with compounds such as tetracyanoethylene, p-chloranil and chloranilic acid. Nitrobenzene and/or aniline have been captivating the attention of the researchers and these derivatives have been considered as the most efficient organic crystals developed up to now. While, it is observed that orthorhombic modifications of nitroaniline, nitrobenzene and nitrophenol crystals exhibit optical nonlinearity described by third rank polar tensors and interesting potentiality have been verified in their nonlinear optical properties. In addition to this, nitro group consist of two additional acceptor sites making substituted aromatic amine to form an extended hydrogen-bonding networks. Extension of π conjugation bonds, good planarity and strong electron donor to acceptor ratio at opposite ends of the molecule are the attractive structural features of the investigated crystals, as they possess added advantages of containing high density of chromospheres and good thermodynamic stability. Hence to develop and design materials for nonlinear optical activities and to enhance first order hyperpolarizabilities a wide approach utilized is the cocrystallization of two chromophores, effectively an acid and base [4-6]. The hydrogen bonding networks exhibited by the title compound are discussed and reported earlier, herein we synthesized the title compound and grown material was subjected to optical characterization.

2. Experimental

2.1 Material synthesis and crystal growth

Synthesis scheme of the investigated compound have been outlined in Fig. 1. The title compound was prepared by taking analar grade o-Phenylenediamine ($C_6H_8N_2$., 10.81 g) as donor and 4-Nitrobenzoic acid ($C_7H_5NO_4$., 16.71g) as acceptor. Initially, various polar solvent combinations such as methanol, acetonitrile, and water were employed according to the solubility of products. It is then resolved that methanol solvent is more suitable for selective growth of PD4NB crystals in accordance to crystal characteristics, as for other polar solvents utilized the crystallization was not suitable. The compounds were dissolved in 100 ml of methanol solvent. The solution was allowed to stir for 6hrs to guarantee the dissolution and homogenization of all ingredients. The saturated solution was filtered and covered by polythene sheet with single perforation at the center. Good optical quality crystal with size upto 4 x 4 x 1 mm^3 was obtained after the growth period of 1 week as shown in Fig.2.

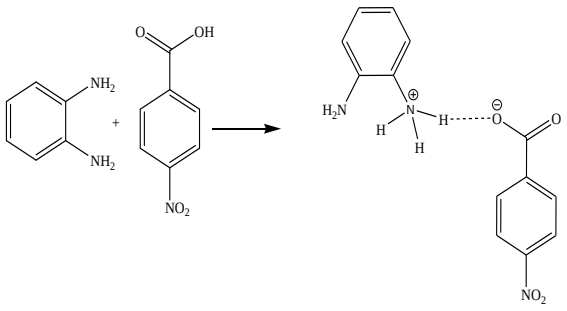

Fig -1: Synthesis Scheme of PD4NB

Fig – 2: Photograph of as grown PD4NB

3. Results and Discussions

3.1 X- Ray Diffraction analysis

The crystallographic lattice parameters of the grown PD4NB crystal were determined using Bruker Kappa APEXII CCD Single Crystal X-Ray Diffractometer and it shows that PD4NB crystal belongs to orthorhombic crystal system with non-centrosymmetric $P2_12_12_1$ space group. The estimated cell dimension are a = 3.7490 (7) Å, b = 10.2865 (19) Å, c =17.237 (4) Å , V = 664.8 (5) $Å^3$and it agree very well with the reported data [7].

3.2 Spectral studies

The IR spectra of the o-Phenylenediamine and 4-Nitrobenzoic acid gave information regarding their mode of coordination and were analyzed in a careful comparison with those of the free o-phenylenediamine and 4-nitrobenzoic acid (Fig -3). The IR spectra appeared around (*br*, 3353 cm^{-1}) and (*m*, 1510 cm^{-1}) is due to the ν(N-H) stretching of amino group of phenylenediamine, respectively [8,9]. The stretching vibration in the region around (*m*, 830 cm^{-1}) corresponds to υ(C-N). The IR spectra of complexes revealed significant difference from those of free o-phenylenediamine and 4-nitrobenzoic acid. The formation of complexes is confirmed by significant changes in frequencies of the ν(N-H), ν(C-N) and ν(COOH) groups, respectively. Upon complexation, these bands were shifted to lower frequencies 3420 cm^{-1} (*m*), 1560 cm^{-1} (*w*) and 940 cm^{-1} (*w*), respectively. The carboxylic -(COOH) vibrations of the free acceptor appeared around 1680 cm^{-1} in free 4-nitrobenzoic acid, which disappeared in the spectrum of complex .

The withdrawing groups attached to 4-nitrobenzoic acid facilitate to liberate the proton of carboxylic group to make intermolecular hydrogen bonds with the nitrogen atom of the amino groups of o-phenylenediamine. The donation process seems to be carried out by -NH_2 group in case of o-phenylenediamine [10,11]. This behavior is in accordance with the proton migration from the acceptor to the donor, which is giving rise to an additional evidence for the involvement of the nitrogen atoms of the donor and carboxylic proton of the acceptor.

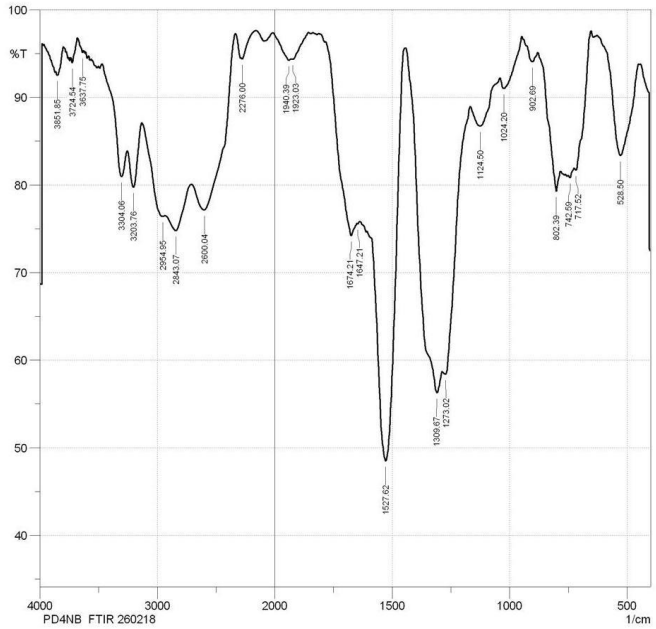

Fig – 3: FTIR spectra of PD4NB

3.3 HRXRD

The crystalline perfection of PD4NB single crystal was studied by high-resolution X-ray diffraction (HRXRD) by employing a multi-crystal X-ray diffractometer with Mo$K\alpha_1$ radiation. Fig. 4 shows the high-resolution diffraction curve (DC) recorded using symmetrical Bragg geometry. As seen in the figure, the DC contains a single peak and indicates that the specimen is free from any structural grain boundaries. The FWHM of the curve is found to be 17 arc s which is slightly more than that expected value for an ideal crystal from the plane wave theory of dynamical X-ray diffraction [12], but it is close to that expected value for a nearly perfect real life crystal. It is also observed from Fig.4 that the DC is not symmetric but greater in the positive direction than in the negative direction due to interstitial type of defects present in the crystal. It is also noticed (As seen from inset of the figure) the top of the diffraction curve is neither sharp nor smooth and extended in an angular range of around few arc s. These type of structural defects observed in the present specimen are probably due to strains developed in the crystal which may be due to entrapment of solvent molecules, thermal fluctuations and/or mechanical disturbances during the growth process [13,14]. The influence of such defects may not influence much on the NLO properties of grown crystal.

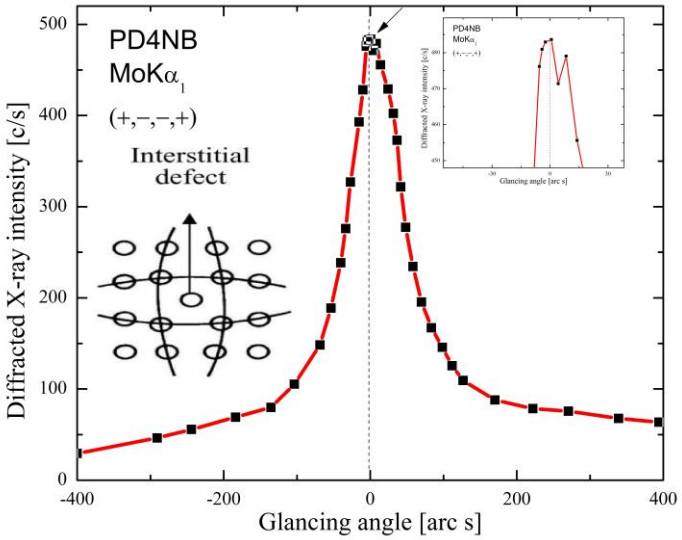

Fig – 4 : HRXRD spectrum of PD4NB

3.4 UV visible transmission spectral studies

Ultraviolet-visible transmittance studies was performed on the 1mm thick PD4NB crystal sample and the spectrum recorded is in the wavelength range 190-900 nm as shown in Fig.5. The lower cut-off wave length was found to be 269 nm and the material was transparent up to 65%.

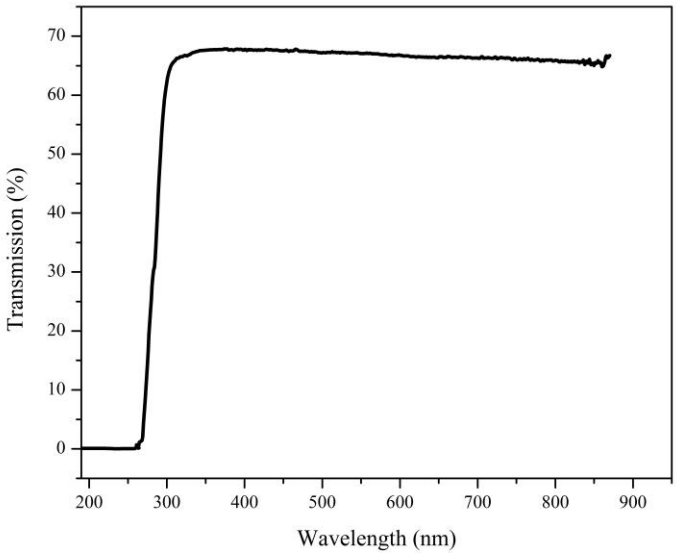

Fig – 5 : UV transmission spectrum of PD4NB

3.5 Optical bandgap energy (E_g) calculation

The optical absorption coefficient (α) was calculated using the relation,

$$\alpha = (1/d) \log (1/T) \qquad (1)$$

where d is the thickness of the crystal and T is the transmittance. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\upsilon$),

$$h\upsilon\alpha = (h\upsilon - E_g)^{1/2} \qquad (2)$$

where A is a constant, E_g is the optical band gap, h is the Planck's constant, and υ is the frequency of the incident photons [15]. The band gap of grown PD4NB crystal was estimated by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ and it is shown in Fig.6. The band gap energy of grown PD4NB crystal was found to be 4.59 eV. Therefore, from the band gap energy, it is observed that the grown material has added advantages for optical and optoelectronic device applications.

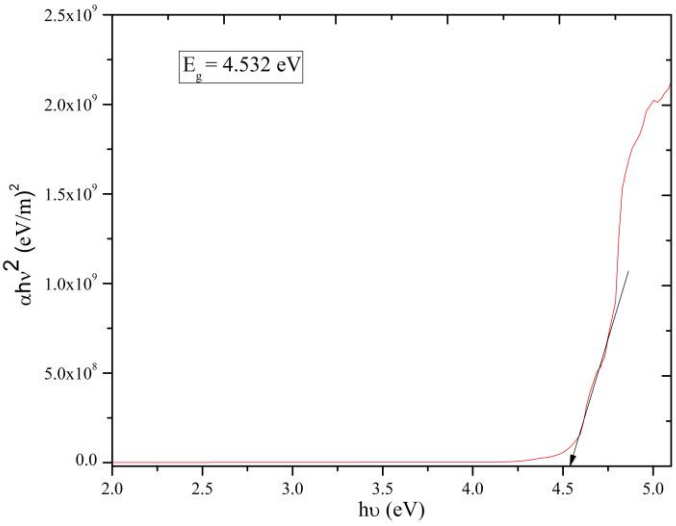

Fig – 6 : Tauc's plot of PD4NB

3.5 PHOTOLUMINESENCE

The strength of the electron–phonon interaction could be ascribed to the difference between the excitation and emission maximum. An intense emission band has appeared in the range 280–550 nm, owing to the emission of ultraviolet radiation. PL spectrum of the grown crystal sample (Fig.7) showed a sharp emission peak at 350 nm (3.53 eV). On the short-wavelength end of the visible spectrum is the near ultraviolet (near-UV) band ranging from 320 to 400 nm which corresponds to the near band-edge exciton of crystal sample [16]. Potentiality of the grown material in UV filters and optoelectronic device application was confirmed from the PL analysis.

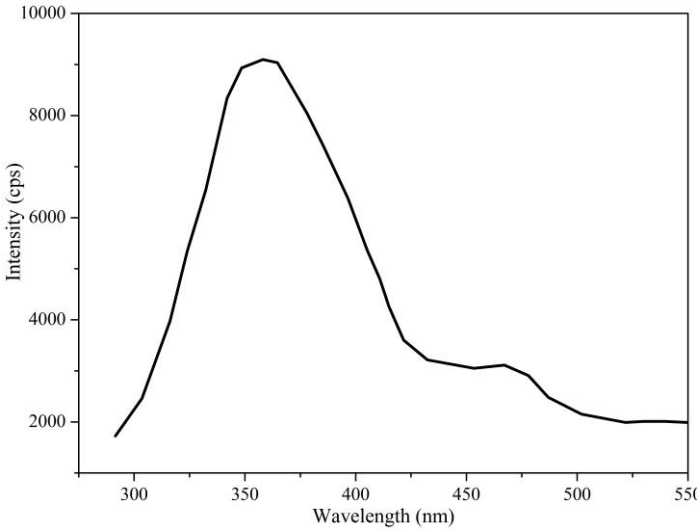

Fig – 7 : PL spectrum of PD4NB

3.6 LASER DAMAGE THRESHOLD

Nonlinear optical materials should tolerate high laser intensity which possesses its suitability in laser application. Laser damage threshold measurement was carried out for PD4NB crystal by using Nd:YAG laser system, which delivered laser pulses at 1064 nm with pulse width 6 ns and repetition rate 10 Hz. The surface LID threshold of PD4NB crystal was calculated using the relation,

$$P(d) = E/\tau A$$

where E is the intensity of the irradiant laser beam (245 mJ), τ is the pulse width (6 ns) and A is the area of the circular spot size (cm^2). For PD4NB crystal, the multiple shot laser damage threshold energy density obtained from the Q-switched Nd:YAG laser was found to be 5.20 GW/cm^2 compared to KDP reference crystal (0.20 GW/cm^2).

3.7 SECOND HARMONIC GENERATION

The NLO property of the grown PD4NB crystal was studied by Kurtz–Perry powder technique with KDP crystal was used as reference. The second harmonic generation (SHG) measurement was carried out using 1064 nm Q-switched mode locked Nd:YAG laser. The pulse width of 8 ns and10 Hz repetition rate with pulse energy of 1.2 mJ/pulse laser was used to fall normally on the sample cell. Second harmonic generation property for PD4NB crystal was confirmed by intense green light (λ = 532 nm) emission from the sample. The SHG signal voltages for PD4NB and KDP were measured to be 918 mV and 120 mV. Thus it is observed that SHG efficiency of the grown o-Phenylenediaminium 4-Nitrobenzoate crystal is 7.65 times higher than that of KDP crystal.

4. CONCLUSION

The title compound of o-Phenylenediaminium 4-Nitrobenzoate was successfully synthesized and the single crystal was grown by slow evaporation solution growth method. Single crystal X-ray diffraction study confirms orthorhombic crystal system with space group $P2_12_12_1$. The structure and crystalline perfection of the grown crystal were confirmed by FTIR and High Resolution X-ray Diffraction study. UV cut-off wavelength (269 nm) and transparency (above 65%) over the entire range of UV–visible region show that PD4NB is a good candidate for NLO applications. PL spectral study revealed the electron excitation wavelength (350 nm) in the grown crystal. The laser damage threshold value was found to be 5.22 GW/cm^2. The second harmonic generation relative efficiency of the grown crystal was found to be 7.65 times that of KDP crystal.

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