Crystal Growth and Characterization of a Novel Non Linear Optical Single Crystal of Urea Phthalic Acid

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Abstract. The Nonlinear optical (NLO) material of Urea Phthalic acid (UPA) was grown by slow evaporation method. The unit cell parameters were determined by single crystal XRD. The fundamental frequency vibrations of UPA were identified by FTIR analysis. The optical properties of UPA were determined by UV-Vis spectral studies. The Laser damage threshold value of UPA single crystal was found to be 5.3 GW/Cm². Z-scan techniques with He–Ne laser has measured the optical nonlinearity of UPA crystal.

1. Introduction
Developments of novel nonlinear optical (NLO) materials and crystal design technique for assembling the materials are used for many device applications in the domain of opto-electronics and photonics [1]. In particular, Organic NLO crystals are attracting a great deal of attention due to their high NLO coefficient, high damage threshold, high thermal stability and mechanical strength. The crystal engineering technology of the nonlinear optical material is based on the anchorage of organic molecules exhibiting a large NLO efficiency on the amino acid groups [2]. The unique optoelectronic properties of organics are due to the formation of weak Vander waals and hydrogen bonds hence, it shows high degree of localization. Urea is one of such organic NLO materials which have been explored as a first for NLO device for second to fifth harmonic generation [3]. In addition to this, the potentiality of urea as a first organic parametric oscillator is having extended transparency in the UV region, large birefringence and high optical damage threshold. The significant efforts were being made by many researchers to explore the potentialities of urea mixed systems and its derivatives through molecular engineering procedure. Such attempts involve the doping of other organic and inorganic NLO materials with urea. Many such efforts have become successful [4,5].With this reported background, we have ventured into growth and characterization of Urea Phthalic acid (UPA) single crystal and it is expected that this would be a non-centrosymmetric complex, but to our surprise it has been formed as a centrosymmetric structure in which third order nonlinearity which is more favourable and prominent. Similar results of third order nonlinear optical properties have been reported earlier [6]. In the present paper, the synthesis, crystal growth and characterizations by Single
crystal XRD, FTIR, UV-Visible, LDT and Z-Scan of Urea Phthalic Acid (UPA) single crystal are reported in detail.

2. Experimental Details
The UPA crystal was synthesized by taking Urea and Phthalic acid in a 1:1 stoichiometric ratio in methanol and stirred separately for about half an hour using a magnetic stirrer. After that these solutions were mixed together and stirred well for about 1h and filtered. The filtered solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation technique. The purity of the synthesized crystal was improved by successive recrystallization process thereby good optical quality colorless single crystals were obtained in 30 days which is shown in Figure 1.

3. Results and Discussion
3.1. XRD analysis
The single crystal X-ray diffraction analysis for the grown UPA crystal has been carried out to identify the cell parameters using an ENRAF NONIUS CAD4 automatic X-ray diffractometer. The UPA crystal retained its triclinic structure with lattice parameters of \( a=7.402 \ \text{Å}, b=7.654 \ \text{Å}, c=10.052 \ \text{Å} \) and \( \alpha=85.92^\circ, \beta=81.94^\circ, \gamma=65.20^\circ \) and the volume of the crystal \( V=511.9 \ \text{Å}^3 \) with Centro symmetric group \( P1 \). The lattice parameters are in good agreement with the reported values [7].

3.2. UV-Vis Absorption spectroscopy
The UV-Vis spectral analysis of UPA was carried out using Varian Cary 5E spectrophotometer in the wavelength range 200 to 900 nm. The resulting spectrum is shown in figure. 2. The cut off wavelength as observed from the spectrum for UPA is 258 nm. It is due to the direct transition of an electron from a non-bonding ‘n’ orbital to an anti bonding ‘\( \pi^* \)’ orbital (n →\( \pi^* \)). It is important that for efficient NLO crystal, lower cut-off wavelength should be in the range of 200 to 400 nm. The steep decrease in the absorption of the compound around 276 nm may be assigned to the electronic excitation in coo’ group. As there is no appreciable change in the transmittance in the entire visible region upto 900 nm, the material can be useful as optical windows in the spectral instruments in the wavelength studied. The material is found to be transparent to all radiation in the wavelength range of 300-900 nm. The wide optical transmission window is an encouraging optical property seen in UPA and is of vital importance for NLO materials.
3.3. *FT-IR analysis*

The FTIR spectra of the grown UPA single crystal were observed on the powder sample is shown in Figure 3. The spectrum of UPA crystal was recorded using the Brukers IFS66 spectrometer in the range 4000 – 400 cm\(^{-1}\) by KBr pellet to identify the functional group present in the crystal. In the high energy region the broad band in the range 3458 cm\(^{-1}\) is due to N-H stretching vibrations. The symmetric and asymmetric stretching vibrations of NH\(_2\) are observed in range of 3233 cm\(^{-1}\) and 3337 cm\(^{-1}\) respectively. The absorption peaks at 3136 cm\(^{-1}\) and 1687 cm\(^{-1}\) are due to the symmetric and asymmetric stretching vibrations of C=O carboxylic group. The absorption peak at 1441 cm\(^{-1}\) is assigned for NH\(_2\) bending which shows the presence of urea. The peaks observed at 1372 and 1014 cm\(^{-1}\) are corresponding to N-C-N stretching vibrations. The peak at 922 cm\(^{-1}\) is due to O-H out of plane bending vibration. All these observations clearly show the formation of the urea phthalic acid crystal.

![Absorption spectrum for UPA crystal](image1)

**Figure 2.** Absorption spectrum for UPA crystal

![FT-IR vibrational spectrum of UPA crystal](image2)

**Figure 3.** FT-IR vibrational spectrum of UPA crystal.
3.4. Laser Damage Threshold Studies
To measure laser-damage threshold for our UPA crystals, we used the laser with the pulse width 10 ns, the repetition rate 10 Hz and the fundamental wavelength 1064 nm. The laser beam with the diameter of 1 mm was focused on the sample. The sample was placed at the focus of a planoconvex lens (the focal length 30 cm). The energy of laser pulses was varied using attenuator that included a polarizer and a half-wave plate. The pulse energy of each laser shot was measured with a combination of a phototube and an oscilloscope. Finally, the surface damage threshold was calculated using the following relation for the power density (\(P_d\)),
\[
P_d = \frac{E}{\tau \pi r^2}.
\]
Here E is the input energy in mJ, \(\tau\) the pulse width in ns and \(r\) the radius of the spot in mm. As a result, the laser damage threshold for the UPA crystals is found to be 5.3 GW/Cm², which is higher than that of Urea tartaric acid (4.6 GW/Cm²) [8].

3.5. Z-Scan analysis
The Z-scan method has gained rapid acceptance by the NLO community as a standard technique for determining the nonlinear changes in refractive index and nonlinear optical absorption. The nonlinear absorption and refractive index of UPA crystals were estimated using the single beam Z-scan method with laser beam intensity of 60mW and the wavelength of source used for the measurement was 632.8 nm. The study of nonlinear refraction by the Z-scan method depends on the position (Z) of the thin samples under the investigation along a focused Gaussian laser beam. The sample causes an additional focusing or defocusing, depending on whether nonlinear refraction is positive or negative. Such a scheme, referred to as an “Open aperture” Z-scan and it is suited for measuring nonlinear absorption in the UPA crystal. Results obtained from a typical closed aperture and open aperture of Z-scan study for the grown UPA crystals are represented by Figure. 4a and b. The nonlinear refractive index (\(n_2\)) of the crystal was calculated using the standard relations \(\Delta T_{p-v} = 0.406(1-S) 0.25/\Delta \phi_o\). Where \(S = 1- \exp (-ra^2/\omega a^2)\) is the aperture linear transmittance, \(\Delta \phi_o\) is the on-axis phase shift. The on-axis phase shift is related to the third-order nonlinear refractive index by \(|\Delta \phi_o| = kn_2L_{eff} I_o\). 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, \(I_o\) is the on-axis irradiance at focus and \(n_2\) is the third-order nonlinear refractive index. The calculated values of third order nonlinear refractive index (\(n_2\)) is 2.24 x 10⁻¹¹ cm²/W, nonlinear absorption coefficient (\(\beta\)) = 3.481 x 10⁻⁶ cm/w. The positive value of nonlinear refraction reveals the self-focusing nature and nonlinear absorption co-efficient (\(\beta\)) exhibits the two-photon absorption process. Real and imaginary value of third order susceptibility of UPA is 9.98 x 10⁻⁸ esu and 7.887 x 10⁻⁶ esu respectively. The third order susceptibility (\(\chi^{(3)}\)) is 7.88 x 10⁻⁶ esu and it is due to the π-electron cloud movement from the donor to acceptor which makes the molecule highly polarised.

![Figure 4](image-url)  
Figure 4. Z-scan spectrum of UPA (a) Open aperture (b) Closed aperture.
4. Conclusion
The novel single crystal of Urea Phthalic acid (UPA) was successfully grown from the methanol solvent by slow evaporation technique. The crystal structure has been confirmed and the lattice parameters have been calculated by single crystal X-ray diffraction studies. The absence of significant absorption in the entire visible region and lower cut-off wavelength indicates the suitability of UPA for optical applications. The vibration spectral analyses confirm the different functional groups in UPA. The laser damage threshold value for the grown crystal is 5.4 GW/cm². The third order nonlinear refractive index, absorption coefficient and optical susceptibility was calculated by the Z-scan techniques and it reveals that the UPA crystal possess self-focusing and two-photon absorption process.

Acknowledgments
The corresponding author gratefully acknowledges the support from the Department of Science and Technology (DST), Government of India for the research project (SB/EMEQ/248/2014).

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