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Growth and Characterization of Urea Phthalic Acid Single Crystals.

Indumathi N¹, Deepa K², Venkatesan A³, Rajasaravanan ME³, Madhavan J², and Senthil S^{1, *}.

¹Department of Physics, Government Arts College for Men, Nandanam, Chennai - 600 035, Tamil Nadu, India.

²Department of Physics, Loyola College, Chennai - 600 034, Tamil Nadu, India.

³Department of Physics, Government Arts College, Salem - 636 007, Tamil Nadu, India.

ABSTRACT

Single crystals of Urea phthalic acid (UPA) were grown by slow evaporation method at room temperature. The lattice parameters of UPA were calculated by single crystal X – ray diffraction analysis and it belongs to triclinic system with centrosymmetric space group (P1). The presence of various functional groups has been identified by FTIR spectral analysis. UV – Vis absorption spectrum was recorded to study the optical absorbance of UPA single crystal. Thermal analysis was performed to study the thermal stability of the grown crystals. The surface laser damage threshold (LDT) for the crystal has been analysed.

Keywords: Crystal growth, X-ray diffraction, FTIR, Optical properties, TG/DTA, LDT.

**Corresponding author*

INTRODUCTION

Crystal growth plays an important role in modern technology. Single crystals find a wide range of applications in laser technology, optoelectronics, light emitting diodes, thermography etc, therefore growth of single crystals is of at most importance for further development in materials research [1,2]. Urea or carbamide was the first synthesized organic molecule, as well one of the simplest organic compound. With urea, the enhancement is achieved through the two hydrogen-bonding acceptor sites on the carbonyl oxygen and the four proton donor sites on the two amine nitrogen's. This capability was illustrated to build the structure of urea where all potential sites are utilized, giving six interactions through the oxygen atoms (three-centre) and both amine nitrogen's [3]. Amino acids with organic salts are prominent promising materials for the application of device fabrications [4]. The combination of urea with the organic compounds such as urea with tartaric acid [5] and urea with L-Malic acid [6] forms with interesting properties are reported. In this paper, we report the growth and characterization of Urea Phthalic acid (UPA) single crystal such as single crystal XRD, Fourier transform infrared spectroscopy (FTIR), UV-Vis-NIR spectroscopy, Dielectric studies, TG/DTA, The surface laser damage threshold for the crystal has been analysed.

EXPERIMENTAL PROCEDURE

MATERIAL SYNTHESIS

Urea phthalic acid (UPA) was synthesized by using Urea and Phthalic acid. Urea and Phthalic acid were taken in the ratio of 1:1 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 the saturated solution was filtered and covered to avoid contamination. The synthesized crystal of UPA was recrystallized several times using methanol at room temperature. Recrystallized optically clear and well shaped UPA crystal is harvested in the period of 30 days.

RESULTS AND DISCUSSION

SINGLE CRYSTAL X - RAY DIFFRACTION

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 $a=7.402 \text{ \AA}$, $b=7.654 \text{ \AA}$, $c=10.052 \text{ \AA}$ and $\alpha=85.92^\circ$, $\beta=81.94^\circ$, $\gamma=65.20^\circ$ and the volume of the crystal $V=511.9 \text{ \AA}^3$ with Centrosymmetric space group of P1. The lattice parameters are in good agreement with the reported values [7]. The Fig.1 shows the photograph of UPA single crystal.

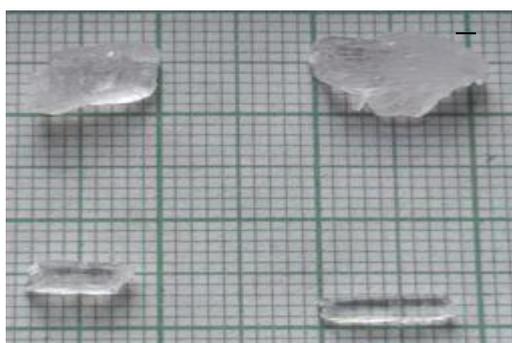


Fig 1. Photograph of UPA single crystal

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fig. 2 shows the FTIR spectrum of UPA crystal. From the spectrum reveals that, in the high energy region the broad band in the range 3458 cm^{-1} is due to N-H stretching vibrations [8]. The symmetric and asymmetric stretching vibrations of NH_2 are observed in the 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. Other characteristic vibrations are identified and the functional groups present in the UPA crystals are represented in Table.1. All these observations clearly show the formation of the urea phthalic acid crystal.

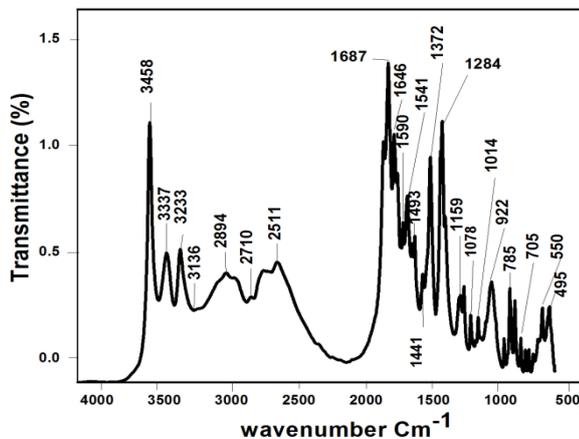


Fig 2. FT-IR vibrational spectrum of UPA crystal.

Table 1: Frequency Assignments For UPA Crystals

Sl. No.	Energy (mJ)	No. of Laser pulses	Time(s)	Observation
1	45	20	20	No damage
2	55	20	20	No damage
3	65	20	20	No damage
4	70	20	20	No damage
5	73	20	20	Damaged

OPTICAL ABSORPTION STUDIES

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 Fig. 3. The cut off wavelength as observed from the spectrum for UPA is 285 nm. It is due to the direct transition of an electron from a non-bonding 'n' orbital to an anti bonding ' π^* ' orbital ($n \rightarrow \pi^*$). The steep decrease in the absorption of the compound around 276 nm is due to the electronic excitation of 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 crystal [9].

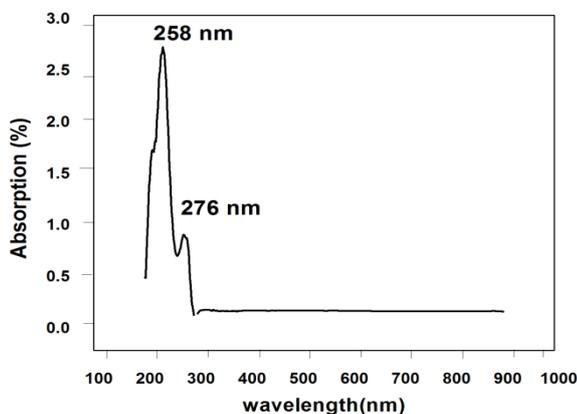


Fig 3. UV Absorption spectrum for UPA crystal

THERMAL ANALYSIS

Differential thermogram analysis (DTA) and Thermogravimetric analysis (TGA) give information regarding phase transition and different stages of decomposition of the crystal system. The TGA/DTA analysis of UPA crystal was carried out using SII Nanotechnology TG/DTA in the temperature range of 50-350°C with a heating range of 2°C/min in the nitrogen atmosphere. The TG-DTA curve of UPA is shown in Fig.4. In the DTA, there is an endotherm with a maximum at 178°C. It coincides with the weight loss in the TGA trace. The second endotherm is observed at 236°C. The endotherm at 178°C represents the melting point of the compound which is also confirmed by melting point apparatus. Another important observation is that, there is no phase transition and colour change till the material melts and this enhances the temperature range for the utility of the crystal for device fabrications.

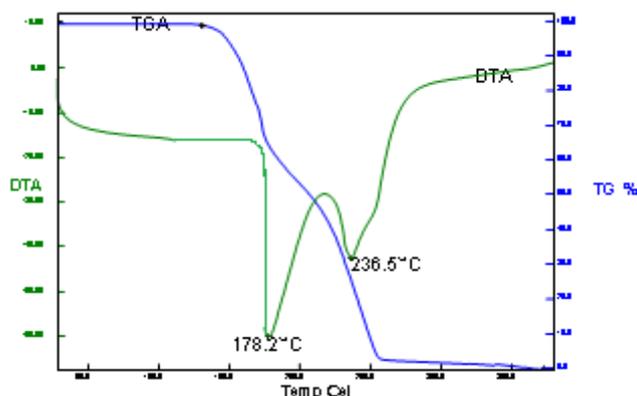


Fig 4. TG/DTA spectrum of UPA crystals

LASER-INDUCED DAMAGE THRESHOLD

For industrial fabrication of any materials, it is necessary to calculate the thermal stability or bind strength of the single shot and multi shot of laser using laser damage threshold technique. Multiple mode laser damage measurement is made on the UPA crystal. A Q-switched Nd YAG laser was used as the source at 1064 nm, pulse width of 6 ns and repetition rate of 10 Hz. The sample was placed at the focus of a Plano convex lens of focal length 20 cm focused on the crystal. The surface damage threshold of the crystal was calculated using the expression, Powder density (Pd) = $E / \tau \pi r^2$ W/cm². Where E is the energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). In the present work, laser damage threshold value of the UPA crystal was found to be 5.3 GW/Cm² (Table 2), which is higher than that of Urea tartaric acid (4.6 GW/ Cm²) [10]. The high damage threshold reveals that the compound is chemically stable and neither hygroscopic nor soluble in water.

Table 2: The laser damage threshold value of UPA Crystal

Wavenumber(cm ⁻¹)	Assignments
3337	NH ₂ asymmetric stretching vibration
3233	NH ₂ symmetric stretching vibration
3136	C=O symmetric stretching vibration
1687	C=O asymmetric stretching vibration
1590	COO ⁻ asymmetric stretching vibration
1493	C-O asymmetric stretching vibration
1372	N-C-N asymmetric stretching vibration
1014	N-C-N symmetric stretching vibration
922	O-H out of plane bending
785	C-H out of plane bending
550	COO ⁻ bending
495	C-OH in plane bending

CONCLUSION

The novel single crystal of 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 X-ray diffraction studies. The absence of significant absorption in the entire visible region and lower cut-off wavelength 258 nm indicates the suitability of UPA for optical applications. The vibration FT-IR spectral analyses confirm the different functional groups in UPA. TG/DTA analysis show thermal stability of the materials up to 178°C. The laser damage threshold value for the grown crystal is 5.4 GW/cm². Nonetheless, the above results shows that the grown UPA crystal is the promising candidate in the fabrication of optical devices since it possess substantial transparency and sufficient thermal stability.

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