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Studies on growth and characterization of L-prolinium picrate— A nonlinear optical crystal

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ABSTRACT

Single crystals of L-Prolinium Picrate (LPP) an organic non-linear optical material has been grown from solution by slow evaporation method at room temperature. The grown crystals were subjected to single crystal X Ray diffraction technique and cell parameters of the crystal were determined. The title compound crystallizes in monoclinic system with a noncentrosymmetric space group of $P2_1$ with unit cell parameters a = 10.8973 Å, b = 5.3495 Å, c = 12.4830 Å, β = 109˚ and V = 687.29 A^3. The thermal stability of the crystal was determined from Thermal analysis curve. The functional groups of the crystal were determined using Fourier Transform Infrared (FTIR) Analysis. The second harmonic generation (SHG) efficiency of the crystal was obtained by classical powder technique using Nd:YAG laser.

Keywords: X- ray Diffraction; LPP; FTIR; SHG efficiency

INTRODUCTION

Non linear optics is concerned with the interaction of electromagnetic fields with various media to produce new electromagnetic fields altered in phase, frequency of amplitude from the incident fields. Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging opto electronic technologies [1,2]. Amino acids are interesting materials for NLO application as they contain the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second-order nonlinearity. Single crystal of L-Proline shows no center of symmetry and its NLO coefficients have been examined by Boomadas et al [3]. Picric acid forms crystalline picrates with amino acids like L-valine [4], glycine [5], L-aspargine [6] and L-proline [7]. Here L-proline acts as donor and picric acid as electron acceptor. Here the CH-O hydrogen bond plays an important role in the supramolecular packing. In the present work we are going to present the investigation of growth and characterization of LPP from a mixed solvent of water and acetone.

MATERIALS AND METHODS

1.1 Crystal Growth

Growth of organic crystals with well developed faces and good optical quality mainly depends on the selection of suitable solvents. Single crystals of L-Prolinium Picrate have been grown successfully by slow-evaporation method. LPP was synthesized by the reaction between picric acid and L- proline in equimolar ratio. The reactants were thoroughly dissolved in double distilled water and acetone in 1 : 1 ratio and stirred well using a temperature controlled magnetic stirrer to get a homogeneous mixture of the solution, which is filtered and left for slow evaporation at room temperature. For the experimental work the de-ionized water was got from Millipore water pre-filtration unit. The resistivity of the used de-ionized water is 18.2 MΩcm.

After a growth period of 15 days, fine needle shaped crystals of dimension of about 5 x1 x 2 mm^3 were harvested and is shown in Fig 1.

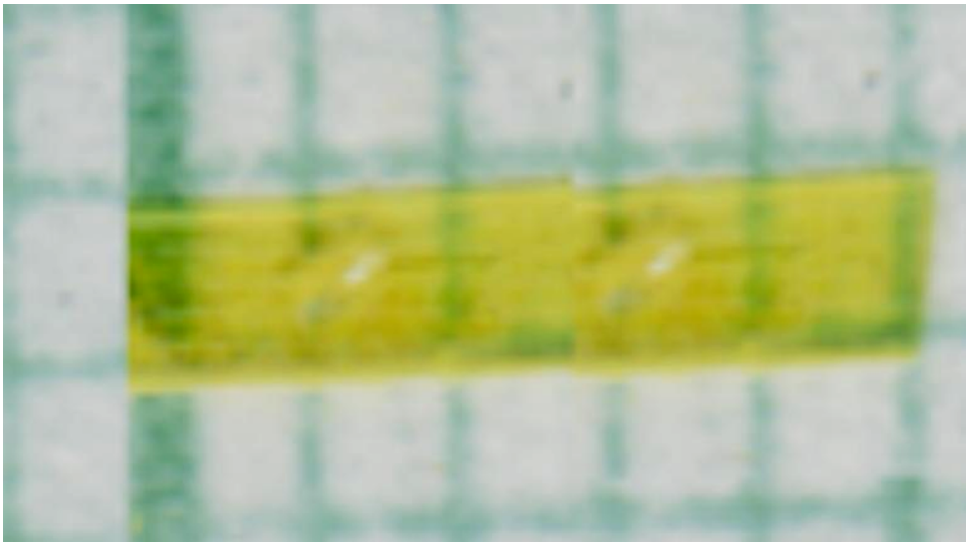

Fig. 1 LPP crystal

2. Characterization

2.1 X- Ray Diffraction Analysis

Single crystal diffractometers are most often used to determine the molecular structure of new materials. The grown crystals were subjected to single crystal X- ray diffraction to determine the unit cell dimensions. A good quality crystal was selected for the X- ray diffraction studies. From Table 1, one can observe that the unit cell parameters derived are in very good agreement with the reported values [8,9].

Table 1. Comparison of single crystal X-Ray data of LPP crystal

Parameters	*Present work*	*T. Uma Devi et.al.[8]*	*Anitha et.al.[9]*
a(Å)	10.897	10.901	10.909
b(Å)	5.3495	5.351	5.352
c(Å)	12.4830	12.466	12.474
V(A^3)	687.29	687	688
System	Monoclinic	Monoclinic	Monoclinic
β (°)	109	109.11	109.142
Space Group	$P2_1$	$P2_1$	$P2_1$

Fig 2 represents the ORTEP of the molecule with thermal ellipsoids at 50% probability. The molecular structure consists of benzene rings.

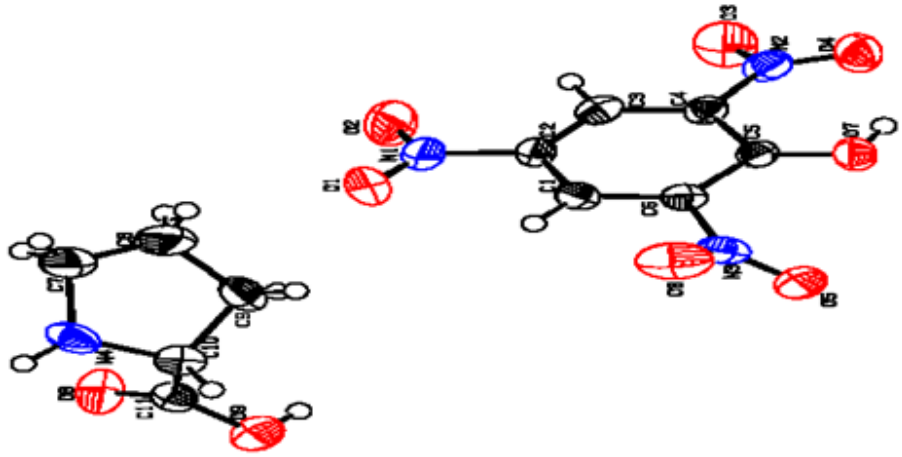

Fig 2. Molecular structure of LPP

2.2 Fourier Transform Infrared (FTIR) Analysis

FTIR spectrum of LPP crystals were recorded using Perkin Elmer Spectrum 1 in the range of 500-4000 cm^{-1} by KBR pellet technique. The FTIR spectra of the grown crystal is given in Fig. 3. The C=O symmetric stretching is found at frequency 1716.57 cm^{-1}. O-H bending appears at frequency 1268.32 cm^{-1}. NO_2 scissoring is found at frequency 786.55 cm^{-1}. NO_2 rocking curve appears at frequency 545.464 cm^{-1}. Asymmetric stretching of COO is found at frequency 1567.27 cm^{-1}. The phenolic vibration produces a peak at 1162 cm^{-1}. Also, it reveals that picric acid necessarily protonates the carboxyl group. The observed vibrational frequencies and the tentative frequency assignments of LPP are given in Table 2 along with a comparison of the corresponding reported values of LPP and L-asparaginium picrate (LASP) [10]. The corresponding vibrational frequencies of LPP and LASP compare well.

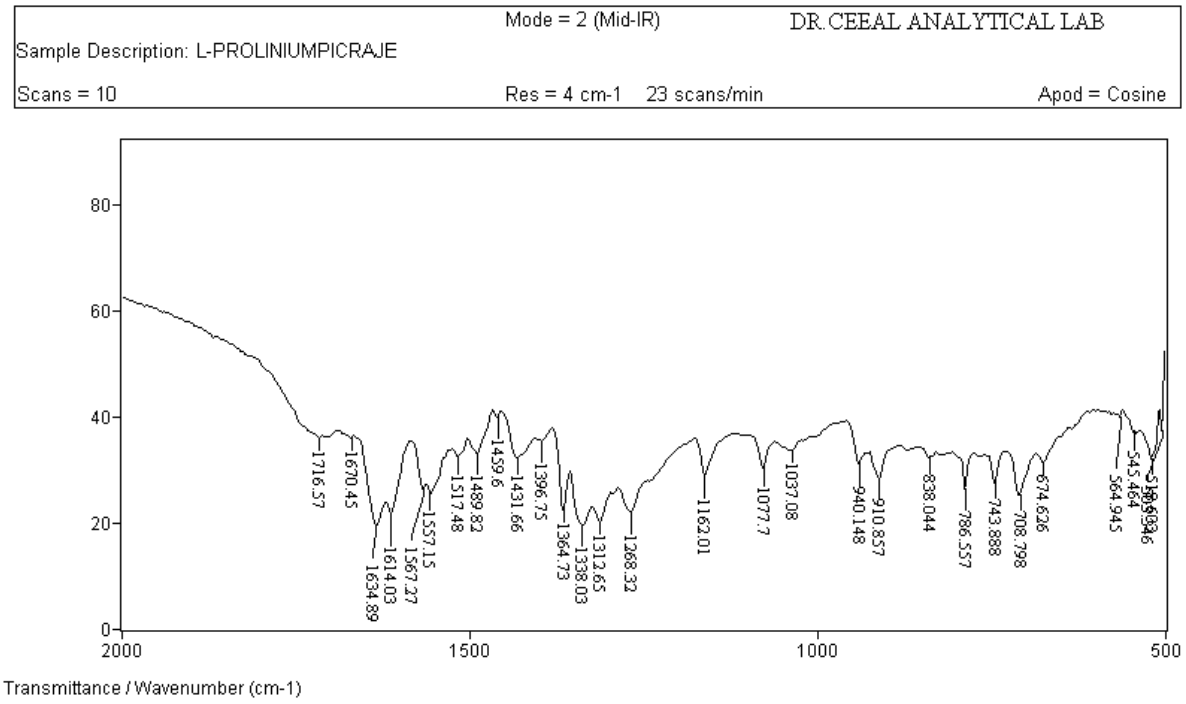

Fig 3 FTIR graph of L-Prolinium picrate

Table 2 Vibrational Band Assignments for LPP Crystal

Vibrational Band Assignment	LPP present work cm-1	LPP (cm-1)[8]	L-Asparaginium Picrate (cm-1)[10]
Symmetric stretching (C=O)	1716.57	1726	1740
Bending (N-H)	1634.89	1632	1633
Asymmetric stretching (COO)	1567.27	1563	1562
Symmetric stretching (NH2)	1489.82	1488	1485
Symmetric stretching (COO)	1431.66	1435	1437
Symmetric stretching (NO2)	1338	1335	1335
Bending (OH)	1268.32	1271	1271
Phenolic O	1162.01	1160	1159
Bending (C-N in plane)	940.148	936	937
Bending (C-N in plane)	910.85	907	906
Scissoring (NO2)	786.56	793	795
Bending (NO2)	743.89	743	745
Bending (ring)	708.79	705	706
Rocking (NO2)	545.46	545	523

3.3 Thermal Analysis

The TG/DTA thermogram of LPP crystals was obtained using NETZSCH STA 409C thermal analyser and the resultant thermogram is shown in figure 4. The TG thermogram reveals that decomposition starts for pure LPP at 216.98 ˚C and steps at 246.9 ˚C. During this decomposition mass of the sample reduces by 49.19%. The decomposition is also accompanied by the melting of the sample at 238.77 ˚C as shown by DSC. The second stage of decomposition is from 329.58˚C to 375.72˚C resulting in a mass reduction of 18.8%. The residue at the end at 774.78˚C is just 0.2066%. This shows that the sample is undergoing complete decomposition in this study.

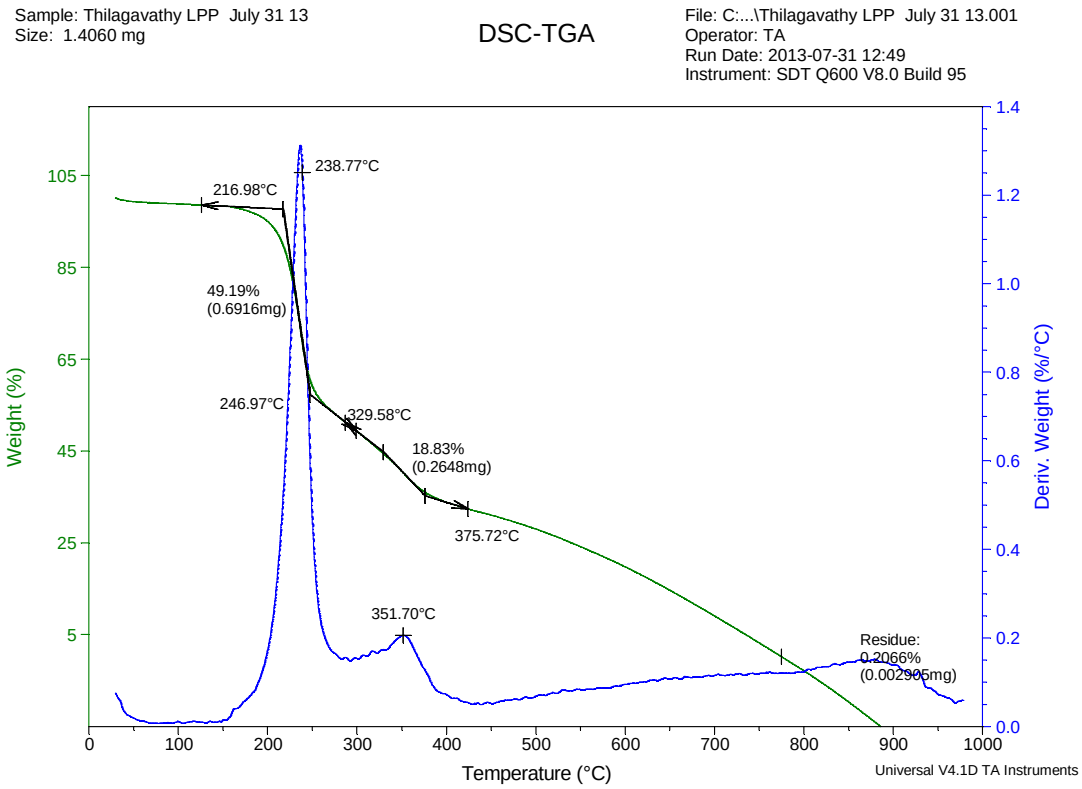

Fig. 4 TG/DTA of LPP crystal

3.4 SHG Efficiency

The SHG behavior of LPP crystal was observed using Q-Switched Nd:YAG laser beam of wavelength 1064 nm, with an input power of 0.68 mJ. The grown single crystal of LPP was powdered to a uniform particle size and then

packed in a microcapillary of uniform bore and exposed to laser radiations. The generation of the second harmonics was confirmed by the emission of green light. The SHG output power from LPP is found to be about 10.08 mJ. A strong bright green emission emerging from LPP crystal shows that the sample exhibits good NLO property.

CONCLUSION

The organic NLO crystal of L- Prolinium picrate (LPP) was grown by slow-evaporation method. Single crystal X-ray diffraction study reveals that the LPP crystal belongs to monoclinic system. Vibrational frequencies were assigned from FTIR spectral analysis, which confirms the presence of functional groups. TGA shows the decomposition behaviour of the crystal. SHG efficiency is tested by Nd:YAG laser as a source.

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