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Synthesis, growth and spectral, optical and thermal characterization studies on L-Tryptophan p-nitrophenol (LTPN) single crystals for NLO applications

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ABSTRACT:

The novel nonlinear optical single crystal of L-Tryptophan p-nitrophenol (LTPN) has been successfully synthesized by taking the appropriate amount of L-Tryptophan and p-nitrophenol. The single crystals have been grown by slow evaporation solution growth technique. The single crystal XRD studies confirmed that the grown crystal belongs to the monoclinic system. The various functional groups presented in the crystal were confirmed by FT-IR and ^{1}H-NMR spectroscopic studies. The absorptions of the grown crystals were analyzed using UV-Vis-NIR spectral studies. The thermal analysis was performed to study the thermal stability of the grown crystals. The second harmonic generation behavior of L-Tryptophan p-nitrophenol crystal was tested by Kurtz–Perry powder technique.

Keywords: crystal growth, solution growth, thermal studies, NLO crystals

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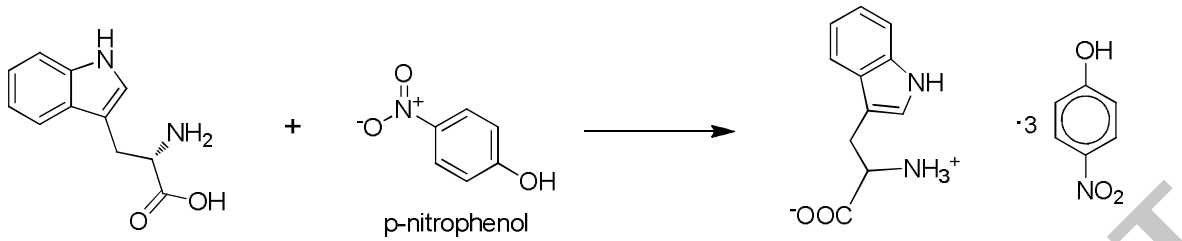
Introduction

Non-linear optical materials (NLO) exhibiting second harmonic generation have been in great demand over the last few decades due to technological importance in the fields of optical communication, signal processing and instrumentation [1-3]. Most of the organic NLO crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency. Also it is difficult to grow large size optical-quality crystals of these materials for device applications. Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity because of the lack of extended π-electron delocalization [4, 5]. Hence it may be useful to prepare semi-organic crystals which combine the positive aspects of organic and inorganic materials resulting in useful NLO materials. In semi-organic materials, the organic ligand is ionically bonded with inorganics. These crystals have higher mechanical strength, chemical stability, and large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [6, 7]. Amino acids are interesting materials, as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino ($-NH_2$) group which provide the ground state charge asymmetry of the molecule required for second order nonlinearity [8, 9]. Literature survey reveals that amino acid impurities have improved the material properties [10]. In this article, we report the growth, spectral optical and thermal aspects of the LTPN crystal.

Materials and Methods

LTPN salt was synthesized using L-Tryptophan and p-Nitrophenol (AR grade) in the stoichmetric ratio 1:2. The required quantity of L-Tryptophan and p-Nitrophenol was estimated according to the following reaction:

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L-Tryptophan p-nitrophenol L-Tryptophan p-nitrophenol

The calculated amount of L-Tryptophan was first dissolved in the hot methanol. Then p-Nitrophenol was added to the solution slowly with stirring. The prepared solution was allowed to dry at room temperature. The purity of the synthesized salt was improved by successive recrystallization. The careful observation was taken for drying the prepared solution and the temperature was never allowed to exceed 50 °C so as to avoid decomposition of the solute molecules. The prepared solution was filtered with Whattman filter paper. The solution was taken in vessels and closed with covers and kept in a dust-free atmosphere. The crystals were harvested when they attained an optimal size and shape.

To determine the structure and to estimate the lattice parameter values the cell parameters of LTPN crystals, single crystal XRD study of was carried out using ENRAF NONIUS CAD4 X-ray diffractometer. To get the information about the structure of a compound, the FT-IR spectrum was recorded using BRUKER IFS-66V spectrometer by KBr pellet technique in the range of 400-4000 cm^{-1}. To find the position of proton in LTPN, the ^{1}H-NMR spectrum was recorded using JOEL GSX 500 instrument in DMSO d_6 solvent. To study the optical behavior of LTPN, the UV-Vis-NIR spectrum was recorded using VARIAN CARY 5E spectrometer in the range of 200-900 nm. The thermal behavior of the grown sample was studied using STA 1500 thermal analyzer. The grown LTPN crystals were subjected to Kurtz-Perry powder SHG test to study their NLO efficiencies using Spectra Physics Quanta Ray an Nd:YAG laser.

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Single crystal XRD studies

From the single crystal XRD studies it was observed that the grown LTPN crystal belongs to monoclinic structure space group P_{21}. The Lattice parameter values of LTPN single crystals are listed in Table 1. The observed data were in very good agreement with the reported values [11].

Table 1. Lattice parameters of LTPN crystal

Sample	Lattice parameters						Volume
LTPN	a (Å)	b (Å)	c (Å)	α (˚)	β (˚)	γ (˚)	V $(Å)^3$
	6.699	13.190	17.275	90	104.236	90	1479.401

FT-IR spectral studies

The FT-IR spectrum of LTPN (Fig. 1) shows very sharp peak at 3438 cm^{-1} corresponding to N-H stretching, the frequency of tryptophan group. The weak singlet at 2932 cm^{-1} is due to alkyl group present in the tryptophan moiety. The peaks appeared from 2560 to 2400 cm^{-1} are due to the presence of hydrogen bonding in carboxylic acid group. The absorptions at 1660 and 1614 cm^{-1} are due to carboxyl and aromatic nature of LTPN. The signals at 1452 and 1164 cm^{-1} are due to the presence of NO_2 group. The FT-IR spectrum confirmed the presence of amino acid in the sample qualitatively.

^{1}H-NMR spectral analysis

The ^{1}H-NMR spectrum of the compound LTPN (Fig. 2) the ^{1}H-NMR spectrum of LTPN shows sharp doublets at 7.05 and 8.13 ppm corresponding to the two types of protons of the nitro phenol molecule. The singlet at 7.05 ppm is due to proton attached ortho to hydroxyl group and

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the signal at 8.08 ppm is due to proton attached ortho to nitro group. The spectrum also shows three doublets at 7.64, 7.34 and 7.15 ppm are due to three types of protons of benzene ring of tryptophan. The singlet at 7.21 ppm corresponds to the aromatic proton of the indole NH. The two triplets at 3.34 and 3.01 ppm are due to the alkyl groups of the tryptophan. The three singlet's at 11.0, 10.2 and 5.13 ppm can be attributed to the carboxylic acid (-COOH), indole ring (-NH) and amine ($-NH_2$) protons respectively. From the intensity of NMR spectrum obtained it can be concluded that there is formation of 1:2 formation of complex between tryptophan and nitrophenol molecules.

UV-Vis-NIR spectral studies

UV-Visible techniques are helpful in the investigation of NLO materials making it possible to check, both NLO responses and spectroscopic absorbance in the appropriate wavelength range [12]. The UV-Vis-NIR transmission spectrum of LTPN (Fig. 3) shows a λ_{max} (wavelength maximum) at 250 nm. This is a characteristic for $\pi \rightarrow \pi^*$ transition in aromatic ring. There is no remarkable absorption in the entire region of the spectra. This is good enough for the production of shorter wave length violet-green radiation from the infrared laser sources.

Thermal studies

The TGA and DTA were carried out in nitrogen atmosphere at a heating rate of 20 °C /min from 25 to 610 °C. The TGA thermogram of LTPN (Fig. 4) shows one major weight loss starting at 163 °C and completing nearly at 251 °C. So it was observed that the LTPN is found to be stable up to 163 °C. The DTA curve of LTPN shows very sharp endotherm at 146 °C corresponding to the melting of LTPN. This is an intermediate melting point of p-nitrophenol and tryptophan.

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NLO/SHG studies

The SHG property of the grown LTPN crystal was tested by the Kurtz–Perry powder method [13]. The crystal was illuminated by spectra physics Quanta-ray Nd:YAG laser using the first harmonic output of 1064 nm, with a pulse width of 8ns. The emission of green radiation from the LTPN confirms the second harmonic generation in the crystal. It is observed that the measured second harmonic generation efficiency of LTPN crystal was 1.25 times that of KDP.

Conclusion

We have successfully grown the crystals of L-Tryptophan p-nitrophenol (LTPN) by slow evaporation technique. The crystal system was identified from single crystal X-ray diffraction. The functional groups of the grown compound have been identified by FT-IR and ^{1}H-NMR spectral studies. The UV-Vis-NIR spectral studies revealed its transparency. It was found that the grown crystal has been transparent for a wide range which highlights their prospects of applications as NLO materials in the photonics field. Thermal analysis clearly illustrates that the crystal undergoes decomposition above 163 °C. NLO property was confirmed using ND:YAG laser of wavelength 1064nm and the efficiency was estimated to be 1.25 times higher than KDP.

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References

[1] R.W. Boyd, Non Linear optics, Academic Press, San Diego, 1992, 155.

[2] B.E.A. Salch and M.C. Teich, Fundamentals of Photonics, Wiley, New York, 1991, 113.

[3] D.S. Chemla and J. Zyss, Non-linear optical properties of organic molecule and crystals Vol I and Vol II, Academic Press, New York, 1987, 71 and 123.

[4] M.H. Jiang and Q. Fang, Adv. Matter 11 (1999) 1147-1151.

[5] M.D. Aggarwal, J. Choi,W.S.Wang, K. Bhat,R.B. Lal, A.D. Shields,B.G.Penn, D.O. Frazier, J. Cryst. Growth 204(1) (1999) 179-182.

[6] T. Thaila and S. Kumararaman, Archives of Applied Science Research 4(3) (2012) 494-1501.

[7] S.Velso, Laser Program Annual Report Lawerence UCRL-JC105000, Lawerence Livermore, National Laboratory Livermore CA, 1990.

[8] Pal Tanusri, Kar Tanusree, Mater. Chem. Phys. 91 (2005) 343-347.

[9] T. Malik, T. Kar, G. Boce III, A. Musatti, Cryst. Res. Technol. 41 (2006) 280-284.

[10] K.D. Parikh, D.J. Dave, B.B. Parekh and M.J. Joshi, 30(2) (2007) 105-112.

[11] V. H. Rodrigues, M. M. R. R. Costa, M. Belsley and E. de M. Gomes, Acta. Cryst. E68 (2012) o920.

[12] J. Kulakowska, S. Kucharski, Eur. Polym. J. 36(9) (2000) 1805-1815.

[13] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798-3814.

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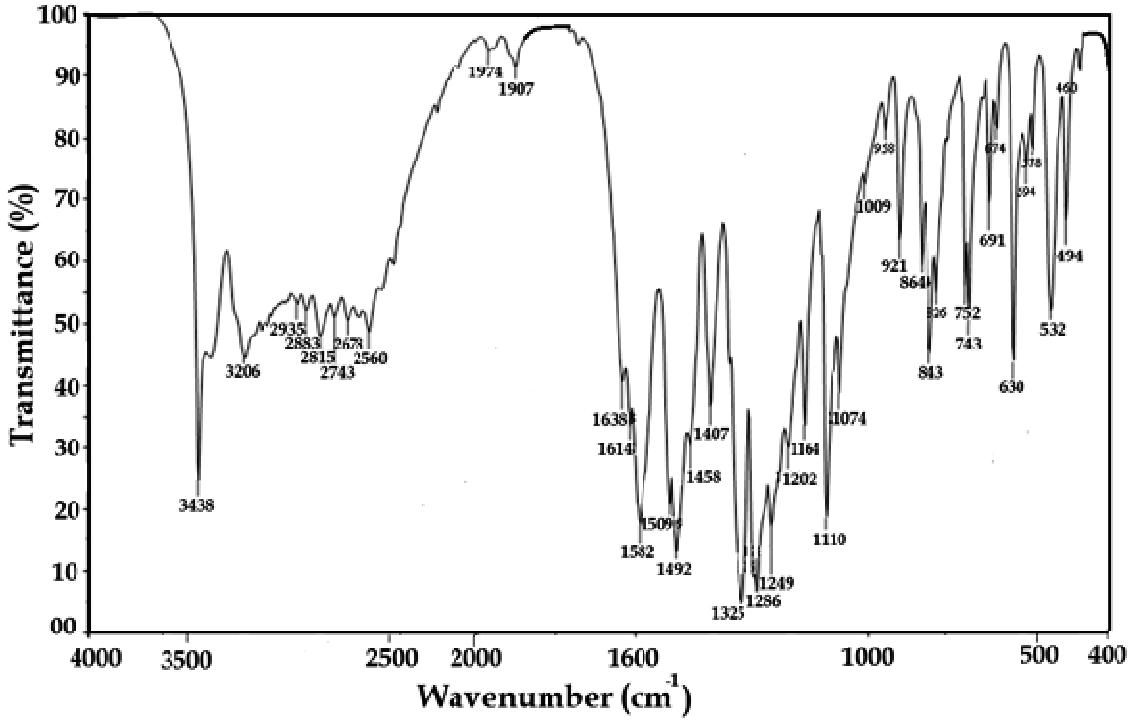


Fig. 1. FT-IR spectrum of LTPN

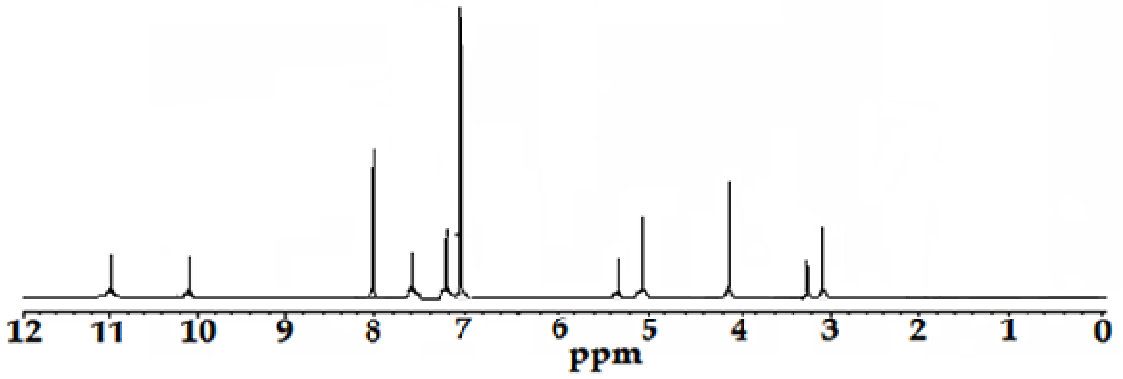


Fig. 2. ^{1}H-NMR spectrum of LTPN

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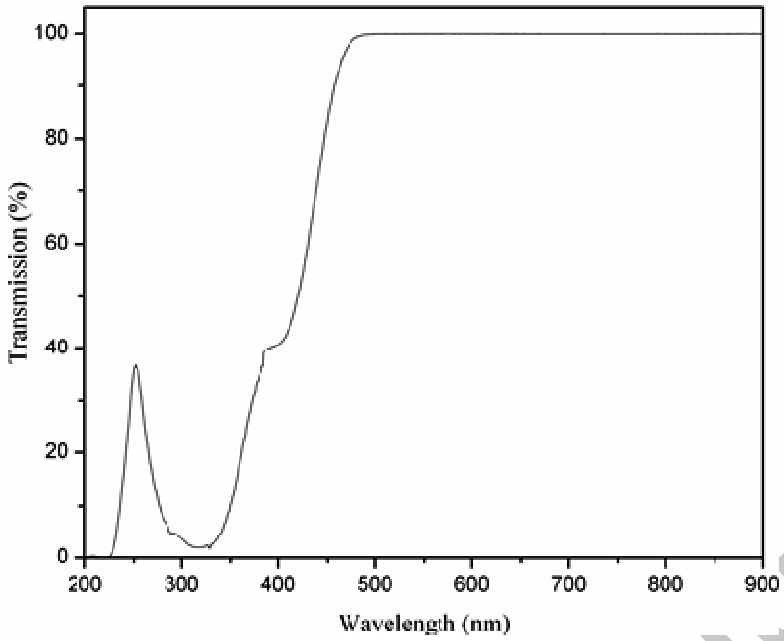


Fig. 3. UV-Vis-NIR transmission spectrum of LTPN

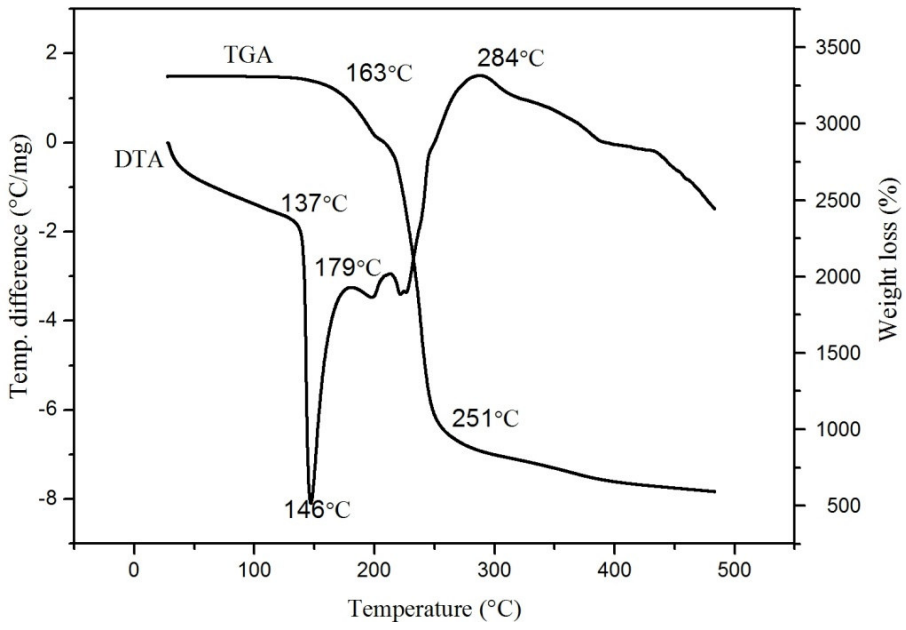
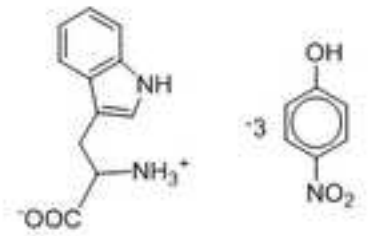


Fig. 4. TG/DTA curves of LTPN

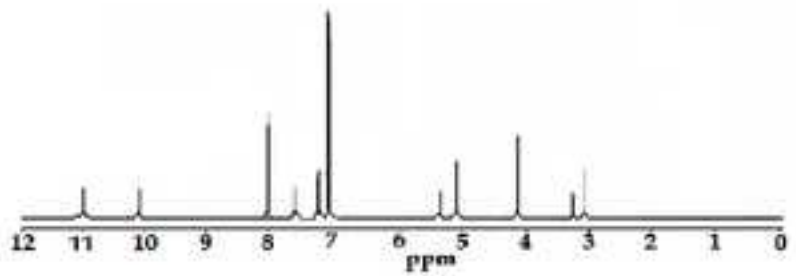
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L Tryptophan p-nitrophenol (LTPN)



As grown crystals of LTPN



^{1}H-NMR spectrum of LTPN

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Highlights:

- Crystals of L-Tryptophan p-nitrophenol (LTPN) are grown by slow evaporation technique.
- The crystal system was identified as monoclinic from single crystal XRD studies.
- The material was characterized by FT-IR, ^{1}H-NMR and UV-Vis-NIR spectra.
- The crystal was found to be thermally stable up to 163 °C from TG/DTA analysis.
- The NLO efficiency of the crystal was estimated to be 1.25 times higher than KDP.

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