Thermal and nonlinear optical properties of semiorganic single crystal: L-Threonine p-nitrophenolate (LTPNP)

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Abstract. The single crystal of L-Threonine 4-nitrophenolate developed by uncomplicated solution growth process. The grown crystal is analysed by using various characterization techniques. The structural analyses have been carried out by using Powder XRD method. Fourier Transform Infrared and Nuclear Magnetic Resonance spectra analysis confirms the functional groups exist in grown crystal. The thermal steadiness of L-Threonine 4-nitrophenolate crystals analysed by Thermo-gravimetric (TG) and Differential Thermal analyses (DTA). The sharp diffraction peaks in XRD pattern confirms the well crystalline nature of the synthesized sample. TG and DTA analysis prove that the synthesized sample possess good thermal constancy up to150°C. The UV-visible absorption studies show that the crystal is clearly visible in the whole visible region of the spectrum. Kurtz -Perry powder technique and Z-scan technique reveals the excellence of the synthesized samples for nonlinear optical (NLO) uses.

1. Introduction
Recent research trend move towards the growth of nonlinear optical crystals with emission of blue and green light for various uses like to store the data via optics, optical amplifiers, image processing and frequency conversion. In general the semi-organic NLO materials show large potential nonlinearities and give immediate response in electro-optic effect. Also semi-organic NLO possess the unique properties like very high nonlinearity, high electronic susceptibility and fast response [1]. The aromatic organic molecules having good optical nonlinearity property due to its unique structure such as acceptor and donor group bonded of the molecule. They are used in many industrial applications, such as optical switches and optical data storage [2]. Due to the demands in various technologies, many non linear optical (NLO) organic crystals have been introduced, like DAST (1-methyl-4-{2-[4-(dimethylamino) phenyl][ethenyl]pyridinium p-toluenesulfonate) and other grown crystals are reported in the previous research results [3-6]. The synthesized crystal L-arginine 4-nitrophenolate 4-nitrophenol dehydrates (LAPP); show the high second order nonlinear coefficient [7, 8]. In this research work, we look into the optical and thermal possessions of L-threonine p-nitro phenolate crystal which was grown from aqueous solution of L-therionine and 4-nitrophenol. The growth process, its crystal structure, thermal possessions and linear and nonlinear optical studies are reported.

2. Experimental Method

2.1. Fabrication of Crystal development Method
The compound of L-threonine p-nitrophenolate (LTPNP) was fabricated by taking equimolar ratio of L-Threonine and 4-nitrophenol in water as solvent. In a beaker, a calculated amount of L-Threonine is dissolved in double distilled de-ionized water using magnetic stirrer. Then, the amount of 4-nitrophenol is added slowly and stirred vigorously for three hours. To steer clear of impurities, the homogeneous solution is filtered and then transferred to beaker. Then the solution is kept at room temperature and allowed to evaporate slowly. After the evaporate process, three times re-crystallized material is used further to grow as single crystal. After 35 days, semitransparent yellow colored grown single crystal of dimension around $10 \times 4 \times 3$ mm$^3$ in the solution were cautiously cropped. The grown crystals were tested by various techniques and found that they are L-Threonine 4-nitrophenolate single crystals. Figure 1a & figure 1b represents the pictures of grown single crystal LTPNP.

![Figure 1. (a) As grown single crystal of LTPNP.](image1)

![Figure 1. (b) Single crystal of LTPNP.](image2)

2.2 Characterization Techniques

The phase analysis of grown crystal L-Threonine 4-nitrophenolate was done by using X’PERT PRO diffraction. The Nuclear Magnetic Resonance spectrum of the grown crystal is evidenced from AMX NMR spectrometer. Fourier transform infrared spectroscopy spectrum of the L-Threonine 4-nitrophenolate was traced to confirm the existence of many functional groups in synthesized crystal. NMR spectrum of LTPNP material was recorded. The thermal characteristics of the crystal were approved by TGA/DTA. The optical property of the sample was characterized by UV-Vis-NIR Spectrophotometer and nonlinear optical studies performed by Kurtz and Perry powder method [11].
The Z-scan experiment was done by using a 532 nm neodymium yttrium aluminium garnet Laser, which was focused by a lens with focal length of 3.5 cm, Rayleigh length is 1.48 mm and laser beam waist at 15.84 μm. A 1 mm wide optical cell containing LTPNP in distilled water is translated across the focal region along the axial direction that is the direction of the propagation laser beam.

3. Results and Discussions

3.1 Phase Analysis Study

The phase analysis was carried out between 10° and 50° of diffraction angles with the wave length of 1.5460 Å. Synthesized powder sample of LTPNP was subjected to analysis with a monochromatic CuKα radiation (λ=1.54060 Å). The angle of 2θ and the scan step time in the range of 0.0289° and 30.6° seconds. The well defined diffraction peaks ensures well crystalline nature of the synthesized sample. The (hkl) parameters were intended and XR diffraction peaks were indexed from obtained lattice parameters and d spacing [9]. The figure 2 represents the phase analysis of LTPNP.

![Figure 2. Powder X-ray diffraction pattern of LTPNP.](image)

3.2 FTIR Spectral analysis

The Fourier infrared spectrum is performed to investigate the various elemental groups exist in the crystal. Figure 3 shows the FTIR of synthesized sample in the frequency range between 4000 and 480 cm⁻¹ of. The existence of modes of vibrations makes the spectrum to be more complex [10]. Broad peak near 3400 cm⁻¹ corresponds to the symmetric and asymmetric stretching vibrations of hydroxyl bond in water. The peak at 1687 cm⁻¹ shows the H-O-H of water molecule. The peak at 1112 cm⁻¹ is due to C-O vibration of stretching mode. Also another vibration peak also observed around 856 cm⁻¹. The peak at 1310 cm⁻¹ represents the NO₂ vibration and the asymmetric stretching vibration is observed at 1590 cm⁻¹. The peak at 500 cm⁻¹ confirms the existence of hydrates. The vibration of the C-H is obtained at 1490 cm⁻¹. Based on obtained bands the functional groups in synthesized sample were deep-rooted.
3.3 Proton NMR Spectral Study

Nuclear magnetic resonance (NMR) spectroscopy is an additional instrument to recognize the fabricated crystal. The LTPNP crystal is undergone to proton NMR spectral analyser. The various chemical elements gives their signal at different chemical shift (δ) position due to presence of hydrogen atoms. The ortho hydrogen bond exists in the nitro phenol associated to parallel or in opposite and end to resonance. Hence the ortho hydrogens appear as distorted doublet and give their signals at 8.05 and 6.82 ppm [11-13]. The presence of amine groups in the L-threonine molecules attributes multiple splitting in these signals. The CH and CH₂ groups in the samples produce the signals at different δ value according to their shielding nature. The Proton NMR spectral study has also been performed to corroborate the configuration of the crystal. The obtained spectrum is given in figure 4. Along with the peak at 4.18 ppm, two signals also noticed. The ortho hydrogen in the aromatic structure is associated to parallel or antiparallel and usually ends to resonance twofold. In this study we observed the outputs with multiple splitting at 6.8. This attributes to the ortho hydrogen of benzene ring and the signal at 6.9 represent the meta hydrogen in benzene ring [11].

**Figure 3.** FTIR spectrum of LTPNP.

**Figure 4.** Proton NMR spectrum of LTPNP
3.4 Linear and Nonlinear Optical properties

The NLO crystal must possess good optical transparency in green visible region. Figure 5 represents the UV absorption spectra from the wavelength between 400 – 800 nm. It is observed that characteristic absorption band of LTPNP occurs at 435.2 nm. Also the crystal is clearly visible in the entire visible region of the spectrum. From the ultra violet absorption spectra, the energy band gap is obtained as 4.5eV.

![Figure 5. UV-Vis absorption spectrum of LTPNP.](image)

The second order harmonic generation studies were carried out for the LTPNP crystal by Kurtz and Perry technique [12-14]. The second harmonic generation (SHG) effectiveness of material is two times more than that of standard reference KDP and four times greater than Urea materials. Hence this crystal is promising materials for various applications in electronics.

3.5 Third order nonlinear characterization

The Z-scan performance is used to establish nonlinear absorption coefficient \( \beta \) and nonlinear index of refraction \( n_2 \) [15]. Real part of the third-order susceptibility, \( \text{Re} \chi^{(3)} \) is proportional to the nonlinear index of refraction and the \( \text{Im} \chi^{(3)} \) is proportional to nonlinear absorption coefficient.

The Z-scan experiments were conducted by using neodymium Laser at 532 nm, which was focused using a 3.5 cm\(^{-1}\) focal length lens. A 1 mm wide optical cell containing LTPNP in distilled water is translated across the focal region along the axial direction which is the direction of the propagation of laser beam. Rayleigh length was found out to be 1.48 mm and since our path length is 1 mm, thin sample approximation holds good. The transmission of the beam was measured by an aperture placed in the far field using photo detector connected to the digital power meter (Field master GS-coherent). For an open aperture Z-scan, a lens is used to collect the entire transmitted beam through the sample. The Closed, open and ratio of the closed-to-open normalized Z-scan of LTPNP sample in distilled water at 63% transmittance is as given in figure 6. Both the refractive and absorptive nonlinearities of the sample have been studied by doing the Z-scan with and without aperture. The sign of negative refractive nonlinearity observed from the pattern of peak followed by a valley, i.e., self-defocusing. Due to the continuous exposure to laser, local dissimilarity in the refractive index with the temperature happens resulting in self-defocusing effect. The figure 6b, open aperture curve shows the material to exhibit saturable absorption [15]. The evaluated nonlinear parameters are shown in Table 1.
Figure 6. (a) Closed aperture; (b) Open aperture z-scan.

Figure 6. (c) Ratio of closed to open aperture z-scan.

Table 1. Non-linear parameters of LTPNP in distilled water.

| $n_2 \times 10^{-8}$ cm$^2$/W | $\beta \times 10^{-4}$ cm/W | Re $\chi^{(3)} \times 10^6$ esu | Im $\chi^{(3)} \times 10^6$ esu | $\chi^{(3)} \times 10^6$ esu |
|-------------------------------|---------------------------|-----------------|-----------------|-----------------|
| 3.88                          | 0.28                      | 1.15            | 1.76            | 1.17            |

3.6 Thermal Analysis

To aware of the thermal performance such as thermal constancy and melting point of the material, thermal analysis was carried out. The thermal properties of LTPNP have been analyzed by obtaining TG/DTA curves as represent in figure 7. From the TG curve it is observed that less than 3 % of weight reduction bellows 150°C due to loss of physically absorbed moisture by the crystal surface. A careful observation in the DTA curve infers that there are no phase transitions below 150°C. The first transition occurs at 168.8°C due to the melting of the material and it is associated with the major weight loss of around 72 %. This study confirmed that the sample is steady till 150°C which agreed with the result of literature [9]. Hence, this material has good thermal constancy up to 150°C and makes the requirement for the many electronic apparatus production.
Figure 7. Thermo gravimetric (TG) and Differential Thermal Analysis (DTA) curves of LTPNP.

4. Conclusion
Semi-organic NLO crystal with high quality of L-Threonine para nitrophenolate (LTPNP) was successfully developed by slow evaporation method. The phase analysis of the LTPNP was performed. The functional groups present in the synthesized sample were confirmed by FTIR and NMR spectral analysis. Thermal stability of the L-Threonine para nitrophenolate crystal was analyzed by TG/DTA analysis and melting point of the synthesized sample was recognized to be 168 °C which shows that the materials can be effectively used in various device applications. The UV-Vis-NIR spectrum of the grown sample shows blue shift in the absorbance near visible region 435.2 nm and entire near NIR region. The second harmonic competence value of the LTPNP is two times elevated than that of referenced KDP and four times higher than value of Urea. The z-scan characterization results confirmed that the synthesized LTPNP crystal is suitable for various non linear optical applications.

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