Investigations on synthesis, growth and characterisations of a NLO material: L-Tryptophanium phosphite (LTP)

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The nonlinear optical material L-Tryptophanium phosphite (LTP) was synthesised and grown by the process of slow evaporation solution growth. Characterisations like single crystal XRD, FT-IR, and H^1NMR spectral measurements were done to find the crystal structure and functional groups. The crystal was found to possess good transparency for the whole visible region from the UV-Vis-NIR spectral analysis. The thermal behaviour like stability and breakdown of the crystal were assessed using TG-DTA analyses. The hardness of the crystal was determined using Vickers micro hardness study. The Kurtz-Perry approach was used to study the nonlinear optical (NLO) characteristics of the crystal. A good value of conversion efficiency in second harmonic generation (SHG) makes the generated crystal suitable for frequency conversion.

(Received February 15, 2024; Accepted May 15, 2024)

Keywords: Solution growth, Amino acid, XRD, FT-IR, NLO

1. Introduction

Many researchers looking for innovative materials have been fascinated by the potential uses of crystal research, notably in the discipline of nonlinear optical (NLO) characteristics. The applications of NLO include optical communication, optical data storage, optical switching, and others [1, 2]. Moreover, NLO materials have been used as sensitive probes in environmental and biological sciences [3 – 5]. According to crystal engineering research, the alignment of donor-acceptor chromophores in noncentrosymmetric arrangement determines the formation of efficient second order nonlinear optical behaviour in the materials. The researchers have presented many practical ways in this respect [6–8]. Amino acids have carboxyl acid groups (COOH) which are proton-donors and amino groups (NH_2) which are proton-acceptors, making these materials for NLO applications. These are commonly employed because their chiral carbon atoms directly crystallize into non-centrosymmetric space groups and their zwitter ionic nature results in crystal toughness. An amino acid that occurs naturally, the L-tryptophan has no net charge and non-polar chain at physiological pH. The L-tryptophan shows non-exponential degradation of fluorescence in an aqueous solution. The observed decay could be attributed to the emission originating from the non-interconverting rotamers, that possess distinct lifetime as a result of varying rates of intermolecular charge transfer [9, 10]. Phosphonium salts are frequently transformed into ylides by the application of potent bases, however relatively weaker bases can also be employed provided that the salt exhibits sufficient acidity. Phosphonium salts, as photo-resistive materials, have potential applications in communication technologies [11]. This study focuses on the synthesis and

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https://doi.org/10.15251/JOR.2024.203.325

development of L-Tryptophanium phosphite (LTP) single crystals using slow evaporation solution growth approach. The single crystal XRD analysis, FT-IR, H^1NMR, UV-Vis-NIR spectral analyses, TG-DTA analyses and NLO investigations were used to describe the produced crystals.

2. Materials and methods

The crystal of L-Tryptophanium phosphite (LTP) was created by combining highly pure L-tryptophan with phosphonic acid (Sigma Aldrich 99%). The appropriate amount of L-tryptophan was completely dispersed by adding double distilled water according to solubility and stirring vigorously for about five hours in a magnetic stirrer. A few droplets of phosphonic acid have been added to an aqueous L-tryptophan solution. Using Whatman filter paper, the mixture was filtered to eliminate insoluble contaminants. The completely saturated solution of L-Tryptophanium phosphite (LTP) was then placed in one beaker with perforated cover which regulates the rate of evaporation and allowed to crystallize at the room temperature. Then, after nearly 40 days of gradual evaporation, clearly defined single crystals were recovered. Fig.1 shows an image of a grown crystal of L-Tryptophanium phosphite (LTP).

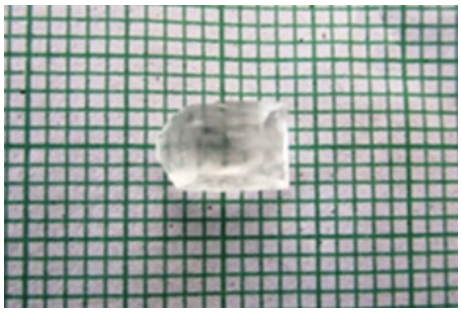

Fig. 1. The grown crystal of LTP.

3. Results and discussions

3.1. Single crystal XRD analysis

The LTP single crystal was subjected to single crystal X-ray diffraction (XRD) analysis to ascertain the cell structure and space group. The single crystal XRD pattern was acquired using BRUKER AXS diffractometer instrument which uses MoKα radiation of wavelength, λ= 0.7170 Å. The determined out cell parameters were, a = 5.533Å; b = 27.320 Å; c = 8.320 Å, and calculated cell volume, V = 1257.664 $Å^3$. The single crystal XRD data revealed that LTP has orthorhombic crystal structure with the space group $P2_12_12_1$ which is noncentrosymmetric. The estimated lattice parameters of LTP agree well with stated values. [12].

3.2. FT-IR spectral analysis

The whole molecular construction of this substance LTP under investigation may be found in the FT-IR spectrum. With this method, practically every functional group in a molecule absorbs distinctively at a certain frequency range. [13]. The FT-IR spectrum shown in Fig.2 was recorded for a range from 4000 to 400 cm^{-1} in a BRUKER IFS-66V spectrometer for validating the functional groups of LTP with the use of KBr pellet method. As seen in Fig.2, the same is utilized to qualitatively check the presence of the amino acids in the sample. The reason for the steep peak at 3406 cm^{-1} may be credited to NH stretching in tryptophan. The prominent cum wide peak that emerges at around 3232 cm^{-1} indicates the OH stretching. A signal seen at 2398 cm^{-1} indicates alkyl stretching of tryptophan. Due to NH bending and the P=O group, the signals are obtained respectively at 1542 cm^{-1} and 1176 cm^{-1}. A band seen at 1616 cm^{-1} confirms the stretching vibration of aromatic C=C.

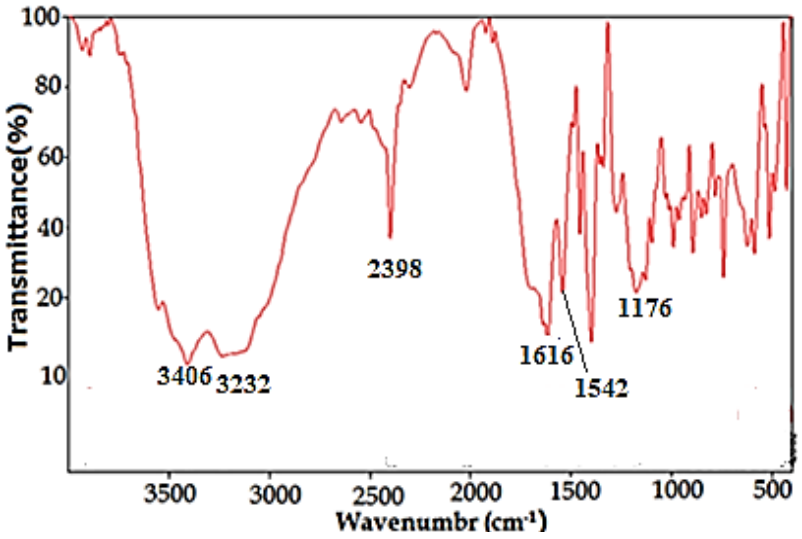

Fig.2. FT-IR spectrum of LTP.

3.3. UV-VIS-NIR spectral analysis

To be used in optical fabrications, the grown materials must have a broad wavelength range with high transparency. The transparency of LTP crystals was investigated from the 200 to1000 nm range using the VARIAN CARY 5E UV-Vis-NIR spectrophotometer. The UV-Vis-NIR spectrum gives insight of the chemical structure responsible for the excitation of the electrons in σ as well as π orbitals from their ground state to an energetically higher state, triggered by absorption of UV and visible light. [14, 15]. The absorption peaks can be seen at 314 nm for the LTP as shown in Fig.3. This can be explained by the tryptophan moiety's π–π* transition. It is clear that an LTP crystal is a necessary component of the diode and solid-state laser frequency doubling processes.

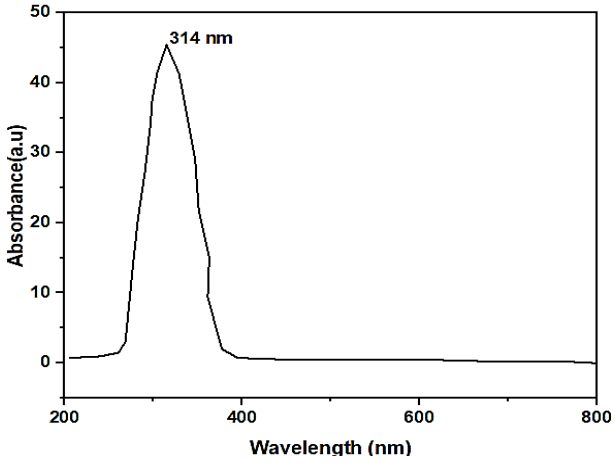

Fig. 3. UV-VIS-NIR spectrum of LTP.

3.4. Optical absorption analysis

Optical characteristics are crucial for a material because they make available the details on its electronic band structures, its localized states and also its types of optical transitions [16]. The optical band gap is a crucial factor for the NLO applications involving lasers and waveguides. The ability to transmit light is reliant only upon absorption coefficient. For a material, the absorption

coefficient (α) indicates the ability to reduce the incident beam intensity when it passes through the material [17]. The link between the optical absorption coefficient and energy of photon enables researchers to investigate on the band structure andtype of electron transition. Using the following relationship, the optical absorption coefficient (α) has been determined through its transmittance.

$$\alpha = \frac{2.303 \log(\frac{1}{T})}{t} \quad (1)$$

Here, the transmittance is represented as T and the thickness of crystal as t.

The value of absorption coefficient which depends on energy suggests the direct band gap existence in the regions of high photon energy. The crystal being studied is a semiconductor with direct band gap and its absorption coefficient (α) follows the given relation at the high photon energies (hv)

$$(\alpha h\nu)^2 = A \times (E_g - h\nu) \quad (2)$$

E_g represents the optical band gap and A represents a constant. The Fig.4 shows the graph plotted between $(\alpha h\nu)^2$ and $h\nu$. The determination of the band gap involves extrapolating the linear portion of the curve, resulting in an estimated value of 4.18 eV. The crystal under examination has high transmittance in visible range as a result of its broad band gap [18]

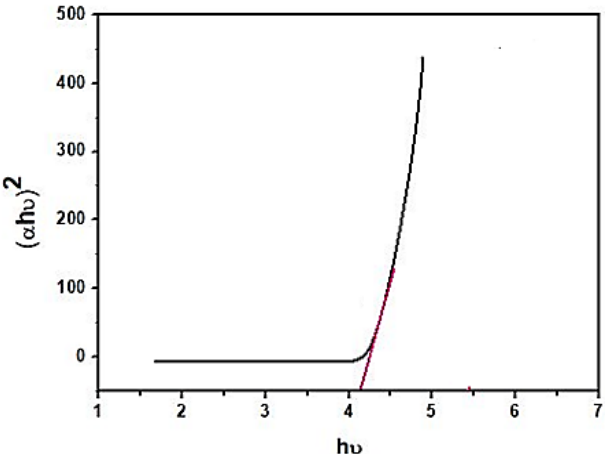

Fig. 4. Tauc's Plot of LTP.

3.5. H^1NMR analysis

Any research project's identification of a chemical is crucial, and methods like NMR spectrum analysis greatly aid in this process. The H^1NMR spectra for the LTP crystal dissolved in DMSO-d6 was acquired using a JOEL GSX 400 NB FT NMR spectrometer at 400 MHz. Figure 5 depicts the ^{1}H-NMR spectrum of LTP. The spectrum shows a sharp singlet at 11.00 ppm corresponding to carboxylic acid proton of the amino acid. It shows a multiplet around 5.8-6.05 ppm which is attributed to the aromatic protons of the tryptophan moiety. The doublet at 6.8 ppm and a sharp singlet at 5.1 ppm are owing to the C-H proton and N-H proton of indole ring respectively. The spectrum also shows a sharp singlet at 4.3 ppm owing to the amine proton of the amino acid. A triplet at 3.5 ppm and doublet at 1.3 ppm correspond to CH and CH_2 proton of the aliphatic side chain of the tryptophan.

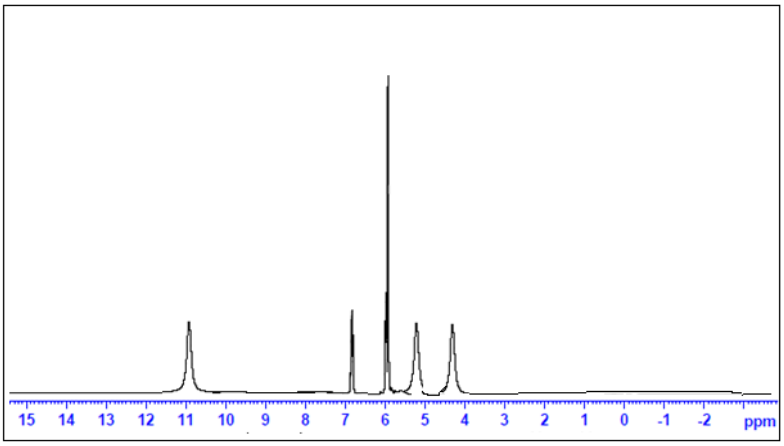

Fig. 5. ^{1}H-NMR spectrum of LTP.

3.6. TG-DTA analyses

The simultaneous TG/DTA curves identify a crystal's thermal stability. Thermal studies were conducted in an alumina crucible in the instrunent NETZSCH STA 409 C/CD at temperatures ranging from 20 °C to 800 °C and at heating rate of 20 °C min^{-1} in the Nitrogen atmosphere. Fig.6 depicts the TG/DTA curves of LTP crystal. From the curves, it was noticed that the decomposition of LTP started at 281 °C.This was supported by the DTA analysis, where the endothermic reaction is observed at 281 °C.It was discovered that the largest weight loss for the first stage occurred at 283°C, whereas the maximum weight loss for the second stage occurred at 396°C. It is possible to conclude from the TGA data that LTP is thermally found to be stable up to 281°C.

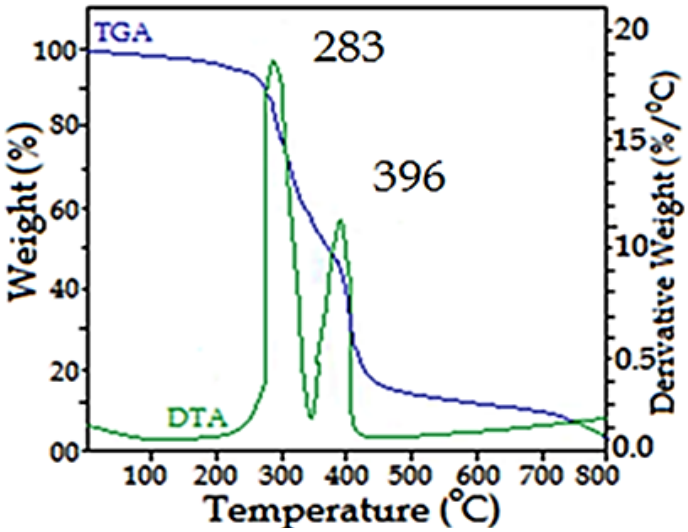

Fig. 6. TG-DTA curves of LTP.

3.7. Microhardness analysis

Mechanical testing examines the mechanical characteristics of crystals, which show particular mechanical features. Hardness measurement is the quickest and most basic sort of mechanical testing. Vickers hardness test is the most often utilized of the several testing procedures. With a diamond pyramidal indentor, the Vickers hardness test was performed for the microhardness investigation [19, 20]. The following equation was used for determining the Vickers microhardness number.

$$H_V = 1.8544 \times \frac{P}{d^2} \quad (3)$$

In the equation, H_V is the Vickers microhardness number, P is the applied load in kg and d is the average diagonal length of the impression in micrometer. Fig.7 depicts the changing of hardness number with applied load.

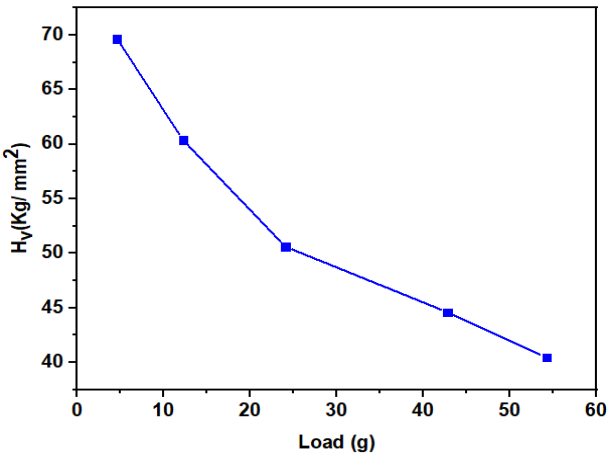

Fig. 7. Microhardness study of LTP.

3.8. NLO analysis

The study on efficiency of the second harmonic generation evaluation was done utilizing the Kurtz-Perry technique with a Nd:YAG laser source of 1064 nm [21]. In this methodology, the pulverized sample consisting of randomly aligned crystallite particles was tightly enclosed within a small capillary tube. Then the material under study was exposed to an output of a Nd:YAG laser which was Q-switched with a power of 2.1 mJs^{-1} and a wavelength of 1064 nm. In terms of output power, the SHG efficiency of LTP was compared with KDP. The LTP was found to have a SHG efficiency of 2.1 times of KDP.

4. Conclusion

The low temperature slow evaporation method was used to grow a novel L-Tryptophanium phosphite (LTP) NLO single crystals based on an amino acid. Based on X-ray diffraction patterns, we can see that the produced crystal has an orthorhombic structure with a space group belonging to non-centrosymmetry. The chemical functional group constituents in the product were confirmed in the FT-IR and ^{1}H-NMR spectral studies. By investigating its optical absorption by employing UV-Vis-NIR spectrum, the applications in the field of optical processing and photonics were validated, which revealed the cut-off wavelength as 300 nm. A value of 4.18 eV is determined for the optical band gap. Thermal analysis using TG and DTA showed that this material was stable up to 281 °C. According to the results of the hardness tests, the hardness value falls with increasing load. The Kurtz-Perry powder method was employed for verifying SHG property. There is no doubt that this crystal might be useful in any NLO-related fields.

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