GROWTH AND CHARACTERIZATION OF L-TRYPTOPHAN (LT) SINGLE CRYSTALS FOR NLO AND OTHER APPLICATIONS

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Abstract: By using the slow evaporation process, L-tryptophan (LT) single crystals have been produced from aqueous solution. Using a single crystal X-ray diffraction (XRD) analysis, the cell dimensions were determined. FTIR (Fourier transform infrared) analysis has been used to confirm the functional groups. Using spectral analysis using Nuclear Magnetic Resonance Spectroscopy (NMR), the location of protons was determined. After conducting optical research, it was discovered that the specimen's transmission propensity with regard to light wavelength makes it practically more appropriate for opto-electronic applications. The thermal characteristics of the as-grown crystal were ascertained by differential thermal analysis and thermogravimetric analysis. Additionally, the efficacy of LT's Second Harmonic Generation (SHG) was ascertained.

Keywords: Crystal growth, Crystal structure, XRD, TG-DTA, SHG, NLO

I. INTRODUCTION

Due to their commercial significance in the domains of optical communication, signal processing, sensing, and instrumentation, as well as their ability to transfer data quickly and with a very high signal to noise ratio, even over long distances, nonlinear optical materials that can efficiently generate second harmonics have been actively sought after over the past three decades [1]. Because of their molecular associations, bond strength, high molecular polarizability, ease of ion integration into the lattice, etc., an organic and inorganic functionalized nonlinear optical material is essential [2,3]. Because of their proton donor carboxyl acid (-COOH) and proton acceptor amino ($-NH_2$) groups, which give the molecule the ground state charge asymmetry needed for second order nonlinearity, their lack of strongly conjugated bonds, which results in wide transparency ranges in the visible and UV spectral regions, and their zwitter ionic nature, which favours crystal hardness, amino acids are intriguing materials [4-6]. The emission from noninterconverting rotamers, which have varying lifetimes because of varying rates of intermolecular charge transfer, has been implicated in the nonexponential fluorescence decay of L-tryptophan in aqueous solutions [7]. In many applications, the process of crystal formation from solution is crucial [8,9]. The growth, spectral, optical, and thermal properties of the formed crystal are reported in this article.

II. EXPERIMENTAL ANALYSIS

A. Solubility Analysis

The commercially available L-tryptophan (LT) was acquired from Sigma Aldrich Company with a stated purity of 99%. The right solvent selection for material growth is crucial in the crystal growth process because

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supersaturation plays a major role in both the growth process and the quality of the crystals. The temperature range used for the L-tryptophan solubility test in deionized water was 30 to 55°C. To guarantee uniform temperature and concentration throughout the solution's volume, the temperature was kept above the desired level and constantly agitated with a motorized magnetic stirrer. After allowing the saturated solution to achieve equilibrium, the solubility was examined using gravimetric analysis. Weighing was done on a sample of L-tryptophan solution in a heated pipette. The 10 ml of solution was evaporated in an oven set at a steady temperature in order to assess the solubility. The solubility curve, which is displayed in Figure. 1, was produced by repeating the same procedure at various temperatures.

B. Growth of Crystal

The current study used the slow evaporation technique to generate L-tryptophan (LT) crystals in a low temperature solution. Since the quality of single crystals depends on the purity of the materials utilized, This purification was achieved through a repeated crystallization process prior to real growth. Since supersaturation plays a major role in both the development process and the quality of the crystals, choosing the right solvent for the material's growth is crucial to the crystal growth process. It was discovered that the best solvent for making the growth solution was deionized water at 40° C. Following a month of gradual evaporation at room temperature after the highly saturated solution was filtered through Whatmann filter paper, optically high-quality crystals were produced, as illustrated in Figure. 2. Greater amount of the initial material can be used to obtain a larger sized crystal.

III. RESULTS AND DISCUSSION

A. SXRD Analysis

Single crystal XRD tests were performed on the sample to verify the cell characteristics of the produced LT crystals. Using an ENRAFNONIUS CAD4-F single X-ray diffractometer with Mok_α (λ = 0.7170 Å) radiation, the single crystal XRD analysis of LT single crystals was conducted. A limited number of reflections from planes were recorded. According to the study, the grown LT crystal has the following cell parameters: a = 11.392 Å, b = 35.102 Å, c = 11.563 Å, and V = 4004.8 $(Å)^3$. It is a member of the triclinic system. These values closely match those that have been reported [10]. Figure 3. and Figure 4. Represent the molecular structure and molecular formula of L-tryptophan respectively.

B. FTIR Spectral Analysis

Using the BRUKER IFS-66V spectrometer, the functional groups of LT are verified by recording the FTIR spectrum in the 4000–500 cm^{-1} region. The KBr pellet technique is used to qualitatively validate the presence of amino acids in the sample (Figure 5.). The L-tryptophan's -NH and -OH stretching vibrations are the cause of the sharp peak at 3400 cm^{-1}. The alkyl stretching vibrations are represented by the peak seen at 3045 cm^{-1}. The presence of intermolecular hydrogen bonds between the carboxylic acid molecules is what causes the signal at 2568 cm^{-1}. The carbonyl stretching frequency of carboxylic acid is represented by the signal at 1667 cm^{-1}. The -NH bending vibrations of the -NH and $-NH_2$ groups are responsible for the peak at 1592 cm^{-1}.

C. H^1NMR Spectral Analysis

Compound identification is a crucial effort that is largely completed by methods such as NMR spectral analysis [11]. The JOEL GSX 400 NB FT NMR spectrometer, operating at 400 MHz, was used to record the proton NMR spectra of the crystal dissolved in deuterated water (D_2O). Figure 6, displays the H^1NMR spectrum of LT. At 10.5 ppm, a sharp singlet represents the indole ring's -NH proton. Additionally, it displays a multiplet of 7.8–6.2 ppm, which corresponds to five aromatic protons. The molecule's alkyl chain is the cause of the multiplet between 3.6 and 3.0 ppm.

D. UV–Vis–NIR Spectral Analysis

Using a VARIAN CARY 5E UV–Vis–NIR spectrophotometer, the UV–Vis–NIR spectral analysis in the 200–900 nm range was done to investigate the transparent nature of LT crystal. From the cutoff wavelength, it is understood that the material exhibits good transmittance and low optical absorption. The wavelength maximum, (λ_{max}) in the UV spectrum of LT is 280 nm. This is a feature of the aromatic ring's $\pi \rightarrow \pi^*$ transition. The graph shown in Figure 7, clearly shows that the LT crystal has a UV cutoff wavelength below 280 nm, which is enough for applications in the blue region such as SHG laser light at 1064 nm.

E. Thermal Analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to determine the thermal stability of L-tryptophan (A NETZSCH STA 409 C/CD system was used to perform the thermal studies in the alumina crucible between 20 and 1000°C at a heating rate of 20°C/min in a nitrogen atmosphere. Figure 8, displays the compound's TGA and DTG thermograms. Two stages of breakdown are shown in the LT's TGA. Decomposition begins in the first stage at 276.9°C and in the second stage at 357.4°C. The maximum weight loss for the first stage was recorded at 286.9°C (41.18%), and the maximum weight loss for the second stage was recorded at 386.3°C (46.44%). It may be deduced from the TGA data that LT is stable at 276°C. At 290.7°C, the DTA of LT displayed a sharp endotherm.

F. Microhardness Analysis

Vickers' microhardness test was used to assess the hardness values of the generated crystal. On the prominent plane, the

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indentations were created at room temperature with a fixed dwell period of five seconds. To prevent indentations from interfering with one another, the space between two indentation sites was kept at more than three times the diagonal length. The load was varied from 10 to 50 grams to create the indentation marks on the surface. Using a Leitz Metallax II microscope, the indentation impression's diagonal length was determined. Three indentations were formed on the sample in order to obtain precise measurements for each given load, and the average diagonal length (d) of the indenter impressions was taken into account.

$$H_v = 1.8544\left(\frac{P}{d^2}\right) \qquad kg/mm^2$$

The above formula was used to determine the crystal's Vickers' microhardness number (H_v). Where P is the applied force and d is the average diagonal length of the indenter impression. It has been noted that work hardening of the surface layer causes the hardness value to increase (H_v = 45.2 kg/mm^2) up to the applied load (P = 50 gm). The hardness value further dropped over 50 gm load because cracks developed as a result of the localized release of internal stress caused by indentation. Figure 9, illustrates how the hardness number changes with load.

G. NLO Analysis

Using the Kurtz and Perry powder method, a Nd-YAG laser with a wavelength of 1064 nm was used to perform the Second Harmonic Generation (SHG) test for LT crystal [14]. After passing via an infrared reflector, the input laser beam was focused on the microcrystalline powder sample that was enclosed in a capillary tube. The light that the sample emitted was picked up by an oscilloscope assembly and a photodiode detector as shown in Figure 10. Green light emission with wavelength 532 nm verified the crystal's SHG. Compared to the reference material KDP crystal, the relative powder SHG efficiency of LT crystal is reported to be almost 1.85 times higher.

IV. CONCLUSION

L-tryptophan (LT) single crystals with acceptable optical quality were formed at room temperature using the slow evaporation solution growth method. The single crystal X-ray diffraction method has been used to determine the lattice parameters. The presence of different functional groups in the formed crystal is revealed by the FTIR and H^{1}NMR spectra. It is a promising contender for optoelectronics and has a strong optical transmittance throughout the visible spectrum, according to the UV-Vis-NIR spectrum. The formed crystal is thermally stable up to 276°C, according to thermogravimetric (TG) and differential thermal analysis (DTA) results. Using a Q-swiched Nd:YAG laser, second harmonic generation was detected, and the SHG efficiency was 1.85 times higher than KDP. L-tryptophan single crystal is therefore a viable material for photonic device applications due to its promising crystal growth characteristics, good optical properties, and modest SHG efficiency.

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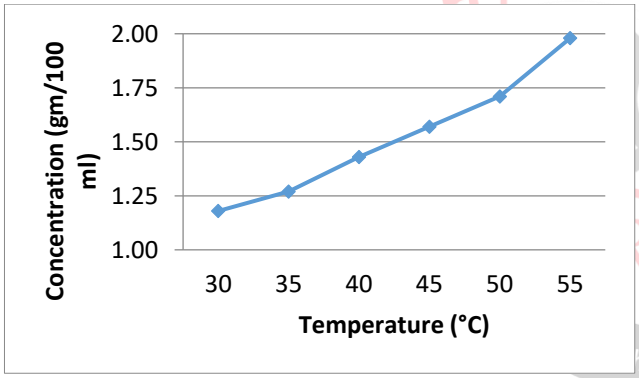

Figure. 1 Solubility curve of LT

Figure 2. As grown crystal of LT

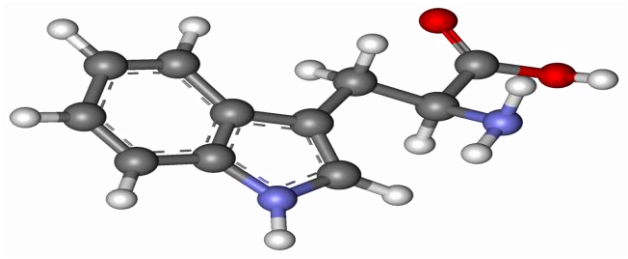

Figure 3. Molecular structure of L-tryptophan - schematic diagram

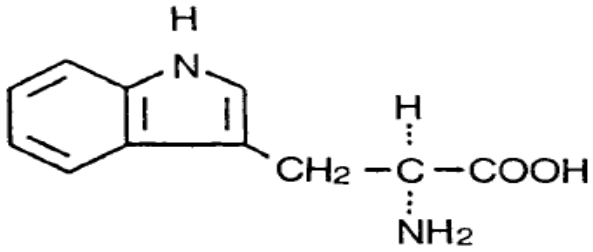

Figure 4. Molecular formula of L-tryptophan

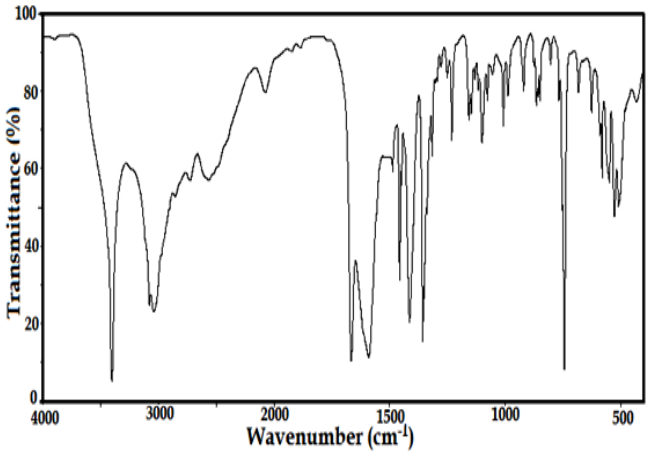

Figure 5. FTIR Spectrum of L-tryptophan

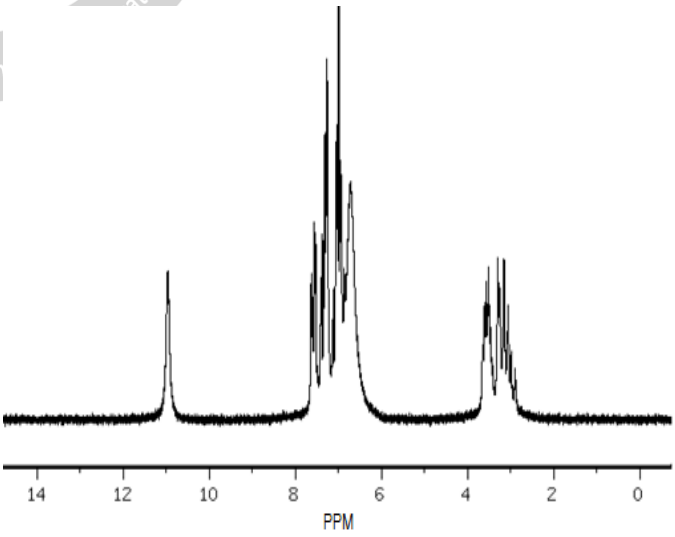

Figure 6. H[1]NMR spectrum of L-tryptophan

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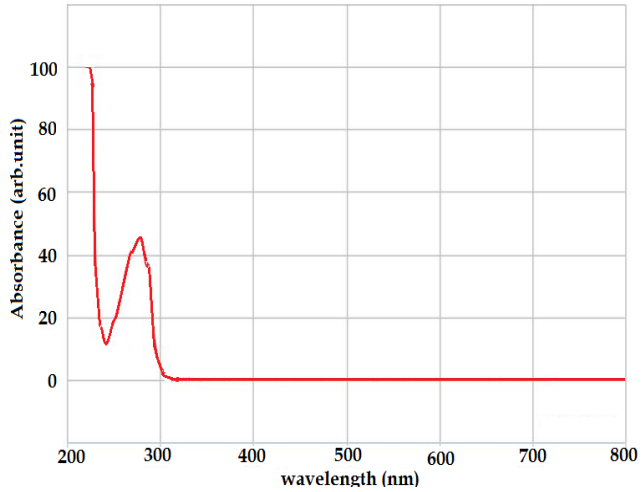

Figure 7. UV-Vis-NIR spectrum of L-tryptophan

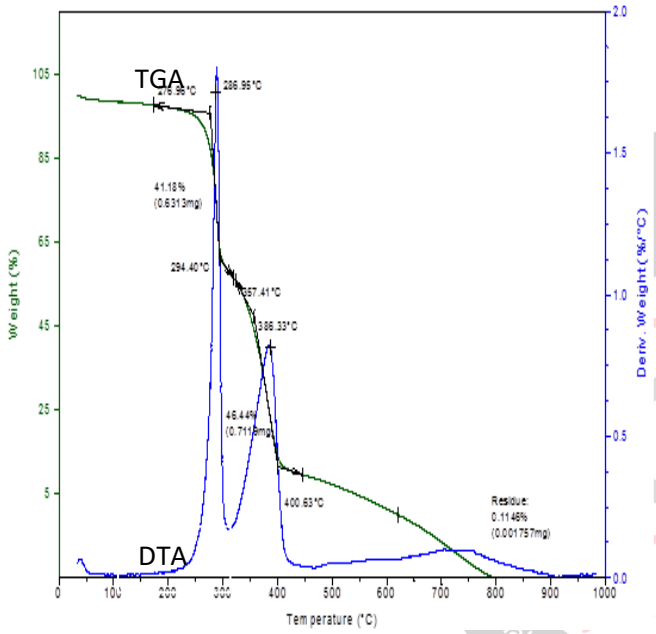

Figure 8. TGA-DTA curves of L-tryptophan

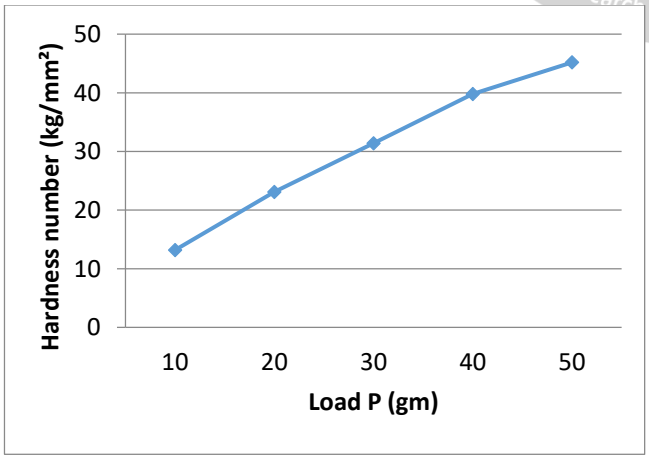

Figure 9. Plot of load Vs hardness number of L-tryptophan

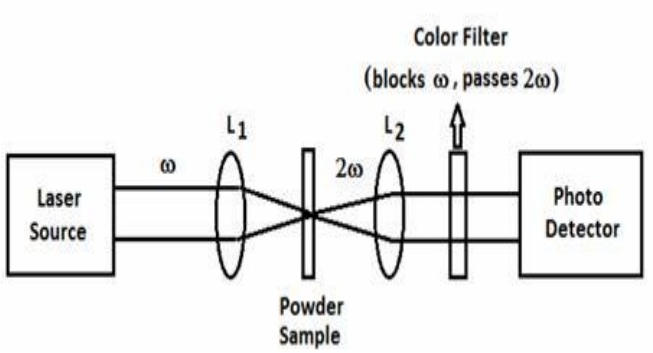

Figure 10. Experimental setup used for the observation of SHG

Table 1. Single crystal data of L-tryptophan

Parameter	Single crystal data
Chemical formula	$C_{11}H_{12}N_2O_2$
Wavelength	MoK_α (λ = 0.7170 Å)
Crystal system	Triclinic
Space group	P_1
Unit cell dimension	a= 11.392 Å, *b*= 35.102 Å, *c* = 11.563 Å
Volume	V = 4004.8 $Å^3$

Table 2. Wave numbers of FTIR absorption peaks of L-tryptophan

Wave number (cm^{-1})	Assignment
3400	NH and OH
3045	Alkyl stretching
2568	Intermolecular H bonding between Carboxylic acid
1667	NH bending of NH_2 groups
1592	Carbonyl stretching of Carboxylic acid

Table 3. Wave numbers of proton H^1NMR peaks of L-tryptophan

Types of Proton	Approximate chemical shift (ppm)
–NH proton of the indole ring	10.5
Five aromatic protons	Multiplet between 7.8 to 6.2
The alkyl chain	Multiplet between 3.6 to 3.0

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