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Synthesis, Growth and Characterization of L-Proline Succinate Crystal for Nonlinear Optical Applications

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Abstract: Crystals of L-Proline Succinate (LPS), an organic nonlinear optical material, was obtained by slow evaporation solution growth method using water as a solvent. Purity of the LPS crystals was increased by the method of recrystallization. The structure, lattice parameters and cell volume of LPS crystals were obtained by powder X-Ray diffraction studies. The LPS crystals were found to be monoclinic in structure. The presence of various functional groups of LPS and their modes of vibration were identified from Fourier Transform Infrared (FTIR) spectral analysis. The crystals of LPS were found to have wide range of transparency in the visible region. The nonlinear optical property of the grown crystals of LPS was measured through second harmonic generation using Kurtz-Perry powder test. Thermal stability of the grown crystals was confirmed using TGA and DTA.

Key words; Crystal growth; X-ray diffraction; FTIR; NLO property; UV; TGA and DTA.

1 Introduction

The extensive research of suitable new nonlinear materials is an important task because of their potential application in telecommunication for efficient signal processing and optical information storage devices [1]. NLO materials are also providing the key functions of frequency shifting, optical logic and optical memory areas [2]. Inorganic materials are widely used in these applications, but the optical nonlinearity of the inorganic materials is very poor. Organic compounds possess high nonlinearity because weak vander waal's and hydrogen bonds provide high degree of delocalization. Hence, they are optically more nonlinear than inorganic materials. A close survey of the literature shows that the various amino acids exhibit enhanced NLO properties [3].

Amino acids are building blocks of proteins. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino ($-NH_2$) group in them. This dipolar nature exhibits peculiar physical and chemical properties in amino acids.

In the present study, an attempt has been made to combine L-Proline with Succinic acid for a better NLO material and is grown by slow evaporation technique at room temperature. The L-Proline Succinate crystals obtained are subjected to various characterization studies such as Powder X-ray diffraction, FTIR, UV-Vis, NLO studies and thermal studies TG/DTA.

2 Experimental procedure

L-Proline Succinate was synthesized from L-Proline and Succinic acid taken in equimolar ratio (1:1). The molecule L-Proline has two groups (Carboxylic and amino group) that can be protonated. The required amount of starting materials for the synthesis of L-Proline Succinate salt was calculated according to the following reaction.

$NH\text{-}CH_2CH_2CH_2\text{-}CH\text{-}COOH + HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$

L-Proline Succinic acid ↓

$NH\text{-}CH_2CH_2CH_2\text{-}CH\text{-}COOH.HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$

L-Proline Succinate

The calculated amount of Succinic acid (5.9045 g) was first dissolved in 50 ml of deionized water. L-Proline (5.7531 g) was then added to the solution slowly by continuous stirring for one hour to yield a homogeneous mixture. Then the solution was left undisturbed. After few days, L-Proline Succinate raw material was collected from the bottom of the beaker. The purity of the synthesized salt was further improved by successive recrystallization. Raw material of L-Proline Succinate was recrystallized twice. Good quality crystals of LPS were obtained after a period of about ten days.

3 Results and Discussion

The Crystals of LPS obtained from second recrystallization process, were subjected to various characterization studies. The Crystal structure, Cell parameters have been determined by powder X-ray diffraction technique. The presence of various functional groups and modes of vibration were identified by FTIR analysis. The optical transmission range of the LPS crystals was determined by UV-Visible spectroscopic analysis. The nonlinear optical property of the grown crystals were confirmed by second harmonic generation using Nd:YAG Laser. TGA and DTA were carried out to study the thermal stability of the grown Crystals.

3.1 Powder X-Ray Diffratction analysis

Powder X-Ray diffraction analysis has been carried out to confirm the crystallinity and also determine the lattice parameter [4]. X-ray diffraction studies of crystlas of L-Proline Succinate was carrried out using Rigaku Corporation, Japan make D/Max Ultima III X-Ray diffractometer with CuKα (λ=1.5418Å) radiation. The sample was scanned over the range 10° to 80° and it was operated in theta-theta vertical mode at a scan rate of 4°/ min. The detector used was a scintillation counter. The graph is drawn between Intensity and 2θ values. The resultant powder X-Ray diffraction pattern of LPS is shown in the fig 3.1.

The X-Ray diffraction pattern of LPS was indexed using PowderX-VB VERSION BY CHENG DONG BASED ON TREOR90. From the diffraction data the cell volume and lattice parameters have been calculated and tabulated (table 3.1). These values confirms that the LPS crystal belongs to Monoclinic system {($a \neq b \neq c$), ($\alpha = \gamma \neq \beta$)}.

Table 3.1. Crystallographic data of L-Proline Succinate crystals

a (Å)	10.399427
b (Å)	10.874266
c (Å)	8.791055
α	90°
β	114.146979°
γ	90°
Unit cell volume = 907.16 $Å^3$	

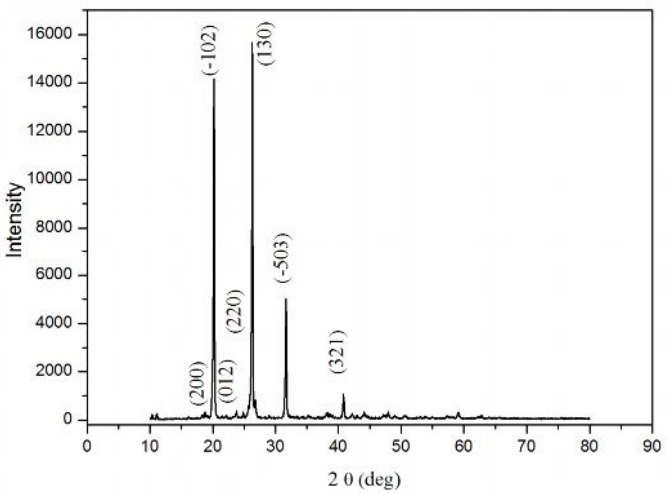

Fig. 3.1. Powder X-Ray Diffraction pattern of LPS crystals

3.2 Fourier Transform Infrared (FTIR) Spectral analysis

FTIR Spectroscopy was used to identify the functional groups present in synthesized crystals of LPS. Functional group with a strong dipole gives rise to strong absorption in the IR region [5]. Different molecular groups present in LPS are identified with the vibrational frequencies of amino acids and their complexes. The IR spectrum of LPS was recorded with a BRUKER-Fourier Transform Infrared spectrometer in the range 4000 cm^{-1} to 400 cm^{-1}.

The observed spectrum of LPS crystals is shown in the figure 3.2. The wavenumbers of various peaks and the assignments corresponding to them are presented in table 3.2 [6].

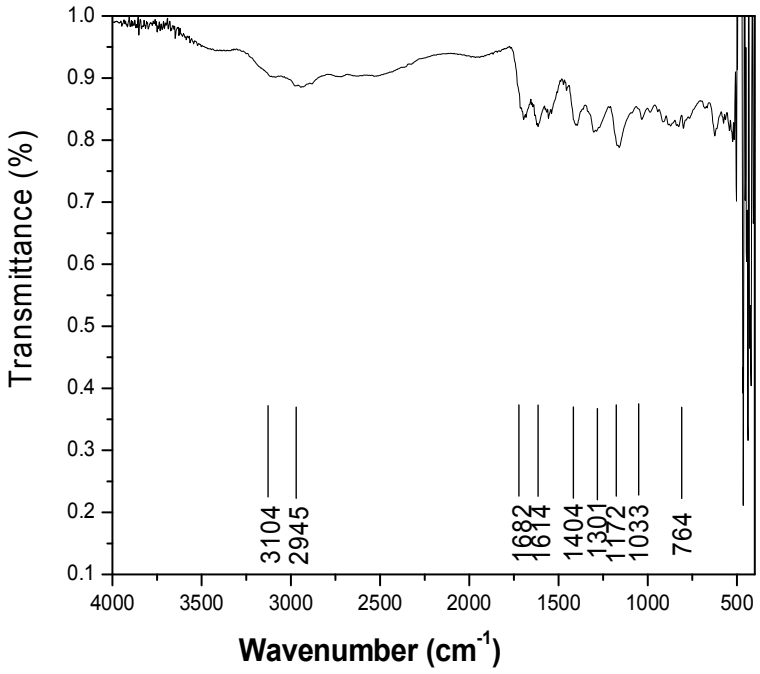

Fig. 3.2. FTIR spectrum of LPS crystals

The observed peak at 3104 cm^{-1} is due to N-H lower frequency region of L-Proline. The presence of NH_2^+ group in LPS is identified at 1682 cm^{-1}. It is due to the protonation of NH group by the COOH group of Succinic acid [5].

The symmetric and asymmetric stretching vibrations of COO- are positioned at 1614 cm^{-1} and 1404 cm^{-1} respectively in LPS crystals. The peaks at 1301 cm^{-1}, 1033 cm^{-1} are due to CH_2^+ wagging. The peak

corresponding to 2945cm^{-1} is due to C-H stretching of L-Proline. The peaks 478 cm^{-1}, 450 cm^{-1} are due to COO^- rocking. The symmetric stretching of COO^- group is identified at 427 cm^{-1}. The peak corresponding to 827 cm^{-1}, 765 cm^{-1} is due to C-H out of plane bending vibration. The stretching and bending vibration of C-C are observed at 883 cm^{-1}, 487 cm^{-1}.

Table 3.2. Vibrational band assignments of LPS

Wavenumber (cm^{-1})	**Assignments**
3104	N-H in lower frequency region
2945	C-H stretching
1682	NH_2^+ weak combination
1614	COO^- asymmetric stretching
1404	COO^- symmetric stretching
1301	CH_2^+ wagging
1172	CH_2^+ rocking
1033	CH_2^+ wagging
912	Rocking NH_2^+
883	C-C stretching
827	C-H out of plane bending
765	C-H out of plane bending
487	C-C bending
478	Rocking COO^-
472	NH_3^+ rocking
450	Rocking COO^-
427	COO^- symmetric stretching

3.3 Nonlinear Optical studies (Kurtz-Perry method)

The second harmonic generation efficiency was carried out by using the Nd:YAG laser. The laser source produces nanosecond pulses (8 ns) of 1064 nm light and the energy of the laser pulse was around 100 mJ. The beam emerging through the sample was focused on to a Czerny-Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infiniium digital storage oscilloscope interfaced to a computer. The powder sample was packed in a triangular cell and was kept in a cell holder. The sample was irradiated by 1064nm laser from Nd:YAG. The monochromator was set at 532 nm. NLO signal was captured by the oscilloscope through the photomultiplier tube. The results are reported in the following table 3.3.

Table 3.3. Comparison of SHG output

Sample	NLO value
LPS	0.128 mV
KDP	0.8122mV

The second harmonic generation efficiency of LPS is found to be 0.16 times of KDP crystals.

3.4 UV-Visible spectral analysis

To find the optical window width of LPS crystals, UV-Visible spectrum was observed using Perkin Elmer make Lambda 35 UV-Visible Spectrometer in the range from 190 nm to 1100 nm and the observed spectrum of LPS crystal is shown in fig 3.3. The observed spectrum of LPS was covering the region near UV, visible region and NIR region respectively. Transparency in the visible region is a desirous property for any NLO material [7].

The observed optical spectrum of LPS crystals shows a good transmittance in the visible region. From the observed spectrum of LPS crystal, there is no significant absorption in the range 201 nm-1100 nm. The

optical transmittance shows that the lower cutoff wavelength occurs at 201 nm for LPS crystals. This makes these crystals suitable for UV tunable laser (Optoelectronic devices) and SHG device applications [6].

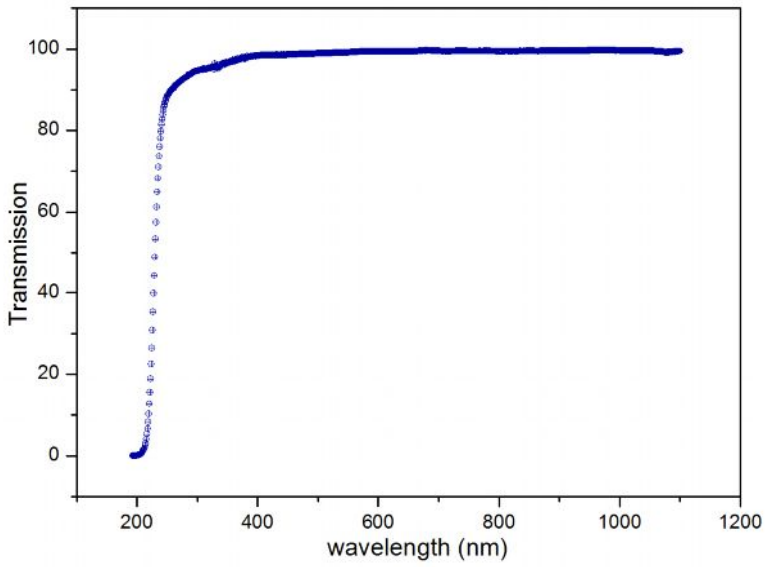

Fig. 3.3. UV-Visible Spectrum of LPS crystals

3.5 Thermal analyses

Thermogravimetric analysis and Differential Thermal analysis for L-Proline Succinate crystals were carried out using CNST thermal analyser. Ceramic crucible was used for heating the sample [8]. The analyses were carried out in a Nitrogen atmosphere at a heating rate of 20 ºC/ min for the temperature ranges from 293 K – 723 K. The initial mass subjected to the analyser was 3.365 mg. The resulting TGA and DTA are shown in following fig 3.4

In TGA, the first transition is observed over the range from 442 K to 545 K due to the melting of the substances. This shows that the material is stable up to 442 K.

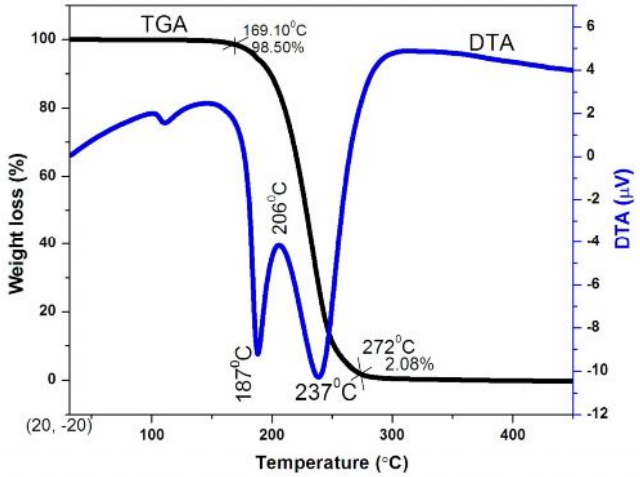

Fig. 3.4. TGA and DTA curve of LPS crystals

In DTA curve, there are two endothermic peaks observed at 460 K and 510 K. The first strong endothermic peak in DTA around 460 K indicates that the removal of N-H during this temperature range. There is another strong endothermic peak in DTA around 510 K indicating the dissociation of the substance and evaporation of volatile substances. There are no other transitions up to 723 K.

4 Conclusion

A new material of L-Proline Succinate (LPS) was synthesized and Crystals of LPS were grown by slow evaporation technique for the first time. The unit cell parameters were found by powder X-ray diffraction analysis and the grown crystals belong to monoclinic system. The presence of various functional groups of the grown crystals was confirmed by FTIR analysis. The UV-Vis transmittance spectra showed that the LPS crystal was transparent in the entire visible region with a lower cut-off wavelength at 201 nm, making it a potential candidate for NLO applications. The relative SHG conversion efficiency of the grown crystals is about 0.16 times higher than that of KDP sample, which indicates the suitability of LPS crystals for photonic and NLO applications. Thermal stability of the grown crystal LPS was studied using TGA and DTA, confirms that the material was stable up to 442 K.

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