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Growth, XRD, FTIR and Second Order NLO studies of Undoped and Zinc Sulphate doped L-Histidine Single Crystals

S. Sudharthini[1,*], P. Selvarajan[2], C. Gnana Sambandam[1], U. Rajesh Kannan[3]

[1]Department of Physics and Research Centre, S.T. Hindu College, Nagercoil, Tamil Nadu, India
[2]Department of Physics, Aditanar College of Arts and Science, Tiruchendur, Tamil Nadu, India
[3]Department of Physics, Kamaraj College, Tuticorin, Tamil Nadu, India

Abstract

Single crystals of pure (undoped) L-histidine and Zinc sulphate doped L-histidine have been synthesized and grown by slow evaporation method using water as the solvent. These grown crystals are characterized by FTIR, XRD and SHG. From Fourier transform infrared (FTIR) spectral analysis, the various functional groups present in the sample have been confirmed. The X-ray diffraction (XRD) study ensures that the grown crystal crystallizes in the orthorhombic system and the corresponding lattice dimensions have been identified. The nonlinear optical conversion efficiency test was carried out for the grown crystals using Kurtz-Perry Powder technique.

Keywords: *Single crystals NLO; Growth from solution. FTIR, XRD, SHG*

****Author For Correspondence*** E-mail: rajeshphymsu@gmail.com

INTRODUCTION

Crystal growth has prominent role to play in the present era of rapid technological and scientific advancement, where the application of crystals has unbounded limits. New materials having attractive nonlinear properties are being discovered at rapid speed in the crystal growth technology. Therefore the commercial development of single crystals with promising NLO properties has been enabled. In recent decades, growth of nonlinear optical crystals has been given much importance, because of their potential applications like waveguides, frequency conversion devices, parametric oscillators, etc. Petrosy AN et al. [1] derived some semi-organic nonlinear optical crystals of L-histidine salts and reported the interaction with various acids. Nonlinear optical (NLO) materials have been attracting a great deal of interest due to their applications such as high-speed information processing, optical communications, optoelectronics and optical data storage [2–5]. As NLO materials, organic materials are considered to be more versatile for their potentially high nonlinearities and rapid response compared to inorganic compounds. Especially the discovery of promising NLO properties in L-arginine phosphate monohydrate (LAP) [6] has stimulated an intense interest in the crystal family. Some complexes of amino acids with organic or inorganic acids exhibit excellent NLO properties [7–12].The structure and various crystalline form of L-histidine have been reported in number of publications [13-16]. In the present work, the effect of zinc sulphate as dopant on the growth of L-histidine by slow evaporation method have been studied and characterized by some advanced techniques such as XRD, FTIR and SHG studies). A comparatively study on the results obtained for undoped L-histidine and Zinc Sulphate doped L-histidine is given below clearly.

SYNTHESIS AND GROWTH CRYSTALS

Analytical Reagent (AR) grade of L-histidine was used for synthesis of single crystals of L-histidine by slow evaporation technique. The calculated amounts of L-histidine salt was dissolved in sufficient volume of double distilled water. The solution was stirred well

using a magnetic stirrer, for an hour till the supersaturation was reached. The solution was filtered using Wattman filter paper. The filtered solution was transferred to the next crystallizer covered with porous paper and this growth vessel was kept in a dust-free atmosphere. The single crystals were harvested after a period of about 30 days and the harvested crystals. The grown crystals were colourless and transparent. Analytical Reagent (AR) grade of L-histidine salt was mixed with zinc sulphate in the molar ratio 1: 0.1.The samples were grinded using Mortar and Pestle. This method was used for the preparation of Zinc sulphate doped L-histidine crystals. [17].

RESULTS AND DISCUSSION

Identification of Functional Groups

The grown pure L-Hystidine and Zinc Sulphate doped L -Hystidine crystals were subjected to Fourier Transform Infrared Analysis. The FTIR spectrum of pure L-Hystidine and zinc Sulphate doped L -Hystidine crystals were recorded using an FTIR spectrometer in the wave number range 400-4000 cm^{-1} with KBr pellet technique and shown in figure 1&2. The various functional groups were assigned and presented in the table 1 & 2. In pure and doped crystals, the bands at 3016 cm^{-1} and 3015 cm^{-1} are assigned to C–H stretching (or) NH^{3+} stretching vibration. The bands at 1634 cm^{-1} and 1633 cm^{-1} are assigned to C = O stretching. The band at 1580 cm^{-1} is assigned to asymmetric mode of—COO- and C = C stretching. The bands around 1459 cm^{-1} and 1458 cm^{-1} are assigned to CH_2 antisymmetric, symmetric deformation. The bands around 1413 cm^{-1} and 1412 cm^{-1} symmetric mode of- COO^- and C–N stretching. The bands around 1339 cm^{-1} and 1338 cm^{-1} are assigned to CH_2 bending. In pure and doped crystals, the bands at 922 cm^{-1} and 921 cm^{-1} are assigned to C–H out of plane bending. The bands around 831 cm^{-1} and 828 cm^{-1} are assigned to C–H out-of-plane deformation. The peak at 790 cm^{-1} in the spectrum is corresponding to N–H wagging. The peak at 733 cm^{-1} in the spectrum is corresponding to CH_2 rocking. The bands around 621 cm^{-1} and 620 cm^{-1} are assigned to Ring deformation or C–N deformation. The bands around 535 cm^{-1} and 534 cm^{-1} are assigned to torsional NH oscillation of NH^{3+}. Thus FTIR studies confirmed that the presence of various possible functional groups in the undoped L-histidine and zinc Sulphate doped L -Histidine crystals. It was good matching with previously observed crystals[18,19]

X-ray Diffraction Studies

To obtain a clear picture of the structure of the crystals there is need for X-ray diffraction studies. The X-ray diffraction studies are a finger print by which crystalline substances are identified. The technique employed in the X-ray diffraction method is the powder diffraction method. The pattern of powder XRD is shown in Figures 3 and 4. Using the INDEXING and TREOR software following procedure of Lipson and Steeple [20]. The reflection peaks have been indexed. The values of 2-Theta, d-spacing, h k l values and relative intensity of the pure L-histidine and Zinc sulphate doped L-histidine are provided in the Tables 3 and 4.

Second Order NLO Studies

The nonlinear optical conversion efficiency test was carried out for the grown crystals using Kurtz-Perry Powder technique. The emission of green light confirmed generation of second harmonic radiation. The relative second harmonic generation efficiency was determined using Q switched mode locked Nd: YAG laser emitting 1064 nm radiation. The crystal was grounded into homogeneous powder of particles and then packed in a capillary of uniform bore and exposed to the laser radiation. KDP is used as the reference material. The second harmonic generation was confirmed by the emission of green light of wavelength 532 nm. [21]. The experiment confirms that the non-linear optical efficiency of as grown zinc sulphate doped L-histidine single crystals. The observed relative SHG efficiency is 0.5612 times that of KDP. Hence it proves that the material is applicable for non-linear optical devices. We have repeated our experiments several times on the title material with different particle sizes to get the actual value of SHG. The observed saturated value of SHG is found to be undoped 0.5612 and doped 0.89 times to that of standard KDP and seems to be the correct value. This kind of particle size dependency on SHG intensity exists only in phase-matchable materials .Hence this crystal can be used as an efficient frequency doubler and optical parametric oscillator

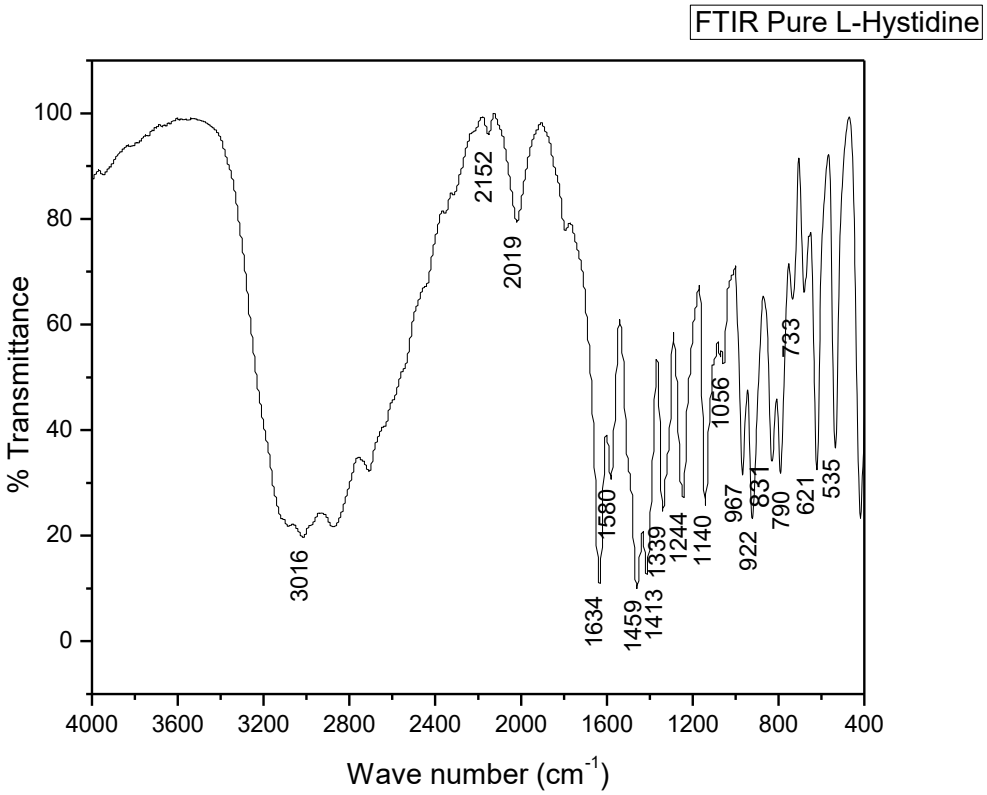

Fig. 1: *FTIR Spectra of Pure L-Histidine.*

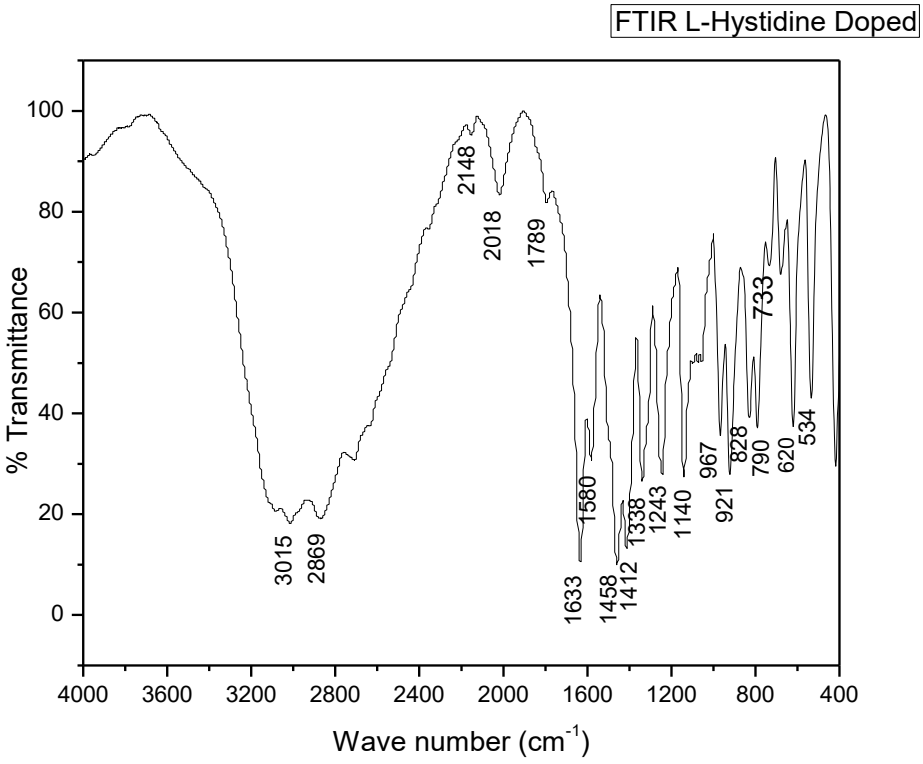

Fig. 2: *FTIR Spectrum of Zinc Sulphate Doped L-Histidine.*

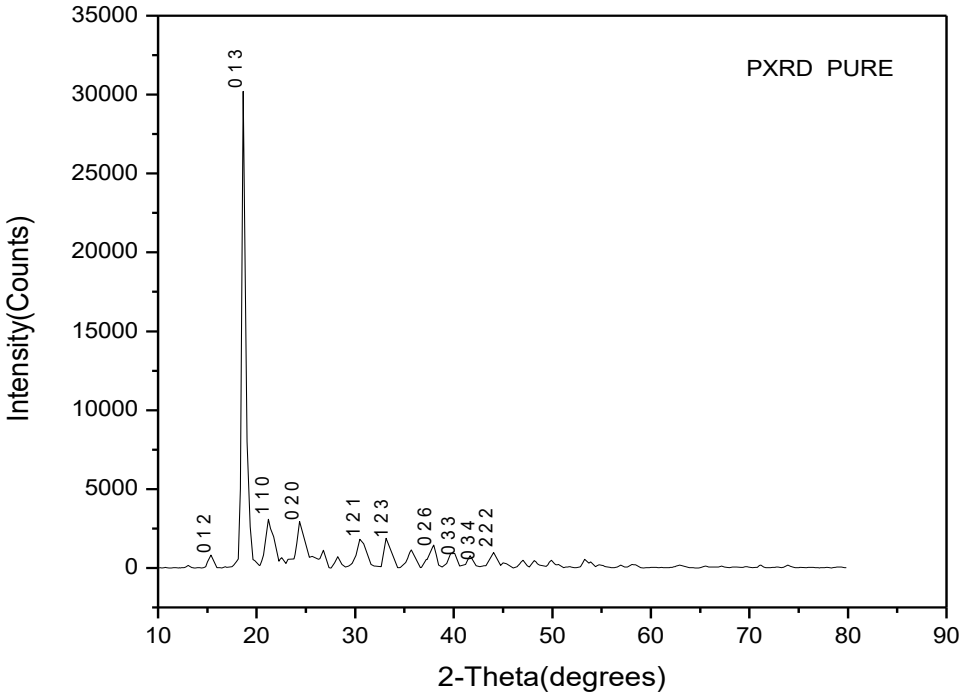

Fig. 3: *Powder X-ray Diffraction Pattern of Pure L-Histidine.*

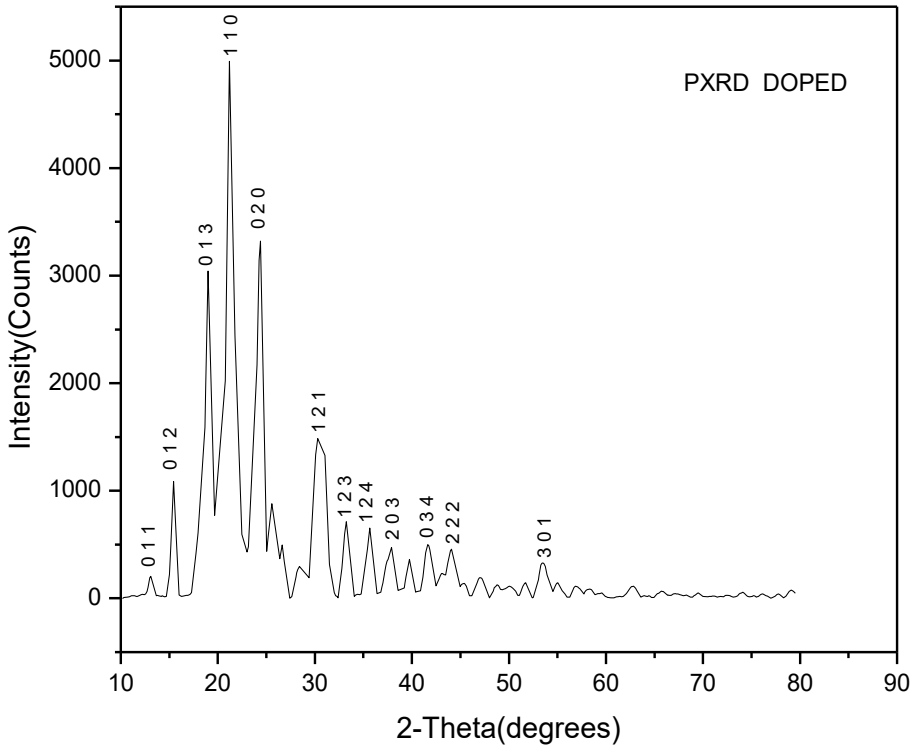

Fig. 4: *Powder X-ray Diffraction pattern of Zinc Sulphate Doped L-Histidine.*

***Table 1**: FTIR Bands and Their Assignments for Pure L-Histidine.*

Wave number (cm^{-1})	Assignments
3016	C–H stretching (or) NH^{3+} stretching vibration
1634	C = O stretching
1580	Asymmetric mode of—COO- and C = C stretching
1459	CH_2 antisymmetric ,symmetric deformation
1413	Symmetric mode of—$COO^-$and C–N stretching
1339	CH_2 bending
1056	C–O stretching of carboxyl group
922	C–H out of plane bending
831	C–H out-of-plane deformation
790	N–H wagging
733	CH_2 rocking
621	Ring deformation or C–N deformation
535	Torsional NH oscillation of NH^{3+}

***Table 2:** FTIR Bands and their Assignments for Zinc Sulphate Doped L-Histidine.*

Wave number (cm^{-1})	Assignments
3015	C–H stretching (or) NH^{3+} stretching vibration
2869	C–H aliphatic stretch
1633	C = O stretching
1580	Asymmetric mode of—COO- and C = C stretching
1458	CH_2 antisymmetric ,symmetric deformation
1412	Symmetric mode of—$COO^-$and C–N stretching
1338	CH_2 bending
921	C–H out of plane bending
828	C–H out-of-plane deformation
790	N–H wagging
733	CH_2 rocking
620	Ring deformation or C–N deformation
534	Torsional NH oscillation of NH^{3+}

***Table 3:** Values of Data from the Powder XRD Analysis for the Sample of Pure L-Histidine.*

Peak Number	2-Theta (degrees)	d-spacing (Å)	h k l	Relative Intensity (%)
1	15.357	5.764951213	0 1 2	2.728
2	18.633	4.75810412	0 1 3	100
3	21.188	4.189755959	1 1 0	10.246
4	24.357	3.651342742	0 2 0	9.789
5	30.458	2.932416192	1 2 1	6.042
6	33.136	2.701285782	1 2 3	6.221
7	37.97	2.367756555	0 2 6	4.824
8	39.689	2.269076022	0 3 3	2.963
9	41.622	2.168053537	0 3 4	2.559
10	44.037	2.054595301	2 2 2	3.268

***Table 4:** Values of Data from the Powder XRD Analysis for the Sample of Zinc Sulphate Doped L-Histidine.*

Peak Number	2-Theta (degrees)	d - spacing (Å)	h k l	Relative Intensity (%)
1	13.093	6.756276856	0 1 1	4.107
2	15.452	5.729720986	0 1 2	21.735
3	18.975	4.673109596	0 1 3	60.938
4	21.208	4.185850001	1 1 0	100
5	24.379	3.648097507	0 2 0	66.546
6	30.31	2.946396879	1 2 1	29.788
7	33.252	2.692126925	1 23	14.243
8	35.648	2.516481	1 2 4	13.081
9	37.898	2.372089223	2 0 3	9.495
10	41.721	2.163137494	0 3 4	9.836
11	44.094	2.052071484	2 2 2	9.175
12	53.486	1.711773884	3 0 1	6.591

CONCLUSIONS

Good quality undoped and doped single crystals of L-histidine are grown by slow evaporation technique in a period of 30 days. The functional group assignments were given by using FTIR spectrum. Miller indices, inter-planar spacing and scattering angle were measured by using XRD spectrum. Both the crystals are found to be crystallizing in orthorhombic structure. The observed relative SHG efficiency is undoped 0.5612 and doped 0.89 times that of KDP.

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