



**HAL**  
open science

# Synthesis, Growth and Characterisation of New Organic Crystal: L-Histidinium 5 Sulfo Salicylate for Second Order Nonlinear Optical Applications

R Usha, N Hema, V Revathi, Ambika D Shalini, D D Jayalakshmi

► **To cite this version:**

R Usha, N Hema, V Revathi, Ambika D Shalini, D D Jayalakshmi. Synthesis, Growth and Characterisation of New Organic Crystal: L-Histidinium 5 Sulfo Salicylate for Second Order Nonlinear Optical Applications . Mechanics, Materials Science & Engineering MMSE Journal. Open Access, 2017, 9, 10.2412/mmse.92.96.883 . hal-01504656

**HAL Id: hal-01504656**

**<https://hal.science/hal-01504656>**

Submitted on 10 Apr 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

## Synthesis, Growth and Characterisation of New Organic Crystal: L-Histidinium 5 Sulfo Salicylate for Second Order Nonlinear Optical Applications

R. Usha<sup>1</sup>, N. Hema<sup>1</sup>, V. Revathi<sup>1</sup>, Ambika D. Shalini<sup>1</sup>, D. Jayalakshmi<sup>1, a</sup>

1 – PG and Research Department of Physics, Queen Mary's College (A), Chennai-600 004, Tamilnadu, India

a – [djayalakshmi2016@gmail.com](mailto:djayalakshmi2016@gmail.com)



DOI 10.2412/mmse.92.96.883 provided by [Seo4U.link](http://Seo4U.link)

**Keywords:** monoclinic, FT-IR, UV and NLO.

**ABSTRACT.** L-Histidinium 5 Sulfo Salicylate, an organic NLO crystal was grown for the first time by slow evaporation solution technique. Single crystal X ray diffraction analysis reveals that H5S belongs to monoclinic crystal system with non-centro symmetric space group  $P2_1$ . The determined parameters are  $a=9.5707(17)\text{\AA}$ ,  $b=19.038(4)\text{\AA}$ ,  $c=8.315(2)\text{\AA}$ ,  $\beta=90.711(14)$  and  $V=1514.8(6)\text{\AA}^3$ . FT-IR and FT Raman studies were carried out to identify the functional groups present in H5S. Optical absorption study showed a UV cut off wavelength of 304 nm. The mechanical properties of the grown crystal has been analyzed by Vicker micro hardness method. The second harmonic generation was confirmed for LH5SS.

**Introduction.** Great efforts have been devoted to the research and design of highly efficient nonlinear optical (NLO) materials due to their widespread applications such as high-speed information processing, optical communications, and optical data storage [1] Amino acid is an organic compound that contains both amine and carboxyl functional groups and one can produce outstanding materials with the help of organic and inorganic counterparts. Amino acids are identified as potential candidates for the growth of single crystals combining with some organic acids which exhibits the most essential nonlinear optical (NLO) property for frequency conversion applications [2,3]. Among the twenty amino acids, the most basic amino acid is l-histidine. Due to its basic nature, it forms a number of salts with different organic and inorganic acids which possess NLO properties. Some of the l-histidine compounds exhibit high second harmonic generation (SHG) conversion efficiency compared to the standard material KDP [4-10]. According to coordination chemistry, the ligand 5-sulfosalicylic acid (H3SSA) has three potential coordination groups:  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  and  $-\text{OH}$ . Both  $-\text{COOH}$  and  $-\text{SO}_3\text{H}$  are versatile coordinating groups and can coordinate with metal ions in a variety of modes [11], and there is a high possibility of proton transfer in organic salts, mainly N-heterocyclic, leading to tunable optical properties. The present investigation is on the growth of L-Histidinium 5 Sulfo Salicylate grown from slow evaporation method and on characterization of the grown crystal that is done using various techniques.

**Materials and methods.** L-Histidinium 5 Sulfo Salicylate crystals were grown from an aqueous solution by slow evaporation technique. l-Histidine (99% pure) and 5 sulfosalicylic acid were taken in the stoichiometric ratio 1:1 and dissolved in double distilled water. The reaction is as follows,



The solution was filtered using whatmann filter paper and left undisturbed in a covered beaker. The growth condition was optimized and the grown crystals were further purified by successive recrystallization. Seed crystals of LH5SS were harvested after a span of 10 days. The photograph of the as grown crystal is shown in Fig. 1.



*Fig. 1. Photograph of L-Histidinium 5 Sulfo Salicylate crystal.*

## Results and discussion

**Single-crystal X-ray diffraction.** The single-crystal XRD analysis of L Histidinium 5-Sulfo Salicylate (LH5SS) crystal was carried out using Bruker kappa APEX II single-crystal X-ray diffractometer with graphite monochromated MoKa radiation ( $k = 0.71073 \text{ \AA}^\circ$ ) at 293 K. A single crystal was selected for crystal structure determination. LH5SS crystallized in the monoclinic system within the non-centrosymmetric space group  $P2_1$ , its lattice parameters are:  $a = 9.5707(17) \text{ \AA}^\circ$ ,  $b = 19.038(4) \text{ \AA}^\circ$  and  $c = 8.315(2) \text{ \AA}^\circ$  and volume =  $1514.8(6) \text{ \AA}^3$

**FT-IR analysis.** Infra red spectroscopy has been used to identify the functional groups and to determine the molecular structure of the synthesized compound. The FTIR analysis of LH5S was carried out between  $4000$  and  $450 \text{ cm}^{-1}$  using Perkin Elmer model spectrometer is shown in the fig.(1) The band observed at  $3157 \text{ cm}^{-1}$  in spectra is due to the symmetric stretching of  $\text{NH}_3^+$  group of L-histidinium ion [12]. Most of the aromatic compound has some peaks in the region  $3110 - 3000 \text{ cm}^{-1}$  and they are being due to the stretching vibrations of the ring CH bonds. The peak observed at  $3019 \text{ cm}^{-1}$  is assigned to the CH stretching vibrations. The  $-\text{CH}_2-$  group of histidine produce peak at  $2862.2 \text{ cm}^{-1}$  due to its asymmetric stretching mode. The stretching vibrations of the C-C bond is identified in the peak  $1619 \text{ cm}^{-1}$ . [13]. The peaks at  $1,477$  and  $925 \text{ cm}^{-1}$  are due to S=O asymmetric stretching [14] and S-O as stretching of para-substituted sulfonic group ( $\text{SO}_3\text{H}$ ) in aromatic ring, respectively. The aromatic C-H in-plane bending vibration is observed at  $1,161 \text{ cm}^{-1}$ . The peak at  $836 \text{ cm}^{-1}$  is due to C-H out-of-plane bending [15]. All these observations clearly demonstrate the formation of L Histidinium 5-sulfosalicylate single crystal. Frequency assignment of the absorption peaks are presented in Table 1.

*Table 1. FT-IR of the LH5SS crystal.*

Wavenumbers $\text{cm}^{-1}$	Assignments
3157	$\text{NH}_3$ asymmetric stretching
3030	C-H stretching
2862	$\text{CH}_2$ asymmetric stretching
1475	$\text{SO}_3$ asymmetric stretching
1084	CO stretching of COO group
925	S-O asymmetric stretching

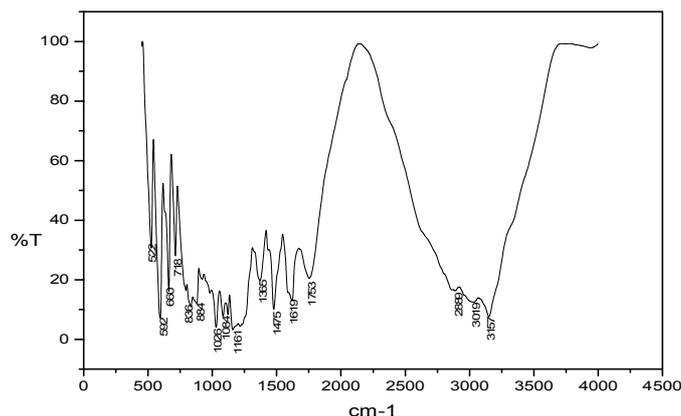


Fig. 2. FTIR spectrum of LH5SS.

**UV-Vis Spectral studies.** The optical absorption plays an important role in identifying the potential of the NLO material. Materials having wide absorption window with reduced absorption around the fundamental and second harmonic NLO application. Optical absorption data were taken on this polished crystal sample of about 3mm thickness using Perkin elmer lamda 35 model spectrometer between 200 – 800nm. The spectrum indicates that the UV cut-off wavelength of LHPT occurs at 304 nm. The band gap is found to be 4.09eV. It is well known that the efficient NLO crystal has an optical transparency at lower cut-off wavelength between 200 and 400 nm [16]. Also, it is observed that there is no significant absorption in the entire visible region which reveals that it suitable for the optoelectronic devices

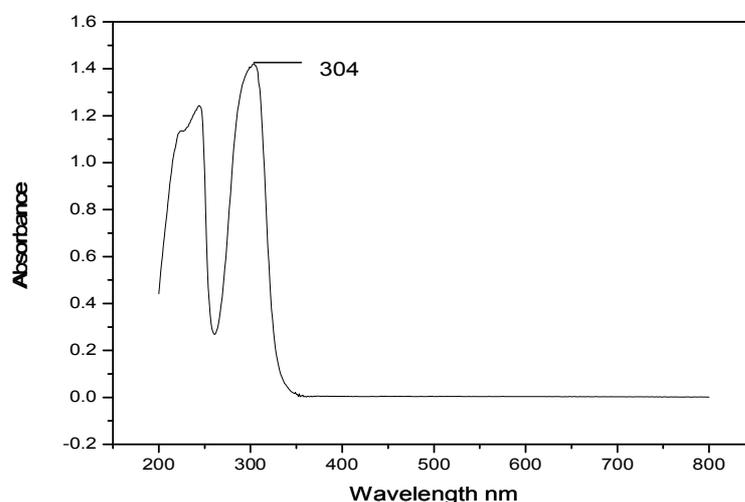
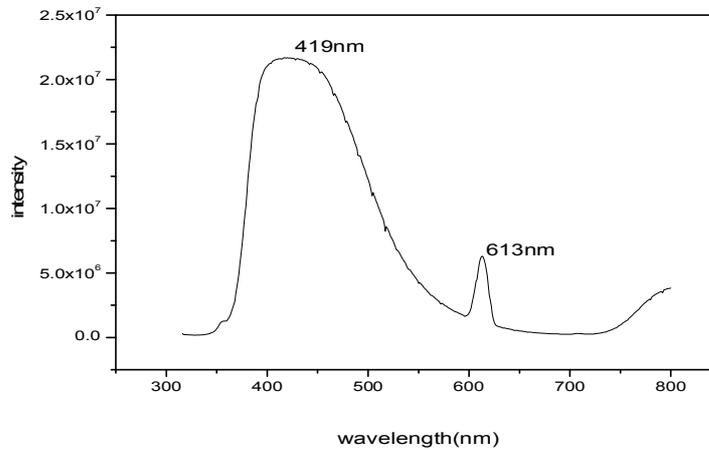


Fig. 3. UV-Vis absorption spectrum of LH5SS.

**Photoluminescence studies.** Photoluminescence (PL) measurement is a prominent tool for determining the crystalline quality of a system as well as its exciton fine structure [17]. Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material. The emission spectrum was recorded for the LH5SS crystal in the range of 304–800 nm and the sample was excited at 304 nm. The emission

spectrum (PL spectrum) and excitation spectrum are presented in the Fig 4. The PL spectrum of the LH5SS sample consists of two emission bands: strong UV peak at 613 nm shows the emission of red color and a broad band at 419 nm shows the emission of violet color. The additional peak at 419 nm may represents the defect level existed due to the presence of low angle grain boundaries.



*Fig. 4. Photoluminescence Spectrum.*

**NLO property.** The nonlinear optical property of the grown crystal was tested using Kurtz-Perry powder technique by passing a Q switched , mode locked Nd:YAG laser of 1064 nm and pulse width of 8 ns (spot radius of 1mm) on the powder sample of LH5SS. The input laser beam was passed through an IR reflector and then directed on micro crystalline powdered sample. Photodiode detector and oscilloscope assembly detected the green light emitted by the sample. The SHG efficiency was evaluated by taking the micro crystalline powder of KDP as the reference material. Input laser energy incident on the sample was 0.68J. The SHG efficiency LH5SS is 1.5 times greater than the KDP. **Microhardness Measurement.** Hardness is an important mechanical property required for the fabrication of electronic and optical devices. The LH5SS crystal placed on the platform of the microhardness tester and loads of different magnitudes (10,25,50g) were applied over a fixed interval of time (10s). The hardness was calculated using the relation:

$$H_v = (1.8544 P/d^2) \text{ kg/mm}^2 \quad (2)$$

where  $P$  is the applied load in kg and  $d$  is the average diagonal length of the indentation in mm. It is observed from the graph that the hardness value increases with the load increases.

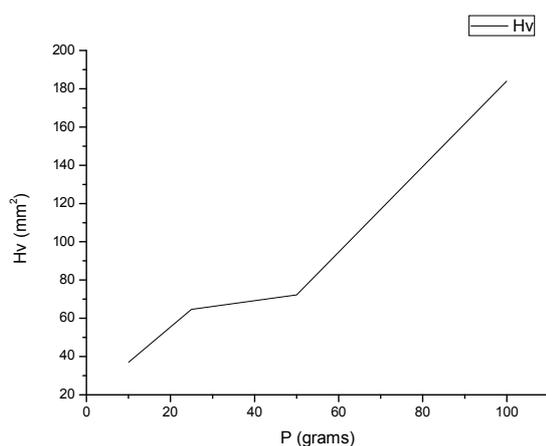


Fig. 5. Microhardness graph.

**Summary.** Single crystals of LH5SS, an organic nonlinear optical material, were grown by slow evaporation method at room temperature. The single crystal XRD analysis confirms the grown crystal belongs to monoclinic system. The functional groups of the grown crystal were identified using FTIR spectrum. The optical transmittance study shows the crystal has good transmittance in the entire visible region and wide band gap. The Kurtz and Perry powder SHG method confirm the SHG efficiency of LH5SS is 1.5 times that of KDP and phase- matching property. The mechanical property of the material was studied by Vicker's hardness measurement.

## References

- [1] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991; (b) T. Pal, T. Kar, G. Bocelli, L. Rigi, Cryst. Growth Design 3 (2003) 13.
- [2] D. Xu, M. Jiang, Z. Tan, A new phase match able nonlinear optical crystal L-arginine phosphate monohydrate, Acta Chem. Sin. 41 (1983) 570–573.
- [3] G. Ramesh Kumar, S. Gokul Raj, R. Sankar, R. Mohan, S. Pandi, R. Jayavel, Growth, structural, optical and thermal studies of non-linear optical l-threonine singlecrystals, J. Cryst. Growth 267 (2004) 213–217
- [4] B. Dhanalakshmi, S. Ponnusamy, C. Muthamizhchelvan, Growth and characterization of a solution grown, new organic crystal: l-histidine-4-nitrophenolate4- nitrophenol (LHPP), J. Crystal Growth 313 (2010) 30–36.
- [5] S.A. Martin Britto Dhas, J. Suresh, G. Bhagavannarayana, S. Natarajan, Growth and characterization of a new organic non-linear optical (NLO) material: l-histidinium trifluoroacetate, Open Cryst. J. 1 (2008) 46–50.
- [6] Madhavan, S. Aruna, K. Prabha, J. Packium Julius, Joseph Ginson P., S. Selvakumar, P. Sagayaraj, Growth and characterization of a novel NLO crystal l-histidine hydrofluoride dihydrate (LHHF), J. Crystal Growth 293 (2006) 409–414.
- [7] S. Aruna, M. Vimalan, P.C. Thomas, K. Thamizharasan, K. Ambujam, J. Madhavan, P. Sagayaraj, Growth and characterization of semi organic nonlinear optical LHPCL crystals, Cryst. Res. Technol. 42 (2007) 180–185.
- [8] Anandan Pandurangan, Jayavel Ramasamy, Crystal growth and characterization of semi organic single crystals of l-histidine family for NLO applications, J. Crystal Growth 322 (2011) 69–73.

- [9] S.A. Martin Britto Dhas, S. Natarajan, Growth and characterization of two new NLO materials from the amino acid family: l-histidine nitrate and l-cysteine tartrate monohydrate, *Opt. Commun.* 281 (2008) 457–462.
- [10] K. Moovendarana, S.A. Martin Britto Dhasb, S. Natarajana Growth and characterization of l-histidinium 2-nitrobenzoate single crystals: A new NLO material. *Optik* 124 (2013) 3117– 3119
- [11] J.F. Ma, J.Y. Li, G.L. Zheng, J.F. Liu, *Inorg. Chem. Commun.* 6,581 –583 (2003)
- [12] H.M. Albert ,J.JosephArulPragasam, G.Bhagavannarayana, C.Alosious Gon- sago, Investigation on structural ,spectral, and thermal properties of L-histidinium glutarate monohydrate(LHG), *J.Therm.Anal.Calor.*118(2014) 333–338.
- [13] Investigations on spectroscopic, optical, thermal and dielectric properties of a new NLO material: L –histidinium p- toluenesulfonate [LHPT] M. Suresh, S. Asath Bahadur and S. Athimoolam
- [14] P.U. Singare, R.S. Lokhande, R.S. Madyal, *Open J. Phys. Chem.*1, 45–54 (2011)
- [15]. V.K. Rastogi, M.A. Palafox, R.P. Tanwar, L. Mittal, *Spectrochim. Acta A* 58, 1989–1994 (2002)
- [16] Y. le Fur, R. Masse, M. Z. Cherkaoui, and J. F. Nicuod, *Zeitschrift für Kristallographie* 210 (1995) 856-860.
- [17] L. Kumari, W.Z. Li, Synthesis, structure and optical properties of zinc oxidehexagonal microprisms, *Cryst. Res. Technol.* 45 (3) (2010) 311–315.

Cite the paper

R. Usha, N. Hema, V. Revathi, Ambika D. Shalini, D. Jayalakshmi (2017). [Synthesis, Growth and Characterisation of New Organic Crystal: L-Histidinium 5 Sulfo Salicylate for Second Order Nonlinear Optical Applications](#). *Mechanics, Materials Science & Engineering*, Vol 9. [10.2412/mmse.92.96.883](#)