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Research Article

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XRD and FT-IR Studies on Lead (II) Nitrate doped Histidine Picrate crystal: A nonlinear optical material

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ABSTRACT

Single crystals of Lead(II)nitrate doped Histidine Picrate crystal has been grown successfully by solution growth method from its aqueous solution. The grown crystals have been subjected to X-ray diffraction (XRD) studies to identify the morphology and structure. The FTIR study reveals bonding interaction of PbNO3 and Histidine in the crystal. The NLO property of the crystals has been confirmed.

Keywords: NLO crystal; Histidine; solution method; XRD; crystal structure; FTIR;

INTRODUCTION

The organic non-linear optical (NLO) crystals with aromatic rings have attracted much attention because of their wide transparency range, fast response and high damage threshold for device applications. However, the shortcomings of aromatic crystals, such as poor physicochemical stability, low hardness and cleavage tendency hinder their device applications [1- 3]. Inorganic NLO materials have excellent mechanical and thermal properties but possess low laser damage threshold and low optical nonlinearities [4, 5].

Semi organic materials possess large optical linearity, high resistance to laser induced damage, inherent ultra fast response times, low angular sensitivity and good mechanical stability [6-8]. The amino acid Histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. Histidine frequently occurs at the active sites of enzymes and co-ordinates ions on large protein structures [9]. There has been a great interest in synthesizing novel nonlinear optical (NLO) samples by combining Histidine with organic and inorganic acids and salts. Usually, Histidine complexes belong to non-centro symmetric space groups and it is an essential criterion for nonlinear optical (NLO) application. Histidine Picrate (LHB) is an NLO material and thorough scan on literature reveals that only a limited work on various properties of this complex has been reported [10-11].

It has been reported that doping NLO crystals with organic impurities can alter various physical and chemical properties and doped-NLO crystals may also find applications in optoelectronic devices like pure NLO crystals [12-14]. Semi organic NLO materials are synthesized in such a way that they take the advantages of both organic and inorganic materials. A typical semi-organic NLO material is formed by combining an organic ion and an inorganic counter ion to have a favorable high optical nonlinearity, low damage threshold, excellent mechanical and thermal properties. The research on the synthesis of semi-organic complexes have increased enormously in the last few years specifically, amino acids and strong inorganic salts are good raw materials to produce semi-organic crystals [15-17]. The interesting amino acid-family of semi-organic crystals such as L-arginine hydrochloride, Histidine tetrafluoro borate, L-arginine phosphate, Histidine bromide, Histidine dihydrogen phosphate, L-alanine tetrafluoro borate etc have been already grown and reported[18-21]. Motivated by the earlier reports on amino acid-family of semi-organic crystals, we synthesize and grow a new semi organic NLO crystal PbNO3 doped Histidine Picrate crystal in this work.

Histidine is one of the optically active amino acids and when it is combined with a suitable inorganic material, it easily forms an eccentric crystal having a point group lacking centre symmetry. This crystal derived from organic-inorganic complex combines the high optical non-linearity of a purely organic compound with favorable thermal properties. The aim of this paper is to report the synthesis, growth of PbNO3 doped Histidine Picrate crystals and to report the results of XRD and FTIR studies of the grown crystals.

EXPERIMENTAL SECTION

Exactly one molar picric acid and Histidine are weighed. Equimolar solutions are prepared and heated separately for five minutes. They are mixed thoroughly with stirring while in hot Condition. It is filtered and added with the doping Lead Nitrate test tube which is also maintained In the hot condition .this is kept aside until it attains the room temperature. After that this is cooled in the ice Bath till the precipitate is formed.

It is filtered, dried and a portion is taken for preparing the saturated solution. The saturated solution is prepared and heated to about 60 degree centigrade for 5 Minutes. It is filtered and kept undisturbed. The induction time is noticed. The fine crystals are harvested within a span of three to five days. The Lead Nitrate doped Histidine crystals are characterized using FTIR and XRD studies.

Instrumentation for characterization of crystals

X-ray Diffraction (XRD) provides an efficient and practical method for the structural characterization of crystals. This method helps in determining the arrangement and the spacing of atoms in a crystalline material.

The grown crystals were subjected to X-ray diffraction (XRD) studies using an XPERT-PRO Philips X-diffractometer with CuKα1, CuK α2 and CuKβ radiation to identify the crystal structure, to find lattice parameters, space group and number of molecules per unit cell(Z). The FTIR spectrum of the sample was recorded using a Perkin Elmer FTIR spectrometer by the KBr pellet technique in the range 400-4000 cm-1. The infrared spectroscopy is effectively used to identify the functional groups of the grown crystals.

RESULTS AND DISCUSSION

FTIR studies

The spectrum was recorded for the wavelength range 500-4000 cm-1. This is shown in the figure 1 and Table 1. The pure N-H stretch of Histidine appears at the peak at 3454.9 cm-1. The broad peaks at 3080.4 cm-1 may be assigned to N-H symmetric stretches of the same group and also protonated NH2 which are varyingly H-bonded to the environment. The anionic nature of carboxylate group in crystal is clearly evident from the C = O stretch at 1636 cm-1. The peak at 1557.9 cm-1 may be due to the skeletal vibrations of the imidazole ring in Histidine.

The band at 1333 cm-1 and 1074 cm-1 is assigned to the OH plane deformation in COOH and NH symmetric stretch respectively and its shoulder at 1154 cm-1 is assigned to COO- stretch of the carboxylate anion in the ring of Histidine. The sharp peak at 3454 cm-1 is the convincing evidence for the protonated form of the Histidine ring nitrogen and NH2 group, which actually stands as the evidence for the bonding interaction between lead nitrate and Histidine in the crystal lattice. The peak at 833.3cm-1 may be due to the NH2 wagging vibrations.

The peak at 1487.2 cm-1 may be due to the NH3+ symmetric deformation vibrations. The peak at 1268.3 cm-1 may be due to the NH3+ rocking vibrations of the imidazole ring in Histidine.

The peak at 707.5 cm-1 may be due to the CH2 rocking vibrations. The peak at 536.3 cm-1 may be due to the C-O-O rocking vibrations. The peak at 1557.9 cm-1 may be due to the skeletal vibrations of the imidazole ring in Histidine.

The peak at 616.6 cm-1 may be due to the C-O-H bending vibrations. The peak at 906.2 cm-1 may be due to the NH2+ rocking vibrations. The peak at 791.9 cm-1 may be due to the CC stretching vibrations. The peak at 1764.1 cm-1 may be due to the C=O stretching vibrations.

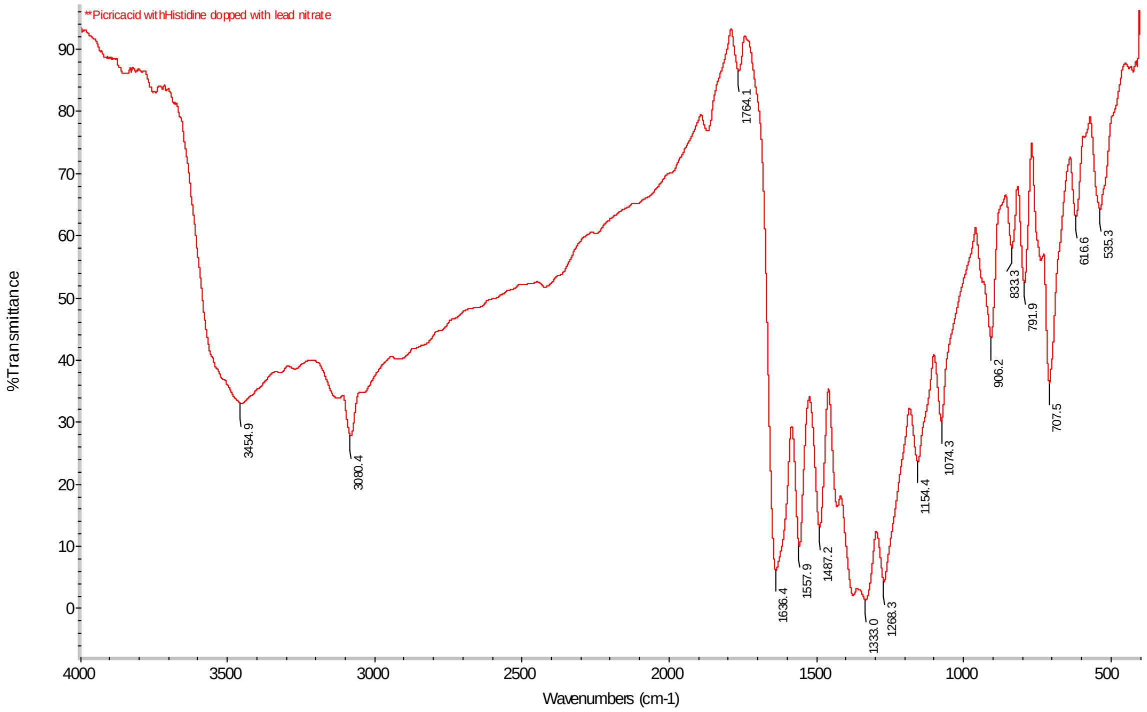

Fig-1 : F.T.I.R Spectrum of Histidine-Picrate Doped with Lead(II)nitrate

Functional groups	Wave Numbers,Cm-1
N-H stretch	3454.9 cm-1
N-H symmetric stretches	3080.4 cm-1
C = O stretch	1636 cm-1
skeletal vibrations of the imidazole ring in Histidine	1557.9 cm-1
OH plane deformation in COOH	1333 cm-1
NH symmetric stretch	1074 cm-1
COO- stretch of the carboxyl ate anion	1154 cm-1
NH2 wagging	833.3cm-1
NH3+ symmetric deformation	1487.2 cm-1
NH3+ rocking	1268.3 cm-1
CH2 rocking	707.5 cm-1
C-O-O rocking	536.3 cm-1
imidazole ring in Histidine	1557.9 cm-1
C-O-H bending	616.6 cm-1
NH2+ rocking	906.2 cm-1
CC stretching	791.9 cm-1
C=O stretching	1764.1 cm-1

Table 1

XRD STUDIES

The grown specimen was first lapped and chemically etched in a non preferential etchent of water and acetone mixture in 1:2 volume ratio to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity of the specimen. Fig. 2 shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen Lead Nitrate doped Histidine picrate crystal (001) diffracting planes in symmetrical Bragg geometry by employing the XPERT-PRO Philips X-ray diffractometer (0000000011024644) with CuKα1 radiation from Alagappa University, Karaikudi.

The structure was solved by XRD analysis by direct method and refined by the full matrix least square technique using SHELXL program. The obtained data from XRD studies are presented in the table 2. From the data, it is observed that the grown crystal which is recognized as noncentro symmetric thus satisfying one of the essential material requirements for the (Second Harmonic Generation) SHG activity of the crystal.

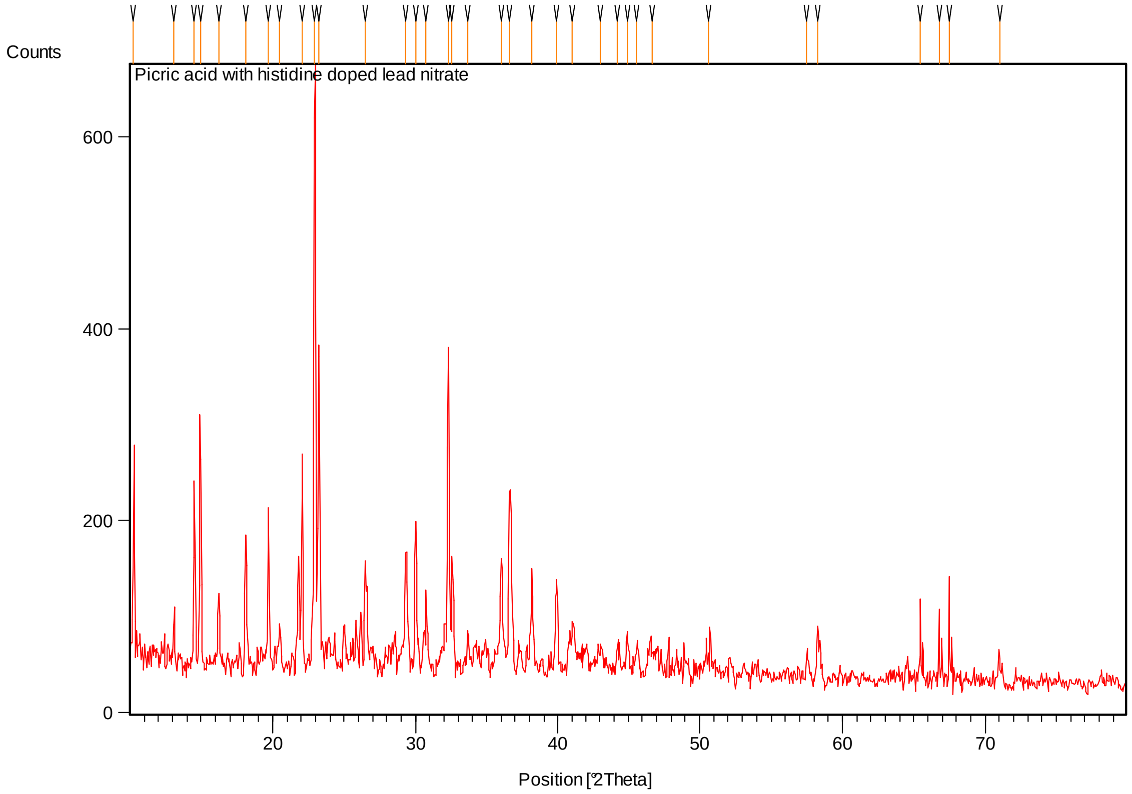

Fig-2: XRD Spectrum of Histidine-Picrate Doped with Lead (II)Nitrate

From the literature, it is noticed that the space group P21 is one of the most popular space groups and it allows maximal contribution of the molecular non linearity to the macroscopic crystal nonlinearity [16]. As seen in the figure, in addition to the main peak at the 22.9 arc s, this curve contains 34 more additional peaks. The solid line in these curves which is well fitted with the experimental points is obtained by the Lorentzian fit. The additional peaks between 10 and 71 (Table 2) arc s around the main peak are due to internal structural very low angle (≤ 1 arc min) grain boundaries [22]. The tilt angle i.e. the mis orientation angle of the boundary with respect to the main crystalline region for all the observed very low and high angle boundaries are 10 and 71arc s.

The full width at half maximum (FWHM) values for the main peak and the all other low and high angle boundaries are respectively given in the table. Though the specimen contains very low angle boundaries, the relatively low angular spread of around 5 arc min of the diffraction curve and the low FWHM values show that the crystalline perfection is (T. Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthy, G. Bhagavannarayana Vol.8, No.10) reasonably good. The affect of such low angle boundaries may not be very significant in many applications, but for the phase matching applications, it is better to know these minute details regarding crystalline perfection. It may be mentioned here such very low angle boundaries could be resolved only because of the high-resolution of the X'Pert Pro Philips X-ray diffractometer used in the present investigation.

Experimental d values of pure samples are in well agreement with standard JCPDS values [23]. The variations in intensity of peaks of doped crystals may be attributed to the incorporation of dopants in crystal lattice.

Start Position [°2Th.]	10.0251
End Position [°2Th.]	79.9251
Step Size [°2Th.]	0.0500
Scan Step Time [s]	10.1382
Scan Type	Continuous
PSD Mode	Scanning
PSD Length [°2Th.]	2.12
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	0.4785

Specimen Length [mm]	10.00
Measurement Temperature [°C]	25.00
Anode Material	Cu
K-Alpha1 [Å]	1.54060
K-Alpha2 [Å]	1.54443
K-Beta [Å]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	30 mA, 40 kV
Diffractometer Type	0000000011024644
Diffractometer Number	0
Goniometer Radius [mm]	240.00
Dist. Focus-Diverge. Slit [mm]	91.00

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
10.2708	205.71	0.0965	8.60580	33.18
13.0997	56.26	0.0842	6.75301	9.08
14.5142	180.11	0.1149	6.09791	29.05
14.9332	256.33	0.0979	5.92772	41.35
16.2103	73.66	0.1639	5.46351	11.88
18.1228	138.50	0.1235	4.89102	22.34
19.6971	150.17	0.0755	4.50351	24.22
20.4751	44.39	0.2518	4.33410	7.16
22.0464	214.43	0.0918	4.02862	34.59
22.9426	619.93	0.1100	3.87325	100.00
23.2363	326.60	0.0915	3.82495	52.68
26.5105	101.31	0.1942	3.35950	16.34
29.3359	115.26	0.1837	3.04205	18.59
30.0056	135.24	0.0957	2.97567	21.82
30.7361	53.33	0.2993	2.90659	8.60
32.3047	295.55	0.1029	2.76894	47.67
32.5902	94.57	0.0792	2.74534	15.26
33.6510	31.24	0.2952	2.66338	5.04
36.0064	96.41	0.2066	2.49231	15.55
36.6186	202.66	0.1829	2.45204	32.69
38.1521	86.73	0.2127	2.35693	13.99
39.8565	96.92	0.1649	2.25998	15.63
40.9817	48.42	0.5568	2.20049	7.81
43.0682	30.14	0.5904	2.10033	4.86
44.2145	29.03	0.2952	2.04850	4.68
44.9385	48.86	0.1476	2.01717	7.88
45.6010	34.42	0.2952	1.98939	5.55
46.7149	31.48	0.5904	1.94452	5.08
50.6388	24.52	0.5904	1.80267	3.96
57.5021	27.58	0.5661	1.60144	4.45
58.2944	56.97	0.2404	1.58154	9.19
65.4691	89.28	0.0833	1.42451	14.40
66.7711	65.35	0.0912	1.39986	10.54
67.4823	100.64	0.0601	1.38682	16.23
71.0563	26.17	0.3600	1.32558	4.22

Table 2

CONCLUSION

Optically good quality crystal of Lead (II) nitrate doped Histidine Picrate crystal was grown using evaporation technique. A XPERT-PRO Philips X-diffractometer with CuKα1 radiation study reveals the crystalline perfection of the crystal without any internal structural grain boundaries. The functional groups were identified using FTIR technique.

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