Crystal Growth and Characterization of an Organic Nonlinear Optical Material: L-Histidinium Maleate (LHM)

C. Alosious Gonsago, Helen Merina Albert, S. Janarthanan, and A. Joseph Arul Pragasam

***Abstract*—L-histidinium maleate, a new amino acid organic nonlinear optical material has been successfully grown from aqueous solution by slow solvent evaporation method. The grown crystal was subjected to single crystal X-ray diffraction study for the identification of the structural arrangement. The chemical composition of the grown crystal was estimated by Energy dispersive X-ray analysis. In order to confirm the molecular structure of the grown crystal, FT-NMR spectral analysis was carried out. The percentage of optical transmittance by the grown crystal was ascertained by UV–visible spectral study. The nonlinear optical property of the grown material was identified by the powder technique of Kurtz and Perry. The HR-SEM analysis shows the surface morphology of the grown crystal. The thermal stability of the grown crystal was found by differential thermal analysis.**

***Index Terms*—NLO, XRD, EDAX, FT-NMR, HR-SEM.**

I. Introduction

Nonlinear optical (NLO) materials have been extensively studied in the recent years, due to their potential applications in various fields like optical data storage, optical switching, image processing and manipulation [1]–[3]. Organic nonlinear materials are drawing a great deal of attention, due to their efficient nonlinearities and rapid response in electro-optic effect when compared with the inorganic nonlinear materials. A number of organic nonlinear optical materials have been accounted in literature owing to their nonlinear optical and photonic applications [4], [5]. Amino acids are interesting and useful materials for NLO applications. The salts of basic amino acid L-histidine added much interest as a promising nonlinear optical material after the works of Marcy et al., which reports that the nonlinearity of L-histidine tetraflouroborate is much higher than that of potassium dihydrogen phosphate [6]. Maleic acid, basically a dicarboxylic acid with large π-conjugation has attracted a great deal of attention [7]. On the basis of earlier reports on L-histidine salts, we have successfully grown monoclinic form of L-histidinium maleate (LHM), a new organic compound. Several authors have followed the spectral, optical, and thermal studies for material characterization [8]–[11]. In this paper, the crystal growth and its characterization by single crystal XRD, energy dispersive X-ray analysis (EDAX), FT-NMR, UV–Visible, NLO and differential thermal analysis are reported for the grown compound.

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II. Experimental

Good quality single crystal of L-histidinium maleate was grown from aqueous solution by slow solvent evaporation method. The title compound was prepared by dissolving equimolar ratio of L-histidine (purity 99%) and maleic acid in double distilled water. The salts were stirred well for nearly 6 h using a magnetic stirrer in order to obtain a uniform mixture of the solution over the entire volume. The substance was purified by successive crystallization process. After repeated crystallization, saturated solution was prepared at 32 ℃ using the synthesized salts. The solution was finally filtered twice using micro-whatmann filter papers to eliminate unwanted impurities. Two drops of H_2O_2 were added to the mother solution to inhibit the growth of any microorganism [12]. The filtered solution was kept in a crystallizing vessel, covered with a perforated sheet and placed in a dust free atmosphere. A good quality single crystal of optimum size was obtained within a period of 4 weeks at room temperature (32 ℃). The photograph of as grown crystal of L-histidinium maleate is shown in Fig. 1.

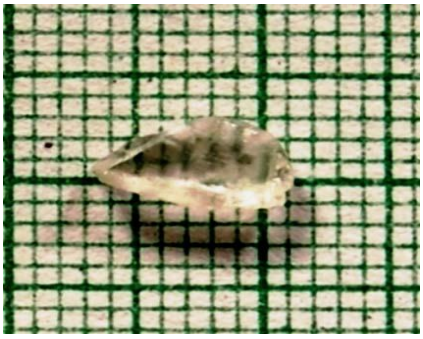

Fig. 1. Photograph of as grown crystal of lhm.

III. Result and Discussion

A. Single Crystal XRD

In order to find the crystal structure and lattice parameters of the grown crystal, single crystal X-ray diffraction analysis was carried out using BRUKER AXS kappa apex2 CCD

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diffractometer. The unit cell dimensions were measured using MoKα radiation source of wavelength 0.7107 Å. The X-ray crystallography data shows that the crystal belongs to monoclinic system with $P2_1$ space group, Z=4. The molecular formula of the crystal is $C_{10}H_{16}N_3O_{7.5}$. The observed values of lattice parameters are a = 11.4656(7) Å, b = 8.0530(5) Å, c = 14.9705(9) Å, V = 1353.75(14) Å^3, α = γ = 90 ºand β = 101.657 º. A detailed study on crystal structure is reported elsewhere [13].

B. EDAX Analysis

Energy dispersive X-ray analysis (EDAX) is a micro-analytical technique, used to obtain information about the chemical composition of the grown crystal. In this work, the grown crystal was subjected to EDAX analysis using the instrument FEI QUANTA 200F energy dispersive X-ray micro analyzer. The EDAX spectrum of the crystal is shown in Fig. 2. The weight percentage (wt %) of *C*, N and O as obtained from EDAX analysis is in concurrent with the theoretical values and listed in Table I.

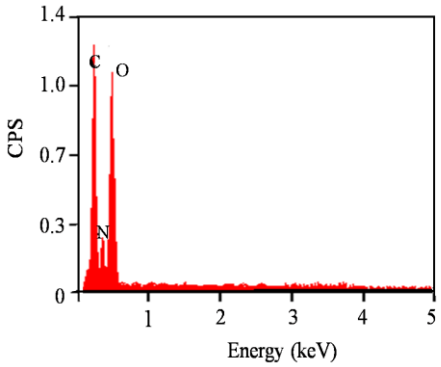

Fig. 2. Edax spectrum of lhm crystal.

TABLE I: EDAX QUANTIFICATION TABLE OF LHM

Element	Wt (%) Experimental	Wt (%) Theoretical
Carbon	43.32	42.58
Nitrogen	14.85	14.89
Oxygen	41.83	42.53

C. FT-NMR Spectral Study

Nuclear magnetic spectroscopy provides detailed information about the structure, dynamics and chemical environment of molecules. In order to confirm the molecular structure of the grown crystal, FT-NMR spectral studies were carried out using the instrument Bruker 300MHz (Ultrashield) TM instrument. The ^{1}H NMR and ^{13}C NMR spectra of LHM are shown in Fig. 3. The ^1H NMR spectrum (Fig. 3a) is recorded at 298 K with DMSO as the solvent. The chemical shifts of the compound are represented in δ ppm. The chemical shifts are assigned and are presented in table 2. In the ^{1}H NMR spectrum, the resonance peaks at δ = 8.261ppm and 7.180ppm are due to the existence of CH groups of the imidazole ring of L-histidine. The sharp intensive peak at δ = 6.058ppm is due the presence of CH group of maleate anion. The signal at δ = 3.935ppm is due to CH(NH_2) group and it is split into a triplet due to the coupling of two neighboring protons (CH_2) of the side chain. The signal at around δ = 3.139ppm is due to CH_2 group of the side chain of L-histidine and it is split in to a quartet due to the interactions of neighboring aliphatic CH groups. The quartet at around 3.028ppm is due to the influence of solvent DMSO.

The ^{13}C NMR spectrum (Fig. 3b) of LHM is recorded at 299.6 K with DMSO as the solvent. The peak appearing at δ = 170.896ppm is due to CO group of side chain of L-histidine and the peak at δ = 167.794ppm is due to CO group maleate anion. The peaks resolved at δ = 136.382ppm and 116.762ppm are due to the presence of CH groups of imidazole ring. The signal at δ = 135.101ppm is due the presence of *C* atom of the imidazole ring. The signal at δ = 131.700ppm is due to the presence of CH of maleate anion. The resonance peak appearing at δ=53.138ppm is due to the presence of CH group of side chain. The peak resolved at 27.276ppm is due to the presence of CH_2 group of the side chain of L-histidine. The peak at δ = 39.940ppm is split into septet due to the effect of solvent DMSO.

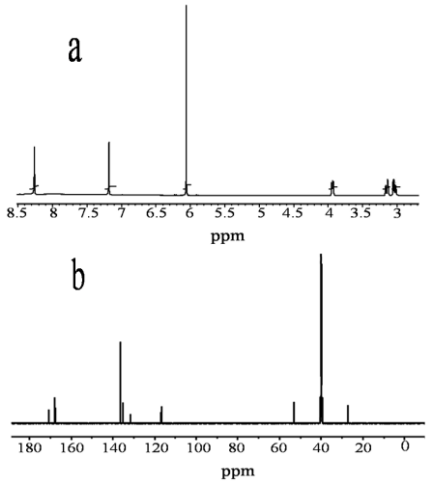

Fig. 3. a) ^{1}h nmr and b) ^{13}c nmr spectra of lhm.

TABLE II: FT-NMR ASSIGNMENTS OF LHM

Spectrum	Signal at δ (ppm)	Functional groups
1H NMR	3.028	DMSO (solvent)
	3.159	CH_2 group
	3.935	CH group
	6.058	CH of side chain
	7.180, 8.261	CH of imidazole ring
13C NMR	27.276	CH_2 group
	39.940	DMSO (solvent)
	53.138	CH of side chain
	131.700	CH of maleate anion
	135.101	C of imidazole ring
	136.382, 116.794	CH of imidazole ring
	167.794	CO of maleate anion
	170.896	CO of side chain

D. Optical Transmittance Study

The optical transmittance study is an important tool in identifying the usefulness of a NLO material in the visible and blue regions. The UV–visible transmittance spectrum was recorded for the grown compound in the wavelength

range of 200–1000 nm using a Varian Carry-5E UV–vis Spectrophotometer. The optical transmittance spectrum of LHM is shown in Fig. 4. From the transmittance spectrum, it is observed that the grown crystal is completely transparent in the UV and visible spectral regions with the lower cut off wavelength around 280 nm thereby confirming the advantages of the crystal. Complete transparency of the crystal between the region 280–1000 nm is an advantage of the crystal for optoelectronics and nonlinear optical applications [14].

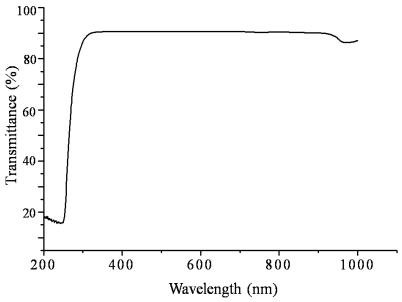

Fig. 4. Optical transmittance spectrum of lhm.

E. Non linear Optical Property

The nonlinear optical property of crystal was examined by the Kurtz and Perry powder technique [15]. In this technique, the grown sample was grounded into fine microcrystalline powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser operated at the fundamental wavelength 1064nm with 8 ns pulse width and 10 Hz pulse rate was allowed to pass through the sample cell. The amplitude of the SHG output was measured using photomultiplier and digitalizing oscilloscope assembly. The final output was displayed on a digital storage oscilloscope. The frequency conversion efficiency of the crystal was confirmed by the emission of green radiation from the sample. Here, the conversion efficiency of LHM sample is compared with standard reference potassium dihydrogen phosphate sample. The SHG efficiency of L-histidinium maleate is comparable with the standard potassium dihydrogen phosphate (KDP) sample.

F. HR-SEM Analysis

In order to analyze the nature and surface morphology of the grown crystal, HR- SEM analysis was employed. The crystal was cut into few mm for observing the surface morphology. The SEM images of LHM crystal taken in two different magnifications are shown in Fig. 5. The images show step-like growth, which suggests the existence of grain boundaries and striations. The surface is smooth and free from any visible inclusions. The micrographs also show the presence of few cracks on the crystal surface. This may be due the temperature oscillations during the crystal growth.

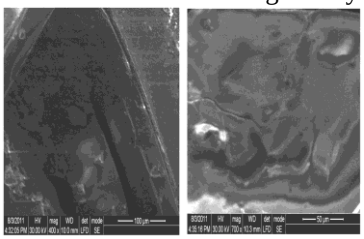

Fig. 5. Hr-sem micrographs of lhm.

G. Thermal Analysis

Differential thermal analysis (DTA) provides useful information regarding the transformations that have occurred, water of crystallization and melting point of the compound [16]. The DTA analysis was employed using the instrument NETSZCH STA 409 C/CD under nitrogen atmosphere. Powdered sample of about 5 mg was used for the analysis. The typical DTA curve of the grown crystal is shown in Fig. 5. The DTA curve shows a sharp endothermic peak at around 120 ℃ which is attributed to water of crystallization. This is followed by two consecutive peaks at around 139 ℃ and 279 ℃ which are attributed to the decomposition and volatilization of the compound. Hence, the melting point of the compound is found to be 139 ℃. The crystal can be used for device application below this temperature.

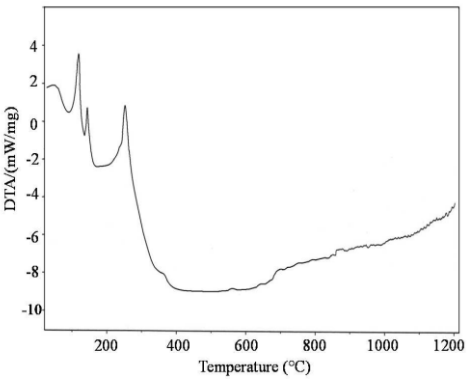

Fig. 6. Dta trace of lhm.

IV. Conclusion

Single crystal of L-histidinium maleate (LHM) was grown successfully by slow evaporation solution growth technique at room temperature. The crystal structure and lattice parameters were identified by single crystal XRD analysis. The chemical composition of the grown crystal was ascertained by EDAX analysis. The molecular structure of LHM was confirmed by FT-NMR spectral analysis. The optical transmittance study reveals the transparency of the crystal which shows that the percentage of optical transmittance is much higher in the range 280 to1000 nm. The emission of SHG from the grown crystal is confirmed by Kurtz and Perry powder method. The HR-SEM analysis shows the surface morphology of the grown crystal. The thermal stability of the grown crystal was analyzed by DTA technique. The above results clearly indicate that the grown L-histidinium maleate crystal can be used as a potential candidate for nonlinear optical applications.

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