L-Histidinium Maleate Crystals for Nonlinear Frequency Conversion

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

***Abstract*—A new amino acid organic nonlinear optical material L-histidinium maleate (LHM), has been synthesized and successfully grown from aqueous solution by slow solvent evaporation method at room temperature. The solubility of the compound was measured in aqueous solution at different temperatures. The grown crystal was subjected to single crystal XRD and powder XRD studies in order to identify the structural arrangement. The chemical composition of the grown crystal was confirmed by Energy dispersive X-ray analysis (EDAX). The percentage of optical transmittance by the grown crystal was identified 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 and differential scanning calorimetry.**

***Index Terms*—DTA, DSC, EDAX, HR-SEM, NLO, XRD.**

I. Introduction

Nonlinear optics is a new frontier in the field of science and technology which plays an important role in the emerging era of photonics. 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]. Materials with large second-order optical nonlinearities, good optical transparency, short lower cut-off wavelengths, and stable physicochemical performances are required in order to realize many of these applications [4]. Organic nonlinear materials are drawing a great deal of attention, due to their potential nonlinearities and rapid response in electro-optic effect when compared with the inorganic nonlinear materials. Recently, a number of organic nonlinear optical materials have been reported in literature owing to their nonlinear optical and photonic applications [5]–[7]. Among these classes of materials, amino acids are interesting and useful materials for NLO applications.

The salts of basic amino acid L-histidine gain much interest as promising nonlinear optical materials after the early works of Marcy et al., that the nonlinearity of L-histidine tetraflouroborate is much greater than that of potassium dihydrogen phosphate [8]. Due to its basic nature L-histidine forms a number of salts with different organic and inorganic acids which have shown NLO properties. Maleic acid, basically a dicarboxylic acid with large π-conjugation has attracted a great deal of attention [9]. Based on the previous reports of L-histidine salts and their NLO properties, we have successfully synthesized L-histidinium maleate, a new analog of L-histidine salt. It is observed that several authors have followed the spectral, optical, and thermal studies for material characterization [10]–[15]. In this paper, we report the crystal growth and its characterization by XRD, energy dispersive X-ray analysis, UV–Visible, NLO, HR-SEM, differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

Manuscript received December 22, 2011; revised January 26, 2012.

C. Alosious Gonsago is with the Physics Department, Faculty of Science and Humanities, A.J. College of Engineering, Affiliated to Anna University, Chennai, India, (email: c.alosious@gmail.com).

S. Pandi was with the, PG & Research Department of Physcs, Presidency College, Chennai, India, (email: pandisangu@gmail.com).

H. M. Albert and A. J. A. Pragasam are with the, Physics Department, Sathyabama University, Chennai-600119, India, (email: merinagonsago@gmail.com, drjosephsu@gmail.com).

II. Material and Methods

A. Solubility Study

AR grade of L-histidine and maleic acid were used for the solubility measurements and crystal growth. Aqueous solution of LHM was prepared by dissolving equimolar ratio of L-histidine and maleic acid in double distilled water. Here, the solubility is the amount of solute (gram) present in 100 ml of saturated solution at certain temperature. The solubility study is generally carried out to find out the quantity of the material available for the crystal growth. The solubility curve of LHM sample in double distilled water at different temperatures ranging from 30 to 50 °C is shown in Fig.1. From the curve, it is noted that solubility increases with increase in temperature. The sample of this study has positive temperature coefficient of solubility and hence, the LHM crystals can be grown from aqueous solution by slow solvent evaporation method.

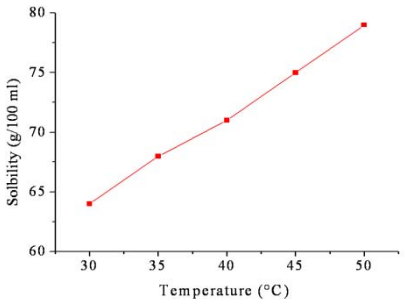

Fig. 1. Solubility curve of LHM sample.

B. Crystal Growth

According to the solubility data, the title compound L-histidinium maleate (LHM) has been grown by dissolving

1:1 molar ratio of L-histidine and maleic acid in double distilled water at room temperature (32 °C). The salts were stirred well for nearly 2 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 recrystallization process, saturated solution was prepared at 32 °C using the synthesized salts. The solution was finally filtered twice or thrice 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 [16]. The filtered solution was kept in a crystallizing vessel, covered with a perforated sheet and placed in a dust free atmosphere for constant growth. A good quality single crystal of optimum size was obtained in a period of 25 days at room temperature. The photograph of as grown crystal of LHM crystal is shown in Fig. 2.

Fig. 2. Photograph of as grown crystal of LHM.

III. Result and Discussion

A. XRD Studies

Single crystal XRD and powder XRD studies were carried out for the grown crystal, in order to find the crystal structure and lattice parameters. The single crystal X-ray diffraction analysis was carried out using BRUKER AXS kappa apex2 CCD 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 P21 space group, Z=4. The molecular formula of the compound is C10H16N3O7.5. 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) Å3, α = γ = 90ºand β = 101.657º.

The grown crystal was characterized by X-ray powder diffraction technique using a JEOL JDX services instrument with CuKα radiation source of wavelength λ = 1.5406 Å. The grown crystal was crushed to a uniform fine powder and subjected to powder X-ray diffraction. The 2θ range analyzed was from10° to 70° by employing continuous scan mode. The powder XRD pattern of the sample is depicted in the Fig. 3. The sharp and well defined peaks at specific 2-theta values indicate good crystalline nature and purity of the sample.

B. EDAX Analysis

Energy dispersive X-ray analysis (EDAX) is a micro-analytical technique which is used to obtain useful information regarding 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. A fine beam of X-rays was made to fall into the LHM sample. The number and energy of the X-rays emitted by the sample was measured by an energy-dispersive spectrometer. Since the energy of the X-rays emitted from the sample is attributed to the energy difference between the two shells and of the atomic structure of the compound, the elemental composition of the specimen can be measured. The EDAX spectrum of the crystal is depicted in Fig. 4. The weight percentages (wt %) of C, N and O as obtained from EDAX analysis are in concurrent with the theoretical values and are listed in TABLE I.

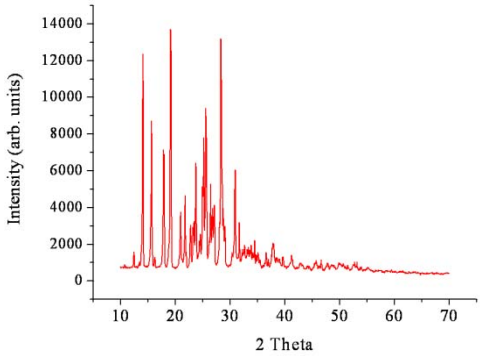

Fig. 3. Powder XRD pattern of LHM crystal.

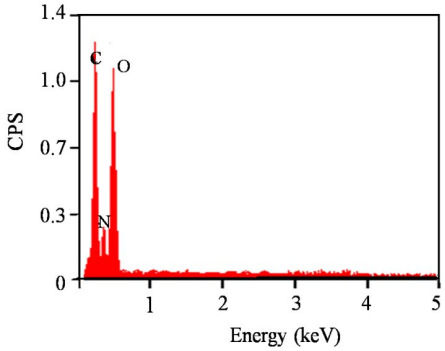

Fig. 4. EDAX spectrum of LHM crystal.

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. Optical Analysis

The optical transmittance study is an effective tool in identifying the usefulness of a nonlinear optical material in the visible and blue regions. The UV–visible transmittance spectrum was recorded for the grown crystal in the wavelength range of 200–1000 nm using a Varian Carry-5E UV–vis Spectrophotometer. The optical transmittance spectrum of LHM is depicted in Fig. 5. 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 at around 280 nm,

thereby confirming the advantages of the crystal for photonics applications. Complete transparency of the crystal between the region 280–1000 nm is an important prerequisite for NLO applications [17]. It is well known that optical absorption in the near UV region arises from the electronic transitions associated within the crystal. The optical band gap of the crystal is calculated using the formula Eg=1240/λ (nm) and is found to be 4.43 eV. Hence, due to wide band gap, the grown crystal has wide transmittance window in the visible and UV regions.

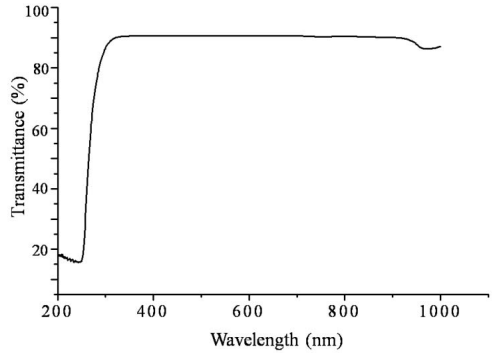

Fig. 5. UV-Visible transmittance spectrum of LHM crystal.

D. NLO Property

The nonlinear property of LHM crystal was studied by employing Kurtz and Perry powder technique [18]. In this technique, the grown sample was powdered into fine microcrystalline samples and then densely packed between two transparent glass slides. A Q-switched mode Nd:YAG laser operated at the fundamental wavelength 1064 nm with 8 ns pulse width and 10 Hz pulse rate was used as the radiation source. The experimental set-up of second harmonic generation was reported elsewhere [19]. The laser beam was allowed to pass through the sample cell. The output beam from the sample was filtered by an IR detector and then identified by a photomultiplier tube. A color filter was used to absorb IR radiation and transmit that of second harmonic radiation of wavelength 532 nm. The final output was displayed on the oscilloscope. The frequency conversion efficiency of the crystal was confirmed by the emission of green radiation from the sample.

E. 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 highly transparent region of the crystal was chosen for analysis. The SEM images of LHM crystal taken in different magnifications are shown in Fig. 6. The images show step-like growth, which suggests the existence of grain boundaries and striations. The micrographs also show the presence of few cracks and visible inclusions on the surface of the crystal. This may be due the temperature oscillations during the crystal growth.

F. DTA Analysis

Differential Thermal Analysis (DTA) is a very popular thermal analysis technique used to find endothermic and exothermic transitions as a function of temperature. The DTA provides useful information regarding the transformations that have occurred, water of crystallization and melting point of the compound [20]. The DTA analysis was employed using the instrument NETSZCH STA 409 C/CD under nitrogen atmosphere between the temperature range 20–1200 °C in steps of 10 °C. The typical DTA curve of LHM crystal is shown in Fig. 7. The DTA curve shows a sharp endothermic peak at around 120 °C which is attributed to water of crystallization. This is followed by two consecutive peaks at around 139 °C and 279 °C which are attributed to the decomposition and volatilization of the compound. Although the melting point of the compound is around 139 °C, the compound loses its structure at around 120 °C due to the presence of water molecules.

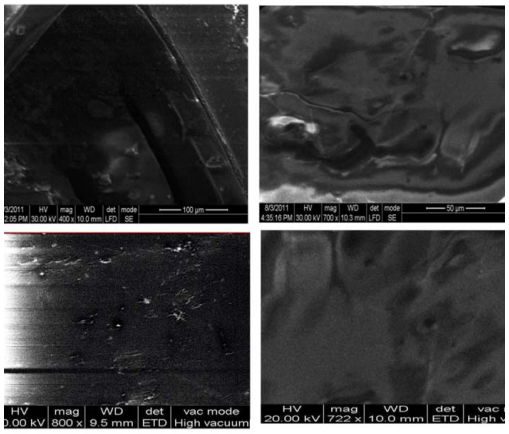

Fig. 6. SEM images of LHM crystal.

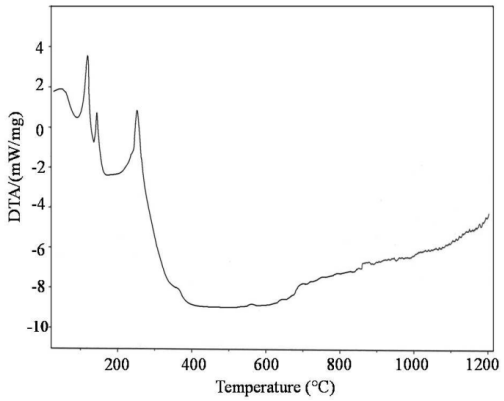

Fig. 7. DTA curve of LHM crystal.

G. DSC Analysis

The differential scanning calorimetry (DSC) is a thermo-analytical technique used to determine melting temperature, water of crystallization and heat of fusion. Differential scanning calorimetry measures heat flow to or from the material as a function of temperature and time. The DSC analysis was carried out for the LHM crystal between 25 °C and 200 °C at a heating rate of 10 °C /min in the nitrogen atmosphere using the instrument NETZSCH DSC 204. The typical DSC curve of LHM is shown in Fig. 8. The DSC curve shows almost the same changes shown by DTA curve. The curve is smooth up to 110 °C and then shows two sharp endothermic peaks at 117.5 °C and 136 °C respectively. The first peak is due to the removal of weakly entrapped lattice water from the crystal and the second peak is due to the

partial decomposition of the compound. The DSC analysis clearly indicates that the grown crystal is hydrated in nature and is found to be thermally stable up to 117.5 °C. The smoothness of the DSC curves reveals the purity of the crystal.

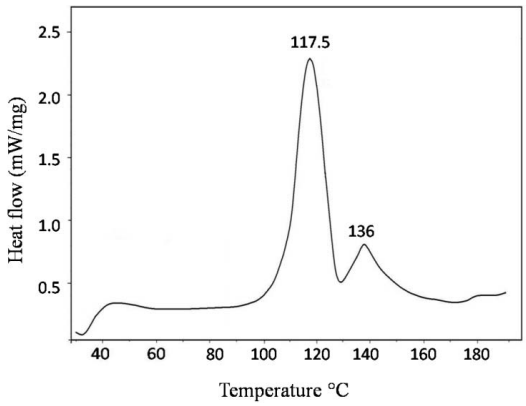

Fig. 8. DSC curve of LHM crystal.

IV. Conclusion

Good quality single crystal of L-Histidinium maleate has been grown successfully by slow evaporation solution growth technique at room temperature. Single crystal and powder X-ray crystallographic data indicate that the LHM crystal belongs to monoclinic system with the space group P21. The chemical composition of the grown crystal was ascertained by EDAX analysis. The UV–visible transmittance spectrum 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 was confirmed by the emission of green radiation using Kurtz and Perry powder method. The HR-SEM analysis reveals the existence of grain boundary and striations on the surface of the grown crystal. The thermal stability of LHM crystal was analyzed by DTA and DSC techniques which indicate that the crystal is stable upto 117.5 °C and it can be used as potential material for nonlinear optical applications below this temperature.

Acknowledgment

The authors sincerely thank Sophisticated Analytical Instrument Facility (SAIF), IIT-Madras and Sathyabama University, Chennai for providing experimental facilities. The authors also acknowledge the Department of Physics, B.S. Abdur Rahman University, Chennai for extending the NLO characterization facility.

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