IOP Conf. Series: Materials Science and Engineering **360** (2018) 012044 doi:10.1088/1757-899X/360/1/012044

Growth and Characterization of L-Leucenium Hydrogen Maleate Single Crystals for Nonlinear Optical Applications

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Abstract. Good quality single crystals of amino acid based L-Leucenium maleate (LLM) has been grown from aqueous solution by slow evaporation method at room temperature. The crystalline nature of the crystal has been confirmed by the X-ray diffraction analysis Using Cuk_{α} radiation of wavelength of 1.54 A°. The presence of various functional groups in the LLM is confirmed by FT-IR using the Bruker IFS66 spectrometer. The functional groups present in the sample were also confirmed by FT-RAMAN spectral analysis. The thermal stability of LLM crystal has been analyzed by TGA and DTA studies. Second harmonic generation test was done on the LLM sample using Kurtz and Perry technique. The NLO efficiency of the grown crystal is nearly 0.6 times that of the standard KDP crystal. The transparent nature of the sample has been conformed from the UV-Vis-NIR spectrum and optical band gap of the LLM crystal also calculated.

1. Introduction

Nonlinear optical materials have been extensively studied in the recent years due to their potential applications in various fields like optical data storage, optical switching images, processing and manipulation. Therefore, there is a need to produce high efficiency NLO materials. Among the class of NLO materials, organic NLO materials are generally preferred to be more efficient than the inorganic counterpart due to their favorable nonlinear responds [1]. Amino acid crystals have subjected to extensive investigation by several researchers for their excellent characteristics. Amino acids are interesting useful organic materials for NLO applications as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (NH_2) group in them, known as zwitterions which produce hydrogen bonds. Due to this dipolar nature, amino acids have physical properties which make them ideal candidates for application [2]. Among the various amino acids, L-Leucine has

formed several complexes, which are promising materials for second harmonic generation. Maleic acid, basically dicarboxylic acid with large π conjugation has attracted a great deal of attention [3]. The intermolecular hydrogen bond in maleic acid is very strong. Maleic acid forms crystalline maleate of various organic molecules through hydrogen bonding and π -π interaction [4]. On the basis of earlier reports on L-Leucine salt [5], we have successfully grown a good quality crystal of L-Leucinium hydrogen maleate, a new organic compound. In this paper, the crystal growth and its characterization by powder XRD, FT-IR, FT-RAMAN, UV-Vis-NIR, NLO and Thermal analysis are reported for the grown compound.

2. ExperimentalProcedure

L-Leucinium hydrogen maleate (LLM) crystal was synthesized from highly pure L-Leucine and L-Maleic acid and they were taken in the equimolar ratio of 1:1. The required quantity of L-Leucine and L-Maleic acid was thoroughly dissolved by adding double distilled water according to their solubility data and stirred well for about five hours using a magnetic stirrer to obtain a homogenous mixture. The solution was filtered to remove insoluble impurities using Whatman filter paper of pore size ten micrometers. Then, saturated solution was taken in a beaker and tightly covered with a polythene paper of perforated sheet in order to control the evaporation rate and kept undisturbed at room temperature for crystallization. Finally, a well-defined single crystal was obtained after 35 days by slow evaporation method. The photo graph of the as grown crystal of LLM is shown in Figure. 1.

Figure1. Photograph of as grown single crystal of LLM

3.Results and Discussion

3.1. .X-ray diffraction analysis

The crystalline nature of the grown crystal was checked by taking the X-ray diffraction pattern of powder samples of L-Leucinium hydrogen maleate (LLM) with Cuk_{α} (λ = 1.5406 A˚) radiation. The sample was scanned over a 2θ in the range of 10 -30˚ at the rate of 2˚per min. From this measurement we found the lattice dimensions as a=21.132 A˚, b=5.226 A˚, c=31.452 A˚, β=98.439° having the space group C2, it is crystallize in monoclinic system and is well matched with the reported literature [5]. The presence of a sharp and well defined peak confirms the good crystalline nature of the L-Leucinium hydrogen maleate (LLM) crystal. The differences in the peak amplitude can be attributed to the different sizes and orientation of the powdered grains. The recorded powder XRD pattern is shown in Figure 2.

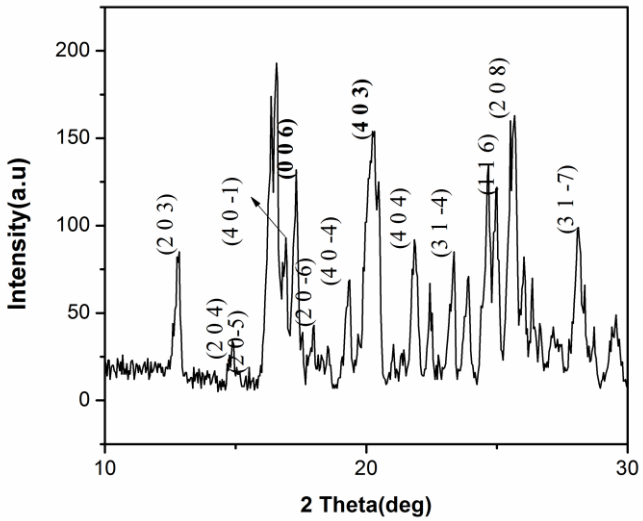
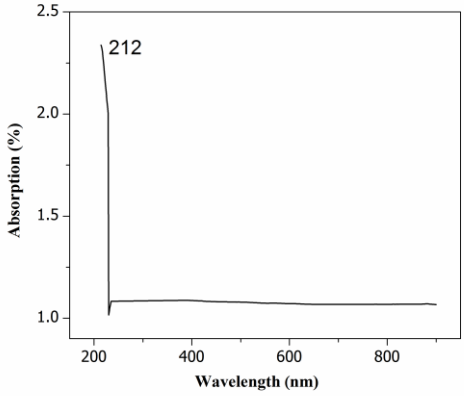


Figure 2. Powder X-ray diffraction pattern of the LLM crystals

3.2. UV-Vis Absorption spectroscopy

The optical absorption study is an important tool in identifying the usefulness of a NLO material in the visible regions. The UV-Visible absorption spectrum was recorded for the grown compound in wavelength range of 200 - 900nm using Varian carry 5E model UV-Vis spectrometer. There is no appreciable absorption of light in the entire visible range as in the case for all amino acids [6]. No absorption was found in the entire visible region of the UV-Vis-NIR spectra. UV-Vis-NIR studies also give important structural information because absorption of UV and visible light involves promotion of the electron in π and n orbital from the ground state to higher energy state [7]. The optical absorption spectrum of LLM is shown in Figure. 3a. The lower cut of wave length is around 212nm. There is no sufficient absorption from 200nm to 900nm. This is an advantage of the use of grown crystal, where the absence of strongly conjugated bonds leads to wide transparency ranges in the visible and UV spectral regions. The optical absorption coefficient of photon energy helps to study the band structure and explains the type of transition of electrons.



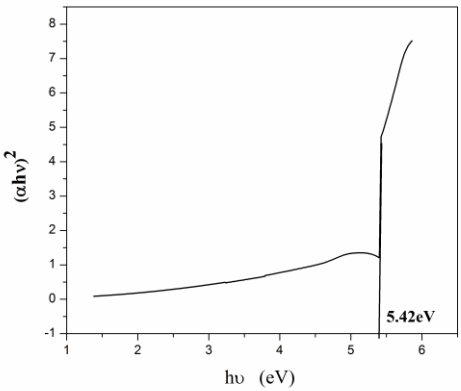


Figure 3.(a) UV-Vis absorption spectrum of LLM **Figure 3. (b)** Plot of $(\alpha h\nu)^2$ versus hν of LLM

The optical absorption coefficient α is calculated using the following relation α = Abs/t where Abs is the absorbance and t is the thickness of the crystal [8]. The optical energy band gap of the crystal is determined from the transmittance spectra using the relation $\alpha h\nu = A(h\nu - E_g)^{1/2}$ where A is a constant which varies with transitions, h is the Plank's constant, ν is the frequency of the photon, Eg is the band gap of the material. The band gap of LLM crystal was estimated by plotting $(\alpha h\nu)^2$ versus hν as shown in Figure. 3b. As per Tauc's idea, the optical band gap has been calculated from the extrapolation of linear part at absorption edge. The value of band gap was found to be 5.42 eV. As a consequence of wide band gap, the grown crystal has large absorption in the visible region.

3.3. FT-IR analysis

The FTIR spectra of the grown LLM single crystal were observed on the powder sample is shown in Figure. 4. The FTIR spectrum of LLM crystal was recorded using the Brukers IFS66 spectrometer in the range 4000 – 400 cm^{-1} by KBr pellet to identify the functional group present in the crystal. The medium intensity band at 3131 cm^{-1} appearing in IR spectrum is due to the NH_3^+ asymmetric stretching mode [9]. The stretching vibrations of the CH_2 group have been observed in the region 2960–2840 cm^{-1}. The position and intensity of the peaks are at 2959 cm^{-1} [10,11] and 2873 cm^{-1} is due to the asymmetric and symmetric stretching of CH_2 group of LLM [4,9]. The combination and overtone vibrations overlap in the range 2653 – 1880 cm^{-1} [4]. The strong carboxyl absorption at 1730 cm^{-1} is assigned to C=O stretching confirms the –COOH and $COO^{-1}$of compound [1,2]. The presence of N-H bending observed at 1572 cm^{-1} confirms presence of amino acid in the crystal lattice [9]. The absorption at 1390 cm^{-1} is due to the COO- ions. CH_2 wagging vibration is absorbed due to the peak at 1321 cm^{-1}[8,12]. The symmetric C-O stretching frequency is observed at 1241 cm^{-1} in the spectrum[13,4]. The broad band of CH_2 wagging vibration absorbed at 1035 cm^{-1} and CH_2 rocking vibration between 839 – 894 cm^{-1}. The strong band of the C-C stretching is observed at 867 cm^{-1} [3,4]. The COO^{-1} bending, scissoring, wagging vibrations observed at 749, 662, 589 cm^{-1}. The vibrational study confirms the LLM exists as zwitterions in which the carboxyl group is present as COO^- Carboxylate ion and the amino group exists as NH_3^+ ammonium ion.

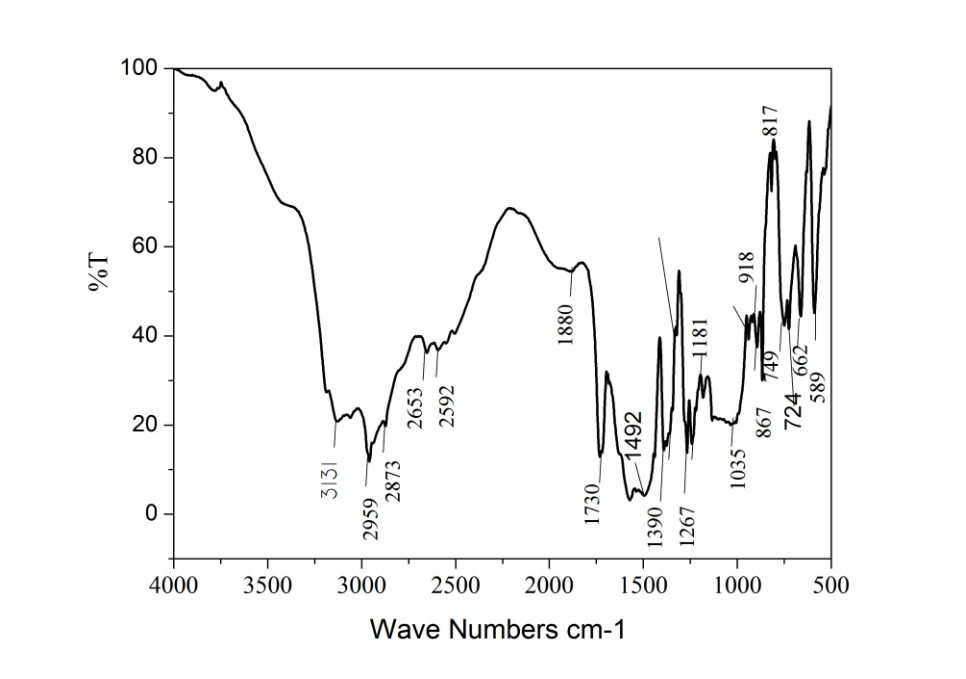


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Figure 4 FT-IR spectrum of the grown LLM crystal

3.4. FT-RAMAN analysis

Figure 5 shows the Raman spectra of LLM crystals recorded in the range of 500 – 3500cm^{-1} at room temperature using Bruker IFS27 Raman spectrograph. The peaks at 3058.47 cm^{-1} confirm NH_3^+ stretching of amino group. The strong band at 1695 cm^{-1} and a shoulder at 1623 cm^{-1} are attributed to NH_3^+ asymmetric deformation mode. The peak against 2961 cm^{-1} and 2936 cm^{-1} are corresponding to the CH_2 asymmetric stretching vibrations. NH_3^+ rocking is observed at 1179 cm^{-1}. Symmetric stretching of CH band in the Raman spectrum is at 2871 cm^{-1}. C-C stretching revealed due to the peak at 1460 cm^{-1} 897 cm^{-1}. The corresponding COO^{-1} symmetric and COO^- wagging are confirmed due to the peaks at 1390 cm^{-1} in FT Raman spectrum. NH_3^+ rocking is observed at 1179 cm^{-1} and 962 cm^{-1}. Therefore the functional groups identified by FT-IR spectrum are also confirmed by FT-RAMAN spectrum.

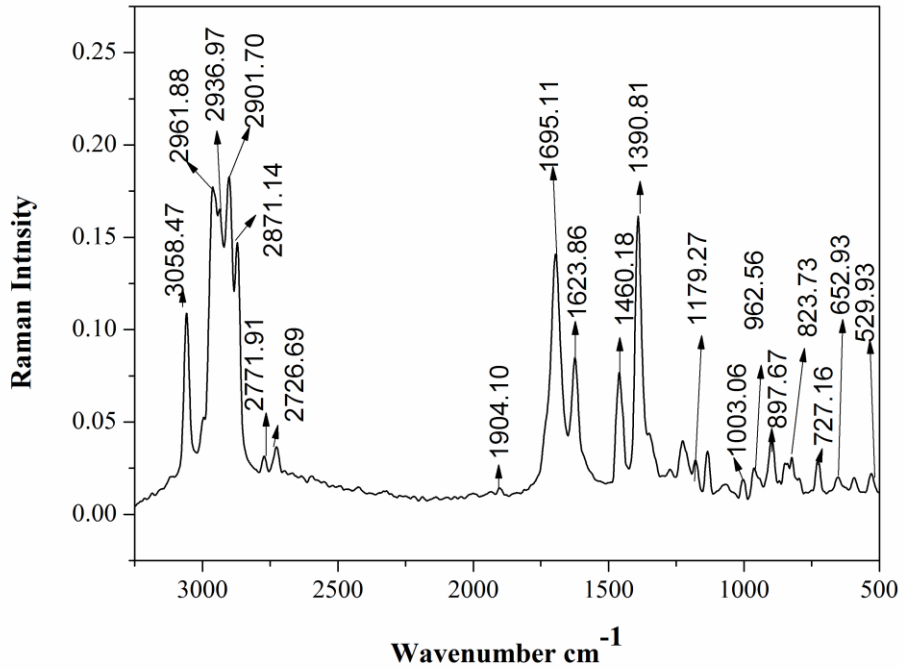

Figure 5. FT –Raman spectrum of the grown LLM crystal.

3.5. Thermal analysis

Thermo gravimetric and Differential thermal analysis gives information regarding phase transition, water of crystallization and different stages of decomposition of the crystal. The Thermo gravimetric analysis (TGA) and Differential Thermal analysis (DTA) of the crystal were carried out between 25˚C to 650˚C at a heating rate of 10K/min in the nitrogen atmosphere. The resulting spectrum is shown in Figure 6. There was no weight loss up to 140˚C, hence the material is free of any solvent entrapped in the crystal lattice. The TGA curve shows a weight loss in one stage and the same near 150˚C .is assigned to loss of water. The weight loss due to water is also associated with melting of the sample, which is clearly observed in the DTA curve as an endothermic transition occurred at 142˚C. At this temperature, LLM and water molecule were dissociated from the compound and the LLM started to melt as its melting point is nearly 150˚C, an exothermic transition as observed at 478˚C and 554˚C in the DTA curve. From the results of DTA it is established that no

transformation in structure was observed before melting. Hence the material can be exploited for any suitable application up to its melting.

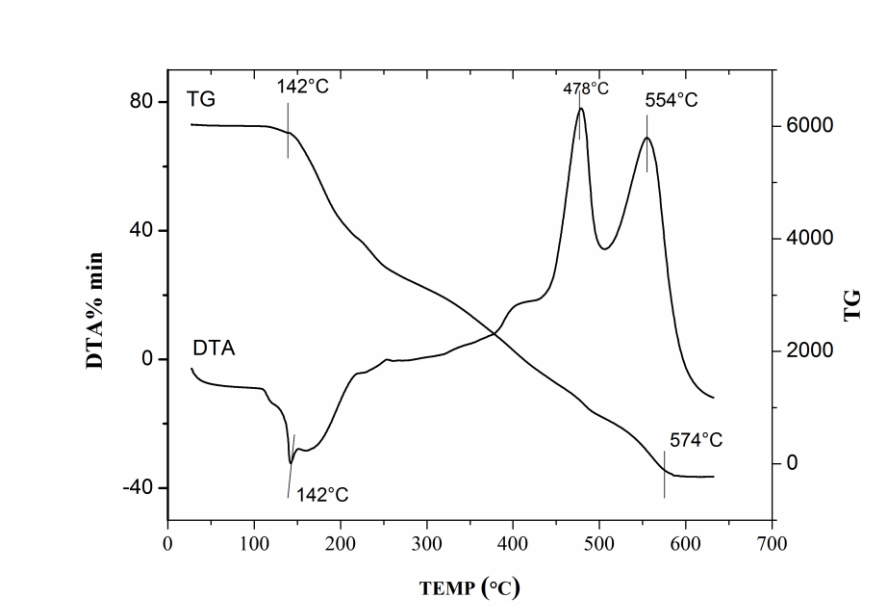

Figure 6.TG/DTA curve for LLM crystal

3.6. Nonlinear optical studies

Second harmonic generation efficiency of the grown crystal was confirmed using Kurtz and Perry powder technique [14]. A Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064nm and a pulse width of 8ns with a repetition rate of 10 Hz was used. The incident input energy of 0.7J/s was incident on the crystalline powder packed between two transparent glass slides. The emission of green light from the sample confirmed the frequency doubling of LLM crystal. The second harmonic generation output signal of 2.98mW obtained for LLM crystal whereas the standard KDP crystal gave an SHG signal of 5.03mW for the same input energy. Hence, SHG efficiency of LLM crystal was 0.6 times that of potassium dehydrogenate phosphate (KDP) crystal.

4. Conclusion

Single crystals of L-Leucenium maleate (LLM) were successfully grown by slow evaporation technique at room temperature. Powder X-ray diffraction analysis reveals the monoclinic crystalline nature of the LLM crystal. The UV-Vis-NIR studies shows that these crystals are transparent in the entire visible region with a lower cut-off wavelength 212 nm and band gap value were calculated for LLM crystal. The presence of various functional groups was identified by FT-IR analysis and is confirmed by FT-Raman. The TG/DTA studies established that the compound undergoes no phase transition and is stable up to 150°C. The SHG efficiency studies show the suitability of the crystals for NLO application.

Acknowledgments

The corresponding author gratefully acknowledges the support from the Department of Science and Technology (DST), Government of India for the research project (SB/EMEQ/248/2014).

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