Growth and characterization of a nonlinear optical crystal of L-histidine salt

C.Alosious Gonsago[1], Helen Merina Albert[2], A.Joseph Arul Pragasam[2*]
[1]Department of Physics, A. J. College of Engineering, Chennai-302, (INDIA)
[2]Department of Physics, Sathyabama University, Chennai-119, (INDIA)
E-mail : drjosephsu@gmail.com

ABSTRACT

A semi-organic nonlinear crystal L-histidine methyl ester dihydrochloride, an analog of L-histidine has been grown successfully by slow evaporation solution growth method at room temperature. The grown crystal was characterized by crystal XRD and FT-NMR studies. The optical transmittance of the grown crystal was analyzed by UV–vis–NIR spectral study which shows that the crystal has a wide transmittance window in the entire visible region. The surface morphology of the grown crystal was analyzed by HR-SEM analysis. The second harmonic generation of the grown crystal was tested by the powder technique of Kurtz and Perry. The thermal stability of the crystal was ascertained by differential scanning calorimetry (DSC) technique. The Vickers microhardness test was performed and the load dependence hardness was estimated.   © 2012 Trade Science Inc. - INDIA

INTRODUCTION

An enduring need persists to build up new class of nonlinear optical materials useful for frequency conversion in the UV to near-IR spectral region. Substantial efforts have been made to combine amino acids with inorganic and organic compounds to produce excellent materials having desirable characteristics suitable for nonlinear optical applications. A number of semi-organic crystals have been explored with high optical nonlinearity, favorable thermal and mechanical properties[1-3]. In semi-organic materials, polarizable organic molecules are stoichiometrically bound within an inorganic host. The salts of L-histidine such as L-histidine tetraflouroborate[4], L-histidine hydrochloride monohy-

drate[5], L-histidine diphosphate[6], L-histidine bromide[7], L-histidine nitrates[8], L-histidine hydroflouride dihydrate[9] and L-histidine perchlorate[10] have been already reported and found to be promising materials for nonlinear applications.

Inspired by the previous works, we have grown L-histidine methyl ester dihydrochloride (LHMED), a semi-organic nonlinear optical material by slow solvent evaporation method. The molecular structure of LHMED was first reported by Victor H. Vilchiz et al.[11] with very small crystals. Preliminary studies suggest that LHMED crystal is promising a material for NLO applications. In this work, the structure of the grown crystal was analyzed by single crystal XRD, and nuclear magnetic resonance (NMR) studies. The linear and nonlin-

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ear optical properties were studied by UV-Vis-NIR and Kurtz and Perry techniques. The thermal stability of the grown crystal was measured by DSC technique. Hardness of the crystal is estimated by microhardness study.

EXPERIMENTAL

The title compound L-histidine methyl ester dihydrochloride (AR grade) obtained from Sigma-Aldrich Company was purified by repeated recrystallization process in double distilled water. After successive recrystallization, the salts were completely dissolved in double distilled water at 32 °C and stirred well using magnetic stirrer for about 2 hours to obtain homogeneous mixture of the saturated solution. The prepared solution was then filtered twice using micro-whatman filter paper to eliminate any unwanted impurities. The filtered solution was kept in a borosil beaker which was covered with perforated polyethylene paper for controlled evaporation of the solvent. In order to avoid temperature variations and to maintain a constant growth, the solution was placed in a constant temperature water bath kept at 32 °C. To restrain the growth any microorganism, two drops of H_2O_2 were added to the saturated solution[12]. The crystal with adequate transparency and size was grown within a period of 30 days.

RESULTS AND DISCUSSION

Single crystal XRD

Single crystal X-ray diffraction study has been carried out to identify the crystal structure and lattice parameters of the grown LHMED crystal. The XRD study was employed using the instrument BRUKER Kappa Apex 2 CCD diffractometer with $MoK\alpha$ radiation of wavelength 0.7107 Å. The X-ray crystallographic data shows that the grown crystal is monoclinic in structure with space group $P2_1$. The observed lattice parameters are a=8.221Å, b=7.108 Å, c=9.505 Å, V=555.42 Å, $\alpha=\gamma$=90º and β=94.56°. These values are in concurrent with the reported values[11].

FT-NMR Spectral analysis

In order to confirm the molecular structure of the

grown crystal, ^{1}H NMR and ^{13}C NMR spectral studies were carried out using the instrument Bruker 300MHz (Ultrashield) TM instrument at 25.7 °C with DMSO as the solvent. The recorded ^{1}H NMR spectrum of LHMED is shown in Figure 1. The chemical shifts of the compound are represented in δ ppm. The chemical shifts are assigned and are presented in TABLE 1. In the ^{1}H NMR spectrum, the resonance peaks at δ = 9.098ppm and 7.531ppm are due to the existence of CH groups of the imidozole ring of L-histidine. These peaks are split into a doublet and triplet due to the interactions of the neighboring proton (NH) of the imidazole ring. The signal at δ = 4.508ppm is due to $CH(NH_2)$ and it is split into a triplet due to the coupling of two neighboring protons (CH_2) of the side chain. A sharp resonance peak observed as a singlet at δ = 3.717ppm is due to the presence of methyl group (CH_3) of ester. The signal at δ = 3.337ppm is due to CH_2 group of the side chain and it is split in to a doublet due to the interactions of neighboring aliphatic CH groups. The peak at 2.532ppm is due to the influence of solvent DMSO.
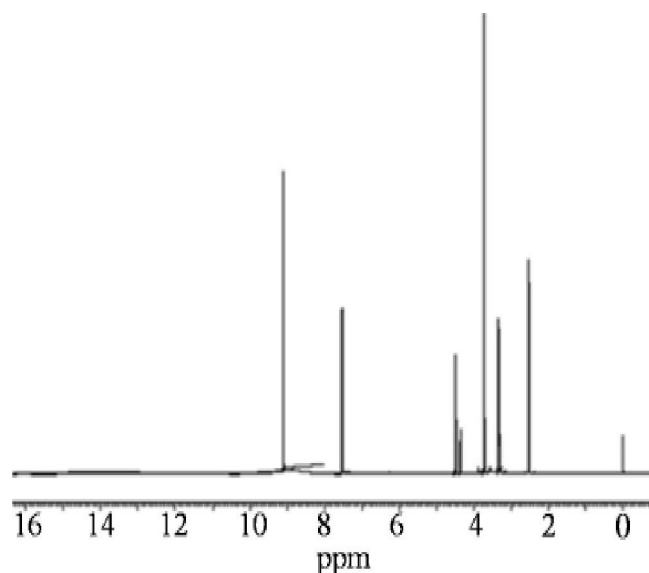

Figure 1 : ^{1}H NMR spectrum of LHMED

The ^{13}C NMR spectrum of LHMED shows eight resonance peaks and is displayed in Figure 2. The resonance peak resolved at δ = 168.982ppm is due to CO group of side chain. The peaks resolved at = 134.427ppm and 118.540ppm are due to the presence of CH groups of imidazole ring. The peak at 127.088ppm is due the presence of C atom of the ring. The resonance peak observed at δ=53.503ppm is due

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to the presence of CH group of side chain. The peak resolved at $\delta = 51.467$ ppm is due to the presence of OCH_3 group of ester and the peak at 25.551 ppm is due to the existence of CH_2 group of the side chain of L-histidine. The peak at $\delta = 41.126$ ppm is split in to multiplet due to the effect of solvent DMSO.
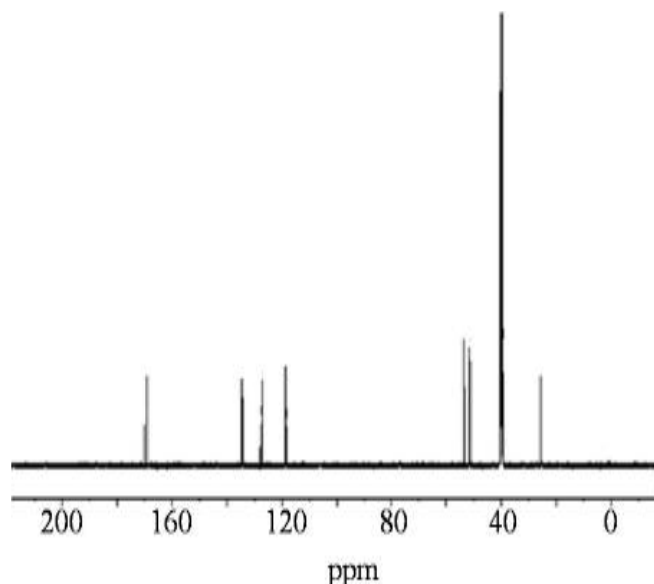

Figure 2 : ¹³C NMR spectrum of LHMED

TABLE 1 : The chemical shifts in ¹H and ¹³C NMR spectra of LHMED

Spectrum	Signal at δ (ppm)	Functional groups
	2.532	DMSO (solvent)
	3.337	CH_2
¹H NMR	3.717	CH_3
	4.508	CH of side chain
	7.531, 9.098	CH of imidozole ring
	25.551	CH_2
	41.126	DMSO (solvent)
¹³C NMR	51.467	OCH_3
	53.503	CH of side chain
	127.088	C of imidazole ring
	118.540, 134.427	CH of imidazole ring
	168.982	CO

UV-vis-NIR spectral analysis

The UV–Vis–NIR spectral study was carried out in the wavelength range 200-1000 nm using the instrument Varian Carry-5E UV-Vis spectrophotometer to identify the suitability of LHMED crystal for optical applications. The optical transmittance spectrum is shown in Figure 3. The crystal shows complete transparency

visible and near UV region which enables it to be a potential material for nonlinear and optoelectronic applications[13]. The transmittance spectrum shows that the transparency of the crystal extends up to the wavelength 230 nm which corresponds to the lower cut-off wavelength or fundamental absorption of the crystal. The wide transparency window between 230 nm and 1000 nm is sufficient for the second harmonic generation of light from the crystal using the Nd:YAG laser.
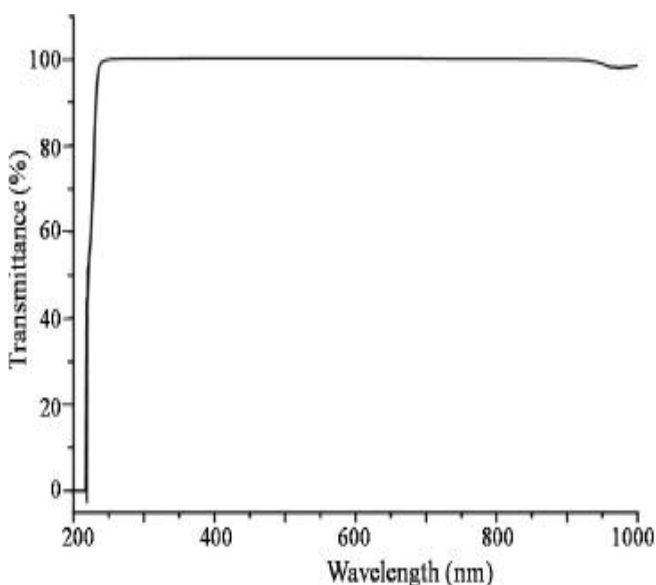

Figure 3 : Optical transmittance spectrum of LHMED crystal

Second harmonic generation

The second harmonic generation of LHMED was tested by the Kurtz and Perry powder technique[14]. A Q-switched Nd:YAG laser operating at the fundamental wavelength 1064nm, producing pulse width 8 ns with the repetition rate of 10 Hz was employed . The grown crystal was ground in to fine powders and densely packed in between two glass plates. It is observed that the sample converts the input radiation of wavelength 1064 nm in to green radiation of wavelength 532 nm. The conversion efficiency of the LHMED is compared with the microcrystalline KDP sample and it is observed that conversion efficiency of the grown crystal is higher than that of standard KDP.

HR-SEM analysis

The high resolution-Scanning electron microscopy (HR-SEM) provides useful information regarding the surface morphology and crystalline nature of the grown compound. The transparent region of the crystal was

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cut into few mm and was used for observing the surface morphology. The SEM images of LHMED taken in two different magnifications are provided in Figure 4. From the Figure 5a, it is clear that the crystal surface is smooth and free from any dislocations. The Figure 5b shows that the surface has step-like growth, which suggests the existence of grain boundaries and striations.
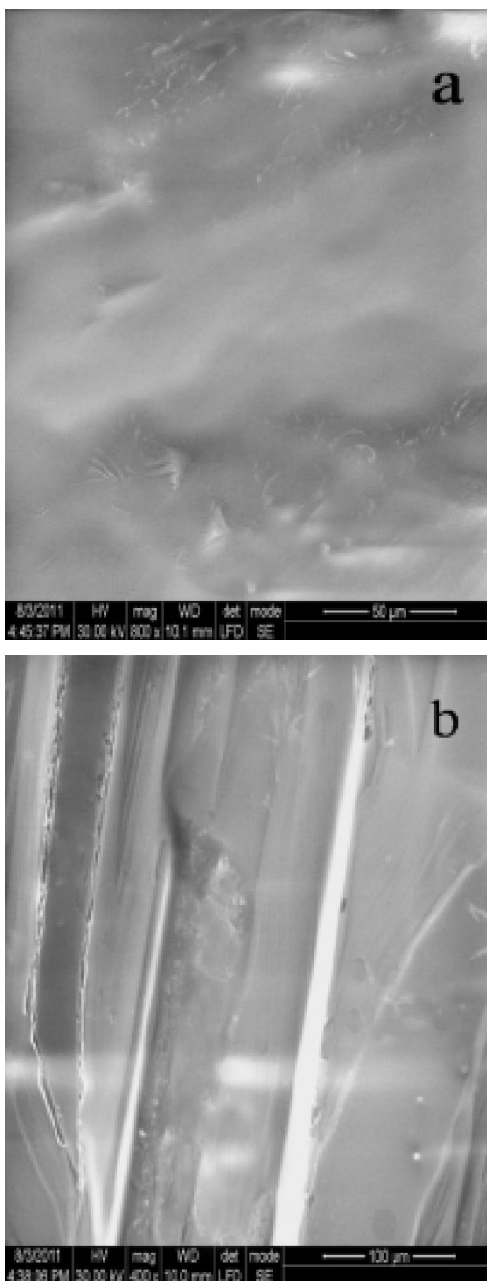

Figure 4 : HR-SEM images of LHMED

DSC analysis

Differential scanning calorimetry (DSC) is a thermo analytical technique which is useful in observing the fu-

sion and crystallization process. The DSC analysis of LHMED crystal was employed using the instrument Perkin-Elmer Thermal analyzer. The DSC analysis was carried out between 25 °C and 250 °C at a heating rate of 20 °C/min in the nitrogen atmosphere. The recorded DSC trace is shown in Figure 5.
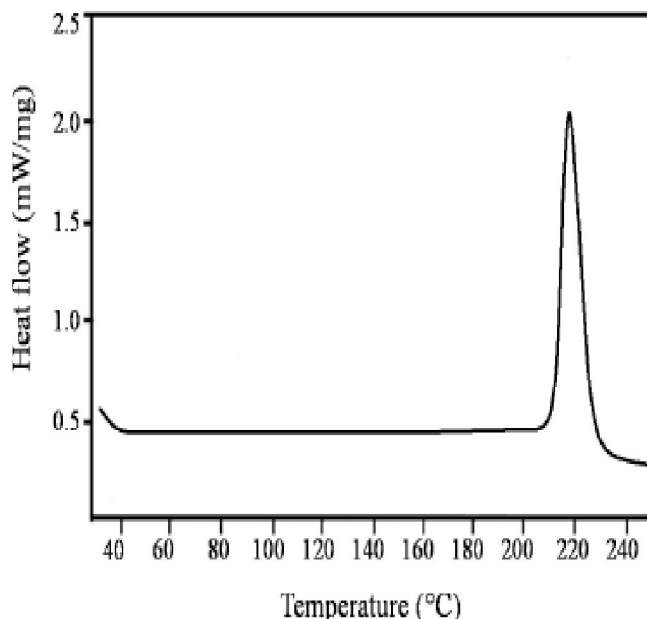

Figure 5 : DSC curve of LHMED

The DSC trace gives the complete picture of decomposition of the material. It is observed that the DSC trace is smooth and rectilinear up to 210 °C and then it shows an endothermic peak at around 218 °C. The onset of the endothermic peak begins at 212 °C and hence the process will be melting. This onset temperature corresponds to the melting point of the crystal which matches with the previously reported value[15]. The peak is broadened between 212 °C and 230 °C which represents the degradation of the material in to fragments. The smoothness of the trace indicates the purity of the compound. The DSC study reveals that the crystal is thermally stable up to 212 °C and suitable for photonic applications where it is necessary to undergo high temperatures.

Microhardness studies

Microhardness testing is very useful technique to understand the mechanical behavior of materials[16]. Mechanical property of the material was analyzed by measuring the micohardness number with different loads. The hardness value of an ideal crystal should be inde-

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pendent of the applied load. But in practice, the load dependence is observed due to normal indentation side effect[17]. The static indentations were made on the crystal for various loads from 10 to 50 g at 32 °C with a constant indentation time of 10 s. The microhardness of the LHMED crystal was estimated for the (010) face. Due to the formation of cracks at higher loads, the maximum applied load was limited to 50 g. The Vickers microhardness number Hv of the crystal was estimated using the formula $Hv = 1.8544 \ P/d^2 \ kg/mm^2$ where, P is the applied load in kg and d is average diagonal length of the indentation in mm. A graph is plotted between hardness number (Hv) and applied load (P) and is shown in Figure 6. It is observed from the plot that the hardness of LHMED crystal decreases with increasing load, which is attributed to normal indentation size effect.

CONCLUSIONS

The LHMED single crystal was grown from solution by slow evaporation method at 30 °C. Single crystal XRD study reveals that the grown crystal belongs to monoclinic system with the space group $P2_1$. The chemical structure of the grown was established by FT-NMR spectral study. The UV-Vis-NIR spectral study shows that the crystal is highly transparent in the UV and visible region and thus confirms the suitability of the crystal for nonlinear applications such as frequency conversion, optical communications, data storage and image processing. The surface morphology of the crystal was analyzed by HR-SEM analysis. The SHG test shows that the sample converts the input radiation of wavelength 1064 nm in to green radiation of wavelength 532 nm. The hardness of the crystal was established by Vickers micrhardness study. The DSC analysis clearly indicates that the crystal is highly stable and making it suitable for possible applications in laser, where the crystal is endured to withstand high temperatures.

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