Structural, Thermal And Optical Properties Of L-Histidine Nitrate Single Crystals

Prakash.P

Department of Physics, Sasurie College of Engineering
Tirupur - 638 056, Tamilnadu, India

Phone: +91-9688851699
E-mail: prakash_19@live.com

Abstract

Single crystals of L-histidine nitrate (LHN), a semi-organic nonlinear optical material were grown by slow evaporation solution growth method at the room temperature. Structural characterization of the grown crystals was carried out by single crystal X-ray diffraction (XRD) method and it is observed that the samples crystallize in orthorhombic system with non-centrosymmetrics pace groups. Fourier transform infrared (FT-IR) studies reveal the presence of functional groups present in the grown crystal. UV–visible study was performed to analyze optical transparency of the grown crystals and found that the crystal was transparent in the entire region. The thermal stability of the grown crystal was studied by thermo-gravimetric (TGA) and differential thermal analysis (DTA). The mechanical strength and the work hardening co-efficient were determined from Vicker’s microhardness measurements for different loads. The NLO property of the crystal was confirmed by Kurtz second harmonic generation (SHG) test, and the output power generated by the crystal was compared with that of KDP

Keywords: crystals, L-histidine, nonlinear optics, second harmonic generation.

1. INTRODUCTION

Over the past several decades, great efforts have been devoted to the research and design of highly efficient nonlinear optical (NLO) materials due to their extensive applications such as laser technology, high-speed information processing, optical communications and optical data storage [1-3]. Recently, inorganic and organic materials are being replaced by semi-organics owing to their large non-linearity. Semi-organic crystals have been proposed as a new approach for materials with interesting nonlinear optical properties including high optical damage threshold, large nonlinearity also the excellent physical properties such as large thermal conductivity and good mechanical characteristics [4].

There is a considerable interest on the synthesis of new materials with a large second-order non-linearity with the favorable thermal and mechanical properties. Among the most widely used crystals, amino acids based materials are interesting candidates for NLO applications as they contain a proton donor carboxyl acid (COOH) group and proton
acceptor amino (NH$_2$) group in them [5]. Amino acids are widely utilized because they not only contain chiral carbon atoms directing the crystallization process in the noncentrosymmetric space group, but also possess zwitter ionic nature favouring crystal hardness [2]. Histidine (α-amino-β-imidazole propionic acid) is characterized among the amino acids by the presence of the imidazole ring. It is the only standard amino acid having an imidazole side chain with pKa near neutrality. In particular, histidine is an interesting amino acid because it serves as a proton donor, proton acceptor and a nucleophilic reagent. L-histidine salts can display high NLO properties due to the presence of imidazole group in addition to amino-carboxylate [6,7].

In the present investigation, LHN crystals were grown by slow evaporation solution technique (SEST) and grown crystals has been subjected to various characterization methods such as XRD, FTIR studies, UV-Visible measurements, TG/DTA, microhardness and second harmonic generation studies.

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2. EXPERIMENTAL

LHN crystals were synthesized by slow evaporation solution technique (SEST) [4] by dissolving stoichiometric amounts (1:1 ratio) of L-histidine and nitric acid in water. The mixture was stirred continuously for 3 hours to obtain a homogenous solution. The solution was filtered to remove the solid impurities in the mother solution using a filter paper. The solution was left for slow evaporation. The seeds were obtained and the seed crystal was kept in the
mother solution for 15 days. The obtained crystals are optically transparent and non-hygroscopic. Fig.1 shows the optically transparent LHN crystals grown by conventional slow evaporation technique.

![Fig. 1 LHN Crystals Grown by Slow Evaporation Solution Technique](image)

**3. RESULTS AND DISCUSSIONS**

**3.1 SINGLE CRYSTAL X-RAY DIFFRACTION**

In order to determine the lattice parameter values of the grown crystals, single crystal X-ray diffraction studies were carried out using a Bruker AXS Kappa APEX II single crystal X-ray diffractometer equipped with graphite-monochromated MoKα radiation (λ=0.71073Å) at room temperature with a crystal dimension of (0.35 × 0.25 × 0.2) mm³. The calculated lattice parameter values are tabulated in Table 1. It is observed from the X-ray diffraction data that the LHN crystal is orthorhombic in structure with space group of P2₁2₁2₁ [2].

**3.2 TABLE**

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₆H₁₀N₄O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁₂₁₂₁</td>
</tr>
<tr>
<td>a(A°)</td>
<td>5.2505(4)</td>
</tr>
<tr>
<td>b(A°)</td>
<td>7.1197(4)</td>
</tr>
<tr>
<td>c(A°)</td>
<td>25.0428(16)</td>
</tr>
<tr>
<td>α°</td>
<td>90°</td>
</tr>
<tr>
<td>β°</td>
<td>90°</td>
</tr>
<tr>
<td>γ°</td>
<td>90°</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>936.15(11)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (mg/m³)</td>
<td>1.548</td>
</tr>
</tbody>
</table>

**3.3 FT-IR SPECTRAL ANALYSIS**

The Fourier Transform infrared (FTIR) spectrum of L-histidinine Nitrate single crystal was recorded on a Perkin Elmer spectrophotometer in the range 450 – 4000 cm⁻¹ using KBr pellet method at room temperature. Various functional groups present in the grown crystal were identified. The characteristic vibrational frequencies of the functional groups and hydrogen bonds observed in FT-IR spectra are represented in Fig. 2. In the case of LHN the peak observed at 3229 cm⁻¹ is due to NH₃⁺ asymmetric stretching. The peak at 2920 cm⁻¹ is due to the C-H stretching
frequency. The peak at 1630 cm\(^{-1}\) is assigned to C=O stretching. The weak hydrogen bonds are characterized by strong, broad, and multicomponent absorption extending into the regions 3227–2373 cm\(^{-1}\), while the strong ones give broad and very strong absorption below 2000 cm\(^{-1}\). The peaks at 1133 and 1089 cm\(^{-1}\) are due to the C-N-C and C-O-C stretching vibrations respectively [1,8].

![FTIR spectrum of LHN crystal](image)

**Fig. 2 FTIR spectrum of LHN crystal**

### 3.4 UV-VIS SPECTROSCOPY ANALYSIS

The UV-Visible spectrum of the grown crystal was recorded using UV-2450 pc spectrophotometer in the range 200 - 800 nm is presented in Fig. 3. From the spectrum, it is inferred that, the absorption near 300 nm is due to the \(\pi-\pi^*\) transition of the compound. LHN crystals have lower cut off wavelength at 340 nm. And also it can be noted that there is no absorption in the entire visible region, which is the key requirement for the material to exhibit second harmonic generation (SHG) and makes it suitable for optoelectronic applications [5]. The absence of absorption band in the visible region is an intrinsic property of all the amino acids. The optical band gap of the LHN was calculated using the formula E\(=\)hc/\(\lambda\), and the band gap is found to be 3.64 eV for the prepared crystal.

![UV-VIS absorption spectrum of LHN](image)

**Fig. 3 UV-VIS absorption spectrum of LHN**

### 3.5 TG/DTA ANALYSIS
To estimate the thermal stability of LHN single crystal, TG/DTA experiments were carried out and the thermogram is illustrated in Fig. 4. The DTA curve of the crystal reveals that no endothermic/exothermic peak is observed below 234°C suggesting its structure is stable up to this temperature range. Also there is no phase transition in the respective region. This ensures the suitability of the material for possible application in lasers, where the crystal is required to withstand high temperatures [2]. The endothermic peak in the DTA curve at 228°C represents the melting point of the sample and the exothermic peak at 259°C indicated the decomposition of the compound.

3.6 MICROHARDNESS TEST

Hardness is an important mechanical property. The mechanical characterization of the LHN crystal was carried out by Vickers hardness test at room temperature. Crystal free from cracks with flat and smooth faces was chosen for the static indentation tests. The LHN crystal was placed on the platform of the micro-hardness tester and the loads of different magnitudes (5, 10, 20, 25 and 50g) were applied over a fixed interval of time (10s). Maximum applied load was restricted to 50g as micro cracks were developed at higher loads. The relation between hardness number \( H_v \) and load \( P \) for LHN is shown in Fig. 5. It is evident from the Fig. that the vickers hardness number increases with increase in load. The workhardening coefficient \( n \) was calculated by plotting \( \log P \) vs \( \log D \). According to onistch concept if \( n > 1.6 \) the material comes under soft material, if \( n < 1.6 \) the material comes under hard material [9]. In our present case \( n = 0.31 \), so LHN comes under hard material category.

Fig. 4 TG/DTA curves of LHN
3.7 SECOND HARMONIC GENERATION STUDIES

The SHG behavior of the LHN crystal was tested using the Kurtz and Perry method. Fine powders of L-histidine nitrate were exposed under 1064 nm laser beam to a pulsed Nd:YAG laser having a repetition rate of 10 Hz and pulse width of 8 ns to test the second harmonic generation (SHG) efficiency. Microcrystalline powder of KDP is taken for comparison. The intensity of the second harmonic output from the sample is compared with that of KDP. The SHG efficiency of the semi-organic compound LHN is about 2.5 times as large as that of the standard KDP crystal.

4. CONCLUSIONS

A semi-organic crystal, LHN has been grown by slow evaporation method from aqueous solution. The single crystal XRD confirmed that the crystal belongs to the orthorhombic system. Various functional groups present in the grown crystal were identified using the FTIR spectra. The TG/DT analysis conforms the crystal structure are stable up to 228°C and indicates its suitability for application in laser fields. The UV–Vis spectral analysis reveals that in the entire visible region, the crystal shows the complete transparent nature. Owing to its good transparency, LHN could be a promising material for NLO applications. Microhardness value was calculated in order to understand the mechanical stability of the grown crystals. The SHG intensity of LHN crystal is found to be 2.5 times greater than that of KDP.

REFERENCES

