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Investigations on the growth aspects and characterization of semiorganic nonlinear optical single crystals of L-histidine and its hydrochloride derivative

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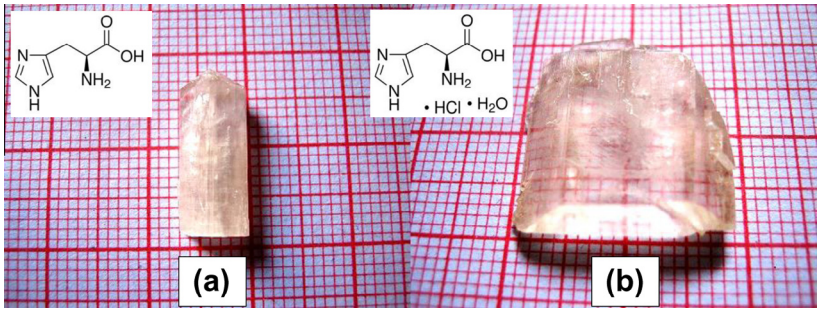
HIGHLIGHTS

- Two different crystals have grown in a single solution made up of L-histidine and HCl.
- Structural optical and thermal properties were studied and compared.
- L-Histidine possesses better properties than L-histidine hydrochloride monohydrate.

GRAPHICAL ABSTRACT



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ABSTRACT

Semiorganic single crystals of L-histidine and L-histidine hydrochloride monohydrate have been obtained in a single solution prepared from the mixture of L-histidine and hydrochloric acid in 1:2 M ratio. Growth aspects of the single crystals have been discussed along with characterization studies. Crystal system and lattice parameters have been identified by X-ray diffraction analyses. It has been observed that the grown crystals possess orthorhombic system but with different set of lattice parameters. Presence of various functional groups has been identified and formation of two different crystals has been confirmed by Fourier transform infrared spectral analyses and FT-Raman studies. Linear and nonlinear optical properties have been studied by UV–Vis spectral analyses and Kurtz–Perry powder technique respectively. The thermal stability of the grown crystals was determined by thermal analyses. From the characterization studies it is found that both the crystals are useful for second harmonic generation applications.

Introduction

Crystals are classified into three categories which are organic, inorganic and semiorganic single crystals by the raw materials used for the growth of single crystals. Crystal growth is one of the thrust areas of research for the past few decades because of

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various industrial applications of single crystals. Since the semiorganic single crystals possess the attractive properties of both organic and inorganic crystal, Scientists and Researchers focused their interest in growing as many semiorganic single crystals [1,2]. Amino acids are identified as potential candidates for the growth of single crystals with some inorganic acids which exhibits the most essential nonlinear optical (NLO) property for frequency conversion applications [3–5]. In recent decade the derivatives of amino acids like alanine, valine, lucene etc., are identified as potential candidates for the NLO device fabrication [6–9].

L-histidine is one such amino acid which gave a huge number of derivatives of semiorganic single crystals with NLO property. Recently many authors have grown and investigated the properties of L-histidine derivative crystals and identified as potential candidates for NLO applications [10–13]. Investigation on the possibility of formation of L-histidine derivative with various acids have been reported and also found that the L-histidine gave two different crystal structures with hydrochloric acid as well as hydrobromic acid when it is mixed in 1:2 M ratios, respectively [14]. The lattice parameters and crystal structure of L-histidine dihydrochloride were determined and reported quite long back [15]. Whereas the bulk growth have been reported recently [16]. But still, there is lack of literature on the properties of L-histidine dihydrochloride. In order to study the growth aspects and properties of the crystals grown in the solution of the above said molar ratio, in the present study, attempts have been made to grow bulk crystal of L-histidine dihydrochloride. But, in contradiction to the expectations two different crystals of L-histidine were obtained in the said solution. The grown crystals were identified as L-histidine and L-histidine hydrochloride monohydrate (LHHC). Characterization on structural, optical and thermal properties of L-histidine has not been reported so far. The growth aspects of the obtained two crystals and their properties were studied and discussed in this paper.

Experiment

Synthesis and growth aspects

L-histidine (99% pure) and hydrochloric acid (HCl) (Merk Product) were taken in 1:2 M ratios in excess of double distilled milli pore water as the starting material. The calculated amount of L-histidine was mixed in excess of double distilled milli pore water and the measured amount of HCl was added slowly with stirring to the mixture of water and L-histidine. After the solution become homogeneous (i.e., after continuous stirring for two hours), the solution was filtered to avoid the inclusion of impurities during the stirring and maintained at room temperature (300 K) by using a constant temperature bath controlled to an accuracy of ±0.01 K. The excess water was allowed to evaporate slowly so as to reach the saturation level of the solution. After the solution has attained the saturation level, well controlled evaporation was maintained to avoid the spurious nucleation. Though the evaporation was controlled carefully, single crystals were grown with two different external morphologies in the same solution. For the first twenty days only the needle like crystals had grown. After twenty days, the secondary nucleation was observed in the same solution and the crystals grown thereafter were in different morphology (bulk in shape) to the previous ones. Several attempts were made by adopting the same procedure and the growth aspects have been confirmed. Seed and grown crystals were carefully harvested from the solution and the photographs of as grown crystals are shown in the Fig. 1. The needle type crystals have been identified as L-histidine and the bulk one as L-histidine hydrochloride monohydrate (LHHC). The measured dimensions are $7 \times 6 \times 30\ mm^3$ and $18 \times 10 \times 20\ mm^3$ for the grown crystals of L-histidine and LHHC respectively.

The dimensions of the crystals have been measured by the digital Vernier caliper and the average rates of growth along the crystallographic directions (a, b, c) have been compared. In the case of L-histidine crystal, the growth rate along 'c' direction is found to be much greater than that of other two directions. On the other hand, the growth rate along 'a' and 'c' directions of LHHC crystal has been observed to be much greater than that along 'b' direction. Among these two directions, the growth rate along 'c' direction is slightly greater than that along 'a' direction. When comparing the two crystals, the growth rate of LHHC crystal along 'a' direction has been found to be increased and decreased along 'b' and 'c' directions as well. The reduction of growth rate along 'c' direction and increased growth rate along 'a' direction have made LHHC crystal as stubbier one. The growth rates along the three crystallographic directions have been tabulated in Table 1.

Characterization techniques

The powdered crystal samples and as grown good quality seed crystals were used to study the properties using various techniques. Single crystal X-ray diffraction analyses were made using suitable crystal samples to confirm the crystal system and lattice parameter values by ENRAF CAD – 4 diffractomer with Mo Kα (λ = 0.7107 Å) radiation. Powder X-ray diffraction patterns were recorded to study the structural variations of the grown crystal by using XPERT PRO diffraction system. The powder sample was mixed with KBr 1:20 weight ratio and made as a pellet to study the Fourier transform infrared spectral analysis of the grown crystals by using Nicolet iS50 Spectrometer in order to find the presence of various functional groups. FT-Raman spectral analyses have also been done using Bruker RFS model spectrometer and the functional groups were confirmed. Linear optical properties of the crystals were studied by UV–Vis Spectrophotometer and nonlinear optical properties were tested by Kurtz Perry powder technique [17]. Thermal analyses were carried out in the nitrogen atmosphere from room temperature to 600 °C using an instrument EXSTAR TG/DTA 6200 model supplied by SII Nanotechnology, Japan.

Results and discussion

Single crystal X-ray diffraction analyses

Single crystal X-ray diffraction analysis has been carried out to determine the lattice parameters. The data have been collected at 293 K using Mo Kα (λ = 0.71069 Å) radiation. The grown crystals possess orthorhombic structure and the lattice parameter values of the grown crystal are tabulated in Table 2. The lattice parameters of the different samples of each category have been measured and the formation of two different crystals has been confirmed. The lattice parameters of needle like crystals have very good agreement with the reported lattice parameters of L-histidine crystals [18]. On the other hand, the lattice parameters of bulk samples do not agree with L-histidine dihydrochloride [15] but agree with L-histidine hydrochloride monohydrate crystal as well [16,19,20]. Fortunately, there were no reports on the bulk growth and characterization of L-histidine single crystals. Hence, it is decided to study the structural, optical and thermal properties and discussed in succeeding sections.

Powder X-ray diffraction analyses

The grown crystals were also subjected to powder X-ray diffraction analyses. The data have been collected at 298 K between 10° and 80° of diffraction angles with the source wave length of 1.5460 Å. The