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Growth and characterization of l-histidine cadmium chloride monohydrate a semiorganic nonlinear optical crystals

J. Chandrasekaran [a,*], P. Ilayabarathi [b], P. Maadeswaran [c], P. Mohamed Kutty [b], S. Pari [d]

[a] Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India
[b] Research and Development Centre, Bharathiar University, Coimbatore – 641 046, Tamil Nadu, India
[c] Department of Physics, K S Rangasamy College of Technology, Tiruchengode – 637 215, Tamil Nadu, India
[d] Department of Physics, National College, Tiruchirapalli – 620 001, Tamil Nadu, India

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ABSTRACT

L-histidine cadmium chloride monohydrate (LHCCM), a semiorganic nonlinear optical material was grown from aqueous solution by slow solvent evaporation method at room temperature. The LHCCM crystals were characterized by X-ray powder diffraction analysis. The presence of functional groups was identified through fourier transform infrared spectroscopy. Thermogravimetric and differential thermal analysis confirms that the crystal is stable up to 277 °C. The dielectric constant was studied as a function of frequency for various temperatures. The mechanical properties of the grown crystals have been studied using Vickers microhardness tester. The second harmonic generation behavior of LHCCM crystal was tested by modified Kurtz–Perry powder technique.

1. Introduction

Nonlinear optical materials are used in optical computing, optical communication, harmonic generators, medical diagnostics, frequency mixing and optical switching. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible, ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [1–3]. In past decades, complexes of amino acids have been surveyed as attractive materials for NLO applications [4]. Amino acids are interesting materials for nonlinear optical applications, they contain a proton donating carboxyl group (COO^-) and a proton accepting amino (NH_3^+) in them except for glycine [5]. Complexes of amino acid with inorganic salts are promising materials for optical SHG, as they have a tendency to combine the advantage of the organic amino acid with that of the inorganic salt. Hence L-arginine, L-histidine, L-threonium L-alanine and L-valine have been subjugated for the formation of salts with different inorganic acids. As a result very good semiorganic nonlinear optical materials such as L-valine hydrochloride [5], L-arginine phosphate monohydrate (LAP) [6], L-histidine hydrochloride [7], L-alanine cadmium chloride [8] and L-valine cadmium chloride [9] are some of the good examples which proved very suitable materials for NLO applications.

In this work, the crystal growth, powder X-ray diffraction, fourier transform infrared spectroscopy, optical property, thermal, dielectric, microhardness and second harmonic generation studies of LHCCM are presented.

2. Experimental

2.1. Material synthesis

LHCCM was synthesized from an aqueous solution of L-histidine and cadmium chloride monohydrate in the equimolar ratio of 1:1as per the reaction:

$$C_6H_9O_2N_3 + CdCl_2.H_2O \rightarrow Cd(C_6H_9O_2N_3)Cl_2.H_2O \quad (1)$$

2.2. Growth of single crystals

Single crystal of L-histidine cadmium chloride monohydrate was grown from aqueous solution by slow solvent evaporation method at room temperature. In order to avoid co-precipitation of multiple phases the mixture of the reactants had to be stirred well. Few holes were made on the paper and kept undisturbed. Good transparent crystals were harvested after a growth period of 20–25 days. The purity of the solution was improved by successive recrystallization process. The photograph of as-grown crystal is shown in Fig. 1.

* Corresponding author. Tel.: +91 422 2692461; fax: +91 422 2692676.
E-mail address: jchandaravind@yahoo.com (J. Chandrasekaran).

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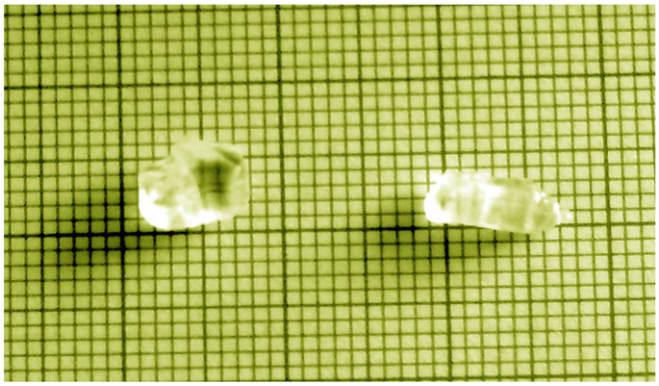

Fig. 1. As-grown LHCCM crystals.

3. Results and discussion

3.1. Powder X-ray diffraction

Powder X-ray diffraction data were collected for the grown single crystals. The pattern was recorded using a JEOL JDX services instrument with CuKα (λ = 1.5406 Å) radiation. The powdered sample was scanned in the range 10–80 °C at a scan rate of 2° /min (Fig. 2). The powder patterns were indexed and the lattice parameter values were calculated by fitting the XRD data with "least square method" using "XRDA" program. The powder XRD studies of LHCCM suggest that the crystal is orthorhombic in structure with space group $P2_12_12_1$. The calculated values of lattice parameters are a = 14.302 Å, b = 8.028 Å, c = 7.049 Å and the cell volume was found to be 809.341 $Å^3$.

3.2. FT IR spectrum

The FTIR spectra was carried out using Thermo Nicolect V-200 FT IR spectrometer by KBr pellet method in the range 4000–400 cm^{-1} as shown in Fig. 3. The wavenumber 3122 cm^{-1} shows the presence of peak due to NH_3^+ asymmetric stretching vibration. The asymmetric vibration of CH_3 leads to the presence of peak 2992 cm^{-1}. The peak around 1637 cm^{-1} is NH_3^+ asymmetric deformation. The peak at 1494 cm^{-1} is due to NH_3^+ symmetric deformation. The peak obtained at 1398 for COO^- symmetric stretching [5]. C–C–N stretching vibration the peak is obtained at 1082 cm^{-1} and CH_2 rocking curve obtained at 935 cm^{-1}. C–H out-of plane bending peak obtained at 667 cm^{-1}. The assignments confirm the presence of various functional groups present in the material, tabulated in Table 1.

3.3. Optical absorption studies

The UV–vis spectra for the grown LHCCM crystal were recorded using JASCO V-530 dual beam spectrophotometer at room temperature in the range 200–400 nm. The UV spectrum of the title compound is shown in Fig. 4. The lower cut off wavelength is observed at around 230 nm for LHCCM crystal. The absence of absorption in the range 240–400 nm suggests good optical transmission of the crystal.

3.4. Thermal analysis

The thermal stability of LHCCM was identified by the thermogravimetric (TG) and differential thermal analyses (DTA). The thermal analyses were carried out simultaneously employing NETZSCH STA 409 C/CD instruments. The TGA and DTA thermogram of LHCCM was investigated and is shown in Fig. 5. A crucible was used for heating the sample and analyses were carried out in an atmosphere of nitrogen at a heating rate of 20 K/min in the temperature range 20–600 °C. The LHCCM sample weighing 26.300 mg was taken for the analysis. The most important and interesting thing noted was the very good thermal stability up to 277 °C. In DTA an endothermic peak noticed at 277 °C corresponds to the melting point of LHCCM. Furthermore, it indicates that there is no phase transition before melting. A systematic weight loss was observed as the temperature further increases above the melting point. It is also noticed that total decomposition of the compound takes place at a temperature above 600 °C.

3.5. Dielectric study

The dielectric study on LHCCM single crystal was carried out using the instrument, AGILENT 4284 A (20 Hz-1 MHz) Precision LCR Meter

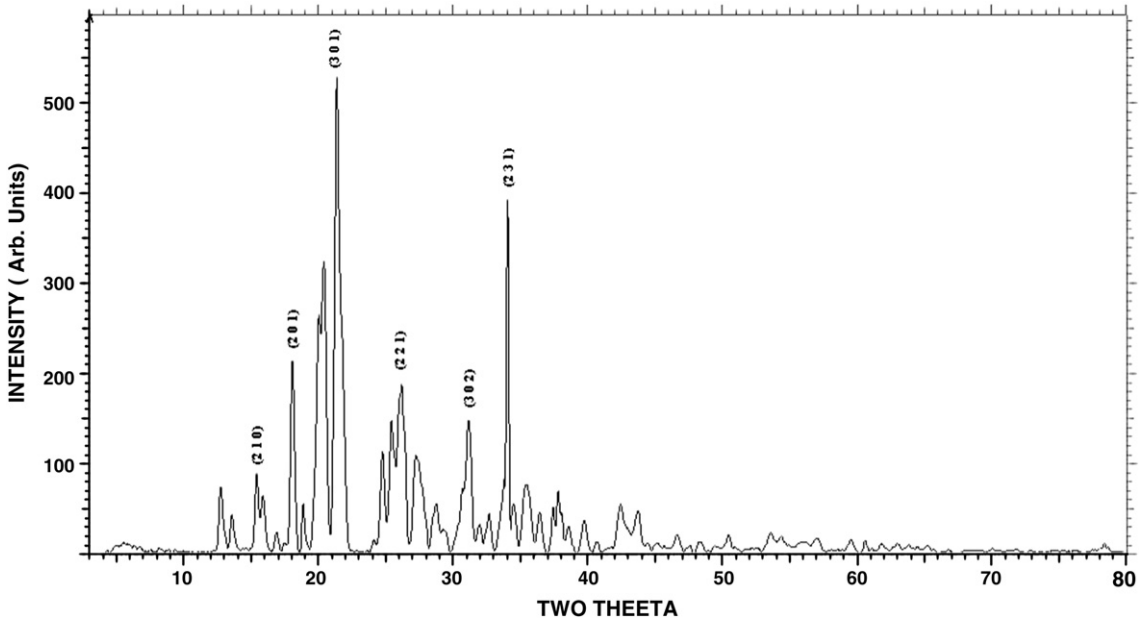

Fig. 2. Powder XRD patterns of LHCCM crystals.