

## Growth and characterization of L-cystine dihydrochloride single crystal

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### ABSTRACT

L-cystine dihydrochloride (LCDHCL) of dimension  $6 \times 4 \times 3 \text{ mm}^3$  was grown from aqua solution. The cell dimensions were obtained by single-crystal X-ray diffraction study. FT-IR, UV-vis-NIR and fluorescence spectral analyses were carried out for the grown crystals. Thermogravimetric and differential thermal analyses were carried out to determine the thermal properties of the grown crystal. Kurtz powder second harmonic generation (SHG) efficiency measurement revealed that the SHG efficiency is about ~6.72 times that of potassium dihydrogen orthophosphate.

**Keywords:** A1. X-ray diffraction; A2. Growth from solution; B2. Nonlinear optical materials

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### INTRODUCTION

In recent years, an intense worldwide effort has been focused on the design and development of highly efficient organic nonlinear optical (NLO) materials. Amino acids and their complexes are promising materials for NLO applications as they contain a proton donor carboxyl acid ( $-\text{COO}$ ) group and the proton acceptor amino ( $-\text{NH}_2$ ) group [1-4]. Nonlinear optical materials, which can generate highly efficient second harmonic blue-violet, are of great interest for various applications including high speed optical communication, wireless optical computing, optical parallel information processing, optical disk data storage, laser fusion reactions, laser remote sensing, color display and medical diagnostics [5-7]. The crystal structure of L-cystine dihydrochloride (LCDHCL) was solved by Gupta et al. [8] and reported that L-cystine dihydrochloride crystallizes in monoclinic system with C2 space group. However no reports are available on the growth and characterization of LCDHCL crystal. Hence optical quality LCDHCL crystals have been grown by the slow evaporation method at room temperature. The grown crystals were characterized by single crystal X-ray diffraction, FT-IR, UV-vis-NIR, fluorescence and Thermal analyses. SHG efficiency of the grown sample was measured by Kurtz and Perry powder [9] method using Nd:YAG laser.

### MATERIALS AND METHODS

#### 2.1. Synthesis and growth of LCDHCL single crystals

L-cystine and hydrochloric acid were taken in 1:2 ratio dissolved in distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which yielded a crystal of LCDHCL. To grow bulk crystal, the saturated solution of LCDHCL was taken in a glass beaker of 100 ml and one of the better quality crystals obtained from slow evaporation of the solvent at room temperature was used as a seed crystal. Slow evaporation at room temperature yielded a good quality single crystal of dimensions  $6 \times 4 \times 3 \text{ mm}^3$  from aqueous solution in a growth period of 25 days and is shown in Figure 1.

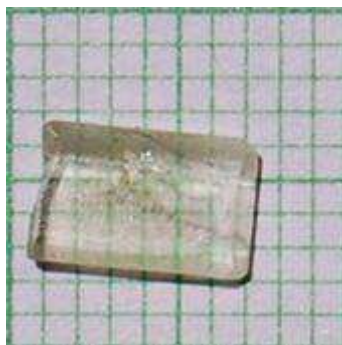


Figure 1. The as-grown LCDHCL crystal

## RESULTS AND DISCUSSION

### 3.1. Single crystal and powder XRD analyses

The powder X-ray diffraction (XRD) was recorded using powder X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Finely crushed powder of LCDHCL crystal was scanned in the  $2\theta$  values ranging from  $10$  to  $80^\circ$  and the XRD peaks were indexed and are shown in Figure 2. Further single crystal XRD studies show that the crystal belongs to monoclinic system with cell parameters of  $a = 18.582(5) \text{ \AA}$  ( $18.582(7)$ ),  $b = 5.247(1) \text{ \AA}$  ( $5.242(2)$ ),  $c = 7.227(3) \text{ \AA}$  ( $7.228(3)$ ).  $\beta = 103.74^\circ$  ( $103.74$ ) and space group C2. The derived unit cell parameters are in good agreement with the corresponding values reported by Gupta *et al.* [8] which are given in the parenthesis.

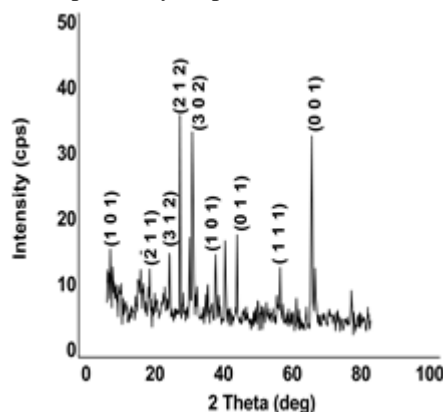


Figure 2. Powder XRD pattern of LCDHCL crystal

### 3.2. FT-IR analysis

The FT-IR spectrum of the grown LCDHCL crystal was recorded in the KBr phase in the frequency range  $400$ - $4000 \text{ cm}^{-1}$  using Perkin-Elmer spectrometer. The observed vibrational frequency and the tentative assignment of LCDHCL are given in Table 1 along with a comparison of the corresponding reported values of L-cystine [10]. The observation confirms the protonation of cystine by hydrochloric acid. From the FTIR studies the presences of the functional groups of the grown LCDHCL crystal was confirmed.

Table 1. Comparison of vibrational frequencies ( $\text{cm}^{-1}$ ) of LCDHCL

Assignments	L-cystine[10]	Present work
$\nu_{\text{as}}(\text{NH})$	3429	3393
$\nu(\text{NH}_3^+)$	2096	2084
$\delta(\text{NH}_3^+)$	1628	1646
$\nu(\text{COO}^-)$	1480	1498
$\delta(\text{CH}_2-\text{CO})$	1408	1424
$\nu(\text{C}-\text{C})$	1342	1350
$\nu(\text{C}-\text{C})$	1194	1189
$\nu(\text{C}-\text{C})$	1126	1132
$\nu(\text{C}-\text{N})$	1043	1048
$\rho(\text{NH}_3^+)$	845	816
$\rho(\text{CH}_2)$	775	746
$\nu(\text{C}-\text{S})$	675	658
$\rho(\text{COO}^-)$	611	658
$\delta(\text{C}-\text{C})$	540	583
$\nu(\text{S}-\text{S})$	457	509

( $\nu$ ) Symmetric stretching; ( $\nu_{\text{as}}$ ) asymmetric stretching; ( $\delta$ ) bending; ( $\rho$ ) rocking.

### 3.3. UV-vis-NIR spectral studies

In order to estimate the optical transparency in the 200-1100 nm region of the electromagnetic spectrum, the optical transmittance study was carried out on the LCDHCL crystal of thickness ~2 mm employing Varian Cary 5E UV-vis-NIR spectrophotometer. There is no appreciable absorption in the entire visible range, as in the case of all the amino acids [11]. The short wavelength cut-off occurs at 270 nm which is one of the most desirable properties of the crystals for the device fabrication [12]. The transmittance between 300 nm and 1100 nm is about 85 % which is an essential parameter required for frequency doubling process [13].

### 3.4. Fluorescence studies

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability [14]. Fluorescence finds wide application in the branches of biochemical, medical and chemical research fields for analyzing organic compounds. The excitation and emission spectra for LCDHCL were recorded using Varian Carry Eclipse, Fluorescence Spectrometer. The excitation spectrum was recorded in the range 200-300 nm (Figure 3). The sample was excited at 242 nm. The emission spectrum (Figure 4) was measured in the range 250-600 nm and the emission peak was observed about 400 nm. Thus the results indicate that LCDHCL crystal has the blue fluorescence emission.

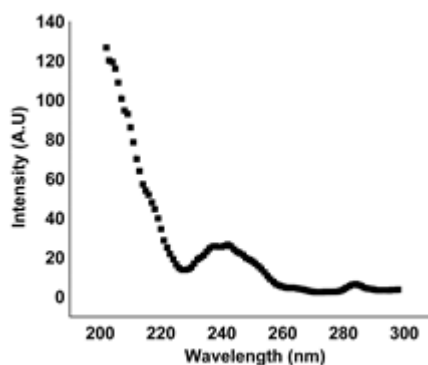


Figure 3. Excitation spectrum of LCDHCL

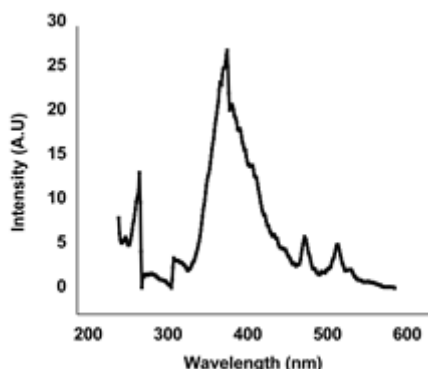


Figure 4. Emission spectrum of LCDHCL

Vickers microhardness test was carried out on (101) face of the LCDHCL crystal using microhardness tester fitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for various loads from 25 to 200 g. The diagonals of the impressions were measured using Shimadzu (Japan); Model HMV-2 hardness instrument. The indentation time was kept as 25 s for all the loads. Vickers microhardness number ( $H_v$ ) was evaluated from the relation  $H_v = 1.8544(P/d^2)$  Kg/mm<sup>2</sup>, where P is the applied load in kg and d is the diagonal length of the impression in mm. From the Vicker's microhardness studies, it is observed that the hardness value increases upto a load of 100 g. For load above 100 g crack started developing around the indentation mark which may be due to the release of internal stresses [15]. Work hardening coefficient n, a measure of the strength of the crystal is computed from the log P-log d plot and it is found to be 2.3. Onitsch [16] inferred that the value of n lies between 1 and 1.6 for hard materials and for soft materials it is above 1.6. Thus the LCDHCL crystal comes under the soft materials category. A plot of P/d against d drawn following proportional specimen resistance (PSR) model is a straight line, and the slope of which gives the load independent microhardness [17]. The load independent microhardness value is calculated from the slope (P/d<sup>2</sup>), which when multiplied by Vicker's conversion factor 1.8544 gives 64 kg/mm<sup>2</sup> for LCDHCL crystal.

### 3.6. Thermal analysis

Thermogravimetric and differential thermal analyses were carried out using a PYRIS thermal analyzer. A ceramic crucible was employed for heating the sample and the analyses were carried out in an atmosphere of nitrogen at a heating rate of 10 °C /min in the temperature range 40-1200 °C. The initial mass of the material subjected to the analyses was 5.105 mg. The TGA trace shows that the material exhibit small weight loss of about 2.03 % in the temperature range 89.62 °C to 102 °C due to loss of water. As the weight loss is sharp, it may be attributed to loss of lattice water. In the temperature range 150 °C - 900 °C, the compound remains stable. At 944.96 °C the loss of weight is due to the S-S bond cleavage, loss of CO<sub>2</sub> from carboxylic acid group and loss of ammonia from the amino acid group. The DTA curve recorded for the LCDHCL crystal implies that the material undergoes irreversible endothermic transition at 141.08 °C, which assigned to melting point of LCDHCL.

### 3.7. Powder SHG measurement

The study of NLO conversion efficiency was carried out using the modified experimental setup of Kurtz and Perry [9]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 2.8 mJ, and pulse width of 8 ns with a repetition rate of 10 Hz was used. The grown single crystal of LCDHCL was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532 nm component. The generation of the second harmonics was confirmed by the emission of green light. A sample of potassium dihydrogen orthophosphate (KDP), also powdered to the same particle size of the experimental sample, was used as a reference material in the present measurement. Second harmonic generation efficiency of the powdered LCDHCL is ~6.7 times that of potassium dihydrogen orthophosphate.

## CONCLUSION

The potential organic NLO crystal of LCDHCL was grown by slow evaporation method. Single crystal X-ray diffraction study revealed that the LCDHCL crystal grown at room temperature belongs to monoclinic system. FT-IR spectral analysis confirms the presence of functional groups of the LCDHCL. The UV-vis-NIR spectrum of LCDHCL showed that the crystal is transparent in the range 300-1200 nm. Fluorescence spectrum showed that LCDHCL has blue fluorescence emission. Its SHG efficiency tested by high intensity Nd: YAG laser as a source is about ~6.7 times greater than that of KDP. Owing to all these properties LCDHCL could be a promising organic material for NLO applications.

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