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Research Article

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Investigations on growth and characterization of L-cystine hydrochloride

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ABSTRACT

L-cystinehydrochloride(LCH) an intriguing organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. The single crystal XRD was used to identify the crystal system. FTIR spectral was performed for the confirmation of functional groups and chemical composition. The optical behavior such as UV–Vis absorption spectra and second harmonic generation (SHG) conversion efficiency are investigated to explore the linear and nonlinear characteristics of the above material. The dielectric constant and dielectric loss are measured for the grown crystal for different temperatures.

Keywords*:* Slow evaporation; Non-linear optical material; X-ray analysis; FTIR; Dielectric; Photoconductivity.

INTRODUCTION

Extensive studies have been made on the synthesis and growth of non-linear optical materials over a past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching [1]. These applications depends upon the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant, thermal. Photochemical and chemical stability. Organic crystals have large non-linear susceptibilities compared to inorganic crystals. However these crystals have certain limitations such as increased optical absorption, narrow transparency window and poor mechanical and thermal stability. Inorganic crystals have excellent mechanical and thermal properties but possess relatively low optical nonlinearities because of the lack of π- electron delocalization. Combining the high optical nonlinearity and chemical flexibility of organics with thermal stability and excellent transmittance of inorganics, semi-organic materials have been proposed and are attracting a great deal of attention in the field of nonlinear optics [2]. Complexes of amino acids with inorganic salts were promising materials for optical second harmonic generation SHG, as they aptly fit in this context with such properties. Amino acids were bifunctional organic molecules that contain a proton donor carboxyl acid (-COO)group and the proton acceptor amino (-NH_2) group in them. In solid state amino acid contains protonated amino group and deprotonated carboxylic group. This dipolar exhibits peculiar physical and chemical properties. So the efforts have been made on the amino acid mixed crystals in order to make them suitable for device applications. Some complexes of amino acid with organic and inorganic acids exhibits NLO properties [3-6]. L-cystine was one of the sulfur containing protenogenic amino acids formed by oxidation of two cysteine residues which covalently link to make a disulfide bond. In this series, we have reported the growth of bulk crystal of L-cystine hydrochloride (LCH) ($C_6H_{12}N_2O_4S_2$.HCl) by slow evaporation method and its characterization by single crystal XRD, Fourier transform infrared spectroscopy, UV-Vis, dielectric and photoconductivity.

EXPERIMENTAL SECTION

The LCH was synthesized by dissolving 2M of L-cysteine in 1M of hydrochloric acid in double distilled water at 60°C. The solution was stirred continuously for 6 hours to attain homogeneity of mixture and then filtered. The filtered solution was kept for slow evaporation at room temperature under undisturbed condition. Evaporation of solvent yields the good quality crystals. Transparent colorless LCH crystals were harvested within the period of 30 to 35 days with the size of 36 mm × 15 mm × 10 mm and the photograph of the as-grown crystal was shown in Figure1. The above material was synthesized according to the following reaction scheme:

$$2C_3H_7NO_2S + HCl \longrightarrow C_6H_{12}N_2O_4S_2.HCl$$

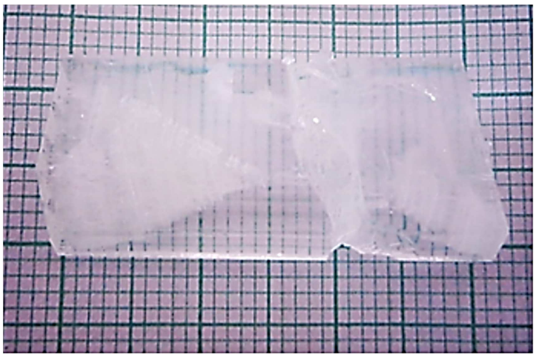

Figure 1. Photograph of LCH crystal

RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction studies have been carried out to confirm the crystallinity and to calculate the lattice parameters of the grown sample. The grown crystal was subjected to single crystal X-ray diffraction studies using ENRAF-NONIUS CAD4 diffractometer with Mo-kα radiation source of wavelength 0.717 Å. From the X-ray diffraction data, it was observed that LCH belonged to monoclinic system with C2 space group. The lattice parameter values of LCH were a=18.73Å, b=5.67Å, c=7.36Å, α=γ=90°, β =102.2°, V= 781.62Å^{3}respectively and these values were in line with the literature value [7]. This confirms that the LCH single crystal retain its own crystal system.

3.2 FTIR studies

The Fourier Transform Infrared spectrum of LCH was recorded at room temperature in the spectral range 600-400 cm^{-1} bythe BRUKER IFS 66V infrared spectrophotometer. The vibration spectrum of a molecule generally consists of two major regions (i) Group frequency region (ii) Finger print region. Group frequencies are vibrations that are associated with certain structural units such as -CH3,-NH2, -C≡N etc., and appear fairly at a constant region in the spectrum. The molecules having similar groups show their vibration in the form of bands is called finger print region [8]. The characteristic absorption peaks are shown in Figure 2. The peak at 1725 cm^{-1}was characteristic of amino acid hydrochlorides [9]. The N-H stretching vibration was assigned at 3403 cm^{-1}.The band located at 2949 cm^{-1}was attributed to CH stretching [10]. The sharp and strong band at 1725 cm^{-1} indicates the C=O stretching of COOH group [11]. The C-H bending mode appears at 1362 cm^{-1}. The C-C stretching vibrations appears between 1113 cm^{-1} and 1219cm^{-1} [10]. The peaks at 812 cm^{-1} was assigned to C-N stretching vibrations. The C-S stretching vibration appears in and around 654 cm^{-1} [7]. The S-S stretching vibrations of LCH was observed at 615 cm^{-1} [12]. This S-S vibration shows the presence of disulfide bond in LCH crystal. The sulfur containing amino acid cystine. The protonation of L-cystine with hydrochloride was also confirmed by the above discussion. Presence of the functional groups of L-cystine and vibrational frequencies were compared in Table 1 with the corresponding frequencies of the parent reactant of L-cystine.

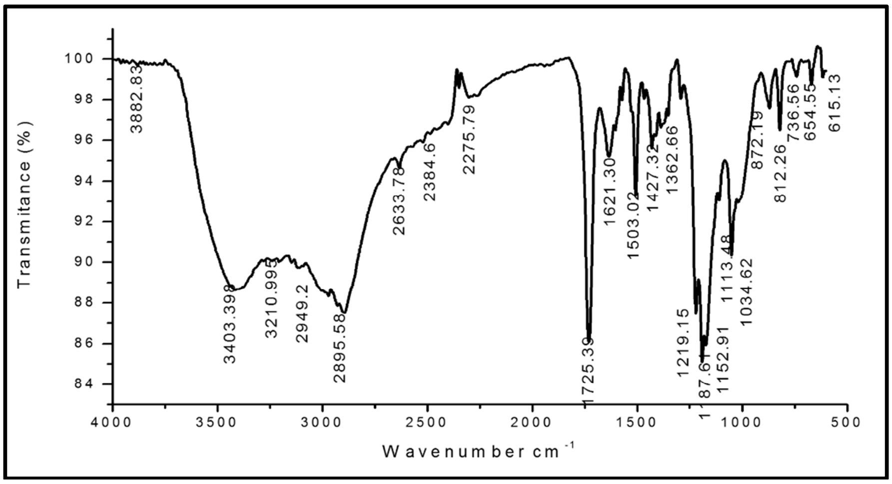

Figure 2. FTIR spectrum of LCH crystal

Table 1. FTIR spectrum of LCH crystal

Wavenumber cm^{-1}		Assignments
L-cystine	LCH	
3429	3403	NH asymmetric stretching
3030	2949	CH broad band stretching
2096	2110	NH_3^+ stretching
1585	1503	NH_3^+deformation
1489	1499	COO^- stretching
1408	1427	CH_2-CO deformation
1342	1362	C-H stretching
1298	1219	CH_2 wagging
1194	1187	C-C stretching
1126	1113	C-C stretching
1090	1034	C-N stretching
1043	1034	COO^- rocking
650	654	C-S stretching
611	615	S-S stretching

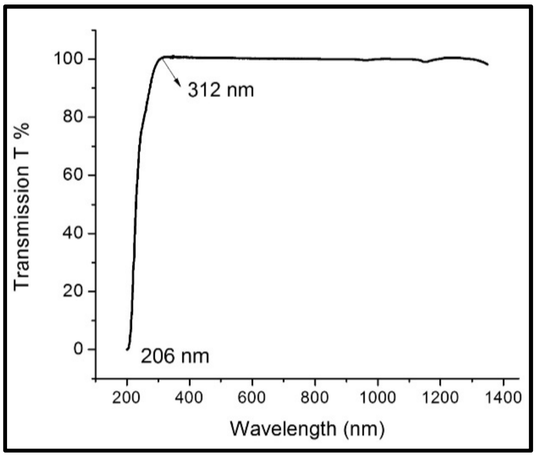

Figure 3. Transmission spectrum of LCH crystal

3.3 UV-Vis- NIR studies

The UV-Visible transmittance spectrum was recorded using Varian Cary 5E model UV-Vis-NIR spectrometers in the range 200- 1400 nm covering the entire UV and Visible region. Fig. 3 shows the recorded optical transmittance spectrum of LCH single crystal. The lower cutoff wavelength are observed at 207 nm which was assigned to electronic excitation in the COO^- group of LCH. A complete transparency in visible region was interesting which was a required for non-linear optical application [13]. From the relation $E_g = 1.243 \times 10^3 / \lambda_{max}$the forbidden energy gap was estimated [14]and was found to be 6.03 eV, which was the typical value of dielectric material [15].The high photo response nature of the material was revealed from the above study.

3.4 SHG efficiency measurement

Kurtz and Perry [16] second harmonic generation (SHG) test was performed to find the NLO property of LCH crystal. The powdered crystalline sample was illuminated using Q-switched, mode locked Nd: YAG laser of wavelength $\lambda = 1064$ nm of pulse width 10 ns. The green radiation of 532 nm was collected by the photomultiplier tube after being monochromated into voltage output at the CRO. The result obtained shows that the powder SHG relative efficiency of LCH was about 0.67 times than that of potassium dihydrogen orthophosphate. As the second order nonlinear efficiency will vary with the particle size of the powder sample, higher efficiencies were expected to be achieved by optimizing the phase matching [17].

3.4 Dielectric Studies

The dielectric study on LCH single crystal was carried out using HIOKI 3532 LCR HITESTER. A sample of dimension 5.41 ×3.99 × 2.13 mm^3 having silver coated on the opposite faces was placed between the copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 50Hz to 5 MHz at various temperatures from 40°C to 100°C. Figure 4 shows the plot of dielectric constant ε_r versus applied frequency. The dielectric constant has high values in the lower frequency region and then it decreases with applied frequency. The dielectric constant has a high value at 50 Hz and decreases at 5 MHz. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its value at higher frequencies may be due to the loss of significance of these polarizations gradually. The dielectric loss was also studied as a function of frequency at room temperature and was shown in Figure 5. These curves suggest that the dielectric loss was strongly dependent on the frequency of the applied field, similar to that of dielectric constant. This behavior was common in the case of ionic system [18-19].

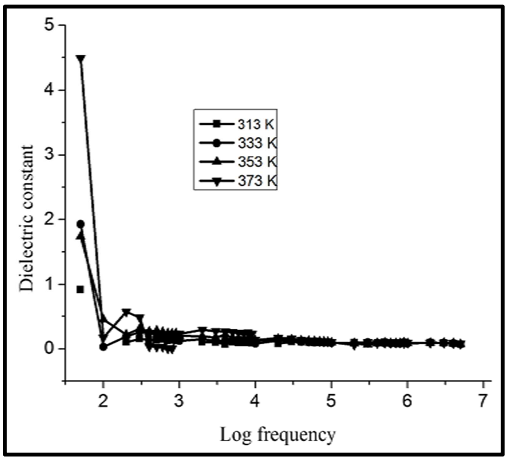

Figure 4. Variation of dielectric constant of LCH

3.5 Photoconductivity studies

Polished sample of LCH was attached to microscope slide and two electrodes of thin copper wire were fixed with silver paint. The sample was connected in series to a DC power supply and a Keithley 480 picoammeter and the corresponding dark current (I_d) was recorded. The sample was then exposed to the radiation from a 100 Whalogen lamp containing iodine vapor and tungsten filament the photocurrent (I_P) was recorded. The field dependence conductivity of LCH crystal was shown in Figure 6. It was observed that both photocurrent and dark current increases linearly with the applied electric field but photo current was observed to be lesser than that of dark current, which was termed as negative photoconductivity. The negative photoconductivity in the present case may be due to the reduction in the number of charge carriers or their lifetime, in the presence of radiation. The Stockmann model also explains the phenomenon of negative photoconductivity successfully with specific reference to semiconducting crystals [20].For a negative photoconductor, forbidden gap holds two energy levels in which one was placed between the Fermi level and the conduction band while the other was located close to the valence band. The second state has higher capture cross-section for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation.

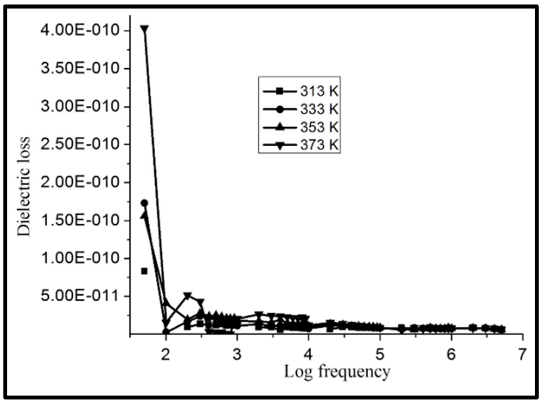

Figure 5. Variation of dielectric loss of LCH

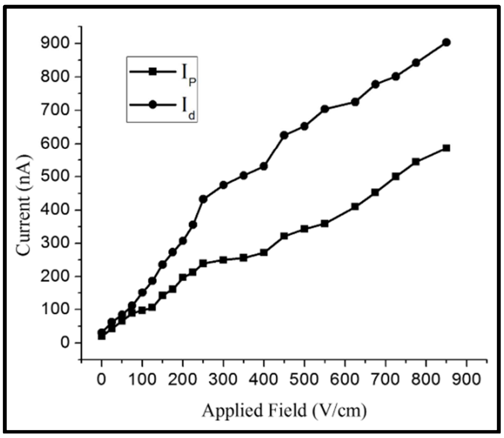

Figure 6. Field dependent conductivity of LCH

CONCLUSION

Single crystals of LCH were grown by slow evaporation method. Single crystal XRD studies confirm that the grown crystal belongs to monoclinic system. FTIR spectrum confirms the presence of all the functional groups such as NH, COO^-, C-C, C-H, C-S and S-S were identified. The UV-Vis-NIR spectrum shows that it has a good optical transmittance with lower cutoff wavelength 207nm and the band gap energy was found to be 6.03eV. The SHG test with 1064 nm wavelength laser showed intense green light and the LCH was 0.67 times than that of KDP. The variation of dielectric constant and dielectric loss were studied with varying frequency at different temperatures. Photoconductivity study revealed the negative photoconductivity nature of the grown crystal. Thus, the above studies indicates the suitability of this crystal for photonics device fabrications.

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