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PHYSICS

SYNTHESIS, GROWTH AND SPECTROSCOPIC STUDIES OF L-ALANINE HYDROGEN CHLORIDE(LAHC) CRYSTALS

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Abstract
L-alanine Hydrogen Chloride (LAHC) salt was synthesized by taking L-alanine and hydrochloric acid in 1:1 molar ratio and the solubility of the synthesized salt in deionized water was determined at different temperatures. Single crystals of L-alanine Hydrogen Chloride (LAHC) were grown by solution method with slow evaporation technique. The grown crystals were characterized by single crystal X-ray diffraction (XRD) analysis, FTIR studies and UV-visible transmittance studies and the NLO activity of the grown crystal has been checked by Second Harmonic Generation (SHG) test.

Keywords: L-alanine hydrogen chloride; solubility; solution growth; FTIR; XRD; SHG

Introduction
Nonlinear optical (NLO) materials have gained considerable attention due to their practical applications in the field of optoelectronics[1,2]. The development of NLO materials led to compounds potentially suitable for application in frequency conversion, optical telecommunication, image processing, optical computing, and data storage devices[3-6]. Amino acid family-type crystals have over the years been subjected to extensive investigation by the researchers for their non-linear optical properties[7,8]. Among the amino acids, L-alanine (CH_3CHNH_2COOH) is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP[9,10] . If L-alanine is mixed with different organic, inorganic acids and salts to form novel materials, it is expected to get improved NLO properties. Keeping this in mind, L-alanine and HCl have been mixed to form a novel NLO material viz. L-alanine Hydrogen Chloride(LAHC). K.Yameda et al reported the details of crystal structure of LAHC [11] and it is observed from the literature survey that there are no detailed studies on the growth and the various properties of LAHC crystals reported. Hence the aim of this paper is to report the growth, spectroscopic studies and NLO activity of LAHC crystals for the first time.

Experimental Methods
Synthesis and solubility
The title compound LAHC was synthesized by taking L-alanine (99% purity) and analar grade Hydrochloric acid (HCl) in the molar ratio 1:1 in deionized water. The reaction of synthesis is adhered by the following chemical equation.

$$CH_3CHNH_2COOH + HCl \longrightarrow (C_3H_8NO_2)^+ Cl^-$$

The synthesized salt was used to measure the solubility of LAHC in water. A 100 ml glass beaker with 10 ml of deionized water was placed inside a constant temperature bath, maintained at 30°C. LAHC salt was added in small amounts at successive stages. The addition of the salt and the stirring were continued till a small precipitate was formed, which confirmed the super saturated condition. The 5 ml of the saturated solution was pipetted out and poured into a petri dish of known weight. The solvent was completely evaporated by warming the solution at 50°C. The amount of the salt present in 5 ml of the solution was measured by subtracting the empty petri dish's weight. From this, the amount of the salt present in 100 ml of the solution was found out[12]. In the same manner, the amount of the salt dissolved in 100 ml at 35, 40, 45 and 50°C was determined. Fig. 1 shows the solubility curve of LAHC salt. From the graph, it is observed that the solubility of LAHC sample in water increases as the temperature increases and hence the title compound has positive temperature coefficient.

Growth of LAHC single crystals
The purity of the synthesized salt of LAHC has been improved by re-crystallization. Using the solubility data, the saturated solution of LAHC in de-ionized water was prepared and it was stirred using a magnetic stirrer for about one hour to get homogenious solution. The saturated solution was filtered using 4 micro Whatmann filter paper. Then the filtered solution was taken in a beaker and

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covered by a perforated cover for controlled evaporation. A typical single crystal with size 14 x 13 x 7 mm^3 was obtained within a period of 25-30 days. The grown crystal is shown in the figure 2.

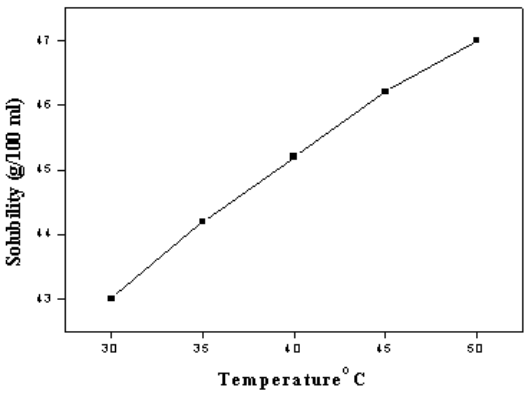

Fig.1: Solubility curve for LAHC crystal

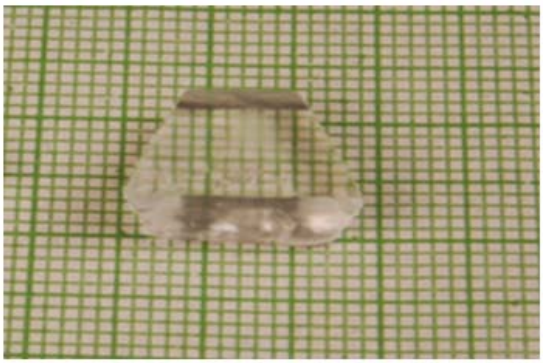

Fig.2: Photograph of as-grown crystal of LAHC

Characterization

Single crystal XRD studies

The grown crystals were subjected to single crystal XRD to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 single X-ray diffractometer. From single crystal X-ray diffraction data, it is observed that the LAHC crystal is orthorhombic in structure with space group $P2_12_12_1$. The lattice parameters are observed to be a=6.193(2) Å, b=9.931(1) Å, c=11.757(3) Å, α=β=γ=90° and V =723.08(2) $Å^3$. The obtained lattice parameters for LAHC crystal in this work are found to be in good agreement with the data reported in the literature[11].

FTIR analysis

The Fourier Transform Infrared (FTIR) spectrum of LAHC crystal was recorded in the region 400 - 4000 cm^{-1} using FTIR SHIMADZU 8400S. The sample was prepared by pressing LAHC with KBr into pellet form. The observed spectrum is shown in the figure 3. The absorption peaks at 3085.89, 1620.09, 1513.37 cm^{-1} are the indication of the presence of NH_3^+ group in the crystal. The peaks at 2812, 2731 and 2560 cm^{-1} are attributed to the C-H stretching mode vibrations. The peaks at 1412, 1306, 1234 and 1113 cm^{-1} are due to COO^- symmetric stretching modes. The absorption peak at 2111.91 cm^{-1} is due to combination band of NH_3^+ degenerate mode and NH_3^+ torsion. The peak at 1591.16 cm^{-1} is due to the asymmetric deformation of NH_3^+. The O-C-O bending mode at 771.47 cm^{-1} has been identified and assigned. The COO^- scissoring mode appears at 648 cm^{-1}. The peak at 540 cm^{-1} represents the COO^- rocking. The assignments for the absorption peaks of the FTIR spectrum have been given in accordance with the data reported in the literature[13].

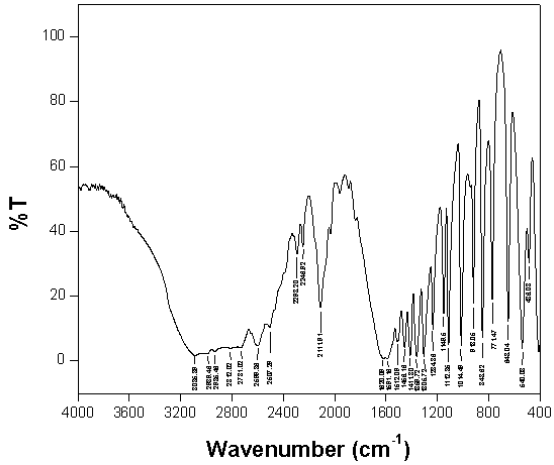

Fig. 3: FTIR spectrum of LAHC crystal

Optical transmission spectral analysis

The UV-Visible transmittance spectrum (Fig.4) of LAHC crystal was recorded in the wavelength range 190-1100 nm, using Lambda 35 spectrometer. Optically polished single crystal of thickness 2 mm was used for this study. This spectral study may be assisted in understanding electronic structure of the optical band gap of the crystal. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. It is noticed from the results that LAHC crystal has transmittance in the entire visible-NIR region of the spectra and the high transmission in the entire visible region and short cut off wavelength facilitates the grown crystals of this work to be potential nonlinear optical materials for second harmonic and third harmonic of Nd:YAG laser. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. The cut-off wavelength (λ) is around 240

nm. Using the formula $E_g = hc / \lambda$, the band gap energy was found to be 5.185 eV.

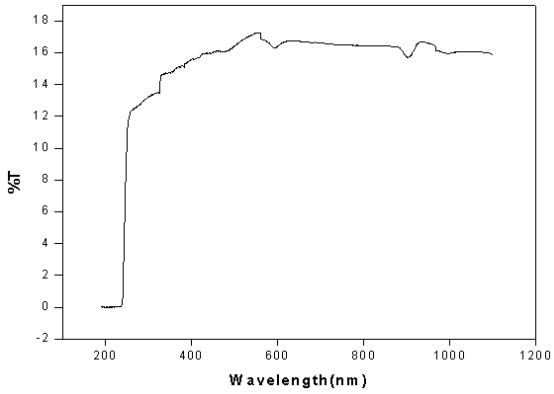

Fig.4: UV-Visible transmittance spectrum for LAHC crystal

Second Harmonic Generation (SHG) test

The Nonlinear Optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique[14] . The LAHC crystal was powdered with uniform particle size using a ball mill and it was packed densely between two transparent glass slides. An Nd:YAG laser was used as a light source. This laser device can be operated in two different-modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multi-shot mode of 8 ns laser pulse with a spot radius of 1mm was used. The experimental setup for measuring SHG efficiency is shown in the figure 5. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample cell(S). The power of the incident beam was measured using a power meter. The filter F1 removes the 1064 nm light and the filter F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength 532 nm. The green light was detected by a photomultiplier tube (PMT) and displayed on a Cathode Ray Oscilloscope(CRO). KDP crystal was powdered into identical size as LAHC crystal and it was used as reference material in the SHG measurement. In the NLO process that taking place in the sample, it converts the 1064 nm radiation into green light (λ=532 nm) when Nd:YAG laser light is passed into the sample and this confirms the SHG . It was found that the efficiency of SHG is 0.76 times that of the standard KDP.

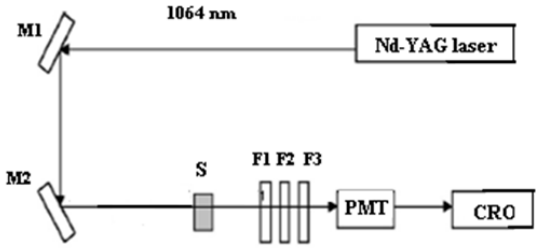

Fig.5: Experimental setup for SHG measurement

Conclusion

LAHC salt was synthesized and solubility was determined at various temperatures. Bulk single crystals of LAHC salt was grown by solution method. It is observed that the grown crystal is transparent, colourless and has good morphological edges. Single crystal X-ray analysis reveals that the crystal belongs to orthorhombic system with space group $P2_12_12_1$. The functional groups present in LAHC crystal are confirmed by the FTIR spectral analysis. The optical absorption study reveals high transparency of the crystal with a UV cut off wavelength of 240 nm. The NLO efficiency of the crystal is found to be 0.76 times that of KDP.

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