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Spectroscopic studies of pure and doped L -alanine hydrogen chloride monohydrate single crystals

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ABSTRACT

Good quality single crystals of pure, zinc and cadmium doped L- Alanine Hydrogen Chloride monohydrate (LAHC) have been grown from aqueous solution by slow evaporation method. The grown crystals were subjected to powder X–ray diffraction studies to study their structural characteristics. FTIR spectral analysis was performed to identify the presence of various functional groups in the crystals. The UV–Visible–NIR spectral analysis was carried out to study the optical properties of the grown crystals. Inductively Coupled Plasma (ICP) studies have been carried out to confirm the presence of dopants in the grown crystal.

Keywords: L- Alanine Hydrogen Chloride monohydrate single crystal, Zinc and Cadmium doped, FTIR, UV-VIS-NIR, ICP OES

INTRODUCTION

Non - linear optical materials are being widely researched currently due to their considerable use in the field of optical telecommunication, space image processing and optical computing. Among the various organic crystals used as NLO materials, amino acids are of much importance because of properties such as (a) molecular chirality, which secures acentric crystallographic structure, (b) absence of strongly conjugated bonds, which gives wide transparency in the UV-Vis spectral regions and (c) Zwitterionic nature of molecules, which results in good crystal hardness. [1, 2]

Among the amino acid family of NLO crystals, L- alanine (molecular formula: CH3CHNH2COOH) is the simplest molecule. L- alanine was first crystallized by Bernal [3] and later by Destro *et al* [4]. In both cases, very small crystals were grown, unsuitable for optical characterization. It was found that, if L –alanine is mixed with different organic, inorganic acids and salts to form novel materials, the so formed crystals improved NLO properties [5,6]. Growth, structural, spectral, mechanical and dielectric characterization of RbCl doped LAHC monohydrate single crystals have been reported [6]. The crystals were grown by solution method with slow evaporation technique/X ray diffraction, spectral and dielectric studies on the grown crystal was carried out and reported. Growth and characterization of semi organic L-alanine acetate crystals were reported by Mohan Kumar *et al* [7]. It is reported that L-alanine acetate crystals exhibit better thermal and mechanical stability with improved optical properties.

In the present work, L-alanine hydrogen chloride monohydrate crystals have been grown with the dopants zinc and cadmium. Their structural, spectral and optical properties of doped and pure LAHC monohydrate crystals have been studied and reported.

MATERIALS AND METHODS

Crystal growth

Analytical grade (AR grade) of L-alanine and concentrated hydrochloric acid were taken in the ratio of 1: 0.05 normality. doubly deionised water was used as the solvent. Single crystals of pure LAHC monohydrate were grown from supersaturated solution at room temperature by slow evaporation method. Good quality crystals were obtained by successive recrystallization.

$$C_3H_7NO_2+HCl+H_2O \rightarrow C_3H_8NO_2^{+}Cl^{-}H_2O$$

The dopants, Zinc chloride and Cadmium chloride were added separately with the pure LAHC solution in definite molecular ratio LAH:X (X is dopant) being 1:0.01 in molar weight. Each solution was stirred for three hours using magnetic stirrer and filtered using Whatman filter paper. The filtered solution was transferred to borosil glass beaker. It was porously sealed and placed in a dust free atmosphere for slow evaporation. The pH of the solution was noted as 4. The grown crystals were harvested after a period of 20 days. Good quality pure and doped crystals were obtained. All the grown crystals were colourless, stable and transparent. The photographs of as grown pure and doped LAHC monohydrate single crystals are shown in fig 1 and fig 2 respectively. The crystals were characterized using FTIR, UV-VIS-NIR spectroscopic techniques, TGA and powder XRD techniques.

Fig1. Photograph of as grown Pure LAHC monohydrate crystal

Fig 2(a). Photograph of as grown Cadmium doped LAHC monohydrate

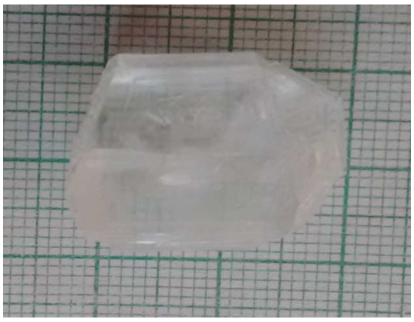

Fig 2(b). Photograph of as grown Zinc doped LAHC monohydrate

Characterization

The FTIR spectra of pure, zinc doped and cadmium doped LAHC crystals were recorded by KBr pellet technique using Perkin Elmer FTIR Spectrophotometer in the range 4000-400 cm^{-1} at SAIF, IIT Madras. The optical properties of the grown crystals were studied in the wavelength region 250-1100 nm at St. Peters University, Chennai. Powder X-ray diffraction pattern was recorded at University of Madras. Inductively Coupled Plasma Optical Emission Spectroscopic studies were carried out at SAIF, IIT Madras to reveal the presence of dopants in the crystal.

RESULTS AND DISCUSSION

FTIR Spectroscopic study

The FT-IR spectra of pure LAHC monohydrate crystal and doped crystal were recorded in the region 4000-400 cm^{-1} using Perkin Elmer at SAIF, IIT madras, Chennai. The sample was prepared by pressing LAHC monohydrate with KBr into pellet form. The observed spectra are shown in fig 3, 4 and 5 respectively.

For CH_3 group frequencies, generally, nine fundamentals can be associated with CH_3 group. The asymmetric stretching vibrations usually occur at higher wave numbers than symmetric stretching vibrations. Also, symmetrical bands are sharper than asymmetrical bands. Asymmetric C-H stretching mode of CH_3 is expected around 2980cm^{-1} and CH_3 symmetric stretching is expected at 2870cm^{-1}.Govindarajan *et al* [8] have assigned the vibrations occurring in the 2900cm^{-1} range to CH_3 asymmetric stretching and bands in the 2800cm^{-1} region to CH_3 symmetric stretching. Also, Gnanam *et al* [9] have assigned peaks occurring at 3223cm^{-1} and 2733cm^{-1} to symmetric stretching bands of N-H and C-H groups. In the present work, the vibrational frequencies occurring at 2811cm^{-1} and 2730cm^{-1} have been assigned to asymmetric and symmetric stretching vibrations of methyl group respectively. The bands occurring at 1455cm^{-1} and 1412cm^{-1} have been assigned to CH_3 bending vibrations. The peak at 1236cm^{-1} has been assigned at O – CH_3 rocking vibrations, based on the vibrational band assignments done by Shettigar *et al* [10].

The C – N stretching frequencies are rather difficult to assign since there are problems in distinguishing these frequencies from other vibrations. For the compound under study, L- alanine hydrogen chloride, the symmetric C-N stretching vibrations are assigned to frequency 1151cm^{-1}, while asymmetric stretching vibration is assigned to 1236cm^{-1}. These assignments are in good agreement with assignments made by previous workers [11, 12].

If a compound contains a carbonyl group, the absorption caused by C=O stretching is generally among the strongest present. If the nature of the carbonyl group can be established by classical chemical tests or by other IR absorptions present, a great deal of structural information can be derived from the exact position of the carbonyl stretching absorption peak. Generally, the C=O absorption occurs in the range 1680cm^{-1} – 1630cm^{-1}. For LAHC crystal, this absorption is assigned the frequency 1618cm^{-1}. This is in correlation with assignments done by Shettigar *et al* [10]. The O-C-O bending mode at 772 cm^{-1} has been identified and assigned. The COO^- scissoring mode appears at 649 cm^{-1} in the FT-IR spectrum of the crystal. The peak at 539 cm^{-1} represents the COO^- rocking. The vibrational band assignments for the absorption peaks of the FT-IR spectrum have been done in accordance with the data reported in the literature [13,14,15].

The N- H group gives rise to six internal modes of vibrations, i.e., symmetric and asymmetric stretching, symmetric deformation, rocking, wagging and torsional modes [16]. For LAHC crystal, the band occurring at 3081cm^{-1} is attributed to asymmetric NH_3^+ stretching, and the one at 2938cm^{-1} is attributed to symmetric stretching. The absorption peak at 2112 cm^{-1} is due to the combination band of NH_3^+ degenerate mode and NH_3^+ torsion. The bands at 1598cm^{-1} and 1519cm^{-1} are due to the bending vibrations of NH_3^+ group. This is in good agreement to the values assigned by Subashchandra bose *et al* [17]. Bands occurring in lower wave number ranges of 501cm^{-1} and 488cm^{-1} in LAHC are attributed to NH_2 wagging, in correlation with vibrational analysis on different compounds by Ramalingam *et al* and Arjunan *et al* [11,12].

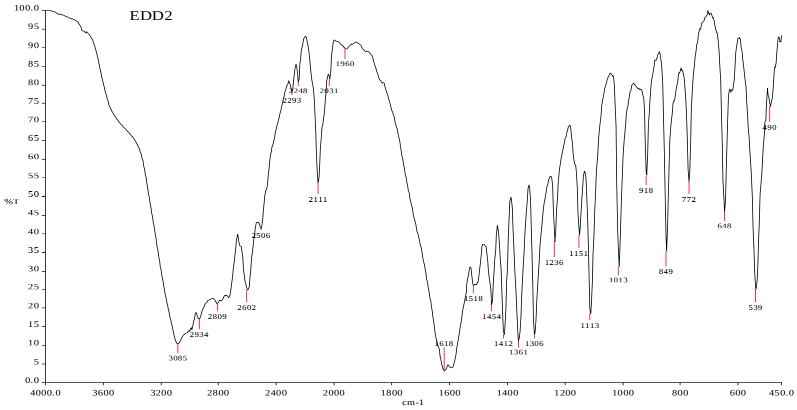

Fig 3. FTIR spectrum of Pure LAHC crystal

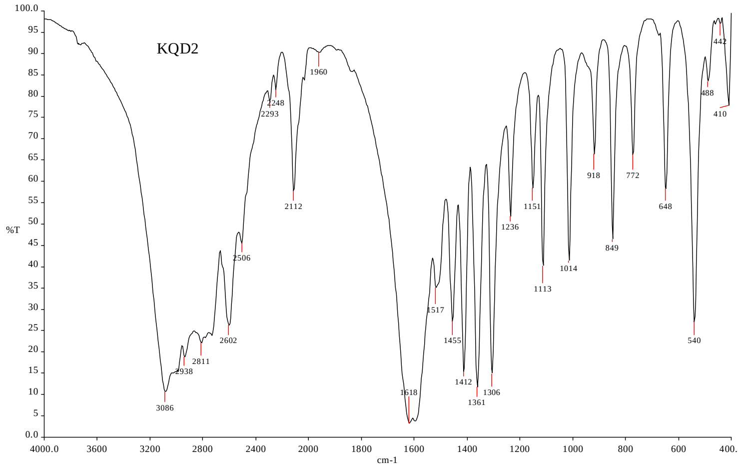

Fig 4. FTIR spectrum of Cadmium doped LAHC crystal

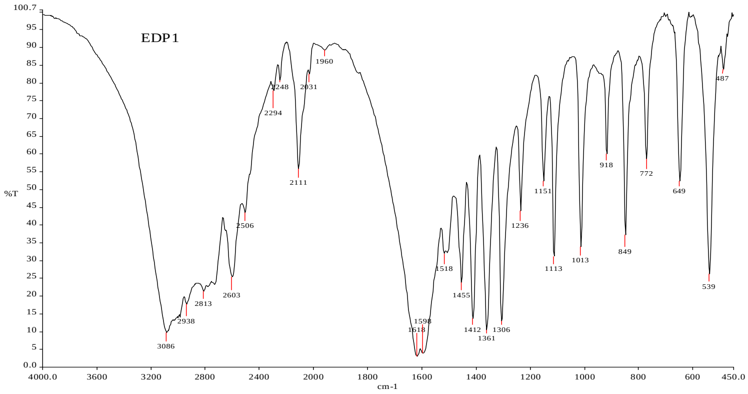

Fig 5. FTIR spectrum of Zinc doped LAHC crystal

Powder XRD Analysis

Powder X-ray diffraction study was conducted to verify the single phase nature of the samples. Figures 7 and 8 show the powder XRD patterns of pure, cadmium doped LAHC monohydrate crystals. Well defined Bragg peaks were obtained at specific 2θ angles indicating that crystals were ordered. The powder XRD studies were done at University of Madras using GE XRD 3003 TT X-ray diffractrometer. The X radiation used was copper (K-Alpha 1) radiation (λ=1.54056Å) operating at a voltage of 40 KV and a current of 20 mA. The scanning rate was maintained at 1.6°/min over a 2θ range of 10-70° employing the reflection mode for scanning. The figures 6 and 7 indicate the sharp peaks and hence the crystalline nature of the grown crystals.

There is a slight shift in the diffracted peaks in the XRD pattern of doped LAHC monohydrate crystals. When compared to that of pure LAHC monohydrate, the intensity of the diffracted peaks was found to vary in both the XRD patterns of doped crystals.

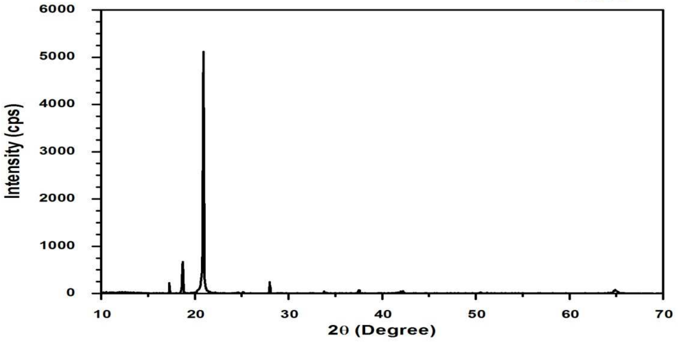

Fig 6. Powder XRD spectrum of pure LAHC crystal

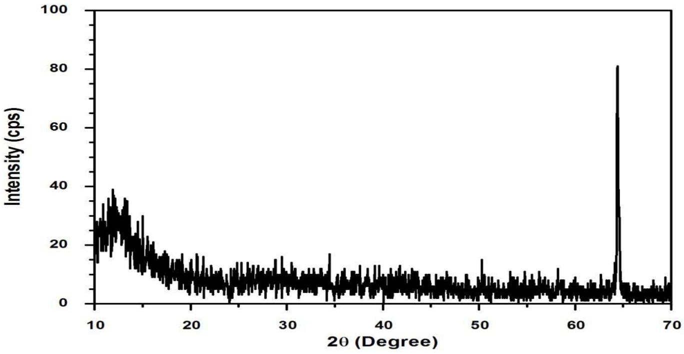

Fig 7. Powder XRD spectrum of cadmium doped LAHC crystal

Optical transmission Spectral Studies

Single crystals of L-alanine are mainly used for optical applications. The study of the optical transmission range of the grown crystals is thus very important. Pure, zinc doped and cadmium doped LAHC monohydrate crystals with a thickness of 2mm without any antireflection coating were cut and used for optical measurements. The UV-Visible-NIR transmission spectra were recorded using Perkin Elmer Lambda 35 UV-Vis NIR spectrophotometer at St. Peters University, Avadi, Chennai in the range 250 nm to 1100 nm.

This spectral study is helpful 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 the electronic structure. This leads to the idea of the band structure of the crystal and to know whether it gets affected in the band extreme or not.

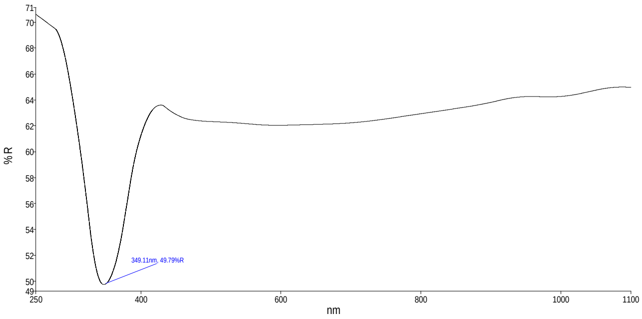

Fig 8. UV-VIS–NIR spectrum of pure LAHC

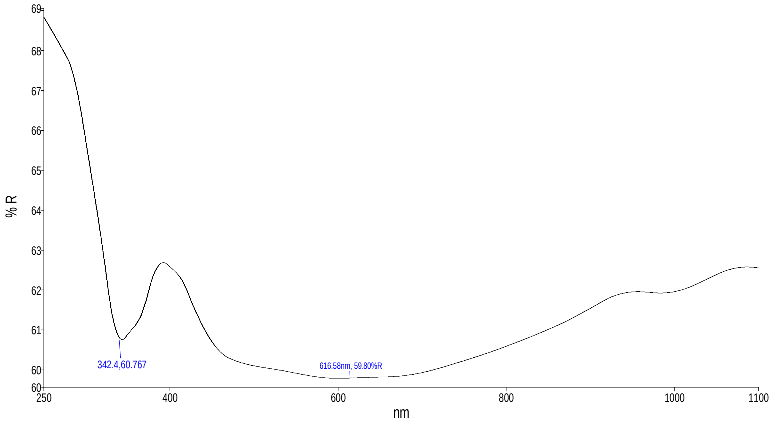

Fig 9. UV-VIS–NIR spectrum of cadmium doped LAHC

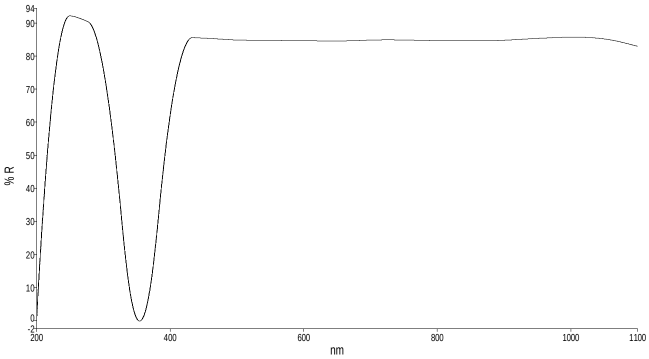

Fig 10. UV-VIS –NIR spectrum of Zinc doped LAHC

From the spectra presented in fig 8-10, it is clear that both the pure LAHC monohydrate and Cd and Zn doped LAHC monohydrate crystals have transmittance in the entire of visible –NIR region of the spectra. High transmission in the entire visible region and short cut off wavelength facilitates the as grown crystals of the present work to be potential candidates for non linear optical materials producing second harmonic and third harmonic of Nd:YAG laser. However, absorption at around 346 nm and 342 nm occur in the near ultraviolet region in pure and cadmium doped LAHC monohydrate crystals. This arises due to electronic transitions associated within the samples. Using cut off wavelength (λ) detail and applying the formula $E_g = hc/\lambda$, the band gap energy was found to be 3.469 eV for pure LAHC monohydrate. The band gap energies for the zinc and the cadmium doped LAHC monohydrate were found to be 3.505 eV and 3.634 eV respectively.

ICP-OES studies

Inductively Coupled Plasma (ICP) technique has been used to detect the presence of dopant in the crystal. Perkin Elmer Optima 5300 DV at SAIF IITM, Chennai was used for the study.

The primary goal of the Inductively Coupled Plasma studies is to get the elements to emit characteristic wavelength specific light, which can then be measured. The presence of zinc in the doped LAHC crystal is confirmed by the ICP- optical emission spectrometry studies. Zinc (Zn) is identified with the wavelength 206.200 nm in the ICP study. The presence of Zinc is confirmed by comparing the emitted wavelength with the characteristic wavelength for Zn (213 nm) in the ICP-OES standard measurements.

Table 1 : ICP test data of doped LAHC monohydrate

Sample weight	Analyte	Concentration
0.15 g	Zn 206.2 nm	3.077 mg/l
0.22 g	Cd 228.8	3.563 mg/l

The weight percentages of Zinc and cadmium present in the doped crystal can be calculated from the formula,

$$\text{Weight \%} = \frac{\text{ppm (mg/l)} \times \text{volume in ml} \times 10^{-4}\text{(dilution factor)}}{\text{Weight of the sample (g)}}$$

Weight % of Zinc and Cadmium were calculated using the above formula as 0.0307% and 0.0809% respectively.

From the ICP spectrometry, it is evident that Zinc and cadmium are present in the doped LAHC monohydrate crystal.

CONCLUSION

Single crystals of pure, Zinc and cadmium doped LAHC monohydrate single crystals were grown by solution method. It was observed that the grown crystals were transparent, colourless and had good morphological edges. The powder XRD of the grown crystals confirmed their crystalline nature. The functional groups present in the crystals were confirmed by the detailed FT-IR spectral analysis. The optical transmission study revealed the high transparency of the crystals. The presence of dopants was confirmed by the ICP optical emission spectral studies.

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