STRUCTURAL AND OPTICAL STUDIES ON SOLUTION - GROWN SEMI-ORGANIC THIOUREA DOPED L-ALANINE HYDROGENCHLORIDE SINGLE CRYSTAL

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ABSTRACT

Optically good quality single crystals of Thiourea L-alanine hydrochloride (TU-LAH) were grown by slow solvent evaporation technique. The grown TU-LAH crystals were confirmed by X-ray powder diffraction studies. Absorptions of these grown crystals were analysed using UV– Vis–NIR studies, and it was found that these crystals possess minimum absorption in the entire visible region. The TU-LAH crystals were characterized by Fourier transform Infrared (FT–IR) studies. Nonlinear optical studies of crystals were carried out and the second harmonic generation efficiency of the powdered sample was measured using Nd:YAG Q-switched laser with first harmonic output of 1064 nm and KDP was taken as the reference material. Scanning electron microscope studies and HR-SEM studies were carried out to show the presence of thiourea dopant in the grown crystal.

Keywords: NLO, Doped, XRD, FTIR, UV- Vis – NIR. HR-SEM,EDAX

I. INTRODUCTION

The chemical flexibility of amino acids is the main reason for the large variety of compounds resulting from reactions of amino acids with inorganic salts, acids or hydroxides [1]. L-Alanine is one of the 20 proteinogenic amino acids and has been currently recognized as one of the most abundant aminoacids in natural proteins [2]. Key functions of frequency conversion and optical switching are provided by nonlinear optical processes and they depend upon the various properties of the materials, such as transparency, laser damage threshold, hardness, thermal and chemical stability [3].In recent years, more promising NLO materials with better properties have been discovered and studied. Materials with large second order nonlinearity, transparency at all wavelengths and stable physicochemical performance are required in order to realize most of these applications [4]. Most of the organic NLO crystals usually have poor mechanical and thermal properties. Inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity. Semi organic crystals are those which combine the positive aspects of organic and inorganic materials resulting in desired nonlinear optical properties [5]. Hence, recent interest is centered on semi organic crystals, which have large nonlinearity, high resistance, low angular sensitivity and good mechanical hardness [6].A series of NLO crystals such as L- arginine diphosphate [7]. L- Histidinium hydrogen maleate [8], L- Lysine monohydrochloride dihydrate [9], L- Histidine hydrochloride monohydrate [10], L- Glutamic acid hydrochloride [11] and L- Cystine dihydrochloride [12] have been reported with moderately high mechanical and chemical stability. L-alanine hydrogen chloride (LAHCl), an NLO crystal, was first reported by Yamada et al [13] and its characterisation was made recently [14]. In the present work, to improve the optical property, an organic dopant such as glycine has been added with LAHCl and the influence of glycine on the growth, structural and optical properties of LAHCl single crystal has been analysed.

II. SYNTHESIS AND CRYSTAL GROWTH

To synthesize TU-LAH, the calculated amount of L-alanine (AR grade from E-Merck India Ltd.) and hydrochloride acid were taken with excess of double distilled water. The concentration of thiourea dopant in the doped crystal was maintained at 0.1 M. The synthesized salts was dissolved in double distilled water and the saturated TU-LAH solution was prepared at room temperature. This saturated solution was placed in a constant temperature bath kept atthe desired growth temperature at 30°C. TU-LAH single crystal was grown within 30 days with a dimension of $15 \times 6 \times 4$ mm^3 and is shown in Fig. (1).

Fig. 1 Photograph of as grown single crystal of TU-LAH

III. CHARACTERISATION

A. X-ray diffraction analysis

Single crystal XRD study of TU-LAH was carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer with $M_O K_a$ radiation. The lattice parameters of the grown crystal are; $a = 6.197$ Å, $b = 9.956$ Å, $c = 11.86$ Å and $V = 730.12$ Å^3. It is observed that the lattice parameters and cell volume of the grown crystal has been slightly modified due to the inclusion of the dopant thiourea and has a very good agreement with the reported literature (13).

B. FTIR analysis

The FTIR spectrum of TU-LAH was recorded on BRUKER IFS FTIR - SPECTROMETER using KBr pellet in the range 4000 - 400 cm^{-1} and is shown in Fig (2). The FT-IR Spectrum of TU-LAH crystal is shown in Figure (2). N-H stretching frequencies of amino group are found between 3100 cm^{-1} and 2600 cm^{-1} for TU-LAH crystal. The TU-LAH compound shows absorption at 1620 cm^{-1} indicating the presence of primary amino group. The characteristic absorption for the – NH group in the aromatic ring is observed at 1307 cm^{-1} for TU-LAH. The broad absorption around 3081 cm^{-1} indicates the co presence of $C = O$ stretching and O-H stretching. The peaks at 1594 cm^{-1} and 1455 cm^{-1} are due to the symmetric and asymmetric stretching modes of NH_3^+ and COO^- respectively. The peak at 1413 cm^{-1} confirms the presence of thiourea dopant in the grown crystal. The FT-IR spectra of TU-LAH confirm the structural aspects.

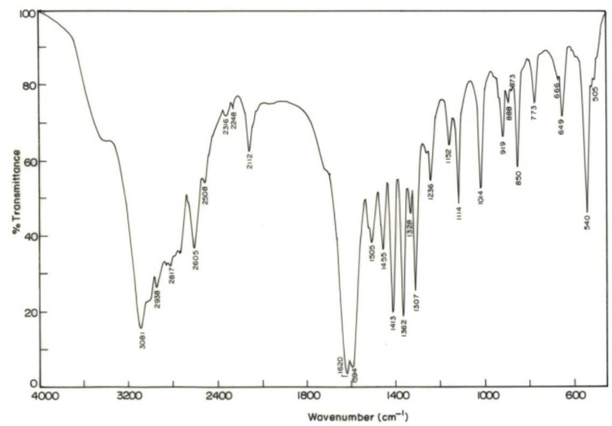

Fig. 2 FTIR spectrum of TU-LAH crystal

C. Optical absorption analysis

The optical absorption spectrum of TU-LAH single crystal were recorded in the region 200 - 1200 nm using a PERKIN - ELMER LAMBDA 25 UV spectrometer and is shown in Fig. (3). The optical transmission analysis revealed that the TU-LAH crystal has a UV cut - off wavelength at 250 nm. It is observed that the grown TU-LAH crystal has a very good transparency throughout the entire visible region, which is an essential property of NLO crystal.

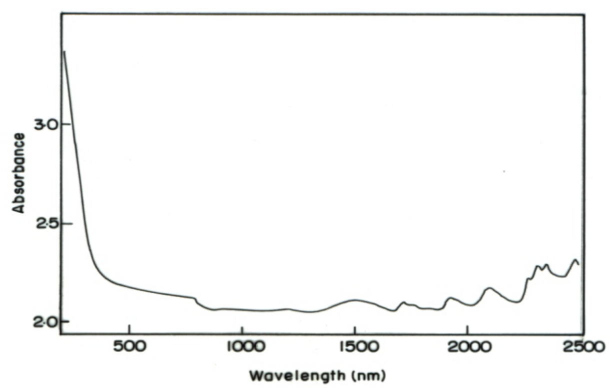

Fig. 3 UV – Vis – NIR spectrum of TU-LAH crystal

D. NLO study

The SHG conversion efficiency of the grown crystal was carried out using the Nd:YAG laser beam of wavelength 1064 nm, using Kurtz powder technique. The second harmonic generation was confirmed by the emission of green radiation of wavelength of 532 nm and NLO efficiency is found to be 1.77 times that of KDP.

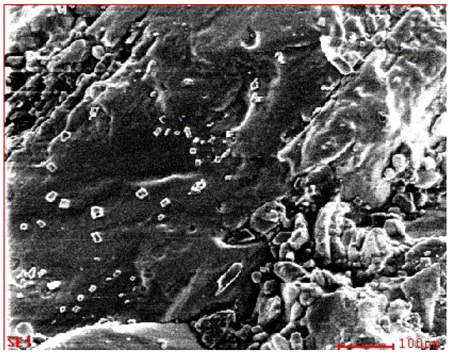

Fig. 4 HR-SEM photograph of TU-LAH crystal

E. HR-SEM analysis

HR-SEM analysis was carried out in order to study the nature and surface features of the grown crystals. The crystals were cut into few mm for observing the surface morphology. The SEM images of both TU-LAH crystal is shown in Fig. 4. It shows the existence of striations and visible inclusions in the grown crystals

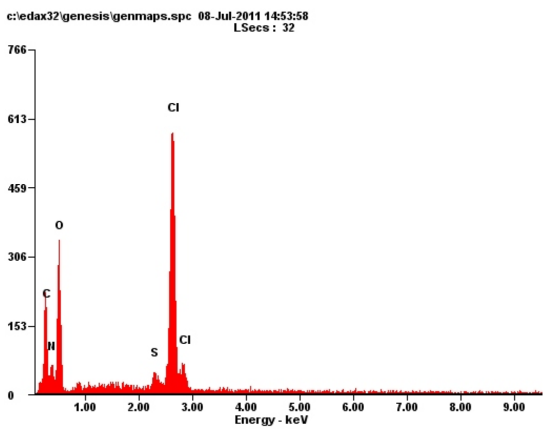

Fig. 5 EDAX of TU-LAH crystal

F. EDAX Analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals. In the present study, the crystal was analysed by INCA 200 energy dispersive X-ray micro analyzer equipped with LED - steroscan 440 scanning electron microscope. The results obtained in EDAX of the doped crystal is shown in Fig. 5 and this confirms the presence of thiourea in the doped sample.

IV. CONCLUSION

Single crystal of thiourea doped L-Alanine hydrogenchloride has been grown by slow evaporation technique at room temperature. Unit cell parameters have been evaluated by XRD technique which has confirmed that the grown crystal belongs to the orthorhombic system. The functional groups present in doped crystal have been confirmed by FTIR spectral analysis. UV- Vis- NIR spectrum has shown the good optical transmittance of the crystal and proves its suitability for NLO applications. The powder SHG measurement has confirmed the NLO property of the grown crystal. The presence of the dopant is verified by EDAX and HR-SEM studies.

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