Crystal Growth and Characterization of a new semiorganic nonlinear optical crystal L-Histidine potassium chloride

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Abstract— A Semiorganic nonlinear optical material L-Histidine Potassium Chloride(LHPC) single crystals were grown by slow evaporation technique. The grown crystal of LHPC is transparent and colourless. The grown crystals were characterized by powder X-ray diffractometry (XRD) method. The XRD pattern confirms the crystalline nature and the purity of the grown crystal. UV-Vis spectrum showed that good optical quality of LHPC. The functional group frequencies were identified and assigned from FTIR spectra. The excitation and emission spectra of LHPC were recorded using spectrofluorometer. The emission peak was absorbed at 306 nm and the optical band gap energy was estimated as 4.06 eV.

Index Terms— Fluorescence, FTIR, LHPC, NLO, Semiorganic, UV-Vis, XRD

1 INTRODUCTION

Nonlinear optical materials are used in optical computing, optical communication, medical diagnostics, harmonic generators, frequency mixing and optical switching. High performance electro-optic switching element for telecommunication and optical information processing are based on materials with high nonlinear optical properties. Developments of novel molecular and crystal design technique for assembling the materials are used for many device applications in the field of opto-electronics and photonics [1]. Hence a variety of materials have been studied for their nonlinear optical properties. A lot of organic chromophores exhibit extremely high and fast nonlinearities much better than those observed in inorganic crystals but they are thermally unstable. Hence, recent search focuses on semiorganic materials due to their large nonlinearity, high laser damage threshold, and good mechanical and thermal stability [2]. In this connection amino acids are promising materials for optical Second Harmonic Generation (SHG) as they contain zwitterions, which create the hydrogen bonds used for the generation of noncentrosymmetric structures favorable for attractive SHG properties of crystal and the complexes of amino acids with inorganic salts have the tendency to combine the advantage of the organic amino acid with that of the inorganic salt [3]. In this work, we report the powder X-ray diffraction, Fourier Transform Infrared (FTIR), UV-Vis and Fluorescence Spectroscopy are studied for L-Histidine Potassium Chloride (LHPC).

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2 MATERIALS AND METHODS

2.1 SYNTHESIS AND GROWTH TECHNIQUE

The starting material was synthesized by taking L-Histidine and Potassium Chloride in a 1:1 stoichiometric ratio. The required amount of starting materials for the synthesis of L-Histidine Potassium Chloride (LHPC) crystal was calculated according to the following reaction:

$$C_6H_9N_3O_2 + KCl \rightarrow K.[C_6H_9N_3O_2].Cl$$

The calculated amount of potassium chloride was first dissolved in deionized water. L-Histidine was then added to the solution. The solution was agitated with a magnetic stirring device for 8h continuously and filtered after complete dissolution of the starting materials. The prepared solution was allowed to dry at room temperature and the crystals were obtained by the slow evaporation technique. The purity of the synthesized crystal was further improved by successive recrystallization process; thereby good optical quality single colorless crystals were obtained in 30 days. The grown crystal of LHPC is transparent and colourless.

2.2 CHARACTERIZATION

The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (LynxEye detector). The powdered sample was scanned in the range 10-80° at a scan rate of 2°/min. The Fourier transform infrared spectrum was recorded by the KBr pellet technique using Bruker germany Vertex 70 Spectrometer. The infrared spectrum of grown crystal was obtained in the range 4000-400 cm^{-1} as shown in

the Fig.3. The grown crystals were crushed to powder and mixed with KBr and palletized. The FTIR spectrum was then recorded using a Bruker germany Vertex 70 Spectrometer. The UV-Vis spectrum was recorded in the range 200-800 nm using Perkin Elmer, Lambda 950 Double beam spectrometer. The excitation and emission spectra of LHPC crystals were recorded in the range 200-400 nm. using FP-6500 spectrofluorometer.

3 RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

Fig 1 shows the X-ray powder diffraction pattern of the grown crystal of LHPC. The sharp and well defined Bragg's peaks at specific 2θ angles confirms the crystalline nature and purity of the crystal. The d spacing and the hkl values of diffraction peaks were listed in Table 1.

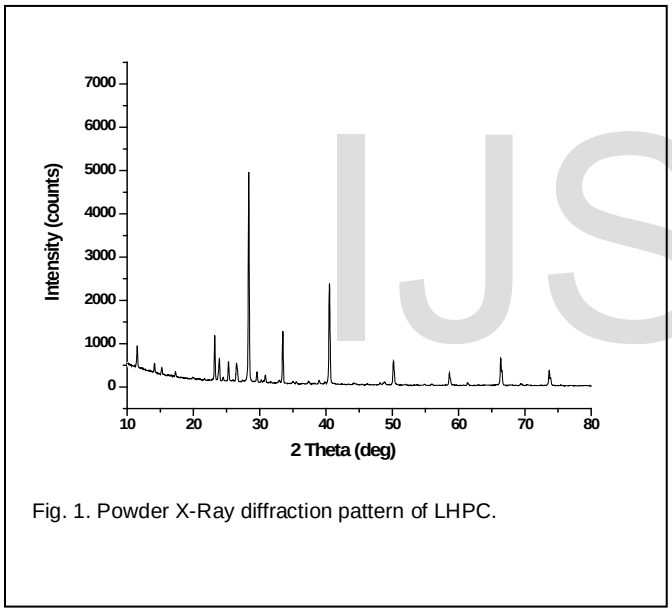

Fig. 1. Powder X-Ray diffraction pattern of LHPC.

TABLE 1
X-RAY POWDER DIFFRACTION DATA OF LHPC CRYSTALS.

2 Theta	hkl	d value (Angstrom)
23.26	112	3.81
24.11	020	3.65
25.35	113	3.48
28.28	114	3.12
33.66	200	2.57
40.64	018	2.22
50.18	041	1.81

3.2 UV-VIS ANALYSIS

Fig.2. shows the UV-Vis spectrum of LHPC, which is evident that the LHPC crystal has a very low cutoff wavelength of 224 nm and there is no absorption in the entire visible region. This transparent nature in the visible region is a desirous property for this material for NLO applications [4]. As well, since there is no significant absorption at 532nm, it can be utilized for Second Harmonic Generation (SHG) and optical application in the blue region [5].

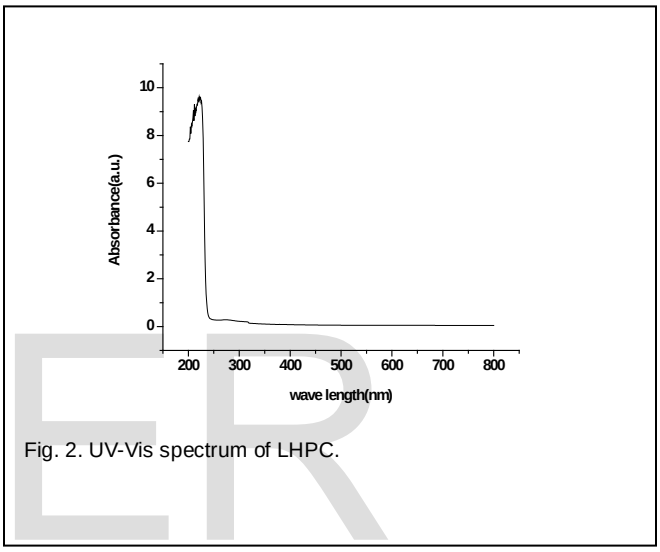

Fig. 2. UV-Vis spectrum of LHPC.

3.3 FTIR STUDIES

Fig 3. shows the Fourier Transform Infrared spectrum of LHPC. The functional groups NH_3^+, CH, CN and COOH were identified and assigned for LHPC. The strong peak at 1335 cm^{-1} is assigned to C-O stretching and 1062 cm^{-1} is due to C-C-N stretching and the peaks at 914 and 960 cm^{-1} are due to NH_3^+ rocking and CH_2 rocking. The intense band at 3410 cm^{-1} is due to asymmetric deformation of NH_3^+ [6]. The peak at 1140 cm^{-1} is assigned to C-C stretching. The peaks appearing at 631 and 699 cm^{-1} are due to COO^- wagging and COO^- inplane deformation. C-H out of plane bending and CH_2 wagging vibrational modes are observed at 820, 1285 cm^{-1} and COO^- asymetric stretching mode is observed at 1605 [7]. CH_2 symmetric stretching is appeared at 3008 cm^{-1} . The assignments confirm the presence of various functional groups present in the material, tabulated in Table 2.

TABLE 2
FTIR ASSIGNMENT OF LHPC

Wave number (cm^{-1})	Assignment
3008	CH_2 symmetric stretching
3410	NH_3^+ asymmetric deformtion
1605	COO^- asymmetric stretching
1497	NH_3^+ symmetric deformtion
1335	C-O stretching
1285	CH_2 wagging
1140	C-C stretching
1062	C-C-N stretching
960	CH_2 rocking
914	NH_3^+ rocking
866	C-C stretching
820	C-H out of plane bending
699	COO^- inplane deformation
631	COO^- wagging
530	COO^- rocking

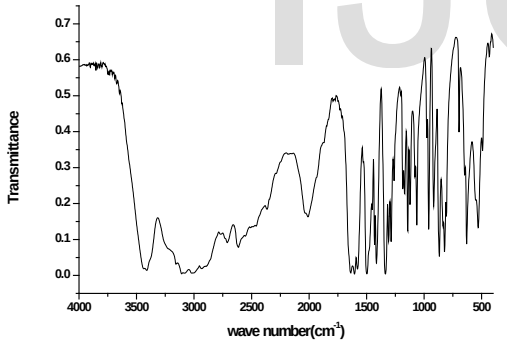

Fig. 3. FTIR spectrum of LHPC.

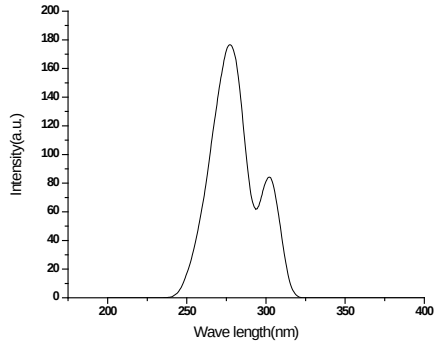

Fig. 4. Excitation spectrum of LHPC..

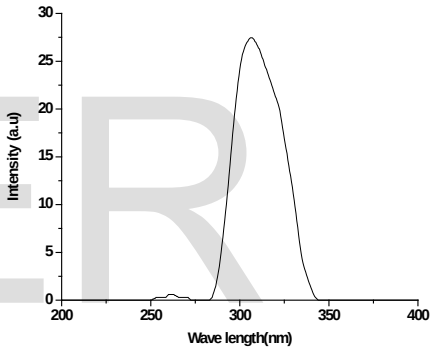

Fig. 5. Emission spectrum of LHPC.

3.4 FLUORESCENCE STUDIES

The spectrum recorded by the emission of photo generated minority carriers is a direct way to measure the band gap energy [8]. Fig. 4 shows the excitation spectrum of LHPC. A peak at 306 nm was observed in the emission spectrum as shown in Fig.5. Band gap energy of LHPC crystal was calculated using the formula E_g=hc/λe. Where h, c and e are constant, λ is the wavelength of fluorescence. The calculated band gap energy is about 4.06 eV.

4 CONCLUSION

A Semiorganic nonlinear optical material L-Valine potassium chloride (LVPC) was synthesized and single crystals of LVPC have been grown using slow evaporation technique in room temperature. The powder X-Ray diffraction pattern was recorded and the sharp well defined Bragg's peaks confirm the crystalline nature of the synthesized material. FTIR analysis confirms the presence of various functional groups. The Fluorescence behavior of the crystal has been confirmed by emission spectrum. From the outcome of above result, it can be considered that the LHPC crystal is a candidate for fluorescence applications.

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