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Investigations on Amino Acid Based L-Prolinium Tartrate Single Crystal.

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ABSTRACT

Optically good quality single crystal of L-Prolinium Tartrate (LPT) was successfully grown by slow solvent evaporation technique at room temperature. The crystals were characterized by optical absorption spectrum, FTIR, FT-Raman and X-ray diffraction studies. The optical absorption spectrum shows that the absorption in LPT is nearly equal to zero in the entire visible region. The powder technique of Kurtz and Perry confirms the NLO property of the grown crystal and the SHG efficiency of LPT was found to be 1.3 times that of KDP crystal.

Keywords: LPT, SHG, EDX, SEM

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INTRODUCTION

The synthesis of new and efficient frequency conversion materials has resulted in the development of new aminoacid based NLO materials. Many of the natural amino acids individually exhibit the nonlinear optical properties because they have a donor NH_2 and COOH and also due to the possibility of intermolecular charge transfer [1]. L-Proline analogs are promising NLO materials. Single crystals of a semi-organic nonlinear optical (NLO) material, L-proline cadmium chloride monohydrate (L-PCCM), were grown by the slow evaporation and slow cooling method [2]. Single crystals of the semiorganic material, dichlorobis (L-proline) zinc (II) (DCBPZ) were grown from aqueous solution. The grown crystals were tested by single crystal X-ray diffraction, energy-dispersive spectrometry, FT-IR, UV–Vis and TG–DTA. The structural perfection of the grown crystals has been analyzed by high-resolution X-ray diffraction (HRXRD) rocking curve measurements. The dielectric and mechanical behavior of the specimen was also studied. The SHG efficiency of DCBPZ is three times greater than that of KDP [3]. A semiorganic material, L-proline lithium chloride monohydrate (LPLCM), was synthesized for the first time. Its solubility and metastable zonewidth in double distilled water were estimated [4]. Unidirectional L-Proline cadmium chloride was reported [5]. The growth and characterization of L – Proline cadmium chloride monohydrate was studied and reported [6]. In this work, we have grown single crystals in larger size and subjected for detailed characterization studies

EXPERIMENTAL

SYNTHESIS AND SOLUBILITY OF LPT

All the starting materials for synthesis of LPT are purchased as AR grade (purity ≥ 99 %). L-Proline and L-Tartaric acid taken in equimolar ratio were dissolved in double distilled water to prepare the aqueous solution of LPT. The reaction that takes place between L-Proline and L-Tartaric acid is as follows:

$$C_5H_9NO_2 + C_4H_6O_6 \longrightarrow C_9H_{15}NO_8$$

The synthesized salt was purified by repeated crystallization process. Solubility corresponds to saturation i.e. to equilibrium between a solid and its solution at a given temperature and pressure. Thermodynamically, this means that the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. The solubility of LPT in the solvent of water is determined using synthesized salt of LPT. A 250 ml glass beaker filled with 100 ml of deionized water was placed inside a constant temperature bath, maintained at 30 °C. LPT salt was added in small amounts at successive stages. The addition of the salt and the stirring were continued till a small amount of precipitate was formed, which confirmed the supersaturated condition. After this, 20 ml of the saturated solution was pipetted out and poured into a petri dish of known weight. The solution is allowed to evaporate completely by warming the solution slightly above the room temperature. The amount of the salt present in 20 ml of the solution is measured. From this, the amount of the salt present in 100 ml of the solution is found out. The same procedure is followed for the temperatures 30, 35, 40, 45, and 50 °C and the amount of salt dissolved in each case are determined. Figure 1 shows the solubility curve of LPT.

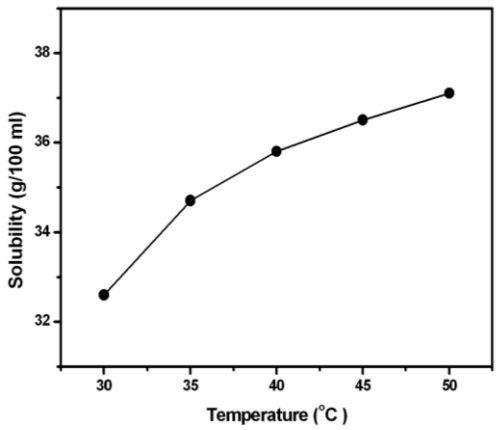

Figure 1: The solubility curve of LPT

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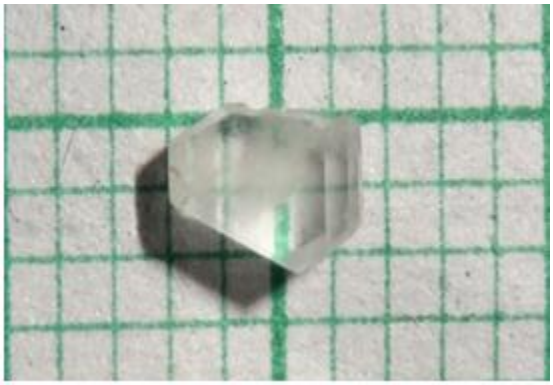

Figure 2: Photograph of as grown LPT single crystal

Supersaturated solution of LPT was prepared in accordance with the solubility data. The spontaneous nucleation results in the formation of large number of crystals of microscopic dimension within 2-3 days. Good optical quality seed crystals, which were free from defects and inclusions, were selected for growing bulk crystals. A few drops of H_2O_2 were added to the mother solution in order to prevent microbial contamination. Good optical grade crystals of dimension upto 4 x 4 x 5 mm^3 were conveniently grown in a period of 30 days. Figure 2 shows the photograph of LPT single crystal grown from its aqueous solution by solvent evaporation technique.

RESULTS AND DISCUSSION

XRD Analysis

In order to confirm the crystallinity and also to estimate the lattice parameter values, the grown crystals were subjected to powder X-ray diffraction analysis. X-ray powder patterns of the crystal were recorded on a SIEFERT X-ray Diffractometer using CuK α (Kα = 1.5408) radiation. The sample was scanned for a 2θ range of 10–40° and at a scan rate of 2°/ min^{-1}. All the observed reflections (figure 3) were indexed and the unit cell parameters were calculated. The XRD data of the crystal indicates that it crystallizes in Monoclinic system with $P2_1$ space group with a = 5.017Å, b = 17.696 Å, c = 6.574 Å and V = 567.8 $Å^3$.

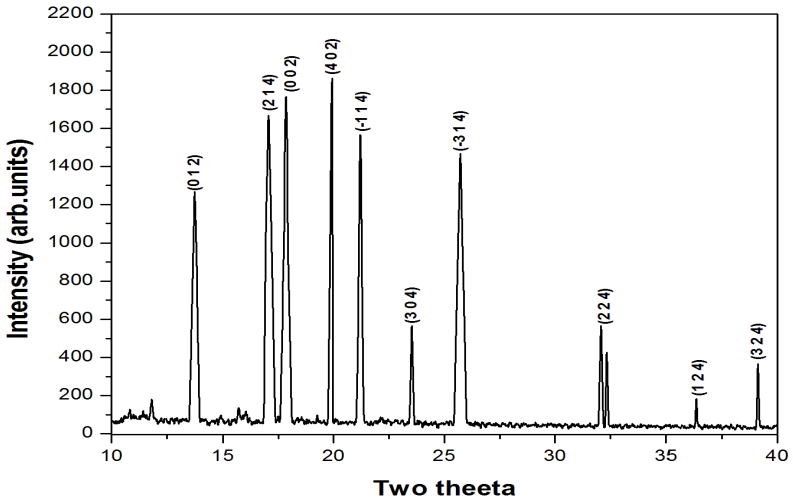

Figure 3: Powder XRD spectrum of LPT crystal

Optical absorption spectrum

The absorption spectrum of LPT is shown in Figure 4. The sharp rise in absorption at 225 nm suggests nearly similar distribution of energies among all molecules of the single crystal and there is no remarkable absorption in the entire region of the spectra. In the entire visible region, the absorbance is less than 1 unit. This transparent nature in the visible region is a desirous property for this material for NLO applications.

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Minimum absorbance is also observed in the near infrared region. Figure 5 shows the plot of $(\alpha h\nu)^2$ *vs* hν, where, α

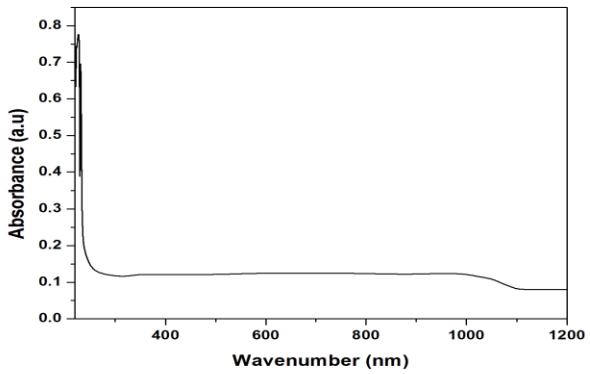

Figure 4: Optical absorption spectrum of LPT crystal

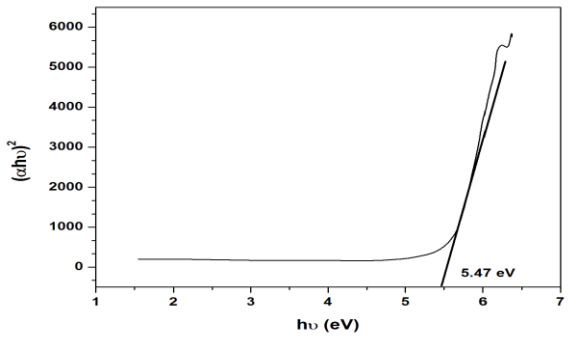

Figure 5 Optical band gap of LPT crystal

Is the optical absorption coefficient and hν is the energy of the incident photon. The energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. The direct band gap energy (E_g) of LPT is found to 5.47 eV.

FT-IR and FT-Raman Analysis

FT-IR spectrum of the grown crystal was recorded in the range 500 cm^{-1} to 4000 cm^{-1}, using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. Recorded FT-IR and FT-Raman spectra are shown in Figure 6 and 7 respectively.

N-H Vibrations

The N-H stretching vibrations generally give rise to bands at 3500–3300 $cm^{-1.}$ [7,8]. In IR 3320 cm^{-1},3270 cm^{-1} and in Raman 3084 cm^{-1}, 3013 cm^{-1} are assigned as a N-H stretching modes these values are well coincides with simulated vibrations. The NH deformation vibrations are assigned to the intense peak at 794cm^{-1} in IR and 783 cm^{-1}in Raman shows good agreement.

COO^- Vibrations

Carboxyl group vibrations give rise to intense characteristic bands due to conjugation or formation of hydrogen bonds. These stretching and bending vibrations of acid group are generally expected in the region 1400–1200 cm^{-1} [9].In the present work COO asymmetric stretching is at 1576 cm^{-1} in IR and 1571cm^{-1} in Raman respectively. Similarly 1209 cm^{-1}, 690 cm^{-1} in IR and 1225 cm^{-1} in Raman exhibit the COO mode vibration.

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C–H vibrations

The C–H vibrations are present in both FT-IR and Raman. The C-H bending vibrations are usually occurred in the region 1465-1281 cm^{-1} [10]. C-H rocking vibration is occurred at 1410 cm^{-1} in the IR and 1462 cm^{-1}in Raman.

C-N Vibrations

C–N stretching absorption is assigned in the region 1382–1266 cm^{-1} [11]. In the present work, the band observed at 1064 cm^{-1} in FT-IR and 1078 cm^{-1} in Raman spectrum has been assigned to C–N stretching vibration.

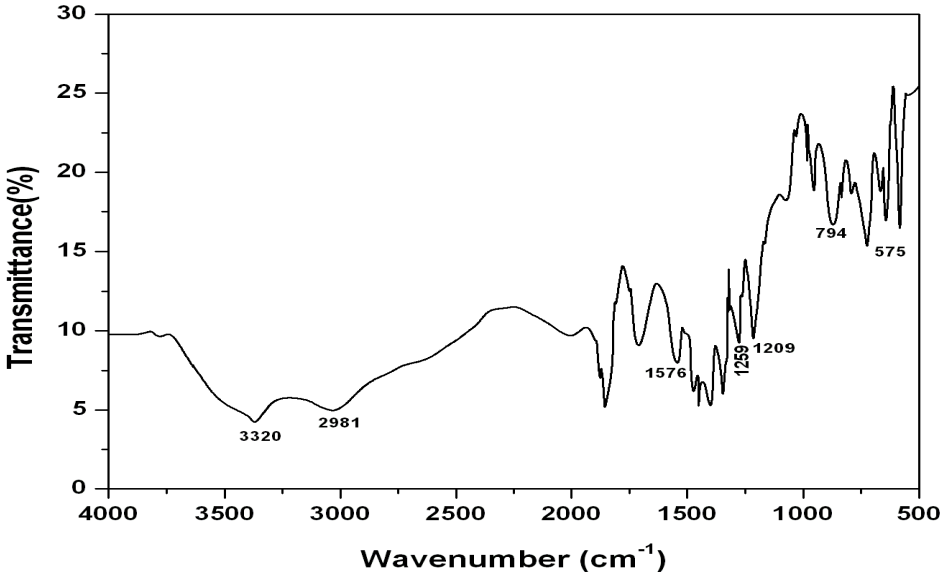

Figure 6: Experimental FT-IR Spectrum of LPT

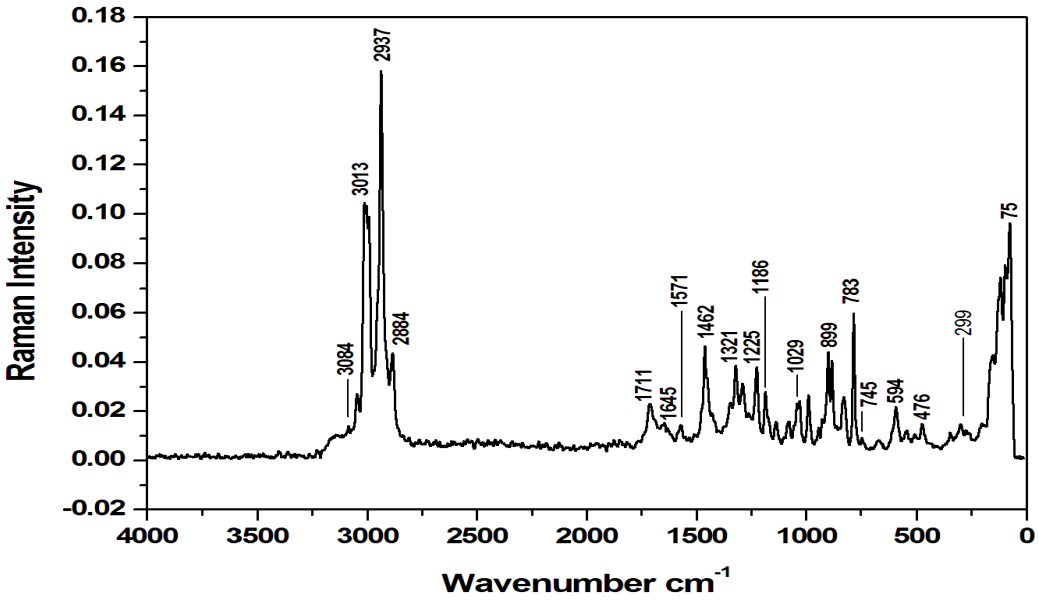

Figure 7: Experimental FT-Raman Spectrum of LPT

SEM analysis

The grown crystal was exploited to SEM analysis using VEGA3 SBH analysis System The quality of the grown crystal can be inferred to some extent by observing the surface morphology of the crystal. From the SEM image (Figure 8) it is clear that the surface of the grown crystal appears smooth though it has pots and

microcrystal on the surface. Overall the surface is very smooth with the appearance of few inclusions, formed on the crystal during growth and they are influenced by the growth conditions. The grain boundaries are clearly seen from the micrograph, which shows the perfect and defect free nature of the grown crystal.

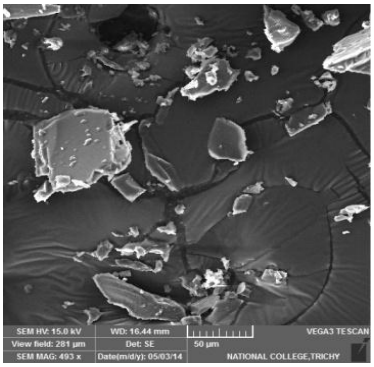

Figure 8: SEM Image of LPT

SHG efficiency studies

The second harmonic generation efficiency of the powdered material was tested using Kurtz and Perry method. The emission of green radiation from the crystal confirms the second harmonic generation in the crystal. Microcrystalline material of KDP was used for comparison with LPT for second harmonic generation experiment. Organic material (crystals) is a potential candidate for frequency doubling. For quantitative work, single crystals of LPT were powdered and then graded by the use of standard sieves to desired range of particle sizes (from <50 to >150 µm). To make relevant comparison with known SHG materials, KDP was also powdered and sieved into the same particle size range. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 10.8 mJ was passed through LPT, second harmonic signal of 532 nm is produced. Then each tube was held within an optical system that collects all the scattered SHG. The generated SHG output signals were monochromated and monitored by a photomultiplier tube and a digital oscilloscope assembly. The second harmonic signal of 71 mV was obtained for LPT with reference to KDP (53 mV). Thus, the SHG efficiency of LPT is nearly 1.3 times higher than KDP.

CONCLUSION

Single crystal of an aminoacid based nonlinear optical material, LPT was successfully grown by slow evaporation technique. XRD data indicates that LPT crystal is of monoclinic structure. The functional groups were identified using FT-IR and FT-Raman analysis. The UV-Vis-NIR spectrum reveals minimum absorption in the entire visible region. The direct band gap energy (E_g) of LPT is found to 5.47 eV. SHG efficiency of LPT was found to be 1.3 times that of KDP crystal.

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