

L-Lysine Doped Organic Nonlinear Optical Crystal

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Abstract— Single crystals of 0.5 mol% L-lysine doped L-Proline Picrate (LPP) an organic non-linear optical material has been grown from solution by slow evaporation method at room temperature. The grown crystals were subjected to single crystal X Ray diffraction technique and cell parameters of the crystal were determined. The title compound crystallizes in monoclinic system with a noncentrosymmetric space group of P21. The thermal stability of the crystal was determined from Thermal analysis curve. The functional groups of the crystal were determined using Fourier Transform Infrared (FTIR) Analysis. The Non linear optical (NLO) response comes from the contribution of charge carriers created by laser excitation in conduction band. The second harmonic generation (SHG) efficiency of the crystal was obtained by classical powder technique using Nd:YAG laser. The SHG output power from 0.5 mol% L-lysine doped LPP is found to be about 15.6 mJ. A strong bright green emission emerging from 0.5 mol% L-lysine doped LPP crystal shows that the sample exhibits good NLO property. The increase of the NLO response supports the general idea that such compounds can be used for multistep switching NLO materials.

Index terms- X-ray Diffraction ; LPP; FTIR; SHG efficiency

I. INTRODUCTION

Nonlinear optics (NLO) has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting and optical data storage for developing technologies in telecommunications and signal processing. Organic materials have been demonstrated in recent years to possess superior second and third order NLO properties compared to the more traditional inorganic materials. The properties of organic compounds can be refined using molecular engineering and chemical synthesis.

A survey of literature indicates that an extensive work has been done on various picrate complexes. Picric acid has a tendency to form stable picrate compounds with various organic molecules due to the presence of active electron cloud and ionic bonds [1]. In the past two decades organic nonlinear optical (NLO) picrate crystals have attracted the scientists and technologists due to their potential applications in the area of photonics including optical information processing [2,3,4,5], high-energy lasers for inertial confinement fusion research, colour display, electro-optic switches, frequency conversion, etc [6]. The organic picrate compounds exhibit larger NLO response than inorganic materials due to the presence of active π -bonds.

However, these materials have poor mechanical strength, thermal stability, laser damage threshold, etc., than the inorganic materials.

Non linear optics is concerned with the interaction of electromagnetic fields with various media to produce new electromagnetic fields altered in phase, frequency of amplitude from the incident fields. Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [7,8]. Amino acids are interesting materials for NLO application as they contain the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second-order nonlinearity. Single crystal of L-Proline shows no center of symmetry and its NLO coefficients have been examined by Boomadas et al [9]. Picric acid forms crystalline picrates with amino acids like L-valine [10], glycine [11], L-asparagine [12] and L-proline [13]. Here L-proline acts as donor and picric acid as electron acceptor. Here the CH-O hydrogen bond plays an important role in the supramolecular packing.

An optical sensing system is basically composed of a light source, optical fiber; a sensing element or transducer and a detector). The principle of operation of a fiber sensor is that the transducer modulates some parameter of the optical system (intensity, wavelength, polarization, phase, etc.) which gives rise to a change in the characteristics of the optical signal received at the detector. Of the huge variety of optical principles, this paper concentrates on optical techniques which provide many possibilities of application of optical principles.

In optical spectroscopy absorbance (or transmittance) is usually monitored have gained increasing interest. The change in amplitude of the radiation is monitored in absorbance and transmittance graph. Remission measurements (changes in the absorbance of reflected light) and fluorescence effects are the most simple sensing methods. Optical sensors have proven in the past to be either very simple and cost-effective devices or enable rather sophisticated multisensor applications. Because of the existence of many different optical principles which can be classified into use of direct optical detection or taking advantage of labelled compounds, in principle many of these methods can be applied to a huge number of applications. It is becoming evident that of the different sensor principles—electronic, electrochemical, masssensitive, or optical devices—none is generally superior, but rather the feasibility

depends on the application. The same holds true for the different optical sensor principles.

In the present work, crystals are grown to observe the optical nature and depending on the optical property the grown crystal can be subjected for its application oriented means. The grown crystal is subjected to linear and nonlinear optical studies to find its absorbance or transmittance property. The same is checked by the nonlinear study, which confirms whether the crystal possesses the nonlinear nature. This property crystals can be used for long distance communication and transfer of energy without any loss.

II. EXPERIMENTAL

Growth of organic crystals with well developed faces and good optical quality mainly depends on the selection of suitable solvents. Single crystals of L-Prolinium Picrate have been grown successfully by slow-evaporation method. LPP was synthesized by the reaction between picric acid and L- proline in equimolar ratio. The reactants were thoroughly dissolved in double distilled water and acetone in 1 : 1 ratio and stirred well using a temperature controlled magnetic stirrer to get a homogeneous mixture of the solution, then 0.5 mol% of l-lysine is doped. This is again stirred for nearly 45 minutes to get a homogeneous mixer. The obtained homogeneous solution is filtered and left for slow evaporation at room temperature. For the experimental work the de-ionized water was got from Millipore water pre-filtration unit. The resistivity of the used dethen-ionized water is 18.2 MΩcm. After a period of 20 days, the size being 8 x1 x 2 mm³ is harvested and the grown crystal is shown in Figure 1.

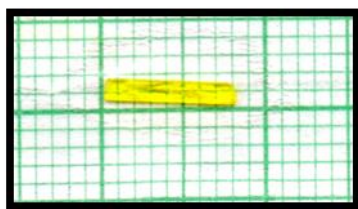


Fig 1. 0.5 mol% L-Lysine doped LPP crystal

II RESULTS AD DISCUSSION

X- Ray Diffraction Analysis

Single crystal diffractometers are most often used to determine the molecular structure of new materials. The grown crystal is subjected to single crystal X- ray diffraction to determine the unit cell dimensions. A good quality crystal was selected for the X- ray diffraction studies. The unit cell parameters of doped LPP crystals were presented in Table 1. It is observed from the table that the cell parameters of doped LPP slightly differ from those of pure LPP, which may be attributed due to the presence of different mol% of dopants in LPP crystals. Both pure and doped crystals are found to be monoclinic and has a space group of P2₁.

Table 1. Single crystal X-ray data of Pure and Doped LPP

Parameters	Pure LPP	0.5 mol% doped L- Lysine
a(Å)	10.897	10.96
b(Å)	5.3495	5.36
c(Å)	12.4830	12.55
V(A ³)	687.29	696
β (°)	109	109.07

Powder X-ray diffraction

Powder X-ray diffraction studies were carried out using Rich Seifort X-ray diffractometer employing CuKα radiation. The intensities of the diffracted peaks of doped LPP crystals were examined. The sharp peaks and low full-width at half maximum (FWHM) values of doped LPP confirms the high crystallinity of the sample. Figures 2 shows the powder XRD spectrum for 0.5 mol% doped L-lysine in LPP.

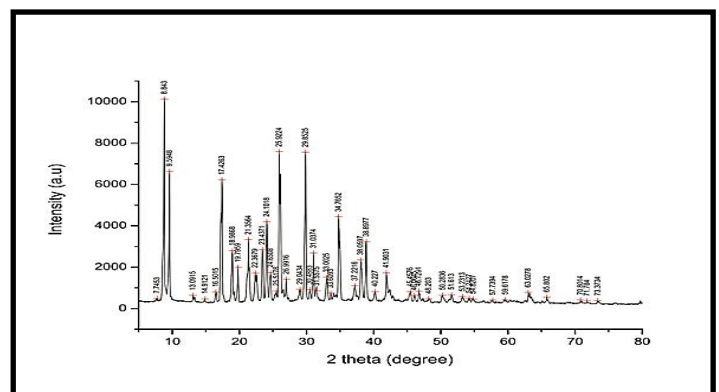


Fig 2. Powder XRD of 0.5 mol% l-lysine doped LPP

Fourier Transform Infrared (FTIR) Analysis

FTIR spectrum of LPP crystals were recorded using Perkin Elmer Spectrum 1 in the range of 500 - 2000 cm^{-1} by KBR pellet technique. The FTIR spectra of 0.5 mol% L-lysine doped LPP grown crystal is given in Fig. 3. The C=O symmetric stretching, O-H bending, NO_2 scissoring, NO_2 rocking curve, Asymmetric stretching of COO are found in all the cases. The phenolic vibration produces a peak at 1160 cm^{-1} . Also, it reveals that picric acid necessarily protonates the carboxyl group. The observed vibrational frequencies and the tentative frequency assignments for doped LPP crystal is given in Table 2.

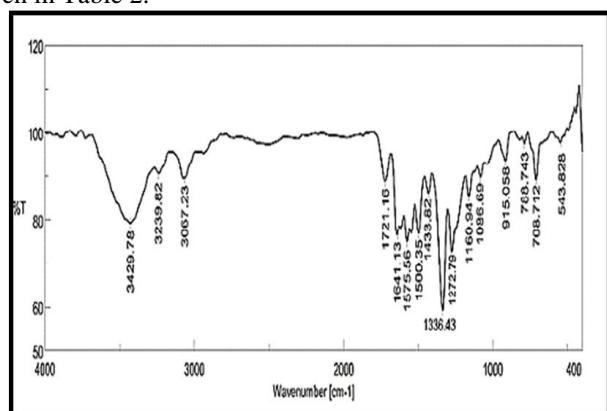


Fig 3. FTIR graph of 0.5 mol% L-lysine doped LPP

Table 2 Vibrational Band Assignments for Pure and doped LPP Crystal

Vibrational Band Assignment	Pure LPP (cm^{-1})	0.5 mol% doped LPP (cm^{-1})
Symmetric stretching (C=O)	1716.57	1721.16
Bending (N-H)	1634.89	1641.13
Asymmetric stretching (COO)	1567.27	1575.56
Symmetric stretching (NH ₂)	1489.82	1500.36
Symmetric stretching (COO)	1431.66	1433.82
Symmetric stretching (NO_2)	1338	1336.43
Bending (OH)	1268.32	1272.79
Phenolic O	1162.01	1160.94
Bending (C-N in plane)	910.85	915.058
Scissoring (NO_2)	786.56	788.743
Bending (ring)	708.79	708.712
Rocking (NO_2)	545.46	543.828

UV –Vis Spectroscopy

UV –Vis Spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electron in atoms and molecules. In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by absorption of UV or visible or near IR radiation. Excitation of a bound electron from the Highest Occupied Molecular Orbital increases the spatial extent of the electron distribution, making the total electron density larger and more diffuse and often more polarizable. A vibrational excited state of the molecule contains rotational excitation and electronic excited state of a molecule also contain vibrational excitation.

Crystal plates of 0.5 mol% of L-lysine doped LPP crystals were taken for observation. Optical transmission spectra were recorded for the crystals in the wavelength region from 200 to 900 nm. The UV –Vis transmittance spectra of L-lysine doped LPP single crystals are shown in Figures 4.

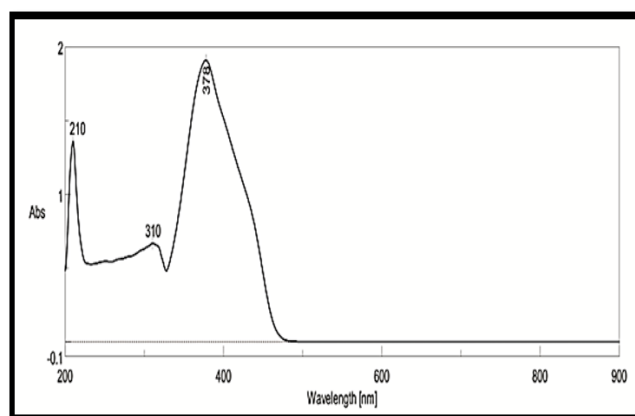


Fig 4. UV of 0.5 mol% L-lysine doped LPP

SHG Efficiency

The SHG behavior of L-lysine doped LPP crystals were observed using Q-Switched Nd:YAG laser beam of wavelength 1064 nm, with an input power of 0.68 mJ. The grown single crystal of pure and doped LPP crystals were powdered to a uniform particle size and then packed in a microcapillary of uniform bore and exposed to laser radiations. The generation of the second harmonics was confirmed by the emission of green light. The SHG output power from 0.5 mol% L-lysine doped LPP is found to be 15.6 mJ. A strong bright green emission emerging from LPP crystal shows that the sample exhibits good NLO property. This property of the crystal confirms that it can be used as optical sensors and switching devices.

THERMAL ANALYSIS

The TG/DTA thermogram of 0.5 mol% L-lysine doped LPP crystals was obtained using Instrument TGA Q500 V20.10 Build 36 thermal analyser and the resultant

thermogram is shown in Figure 5. The DTA curve shows a sharp endothermic peak at 240 °C, which confirms the melting point of the 0.5 mol% of L-lysine doped crystal. The TG thermogram reveals that decomposition starts for 0.5 mol% of L-lysine doped LPP crystals at 170 °C and continues in three distinct stages. The decomposition for 1 mol% doped L-lysine LPP as shown in Figure 5c, starts around 170 °C and proceeds in two stages leaving a little of residue at the end of the heating run at 900 °C. The decomposition is also accompanied by the melting of the sample at 238 °C as shown by DSC. This shows that the sample is undergoing complete decomposition in this study.

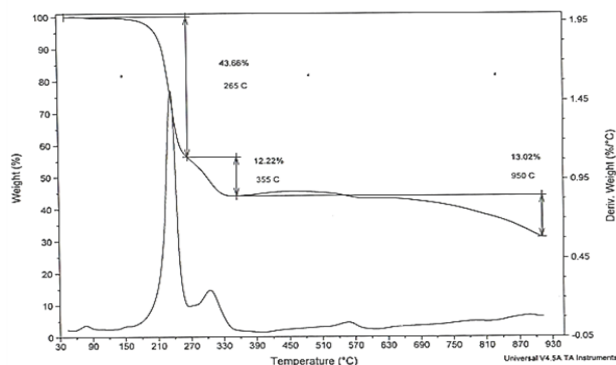


Fig. 5. TG/DTA 0.5 mol% L-lysine doped LPP crystal

IV CONCLUSION

The organic NLO crystal of 0.5 mol% L-Lysine doped, L-Proline picrate crystals were grown by slow-evaporation method at room temperature. Single crystal X-ray diffraction study reveals that the pure as well as doped LPP crystal belong to monoclinic system. Good crystallinity of the grown crystals was observed from powder XRD. Vibrational frequencies were assigned from FTIR spectral analysis, which confirms the presence of functional groups. UV spectral analysis reveals a good transparency window from 377 nm to 900 nm. TGA shows the thermal stability and decomposition behaviour of the crystal. The studies on the NLO property confirmed that the SHG of 0.5 mol% L-lysine doped LPP is better than pure LPP.

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