

COMPARITIVE STUDY OF 1 MOL% L-LYSINE DOPED IN ORGANIC AND SEMI ORGANIC MATERIALS

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Abstract— Single crystals of L-Lysine doped (1 mol %) in organic, L-Proline picrate (LPP) and semi-organic, Potassium hydrogen phthalate (KHP) were successfully grown from solution by slow evaporation method at room temperature. The lattice parameters were confirmed by single crystal X-ray diffraction. The range of optical transmission are represented by recording UV-vis analysis. The Fourier Transform Infrared spectroscopy study confirms the incorporation of L-lysine into the LPP and KHP crystals. The thermal study indicates the dissociating nature of the crystal. The nonlinear optical property of the grown crystals have been confirmed by Kurtz-powder second harmonic generation test. The dopant of 1 mol % in organic material shows higher second harmonic generation than inorganic material.

Index terms- KHP, LPP, FTIR, SHG efficiency.

I. INTRODUCTION

Nonlinear optical crystals can be used in wide range of optical applications including laser harmonic generations, frequency conversion, optical parametric generation and amplification, electro-optical Q-switching or electro-optical modulation. In recent years organic materials have been demonstrated superior second and third order NLO properties compared to the more traditional inorganic and semiorganic materials. The properties of organic compounds can be refined using molecular engineering and chemical synthesis.

In the present work, potassium hydrogen phthalate, often called simply KHP (also known as potassium acid phthalate) is an interesting material as an analyzer material in x-ray spectroscopy [1,2]. KHP, a semi organic compound crystallizes from its aqueous solution in the orthorhombic system with spacegroup $Pca2_1$. Here we are presenting a preliminary report on the growth and characterization of 0.5 mol% L-Lysine doped KHP crystals. Similarly a survey of literature indicates that an extensive work has been done on various picrate complexes. In the past two decades organic nonlinear optical (NLO) picrate crystals have attracted the scientists and information processing [3,4,5,6], high-energy lasers for inertial confinement fusion research, colour display etc. The organic picrate compounds exhibit larger NLO response than inorganic materials due to the presence of active π -bonds, however they have poor thermal stability, laser

damage threshold. 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. In the present work we are going to present the investigation of growth and characterization of 1 mol% of L-Lysine doped LPP from a mixed solvent of water and acetone.

II. EXPERIMENTAL

A. Choice of Growth Method and Solubility

The growth of good quality crystals starts with the solvent selection. Basically materials which have high solubility and have variation in solubility with temperature can be grown easily by solution method. In the solution growth method, the low temperature solution growth was preferred due to its versatility and simplicity. This technique apparently involves the use of two solvents, one in which the material to be crystallized is soluble and a second in which it is insoluble. Here the important one is that the first solvent is more volatile than the second, so the an 'solvent one' evaporates, 'solvent two' remains, eventually reaching a point where solubility of the compound can no longer be sustained. Henceforth the solubility of L-Proline picrate crystal was determined in 1:1 mixed solvent of water and acetone.

B. Growth of Organic Crystal

Crystals of L- lysine doped L-Proline picrate (L-LLPP) were grown from aqueous solution of L-proline and picric acid in the ratio of 1:1 in the presence of equimixed solvents of water and acetone. The reactants were thoroughly dissolved in the solvent using a temperature controlled magnetic stirrer for about 4-5 hours, to get a homogeneous mixture, finally 1 mol% of L-lysine is also mixed in the solution and stirred for homogeneity. Now the homogeneous solution is filtered using whatmann's filter paper and poured in a perforated vessel to enable 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 de-ionized water is $18.2 \text{ M } \Omega \text{ cm}$. After a period of 20 days, yellow coloured L-LLPP crystals with appreciable transparency were harvested having dimensions of $5 \times 1 \times 2 \text{ mm}^3$ as shown in Figure 1. The yellow colouration of the crystals may be attributed due to the inclusion of traces of

picric acid inside the crystal that tinges the outer colouration of the crystal.

C. Growth of Semi-organic Crystal

Crystals of L-lysine doped potassium hydrogen phthalate (L-LKHP) were grown by adding KHP in de-ionized water of resistivity 18.2 M Ω cm. The reactant is thoroughly stirred with the help of magnetic stirrer at room temperature, after getting a homogeneous solution 0.5 mol% of L-lysine is mixed in solution and again stirred for homogeneous solution for nearly 5 to 6 hours. Then the solution is filtered using Whatmann's filter paper and poured in a perforated vessel for slow evaporation. After a period of 25 days fine transparent colourless L-LKHP crystals of size 17 x 14 x 3 mm³ were harvested.

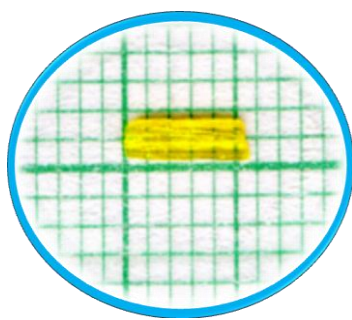


Figure 1: 1 mol% L-lysine doped LPP



Figure 2: 1 mol% L-lysine doped KHP

III. 2.CHARACTERIZATION

A. X-Ray Diffraction Analysis

In order to estimate the crystal data, single crystal XRD analysis was carried out independently for the grown L-LLPP and L-LKHP crystals using Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer with MoKα (λ = 0.71073 Å) radiation. A good quality crystal was selected for the X-ray diffraction studies. The single crystal DRD data of the grown crystal is presented in Table 1. L-LLPP crystallizes in monoclinic system with a space group of P2₁. L-LKHP crystallizes in orthorhombic with space group of Pca2₁.

Table 1 : Single Crystal XRD Data for L-lysine doped LPP and KHP crystals

Lattice Parameters	L-Lysine+ LPP	L-Lysine +KHP
a(Å)	10.96	6.53
b(Å)	5.35	9.71
c(Å)	12.51	13.40

Crystal System	Monoclinic
Orthorhombic	
Space group	P2 ₁ Pca2 ₁

B. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectral analysis of L-LLPP and L-LKHP were carried out in the middle infrared region extending from 400 – 4000 cm⁻¹ using a Perkin Elmer FTIR spectrophotometer with the aid of KBr pellet technique. The obtained spectrum is shown in Figure 3 and Figure 4. From Figure 3, the C=O symmetric stretching, O-H bending, NO₂ scissoring, NO₂ rocking curve, Symmetric stretching of COO are found. The phenolic vibration produces a peak at 1160.94 cm⁻¹. Also, it reveals that picric acid necessarily protonates the carboxyl

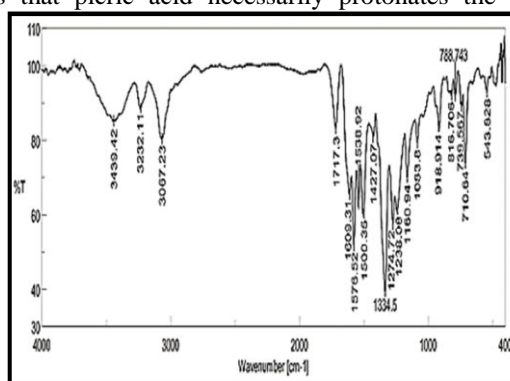


Figure 3: FTIR graph of 1 mol% L-lysine doped LPP group.

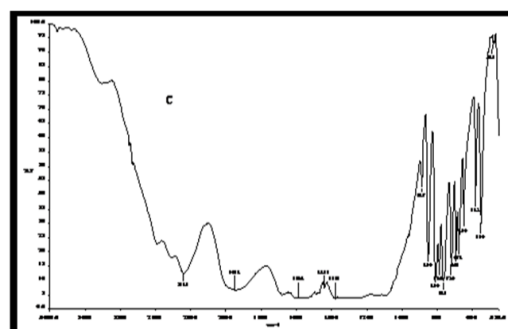


Figure 4: FTIR graph of 1 mol% L-lysine doped KHP

From Figure 4, the broad band lying in the range 3600 – 4000 cm⁻¹ corresponds to NH symmetric stretching. The broad band lying in the range 1800 – 1950 cm⁻¹ corresponds to C=C stretching. There is no NH absorption peaks at higher frequency except OH asymmetric stretch is found at 3752 cm⁻¹, this may be due to 1 mol% doping of l-lysine. This corresponding peak is not found as per literature in pure KHP crystals.

C. Thermal Analysis

The TG/DTA thermogram was obtained using SDT Q600 thermal analyzer and the resultant thermogram is shown in Figure 5 and Figure 6. The sample is found to be thermally stable till 170°C. Around 260°C the weight loss is found to be 75.6%. The residue at 900°C is around 3%. Thus the sample undergoes almost complete decomposition. The melting point of the material is 238°C as shown by DTA .

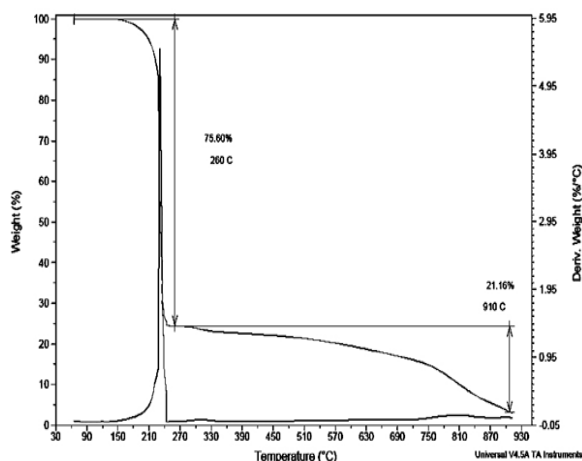


Figure 5: TG/DTA 1 mol% l-lysine doped LPP crystal

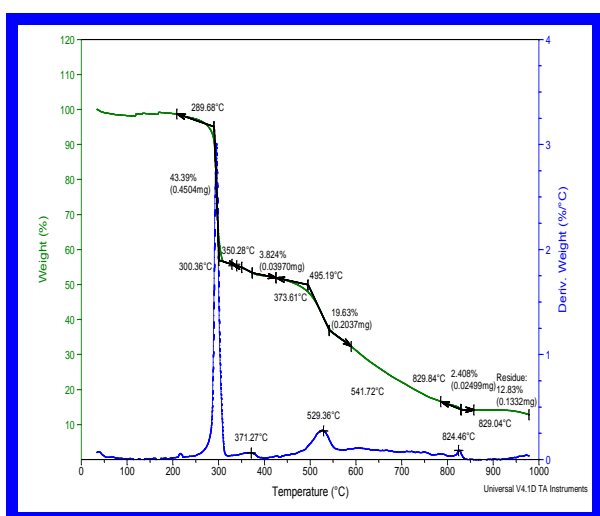


Figure 6: FTIR graph of 1 mol% L-lysine doped KHP

Figure 6 gives the thermogram graph of L-lysine doped KHP crystals. The sample decomposes at different stages. In the first stage the decomposition goes along with the phase change. The residue at the end of the thermal run is just 12.83%. The melting point of the material is at 289.68 °C as shown by DTA. This shows that the sample is undergoing complete decomposition in this study.

D. 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. Crystal plates of 1 mole % 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 1 mol% l-lysine doped LPP single crystals is shown in Figure 7. In the Figure, when the absorption is monitored from longer to shorter wavelength, the absorption is found to be nearly zero in the entire visible region of the spectrum due to the delocalization of electronic cloud through charge transfer. This is the most desirable property of the materials possessing NLO activity. The crystal is highly transparent in the entire UV, visible and near-IR region. The UV cut-off of the crystal in which the transmittance falls exactly zero is found to be 485 to 495 nm. It is clear that the doping of l-lysine does not bring in any favourable change in UV-Vis behaviour regarding the UV-cut off wavelength. The UV –Vis transmittance spectra of 1 mol% l-lysine doped KHP single crystal is shown in Figure 8. It is observed from the figure that the doped KHP has 50% of transmittance.

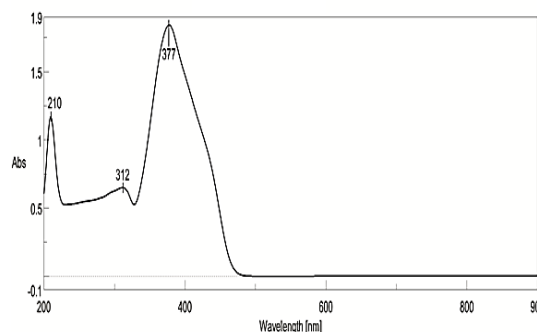


Figure 7: UV of 1 mol% l-lysine doped LPP

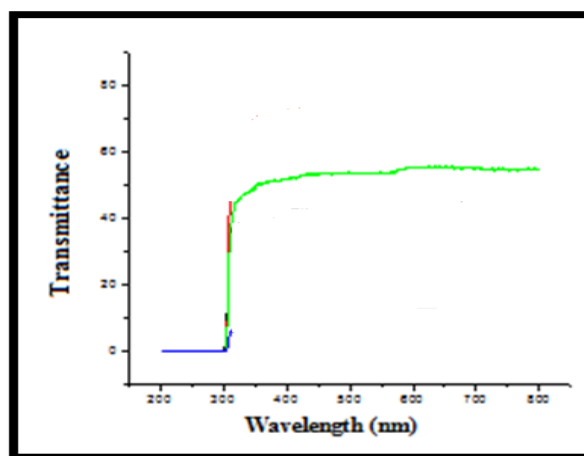


Figure 8: UV of 1 mol% l-lysine doped KHP

E. SHG Efficiency

It is highly desirable to have some technique of screening crystal structures to determine whether they are non centrosymmetric and it is also equally important to know whether they are better than those currently known. Kurtz and Perry [7] proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. The powder sample was packed in a triangular cell and was kept in cell holder. The sample was irradiated with 1064nm laser from Nd:YAG. The monochromator was set at 532nm. NLO signal was captured by the oscilloscope through the photomultiplier tube. The grown single crystal of 0.5 mol% l-lysine 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 1 mol% L-lysine doped LPP was 14.2 mJ. A strong bright green emission emerging from LPP crystal shows that the sample exhibits good NLO property. The powdered material of 1 mol% l-lysine doped Potassium Hydrogen Phthalate (KHP) 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. Second harmonic generation efficiency of the doped l-lysine of 1 mol % crystals was found. The SHG output from 1 mol% doped KHP was 5.6 mV. It is found that doping of l-lysine in organic material has higher SHG efficiency than semi-organic material.

IV. CONCLUSION

The organic and semi-organic NLO crystal of 1 mol% l-lysine doped LPP and KHP were grown by slow-evaporation method at room temperature. Single crystal X-ray diffraction was carried. Vibrational frequencies were assigned from FTIR spectral analysis. The optical transmittance spectrum of doped KHP reveals that 50% transmittance. TGA shows the thermal stability and decomposition behaviour of the crystals. The

studies on the NLO property confirmed that 1 mol% l-lysine doped LPP is better than KHP.

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