# Growth and Characterization of L-Asparagine (LAS) Crystal Admixture of Paranitrophenol (PNP): A NLO Material

Grace Sahaya Sheba, P. Omegala Priyakumari, M. Gunasekaran

*Abstract*—L-asparagine admixture Paranitrophenol (LAPNP) single crystals were grown successfully by solution method with slow evaporation technique at room temperature. Crystals of size 12mm×5 mm×3mm have been obtained in 15 days. The grown crystals were Brown color and transparent. The solubility of the grown samples has been found out at various temperatures. The lattice parameters of the grown crystals were determined by X-ray diffraction technique. The reflection planes of the sample were confirmed by the powder X-ray diffraction study and diffraction peaks were indexed. Fourier transform infrared (FTIR) studies were used to confirm the presence of various functional groups in the crystals. UV–visible absorption spectrum was recorded to study the optical transparency of grown crystal. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz–Perry powder technique and a study of its second harmonic generation efficiency in comparison with potassium dihydrogen phosphate (KDP) has been made. The mechanical strength of the crystal was estimated by Vickers hardness test. The grown crystals were subjected to thermo gravimetric and differential thermal analysis (TG/DTA). The dielectric behavior of the sample was also studied

*Keywords*—Characterization, Microhardnes, Non-linear optical materials, Solution growth, Spectroscopy, XRD.

## I. INTRODUCTION

THE development and focus on new materials possessing high NLO properties have received much attention due to their optoelectronic applications such as high speed information processing, optical communications and optical data storage device [1]. Inorganic materials were also used in these applications due to their high melting point, high mechanical strength and high degree of chemical inertness but their optical nonlinearity is poor [2]. Organic compounds are often formed by weak Van der Waal's and hydrogen bonds and hence possess high degree of delocalization. Thus they are expected to be optically more linear than inorganic compounds because the organic compounds with electron rich (donor) and deficient (acceptor) substituent provide the asymmetric charge distribution in the $\pi$ – electron system and show large nonlinear optical responses [3]. The NLO properties of large organic molecules and polymers have been

the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electrooptic effect and large second or third order hyperpolarizibilities compared to inorganic NLO materials. Thus, there is much impetus to design and understand organic compounds for SHG applications.

Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid $(COO^-)$ group and proton acceptor amino $(NH_2^+)$ group in them [4]. L-Asparagine is one of the twenty nine most common natural amino acids in living organism. It is a very important amino acid because it plays a role in the metabolic control of some cell functions in nerve and brain tissues and is also used by many plants as a nitrogen reserve source besides this being part of different drug and food. L-asparagine monohydrate $C_4H_8O3N_2.H_2O$ single crystal have orthorhombic structure [5] and belong to space group P212121 with four molecules per unit cell and lattice parameters: $a = 5.593Å$, $b = 9.827Å$, $c = 11.808Å$. The molecule is in the zwitterions form and is linked together by seven distinct hydrogen bonds forming a three dimensional network. It is an interesting material to investigate as it crystallizes in structures exhibiting a complex network of hydrogen bonds among asparagines and water molecules. Based on this, asparagine compound materials such as L-asparagine-L-tartaric acid (LALT)[6], L-asparaginium picrate (LASP) [7], L-asparaginium nitrate (LAsN) [8] and L-asparagine cadmium chloride monohydrate [9] are proved to be good NLO application materials.

In this work, an attempt has been made to synthesize and grow L-asparagine admixture Paranitrophenol crystal by solution method as well as to report the growth and characterization of L-asparagine admixture Paranitrophenol in this paper.

## II. EXPERIMENTAL PROCEDURE

### A. Synthesis and Solubility

L-asparagine admixture Paranitrophenol was synthesized using high purity L-Asparagine and AR grade Paranitrophenol from Merck in the stoichiometric ratio 1:1 with distilled water. The reactants were thoroughly dissolved in water and stirred well for about 2 hrs using a temperature controlled magnetic stirrer and yields a homogeneous solution. This solution has been kept for evaporation to dryness at room temperature.

Grace Sahaya Sheba is with the Department of Physics, VV College of Engineering, Tisaiyanvilai (phone: 9965099766; e-mail: gracesahayasheba@gmail.com).

P. Omegala Priyakumari is with the Department of Physics, Dr. G. U. Pope's College of Engineering, Sawyerpuram, Tamil Nadu, India.

M. Gunasekaran is with the Department of Physics, Regional Centre of Anna University, Tirunelveli Region, Tirunelveli – 627 007, Tamil Nadu, India (e-mail: mgunat75@yahoo.com).

Good optically transparent L-asparagine admixture Paranitrophenol crystal has been crystallized with well defined faces in a period of 18 days as shown in Fig. 1.



Fig. 1 Grown crystal of L-asparagine admixture Paranitrophenol

Solubility study was performed using L-asparagine admixture Paranitrophenol grown by slow evaporation method. The crystal was powdered and stirred in the water with different temperature by using magnetic stirrer. Fig. 2 shows the solubility curve for L-asparagine admixture Paranitrophenol salt. From the graph, it was observed that the solubility of L-asparagine admixture Paranitrophenol sample in water increases linearly with temperature, exhibiting a high solubility gradient and positive temperature coefficient, which reveals the fact that slow evaporation technique is the appropriate method to grow single crystal of L-asparagine admixture Paranitrophenol.
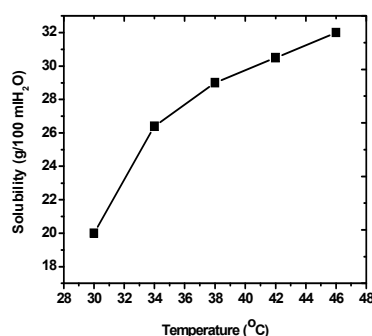


Fig. 2 Solubility of L-asparagine admixture Paranitrophenol

## III. RESULTS AND DISCUSSION

### A. Single Crystal Xray Diffraction

The grown crystals are subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD 4 diffractometer with Mo Ka radiation (k = 0.71073Å) to determine the unit cell dimensions. The structures were solved by the direct method and refined by the full-matrix least-square technique using SHELXL program. The number of molecules per unit cell (z) for the grown crystal is 4. The unit cell parameters of L-Asparagine crystal have reported [7]. The unit cell parameters of pure L-Asparagine obtained in this work are very close agreement with the reported work and marginal difference in lattice parameters have been noticed for the L-Asparagine admixture Paranitrophenol crystal compared to the pure L-Asparagine crystal which is shown in Table I.

These changes in the lattice parameter are due to incorporation of Paranitrophenol in the lattice of L-Asparagine.

### B. Powder XRD Studies

The powder X-ray diffraction analysis has been carried out to confirm the crystallinity of grown crystal by using JEOL JDX services instrument with CuKα ($\lambda$=1.548A$^0$) radiation to verify the correctness of lattice parameter values. Finally, crushed L-asparagine admixture Paranitrophenol crystal was subjected to powder X-ray analysis. The sample was scanned over the range 10-80$^0$ at a scan rate of 2$^0$ min$^{-1}$. The powder X-ray diffraction peaks are indexed from the crystal structure parameters obtained in the present study and are shown in Fig. 3.

TABLE I
CRYSTALLOGRAPHIC DATA FOR L-ASPARAGINE (LAS) ADMIXED PNP CRYSTAL

| Identification code | LAS | LAS admixed PNP |
|---|---|---|
| Crystal color | Colorless | Light Brown Color |
| Symmetry | Orthorhombic | Orthorhombic |
| Space group | P212121 | P212121 |
| a | 5.583(1) A° | 5.587 A° |
| b | 9.738(1) A° | 9.843 A° |
| c | 11.693(1) A° | 11.82 A° |
| Volume | 635.72 A$^0$3 | 649 A$^0$3 |
| Density | 1.569g/cm$^{-3}$ | 1.583 g/cm$^{-3}$ |

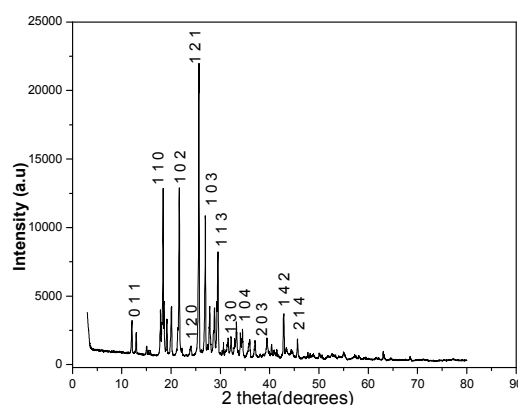cm =centimeter, A$^0$ = amstrong, J = joule, g = gram.



Fig. 3 Powder XRD of L-asparagine admixture Paranitrophenol

### C. FT-IR Spectral Studies

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify mainly, the functional groups present in organic materials. FTIR analysis provides information about the chemical bonds and molecular structure of a material. In order to qualitatively analyze the presence of functional groups in the grown crystals, the FT-IR spectrum were recorded in the range 400–4000cm$^{-1}$ using a KBr pellet on Perkin Elmer RXI FTIR spectrometer and the recorded spectra were shown as Fig. 4.
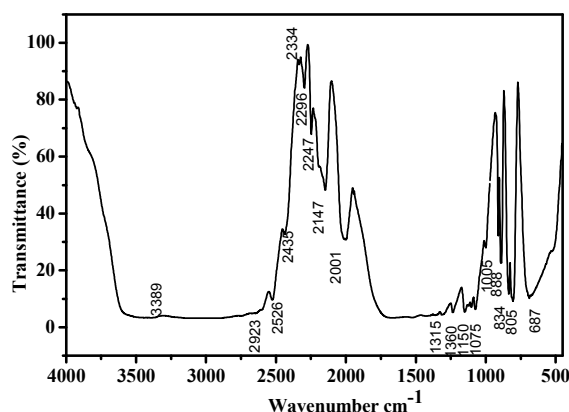
Fig. 4 FTIR of L-asparagine admixture Paranitrophenol

TABLE II
VIBRATIONAL ASSIGNMENTS FOR LAS ADMIXED PNP

| Wave number | | Vibrational Assignments |
|---|---|---|
| Pure LAS | LAS Admixed PNP | |
| 3382 | 3389 | OH bond(absorption) & N-H stretching |
| 2952 | 2923 | C-H stretching |
| 2000 | 2001 | N-H stretching |
| 1643 | 1676 | $NH_3^+$ deformation |
| 1528 | 1523 | $NH_2$ bending |
| 1458 | 1426 | $COO^-$ sym. Stretching |
| 1360 | 1360 | CH bending |
| 1314 | 1338 | $CH_2$ wagging |
| 1235 | 1234 | $NH_2$ rocking |
| 1149 | 1150 | $NH_3^+$ rocking |
| 1074 | 1075 | C-N stretching |
| 910 | 998 | $CH_2$ rocking |
| 807 | 834 | C-C stretching |
| 666 | 687 | $H_2O$ rocking |

The presence of OH is indicated by a broad absorption peak at 3389cm⁻¹ because it is intermolecular polymeric bond. By that broad absorption, the intensity changes and frequency increases on dilution. The peak obtained at 2923cm⁻¹ is due to CH stretching of $CH_2$ vibration of the amino acid. The absorption peaks observed at 1150 and 1075cm⁻¹ respond to C-H group and C-N stretch. The peaks obtained at 1523 and 1426 cm⁻¹ are due to asymmetric and symmetric vibrations of COO−. The peaks observed at 995, 834 and 687cm⁻¹ is attributed to $CH_2$ group while the peak observed at 1676cm⁻¹ is attributed to $COO^-$ group and other prominent frequencies are assigned in Table II.

*D. Optical Absorption*

The optical absorption spectrum of a good quality grown crystal was recorded in the wavelength range 200–1000nm using a Perkin Elmer Lamda 935 UV-vis-NIR spectrometer. The obtained absorption spectrum is shown in Fig. 5, where the lower cut off region is obtained at 246.112nm. The UV spectra show the presence of a wide transparency window lying between 250nm and 1000nm as shown in Fig. 6. This spectral study may be assisted in understanding the electronic structure of the optical band gap of the crystal. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of

whether the band structure is affected near band extreme [10]. Hence, from the analysis of the absorption spectrum, it is evident that the grown crystal is transparent in the entire visible region without any absorption peek, which is the key for any nonlinear optical crystal having applications in second harmonic generation (SHG).
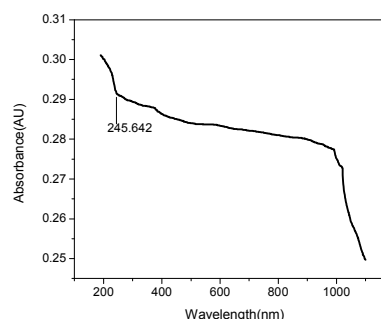


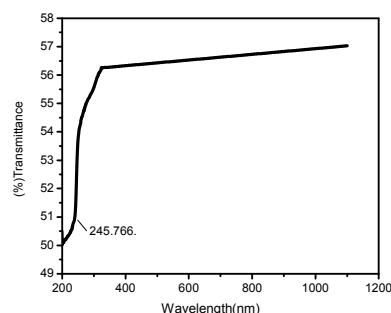Fig. 5 UV Absorption of L-asparagine admixture Paranitrophenol



Fig. 6 UV Transmittance of L-asparagine admixture Paranitrophenol

*E. Dielectric Studies*

The dielectric constant ($\varepsilon_r$) and the dielectric loss (tan δ) of LAPNP single crystal were measured using LCR meter (Agilent 4284A) in the frequency region 1 kHz–1 MHz. Defect free and transparent crystals were selected and used for the electrical measurement. For good conduction, opposite faces of the sample crystals were coated with good quality graphite. The dielectric constant and the dielectric loss were estimated for varying frequencies under different temperature slots from 35 to 100°C. From the graph, it is observed that as the temperature increases, the value of dielectric constant and the dielectric loss increase to a considerable value (Figs. 7 and 8).
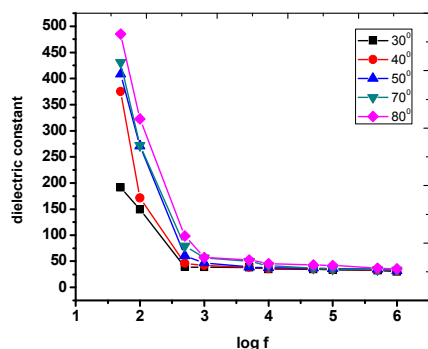
Fig. 7 Dielectric Constant of L-asparagine admixture Paranitrophenol

The high values of $\varepsilon_r$ at low frequencies may be due to presence of all the four polarizations namely, space charge, oriental, ionic and electric polarizations and its low value at high frequencies may be due to the loss of significance of these polarizations gradually. It is to be noted here that space charge polarization is dominant and electronic and ionic polarizations are not very much active in low frequency region [11], [12]. In accordance with Miller's rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient [13]. The low value of dielectric loss at high frequency reveals the high optical quality of the crystal with lesser defects, which is the desirable property for NLO applications.
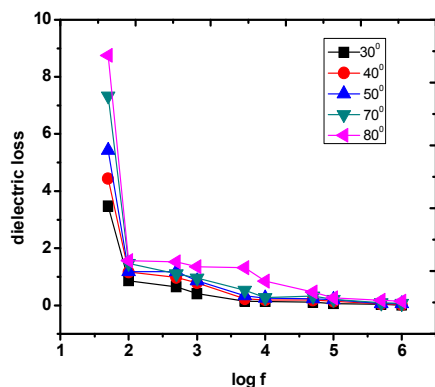


Fig. 8 Dielectric loss of L-asparagine admixture Paranitrophenol

### F. Thermal Studies

The thermogravimetric (TG) and differential thermal analyses (DT) of L-asparagine admixture Paranitrophenol were carried out between 33 and 1000z ∘C at a rate of 20∘C/min in nitrogen atmosphere using a STA 409C analyzer. Fig. 9 shows the simultaneously recorded TGA and DTA of NCS.
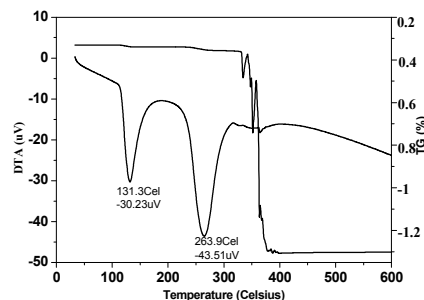


Fig. 9 TG/DTA of L-asparagine admixture Paranitrophenol

The weight loss at about 332.5∘C is assigned to loss of water. The presence of water in the lattice is also identified from the IR results. It is followed by a major weight loss at about 343.5°C. The residue that results after this decomposition also undergoes degradation at about 549°C. Since there is no weight loss below 332.5°C, there might not be any physically adsorbed water on the surface of the crystal. Though the TGA trace shows weight loss at about 332.5°C, the corresponding DTA trace shows weight loss starting at about131.3°C.

### G. Vicker's Microhardness Analysis

Microhardness is an important for good quality crystals along with good optical performance. The Vicker's microhardness study was made on the as grown face of L-asparagine admixture Paranitrophenol for the static indentation tests in air at room temperature. The Vicker's microhardness values were calculated using the formula $Hv = 1.8544P/d^2$ kg/mm$^2$, where P is the applied load and d is the average diagonal length of the indentation. A plot is drawn between the hardness values and corresponding loads is shown in Fig. 10. It was observed that hardness increases with increase in load up to 100g. Beyond the load of 100g multiple cracking were developed in the crystal surface due to the release of internal stress generated locally by indentation.
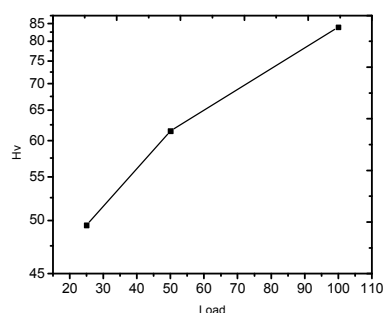


Fig. 10 Microhardness of L-asparagine admixture Paranitrophenol

### H. SHG Measurements

The second harmonic generation property of the grown crystals was investigated using a Q-switched Nd:YAG laser by Kurtz and perry technique [14]. In this technique the sample was prepared by sandwiching the graded crystalline powder with average particle size of about 90m between two

quartz sides using copper spacers of 0.4mm thickness [15]. The sample was ground into very fine powder and tightly packed in a micro capillary tube. The second harmonic generation signal of 8.45 mJ for L-asparagine admixture Paranitrophenol crystal was obtained for an input energy of 0.68 J. But the standard KDP crystal gave an SHG signal of 8.8 mJ for the same input energy. Thus, it is observed that the SHG efficiency of the grown single crystal is nearly equal to the standard KDP crystal. Thus, the grown L-asparagine admixture Paranitrophenol sample has improved NLO properties compared to L-asparagine crystals as in the Table III.

## IV. CONCLUSION

Good quality single crystal of L-asparagine admixture paranitrophenol of size 12mm×8m×3mm has been grown by slow evaporation technique. The solubility of L-asparagine admixture paranitrophenol sample was estimated for water solvent at different temperatures. The X-ray diffraction studies confirmed the orthorhombic structure of the grown crystal. The changes in the lattice parameter are due to incorporation of Paranitrophenol in the lattice of L-Asparagine. The FTIR spectrum reveals the mode of vibration of different molecular groups present in the title compound. The optical studies reveal that grown crystals possess transmittance. SHG studies reveal that L-asparagine admixture paranitrophenol crystal is a promising candidate for NLO applications. The TG/DTA studies confirmed the thermal stability up to 300∘C. The dielectric constant and dielectric loss of the grown L-asparagine admixture paranitrophenol crystal decreases with increase in frequency and these low values at high frequencies reveal the desirable property of the crystal for NLO device applications.

TABLE III
SHG STUDIES OF L-ASPARAGINE ADMIXTURED PARANITROPHENOL

| Material | NLO values |
|---|---|
| L-Asparagine | 8.2mJ |
| Paranitrophenol | 6.2mJ |
| L-Asparagine + Paranitrophenol | 8.45mJ |

mJ =milli Joule.

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