

Synthesis and Characterization of Crystal Structure and NLO Properties of a New Mixed L-Leucine Doped in Ammonium Dihydrogen Phosphate

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Abstract:- Ammonium dihydrogen phosphate (ADP) ($\text{NH}_4\text{H}_2\text{PO}_4$) single crystals were grown by slow evaporation method using doped 1% L-Leucine. The X-ray diffraction analysis of the as-grown ADP crystals showed that it possess tetragonal structure having lattice parameters $a = 7.504 \text{ \AA}$ and $c = 7.6694 \text{ \AA}$. The Fourier transform infrared spectroscopy (FTIR) of as-grown ADP crystal taken between wave-number 400 to 4000 cm^{-1} showed peaks due to vibration and stretching of functional group PO_4 , P-OH and HO-P-OH in 400 to 907.12 cm^{-1} , $\text{P}=\text{O}$, NH_2 and P-O-H in 1099.31 to 1732.22 cm^{-1} and $\text{O}=\text{P-OH}$, P-O-H and O-H-O in 2414.99 to 3260.97 cm^{-1} range. The thermal properties of the as-grown ADP crystals were studied by thermogravimetric analysis (TGA). The thermal activation energy determined from the TGA curve using Broido, Piloyan-Novikova (PN) and Coats Redfern (CR) relations were in good agreement with each other. The relative second harmonic generation efficiency (SHG) was examined by Kurtz powder technique. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1064 nm, generating about 10.3 mJ and pulse width of 10 ns was used for the present experimental study. The obtained results are discussed in details.

Keywords: FTIR, XRD, SHG, UV, L-Leucine.

I. INTRODUCTION

Ammonium Dihydrogen Phosphate (ADP) is a representative of hydrogen bonded materials that possesses excellent dielectric, piezoelectric, anti-ferroelectric, electro-optic and nonlinear optical properties. Growth and studies of ammonium dihydrogen phosphate is a centre of attention to researchers because of its unique properties and wide applications. Single crystals of ADP are used for frequency doubling and frequency tripling of laser systems, optical switches in inertial confinement fusion and acoustic-optical Devices [1]. ADP crystallizes in a body centered tetragonal structure with the space group $I 4 2d$ and has tetra molecular unit cell [2] with unit cell parameters $a = b = 7.504 \text{ \AA}$ and $c = 7.6694 \text{ \AA}$. ADP has been the subject of a wide variety of investigations over the past decades. Reasonable studies have been done on the growth and properties of pure ADP [3, 4]. In recent years, efforts have been taken to improve the quality, growth rate and properties of ADP, by employing new growth techniques, and also by the addition of organic, inorganic

and semi organic impurities [5, 6]. Organic nonlinear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power as compared with inorganic materials. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid ($-\text{COOH}$) group and proton acceptor amino ($-\text{NH}_2$) group in them [7]. Amino acids, when added as impurities, have improved material properties [8]. Amino acid, L-leucine has formed several complexes, which are promising materials for second harmonic generation [9, 10]. In the light of research work being done on ADP crystals, to improve the properties, it was thought interesting and worthwhile to investigate the effect of L-leucine on ADP. In this work, the structural spectral and nonlinear optical behaviour of single crystals of L-leucine added ADP against pure ADP has been studied and reported.

II. EXPERIMENT

Ammonium dihydrogen phosphate and L-leucine (Merck-Germany) along with de-ionised water were used for the growth of single crystals. ADP was mixed with L-leucine in the ratio 1:1 to prepare 300 ml of saturated solution at 35°C. The solution was stirred for four hours using magnetic stirrer and filtered using Whatman filter paper. The filtered solution was transferred to borosil glass beaker. It was porously sealed and placed in a dust free atmosphere for slow evaporate. n. 100 ml of saturated solution of pure ADP was also prepared with de-ionised water at 30°C. The solution was stirred for four hours using magnetic stirrer. It was then filtered using Whatmann filter paper, transferred to borosil glass beaker, porously sealed and kept in a dust free atmosphere for slow evaporation. The grown Pure and 1 mol% L-leucine added ADP crystals were harvested after a period of 30 days. Crystals growth and characterization of ADP and doped ADP crystals were grown from an aqueous solution by slow evaporation and slow cooling techniques. Good quality crystals of reasonable size (40 mm X 8 mm X 7 mm) are obtained for a particular concentration shown in fig 1 and 2.

III. RESULT AND DISCUSSIONS:

3.1 Powder X-Ray diffraction (PXRD) Analysis: Powder of grown pure ADP and L-Leucine doped crystals were analyzed by XRD studies. The powder sample were loaded into X-Ray diffractometer with radiation ($\lambda=1.5406 \text{ \AA}$) with an operating voltage 40kV and current 35mA. Scanning rate was maintained at 32.8s over a 2θ range of 10-80. From this measurement we found the lattice parameters as $a=b= 7.504 \text{ \AA}$ and $c= 7.6694 \text{ \AA}$ for pure ADP and lattice parameter of L-Leucine doped crystals are well matched with the result reported [12], having symmetry space group I42d and result shows that L-Leucine entered into ADP lattice. No additional peaks are present in the XRD spectra of doped ADP crystal, showing the absence of any additional phases besides the tetragonal system, due to doping. The observed prominent peaks of all L- Leucine doped crystals are (101), (200), (112), (202), (301), (213), (114), (204), (323), are shown in fig. (2).The variation in intensity of diffracted peaks is found. The differences in the peak amplitude can be ascribed to the different sizes and orientation of the powered grains. The degree of sharpness of peaks indicates the crystalline of the grown crystals. There is small variation in lattice parameters with concentration.

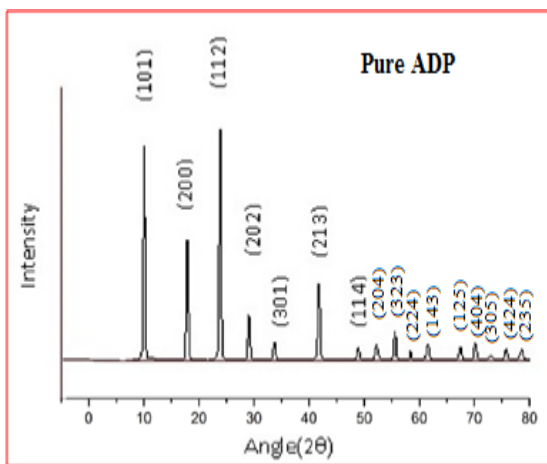


Fig 1 PXRD of pure ADP

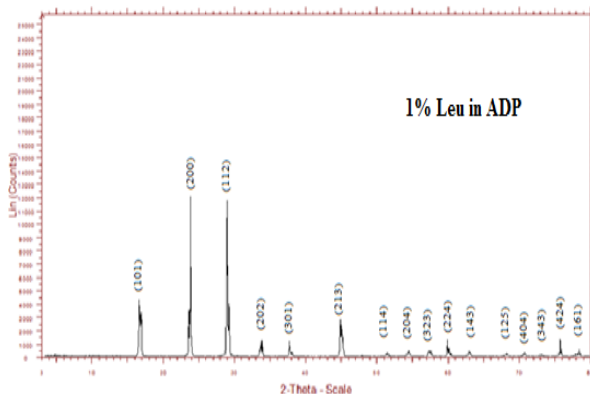
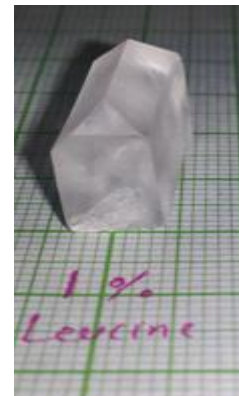


Fig 2 X-Ray Diffraction Pattern for Sample 1% Leu in ADP

3.2 Fourier Transforms Infrared (FT-IR) analysis:

The powdered samples of L-Leucine doped ADP were also attempted to Fourier Transform Infrared (FT-IR) investigation. The spectrum was observed from VARIAN resolution pro FTIR spectrometer in the range 400- 4000 cm^{-1} by KBR pallet technique. The prominent peaks in the FT-IR pattern for different concentration of L-Leucine doped ADP crystals are shown in the fig. 5. The FT-IR spectra of pure ADP and L-Leucine doped ADP shows that band in the high energy region is due to free O-H stretching of water, P-O-H group of pure and L-Leucine doped ADP [13]. Graphs of pure ADP and L-Leucine doped ADP have high similarities which indicate pure ADP peaks are predominant over L-Leucine peaks due to very small doping of L-Leucine. From FT-IR spectrum of pure and L-Leucine doped ADP it is been observed that all major peaks have shifted towards the higher wave number region, which indicates that dopant L-Leucine has brought about this changes.



1% Leu in doped ADP Crystal

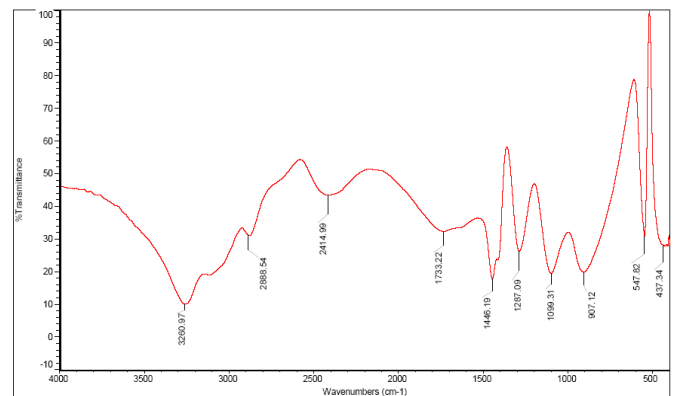


Fig 3 FTIR of 1% Leucine doped ADP

The characteristics absorption frequencies of various functional groups are given in the following table no. 1.

3.3 UV-VIS spectral analysis

The UV-Vis-NIR spectral Absorption was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer with a single crystal of 6 mm thickness in the range of 200-1200 nm. The recorded spectrum is shown in figure. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 250 nm; the transmission percentage of 1% Leucine added in ADP

crystal is around 85%, as compared to pure ADP, which is around 83%.

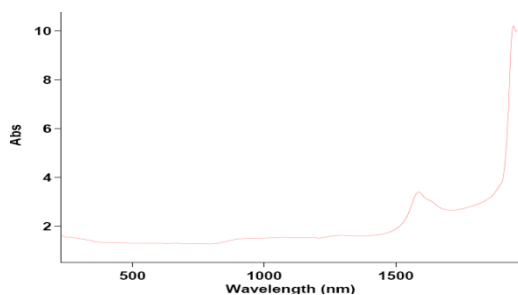


Fig.4 UV-VIS Absorption spectral analysis

CONCLUSION:

Optical quality, colorless and pure and 1 mole%, L-Leucine doped ADP crystals were grown by slow evaporation technique at room temperature. The powder X-ray diffraction studies of pure and L-Leucine doped ADP showed that crystal possesses tetragonal structure having I42d symmetry space group, with lattice parameter in good agreement with JCPDS data card no. 850815. Even after doping crystal system remains unchanged. Intensity peaks of L-Leucine doped ADP crystal resembles with diffraction angle of pure ADP crystal with negligible small variation, while intensity variation observed. The FT-IR spectrum confirms the presence of all functional group of L-Leucine.

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Table 1 FTIR of L-Leucine doped ADP

SN	Functional group	Pure ADP cm ⁻¹	1 %L-Leu+ADP cm ⁻¹
1	O-H-O stretching	3246	3260.97
2	P-O-H asymmetric stretching	2847	2888.54
3	O=P-OH stretching	2379	2414.99
4	O=P-OH stretching	1739	1732.22
5	NH ₂ bending	1500	1416.19
6	P=O stretching	1281	1287.09
7	P=O stretching	1089	1099.31
8	P-O-H stretching	897	907.12
9	HO-P-OH bending	557	547.82
10	PO ₄ vibration	447	437.43