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Growth, Structural, Spectral Comparative Study of 0.4 % L- Leucine & L-Histidine Doped Ammonium Dihydrogen Phosphate Single Crystals

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Abstract
Single crystals of pure and L-Leucine & L- Histidine doped Ammonium Dihydrogen Phosphate (ADP) were grown from aqueous solutions, employing slow evaporation technique at room temperature. The grown crystals were subjected characterized by powder X-ray diffraction to analyze their structural parameters. Fourier transform infrared (FTIR) spectral analysis was performed to identify the presence of various functional groups in the crystals. The UV-Visible-NIR spectral analysis was carried out to confirm the improvement in the transparency of the ADP crystal on the addition of L-Leucine & L- Histidine. The studies performed have revealed the incorporation of L-Leucine & L- Histidine into the lattice of ADP crystal. EDAX And Micro hardness Study.

Keywords: ADP, L-Leucine & L- Histidine; Crystal growth; X-ray diffraction; Single crystal, UV, FTIR, EDAX, Micro Hardness.

1.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 = 7.6264 Å and c = 7.7151 Å. 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 (-COOH) group and proton acceptor amino (-NH2) 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.


Fig 1: pure ADP **Fig 2:** 0.4%

2. 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 1:0.04 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 0.4 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 X8 mmX 7 mm) are obtained for a particular concentration shown in fig 1 and 2.

3. 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 (λ=1.5406 Å) with an operating voltage 40kV and current 35mA. Scanning rate was maintained at 32.8s over a2θ range of 10-800.From this measurement we found the lattice parameters as a=b= 7.510 Å and c= 7.654 Å 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. 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 crystallinity of the grown crystals. There is small variation in lattice parameters with concentration.

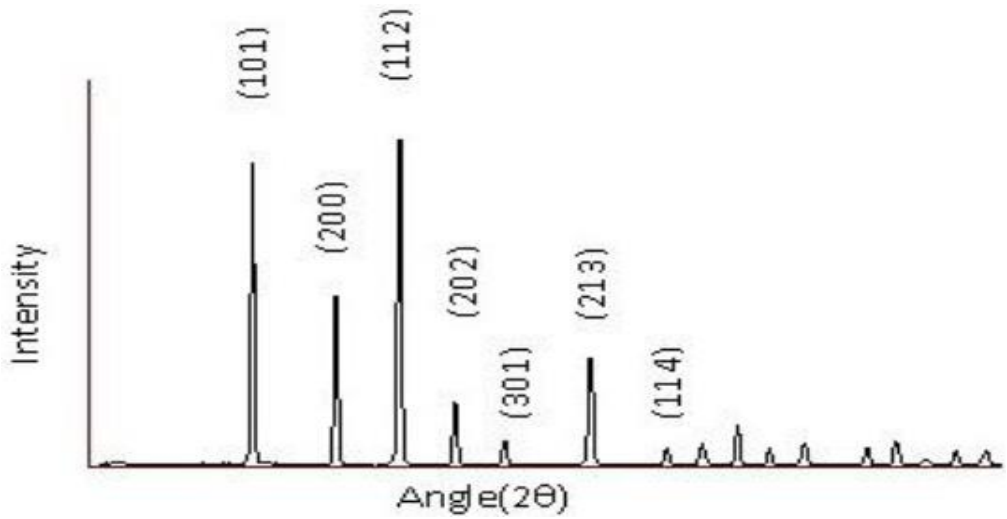


Fig 3: PXRD of pure ADP

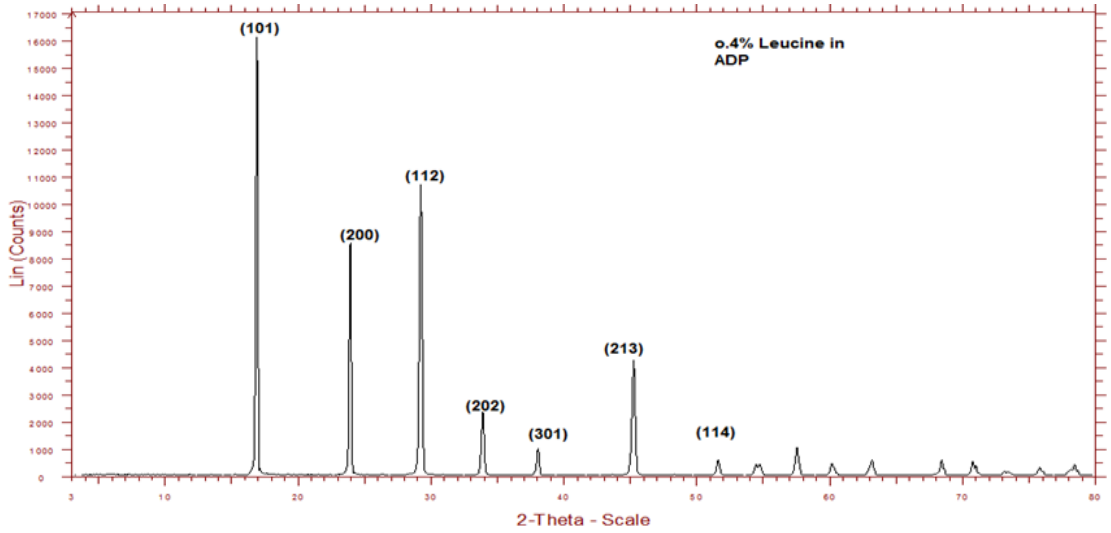


Fig 4 PXRD of 0.4% Leucine doped in ADP

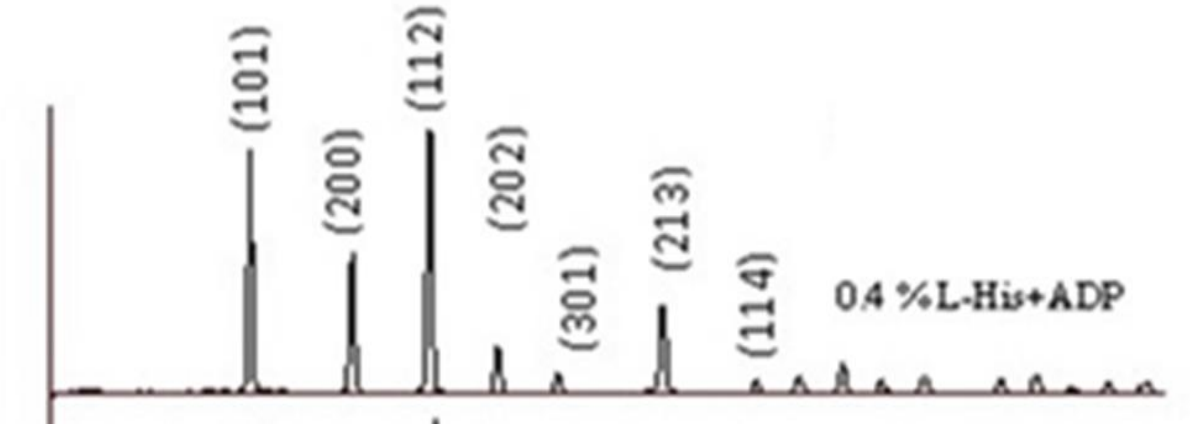


Fig 5 PXRD of 0.4% L-Histidine doped in ADP

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 these changes.

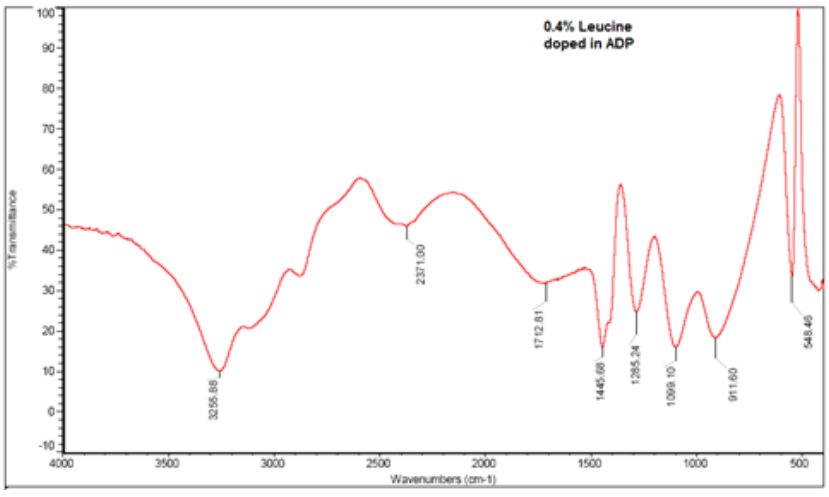


Fig 6: FTIR of 0.4% Leucine doped ADP

Table 1: Bond assignments of various frequency.

Sr.no	Frequency Range	0.4 mole%+ADP Histidine	0.4 mole%+ADP L-Leucine	Bond Assignments
1	3700-3100	3406	3255.88	O-H Stretching
2	2800-2400	2371	2371.00	Vibration of combination bond
3	1450-1200	1298	1445.65	Bending vibration of NH2
4	1100-900	897	1099.10	P-O-H vibration
5	550-430	550	548.46	PO_4 Vibration

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

Thermal study of L-Leucine & L-Histidine doped ADP single crystal

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) gives information regarding phase transition, crystallization and different stages of decomposition of the crystal system. Thermal stability is an important parameter of single crystals. TGA/ DTA studies can be exploited for routine quality control measurements, where automation capability and simple operation is the exothermal curing reaction of an epoxy resin allows the determination of the kinetic parameters. They are used to predict the reaction at other curing temperatures. Thus, valuable information on the application of thermo sets is obtained which is in research, where high sensitivity and flexibility are important aspects. TGA /DTA are powerful tool to investigate the melting behavior, Glass Transition, Crystallization, Oxidation Stability, Kinetics, Purity, and Specific Heat. TGA graph of L-Histidine doped ADP is shown in fig.

Perkin Elmer Diamond instrument was used for measurement of TGA /DTA in the variable temperature range 30-1550 ^{0}C. The measurement can also be carried out in nitrogen gas atmosphere at the rate of flow 20 ml/min. Thermal analyzer has carried out measurements at the heating rate 10 ^{0}C/ min ranging from 30 to 300 ^{0}C in the inert nitrogen atmosphere. Crystal is thermally stable up to 190-195 ^{0}C as shown in figure, after this temperature crystal starts decomposition around 330 ^{0}C and completely decomposes at 670 ^{0}C.

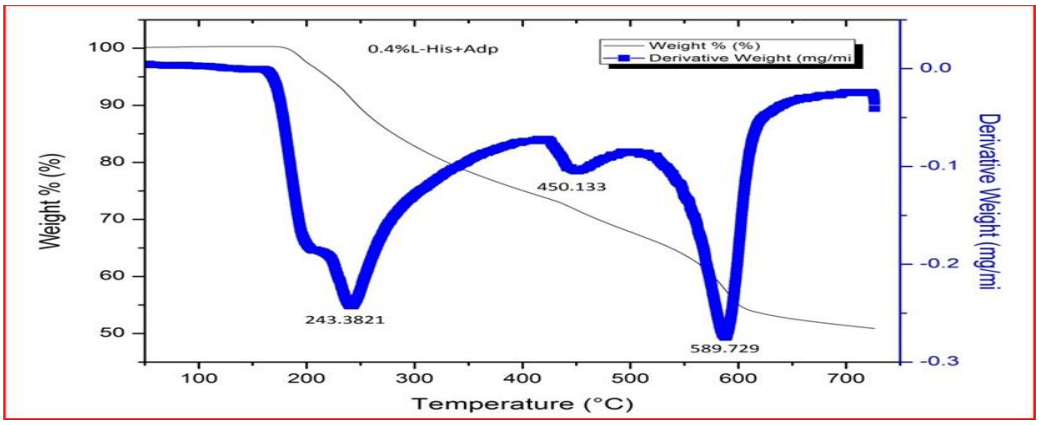


Fig 7: TGA/DTA of 0.4%L-Histidine doped ADP

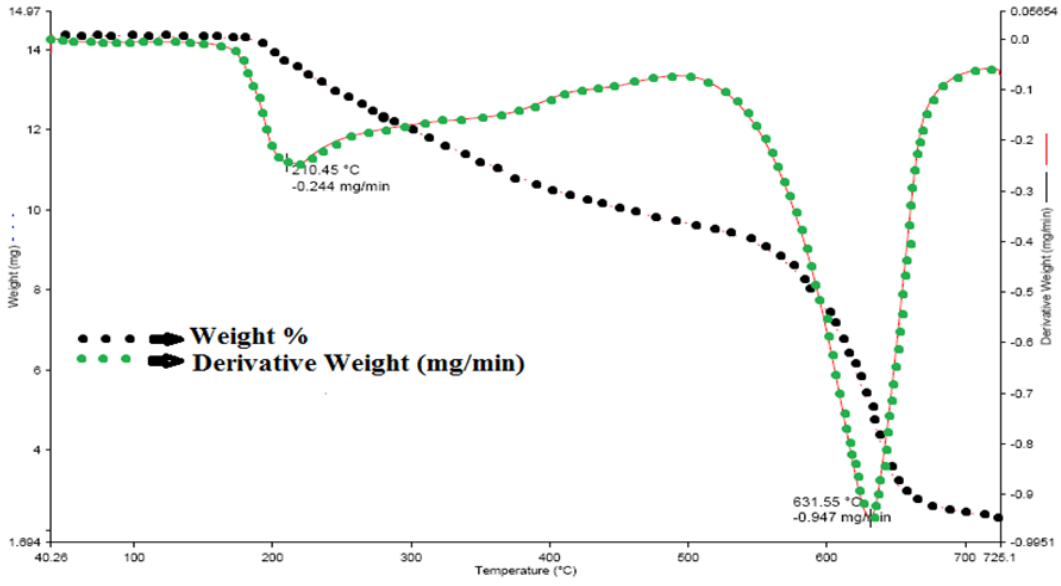
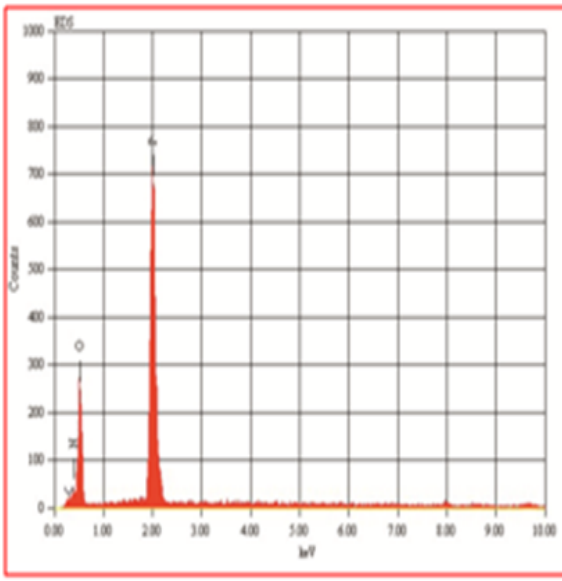


Fig 8. TGA/DTA of 0.4%L-Leucine doped ADP

EDAX characterization

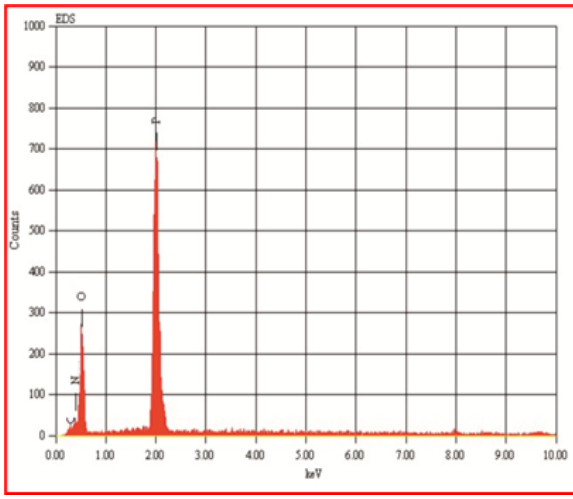
The presence of L-Histidine was confirmed from EDAX studies performed on various samples. Energy dispersive X-ray analysis (EDAX) is a micro-analytical technique, used to obtain information about the chemical composition of the grown crystal. Energy dispersive X-ray analysis (EDAX) is used in conjunction with all types of electron microscope. It has become an important tool for characterizing the elements present in the crystals. In the present investigation, the chemical composition of the crystal was analyzed by INCA 200 energy dispersive X-ray micro analyzer equipped with LEO Steroscan 440 Scanning electron microscope. The EDAX spectrum of the 0.4 mole % L-His doped ADP are shown in figure 6.4 (a),(b),(c),(d) &(e). The weight percentage (wt %) of C, N, P and O as obtained from EDAX analysis are given in the respective table

In the energy dispersive X-ray analysis, the sample is irradiated with high energy electrons. The energy of the consequent radiation emitted from the specimen is related to the atomic number of the elements present in the sample. The EDAX spectrum is a relation between intensity and binding energy of the emitted photoelectron. It is interesting to note that the peak height and area of the peaks are measures of the quantity of the elements incorporated in the specimen.



Element	(keV)	Wt %	At%
C K	0.277	0.39	0.19
N K	0.392	3.43	5.99
O K	0.525	23.98	36.66
P K	2.013	72.2	57.16
Matrix		Correction	ZAF

Fig 9: EDAX of 0.4% L-Histidine doped ADP.



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Matrix		Correction	ZAF

Fig 10: EDAX of 0.4% L- Leucine doped ADP.

Vickers's Microhardness Analysis

Hardness is a measure of a materials resistance to localized plastic deformation. The mechanical property of the materials is useful for determination of device fabrication and it is directly related to its bonding and crystallographic orientation. Vickers indentation test studied by Mitutoyo Microhardness tester on cut and polished plate of (100) plane of thickness 5 mm in size with load using Vickers hardness tester with diamond indenter attached to an incident light microscope and the indentation time was kept as 20 sec for all loads. Crystals with flat and smooth faces, microscopically free from signs of any damage are selected for indentation studies. The indented impressions are approximately pyramidal in shape. The distance between two indentation points was maintained to be more than three times the diagonal length, in order to avoid any mutual influence of indentations

Table 2 shows the Vickers hardness (Hv) for the 0.4 mole%, of L-Leu doped ADP crystals at constant load, that at 50 g the Hv of doped ADP are in the range 66 to 79 Hv. This shows that as the concentration of dopant increases the hardness property of crystals.

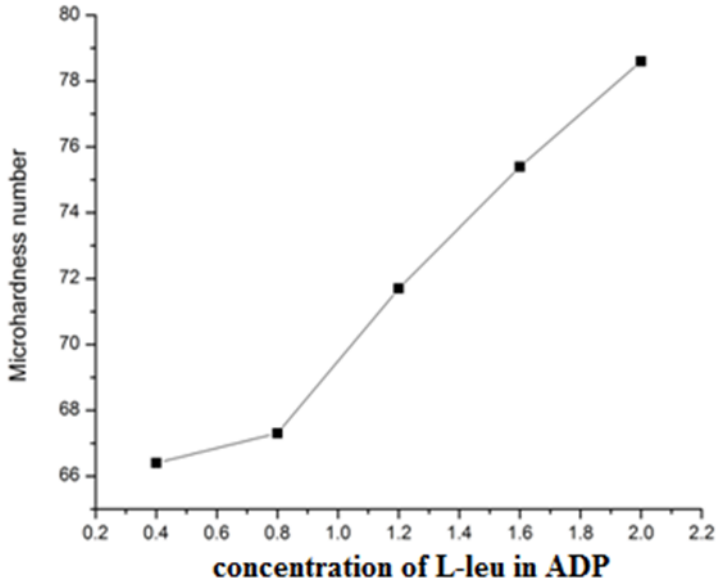

Fig. 11: Variation of Hv with Concentration of L-His L-Leu in ADP.

Table 2: Variation of Hv for constant load.

Sample	Micro hardness number	Load used
0.4%Leu &L-His +ADP	66.4 Hv	50 gm

Conclusion

Optical quality, colourless and transparent single crystals of pure and 0.4 mole% L- Leucine & L-histidine doped ADP were grown employing slow evaporation solution growth technique. The morphological parameters were discussed in order to confirm the crystal structure. The powder XRD studies reveal that tetragonal structure is preserved and that the lattice of ADP crystal is slightly distorted due to the addition of L- Leucine & L-histidine. The FTIR spectra confirm the presence of all the functional group and the presence of L- Leucine & L-histidine in the grown crystal. The optical transmission spectrum shows good transmission in entire visible and NIR region for the crystals with higher transmission for the .4 mole% L-Leucine & L-histidine doped crystal. Thus, the grown .4 mole% L- Leucine & L-histidine doped ADP crystals better than pure ADP for optoelectronic and laser applications. Synthesized crystals are subjected to EDAX, TGA-DTA and Vickers, micro hardness test. EDAX confirms the presence of dopant (.4 mole% L- Leucine & L-histidine) according to mole% of L-histidine. TGA analysis revealed the thermal stability of .4 mole% L- Leucine & L-histidine doped ADP.

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