Growth and Characterization of L- Histidine Doped Ammonium Di-Hydrogen Phosphate Single Crystal by Slow Evaporation Method.

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Abstract:
Pure Ammonium Di-hydrogen Phosphate (ADP) and Ammonium Di-hydrogen Phosphate doped with different concentration in terms of weight % of L- Histidine have been synthesized by *Slow Evaporation method* at constant temperature 35^0 C in a dust free atmosphere. The prepared crystal studied by powder XRD to determine the lattice parameters which helps to know the structure .The FT-IR analysis is carried out to identify the various functional groups of pure ADP and L- Histidine doped ADP crystal. Presence of carbon, nitrogen, phosphorous and oxygen which are constituents of pure ADP & L- Histidine doped ADP is studied from EDAX, measurement. The Dielectric properties and Micro hardness test are also done of grown crystals.
Keywords: ADP, Crystal growth, L- Histidine, PXRD, FT-IR, EDAX, Micro hardness test.

1. Introduction:

Ammonium dihydrogen phosphate (ADP) $(NH_4)H_2PO_4$ is an interesting material with wide application as a piezo-electric material in transducer devices, nonlinear optics (NLO), electro-optics, and as monochromators for X-ray fluorescence analysis[1 -6]. ADP was the first material that was used and exploited for their non-linear optical (NLO) and electro-optic (EO) properties [7]. They are used as the second, third and fourth harmonic generator in Nd:YAG and Nd:YLF lasers. Studies on ADP crystals still attract interest because of their unique nonlinear optical, dielectric and antiferroelectric properties [8-10]. L- Histidine (Amino Acids) doped ADP crystals act as sharp tool in non linear optics. In many complexes L- Histidine enhances the properties of ADP crystal. The literature shows that mostly the ADP crystals are grown by solution growth methods. Thus the authors used slow evaporation method for growth of ADP crystals. In this paper, the authors report growth of ADP single crystals by *Slow Evaporation method* and its structural, optical, thermal characterization studies. The results obtained for pure ADP and different concentration in terms of mole% of L- Histidine doped ADP crystals are given below.

2. Experimental:

2.1.1 Crystal growth.

Solution of Ammonium Di-hydrogen Phosphate (ADP) of analytical reagent (AR) grade was prepared with triple distilled water and stirred for four hours on an automatic heated magnetic stirrer. The prepared solution kept in constant

temperature bath which was maintained at 35⁰C temperature in dust free atmosphere. Within nearly 25-30 days good quality colorless & transparent crystals are formed.

Similarly, L- Histidine doped ADP crystals with 1.4 mole% and 2.0 mole%, concentrations of L- Histidine were by *slow evaporation method.*

The grown pure ADP and with various concentration of L- Histidine doped ADP crystal of good quality are as shown in fig. 1.
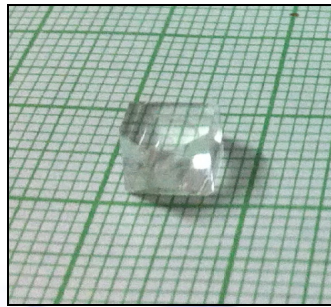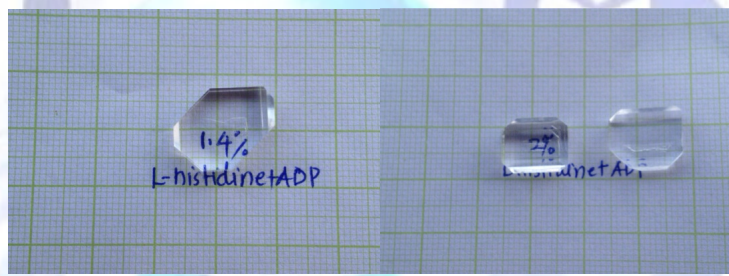

Fig. 1(a) photograph of pure ADP

Fig.1. (b) photograph of L- histidine doped ADP

3. Characterization

3.1 *Powder X-Ray diffraction (PXRD) Analysis*

Powder of grown pure ADP and L- Histidine 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 a 2θ range of 10-80⁰.From XRD measurement we have observed that the lattice parameters as a = b = 7.510 Å and c = 7.654Å for pure ADP and lattice parameter of L- Histidine doped crystals are well matched with the JCPDF data file no. 085-0815 (Delci *et al* 2013), with crystal symmetry space group I$\bar{4}$2d. The observed prominent peaks of all L-histidine 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 degree of sharpness of peaks indicates the crystallinity of the grown crystals. There is small variation in lattice parameters with concentration. The results showed that L-

Histidine entered into ADP lattice. The sharp peak indicates the crystalline nature of grown crystals. It showed that the crystal structure of ADP remains unaltered even after doping.

No additional peaks are present in the XRD spectra of doped ADP crystal, showing absence of additional phase beside the tetragonal system, due to doping. The variation in intensity of diffracted peaks is found. The differences in the peak amplitude can be as described to the different sizes and orientation of the powered grains.
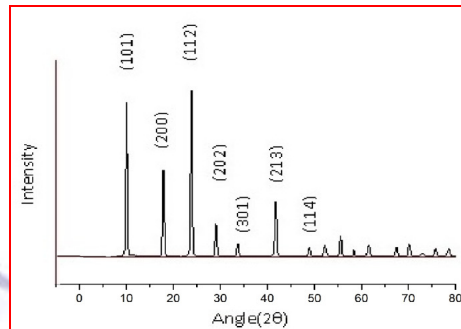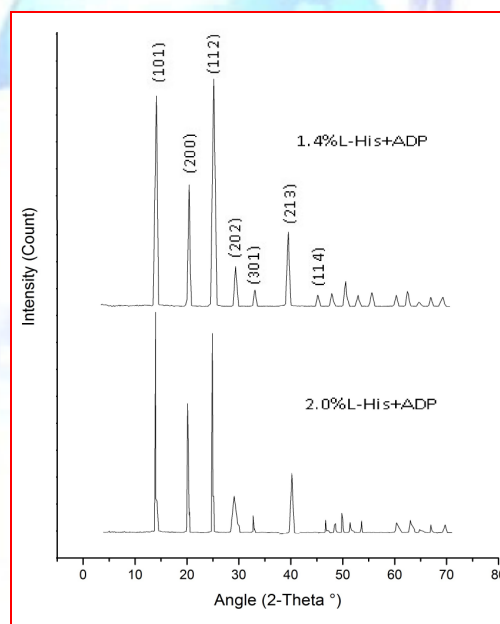

Fig2 (a) PXRD of pure ADP

Fig. 2(b) PXRD of L- Histidine doped ADP

3.2 Fourier Transforms Infrared(FT-IR) analysis:

The powdered samples of L- Histidine doped ADP were also attempted to Fourier Transform Infrared (FT-IR) Investigations. 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- Histidine doped ADP crystals are shown in the fig (3).
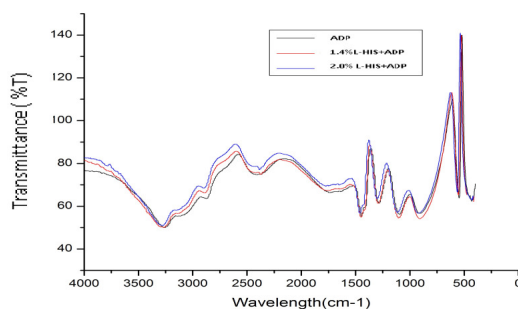
Fig. (3) FT-IR of L- Histidine doped ADP

The characteristics absorption frequencies of various functional groups are given in the following table1.

Table:-1

Sr. No.	Frequency Range	Pure ADP	1.4 mole%+ADP	2.0mole% +ADP	Bond Assignments
1	3700-3100	3259.97	3261.04	3261.86	O-H Stretching
2	2800-2400	2409.6	2410.15	2411.46	Vibration of combination bond
3	1450-1200	1443.79	1443.99	1444.30	Bending vibration of NH_2
4	1100-900	1097.76	1098.06	1198.87	P-O-H vibration
5	550-430	544.56	544.96	545.03	PO_4 Vibration

All functional group which are tabulated in table 1, are present and verified with FTIR standard spectrum data. FTIR spectrum show changes in the absorption wave number due to change in the bond length between O-H and P=O. It is found that the optical properties of pure and doped ADP changed due to the weak force of attraction of the bond between O-H and P=O. This force of attraction may not be only due to hydrogen bonding but also due to the substitution of NH_4^+ ion in the crystal lattice of tetragonal ADP crystal, which is in good agreement with the result of Ananda Kumari *at el* (2009).

3.3 Energy Dispersive X-ray diffraction (EDAX)

The presence of L- Histidine was confirmed by EDAX analysis. In the present study, 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 spectra for pure and L- Histidine doped ADP crystal recorded are shown in fig (4).
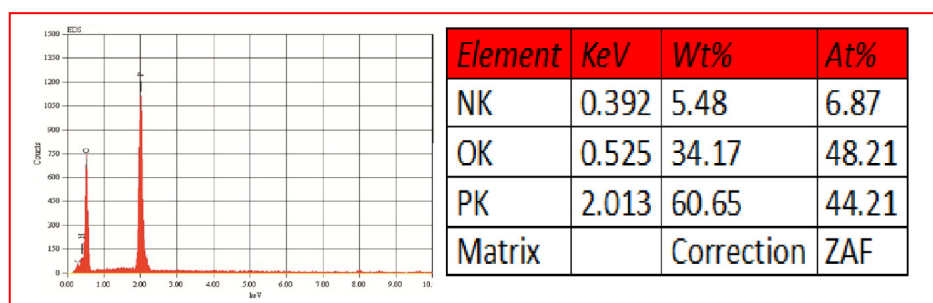

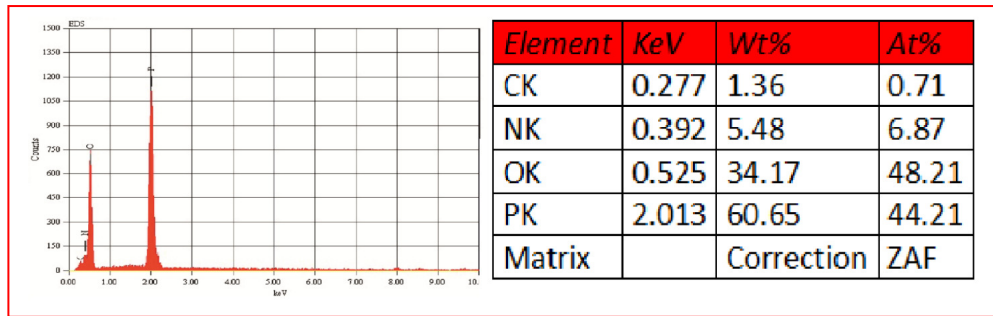| Element	KeV	Wt%	At%
NK	0.392	5.48	6.87
OK	0.525	34.17	48.21
PK	2.013	60.65	44.21
Matrix		Correction	ZAF

Fig. (a) EDAX of pure ADP

Element	KeV	Wt%	At%
CK	0.277	1.36	0.71
NK	0.392	5.48	6.87
OK	0.525	34.17	48.21
PK	2.013	60.65	44.21
Matrix		Correction	ZAF

Fig.4 (a) EDAX of 1.4 mole% L- Histidine +ADP

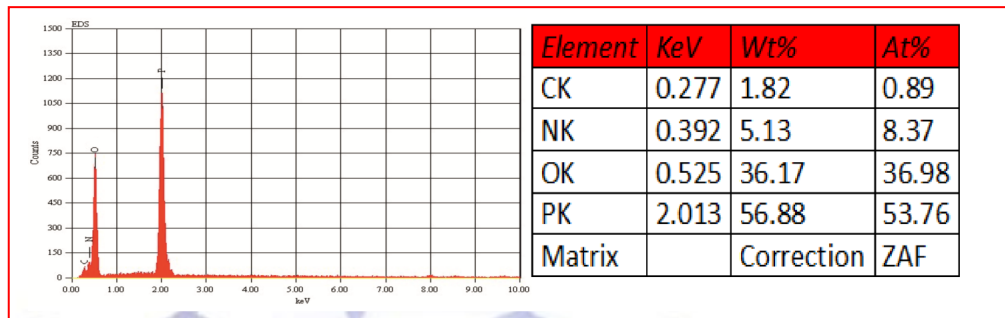| Element	KeV	Wt%	At%
CK	0.277	1.82	0.89
NK	0.392	5.13	8.37
OK	0.525	36.17	36.98
PK	2.013	56.88	53.76
Matrix		Correction	ZAF

Fig.4(c) EDAX of 2.0 mole% L- Histidine +ADP

3.4 Second harmonic generation (SHG) test:

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 1064nm, generating about 10.3mJ and pulse width of 10 ns was used for the present experimental study. The input laser beam was passed through an IR reflector and then incident on the fine powder form of the ADP specimen, which was packed in a glass capillary tube. A photodiode detector integrated with oscilloscope assembly detected the output energy. Second harmonic signal of 532nm was detected when the laser beam was passed through L-Histidine doped ADP specimen. The second harmonic generation efficiency was measured with respect to ADP. From this measurement we found that the relative SHG efficiency of L- Histidine doped ADP slightly changes that of standard ammonium dihydrogen phosphate. SHG of pure ADP is found to be 34mV. SHG efficiency results of various concentration of L- Histidine doped ADP is summarized in the table 2.

Table:-2 SHG of various concentration of L-his doped ADP

Sr. No.	L- Histidine doped%	SHG in mV	SHG Efficiency(Ratio with pure ADP)
1	0.0	34mV	1.00
2	1.4	40mV	1.17
3	2.0	43.86mV	1.29

3.5 Electrical properties

The dielectric constant is one of the basic electrical properties of solids. Dielectric properties are correlated with the electro-optic property of the crystals (Aithal et

al 1997). The capacitance (Ccrys) and dielectric constant of pure and doped ADP crystals were measuredfor temperatures from 313 to 423 ^{0}Kwith frequency (f) of 1 kHz. Good quality transparent crystals of size 3mm in thickness and 2.28mm in diameter were used for the measurements. The dimension of the samples were determined using a digital vernier calliper. A well-polished circular shape specimen of ADP crystal was chosen and surface of samples were coated with good quality silver paste in order to obtain a good ohmic contact. The samples were annealed up to 423 ^{0}K to remove water molecules if present.

Wynne Kerr 6500 (UK) impedance analyzer was used to measure dielectric nature of ADP. The properties that require investigation are the dielectric constant. The dielectric constant ε' of the material was calculated using the relation

$$(\varepsilon') = \frac{C\, d}{\varepsilon_0 A}$$

Where C is capacitance, A is the area of the specimen, d is the distance between the two parallel plates and ε_0 is the absolute permittivity of free space. We observed that as temperature increases the dielectric loss also increases but it decreases with in increasing concentration of L- Histidine in ADP. The high value of the dielectric constant with in increasing concentration of L- Histidine in ADP indicates that there are contributions from all four known sources of polarization, which are electric, ionic, dipolar and space charge polarizations. The dielectric constant variation with temperature is shown in the figure (5). The low value of dielectric loss for higher concentration of L- Histidine in ADP indicates that the grown crystals are of good quality and have negligible defects.
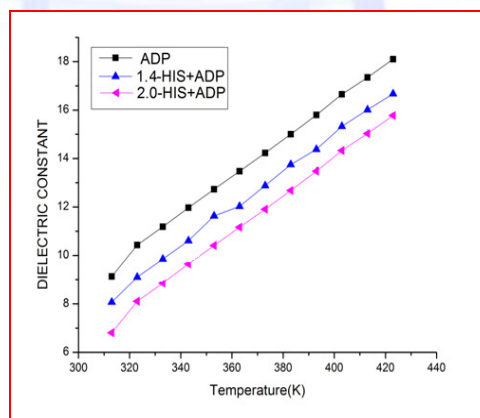

Fig. (5)Dielectric constant versus temperature

4. CONCLUSIONS:

Optical quality, colorless and purity of the 1.4 mole% and 2.0 mole%, L- histidine doped ADP crystals were grown by **slow evaporation technique**. The powder X-ray

diffraction studies of pure and L- Histidine doped ADP showed that crystal posses tetragonal structure having $I\overline{4}2d$ symmetry space group, with lattice parameter has good agreement with JCPDS data card no. 085-0815.

Even after doping crystal system remains unchanged. Intensity peaks of L-Histidine 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 and L- Histidine. As concentration of L- Histidine increases the peaks shifted towards higher wave number side. From the EDAX analysis the presence of L- Histidine is confirmed. The second harmonic generation test revealed that the increasing concentration of dopant (i.e. L- Histidine) enhances the SHG efficiency of ADP crystals.

5. Acknowledgement:-

6. References

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