# XRD, FTIR, TGA, EDX INVESTIGATIONS OF L-LEUCINE DOPED IN AMMONIUM DIHYDROGEN PHOSPHATE (ADP) SINGLE CRYSTAL

B. A. Shingade[#], R. M. Belekar[@], P. S. Sawadh[$], K. G. Rewatkar*
[#]Department of Physics, Bhawabhuti Mahavidyalaya, Amgaon, Gondia, India.-441902
[@]Department of Physics, Government Vidarbha Institute of Science & Humanities, Amravati, India 444604
[$]Department of Physics, B. D. College of Engineering Sevagram, Wardha, India.-442102
[*]Department of Physics, Dr. AmbedkarCollege,Deekshabhoomi, Nagpur, India.-440010
Corresponding author e-mail:bashingade@gmail.com

**Abstract**

**Ammonium dihydrogen phosphate (ADP) ($NH_4H_2PO_4$) single crystals were grown by slow evaporation method using doped 0.8% L-Leucine. The X-ray diffraction analysis of the as–grown ADP crystals showed that it possess tetragonal structure having lattice parameters a = 7.4854 Å and c = 7.5377 Å. 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 O-N=P and $–ONO_2$ in 400 to 912.16 $cm^{-1}$, P=O and O-H in 1100.50 to 1446.67 $cm^{-1}$ and O-H and N-H in 2409.81 to 3253.71 $cm^{-1}$ 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 and Energy Dispersive X-Ray Analysis (EDX). The obtained results are discussed in details.**

**Keywords :FTIR , XRD, TGA ,EDAX, L-Leucine.**

## 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 = 7.4854 Å and c = 7.5377 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 behavior of single crystals of L-Leucine added ADP against pure ADP has been studied and reported.


**Fig.1: Pure ADP and 0.8 % L-Leucine doped crystal**

### *2. Experimental*

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 1:0.08 to prepare 200 ml of saturated solution at 38°C and 100 ml of saturated solution of pure ADP was also prepared with de-ionised water at 35°C. The solution was stirred for four hours using magnetic stirrer[29]. 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 0.8 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 .

### *3. Characterization Analysis*

The grown single crystal of ADP was subjected to different characterization studies such as powder X- ray diffraction, FT-IR and Thermal stability of the sample was tested using DTA and thermo gravimetric analysis (TGA).

### *3.1. X-ray Diffraction Analysis:*

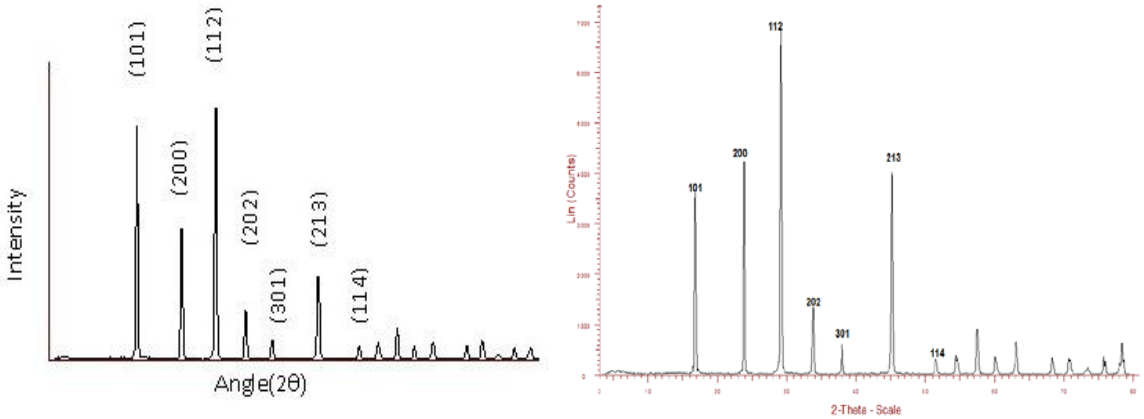



**Fig. 2: XRD of Pure ADP Crystal and 0.8% doped ADP with L-Leucine**

XRD studies were carried out with the grown crystals in powdered form. The powder samples were loaded into Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5417) with an applied operating voltage 40 kV and current 35 mA. Scanning rate was maintained at 18 $min^{-1}$ over a 2Θ range of 10–80°, employing the reflection mode for scanning. From this measurement we found the lattice dimensions as:$a$ = b = 7.4854 A˚, $c$ = 7.5377A˚,α =β=γ=90◦ having space group I42$dd$ and the lattice parameters are in good agreement with the reported values. XRD values of ADP crystallites are in good

agreement with standard JCPDS card No. 850815. There are no other phases that were observed beside the tetragonal system.. The prominent peaks in the XRD pattern have been indexed as shown in Fig2. The differences in the peak amplitude can be attributed to the different sizes and orientation of the powdered grains.

### *3.2. Fourier Transforms Infrared (FT-IR) Analysis:*

The Fourier Transform Infra Red (FTIR) investigations were also carried out on the powdered samples of ADP. The spectrum was observed from Thermo Nicolet, Avatar 370 sectrophotometer in the region 400 to 4000 cm-1 using KBr pellet. The prominent peaks in the FTIR pattern have been indexed as shown in Fig. 2. Many useful observations were observed. The group frequency region was located between 4000 cm-1 to 1300 cm-1 and the fingerprint region 1300 to 630 cm-1. The intermediate frequency range 2500 to 1540cm-1 (unsaturated region) contains triple bond frequencies which appear from 2500 to 2000 cm-1 and double bond frequencies from 2000 to 1540 cm-1. In the region between 1300 to 650 cm-1 there are single bond stretching frequencies and bending vibration of polyatomic systems involving motions of bonds linking a substituent group to the molecule.

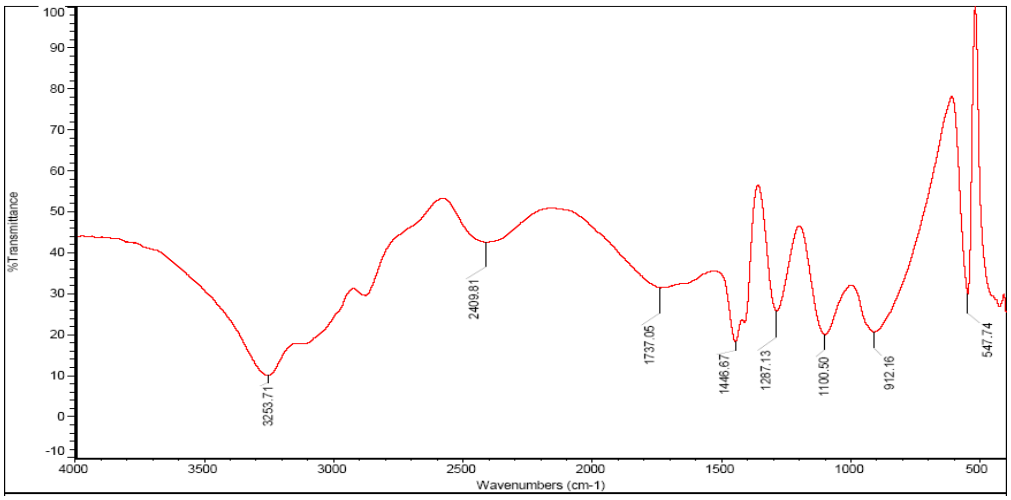



**Fig.3: FTIR of 0.8% doped ADP with L-Leucine**

In the spectrum of ADP, there is a broadband in the higher energy region due to O–H stretching vibration of ADP and water. Hydrogen bonding within the crystal is suggested to be the cause for broadening. Presence of water is supported by its bending vibrations occurring at the band 1737.05cm$^{-1}$ [27]. The bands below1300cm$^{-1}$ is duetoPO4 vibrations. It includes the OH stretch of hydrogen bonded carboxyl groups, the asymmetric stretching mode of NH3+ at 3253.71 cm$^{-1}$ and CH2 stretching mode just below 3000 cm$^{-1}$. The absorption at 1737.05 cm$^{-1}$ is assigned to C = O stretching of –COOH group. The NH 3+ displays its characteristic bending modes at 1446.67 cm$^{-1}$. The strong absorption in the range 1100.50 – 912.16 cm$^{-1}$ is evidently due to thephosphate part of the molecule. The peaks observed at 547.74cm$^{-1}$ is due to NH3+ oscillation [28].

**Table No.1: Bond assignments of various frequencies:**

| Sr.no | Frequency Range | 0.8mole%+ADP | Bond Assignments |
|---|---|---|---|
| 1 | 3700-3100 | 3253.71 | O-H Stretching |
| 2 | 2800-2300 | 2409.81 | Vibration of combination bond |
| 3 | 2000-1500 | 1737.05 | Bending vibration of NH2 |
| 4 | 1500-1000 | 1446.67 | P-O-H vibration |
| 5 | 1500-1000 | 1267.13 | P-O-H vibration |
| 6 | 1500-1000 | 1100.50 | P-O-H vibration |
| 7 | 1000-700 | 912.16 | P-O-H vibration |
| 8 | 700-500 | 547.74 | $PO_4$ Vibration |

| Crystal | a (A◦) | b (A◦) | c (A◦) | Volume (A3) | α=β=γ | System |
|---|---|---|---|---|---|---|
| Ammonium dihydrogen Phosphate (ADP) | 7.5006 | 7.5006 | 7.5490 | 425.8 | 90◦ | Tetragonal |

### 3.4. Thermo Gravimetric Analysis(TGA) :

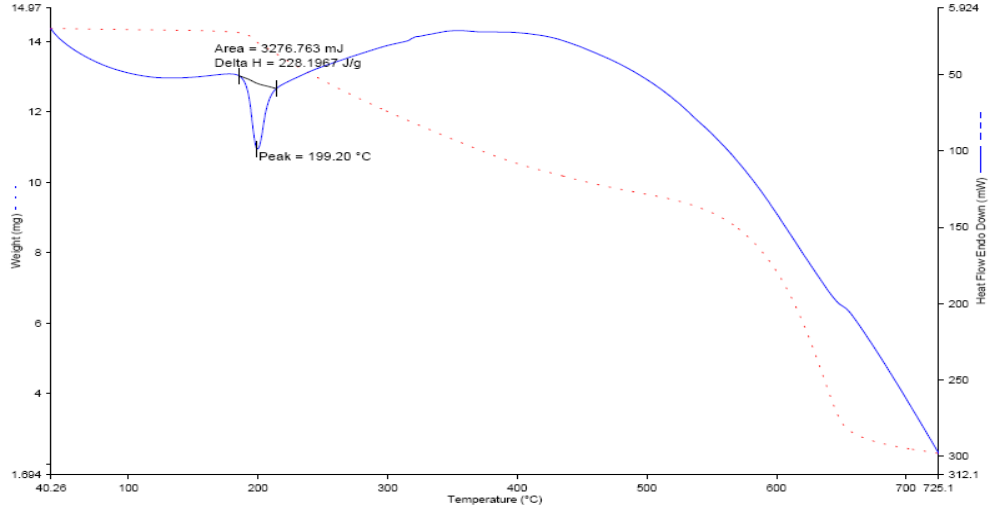



**Fig.4: TGA of 0.8% L-Leucine doped ADP**

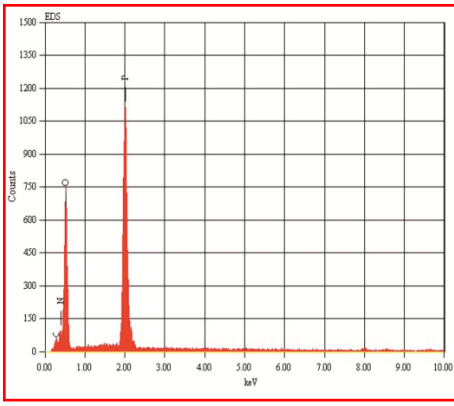
Thermo gravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. The thermo gravimetric analysis of MAP single crystal was carried out between 30 °C and 300 °C in the nitrogen atmosphere at a heating rate of 20 °C $min^{-1}$ using Perkin Elmer, Diamond TG/DTA analyzer. The thermo gram and the differential thermo gravimetric trace of USA are shown in Fig.3. In the first step of the TGA curve, there is negligible weight is lost within the temperature range from 25°C to 180°C, which indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. The second step of the TGA curve shows about 8 wt.% loss at 180°C to 570°C; that is considered as the de-bonding of bonded $H_2O$ and the elimination of organic compounds through oxidation.

It seen that the major weight loss starts at $700^0$C and it continue up to $1020^o$C. The nature of weight loss indicate the decomposition point of the material .However, above this temp no temperature, no weight loss has been observed .In the DTA the strong endothermic peaks located ~$199.20^0$C depict the crystallization of the phase of decomposed material.

### *3.5 EDAX Characterization*

The composition of the synthesized samples was determined using the energy dispersive X-ray spectroscopy (EDX) analysis. The EDX analysis of L-leucine substituted ADP samples clearly shows that the stoichiometric C, P, N and O content increased. Figure 5 Shows few representative EDX spectra of synthesized L-leucine doped ADP.EDX of samples record all peaks associated to elements of crystal like carbon, phosphorus, nitrogen and oxygen shown in Fig.5. The chemical composition quantification for L-leucine 0.8%,is presented in Table. It is noticed that doped samples do not generally show any large variations in the contents of all the metal ions from spot to spot on the sample surface suggesting regular surface and intrinsic homogeneity in the samples.

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 | 0.78 | 0.47 |
| N K | 0.392 | 3.6 | 6.21 |
| O K | 0.525 | 25.39 | 38.37 |
| P K | 2.013 | 70.23 | 54.95 |
| Matrix | | Correction | ZAF |

**Fig**.5.**EDAX Characterization of 0.8% L-Leucine doped ADP**

## 4. Conclusion

Optical quality, colorless and pure and 0.4 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 posses 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. TGA analysis reveals the different stages of decomposition. The thermal stability of doped crystal is found to be improved.

**Acknowledgement**

Authors would like to thank the Principal ,Bhawabhuti Mahavidyalaya Amgaon and express our gratitude towards Dr. P .S. Sawadh , Dr. K. G . Rewatkar, Department of Nanoscienceand Nanotechnology Dr. Ambedkar College Nagpur and UGC for funding and providing necessary support and help.

## 5. References

[1] Ram Kripal, SantwanaShukla, PrashantDwivedi, Physica B 407 (2012) 656-663.

[2] P. Rajesh, K. Boopathi, P. Ramasamy, J Crystal Growth 318 (2011) 751-756.

[3] K. Srinivasan, A. Cantoni, G. Bocelli,,Cryst. Res. Technol. 45(7) (2010) 737-746.

[4] R. AnandaKumari, Ind. J. Pure & Appl. Phys. 47 (2009) 369-371.

[5] Y. Asakuma, Q. Li, H. M. Ang, M. Tade, K. Maeda, K. Fukui, Appl. Surface Sci. 254(15) (2008) 4524-4530.

[6] XiueRen, DongliXu, DongfengXue, J Crystal Growth 310 (2008) 2005-2009.

[7] N. Zaitseva, L. Carman, Prog. Cryst.Growth Charact. 43,1 (2001) .

[8] L. Glasser, Chem. Rev. 75,21 (1975) .

[9] M.J. Gunning, R.E. Raab, W. Kucharczyk, J. Opt. Soc. Am. B18,1092 (2001) .

[10] E. Rushton, Br. J. Appl. Phys. 12.417 (1961).

[11] N. Peres, A. Boukhris, M. Souhassou, G. Gavoille, C. Lecomte, ActaCryst. A55,1038 (1999).

[12] R. Ledzion, K. Bondarczuk, W. Kucharczyk, Cryst. Res. Technol. 39, 161 (2004) .

[13] Glass, A.M. and M.E. Lines, Oxford University Press, Oxford, pp 293, (1977).

[14] Courtens.E, Helv. Phys. Acta., 56:705 (1983).

[15] Ermerl, D. Ferroelectrics, 72:95 (1987).

[16] Zaitseva, N.P., L.N.Rashkovich and S.V. Bogatyreva, J. Crystal growth, 148:-276, (1995).

[17] Dmitriev, V.G., G.G.Gurzadyan and D.N. Nikogosyan,, Springer – verlag, Berlin, Heidelberg, pp : 14 -35, (1991).

[18] A. Jayarama , S.M. Dharmaprakash," Applied Surface Science 253, 944–949 (2006).

[19] A. Claude, V.Vaithianathan, R. Barivava Ganesh, R. Sathiyalakshmi and P.Ramasamy, Journal of Applied Sciences 6 (1): 85 – 89, (2006).

[20] A. Abdel-Kader, J. Mater. Sci. - Mater.Electron.2, 7 (1991).

[21] N. Pe´ere`sy,M. Souhassouyx, B.Wynckey, G. Avoilleyx, A. Coussonzand, J. Phys: Condens. Matter 9, 6555 (1997).

[22] [16] R. Reintjes, E.C. Eckardt, Appl. Phys. Lett. 30, 91 (1977).

[23] R.J. Davey, J.W. Mullin, J. Cryst. Growth 26 ,45 (1974).

[24] R.I. Ristic, J.N. Sherwood, J. Phys. D: Appl. Phys. 24 , 171 (1991).

[25] J. Fontcuberta, R. Rodriguez, J. Tejada, J. Cryst. Growth 44 , 593 (1978).

[26] A. Boujhris, M. Souhassou, C. Lecomte, B. Wyneke, A. Thalal, J. Phys: Condens. Matter 10, 1621 (1998).

[27] C.N. Banwell, E.M. McCash, fourth ed., McGraw-Hill, NewYork, (1994).

[28] T. Balu , T.R. Rajasekaran , P. Murugakoothan, Current Applied Physics 9 435–440 (2009).

[29] S.Goma, C.M.Padma, C.K.Mahadevan. Elsevier Material latter – 60 (2006) 3701-3705