INVESTIGATIONS ON THE GROWTH AND PROPERTIES OF PURE AND L-HISTIDINE DOPED ADP CRYSTAL

A. GANDHIMATHI[a*], O. N. BALASUNDARAM[b], A. E. KUMARAN[c]
[a*]*Research Scholar, Research and Development Centre, Bharathiar University, Coimbatore, India*
[b]*Department of Physics, P. S. G. College of Arts and Science, Coimbatore, India.*
[c]*Departmentof Physics with Computer Applications, L.R.G.Government Arts College for women,Tiruppur, India*

Pure and L-Histidine doped Ammonium dihydrogen phosphate crystal have been grown by slow evaporation solution growth technique.The grown crystals have been investigated through various techniques.The functional group frequencies were identified and assigned from FTIR spectra.The XRD pattern confirms the crystalline nature and the purity of the grown crystals.UV-Vis spectrum showed that good optical quality of the crystal.The optical band gap energy was estimated as 2.7468eV and 2.1807eV respectively using Spectrofluorometer. Thermo gravimetric and Differential Thermal Analysis (TGA-DTA) measurements indicate the thermal stability of the grown crystal.Nonlinear optic measurement has been used to find the SHG efficiency.Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) are presented and discussed. The mechanical property of the grown crystals was also carrying out the Vickers microhardness measurements.

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1.Introduction

Ammonium dihydrogen phosphate (ADP) ($NH_4H_2PO_4$) is an interesting inorganic material with varied application as a piezo-electric material in transducer devices, nonlinear optics (NLO), electro-optics and as monochromators for X-ray fluorescence analysis [1-6]. The search for materials possessing high optical nonlinearity is an important task because of their practical applications in harmonic generation, optical communication, data storage, switching and other optical switching devices [7-11].

Amino acid family crystals are the famous organic materials playing an important role in the field of non-linear optics due to the fact that almost all the amino acids have chiral symmetry and crystallize in non-centrosymmetric space groups such as L-histidine nitrate, L-arginine triflurocetate. An amino acid consists of a free NH_2 (amino) and a free COOH (carboxyl) group. Both are attached to the same carbon atom. Recently several new complexes incorporating the amino acids have been crystallized and their structural, optical and thermal properties have been investigated [12-15].

Semi organic materials possess the advantage of both inorganic and organic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher second harmonic generation and high damage threshold [16-18].Many researchers have carried out studies in pure and doped ADP [19-22]. 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 [23-26]. L-Histidine ($C_6H_9N_3O_2$) is an

[*]Corresponding author: mathiegphysics@gmail.com

essential amino acid, optically active, polar aromatic and is used to develop and maintain a healthy tissue in all parts of the body.From this motivation we select amino acid as dopant for this research work.

We have grown pure and doped ADP crystals by solution growth technique and subjected to different types of characterizations Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), Fluorescence Spectroscopy, Nonlinear optic measurement (NLO), Microhardness, Thermo gravimetric and differential thermal analysis (TGA-DTA).

2. Experimental

Ammonium dihydrogen phosphate of AR (Merck) grade powder was selected as source material. This Powder was initially added with double distilled water and stirred well using magnetic stirrer for one hour continuously. Then the prepared super saturated solution was filtered with micro filter paper with 0.1 μm porosity. This mother solution was poured into two 100 ml beakers. Out of these two beakers one beaker containing the 50 ml of pure ADP solutionwas allowed to evaporate at room temperature and other beaker containing 50 ml of ADP solution was doped with 0.1 mol percent of Histidine.

Doped solution was again stirred well using magnetic stirrer and filtered again using the filter paper then covered with separate perforated paper and placed in the dust free atmosphere in separate places and allowed to evaporation at room temperature.The seed crystals were grown from the respective solutions aftertwo days. The seed crystals were harvested. Each one seed crystals were again placed in the same respective mother solutions and allowed for even growth until to attain the considerable sizes. These crystals were attained considerable size at 17 days. Fig.1 and Fig.2 shows the photograph of as grown pure and doped ADP crystals with an average size of 7x6x4mm and 7x7x3mm respectively.

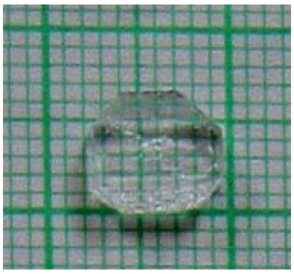

Fig.1. Photograph of as-grown Pure ADP crystal.

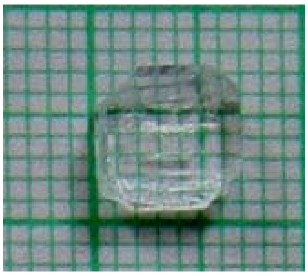

Fig.2. Photograph of as-grown Histidine doped ADP crystal.

3. Results and Discussion

3.1 Single crystal X-Ray Diffraction Analysis

The single crystal X-ray diffraction analyses of pure and doped ADPcrystals were performed using Bruker Kappa APEX II single crystal X-ray diffractometer. It is observed that both pure and histidine doped ADP crystals crystallize in the tetragonal system with the space group $I42dd$. The obtained lattice parameter values confirmed that the addition of histidine did not change the tetragonal structure of ADP.The lattice parameter values were compared with JCPDS values. The lattice parameters are in good agreement with the reported values [27].The lattice parameters are shown in table 1.

Table 1 Lattice parameters of pure and doped ADP crystals

Lattice parameters	Pure ADP Values	Doped ADP Values	JCPDS values for pure ADP
a (Å)	7.515	7.528	7.499
b(Å)	7.515	7.528	7.499
c(Å)	7.537	7.544	7.549
Volume ($Å^3$)	425.65	427.52	424.51

3.2. Powder X-ray diffraction

The powder X-ray diffraction has been recorded for pure and doped ADP crystal using Shimadzu model XRD- 6000 diffractometer.The powdered samples were scanned in the range 10-90° at a scan rate of 2°/min.The powder X-ray diffraction (XRD) patterns of the crystals were shown in the Fig.3. The sharp and well defined peaks at specific 2θ values indicate the high crystalline nature of the crystal. In the case of histidine doped ADP crystals, no new peaks are detected, rather slight shifts in the position of some peaks are observed.

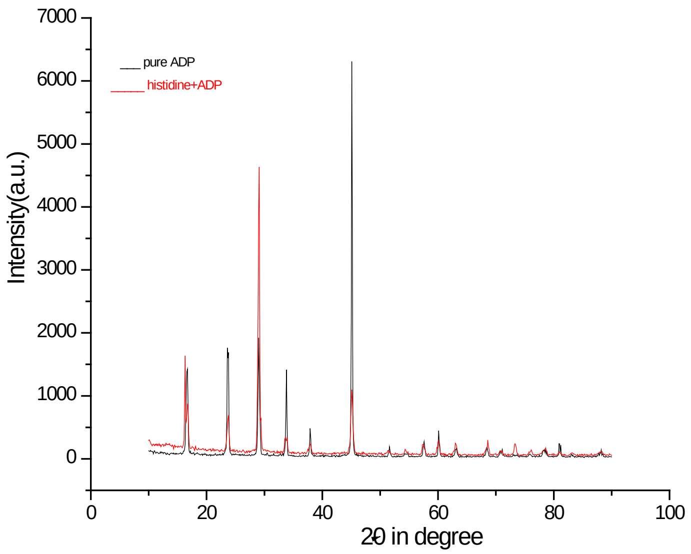

Fig.3. Powder X-Ray diffraction pattern of pure and doped ADP.

3.3 UV-Vis Analysis

Optical absorption spectra of pure and doped ADP crystals were recorded using the Jasco - Vis NIR model V-670 spectrometer in the range 200-800 nm. The large transmission in the entire visible region enables pure and doped ADP to be a good material for electro – optic and NLO applications [28]. Fig.4. shows the absorbance spectra of the grown crystals. The lower cut-off wavelength is found to be nearly 250 nm.

The high transmission in the entire visible region suggests its suitability for second harmonic generation. Good transparency in UV-visible region is due to the delocalization of electrons of bonded oxygen long P=O which is expected to largely destroy the double bond character. The presence of low cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity [29].

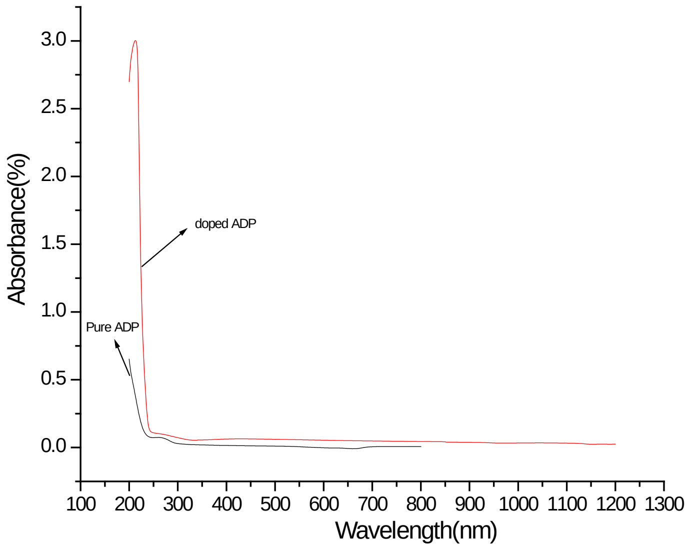

Fig. 4.UV- Vis spectrum of Pure and Doped ADP crystals.

3.4 FTIR Studies

The Fourier transform infrared spectrum of pure and histidine doped ADP crystals were recorded using Shimadzu model IR Perstege-21 spectrophotometer in the range 400 cm^{-1} and 4000 cm^{-1} and are shown in Fig.5.The absorption peaks correspond to the molecular group vibrations are tabulated in table 2. The relations of molecular group vibrations and the characteristics absorption bands were assigned according to the theories of infrared spectra [30]. The slight shoulder absorption peak in 3240 cm^{-1} is the evidence for histidine dopant doped into the crystal site.

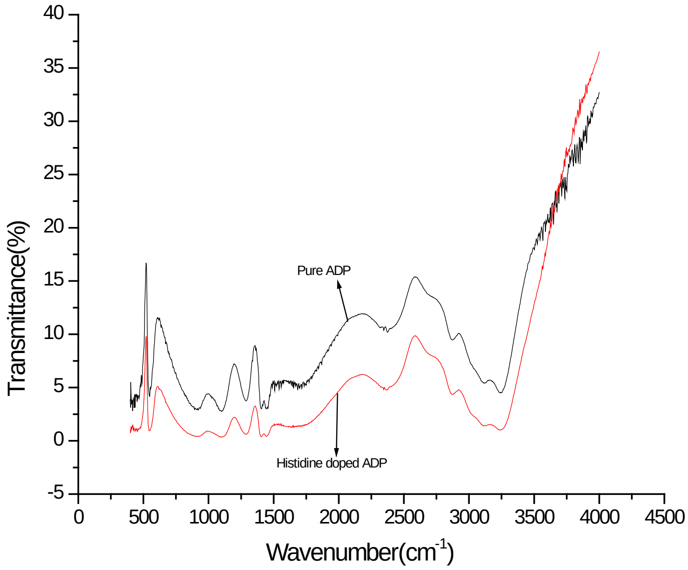

Fig. 5. FTIR Spectrum of pure and doped ADP.

Table 2 Vibrational band assignments of pure and doped ADP crystals

Observed FTIR Frequencies (cm^{-1}) for pure ADP	**Observed FTIR Frequencies (cm^{-1}) for doped ADP**	**Vibrational Assignments**
3238	3240	O-H stretching
2872	2872	Combination bond of Vibration
2378	2375	Combination band of Stretching
1404	1420	Bond vibration of NH_4
1288	1282	Combination band stretching
1101	----	P-O-H stretching Vibration
543	547	PO_4 stretching(Vibration)
430	----	PO_4 vibration

3.5 Fluorescence Studies

The spectrum recorded by the emission of photo generated minority carriers is a direct way to measure the band gap energy [31]. The emission spectra of pure and doped ADP crystals were recorded in the range 300-800 nm using Perkin Elmer model LS-45 spectrofluorometer. Fig.6 and Fig. 7 shows the emission spectrum of pure and doped ADP crystal. The peaks at 452 nm and 569 nm were observed in the emission spectrum. Band gap energy of pure and doped ADP crystals were calculated using the formula Eg= hc/λe. Where h, c and e are constant λ is the wavelength of fluorescence. The calculated band gap energy of pure ADP crystal is 2.7468 eV and doped ADP is 2.1807 eV.

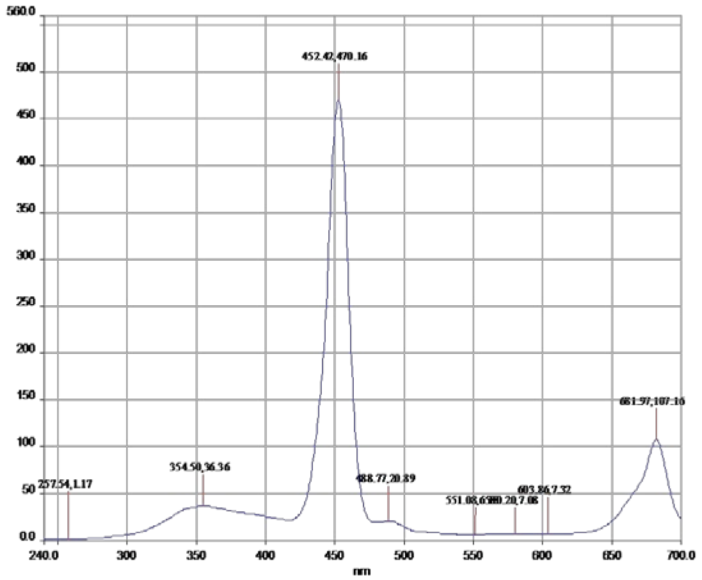

Fig.6.Emission spectrum of pure ADP crystal

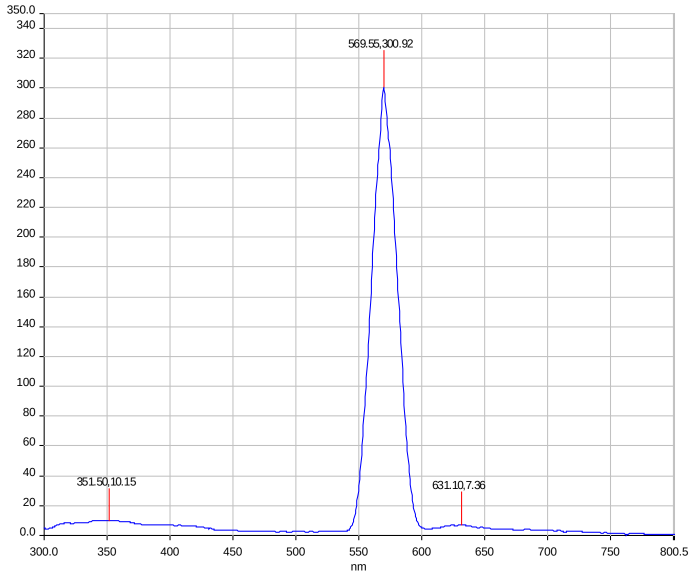

Fig.7.Emission spectrum of doped ADP crystal

3.6 Kurtz and Perry powder SHG test

Kurtz second harmonic efficiency test (SHG) is performed for the comprehensive analysis of second order nonlinearity [32].Non linear optic measurements were carried out by using Kurtz powder technique. A Q-switched Nd: YAG laser beam of 1064nm wavelength with 1.9 mJ/pulse input power, 8ns pulse width and repetition rate 10Hz was used to estimate SHG efficiency of the as grown crystals.The grown crystals of pure and doped ADP were grounded into a fine powder and then packed in a micro-capillary of uniform bore and exposed to laser radiation. The fundamental input radiation (1064nm) was separated or filtered by a monochromator and the output was measured.

Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R5 109). SHG was confirmed by the emission of green light. Using the Potassium dihydrogen phosphate (KDP) crystalline powder as reference material, the output of SHG signal were compared and found that the SHG conversion efficiency of pure ADP is 1.23 times that of KDP and doped ADP is 1.06 times that of KDP.

3.7 Thermo-Gravimetric and Differential Thermal Analysis

Thermal properties of the grown crystals were studied by using Siint model TG/DTA-6200. The analyses were carried out between 30°C and 800°C in the nitrogen atmosphere at a heating rate of 20°C min^{-1}. Fig.8. and Fig.9.Shows Thermo gravimetric and differential thermal analyses give information regarding phase transition and different stages of decomposition of crystals.It is obvious to observe that both pure and doped crystals were thermally stable until 210˚C.This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. However, above this temperature, weight loss has been observed.

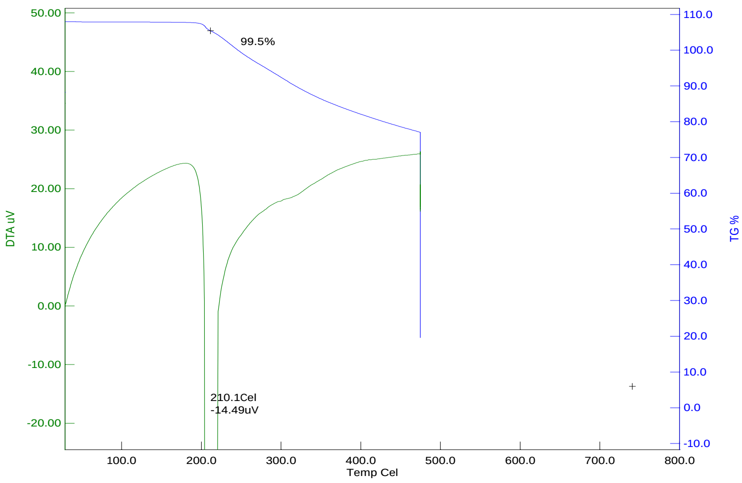

Fig.8.TGDTA curve of pure ADP crystal

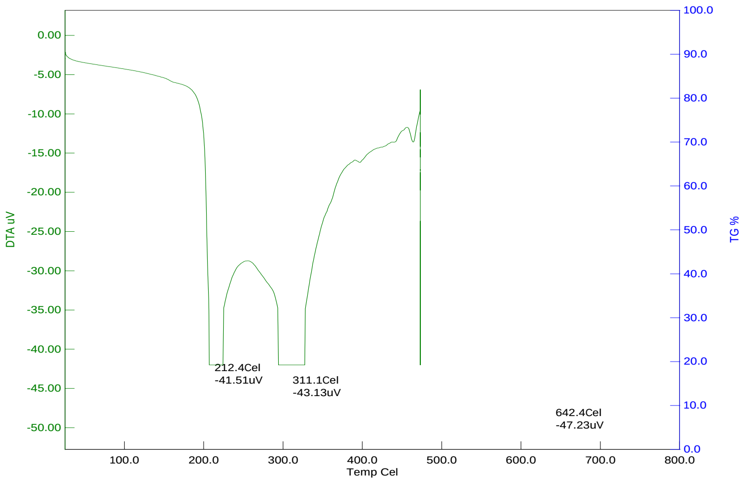

Fig.9.TGDTA curve of doped ADP crystal

3.8 Scanning Electron Microscope (SEM) Analysis

Scanning the surface with a high energy beam of electrons in a raster scan pattern is called Electron microscope. The shape and size of the particles making up the object can be viewed and studied. Scanning electron microscopy (SEM) was performed using the Jeol model JSM – 6390. SEM images were shown in the Fig.10.and Fig.11. for pure and doped ADP crystals. The SEM studies of both crystals show the optical clarity and substance nature of both crystals. The slight change in doped ADP SEM structure proves that the presence of dopant in the doped crystal.

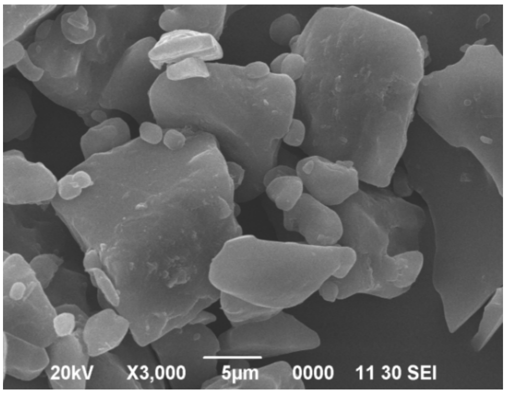

Fig.10.SEM image of pure ADP crystal

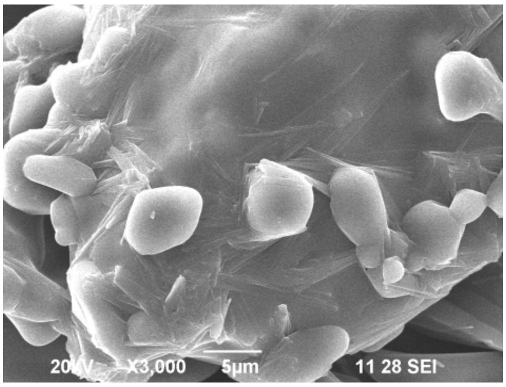

Fig.11. SEM image of doped ADP crystal

3.9 Energy Dispersive X-ray Diffraction (EDAX) Analysis

The Energy dispersive X-ray analysis (EDAX) were performed using the Jeol model JSM – 6390.The EDAX spectra for pure and doped ADP crystals are shown in Fig.12 and Fig.13. It is observed that the introduction of defects by partial cationic substitution in the host framework influences the physical properties. The elements were identified and presented. From EDAX spectrum the chemical composition weight has been calculated. The estimated % of P, O in pure ADP and P, O, C,N in doped ADP crystals are shown in table 3.

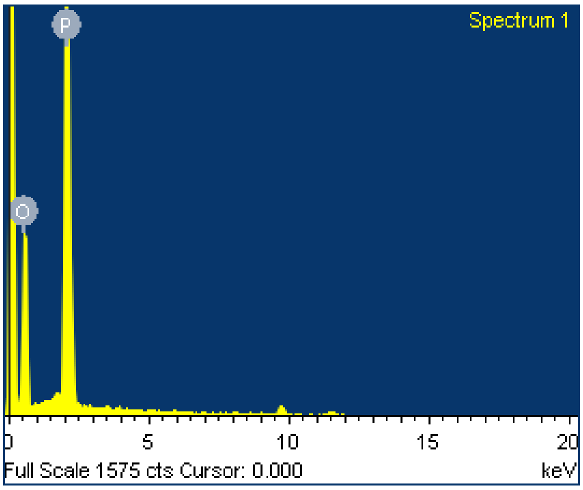

Fig.12.EDAX spectrum of pure ADP crystal

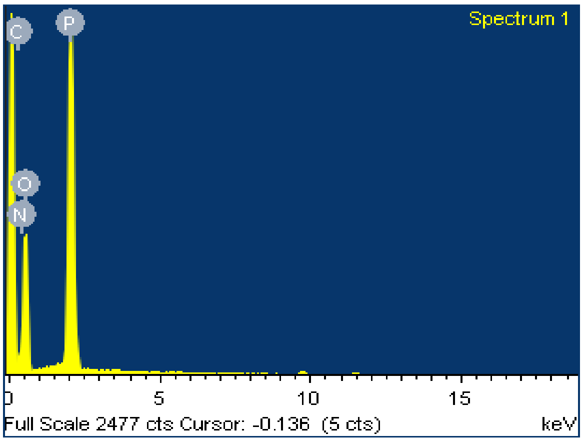

Fig.13. EDAX spectrum of doped ADP crystal.

Table 3 Estimated Weight Percentage of pure and doped ADP crystal

Element	Pure ADP		Doped ADP	
	Weight %	Atomic %	Weight %	Atomic %
OK	55.62	70.81	51.45	53.97
PK	44.38	29.19	21.88	11.86
CK	-	-	11.12	15.54
NK	-	-	15.55	18.63
Total	100	100	100	100

3.10Microhardness test

The good qualities of single crystals needed for device fabrication not only depends on optical performance but also on their mechanical behaviors [33, 34]. Vickers micro hardness test is one of the best methods to understand the mechanical properties of the materials such as brittleness and cracking [35].The as grown pure and doped ADP crystals were subjected to Vickers micro hardness test using Shimadzu model HMV-2T micro hardness tester. The indentations were made on the surface of the grown crystals by varying the load from 25 g to 100 g at room temperature with a constant indentation time of 5s.The graph plotted with load (P) and Hardness number (Hv) is shown in Fig.14. The hardness number is more in the case of doped crystal. Hardness number increases for both crystals up to 50 gram load with slight variations and slight decrease in pure ADP when load was increased compared with doped crystal.

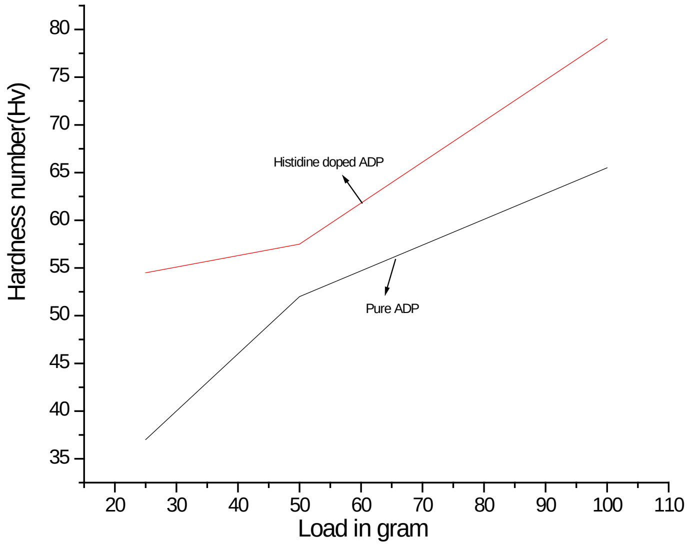

Fig. 14.Plot for Vickers Hardness of pure and doped ADP crystals.

4. Conclusions

Pure ADP and organic impurity L-Histidine doped ADP crystals were grown using slow evaporation technique in room temperature. The X-ray diffraction analysis shows the incorporation of histidine into ADP crystal lattice and the sharp well defined Bragg's peaks confirm the crystalline nature of the materials. FTIR analysis confirms the presence of organic additive histidine in Ammonium dihydrogen phosphate (ADP). The Fluorescence behavior of the crystals was determined and the SHG efficiency was also calculated. The decomposition of these crystals has been studied by Thermal Analysis. SEM reveals that the scan aspects of pure ADP and doped ADP crystals. The presence of chemical composition has been identified by Energy Dispersive X-ray Spectroscopy and its weight percentage has been calculated. From the results, it can be considered that the pure and doped ADP crystals were candidate for fluorescence, mechanical and NLO applications.

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