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Effect of Dicarboxylic Acid Dopant on Adp Crystal by Slow Evaporation Method

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Influence of dicarboxylic acid dopant on growth and characterization of ADP crystal were grown by slow evaporation technique at room temperature. The transparent (ADFU) crystals are yield after a period of 15 days. The X-ray diffraction study reveals that ADFU crystal belongs to tetragonal system. The vibrational modes of grown crystal were confirmed by FTIR spectral analysis. In UV-Vis spectral analysis the absorbance is low than pure ADP which reveals that NLO active of grown crystal is more. The emission spectrum of grown crystal was studied using fluorescence spectral analysis. The nonlinear optical property was analyzed using Kurtz-Perry technique, the SHG efficiency of ADFU crystal has much higher than that of pure ADP. The mechanical behavior includes binding nature and strength for the grown crystal was investigated by Vickers microhardness test.

Keywords: slow evaporation, NLO, XRD, FTIR hardness parameter.

1. Introduction

Ammonium Dihydrogen phosphate (ADP) is a class of hydrogen bonded, inorganic material which has piezoelectric, antiferro-electric and nonlinear optical properties. ADP crystals are mostly used in electro-optic modulator, harmonic generators and Para- metric generators [1]. Because of its birefringence property ADP crystals are widely used in optics. Crystal growth from solvent evaporation method is easy one to grow ADP crystals. The hydrogen bonded ADP can easily accept both organic and inorganic dopants [2]. Dicarboxylic acid still attracts many researchers for their massive practical applications in the field of science and technology [3].

The literature analysis reveals that the doping effect of carboxylic acid namely formic acid [4] oxalic acid, maleic acid [5–7], citric acid [7] and salicylic acid [8] has promising impact on characteristic properties of KDP crystal. The doping effect of oxalic acid and DL-malic acid on crystal growth, optical, mechanical and dielectric performance of ADP crystal has been found to be much interesting [9,10]. The coordination compounds from fumaric acid used in the production of synthetic polymers and in the production of 3D frame structures. Fumaric acid is an organic compound which exhibits luminescent, magnetic and dielectric properties have been reported in literature [11].

In the present investigation, Fumaric acid was used as dopant on the properties of Ammonium Dihydrogen Phosphate (ADFU) by slow evaporation solution growth technique. An added advantage is that large single transparent crystals are found. The details about crystal structure and properties can be found with a help of diffraction and spectroscopic techniques. The grown crystals were followed by various characterization techniques, including single and powder X-ray diffraction, FT-IR, UV-Vis and fluorescence spectral analysis, nonlinear optical test and microhardness study.

2. Experimental Procedure

Commercially available Analytical Reagent grade (AR) samples of ADP and Fumaric acid were used as solute and deionized water was used as solvent for the growth of ADFU single crystals. The 2 mol% fumaric acid dopant on ADP crystals were grown by slow evaporation technique. The solution was stirred for three hours to obtain the homogenization utilizing magnetic stirrer and filtered by whatmann filter paper. The filtered homogeneous solution was brought into Borosil glass beaker. The beaker was covered with perforated cover. Small holes were facilitated on the paper and it was left to solvent evaporation at room temperature to yield a crystal. Re-crystallization and filtration was performed to improve the purity of the crystal. After a period of 15 days the transparent, colorless crystals were harvested. The photograph of the grown crystal is shown in the Fig. 1 and the growth conditions are tabulated in the Tab. 1.

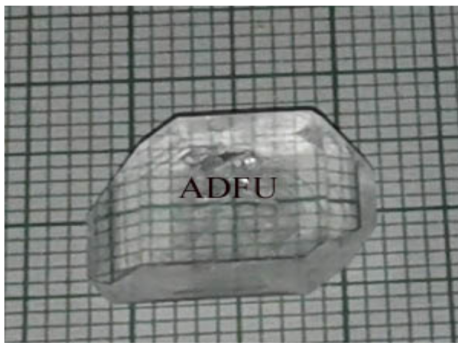

Figure 1 Photograph of ADFU crystal

Table 1 Growth Conditions of ADFU crystal

Solute	Ammonium Dihydrogen Phosphate, Fumaric acid
Solvent	deionized water
Method	slow evaporation
Growth period	15 days
Purification	re-crystallization and filtration
Size of the crystal	1.3×1.0×2.25 mm^3

3. Results and Discussion

3.1. *Single X-ray Diffraction*

The grown ADFU crystal was subjected to Single X-ray diffraction to find the unit cell parameters or lattice constants and space group. The lattice constants of the unit cell for pure ADP [12] is $a = b = 7.506$Å, $c = 7.555$Å, α=β=$\gamma = 90°$. The lattice constants of the unit cell for doped ADP is $a = b = 7.5025$Å, $c = 7.5470$Å, α=β=$\gamma = 90°$. The obtained structural parameters confirm that the grown ADFU crystallize in the tetragonal system. It may also be noted that slight variations are observed in lattice constant due to the inclusion of dopant and thus no change in their original structure.

3.2. *Powder X-ray Diffraction*

The analysis of room temperature powder X-ray diffraction pattern was recorded for ADFU crystal using Bruker D8 advance diffractometer with Cu $k\alpha(\lambda = 1.5406$Å$)$ radiation to determine the crystalline perfection. The sample was scanned through a range of 2θ angles to achieve all the possible diffraction directions of the lattice from the powdered material. The powder X-ray diffraction index pattern of present study is shown in the Fig. 2.

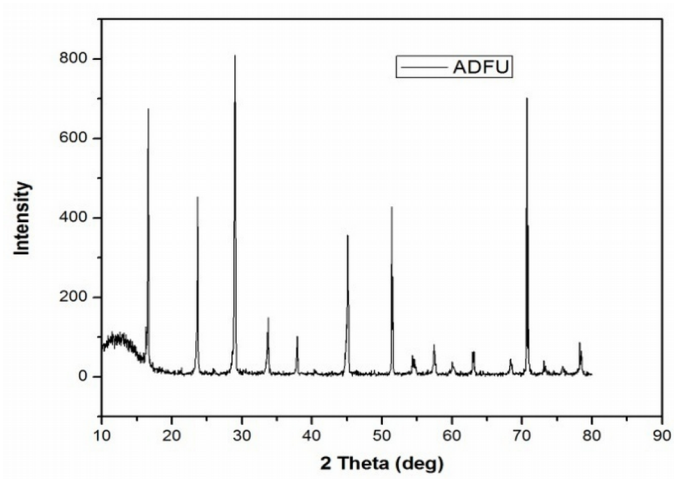

Figure 2 Powder X-ray diffraction pattern of ADFU

The presence of sharp peaks indicates the crystalline nature of the grown crystal. The obtained sharp peaks are in the plane (110), (200), (112), (211), (321), (114), (404). The crystallite size of the compound was determined associated with the sharp peak (112). Crystallinity has great impact on the application of crystal properties like mechanical, optical, thermal etc. To increase the crystallinity of the material is ascribed to its crystallites. The crystallite size and strain was calculated and compiled in Tab. 2.

Table 2 2θ, d, crystallite size (D), strain (ε) for ADFU crystal

Sample	2θ(o)	d(Å)	D(nm)	ε(lin^{-2} m^{-4})
ADFU	29.01	3.07725	63	0.031

3.3. *Fourier Transform Infrared Spectroscopy*

In order to find out the presence of functional groups in the sample, the Fourier transform infrared (FT-IR) spectrum was recorded using a Perkin-Elmer spectrometer by KBr pellet technique in the range 4000–400 cm^{-1}. The recorded FT-IR spectrum of doped ADP is shown in Fig. 3. The strong and broad band at 3129 attributes to OH stretches and water bending. The N-H bending vibrations are assigned to weak band at 1648 cm^{-1}. The peak at 913 cm^{-1} indicates the O-H vibration [13]. The presence of band 1404 cm^{-1} is due to bending vibration of ammonium. Also the reduced in the shift P=O deformation at 456 cm^{-1} is compared with pure ADP confirms the presence of doping fumaric acid in the crystal which influence the P=O functional group. A detailed assignment of the frequencies observed in the FTIR spectrum and its reference is given in Tab. 3. The assignments of the present work were compared with pure ADP which is consistent with literature value [14].

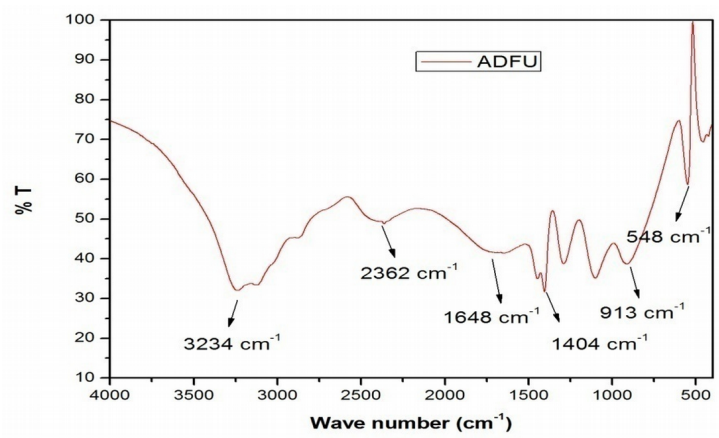

Figure 3 FTIR spectrum of ADFU crystal

Table 3 Tentative Assignments

Pure ADP	Present work	Reference [16]	Mode of Vibrations
459	456	457	Vibration of PO_4
552	548	565	$(PO4)^3$ Vibration
910	913	908	P-O-H Vibration
1090	1101	1097	P-O-H stetching vibration
1288	1290	1290	PO4 Stretching
1409	1408	1409	Ammonium bending vibration
1651	1648	1640	N-H bending of NH4
2353	2362	2432	Combination of vibrational band
3125	3129	3152	O-H stretching.

3.4. *UV-Visible Spectral Analysis*

The UV-Vis analysis is a significant tool for studying optical applications. It helps to find the optical behavior of the material. The optical absorption spectrum was recorded with a help of Perkin Elmer Lambda 35 spectrophotometer in the wavelength region 190–1100nm. The crystal which exhibits optical transparency and lower cutoff wavelength between 200–400nm is said to be an efficient non linear optical material [15]. Optical absorption spectrum of doped ADP is shown in the Fig. 4.

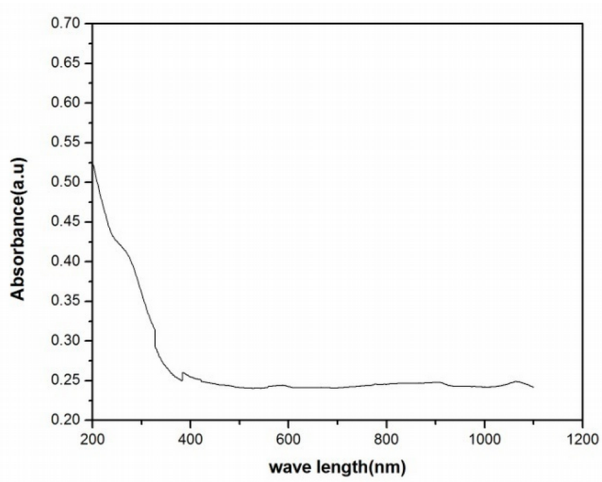

Figure 4 Absorbance spectrum of ADFU

The lower cut of wavelength is found to be 384 nm which is consistent with literature value [13]. The optical transmittance in bulk crystal medium is facilitated by optically active functional units and scattering/absorption of light due to defect centers [16]. The observed low absorption offered by ADFU crystal reveals the presence of high optical homogeneity and lesser defects. Literature survey reveals that

if the UV-Vis spectrum exhibits minimum absorbance then the possibility of that crystal is NLO active is high [13]. From the knowledge of absorption coefficient and photon energy, the band gap Eg can be estimated as 2.5eV respectively.

3.5. *Fluorescence Spectral Analysis*

The fluorescence is the most crucial nondestructive tool to evaluate the defects, surface interfaces and transition associated with the energy states. It therefore finds huge application in biomedical, photonics, and chemical applications [17]. The emission spectrum of grown ADFU crystal was recorded in the range of 280-700nm by means of Perkin Elmer model LS-45 fluorescence spectrometer. The emission behavior of the material is required to determine the surfaces, interfaces and impurity levels and to probe the alloy disorder and interface roughness. The emission spectrum of doped ADP is depicted in Fig. 5. The grown crystal has green fluorescence emission.

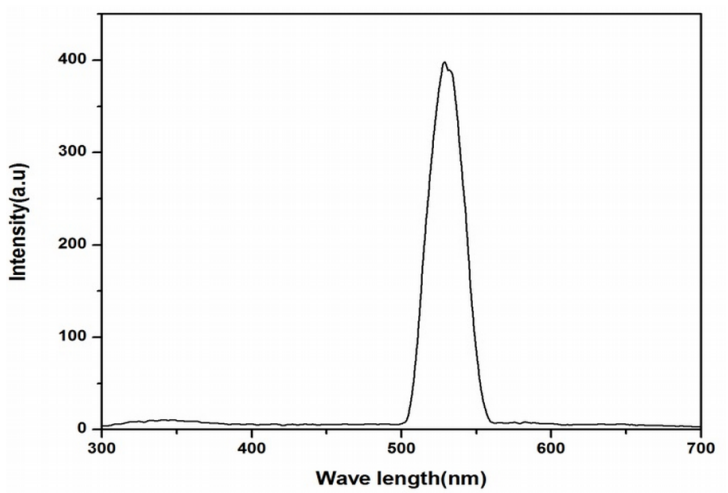

Figure 5 Emission spectrum of ADFU

3.6. *Nonlinear Optical Study*

The non-linear optical property was analyzed by Kurtz Perry powder technique. The grown ADFU crystal was subjected to second harmonic generation utilizing Q-switched high energy Nd-YAG laser of wavelength 1064 nm with repetition rate 10 Hz. The output energy of pure [18] and doped ADP is 3.6 mJ and 21.37 mJ. The result clears that SHG efficiency of doped ADP has nearly 5.9 times that of Pure ADP. The improved SHG efficiency of synthesized compound may be due to inclusion doping in ADP.

3.7. *Vickers Microhardness Study*

The microhardness study helps to assess the mechanical aspects such as crystalline stability, dislocation resistance to applied load, interatomic bonding and lattice en-

ergy of the system which play crucial role for the selectivity of the material for specific application [19]. The Vickers microhardness method is very useful in determination of strength of the crystal. Hardness of the material is essential parameter to study the mechanical application. The grown ADFU crystal was fitted with Vickers diamond pyramidal indenter at room temperature for a constant indentation period of 15 S. The experiment was carried by varying the load 25, 50 and 100 kg. The vicker's microhardness number Hv is calculated using the below expression [15].

$$Hv = 1.8544\, P/d^2 \text{ Kg/mm}^2 \tag{1}$$

where P is the applied load in g and d is the diagonal length of the indentation in millimeter. The variation of Hv with applied load is shown in Fig. 6.

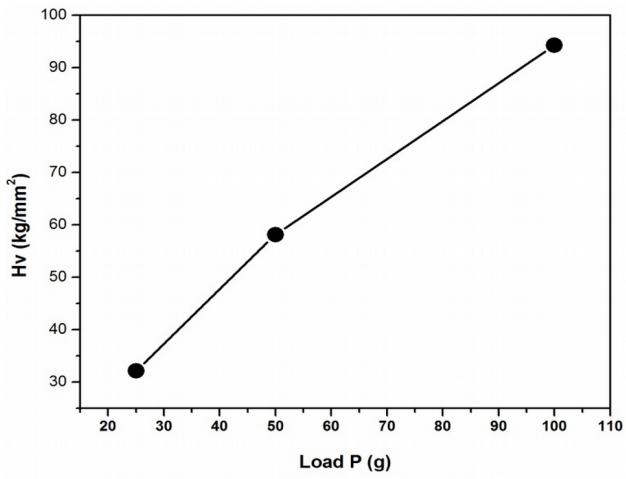

Figure 6 Load P vs. Hv

4. Determination of Meyer Index, Elastic Stiffness and Yield Strength

The load and size of indentation related by the following expression,

$$P = Ad^n\,, \tag{2}$$

Where A is a constant, P is the applied load and d is the diagonal length and the exponent n is called Meyer number (or) Meyer index. Meyer index helps to study the nature of the material. It can be evaluated by doing least square fit in the graph of log d versus log P shown in Fig. 7.

The normal ISE behavior occurs when the hardness number increases with increasing load. The reverse ISE behavior occurs, the hardness number decreases with increasing load. According to Onitsch, if $n > 1.6$, those materials are soft materials [20].

In the present investigation, the value of n is found to be more than 2 and which shows that the grown crystal is soft material. Also this shows the behavior of reverse ISE.

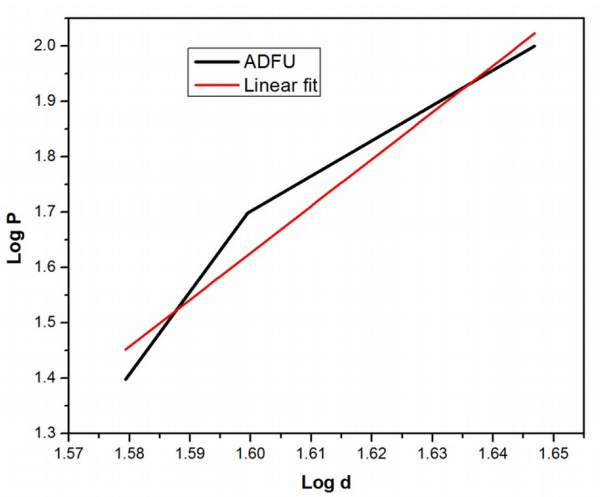

Figure 7 Log d vs. Log P

The yield strength σ_y of the material has been studied using the following expression,

$$\sigma_y = \frac{1}{3} Hv\, 0.1^{n-2}\,. \tag{3}$$

The bonding nature of the material has been determined by elastic stiffness. The elastic stiffness constant C_{11} of the material can be calculated from Wooster's expression,

$$C_{11} = Hv^{7/4}\,. \tag{4}$$

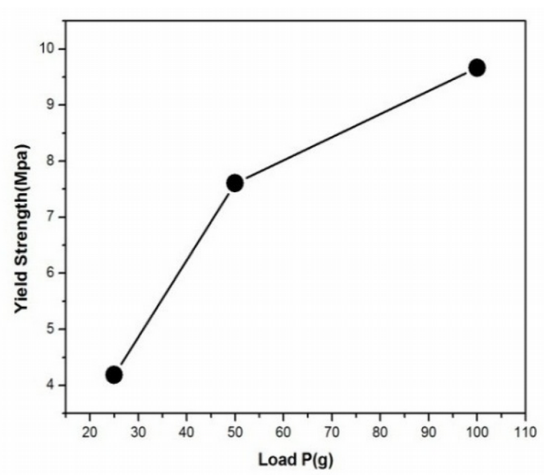

Figure 8 Load P vs. Yield strength

From the Figs. 8 and 9, the yield strength and elastic stiffness constant of the material is found to be increase with increase in load, which implies that ADFU has high mechanical stability. The higher value of elastic stiffness suggests that strong binding force exist between the ions. By using above relations (3) and (4) mechanical parameters of ADFU were calculated and presented in Tab. 4.

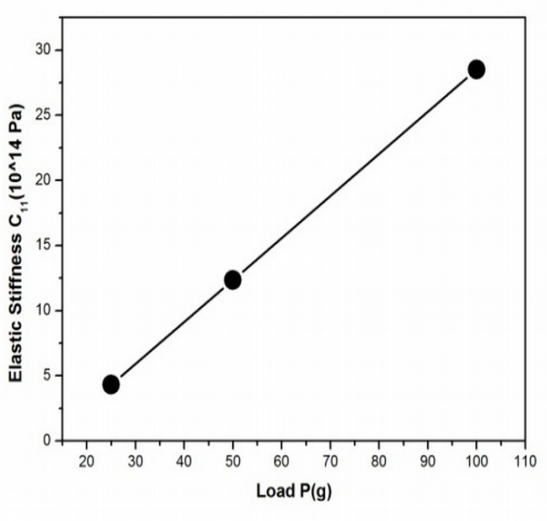

Figure 9 Load P vs. elastic stiffness

Table 4 Mechanical Parameters of ADFU

load P (g)	Yield strength (MPa)	elastic stiffness C_{11} 10^{14} Pa
25	4.184	4.34
50	7.606	12.35
100	9.662	28.50

5. Conclusions

The single crystals of fumaric acid dopant on Ammonium Dihydrogen Phosphate were grown successfully by slow evaporation technique. The grown crystals were characterized to examine the properties. The structural parameters and crystalline nature was studied by X-ray diffraction. The functional group present in the grown crystal was confirmed by FTIR spectrum and exhibits all salient features reported in the literature. The lower absorbance in the absorbance spectrum indicates that probability of NLO active is more for ADFU crystal. The green fluorescence emission of grown crystal was found by fluorescence spectral analysis. The high SHG efficiency of fumaric acid doped ADP than pure ADP was confirmed utilizing NLO study. The mechanical stability was analyzed using Vicker's hardness test. The hardness parameter includes elastic stiffness, yield strength and Meyer's index have

been calculated. The result suggest that the grown crystal suitable for NLO applications.

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