

GROWTH AND CHARACTERIZATION OF AMMONIUM DIHYDROGEN PHOSPHATE CRYSTAL DOPED WITH β - ALANINE

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ABSTRACT:

Unique non-linear optical compound of ammonium dihydrogen phosphate and ammonium dihydrogen phosphate doped with β -alanine crystals were grown by slow evaporation technique at room temperature. These crystals are analysed by powder XRD, FT- IR, FT- Raman, UV- Visible spectroscopy and SEM with EDAX examines. The powder XRD pattern affirms the crystalline nature of these crystals. The FT- IR and FT- Raman spectroscopy concentrates on affirm different functional groups present in the title compound. From the UV- Visible spectroscopy study, the grown crystals have a good transparency in the entire visible region. The morphology of the developed precious crystal recognized from the SEM microphotograph. The EDAX examination affirms the presence of the β -alanine with the ADP precious crystal.

KEYWORDS:

Ammonium dihydrogen phosphate; XRD; FT-IR; FT-Raman; UV-Visible spectroscopy; SEM; EDAX

INTRODUCTION

Examines on Ammonium dihydrogen phosphate crystal still draws in interest due to their special non-linear optical, dielectric, piezoelectric and antiferroelectric properties and their assortment of employments, for example, electro-

optic modulators, symphonies generators and parametric generators [1]. A few examination works have been completed on immaculate and doped ADP crystals [2–6]. As of late, endeavours have been taken to enhance the quality, development rate and properties of ADP by utilizing new development strategies further more by the expansion of natural, inorganic and semi natural pollutions [7–9]. Inorganic non-straight optical materials have extensive optical susceptibilities, inborn ultrafast reaction times, and high optical edges for laser power [10, 11]. In the present study, we are intrigued to develop unadulterated ADP and ADP doped with β -alanine crystals by slow evaporation technique. The grown crystals were investigated by the Powder XRD, FT-IR, FT-Raman, UV-Visible Spectroscopy and SEM with EDAX systems and their results are condensed in the present study.



MATERIALS AND METHODS

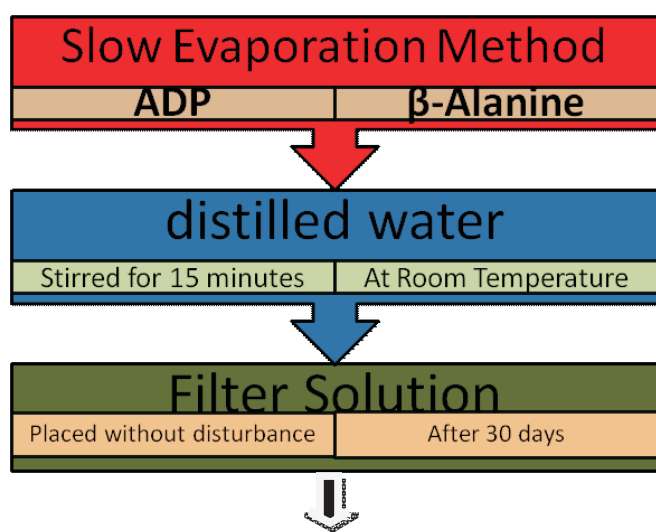
MATERIALS

The raw materials are used for crystallization (Ammonium dihydrogen phosphate (ADP), β -alanine) were purchased from the Merck India Ltd, Mumbai.

CRYSTAL GROWTH BY SLOW EVAPORATION METHOD

The Equimolar (1:1) ratio of ADP and β -Alanine salts are dissolved with distilled water. The dissolved solution stirred with magnetic stirrer for 15 minutes. After the stirring process the solution is filtered by

filter paper and the solution is placed in the petri dish. The mouth of the petri dish tightly covered by newspaper or any cover with small holes. The block diagram of the slow evaporation method is shown in Fig. 1. The photographic view of the harvested colourless crystals of pure ADP and ADP doped with β -alanine complex crystals are shown in Fig. 2. The Molecular structure of pure ADP and ADP doped with β -alanine crystals are shown in Fig. 3.



ADP crystal doped with β -Alanine

Fig. 1: Block diagram for Slow Evaporation Method

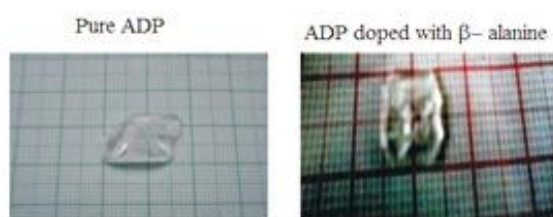


Fig. 2: Photographic view of the harvested pure ADP and ADP doped with β -alanine crystals

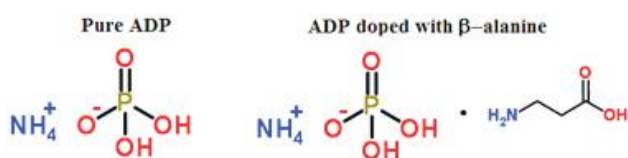


Fig. 3: The Molecular structure of pure ADP and ADP doped with β -alanine crystal

CHARACTERIZATION TECHNIQUES

Powder X-ray diffraction example was recorded utilizing aXPERT-PRO X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda=1.5418\text{\AA}$) radiation. The FTIR spectra of immaculate ADP, ADP doped with β -alanine precious stones were recorded by SHIMADZU FT-IR Spectrometer in the extent $4000\text{-}400\text{ cm}^{-1}$. The Raman spectra of unadulterated ADP and ADP doped with β -alanine precious stones were recorded over the reach $4000\text{-}80\text{ cm}^{-1}$ using the BRUKER RFS 27 FT-Raman spectrometer. The sources utilized as a part of this gadget was the Nd:YAG laser worked at 1064 nm with the episode force of 100 mW for excitation. The optical retention spectra of unadulterated ADP and ADP doped β -alanine precious stones were recorded with SHIMADZU-UV 1800 twofold pillar spectrometer. The surface morphology and the compound structure of the immaculate ADP and ADP doped with β -alanine gems have been recognized by SEM with EDAX examination utilizing the CARLZEISS EVO18 check magnifying lens.

RESULT AND DISCUSSION

The ammonium dihydrogen phosphate crystals and ammonium dihydrogen phosphate doped with β -alanine complex crystals were grown by slow evaporation method. These crystals are analysed by the powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy and SEM with EDAX investigation.

CRYSTAL DENSITY MEASUREMENT

The density of the grown crystals is determined by flotation method. The density values are given in Table 1.

Table 1: Density values of parent and complex Crystal

Compounds	Density(g/cm^3)
ADP	1.80
$\hat{\alpha}$ -Alanine	1.44
Complex	1.57

By employing the above floatation method, the density of the grown complex crystal has been

determined as 1.57 g/cm³.

POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction pattern study of pure ADP and ADP doped with β-alanine crystals were recorded by using a Philips XPERT-PRO X-ray diffractometer with CuKα (λ=1.5418Å) radiation [12-14]. The Powder X-ray diffraction patterns for pure ADP and ADP doped with β-alanine crystals are shown in Fig. 4. The sharp and well defined peaks indicate the crystalline nature of the compound. The complex crystalline nature has been identified by comparing the interplanar spacing and 2λ values of the powder pattern with the pure ADP and doped ADP crystal. The d-spacing and 2λ values of complex crystal are different from that of the pure ADP. This result confirms the formation of ADP doped with β-alanine complex crystal.

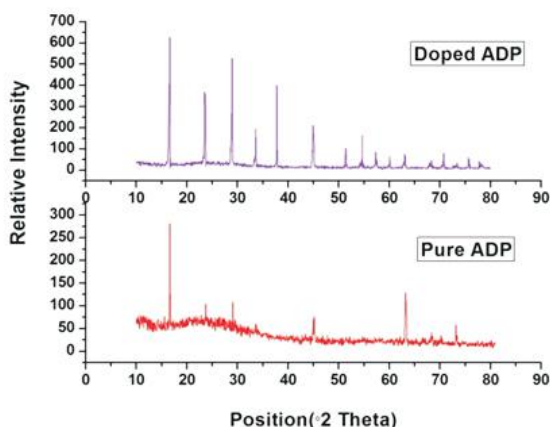


Fig. 4: Powder X-ray diffraction pattern for pure ADP and ADP doped with β-alanine crystals

Table 2: Powder XRD data of pure ADP and ADP doped with β alanine complex crystals

Pure ADP				ADP doped with β-alanine			
Position [°2θ]	d-spacing [Å]	FWHM Left [°2θ]	Particle size D=0.9λ/βcosθ [nm]	Position [°2θ]	d-spacing [Å]	FWHM Left [°2θ]	Particle size D=0.9λ/βcosθ [nm]
16.6414	5.32732	0.1476	54.4197	16.5866	5.34481	0.1476	54.4159
45.1014	2.01026	0.3936	21.8643	23.6189	3.76696	0.1968	41.2585
63.1936	1.47143	0.1968	47.4140	28.9594	3.08330	0.1476	55.6134
68.4214	1.37119	0.2952	32.5565	33.6201	2.66576	0.1476	56.2505
73.1372	1.29399	0.1476	67.0451	37.8144	2.37917	0.1476	56.9179
-	-	-	-	44.9845	2.01521	0.2952	29.1401
-	-	-	-	51.3723	1.77864	0.1968	44.8135
-	-	-	-	54.6530	1.67938	0.2952	30.3054
-	-	-	-	57.4049	1.60525	0.2952	30.6950
-	-	-	-	60.1386	1.53865	0.2952	31.1103
-	-	-	-	63.1405	1.47254	0.2952	31.6003
-	-	-	-	68.1541	1.37592	0.7872	12.1893
-	-	-	-	70.7918	1.33098	0.3936	24.7710
-	-	-	-	73.4150	1.28977	0.5904	16.7915
-	-	-	-	75.7641	1.25552	0.3936	25.5837
-	-	-	-	78.1509	1.22304	0.5904	17.3405

The d-spacing and 2θ values of pure ADP and ADP Doped with β-alanine crystals are shown in Table 2. The particle size is determined by Debye-Sherrer formula using powder X-ray diffraction data

$$D = 0.9\lambda / \beta \cos\lambda \text{ (nm)}$$

The average crystallite size is found to be as 47 nm and 31 nm for pure ADP and ADP doped β-alanine crystals respectively with by using the above relation. From this powder XRD studies, 2λ and d-spacing values reveal the significant change of X-ray diffraction peaks. Comparing the pure ADP and ADP doped with β-alanine data, the minimum numbers of peaks are observed in pure ADP and most of the peaks are presented newly in ADP doped with β-alanine.. This confirms the β-alanine compound is doped with ADP crystal.

VIBRATIONAL ANALYSIS

The infrared and Raman spectroscopy analysis are employed here for the identification and assignment of the various functional groups present in the molecule. The FT-IR and FT-Raman spectra of pure ADP and ADP doped with β-alanine complex crystals are shown in Fig. 5 and Fig. 6 respectively. The title compound has PO₄, P-O-H, P=O, O-P-O, NH₄⁺, O-H, C=O, C-O-H (in COOH-carboxylic group), CH₂ (methylene group) and NH₂ (amine group) groups. The detailed assignments of absorption bands /peaks observed in the FT-IR and FT-Raman spectra of pure

ADP and ADP with β alanine complex crystals are shown in the Table 3.

VIBRATIONS OF ADP

Based on the literature data and correlation with well observed wave numbers, the special assignments are given Table 3. In the present work, the vibration of various functional groups of ADP molecules such as PO_4 , P-O-H, P=O, O-P-O, NH_4^+ , O-H are discussed in detail.

PO_4 VIBRATION

The PO_4 antisymmetric stretching wave numbers normally occur in the region between $1280-1300\text{ cm}^{-1}$ [15]. In the present investigation, the very strong band at 1292 cm^{-1} is obtained in the FT-IR spectrum which is assigned to PO_4 vibration. This band is slightly shifted to 1288 cm^{-1} in the FT-IR spectrum of ADP doped with β -alanine crystal and is due the formation of hydrogen bonding. There is no its counterpart in the FT-Raman spectra for this region. The PO_4 bending wave numbers normally occur in the region of $547-439\text{ cm}^{-1}$ [15]. In present investigation, wave numbers of pure ADP are observed at $547, 445\text{ cm}^{-1}$ and $540, 477\text{ cm}^{-1}$ in the FT-IR and FT-Raman spectra for PO_4 bending mode respectively. These wave numbers of pure ADP are compared with the ADP doped with β -alanine complex crystal and are observed at $547, 432\text{ cm}^{-1}$ and $535, 474\text{ cm}^{-1}$ in both spectra. P-O-H Vibration

In this phosphate group, the stretching vibrations of P-O-H is assigned at near 3150 cm^{-1} and another stretching vibration region at $1100-906\text{ cm}^{-1}$ [16]. In the present investigation, the bands are observed at $3101(w), 1022(w), 920(w)\text{ cm}^{-1}$ for pure ADP and $3124(w), 1024(w), 920(s)\text{ cm}^{-1}$ for ADP doped with β -alanine complex crystal in the FT-IR spectrum is assigned to the P-O-H stretching mode.

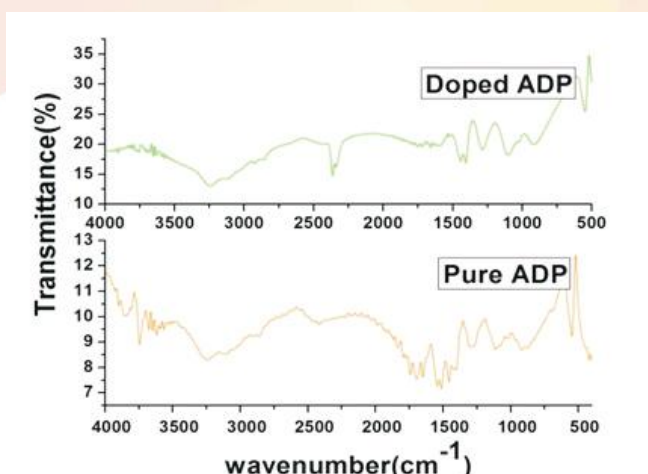


Fig. 5: FT-IR spectra of pure ADP and ADP doped with β -alanine complex crystals

P=O AND O-P-O VIBRATIONS

In this phosphate group, the stretching vibrations of P=O and O-P-O bands are assigned at the region of $1200-1100\text{ cm}^{-1}$ and $1100-1000\text{ cm}^{-1}$ respectively [14, 15]. In present investigation, the FT-IR spectra of pure ADP and ADP doped with β -alanine crystals are show the bands at 1112 and 1101 cm^{-1} which are very strong bands of P=O stretching vibrations. Also the O-P-O stretching vibrations are observed as the weak bands at 1022 and 1024 cm^{-1} for pure ADP and ADP doped with β -alanine crystals.

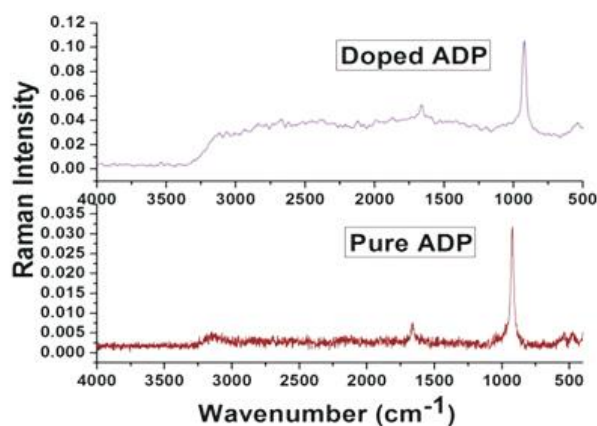


Fig. 6: FT-Raman spectra of pure ADP and ADP doped with β -alanine complex crystals

Table 3: Observed wave numbers in FT-IR spectrum and FT-Raman spectrum and their assignments for ADP and ADP doped with β -alanine complex crystals.

Pure ADP		ADP doped with β -alanine		Assignment
FT- IR ($??/cm^{-1}$)	FT- Raman ($??/cm^{-1}$)	FT- IR ($??/cm^{-1}$)	FT- Raman ($??/cm^{-1}$)	
3240(s.br)	-	3246(s.br)	-	\dot{f} (O-H); \dot{f}_s (NH ₄ ⁺); \dot{f} (NH ₂)
-	3152(sh)	-	-	\dot{f} (NH ₄ ⁺)
3101(w)	-	3124(w)	-	\dot{f} (P-O-H); \dot{f} (NH ₄ ⁺)
-	-	2924(s)	-	\dot{f}_{as} (CH ₃); \dot{f} (O-H); \ddot{a} (C-OH); \dot{f} (NH ₄ ⁺)
2858(w)	-	2858(w)	2840(m)	\dot{f}_s (NH ₄ ⁺)
-	-	-	2670(w)	\dot{f}_s (NH ₄ ⁺); \dot{f} (O-H)
-	-	-	2618(w)	\dot{f}_s (NH ₄ ⁺); \dot{f} (O-H)
-	-	2369(vs)	-	Overtones and combination bands
-	-	2329(vs)	-	
1793(w)	-	-	-	
1772(w)	-	1778(sh)	-	
1741(s)	-	1753(sh)	-	
-	-	1720(sh)	-	\dot{f}_{as} (C=O)
-	-	1707(sh)	-	\dot{f}_{as} (C=O)
1697(s)	-	-	-	\ddot{a} (NH ₄ ⁺)
-	-	1683(sh)	-	\dot{f}_{as} (C=O)
-	-	-	1662(s)	\dot{f}_{as} (C=O)
1649(s)	1657(s)	-	-	\ddot{a} (O-H); \ddot{a} (NH ₄ ⁺); \ddot{a} (NH ₂)
-	-	1600(sh)	-	\ddot{a}_{as} (NH ₂)
1541(s)	-	1546(w)	-	\ddot{a} (NH ₃ ⁺)
1512(s)	-	-	-	\ddot{a} (NH ₃ ⁺)
1456(vs)	-	-	-	\ddot{a} (NH ₄ ⁺)
-	-	1442(vs)	-	\ddot{a} (CH ₂)
-	-	1404(vs)	-	\ddot{a} (O-H); \ddot{a} (CH ₂); \ddot{a} (C-O-H)
1292(vs)	-	1288(vs)	-	\dot{f}_{sw} (PO ₄)
1112(vs)	-	1101(vs)	-	\dot{f} (P=O)
1022(w)	-	1024(w)	-	\dot{f} (P-O-H); \dot{f} (O-P-O)
920(w)	922(vs)	920(s.br)	923(vs)	\dot{f} (P-O-H)
877(vw)	-	-	-	\ddot{u} (N H ₂)
694(vw)	-	675(vw)	-	\ddot{u} (N H ₂)
547(vs)	540(m)	547(vs)	535(m)	\dot{f} (PO ₄); \ddot{a} (PO ₄)
445(w)	477(m)	432(vs)	474(m)	\dot{f} (PO ₄); \ddot{a} (PO ₄)

s- strong; vs- very strong; vvs- very very strong; m- medium; w- weak; vw- very weak; sh- shoulder; v- stretching; λ_s - symmetric stretching; λ_{as} - asymmetric stretching; λ - wagging; β - in plane; d- bending; d_s - symmetric bending; d_{as} - asymmetric bending; def- deformation.

Also the samemode is observed at 922 and 923 cm-1 in FT-Raman spectra of pure ADP and ADP doped with β -alanine crystals respectively.

VIBRATIONS OF [NH₄]⁺

In pure ADP, the λ_3 vibrational spectrum of the free ammonium ion [NH₄]⁺ is presented. In this molecule, H atoms are bonded with one N atom as in Td symmetry. The [NH₄]⁺ vibration splits into N-H, NH₂ and [NH₃]⁺vibrations. Also β -alanine has the same amine group i.e., NH₂. The characteristic -NH₂ bands around at 3200 cm⁻¹ usually appears. Also [NH₃]⁺assignments are supported by [NH₂]⁺vibrations.

Now, the [NH₄]⁺ stretching vibrations are assigned at the region between 3500-2600 cm⁻¹ [16].

In present investigation, 3101(w), 2858(w) and 3124(w), 2924(s), 2858(w) bands are observed due to [NH₄]⁺ stretching vibrations in FT-IR spectrum for pure ADP and ADP doped with β -alanine crystals. Also, 3152 cm⁻¹ and 2840, 2670, 2618 cm⁻¹ bands are observed due to [NH₄]⁺ stretching vibrations in FT-Raman spectra for pure ADP and ADP doped with β -alanine crystals. Particularly, in symmetric (λ_1) and antisymmetric (λ_3) stretching vibrations are assigned at near 3270 cm⁻¹ and 3343 cm⁻¹ respectively [15]. In present investigation, only the symmetric stretching of [NH₄]⁺ vibration is observed as the strong band at 3240 and 3246 cm⁻¹ in pure ADP and ADP doped with β -alanine crystals from FT-IR spectra respectively. Also, symmetric (λ_2) and antisymmetric (λ_4) bending vibrations are assigned at near 1669 cm⁻¹ and 1447 cm⁻¹ respectively [16]. In present study, the symmetric bending of [NH₄]⁺ vibration is observed as the strong bands at 1697, 1649 cm⁻¹ and 1657 cm⁻¹ in FT-IR spectra and FT-Raman spectra for pure ADP respectively. Also, the antisymmetric bending of [NH₄]⁺ vibration is observed as the very strong band at 1456 cm⁻¹ in FT-IR spectrum for pure ADP crystal.

Now, the characteristic -NH₂ bands around at 3200 cm-1 usually appears [16]. The stretching and bending vibrations of -NH₂ are assigned at the region between 3500-3200 cm⁻¹ and 1650-1590 cm⁻¹ respectively [16]. In present investigation, 3240 and 3246 cm⁻¹ band are observed due to -NH₂ stretching vibrational mode in FT-IR spectra for pure ADP and ADP doped with β -alanine crystals. The strong bands at 1649 and 1657 cm⁻¹ are observed due to -NH₂ bending vibrational mode in FT-IR and FT-Raman spectra for pure ADP crystal. Already these bands are reported to [NH₄]⁺vibrations. The vibration of -NH₂ wagging is assigned at the region between 900-660 cm⁻¹ [15, 16]. The band at 877 cm⁻¹ is observed in FT-IR spectrum for pure ADP crystal. From FT-IR spectrum, the band at 694 cm⁻¹ for pure ADP is downshifted to 675 cm⁻¹ for ADP doped with β -alanine crystals due to formation of hydrogen bonding.

Also [NH₃]⁺ assignments are supported [NH₄]⁺ vibrations. The [NH₃]⁺ displays its characteristics bending modes at 1475-1600 cm⁻¹ [15, 16]. The FT-IR

spectrum shows the bands at 1541cm^{-1} for pure ADP is upshifted to 1546cm^{-1} for ADP doped with β -alanine crystals due to formation of hydrogen bonding. The $[\text{NH}_3]^+$ bending vibrations is observed at 1512cm^{-1} in the FT-IR spectrum for pure ADP crystal.

O-H VIBRATION

The functional groups of O-H stretching is assigned at the range $3500\text{-}3200\text{cm}^{-1}$ [17]. In the present analysis, the FT-IR spectrum of the pure ADP and ADP doped with β -alanine crystals show the strong peaks at 3240 and 3246cm^{-1} respectively. It is known that the O-H bending vibration makes a peak at 1642cm^{-1} in FT-IR spectrum. In present study, 1649cm^{-1} and 1657cm^{-1} band are assigned to O-H bending vibration of pure ADP and ADP doped with β -alanine crystals respectively.

VIBRATIONS OF β -ALANINE

The hydrogen bonding leads to several modes of vibration undergoing changes in position and intensity. Based on the literature data and correlation with well observed wave numbers, the spectral assignments are given Table 3. In the present work, the vibration of various functional groups of β -alanine molecules such as O-H, C=O, C-O-H (in COOH-carboxylic group), CH_2 (methylene group), NH_2 (amine group) are discussed in detail.

VIBRATION OF CARBOXYL GROUP

O-H VIBRATION

The O-H stretching vibration of COOH - Carboxylic acid group is assigned in the region between $3300\text{-}2500\text{cm}^{-1}$ [18]. In the present investigation, the strong band at 2924cm^{-1} is occurred in FT-IR spectra of complex crystal which is assigned to the O-H...O stretching vibration of carboxylic acid. Also the FT-Raman spectra are observed the bands at $2670, 2618\text{cm}^{-1}$ in ADP doped with β -alanine crystal. However, the corresponding FT-IR bands are not identified distinctly because the overlapping of CH_2 , O-H, and N-H stretching bands contributes to the broad FT-IR band. This mode is observed only ADP doped with β -alanine crystals,

because COOH-Carboxylic acid group appears in β -alanine.

The O-H in plane bending wave number normally occurs in the region between $1440\text{-}1395\text{cm}^{-1}$ [18, 19]. In the present study, the FT-IR spectrum shows very strong band at 1404cm^{-1} in ADP doped with β -alanine.

C=O AND C-O-H VIBRATIONS

As the carboxyl dimer structure has a centre of symmetry, the antisymmetric carbonyl stretch will be IR active whereas its symmetric stretch will be Raman active. Most carbonyl dimers have an IR band in the range $1720\text{-}1680\text{cm}^{-1}$ due to antisymmetric C=O stretch and it is lower than the absorption for a monomer [20]. In the FT-Raman spectrum, a band is expected between $1680\text{-}1640\text{cm}^{-1}$ due to symmetric C=O stretch. In the present structure, a shoulder FT-IR bands at $1707, 1720, 1683\text{cm}^{-1}$ (Raman inactive) is attributed to the C=O antisymmetric stretching mode and a strong FT-Raman band at 1662cm^{-1} is assigned to C=O symmetric stretching mode of vibration. These bands clearly confirm the occurrence of a cyclic carboxyl dimer in the crystal.

The C-O-H bending wave number normally occur in the region $1440\text{-}1395\text{cm}^{-1}$ whereas CH_2 deformation, O-H in plane vibrations are involved [20]. In the present study, the FT-IR spectrum shows very strong band at 1404cm^{-1} in ADP doped with β -alanine. Also, bending of C-OH vibration is assigned at the region between $3000\text{-}2800\text{cm}^{-1}$ whereas antisymmetric CH_2 stretch, O-H stretch is involved. In present study, strong band at 2924cm^{-1} is assigned to C-OH bend vibration. There are no FT-Raman bands in both groups.

VIBRATIONS OF METHYLENE GROUP

The antisymmetric and symmetric stretching modes of the methylene group were identified together with their deformation modes. In β -alanine, the stretching modes of the CH_2 group are observed at the region between $3000\text{-}2850\text{cm}^{-1}$ [19, 20]. Particularly, the asymmetric stretching and symmetric stretching of CH_2 vibrations occur at the region between $2945\text{-}2910\text{cm}^{-1}$ and $2865\text{-}2835\text{cm}^{-1}$

respectively. In present work, the bands at 2924 cm^{-1} is due to antisymmetric stretching vibration of CH_2 . The vibration due to symmetric bending of CH_2 (deformation) mode is expected to occurs at $1470\text{-}1350\text{ cm}^{-1}$ [20]. In present study, the very strong bands at $1442, 1404\text{ cm}^{-1}$ are obtained in FT-IR spectrum.

VIBRATIONS OF NH2

Bending vibrations of NH_2 is assigned at the region between $1650\text{-}1590\text{ cm}^{-1}$ [20-22]. At present investigation, the shoulder band is appeared at 1600 cm^{-1} in FT-IR spectrum for ADP doped with β -alanine due to NH_2 bending vibration. Also, the vibration of NH_2 wagging is assigned at the region between $900\text{-}660\text{ cm}^{-1}$. From FT-IR spectrum, the band at 694 cm^{-1} for pure ADP is downshifted to 675 cm^{-1} for ADP doped with β -alanine crystals due to formation of hydrogen bonding. The band at 675 cm^{-1} for ADP doped with β -alanine crystals is appeared due to the presences of NH_2 group in β -alanine molecule.

From all the above vibrational assignments, wave numbers of the FT-IR and FT-Raman spectra are identified the various functional groups of pure ADP and ADP doped with β -alanine crystals. The wave numbers are shifted because of the hydrogen bonding formation. These vibrational assignments are used to assess the complex crystal.

UV- VISIBLE SPECTROSCOPY ANALYSIS

The optical absorption spectra of pure ADP and ADP with β -alanine crystals have been recorded with SHIMADZU- UV 1800 double beam spectro meter. Transmittance and absorption data were observed for the crystals in the wavelength range $200\text{-}1100\text{ nm}$ insteps of 1 nm . The slit width chosen was 0.2 nm . The wavelength rate was in fast mode. The observed values of absorbance were recorded and stored in the memory of a computer and plotted.

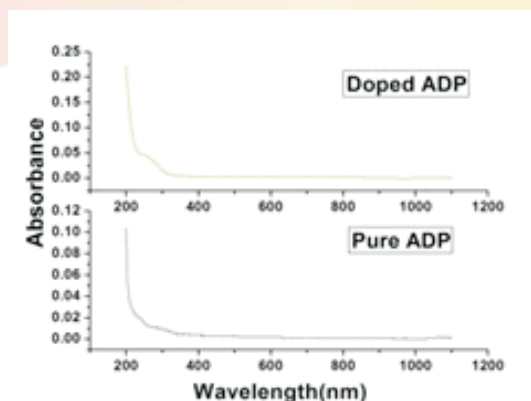


Fig. 7: Absorption spectra of pure ADP and ADP doped with β -alanine complex crystals

From the spectra, the crystals show a good transmittance in the entire visible region. A good optical transmittance from ultraviolet to infrared region is very useful for optical applications. The lower cut-off wavelength is found to be 215 nm and 234 nm for pure ADP and ADP doped with β -alanine complex crystals respectively. The transparency of the pure ADP is decreased in the presence of β alanine which is depicted in the Fig. 7. But there is no change in the optical window for both crystals in the visible region [23, 24].

Table 4:Cut-off wavelength and Band gap of pure ADP and ADP with β alanine complex crystals

Sample	Cut-off wavelength (nm)	Band gap (eV)
Pure ADP	215	6.16
Doped ADP	234	5.50

The energy gap value E_g could be determined by analyzing the optical data with optical absorption coefficient α and the photon energy $h\lambda$ using Tauc's relation [25], $(\alpha h\lambda)^2 = A(h\lambda - E_g)$.The optical band gap was evaluated by plotting $(\alpha h\lambda)^2$ vs. $h\lambda$ as shown in Fig. 8 and extrapolating the linear portion of absorption edge $(\alpha h\lambda)^2$ the photon energy axis gives the optical band gap of the crystal [26].

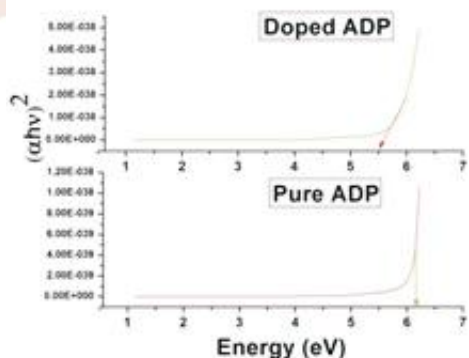


Fig.8: Energy gap curve of pure ADP and ADP with β -alanine complex crystals

From the Fig.8, the band gap values of the crystals were found to be as 6.16 eV for pure ADP and 5.50 eV for ADP doped with β -alanine. The band gap value of pure ADP is decreased in the presence of β -alanine. This result also confirms presence of β -alanine in the complex crystal.

SEM WITH EDAX ANALYSIS

A high energy beam of electrons are scanning the surfaces in a raster pattern is called Electron Microscope. The shape and size of the particles making up the object can be viewed and studied. SEM analysis is carried out using CARLZEISS EVO18 scan microscope. The SEM analysis shows the optical clarity and substance nature. Also, nature of the surfaces and morphology of the crystal are identified by the SEM analysis [27].In present investigation, SEM image shows the highly optical clarity and nature of the substances for pure ADP and ADP doped with β -alanine. The surfaces of the grown crystals are smooth and well defined planes (morphology) for pure ADP and ADP doped with β -alanine which is due to SEM analysis.



Fig. 9: SEM image of pure ADP and ADP doped with β -alanine crystal.

β -alanine complex crystals

Shape and size of microcrystals are different in pure ADP and ADP doped with β -alanine to identify by SEM analysis. This SEM image proves that the presences of dopant.

ENERGY DISPERSIVE X-RAY ANALYSIS

The Energy Dispersive X-Ray Analysis (EDAX) is performed using the CARLZEISS EVO18. The EDAX pattern reveals the presence of chemical compositions of crystals, from the characteristic peaks of the elements and also confirms the absence of impurities. From EDAX spectrum, the chemical composition weight has been calculated [27-29].

Table 5: Estimated Weight Percentage of pure ADP and ADP doped with β -alanine crystals

S.NO	Element	Pure ADP		ADP doped with β -alanine	
		Weight %	Atomic %	Weight %	Atomic %
1.	O	59.46	65.75	48.00	45.55
2.	P	25.31	14.46	11.57	5.67
3.	N	12.57	15.88	12.90	13.99
4.	C	2.66	3.91	27.52	34.79
TOTAL		100	100	100	100

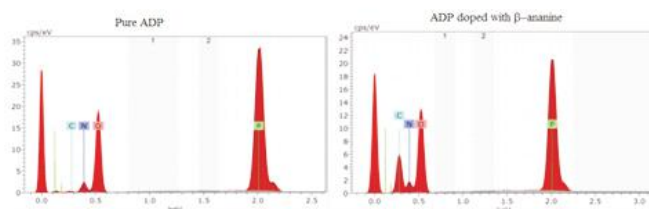


Fig. 10: EDAX Spectrum of ADP doped with β -alanine crystal

From the EDAX analysis, the presence of chemical composition(O, P, N and C) has been identified and its weight percentage has been calculated for pure ADP and ADP doped with β -alanine crystals. From the results, estimated weight percentage (%) and atomic percentage (%) of carbon component of ADP doped with β -alanine reveals the high value than pure ADP. This result confirms that the dopant is existing in the ADP doped with β -alanine crystal.

CONCLUSIONS

The pure ADP and ADP doped with β -alanine single crystals were grown by slow evaporation method. From the Powder XRD studies, 2λ and d -spacing values reveal the significant change of X-ray diffraction peaks. Compared to pure ADP and ADP doped with β -alanine data, the minimum number of peaks are observed in pure ADP and more of the peaks are pronounced newly in the ADP doped with β -alanine. The frequency assignments have been made for various functional groups and they are found to be in good agreement with previously published works. From UV-Visible Spectroscopy, the crystal shows a good transmittance in the entire visible region. The band gap value of pure ADP is decreased in the presence of β alanine. This result also confirms presence of β -alanine in the complex crystal. From SEM image shows the highly optical clarity and nature of the substances for pure ADP and ADP doped with β -alanine. The surfaces of the grown crystals are smooth and well defined planes (morphology) for pure ADP and ADP doped with β -alanine which is due to SEM analysis. From the EDAX analysis, the presence of chemical composition(O, P, N and C) has been identified and its weight percentage has been calculated for pure ADP and ADP doped with β -alanine crystals.

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