Influence of organic dopants (L-alanine and L-arginine) on structural, spectroscopic and thermal properties of ammonium dihydrogen phosphate crystal

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Ammonium dihydrogen phosphate is a popular nonlinear optical crystal used for second harmonic generation efficiency improvement in pump lasers. Due to molecular chirality and zwitterionic structure, amino acids are used to enhance various properties of ADP crystal. The single crystals of ammonium dihydrogen phosphate (ADP) added with different concentrations (0.3 wt.%, 0.4 wt.% and 0.5 wt.%) of amino acids (L-alanine and L-arginine) impurities were grown using slow evaporation solution growth (SESG) technique at room temperature. To study the structural properties, powder XRD study was carried out which revealed that all the grown crystals have tetragonal structural symmetry. The presence of various functional groups was confirmed using FT-IR spectroscopy. The thermal spectra (TGA/DTA/DSC) were recorded for all grown samples to determine their decomposition. Also kinetic and thermodynamic parameters were determined from the thermal study.

Keywords: *crystal growth; powder XRD; FT-IR; force constant, TGA/DTA/DSC, C-R relation*

1. Introduction

Ammonium dihydrogen phosphate (ADP) belongs to a large crystal family MH_2XO_4 (where $M = K, Na, NH_4^+$, $X = As, P$). In ADP crystals, NH_4^+ can form N–H...O–P hydrogen bonding with H_2PO_4 [1]. Below 148 K, ADP is antiferroelectric, belonging to P212121 space symmetric group. Above this temperature, it shows paraelectric behavior and I4/2d symmetry [2, 3]. ADP is used in short-wavelength laser technology, nonlinear and integrated optics as a bulk electro-optical device, as a frequency converter of coherent radiation of high-power picosecond lasers, as an optical parametric oscillator for the infrared spectral region, and as integral optical waveguides [4].

Amino acids have such properties as molecular chirality, absence of strongly conjugated bonds and zwitterionic nature [5]. They have attracted researcher to dope them in ADP [6]. Previously, Delci et al. [7] studied structural, spectroscopic

and thermal properties of pure and L-histidine doped ADP crystals. In the present paper, authors have reported the structural, spectroscopic, thermal properties of ADP crystal doped with L-alanine and L-arginine. Various kinetic and thermodynamic parameters were calculated using Coat and Redfern method.

2. Experimental

The pure and amino acid doped ADP crystals were grown by using slow evaporation solution growth technique at room temperature. All the chemicals used for the study viz. ADP (E. Merck); L-alanine and L-arginine (SRL Chemicals) were of analytical grade. 700 mL double distilled water was taken and pure ADP powder was dissolved till saturation occurred. The saturated solution was stirred continuously using a magnetic stirrer for 4 hours and filtered using Whatman filter paper No. 1. The solution was then subdivided into 7 different glass beakers, each of them containing 100 mL of pure solution. One beaker containing a pure solution was sealed with a porous lid and placed

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in a dust free atmosphere. L-alanine and L-arginine with different concentrations (0.3 wt.%, 0.4 wt.% and 0.5 wt.%) were added into the remaining beakers, all the solutions were stirred again for 4 hours to make them homogeneous. All the solutions were then sealed with porous lids and placed in a dust free atmosphere. Good quality and transparent crystals were harvested from all the solutions after a span of 10 to 15 days.

Powder XRD was carried on Philips X'Pert MPD system and the data were analyzed by software powder-X. FT-IR spectra were recorded in the region 400 cm^{-1} to 4000 cm^{-1} employing Thermo Nicolet 6700 in KBr media. TGA/DTA/DSC study was performed on Linseic STA PT 1600 setup from room temperature to $450\text{ }^{\circ}\text{C}$ in air atmosphere at a heating rate of $15\text{ }^{\circ}\text{C}/\text{min}$.

3. Results and discussion

3.1. Powder XRD study

Fig. 1 shows powder XRD patterns of pure and different (0.3 wt.%, 0.4 wt.%, 0.5 wt.%) L-alanine (AL) and L-arginine (AR) doped ADP crystals. From the figure it can be seen that all the samples show single phase nature and no additional peaks are found due to the doping of L-alanine and L-arginine in pure ADP, which confirms that amino acids do not distort the structure of pure ADP [8]. The variation in intensities of pure and doped samples was found but the angle 2θ remained the same which may be due to the presence of L-alanine and L-arginine. All the crystals belong to the tetragonal crystal system. The unit cell volume of pure and doped samples was calculated using the standard formula for tetragonal crystal system $V = a^2c\text{ \AA}^3$. The lattice parameters were calculated and listed in Table 1. The small variation in lattice parameters may be due to the presence of dopant in ADP.

3.2. FT-IR spectroscopy study

The interaction of amino acids (L-alanine and L-arginine) with ADP crystal was confirmed by FT-IR spectroscopy. From the spectra of pure and different weight percentages L-alanine and L-arginine doped ADP, it is observed that the

Fig. 1. Powder XRD patterns of pure and doped ADP.

Fig. 2. FT-IR spectra of pure and L-alanine (AL) doped ADP.

peak positions of P–O–H and P–O vibrations are shifted from higher to lower side for L-alanine and L-arginine doped ADP crystals with respect to pure ADP. Fig. 2 and Fig. 3 show FT-IR spectra of pure and L-alanine and L-arginine doped ADP, respectively.

Table 1. Unit cell parameters of pure and doped ADP.

Samples	$a = b\text{ [\AA]}$	$c\text{ [\AA]}$	Unit cell volume $[\text{\AA}^3]$
PURE ADP	7.504	7.552	425.25
0.3 AL	7.500	7.556	425.02
0.4 AL	7.521	7.554	427.29
0.5 AL	7.516	7.555	426.78
0.3 AR	7.523	7.572	428.54
0.4 AR	7.518	7.553	426.89
0.5 AR	7.509	7.553	425.88

Fig. 3. FT-IR spectra of pure and L-arginine (AR) doped ADP.

The FT-IR spectrum of pure ADP crystal shows the O–H stretching of water at 3231 cm^{-1} , P–O–H stretching at 1080 cm^{-1} , N–H stretching of ammonia at 2834 cm^{-1} and PO_4 vibration at 575 cm^{-1} and 478 cm^{-1} . The FT-IR spectra of L-alanine (0.3 wt.%, 0.4 wt.%, 0.5 wt.%) and L-arginine (0.3 wt.%, 0.4 wt.%, 0.5 wt.%) doped ADP crystals show that the peak positions shifted from lower to higher wave number due to the presence of L-alanine and L-arginine in the ADP crystals.

For example, the PO_4 vibration of pure ADP is shifted from 478 cm^{-1} to 451 cm^{-1} , 498 cm^{-1} , 461 cm^{-1} in case of 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-alanine doped ADP crystals, while in case of 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-arginine doped ADP crystals the same vibration is shifted at 459 cm^{-1} , 465 cm^{-1} , 494 cm^{-1} . Also the P–O–H-stretching of pure ADP is shifted from 1080 cm^{-1} and 953 cm^{-1} to 1061 cm^{-1} and 912 cm^{-1} , 1097 cm^{-1} and 935 cm^{-1} , 1059 cm^{-1} and 941 cm^{-1} in case of 0.3 wt.%, 0.4 wt.% and 0.5 wt.% doped ADP crystals, while in case of 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-arginine doped ADP crystals the same vibration is shifted at 1080 cm^{-1} and 933 cm^{-1} , 1101 cm^{-1} and 924 cm^{-1} and 1084 cm^{-1} and 935 cm^{-1} .

From the FT-IR band assignment for different functional groups, one can calculate the force constant of diatomic atoms present in the sample. According to Hooke law, if we consider the nuclei as a point mass and interatomic bonds as a massless spring then the interatomic distances are varied sinusoidally due to their vibrations but their center of gravity remains unchanged. Hence, during the vibrations, the atomic displacement is inversely proportional to the masses at any given time.

The relation between the absorption frequency and the force constant can be written as:

$$\nu = 1330F \cdot \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \quad (1)$$

where ν = absorption wavenumber in cm^{-1} , $1330 = (N_A \times 10)^{1/2} / 2\pi C$, N_A = Avogadro number, F = force constant in $\text{N}\cdot\text{m}^{-1}$, C = velocity of electromagnetic wave in vacuum, M_1 and M_2 = molecular masses of atoms u [9].

Table 2. Force constant of pure and doped ADP.

Samples	Force constant for O–H vibration [Nm^{-1}]	Absorption wavenumber [cm^{-1}]
Pure ADP	555	3230
0.3 AL	558	3240
0.4 AL	548	3211
0.5 AL	556	3234
0.3 AR	545	3203
0.4 AR	547	3209
0.5 AR	547	3209

In the present study the force constants for O–H bond were calculated for pure and amino acids doped ADP crystals. From Table 2 it can be seen that the force constant alters when the amino acids interact with the hydrogen bond of ADP.

3.3. Thermal study

Fig. 4 to Fig. 9 show the TGA/DTA/DSC curves for pure and different weight percent L-alanine and L-arginine doped ADP crystals.

The pure ADP remains stable up to 180°C , while 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-alanine

Fig. 4. TGA curves of pure and L-alanine (AL) doped ADP.

Fig. 6. DTA curves of pure and L-alanine (AL) doped ADP.

Fig. 5. TGA curves of pure and L-arginine (AR) doped ADP.

Fig. 7. DTA curves of pure and L-arginine (AR) doped ADP.

doped ADP crystals remain stable up to 196 °C, 195 °C, 198 °C and 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-arginine doped ADP remain stable upto 191 °C, 181 °C, 185 °C respectively, and then decompose slowly. Thereafter, the pure ADP crystal reaches the metastable state at 214 °C with 3.3 % weight loss while 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-alanine doped ADP reach the metastable state at 198 °C, 203 °C, 216 °C with 1.03 %, 1.76 %, 2.61 % weight loss and 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-arginine doped ADP reach the metastable state at 207 °C,

210 °C, 222 °C with 4.08 %, 3.55 %, 3.04 % weight loss, respectively.

The samples are finally decomposed at comparatively rapid decomposition rate to final stable state at 448.4 °C with 31.40 % weight loss for pure ADP, while the final stable state occurs at 447.5 °C, 446.6 °C, 446.4 °C with 20.59 %, 24.39 %, 25.65 % weight loss for 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-alanine doped ADP crystals, respectively, and the final stable state occurs at 449.9 °C, 450 °C, 448 °C with 28.18 %, 17.37 %, 11.43 % weight

Fig. 8. DSC curves of pure and L-alanine doped ADP.

Fig. 9. DSC curves of pure and L-arginine doped ADP.

loss for 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-arginine doped ADP crystals, respectively.

The DTA curve shows an endothermic peak at 211 °C for pure ADP crystal, which corresponds to decomposition of ADP. For the 0.3 wt.%, 0.4 wt.%, 0.5 wt.% L-alanine doped ADP crystals the endothermic peak is shifted to 208 °C, 214 °C, and 211 °C. In the 0.4 wt.% L-alanine doped ADP crystal the DTA peak is shifted to 214 °C and the decomposition temperature of ADP increases by 3 °C, which appears to be adequate as the 0.4 wt.% concentration of L-alanine present inside the crystal could have strengthened the lattice partially. In addition, for a 0.3 wt.%, 0.4 wt.%, 0.5 wt.%

L-arginine doped ADP crystals, the endothermic peaks are shifted to 208 °C, 216 °C, and 214 °C, respectively. Similar to 0.4 wt.% L-alanine doped ADP, for the case of 0.4 wt.% L-arginine doped ADP the endothermic peak is shifted to 216 °C and the decomposition temperature of ADP increases by 5 °C, which may also provide the partial strengthening to the lattice.

3.4. Kinetic and thermodynamic parameters

The use of thermogravimetry data to evaluate kinetic parameters of solid state reaction which involves the weight loss of a sample has been widely reported in literature [10–12]. The kinetic parameters for dehydration process in pure and amino acids (L-alanine and L-arginine) doped ADP crystals were evaluated by using non-isothermal kinetic relation proposed by Coats et al. [13], which is given below:

$$\log_{10} \left[\frac{1 - (1 - a)^{1-n}}{T^2(1 - n)} \right] = \left[\log_{10} \left(\frac{AR}{\alpha E} \right) \left(1 - \frac{2RT}{\alpha E} \right) - \frac{E}{2.303RT} \right] \quad (\text{for } n \neq 1) \quad (2)$$

where $\alpha = (W_0 - W) / (W_0 - W_f)$, W_0 is the initial weight, W is the weight at time t , W_f is the final weight, n is the order of reaction, A is frequency factor, E is the activation energy of reaction, R is the gas constant, a is the heating rate in K/min.

A plot of $\log_{10} [1 - (1 - \alpha)^{1-n} / T^2(1 - n)]$ versus $1/T$ is drawn for different values of n . Fig. 10 to Fig. 12 show C-R relation for pure and 0.3 wt.% L-alanine and L-arginine doped ADP. The best linear fit gives the correct value of reaction order. The activation energy can be calculated from the slope, and frequency factor can be obtained from equation 2.

The kinetic parameters for all the samples are listed in Table 3. The activation energy is considered as a barrier to be surmounted by a reactant to form a product. Hence, from Table 3, it can be seen that the pure ADP crystals have higher activation energy compared to doped crystals, which indicates more stable nature of pure ADP. Thermodynamic

Fig. 10. C-R relation for pure ADP.

Fig. 11. C-R relation for 0.3 wt.% L-alanine (AL) doped ADP.

parameters are evaluated by the standard entropy of activation ΔS [14] what can be expressed as:

$$\Delta S = 2.303 \times R \times \log_{10} [A\hbar/kT_m] \quad (3)$$

where k is the Boltzmann constant, $\hbar$ is the Planck constant, T_m is temperature, A is the frequency factor.

The standard enthalpy of activation ΔH can be calculated by using equation 4:

$$\Delta H = E - 2RT \quad (4)$$

The standard Gibbs energy of activation ΔG can be estimated by relation 5:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Fig. 12. C-R relation for 0.3 wt.% L-arginine (AR) doped ADP.

Table 3. Kinetic parameters of pure and doped ADP.

Samples	Kinetic parameters		
	n	E_a [kJ·mol ⁻¹]	A
Pure ADP	3/2	32.743	51.41×10^{16}
0.3 AL	0	4.301	12.14×10^{14}
0.4 AL	1/4	8.319	24.77×10^{14}
0.5 AL	0	7.759	23.61×10^{14}
0.3 AR	1/2	18.631	23.74×10^{15}
0.4 AR	1/4	3.981	11.85×10^{14}
0.5 AR	0	4.902	16.66×10^{14}

Thermodynamic parameters are listed in Table 4. The positive values of standard entropies of activation (ΔS) indicate the spontaneous reaction for all grown crystals while the negative values of standard enthalpies of activation (ΔH) show that the enthalpy decreases during the process, which suggests the endothermic reaction. The negative value of standard Gibbs free energies (ΔG) suggests the exergonic reaction in which the energy is released in form of heat, which favors the spontaneous reaction for all grown crystals. This is to be verified by DSC curves of pure and amino acids doped ADP crystals.

4. Conclusions

The pure and different weight percentages (0.3 wt.%, 0.4 wt.%, 0.5 wt.%) L-alanine and L-arginine doped ADP crystals were

Table 4. Thermodynamic parameters of pure and doped ADP.

Samples	Thermodynamic parameters		
	ΔS [JK ⁻¹ mol ⁻¹]	ΔH [kJ·mol ⁻¹]	ΔG [kJ·mmol ⁻¹]
Pure ADP	89.07	23.548	-25.707
0.3 AL	37.35	-6.556	-30.946
0.4 AL	43.94	-1.707	-28.203
0.5 AL	43.54	-2.266	-28.521
0.3 AR	63.45	9.435	-25.652
0.4 AR	37.41	-6.544	-8.278
0.5 AR	40.24	-5.622	-31.094

successfully grown by using slow solvent evaporation technique at room temperature. The powder XRD study showed single phase nature of the pure and doped crystals. All the crystals belong to tetragonal crystal system. The FT-IR spectroscopy showed shifting of various vibration modes of functional groups and change in force constant which confirms the presence of dopant in ADP. The TGA/DTA investigation showed that the addition of amino acids in pure ADP improves strength of the lattice and enhances the thermal stability of ADP. The kinetic and thermodynamic parameters calculated from C-R relation showed spontaneous reaction for all the grown crystals, which was also confirmed by DSC.

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