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Unidirectional growth of pure and L-lysine added ADP crystals from aqueous solution

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Pure and L-lysine added ammonium dihydrogen phosphate (ADP) crystals were grown in the ⟨001⟩ direction by Sankaranarayanan-Ramasamy (S-R) method. The grown crystals were characterized by X-Ray diffractometry (XRD), UV-Vis spectroscopy, Fourier Transform Infrared (FT-IR) and Vicker's Microhardness analysis.

XRD spectrum of each of the grown crystals proved its crystallinity. The crystals showed good transparency in the entire visible region. FT-IR spectra of the specimens revealed the presence of functional groups in them. The hardness of the pure and L-lysine added ADP crystals were measured and that of the added one was found higher. Meanwhile, it was found that the ADP crystals (pure and L-lysine added) grown by S-R method had higher hardness compared to ADP crystal grown by conventional method.

Keywords: *crystal growth; ADP; L-lysine; UV-Vis; FT-IR*

1. Introduction

ADP crystal has attracted the attention of many crystal growers because of good piezoelectric properties and nonlinear optical applications. Numerous attempts have been made to improve the quality and characteristics of ADP crystals, for example, a lot of studies have been carried out on pure and doped ADP crystals [1, 2].

ADP belongs to scalenohedral class of tetragonal crystal systems. It has unit cell parameters of a = b = 7.510 Å and c = 7.564 Å [3].

It is known that a very little amount of additives can strongly suppress the metal ion impurities and promote the crystal quality. Oxalic acid and amino acids as additives in ADP crystals give appreciable change in optical, thermal, dielectric and mechanical behaviors [4]. Zion et al has recently reported the enhancement of transparency and NLO efficiency of ADP crystal upon doping with boron additive [5].

In ADP crystal growth, the metallic cations present in the solution, especially those with high valency, were considered to strongly affect the growth habit and optical properties of the crystal. The most dangerous impurities are trivalent metals Cr^{3+}, Fe^{3+}, and Al^{3+} which make also important habit distortions [6]. Minute amounts of additives can effectively suppress the metal ions and promote the crystal quality. The quality of the crystals is much better in the presence of low concentrations of dopant in the growth medium [7]. An impurity can suppress, enhance or stop the growth of crystal completely [8]. Claude et al. have found ADP crystals doped with impurities in the form of dopants to have faster nucleation rates and quicker induction periods [9]. It is substantially known that impurities are one of the significant factors influencing the growth kinetics, morphology and quality of the crystals.

In the present investigation, L-lysine has been used as an additive in growing ADP single crystal unidirectionally. The grown pure and L-lysine added ADP crystals were characterized by XRD, FT-IR, UV-Vis and Vicker's Microhardness analyses.

2. Experimental details and crystal growth

Single crystals of pure and L-lysine added ADP were grown using deionized water as solvent by

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a technique called Sankaranarayanan-Ramasamy (S-R) method. The details of the method are given elsewhere [10]. The ADP seeds necessary for growing bulk crystals were first grown by slow evaporation method. The well faceted crystals were chosen in order to grow pure and L-lysine added ADP bulk crystals. The z-cut and polished seeds were mounted at the bottom of glass ampoules. Two separate saturated solutions at room temperature: one pure and the other having 2 mol % L-lysine were transferred to the growth ampoules. The crystallizer was kept in a water bath to avoid the temperature fluctuation of the daily variation. The temperature of the top and bottom portion of the ampoules was set at 300 K and 297 K (room temperature), respectively. The top heater provided the necessary temperature for solvent evaporation while the bottom one was set at the saturation temperature. After 85 days a good crystal of a size of 20 mm in diameter and 120 mm in length was grown. Fig. 1 shows the as grown single crystal and the cut and polished wafers of ADP.

In the case of growing L-lysine added ADP crystal by S-R method, the saturated solution of ADP contained 2 mol % L-lysine. The temperature of the top and bottom portion was set at 298.5 K and 297 K (room temperature), respectively. After few days, the growth started and it took about 80 days to grow a crystal of about 90 mm length which is shown in Fig. 2.

(a)

(b)

Fig. 1. S-R grown ADP crystal, (a) after removing from ampoule and (b) cut and polished ingot

Table 1. Crystallographic parameters of ADP and ADP added with L-lysine crystals.

Sample	a (Å)	b (Å)	c (Å)
ADP	7.510	7.510	7.564
ADP + L-lysine	7.499	7.499	7.548

3. Results and discussion

3.1. X-Ray diffraction studies

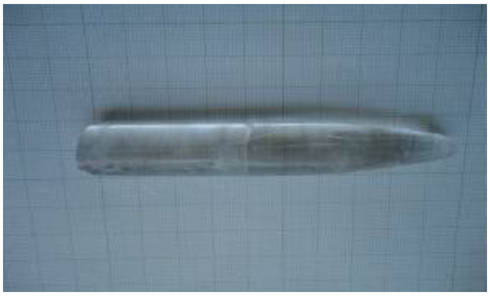
Both the pure and doped ADP crystals were subjected to powder X-Ray diffraction (XRD) analysis using an X-Ray diffractometer (Advance Model D8) with high intensity CuK_α radiation ($\lambda = 1.5406$ Å). Fig. 3 shows the XRD pattern of L-lysine added ADP crystal. The lattice parameters of ADP and ADP added with L-lysine crystals were calculated from the powder XRD patterns and presented in Table 1. From the data, it is observed that both the crystals crystallize in tetragonal system.

It may be noted from Table 1 that all lattice parameters of ADP crystal are larger than those of ADP added with L-lysine.

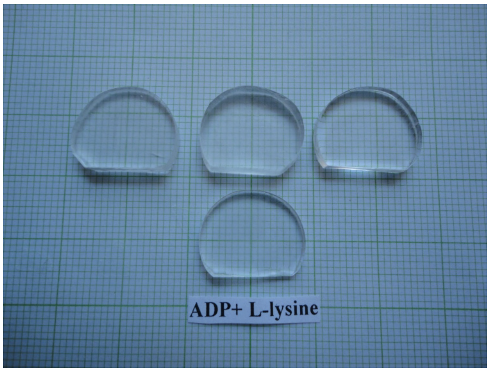
3.2. Fourier transform infrared analysis (FT-IR)

The FT-IR spectra were recorded for pure and doped crystals in the range of 400 – 4000 cm^{-1} using a FT-IR-8400S-SHIMADZU infrared spectrometer by KBr pellet technique.

Fig. 4 shows the FT-IR spectra of the pure ADP and L-lysine-added ADP crystals. It is observed that both the spectra closely resemble each other, hence, no change in the functional groups could be detected. This again confirms that L-lysine has not entered into the crystal lattice. The broad band in the high energy region is due to O–H vibrations in



(a)



(b)

Fig. 2. S-R grown L-lysine added ADP crystal, (a) after removing from ampoule and (b) cut and polished ingot.

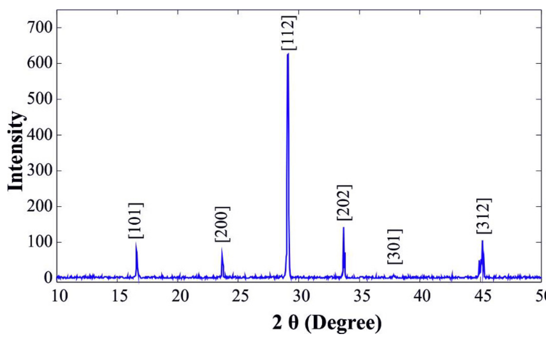


Fig. 3. XRD pattern of L-lysine added ADP crystal.

water, P–O–H group and N–H vibrations of ammonium [11]. Considering curve I, P–O–H vibration occurs in 1094 cm^{-1} and 914 cm^{-1}, and the vibrations of PO_4^{-3} are seen in 570 cm^{-1}, too.

The curve II shows the functional groups of N–H, P–O–H, H–O–H, present in $NH_4H_2PO_4$ crystal. In the spectrum, the peak observed at 1650 cm^{-1} is related to bending vibration of water molecules and the peaks at the wave numbers 3224 cm^{-1} and 3124 cm^{-1} are due to stretched vibrations of N–H. P–O–H occurring at 1095 cm^{-1} and 918 cm^{-1}. The peak observed at 547 cm^{-1} indicates PO_4^{-3} vibrations.

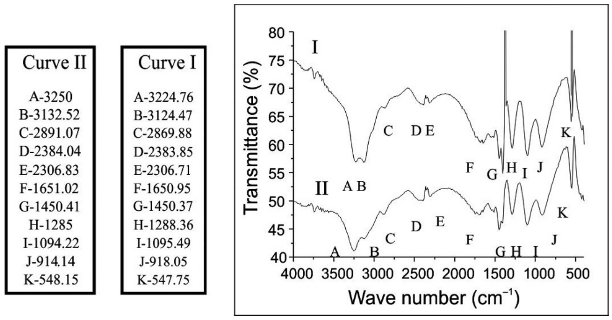


Fig. 4. FT-IR spectra of (I) ADP and (II) ADP + L-lysine crystals.

3.3. Optical transmission studies

Optical transmission spectra have been recorded using Shimadzu (Model UV-1650 pc) spectrophotometer. The recorded transmittance spectra of 2 mm thick pure and L-lysine added ADP crystals in the wavelength range 200 – 1100 nm are shown in Fig. 5. The crystals show good transparency in the entire UV, visible and near IR region. This shows that doping the crystal with L-lysine did not shift the lower cut-off value. It is seen that doping with L-lysine has lowered the transparency of the crystal to some extent.

3.4. Vicker's microhardness studies

Hardness of a material is a measure of the resistance it offers to local deformation. The microhardness measurements were made using Buehler hardness tester with Vickers's diamond pyramidal indenter. Selected (001) faces of pure and doped crystals were subjected to Vickers's static indentation for loads of 10, 25, 50 and 100 g for a dwell time of 10 s. Vickers microhardness number was determined using

$$Hv = 1.81544 f/d^2 (\text{kg/mm}^2),$$

where Hv is the Vickers's microhardness, f the applied force, d the diagonal length of the indentation impression [12].

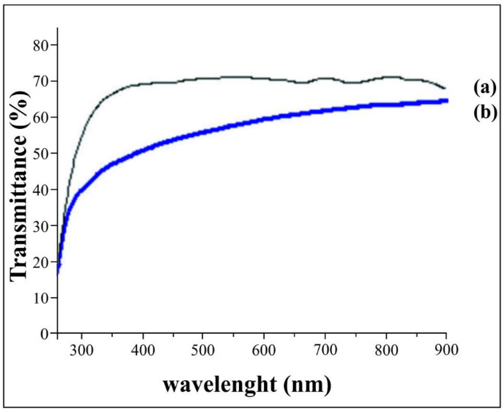


Fig. 5. Optical transmittance spectra of (a) ADP and (b) ADP + L-lysine crystals.

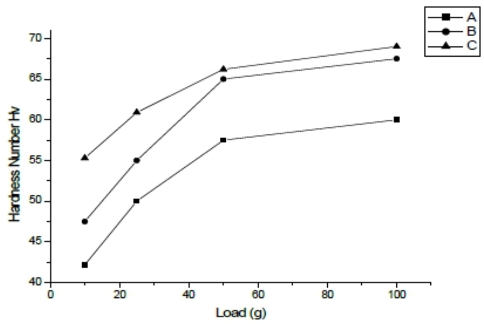


Fig. 6. Comparison of hardness number of ADP crystals grown by (A) conventional method [10], (B) S-R method and (C) ADP + L-lysine crystal grown by S-R method.

Fig. 6 gives a comparison of Vickers microhardness of ADP crystals grown by conventional [13] and S-R methods and L-lysine-doped ADP crystal grown by S-R method. It is found from the results that the doped crystal shows higher hardness than the pure one. This increase in the hardness of doped ADP crystal can be attributed to the presence of additive in it. It is also observed that the hardness of the L-lysine added crystal is higher than that of the pure ADP crystal grown by both conventional and S-R methods.

4. Conclusions

⟨001⟩ directed pure and L-lysine-doped ADP crystals were grown by SR method. Structural studies revealed that both the crystals were of tetragonal structure with lattice parameters of ADP crystal being larger than those of doped one. FT-IR studies showed no change in the functional groups due to additive present in the doped crystal which confirmed that L-lysine had not entered into the crystal lattice.

The crystals exhibited good transparency in the entire UV, visible and near IR region. The crystal doped with L-lysine showed lower transparency compared to the pure one.

Vickers microhardness studies showed that L-lysine added ADP crystal possessed higher hardness than pure ADP crystal regardless the method by which the crystal was grown.

It is obvious that the S-R method of ADP crystal growth from solution without any additives permits getting crystals of more desirable linear size, transparency and hardness.

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