Advance Physics Letter

Thermal and optical properties of l-lysine doped ammonium dihydrogen phosphate, a novel semi-organic crystal

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Abstract : Single crystals of ADP doped with 1% of l-lysine, a semi-organic nonlinear optical (NLO) material, have been grown by slow evaporation method. Good optical quality single crystals with dimensions up to 20 x 5 x 15 mm^3 are obtained. It is observed that growth rate of doped ADP is higher than pure ADP. The grown crystals were characterized by powder XRD, FTIR, UV absorption and transmission studies. The thermal stability of the crystal was studied by thermo-gravimetric analysis (TGA).

Keywords: ADP–L-lysine doped crystal; FTIR, TGA, UV analysis etc.

I. INTRODUCTION

Introduction Ammonium dihydrogen phosphate (ADP), a hydrogen bonded compound, belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. These molecular crystals exhibit low-temperature order–disorder phase transitions. Below148.5K, ADP is antiferroelectric and belongs to P_{212121} space symmetry group while above this temperature it becomes paraelectric having a I42d symmetry [1–3]. Ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) are nonlinear optical materials and have been used as optical modulation Q-switch, quantum electronics and frequency converters. Particularly, optical crystals with lower impurity and higher damage threshold are required for inertial confinement fusion [4, 5]. In recent years, various growth methods and apparatus have been continuously developed to improve the crystal quality and the growth rate [6–8]. One of the obvious requirements for an on-linear optical crystal is that it should have excellent optical quality. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage in applications. It is difficult to grow large optical quality crystals of these materials for device application.

Semiorganic nonlinear optical crystals formed by amino acids with inorganic materials possess the combined advantages of high optical nonlinearity of the organic amino acids and the favorable mechanical and thermal properties of inorganic solids. The importance of amino acids in NLO applications is due to the fact that all the amino acids except glycine contain chiral carbon atom and crystallize in noncentrosymmetric space groups. In solid-state, amino acid contains a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH_3^+). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO applications. L-lysine, l-valine, l-arginine, l-arginine phosphate, l-threonine, l-threonine acetate, l-histidine, l-hisditine hydrochloride, are some of the examples of the amino acids.

In the present studies, our aim is to investigate the thermal, mechanical and other properties of the single crystals of l-lysine doped ADP crystal. ADP doped with l-lysine crystals of dimension up to 20 x 5 x 15 mm^3 have been grown by slow evaporation method at room temperature, and the Fourier transform infrared (FTIR) analyses, Thermal behavior of crystal, microhardness and UV measurements have been studied and discussed.

II. EXPERIMENT

2.1. **Material synthesis**

Crystal growth the commercially available ADP was used for growth, after repeated recrystallization. Single crystals of pure and l-lysine added ADP were grown using deionized water as a solvent by slow evaporation technique. According to the solubility data [9], 400 ml saturated solution of ADP was prepared and filtered at room temperature and the solution was divided equally into two beakers and it was named as A and B. The beaker A was kept closed with porously sealed cover, then1 mol% of l-lysine was added into the beaker B and it was closed with the same type of covers. Solutions in all the beakers were allowed to evaporate in an identical condition. After seven days, tiny crystals were seen in the beaker B, where as in A, it was observed one day later only. All crystals reached maximum size in 30days. The colourless transparent pure ADP crystals harvested were of size up to 15 x 5 x15 mm^3 and doped crystals of size upto 20 x 5 x15mm^3. It was observed that the

growth rate of l-lysine added ADP is faster than the pure ADP and comparably big crystals were obtained in L-lysine added solution. The L-lysine doped ADP is shown in Fig. 1. Ammonium dihydrogen phosphate and L-lysine and L-histidine used in the present study were from Merck, India.

Fig.1. Grown crystals of L-lysine doped ADP

III. RESULT AND DISCUSSIONS

3.1. Powder XRD analysis

An advance X-ray diffractometer (Bruker AXS D8 Advance) was used to recieve the diffraction pattern of the crystals with CuKα radiation of wavelength 1.54056 Å. The samples were scanned over the required 2θ range of 10-80^o at a scan speed of 0.02^o per second. The crystalline phase structure of the samples was identified from the crystallographic parameters such as 2θ, d-spacing, relative intensity and the hkl values (Miller indices). Indexing of a powder pattern consists of assignment of the three numbers h, k and l to each reflection. All the reflections of powder XRD patterns of the grown crystals in powder form were indexed. The indexed X-ray powder diffraction patterns of the grown crystals of pure and doped ADP are shown in the figure 2.

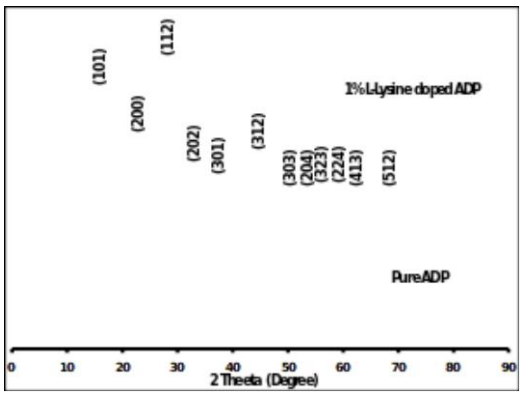

Figure 2: Comparative X-ray Diffraction Pattern of pure and doped ADP crystals

The grown crystal belongs to tetragonal crystal system as confirmed by single crystal XRD study. The unit cell parameters are determined from XRD patterns and data analyzed from it is enumerated in table 1.

The results showed that L-lysine entered into ADP lattice. The sharp peak indicates the crystalline nature of grown crystals. It showed that the crystal structure of ADP remains unaltered even after doping. No additional peaks are present in the XRD spectra of doped ADP crystal, showing absence of additional phase beside the tetragonal system, due to doping. The observed prominent peaks of all crystals are (101), (200), (112), (202), (301), (312), (303), (204), (323), (224), (413) and (512) are shown in figure 2.

Table 1 Powder XRD data of pure ADP single crystal

Sr. No.	Miller Indices			Pure ADP			L-lysine doped ADP		
				a=b =7.4116Å, c=7.4795Å			a=b =7.4911Å, c=7.5786Å		
	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/Io (%)	d_{obs} (Å)	d_{cal} (Å)	I/Io (%)
1	**1**	**0**	**1**	5.2956	5.3009	62.40	5.3166	5.3276	75.09
2	**2**	**0**	**0**	3.7422	3.7420	100	3.7455	3.7455	40.85
3	**1**	**1**	**2**	3.0683	3.0684	32.72	3.0688	3.0819	100
4	**2**	**0**	**2**	2.6544	2.6544	9.59	2.6553	2.6638	17.35
5	**3**	**0**	**1**	2.3708	2.3682	13.54	2.3716	2.3716	6.67
6	**3**	**1**	**2**	2.0075	2.0084	45.06	2.0072	2.0086	29.38
7	**3**	**0**	**3**	1.7730	1.7740	5.06	1.7725	1.7758	5.73
8	**2**	**0**	**4**	1.6811	1.6820	5.39	1.6849	1.6906	5.17
9	**3**	**2**	**3**	1.6013	1.6001	11.06	1.6024	1.6046	7.43
10	**2**	**2**	**4**	1.5368	1.5342	6.32	1.5370	1.5409	6.31
11	**4**	**1**	**3**	1.4715	1.4710	5.06	1.4724	1.4750	5.86
12	**5**	**1**	**2**	1.3702	1.3737	6.59	1.3703	1.3697	3.92

The variation in intensity of diffracted peaks is observed. The differences in the peak amplitude can be as described to the different size and orientation of the powered grains. The degree of sharpness of peaks indicates the crystallinity of the grown crystals.

3.2 FTIR analyses

The FT-IR spectrum was recorded for L-lysine doped ADP crystals using JASCOFT-IR410 spectrometer by KBr pellet technique in the range 400–4000 cm^{-1} and is shown in Fig. 3. The effect of L-lysine on the functional

groups of the pure ADP crystal has been identified by the spectrum. The broad band in the high-energy region is due to the O–H vibrations of water, P–O–H group and N–H vibrations of ammonium. The peaks at 1092 and 932 cm^{-1} represent P–O–H vibrations. The PO_4 vibrations give their peaks at 544 and 470 cm^{-1}. The peak at 2370 cm^{-1} is due to the combination of band of vibrations occurring at 1293 and 1290 cm^{-1}. The broadness is generally considered to be due to hydrogen bonding interaction of $H_2PO_4^-$, $COOH^-$ and $NH3^+$ with adjacent molecules. The bending vibrations of water give its peak at 1646 cm^{-1}. The peak at 1402cm^{-1} is due to the bending vibrations of ammonium. In the structure of ADP strong bonding is there between P and O. The addition of l-lysine can make a small change in the hydrogen bonding of the crystals. The changes in the hydrogen bonds make some variations in the stretching vibrations and in the peak positions.

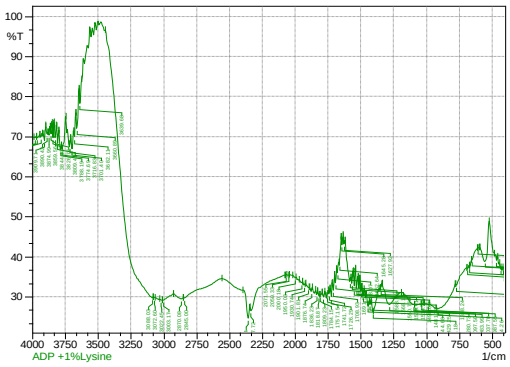

Fig.3 FTIR spectra of L-lysine doped ADP

Although this spectrum also carries similar features of that of ADP, there is a distinct evidence for the presence of l-lysine in the lattice of ADP. The peaks appearing at 1567 and about 1415 cm^{-1} are due to asymmetric mode of —COO and CQC stretching and symmetric mode of —COO and C–N stretching of l-lysine. In addition, shift in the peak positions of P–O–H and PO_4 vibrations compared to ADP established the presence of the additive in the lattice sites of ADP.

3.3. Thermal Analysis

TGA of ADP mixed with 10 mole% of BGSN was carried out between room temperature (28℃) and 600℃ at a heating rate of 10 K min^{-1} as shown Fig. 4. The experiment was performed in nitrogen atmosphere. TG trace representing the decomposition temperature of the crystal. It is seen from the TG that the weight loss started for the pure ADP at 195 ℃, a careful examination of DTA thermogram revealed a endothermic peak around 207.5 ℃. After 195 ℃ weight loss started and a steady decrease in weight observed (63.4%) up to 533℃, which may be due to the decomposition of the sample. At temperatures above 595℃, the final stage of decomposition occurs, giving a total loss equal to 90%. The DTA of L-lysine doped ADP was carried out between 28 and 600 ℃ in nitrogen atmosphere using NETZSCH STA 409 PC at a heating rate of 10 K min^{-1}.

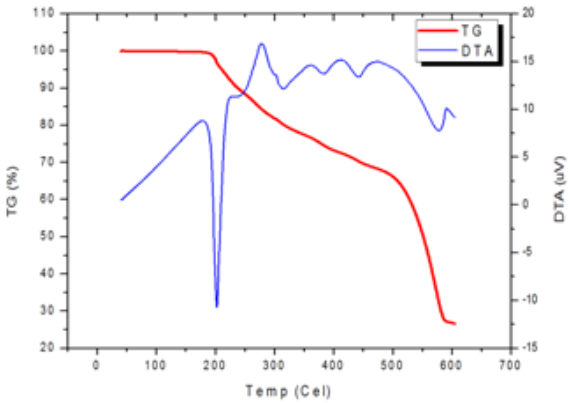

Fig.4. TGA/DTA of ADP doped with 1% L-lysine

The DTA trace indicates a strong endothermic starting at 207.5 ℃ due to its melting of the crystal. Hence, from these thermal studies, it is concluded that the crystal can retain texture up to 207.5℃. Its application is restricted up to 207.5℃ only, which is less than pure ADP (215℃) but greater than other semi-organic materials like L-alanine cadmium chloride (LACC) (110℃), triallyl thiourea cadmium chloride (ATCC) (101℃), triallyl thiourea cadmium bromide (ATCB) (97℃), triallyl thiourea mercury chloride (ATMC) (133℃) and allyl thiourea mercury bromide (ATMB) (125℃) [10 –14].

3.4. UV-visible spectral study

Since single crystals are mainly used in optical applications, the optical transmission range and the transparency cutoff are important. Therefore UV-Vis. transmission spectroscopy was carried out using a Shimadzu spectrophotometer. The absorption spectrum of ADP doped with L-lysine is shown in figure 5. A strong absorption peak corresponding to the fundamental absorption appears at 230 nm.

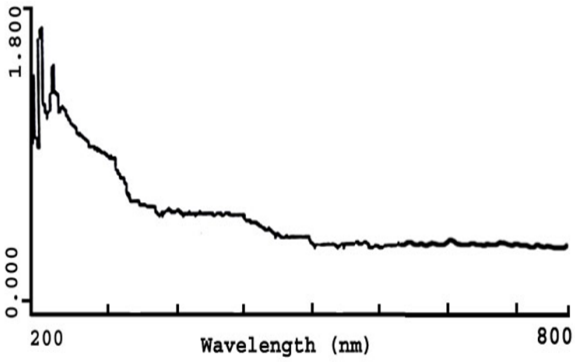

Fig. 5. UV–visible absorption spectrum of pure and doped ADP

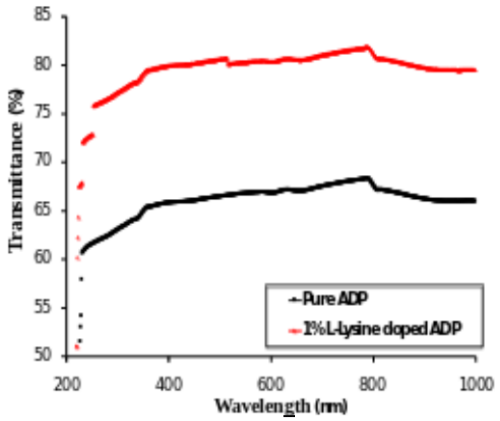

Fig. 6. UV–Visible transmission spectrum of pure and doped ADP

Transmission spectrum of pure and lysine doped ADP is compared in fig. 6. It is observed that the doped crystal shows heigher transmittance of 83 % which prove the good optical quality as compared to pure ADP.

IV. CONCLUSION:

The L-lysine doped ADP single crystal is synthesized by slow evaporation method. The optically good quality of single crystal of maximum size up to 20 x 5 x 15 mm^3 is obtained. It is observed that the growth rate of doped ADP is greater than pure ADP. FTIR analysis confirms the presence of all functional group. From TGA/DTA analysis it is found that the crystal is thermally stable up to 207.5^{0}C. The UV absorption analysis shows a strong absorption peak at 230nm and crystal shows transmittance of 83% which proves a good optical quality.

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