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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1555-1558, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Growth and Characterization of L-threonine doped ADP Crystals

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Abstract: Ammonium Dihydrogen Phosphate (ADP) crystals are one of the most popular crystals used for Nonlinear Optical (NLO) applications. Most of the amino acids also exhibit NLO properties. The effect of doping of L-threonine (amino acid) in ADP crystals has been investigated. The pure and 0.4 wt % of L-threonine doped ADP crystals were grown by slow evaporation method at room temperature. Good quality and transparent crystals were obtained within 8 to 10 days. The Powder XRD study shows the tetragonal structure with lattice parameter a = b = 7.506 Å and c = 7.555 Å. Doping of L-threonine in ADP crystal was confirmed by paper chromatography and FT–IR spectroscopy. Thermal studies (TG/DTA) study carried out for determination of decomposition of pure and L-threonine doped ADP Crystals.
Keyword: Solution growth, PXRD, FT-IR, TGA/DTA.

1. Introduction and Experimental:

Ammonium dihydrogen phosphate (ADP) is one of the most popular crystals used for piezoelectric and non-linear Optical (NLO) applications. ADP belong to a large number 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 belong to $P2_12_12_1$ space symmetric group, above this temperature it gives the paraelectric behavior having I4/2d symmetry [2-3]. One of the earliest applications of ADP was that it was used in design of hydrophone for acoustically active mines, due to its zero aging characteristic ADP remains stable during many year of storage [4]. ADP crystal exhibits properties like second harmonic generation, sum and difference frequency conversion etc, for improvement of NLO performance and other properties various amino acids are used as a dopant. Previously, L-histidine [5], L-lysine monohydrate dehydrate [6] etc were used as dopants in ADP crystals and studied structural, mechanical, optical, electrical, dielectric and SHG properties. The aim of present study is to investigate structural, spectroscopic and thermal properties of pure and L-threonine doped ADP crystals.

The doping of L-threonine into ADP was achieved by adding 0.4 wt. % of L-threonine in ADP solution prepared in double distilled water. The solution was stirred for 3 hours to achieve homogenization. The pure and doped ADP crystals were grown by slow evaporation technique at room temperature. The solution was sealed with porous lid and placed in a dust free atmosphere for slow evaporation. The optically good quality and transparent crystals were harvested in 8 to 10 days.

The powder XRD was carried on PHILIPS X'PERT MPD system and the data were analyzed by software powder-X. The FTIR spectra were recorded in the region 400–4000 cm^{-1} employing THERMO NICOLET 6700 in KBr media. The thermo gravimetric analysis (TGA) was performed on NETZSCH Geratebau GmbH setup from room temperature to 900^{o}C at a heating of 15^{o}C/min in nitrogen atmosphere.

2. Results and Discussion:

2.1 Powder X-Ray Diffraction:

Figure (1) shows the powder XRD pattern of pure and 0.4 wt% L-threonine doped ADP crystals. The powder XRD of Pure and doped ADP crystal shows the slight variation in the unit cell parameters and matching of peaks shows single phase nature of samples. It is also seen that there are not present additional peaks, but only change in the intensity of the peaks takes place. The unit cell parameters are belong to tetragonal crystal system and given in table -1.

Figure 1. Powder XRD patterns of pure and L-threonine doped ADP crystals.

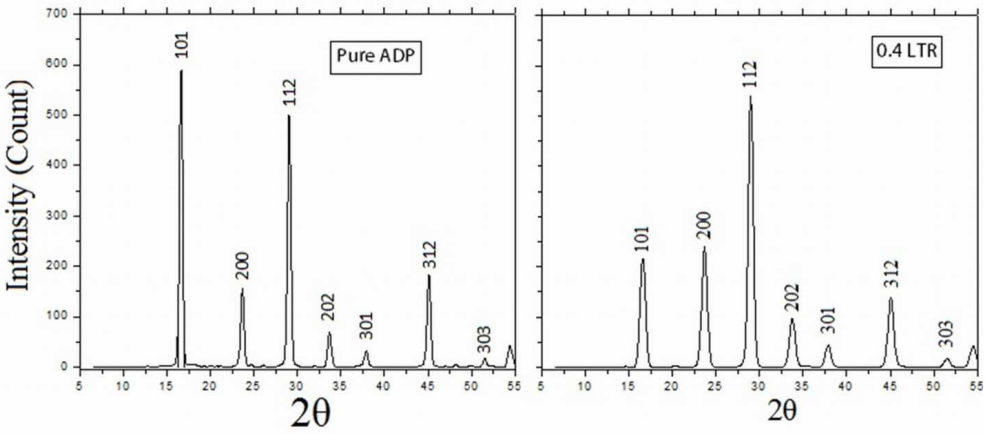


Table 1. Unit Cell Parameters of pure and L-threonine doped ADP crystals

Samples	Lattice Parameter (Å)		Cell Volume ($Å^3$)
	a = b	c	
Pure ADP Crystal	7.506	7.555	425.6
ADP + 0.4 % L-threonine	7.503	7.548	424..9

2.2 FT-IR Spectroscopy Study:

The FT-IR spectra of pure and 0.4 wt% L-threonine doped ADP crystals are shown in figure (2). The confirmation for interaction between ADP and amino acid can be identified with the help of shifting the peak positions of P-OH and PO vibrations compared to pure ADP [7]. In the spectrum of pure ADP, the broad band around ~3230.87 cm^{-1} and ~3123.82 $cm^{-1}$are due to the O-H vibration of P-O-H group and N-H vibration of NH_4 respectively. The band around ~2823.88 cm^{-1} is due to N-H stretching of ammonia. The band observed at

~2314.66 cm^{-1} is due to hydrogen bonding of CH_2. The band around ~1758.17 cm^{-1} is due to O-H bending vibration. The FT-IR spectrum of 0.4 wt% L-threonine doped ADP crystal shows the same absorption bands as of the pure ADP with some additional absorption bands and the absorption band positions have shifted from lower to higher wave numbers due to presence of L-threonine into ADP crystal. In figure (2), the absorption at ~2825.81 cm^{-1} is due to symmetric C-H stretching of L-threonine, the absorption at ~1757.21 cm^{-1} is due to C=O stretching of COOH group and NH stretching of NH_3 group. This confirms that the dopant has entered the crystalline matrix of ADP crystal. The Paper Chromatography of dissolved crystal using nin-hydrin exhibited purple spot, which indicates the presence of amino acid in crystal.

2.3 Thermal Analysis:

Figure (3) shows the TG/DTA curve for pure and 0.4 wt% L-threonine doped ADP crystals. The pure and 0.4 wt% L-threonine doped ADP crystals remain stable up to 180°C and 170°C, respectively and then decompose slowly, thereafter at 214.1°C and 210.7°C temperatures metastable states are observed with 3.3% and 0.77% weight in pure and 0.4 wt% L-threonine doped ADP respectively. Finally the samples are decomposed with comparatively rapid decomposition to final stable state at 641.4°C and 630°C with 43.7% and 32.6% weight for pure and 0.4 wt% L-threonine doped ADP crystals, respectively. The thermo-grams indicate that the doping of L-threonine has made ADP crystals less thermal stable. The DTA curve shows the endothermic peak at 215.6 °C and 213.1° C for pure and for 0.4 wt% L-threonine doped ADP respectively. The endothermic peak corresponds to the decomposition temperature. The reason for shifting of endothermic peak is due to phase change, melting and decomposition of ADP crystal at higher temperature [8].

Figure 2. FTIR spectra of pure and L-threonine doped ADP crystals

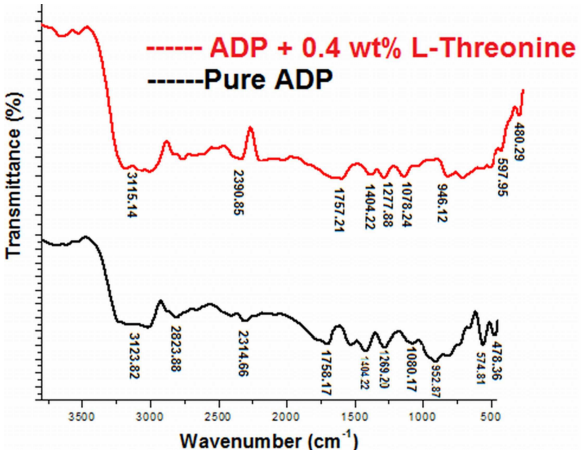
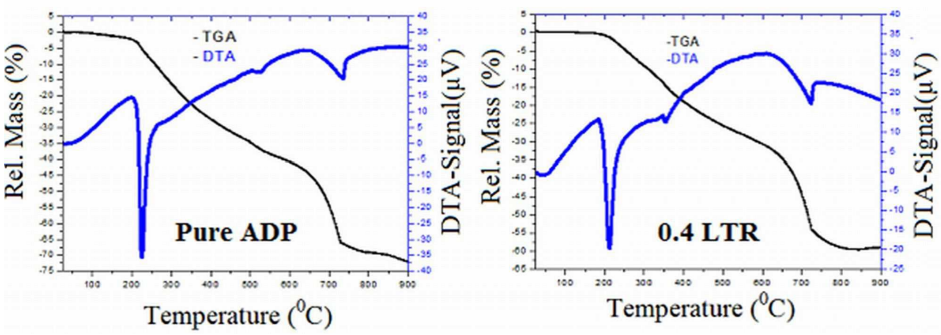


Figure 3. TGA/DTA curve of pure and L-threonine doped ADP crystals.



Acknowledgement:

The authors are thankful to Prof. H. H. Joshi, Head of Department, Department of Physics, Saurashtra University, Rajkot and Dr. S. U. Vora, Principal, Shri M. P. Shah Arts & Science College, Surendranagar, for their encouragement and kind support for carry out present research work.

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