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STUDIES ON SEEDED GROWN CRYSTAL OF POTASSIUM DIHYDROGEN PHOSPHATE WITH ADDITIVES MIXING OF AMINO ACID

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ABSTRACT

A comparative study was carried out on L-valine amino acid doped potassium dihydrogen phosphates (KDP), LV doped KDP were prepared by seed rotating crystal method (SRCM) as well as by solution growth as a solvent evaporation at room temperature. The dopant concentration was taken 0.4 mole % and 0.8 mole % with rotation rate of seed was 30 rpm, for 25 days. The transparent crystals along c axis i.e. along <011> plane with dimensions 10 x 11 x 23 mm, for 0.4 mole % and 10 x 12 x 35 mm for 0.8 mole % were harvested. The parameters of unit cell were determining using powder XRD. FTIR show the influence of L- valine and functional groups were identified. Thermal properties of the crystal have been studied by using Thermo gravimetric (TG) and Differential thermal analysis (DTA).

KEYWORDS: -growth from solution, Powder XRD, thermal properties.

1. INTRODUCTION

A representative hydrogen bonded materials Potassium dihydrogen orthophosphate (KDP) which posses' important piezoelectric, ferroelectric, electro-optic. Mainly NLO properties of KDP crystal material was of great interest in the recent years because of their potential numerous applications. Many investigations are being carried out to synthesize new materials with large second-order optical nonlinearities in order to satisfy day-to-day technological demands. [1]

Organic impurities enhance the NLO properties hence in present communication, we had been present the 2 amino-3methylbutanoic acids (valine) doped KDP crystal. We have made attempt to grow a good transparent crystal by SRCM and slow evaporation solution growth method. The excellent perfection seed crystal prepared should be choosing and which suspended on a smooth seed holder to avoid nucleation. Initially the doping concentration in mother solution was 0.4 mole % and 0.8 mole % with rotation rate of DC motor was about 30 rpm. Fast rotation increase the growth rate as up to 100rpm but which decrease transparency which is wieldy used to study optical properties of crystals. The growths have been observed was about 1mm per day. As driving force, super saturation determines the growth rate along <011> or <101> faces that vary even under the identical environmental conditions and thus the different aspects of crystal. Hence good quality of transparent crystals growth has been harvested with dimensions 10 x 11 x 20 mm, 10 x 12 x 35 mm. The crystal structure has been studied by powder XRD and some changes in the lattice parameters have been recorded. FT-IR spectrum of doped and pure KDP crystals confirms doping of LV in the host crystals.

2. RESULT AND DISCUSSION

2.1 CRYSTAL GROWTH

A.R grade sample of KDP and valine amino acid along with de-ionized water were prepared for the growth of crystals. Solution was prepared in under saturation condition which was thoroughly stirred for 5 to 6 hours for homogenization at 40^{o}C. The KDP with LV-amino acid of 0.4 mole % and 0.8 mole % will dissolve in 250 ml of double distilled water in different beakers to get saturated solutions. The saturated solutions kept at dust free environment at room temperature will produce the seed crystals required for further growth.

The <011> direction of the seed crystal was selected for unidirectional crystal growth. The Schematic diagram of modified solution crystal growth system designed in our laboratory is shown in fig. (1). Firstly processed seed is placed on cylindrical platform which

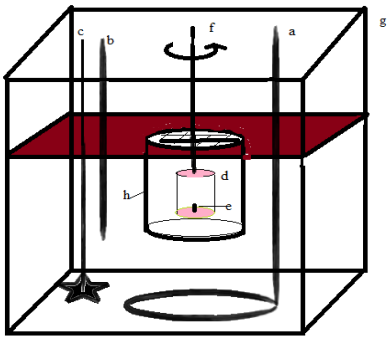

fig .1 Scheme of the crystallizer :(a) Heating element, (b) thermocouple, (c) stirrer, (d)seed holder, (e) growing crystal, (f) rotation system, (g) outer glass chamber, (h) inner growth chamber

was made by using acrylic sheet. The cylindrical platform attached with rotating unidirectional DC motor. This was controlled by electronic dc power supply of 12 V about 30 rpm. Whole assembly placed on rectangular constant temperature bath which was made by glass plate. One constant temperature controller were used which was maintained at 40^0C.

There are different methods to grow high quality pure crystals through a systematic and aligned planning. The crystal growth does depend upon various parameters such as its saturation, temperature, size, mass transfer, type of degree of impurity it contains [2-5]. The history of researches confirms that the different faces of crystal have different growth rate and different face energy. The different planes of single crystal may show different characteristics behavior. In this article the LV doped KDP growth rate is approximately 1mm per day was observed. A good transparent quality of crystal is obtained as shown in fig. (2)

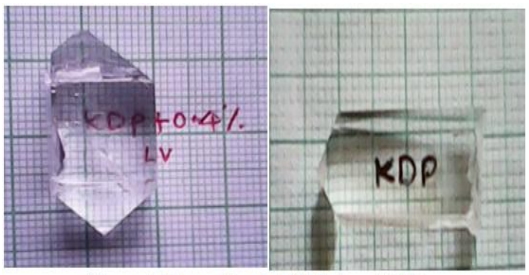

Figure 2: Grown Crystal of LV doped KDP

2.2 Morphology

The pure and doped KDP crystals, show tetragonal morphology it means that there is no change in the structure of crystal. In present work it was observed that when the molar concentration of either of the components increases, the lateral thickness of crystal may decrease. N.P. Zaiteseva et. Al. have suggested that usually growth rate along <100> and <010> planes was zero referred as "dead zone" [6].

2.3 POWDER XRD ANALYSIS

The powder X-ray diffraction analysis for the grown crystals was carried out to identify the cell parameters using an Bruker AXS D8 Advance (λ=1.5406 Å) Vertical, Theta/2 Theta geometry , X-ray diffractometer. The powder sample scanned over the range 10-70^0 at a scan rate of 1^0/min is shown in figure 3. The observed'd' values for different 2θ with (h k l) indices of corresponding reflection planes for the crystal are given in table 1. The XPXD peaks are indexed and unit cell parameters are calculated with help of programmable software of powder X. The unit cell parameters of LV doped KDP crystal are shown which are in good agreement with the result reported [7].

Table 1(a). Powder X-ray diffraction data for LV+KDP

Sample	Crystal system	Space group	Unit cell parameters	Cell volume (Å^3)
Pure KDP	Tetragonal	I-$\bar{4}$2d	a=b=7.448 Å, c=6.977 Å	387.03
0.4 mole%	Tetragonal	I-$\bar{4}$2d	a=b=7.397 Å, c=6.878 Å	376.45
0.8 mole %	Tetragonal	I-$\bar{4}$2d	a=b=7.428 Å, c=6.934 Å	382.58

Table 1 (b) PXRD data of doped KDP

SN	2 θ	$d_{obs.}$	$d_{cal.}$	h	k	l	I/I_0
1	17.487	5.0654	5.0687	1	0	1	20.61
2	23.955	3.7104	3.7140	2	0	0	100
3	29.782	2.9963	2.9959	1	2	1	14.43
4	30.803	2.9004	2.8935	1	1	2	90.72
5	34.112	2.6262	2.6262	2	2	0	27.83
6	35.298	2.5406	2.5344	0	2	2	10.30
7	38.502	2.3363	2.3318	0	3	1	21.64
8	46.521	1.9505	1.9446	1	3	2	61.85
9	55.092	1.6656	1.6610	2	4	0	10.30
10	58.520	1.5759	1.5708	0	2	4	17.52
11	64.042	1.4527	1.4526	3	4	1	13.40
12	69.700	1.3480	1.3430	1	5	2	18.55
13	74.458	1.2732	1.2739	3	5	0	8.24
14	79.510	1.2045	1.2099	0	3	5	13.40

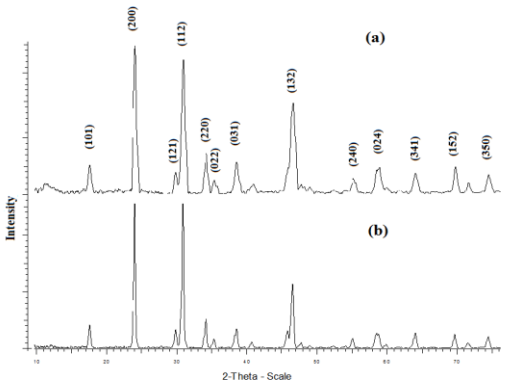

Fig. (3)powder XRD pattern of (a)Pure KDP (b) LV+ KDP

2.4 FTIR STUDIES ANALYSIS.

The vibration frequencies of functional groups of additives used in KDP crystal has been identified by FTIR spectroscopy shown in fig (4). The spectra were recorded in the region of range 400- 4000 cm $^{-1}$ using a Thermo Nicolet, Avatar 370 FTIR spectrometer by KBR beam splitter. Figure 4 shows the FTIR spectra of pure KDP [7] and KDP doped with valine (0.4 mole% and 0.8 mole %). The slope band in the high energy region is due to free O–H stretching of water, P–O–H group of pure and L- valine doped KDP (P. Kumaresan et al.,2008). By Comparing these graphs it shows there is high similarities, it means that pure KDP peaks are predominant over valine peaks due to the low amount of doping valine in the compound compared to pure KDP. These vibrations of amino acids present in the spectra of doped crystals reveals the incorporation of impurities in the crystals.(B Suresh Kumar et al.2008)

Table 2 FTIR frequencies of fundamental vibrations of pure KDP and doped samples/cm-1

SN	Pure KDP cm $^{-1}$	0.4% LV +KDP cm $^{-1}$	0.8% LV +KDP cm $^{-1}$	Assignment
1	3605	---	----	Free O-H stretching Hydrogen bonded of KDP
2	3341	---	3472.45	O-H-O stretching of NH_3^+ amino acid
4	2830	2844.65	2824.74	P-O-H symmetric stretching
5	2466	2484.24	2468.90	O=P-OH stretching
6	2362		2362.94	NH_3^+ Bending superimposed with P-O-H bending of KDP
7	1655	1718.49	1671.25	O=P-OH stretching
8	1299	1297.39	1297.42	C-H bonding of LV
9	1101	1095.92	1097.51	P=O stretching
10	904	899.72	899.72	P-O-H stretching of KDP
11	539	534.66	537.76	Symmetric HO-P-OH bending
12	416	409.81	397.82	PO_4 stretching

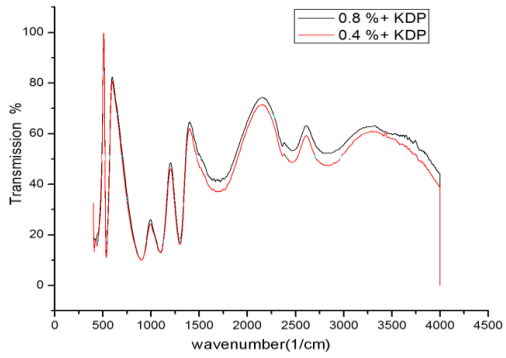

Figure (4) FTIR spectra of LV + KDP crystals.

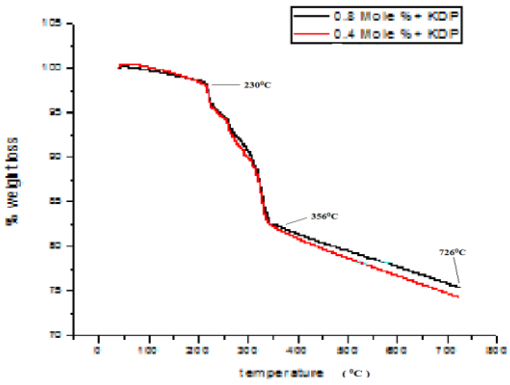

Figure (5) UV spectra of LV+KDP crystals.

2.5 THERMAL ANALYSIS

Thermogravimetric Analysis (TG) determines the weight changes of a sample, whereas Differential Thermal Analysis (DTA) measures changes in temperature between a sample and a reference, as a function of temperature or time which are used to investigate the melting behavior, Glass Transition, Crystallization, Oxidation Stability, Kinetics, Purity, and Specific Heat. TG/DTA carried out with the help of an instrument Perkin Elmer, Diamond using KDP crystals as sample and alumina as reference. The TGA/DTA traces are shown in figure(5).TGA curve sharply decrease at temperature at 230 ℃ it means crystal is thermally stable up to 230 C and after this crystal decomposes at 356 ℃ and completely decomposes at 726 C. DTA graphs show the peaks at 219.70 ℃, 265.39℃ , 297.01 and 323.95 which reveal endothermic reaction. Enthalpy Δ H changes in the endothermic reaction are 241.44 J/gm, 63.75 J/gm.

3. CONCLUSIONS

An NLO property gives versatile importance to KDP crystal. Doping of different concentration of amino acid alter some basic parameters. In present work L-

valinedoped KDP crystal has been investigated through Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Thermo gravimetric and differential thermal analysis (TA/DSC). Powder XRD of LV doped KDP confirms the grown crystal belongs to the tetragonal scalerohedral symmetry with space group $I\bar{4}2d$ having dimensions a=b=7.428 Å, c=6.934 Å. The XRD data is verified by KDP crystal JCPDS Card nos. 35- 0807. Prominent peak of doped KDP (101), (200), (212), (211), (312), (310), (303), (312), were observed. FTIR confirm the presence of organic additive amino acid in potassium dihydrogen phosphate. DTA and TGA of Valine doped KDP shows the addition of organic impurity increase the thermal stability of KDP crystal.

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