Review Of Research
Vol.2, Issue. 10, July. 2013
ISSN:-2249-894X
Available online at www.reviewofresearch.net
ORIGINAL ARTICLE

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NEW MIXED CRYSTAL OF KDP AND ADP WITH DMG AS DOPANT

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Abstract:

Single crystals of a new nonlinear optical material Dimethyl Glyoxime (DMG) doped with DDP and ADP have been grown from aqueous solution by slow evaporation technique with a period of 3 weeks. The presence of DMG in the crystal lattices has been qualitatively determined by powder XRD, FTIR UV and analysis the surface morphology of the as grown specimens which is changed with the nature and concentration of dopants was studied by Scanning Electron Microscopy (SEM). The presence of dopants was confirmed by Energy Dispersive Spectrometry (EDS).

KEY WORDS:

FTIR ; Optical Imaging Microscopy; Dimethyl Glyoxine Solution growth ; XRD;UV,SEM;EDS.

.INTRODUCTION

Potassium Dihydrogen Phosphate (KDP) and Ammonium Dihydrogen Phosphate (ADP) form well defined crystals. Mixed crystals of (K,Rb) $HC_8 H_4 O_4$ are tested as well for their application an X-ray monochromators. For that reason their growth from aqueous solution is widely investigated. KDP and ADP are extensively studied for its crystal morphology [1-8]. The KDP and ADP crystals have been studied by means of many different techniques such as optical light microscope, differential contrast methods, X-ray topography and scanning force microscopy also known as atomic force microscopy. It has been found that mixtures of KDP and ADP are suitable substrate for the oriented growth of organic non-linear optical material [9-16]. The growth kinetics of KDP single crystals with inorganic impurities have already have been reported [17]. This crystal is highly stable in vaccum. The aim of present work is to study the influence of impurities on the morphology and properties of KDP and ADP single crystals. DMG is an organic NLO material. The effect of impurities ie DMG, their Structural, optical and mechanical properties of KDP and ADP crystals have been studied.

EXPERIMENTAL

KDP and ADP (E Merck) sample was purified by recrystallisation process. Preparation of KDP with DMG, ADP with DMG and mixtures of KDP and ADP with DMG were prepared at room temperature with three different proportions are A (5:0.03); B (5:0.02) and C (0.90:0.01:0.03). These were filtered and kept for slow evaporate. The beakers were covered with filter paper. Small holes were made on the filter paper. The solution was allowed to evaporation slowly. Crystals formed were harvested after 3 weeks care was taken it minimise mechanical and thermal variations colourless, bright and transparent crystal was obtained. The seed crystals are shown in figure 1a to figure 1e

Title:SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NEW MIXED CRYSTAL OF KDP AND ADP WITH DMG AS DOPANT Source:Review of Research [2249-894X] E. JASMINE VASANTHARANI , N.LAVANYA AND G.MADHURAMBAL yr:2013 vol:2 iss:10

MEASUREMENT

The powder XRD analysis was performed with a graphite monochromated cute radiation and stepsize of 0.008. The samples were examined within a 2θ range of 10-80. Photographs of the crystals are taken and size of the crystals are measured wing LX400 Optical Imaging Microscopy. UV spectral analysis was carried out in perkin Elmer lambda 35 in the range 100-190nm. A Bruker IFS 66 V spectrometer was used to record the FTIR spectra of the compound, by KBr pellet technique in the frequency range 400-4000 cm^{1}. SEM and EDS observed using oxford model Leo 1550 is used for the morphological and average fibril size study.

4. RESULTS AND DISCUSSION

4.1 Powder X-ray Analysis

XRD Patterns of pure and doped KDP, ADP with DMG revealed that the structures of the doped crystals are slightly distorted compared to the pure KDP and ADP crystals. The diffracted peakes are same in pure and doped crystals. The observed prominent peaks of pure and doped crystals are (101), (200), (112), (202), (301) and (312) but the intensities of the diffracted peaks are found to be varied. The sharp peaks and low full – width at half maximum (FWHM) values confirm that crystallinity of the grown crystals is good (figure 2). The observed values are in good agreement with the reported values [18].

4.2 Optical Imaging Microscope

The samples are photographed using Optical Microscopy LX400 to determine the size. The photographs of the crystals are shown at figure 3a to figure 3e. Pure and mixed crystals are tetragonal in shape. They are colourless and transparent crystals.

4.3 UV spectral analysis

The UV spectra for pure and mixed crystals are shown in figure 4a to figure 4e. In KDP, ADP doped with DMG, the II-II* absorption band shifted to longer wavelength when compared to pure KDP and ADP. The absorption at 280nm for pure KDP and ADP, 279nm for KDP with DMG. In mixed crystal C, the II-II* band have no sharp signal but weak absorption is absorbed. This is because of the formation of band between – CO – NH increase the bond length of >C = 0 and thus smaller energy required for this transition and hence absorption shows red end of the spectrum.

4.4 FTIR spectral analysis

The FT-IR spectra for pure KDP, ADP and doped with DMG are shown in Figure 5a to figure 5e In pure KDP and ADP –OH stretching frequencies are at $3401cm^{-1}$, $3400cm^{-1}$, an adding DMG to both KDP and ADP, the –OH stretching Frequency is gradually increased (Table 1). By comparing the spectra of doped and undoped crystals one can easily find missing absorptions for N-H stretching of NH3+, C-H stretching of CH_2 and CH, indicates that DMG doping is successfully achieved. The IR study on pure and mixed crystals clearly indicates the effect of dopants on the crystal structure of pure crystals, which leads to change in the absorption of IR frequencies and the non-linear optical property of both crystals. DMG mixed with both KDP and ADP also change their optical properties.

4.5 SEM Studies and EDS:

The investigation of the influence of dopant DMG on the surface morphology of KDP and ADP crystal faces reveals the formation of structure defect centers (fig 6). In the presence of DMG in the growth medium, the SEM photograph KDP crystal shows a needle structure, while ADP crystal shows fibrous morphology. Scatter centers are observed in doped KDP, ADP and DMG.

The presence of CK, NK, OK, NaK in the doped specimen is confirmed by EDS (figure 7). It is observed that the introduction of defects by partial cationic substitution in the host framework influences the physical properties. Davey and Mullin [11] have shown that ADP crystals grown in the presence of $CrCl_3$. $6H_20$ contain both Cr^{3+} and Cl- ions. Quantitative determinations indicate the incorporation of Na in the sample increases when increasing the dopant of DMG in the aqueous growth medium. Analysis of the surface at different sites reveals that the incorporation of dopant is not very uniform throughout the surface.

CONCLUSION

Grown single crystals of pure KDP, ADP and doped with DMG are grow by the slow evaporation

method at room temperature. The grown crystals with dopants have similar morphology to the pure. Powder X-ray diffraction analysis confirm the structure and change in lattice parameter values for the doped crystals. The UV and FTIR analysis also confirms the substitution of DMG in KDP and ADP crystals. SEM studies reveal the external morphology of KDP and ADP crystals. EDS confirms the presence of large amount of Na, C and H in the doped specimen.

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Table : 1 Observed and calculated in IR frequency (cm-1) of pure and mixed crystals of KDP and ADP with DMG

Calculated frequencies cm-1	Observed IR frequencies and Intensities					
	KDP	ADP	A	B	C	Assignments
3333	3401	3400	3434	3418	3412	O-H stretching hydrogen bond
2919	2866	2449	2928	-	2923	P-O Assymet Stretching
2494	1705	1640	2437	2415	2483	O || P – OH Stretching
1650	-	-	1647	1638	1676	N-H inplane hending
1400	-	1403	-	1402	1442	N-H bending of the dopant
1295	1298	1297	1302	1295	1382	Assymetric C-C stretching
1100	1098	1098	1091	1089	1095	P=O stretching, Symmetry C-O stretching
904	-	-	927	931	938	C-H out of plan (Stretching)
535	545	549	536	543	551	HO-P-OH bending

Fig:1a

Fig:1b

Fig:1c

Fig:1d

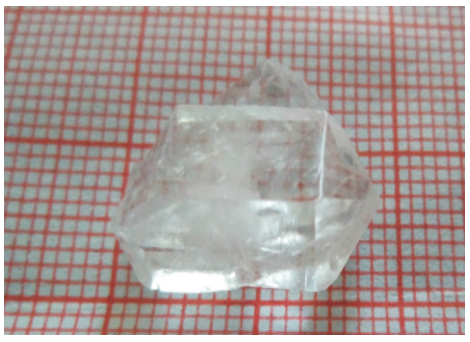
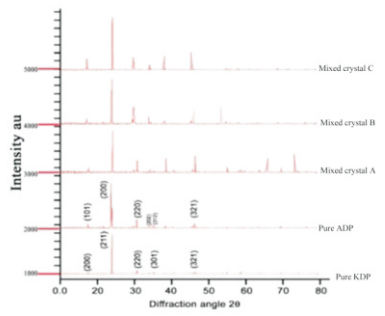


Fig: 1e



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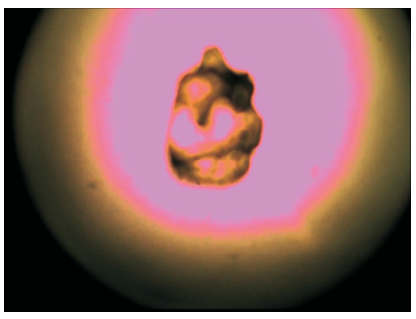

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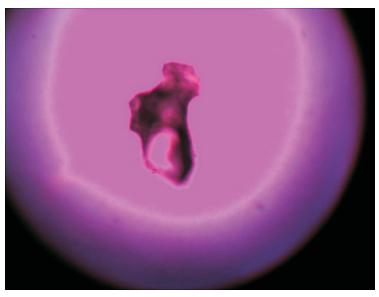

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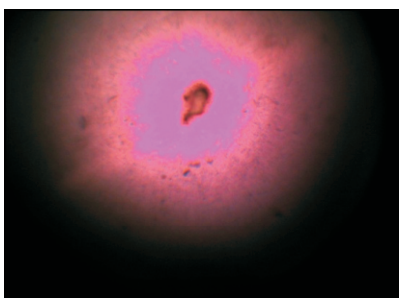

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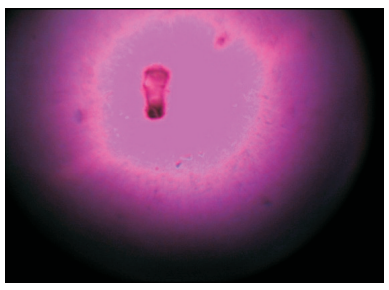

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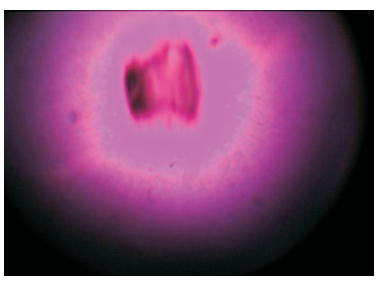

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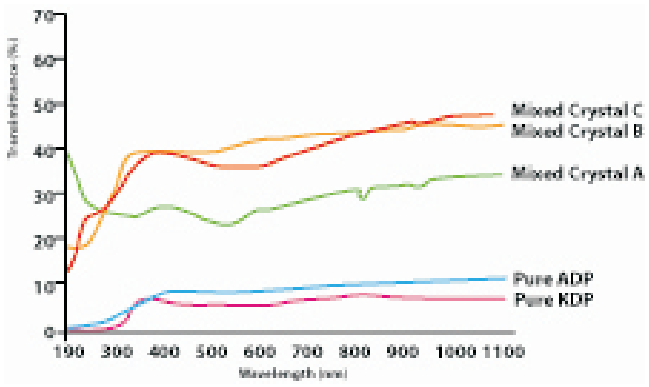

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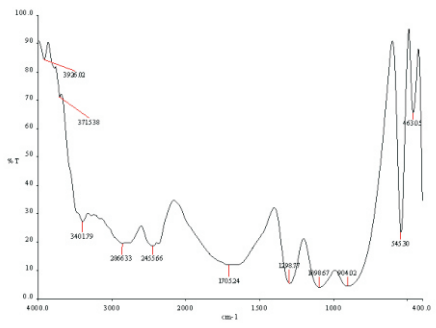

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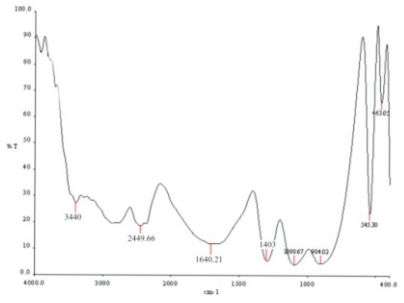
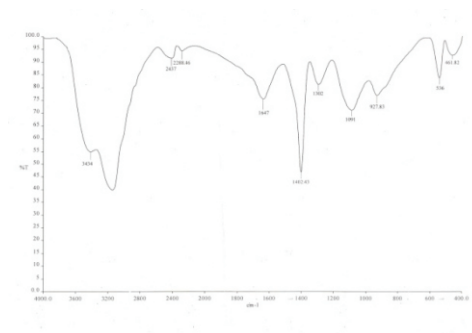


Fig:5b



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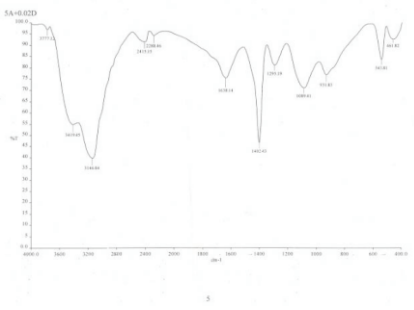

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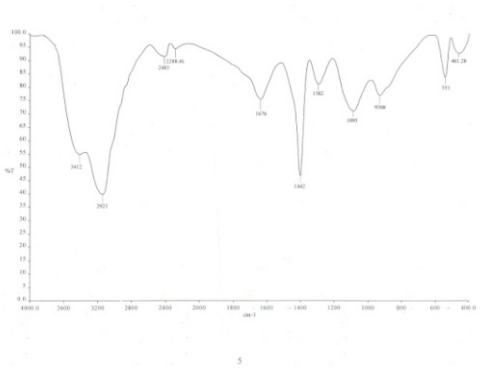

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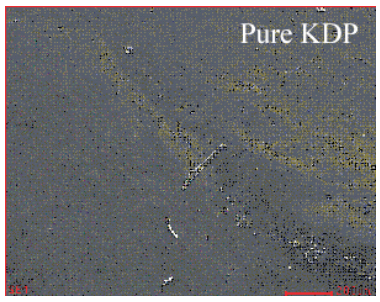
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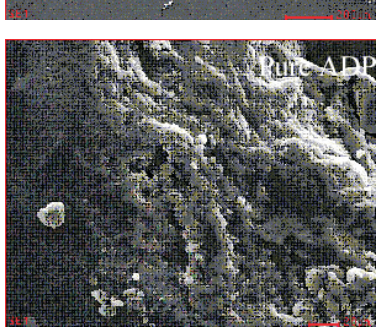
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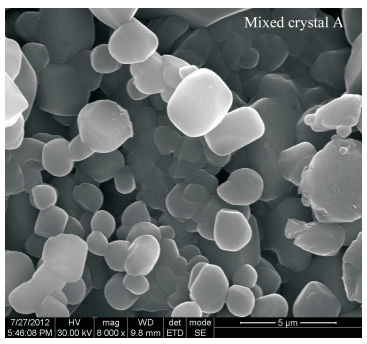
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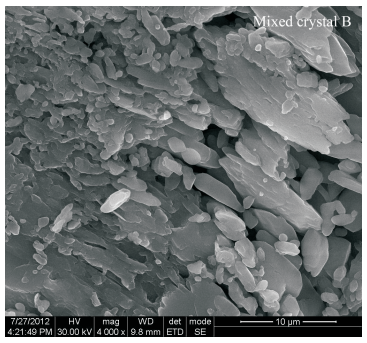
det ETD
mode SE
5 µm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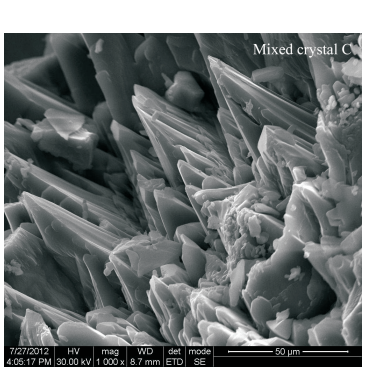
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mode SE
50 µm

Fig :

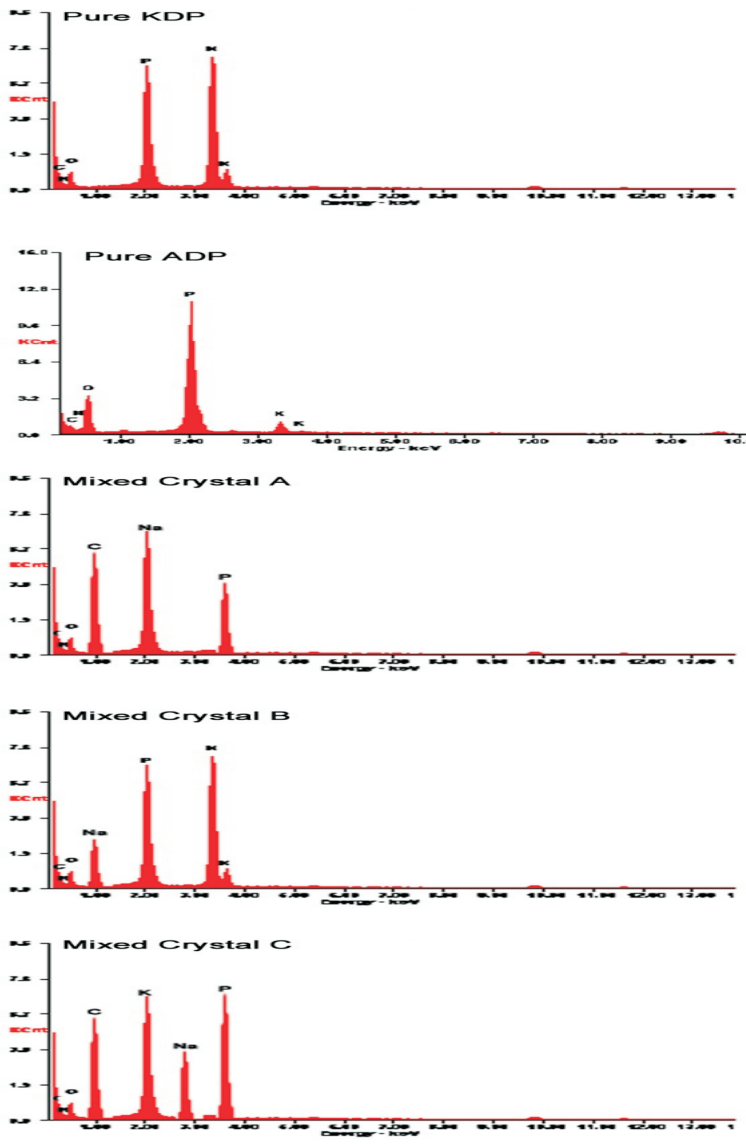
Pure KDP
Pure ADP
Mixed Crystal A
Mixed Crystal B
Mixed Crystal C

Fig : 7