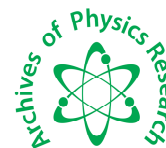




Scholars Research Library

Archives of Physics Research, 2011, 2 (4):60-66
(<http://scholarsresearchlibrary.com/archive.html>)



Scholars Research
Library

ISSN : 0976-0970

CODEN (USA): APRRC7

Growth and characterization of semiorganic NLO L-arginine trifluoroacetate (LATF) added KDP single crystals

T. Prasanyaa and M. Haris*

Department of physics, Karunya University, Coimbatore, TamilNadu, India

ABSTRACT

Potassium dihydrogen phosphate (KDP) and were well known nonlinear optical material for various optoelectronics applications. KDP continues to be interesting materials both academically and industrially. Since amino acids exhibit NLO property, it is of interest to dope them in KDP. In present study single crystals of pure and LATF doped KDP in different ratios has been grown by slow evaporation solution technique. The crystallinity and cell parameters were characterized by X-ray diffraction analysis, the shifting in frequency assignment of different functional group of KDP due to addition of LATF were analyzed by FTIR analysis. The enhancement in transmittance of grown KDP with addition of LATF at different ratios was determined by UV-Visible spectral analysis. The presence of dopant in the sample of grown crystal was confirmed by energy dispersive X-ray analysis (EDAX). The grown crystals subjected to various characterizations will be discussed.

Key words: optoelectronic, aminoacid, organic material, susceptibility.

INTRODUCTION

The Overwhelming success of molecular engineering in controlling NLO properties in last decade has prompted better initiative in crystal engineering. One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Potassium dihydrogen phosphate (KDP) is a model system for nonlinear optical device application. KDP is an effective angle tuned dielectric medium for optical harmonic generation in and near the visible region. The material offers high transmission throughout the visible spectrum and meets requirements for optical birefringe, large enough to bracket its refractive index for even extreme wavelength range over which it is transparent. Among non-linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication [1-4]. KDP finds widespread use as frequency doublers in laser applications for fast and optimum

processing of optical signals. Improvement in the quality of the KDP crystals and the performance of KDP based devices can be realized with suitable dopants [5-7]. To analyse the influence of amino acid based dopants on the non-linear optical property of KDP crystals. Therefore amino acid may be used as dopants and it was observed that there is enhancement in the material properties such as NLO and ferroelectric properties [8-12]. So, efforts were made to dope KDP with with different molar percentage (2M%, 4M%). The effects of the present investigation, the growth aspects of KDP and doped KDP have been studied. Bulk crystals of KDP and doped KDP were grown by slow evaporation technique. The structural, crystallinity of the material were characterized by x-ray diffraction analysis, the frequency assignment of different functional group of pure and doped KDP was determined by FTIR analysis. The optical properties of pure and doped KDP was analysed by UV-Visible spectrometer. The presence of dopant in the sample of grown crystal was confirmed by energy dispersive X-ray analysis (EDAX).

Effect of doping:-

The pure KDP crystals were found to be less perfect (in terms of transparency and morphological development) as compared to LATF doped KDP crystals. This might be due to the higher reactive nature of potassium than that of LATF dopants because slower than the rate of reaction between the ions present in the amino acid complex, greater is the perfection of the grown crystals. It was observed that the maximum size attained by pure potassium dihydrogen phosphate is larger than that of doped crystals of KDP. The size effect may also be attributed to greater reactivity of potassium ions with dihydrogen phosphate ions present in the solution. Due to higher reactivity of potassium ions as compared to ions present in amino acid, the number of the potassium ion reacting with dihydrogen phosphate ions in the solution per unit time is much higher than the dopants and hence lead to bigger size of pure KDP crystals. The crystals of pure KDP is slightly less in transparency whereas the crystals of LATF doped KDP were quite transparent. This might be due to the fact that the doping has entered the lattice of pure KDP led to decrease in number of nucleation centres. Hence the doping affects the size, shape, optical transparency of the pure KDP crystal.

MATERIALS AND METHODS

2.1 Synthesis and growth

Pure LATF was synthesized from the starting materials of l-arginine and trifluoroacetic acid taken in equimolar ratio. LATF was prepared by evaporating its aqueous solution and the synthesized salt was purified by repeated recrystallization.

The solution of KDP salt was prepared in a saturated condition. The solution was stirred well for two hours constantly using magnetic stirrer, then solution was filtered using Whatmann filter paper. This solution was taken in 2 different beakers of 100ml and the amino acid LATF was added to each beaker as 2mole% and 4mole%, and the same was kept for crystallization at room temperature. The spontaneous nucleation takes place and seed crystals in all 2 beakers were obtained. A supersaturated solution of pure KDP, 2 mole% and 4mole mole% LATF doped KDP at temperature 32°C was obtained by constant stirring up to two hours and then filtered. These solutions were loaded in constant temperature bath set at 32°C. After twenty four hours the good quality seeds were suspended in respective beakers using the nylon thread. Slow evaporation

method was employed for the growth. After completion of growth run, the crystal was harvested. The photograph of grown LATF doped KDP crystal is shown below, Fig 1;

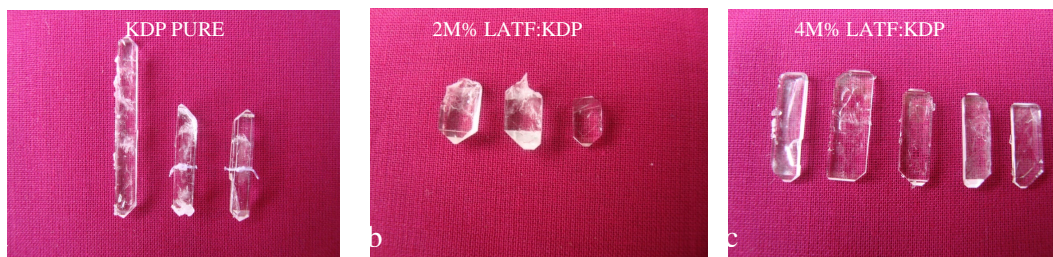


Fig 1:- Shows the photograph of (a) pure KDP; (b) LATF: KDP 2M% ; (c) LATF:KDP4M%

3. Characterization:-

3.1 X-RAY diffraction analysis:-

Powder x-ray diffraction studies were performed on grown crystals to identify the phase formation and degree of crystal perfection. X-ray powder patterns of pure and doped KDP were recorded . The powder diffractograms of pure and doped KDP are shown in fig.2. the crystallinity of both pure and doped crystals is quite clear from diffractograms because of the occurrence of sharp peaks at specific bragg’s angles. From the diffractograms it is clear that the entry of the dopants in the modified composition of KDP crystals lead to a change in the intensity of peaks when compared to the peaks of pure KDP, which shows that the doping has brought about a change in the internal structure of crystals due to change in bond lengths.

FIG 2:-shows the XRD patterns of (a) pure KDP; (b) 2M%LATF:KDP; (c)4M%LATF:KDP

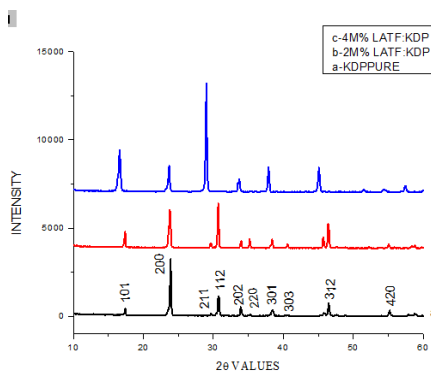


TABLE 1: The datas of lattice parameters of pure and doped KDP

Lattice parameter	Pure KDP	2M% of LATF	4M% of LATF
a (Å)	7.448	7.424	7.472
b (Å)	7.448	7.424	7.472
c (Å)	6.977	6.955	7.003
Cell Volume	387.033	383.330	390.989

Calculation of cell parameters reveals that both pure and doped crystals belong to tetragonal crystal system [$\alpha=\beta=\gamma=90^\circ$]; [$a=b\neq c$]. the table 1 shows the comparison of the cell parameter values of pure and the doped crystals. From the table it is clear that the doping has brought about

a change in the cell dimensions due to the change in bond lengths resulting in to a change in cell volume.

3.2 UV-VISIBLE spectral analysis:-

The transmittance of the grown crystals was measured using a Shimadzu model UV-Visible - 1650 spectrometer in the spectral region 200-800nm. Measurement was carried out on a single crystalline piece which was polished to 1mm thickness. Fig 3, shows the transparency curve of pure and doped KDP crystals. There is a good enhancement in the percentage of transmission in the LATF doped crystals than the pure KDP crystal. The measured percentage of transmission for 2m% is 90% and for 4m% is 88.5% . This is because , the number of inclusions is reduced by the addition of impurities [13],hence the enhancement in the percentage of transparency increases the NLO efficiency of the doped KDP crystals. The curve for pure KDP has cut-off wavelength at 308nm and both the doped KDP crystals has cut-off wavelength at 286nm and this absorption is due to the $n \rightarrow \pi^*$ transition. The spectra of both pure and doped KDP crystals indicate that there is no remarkable absorption in the entire visible region. From the spectra, it is also seen that the doped KDP crystals have better lower cut-off wavelengths than the pure KDP. The required properties for NLO activity are minimum absorption and low cut-off wavelength. These properties are improved in the doped crystals.

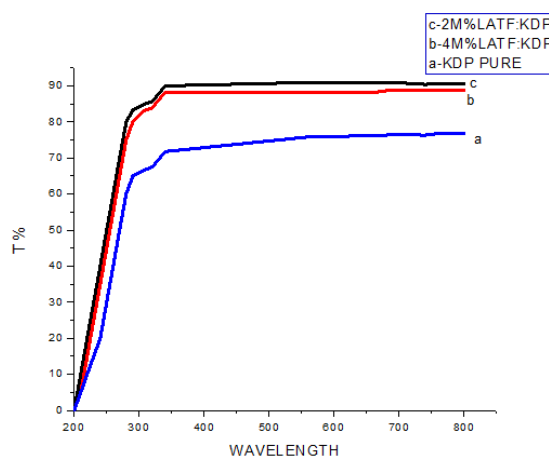


Fig 3:- UV-Vis spectra for pure and doped KDP

3.3 FTIR analysis:-

The FTIR spectra of the grown crystal was recorded with the help of a Shimadzu 8400S. FTIR infrared spectrometer in the region 400-4000 cm^{-1} . A comparison of the band and peaks of FTIR spectra for pure and 2m%, 4m% of LATF doped KDP crystals were given in table 2. There is a strong broad absorption band between 1500 and 1700 cm^{-1} resulting from hydrogen bonded N-H stretching bands. The symmetric deformation of NH_3^+ ion appears at around 1500 cm^{-1} , CH_3 bending vibrations of amino acid present in spectra of doped crystals reveals the incorporation of impurities. some bands of H_2PO_4 overlap with amino acid vibrations, the asymmetric stretching vibration of NH_3^+ of amino acid appear in the region of 3100-3450 cm^{-1} , some of them overlap with the OH stretching of dihydrogen phosphate ion. The bands which appeared at 3600 cm^{-1} in pure KDP are assigned to free O-H stretching. The broad band absorption appears at 3340, 3296, 3255 were assigned to hydrogen bonded O-H stretching frequency in pure KDP. In the pure KDP

3100-3450 indicates the very weak band. In absence of such a very weak band in the dopants added KDP indicates the strong interaction of NH_3^+ of amino acids. This shows the possible entry of these ions in the lattice site of KDP to lower frequency at 2923 in KDP doped with 2M% of amino acid and at 2862 in KDP doped with 4M% of amino acid indicates the interaction with P-O-H group of KDP and the weakening the strength of the band between oxygen and hydrogen. This leads to the decrease in the frequency of O-H stretching and confirms the NLO property of pure and doped KDP at these lattice sites in the crystal. The 1636, 1693 at the dopants added KDP is assigned to N-H bending of dopants, 1640, 1641 is assigned to COO^- asymmetric bending of dopants and the 1300, 1301 frequency of dopants added KDP shows the C-N-H stretching of dopants. The incorporation of carbon atom from amino acid shows the carbon atom has entered the KDP lattice sites and makes the material semi organic. Fig 4, shows the FTIR spectra for pure and doped crystal

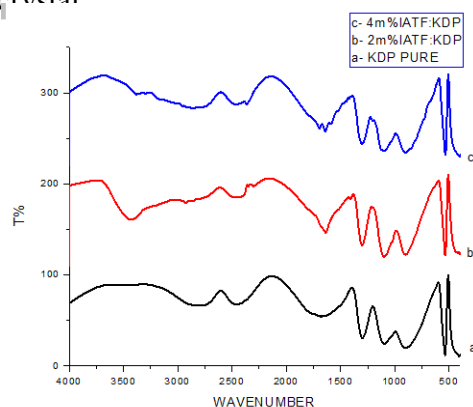


Fig 4:- shows the FTIR spectra for pure and doped crystal.

Table 2:- Shows the comparison of the band and peaks of FTIR spectra for pure and LATF doped KDP crystals

PURE KDP	2M% LATF:KDP	4M%LATF:KDP	ASSIGNMENTS
3600	3429	-	O-H Stretching with NH_3 stretching of amino acid
2924	2923	-	P-O-H asymmetric stretching
2844	-	2862	P-O-H asymmetric stretching
2362	-	2363	P-O-H bending
-	1636	1693	N-H bending of dopants
-	1641	1640	COO^- asymmetric bending of dopants
-	1309	1301	C-N-H stretching of dopants
1101	1098	1101	P=O Stretching
908	901	900	P-O-H Stretching
539	535	533	HO-P-OH bending

3.4 EDAX analysis:-

In order to confirm the presence of the LATF, the sample of grown crystals was subjected to EDAX analysis using JEOL-6360 Scanning Electron microscope. The EDAX spectra for pure and 2m%, 4m% of LATF doped KDP crystals were recorded and analysed, from the spectrum of pure crystals it is clear that there is no peak other than that of potassium and phosphate, as expected from pure KDP crystals. The spectrum corresponding to LATF doped crystals shows peaks of potassium, carbon, oxygen, fluorine and phosphate suggesting thereby that the amino acid dopant has entered in to the crystal lattice of KDP and making it a new semiorganic crystals.

The recorded EDAX spectrum is shown in fig 5. The observed weight percentage of elements in the doped crystals are given in table 3.

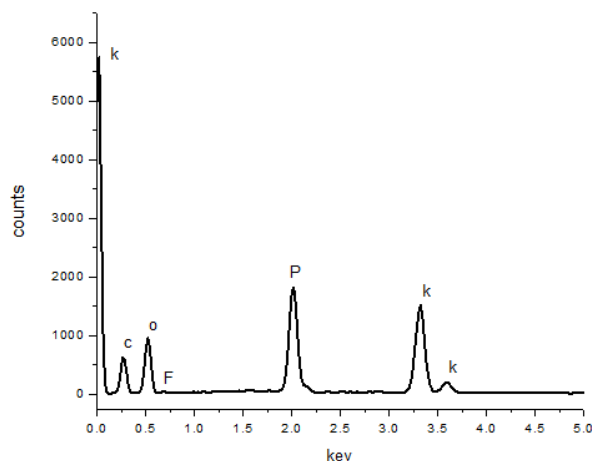


Fig 5:- Shows the recorded EDAX spectrum of LATF doped KDP.

Table 3:- The observed weight percentage of elements in the doped crystals

2M%LATF:KDP	4M%LATF:KDP
CARBON – 7.79%	CARBON – 33.04%
OXYGEN -44.75%	OXYGEN -39.71%
FLUORINE– 0.58%	FLUORINE– 1.52%
POTASSIUM-24.68%	POTASSIUM-13.48%
PHOSPHATE-22.21%	PHOSPHATE-12.25%

CONCLUSION

From the above observations the following conclusions may be drawn:

1. Pure KDP, 2m% and 4m% LATF doped KDP crystals were grown in slow evaporation technique.
2. Entry of amino acid in to the lattice of pure KDP crystals influence the size, perfection , transparency of the grown crystals.
3. The grown crystals were characterized using powder x-ray diffraction and the cell parameters were calculated for both pure and LATF doped KDP crystals.
4. Functional groups and the modes of vibrations of pure doped crystals were identified by FTIR spectroscopy.
5. The UV-Visible spectroscopy shows the optical transparency enhancement in the LATF doped crystals than the pure KDP crystal. Thus the LATF doped crystals increases the optical transparency.
6. The doping of LATF in the pure KDP was confirmed by EDAX analysis. The analysis shows the amount of dopants present in the sample.

Acknowledgement

The authors thank the department of nanoscience and technology of karunya University for providing the facilities for diffraction studies, also we thank the Department of plant physiology Tamilnadu Agricultural University for providing optical studies facility and Amrita University for providing facility for IR studies.

REFERENCES

- [1] H.V. Alexandru, S. Antohe, *J. Crystal Growth.*, (2003), 258 ,149.
- [2] H.V. Alexandru, *J. Crystal Growth.*, (1996) , 169 ,347.
- [3] V.I. Bredikhin, G.L. Galushkina, A.A. Kulagin, S.P. Kuznetsov, O.A. Malshakova, *J. Crystal Growth .*, (2003) ,259 ,309.
- [4] N.A. Booth, A.A. Chernov, P.G. Vekilow, *J. Crystal Growth.*, (2002) , 237–239 ,1812
- [5] M.L. Dalal, M. Rahman, P.D. Tounsand, *Nucl. Instr. and Meth.*, B(1988) , 32 ,61.
- [6] G. Fischfeld, A. Affranchino, A. Di Loreto, C.C. Rocco, *Cryst. Res.Technol.*, (2004) 39,10920.
- [7] G.-W.Lu, H.-R.Xia, S.-Q.Zhang, X.Sun, Z.-S. Gao, J.-Y.Wang, *J. Crystal Growth.*, (2001) , 233 ,730.
- [8] S. S. Hussaini, N.R. Dhumane, V.G.Dongre, P. Ghughare and M.D. Shirsat, *J.Optoelect and Adv. Mat Rapidcommunication .*, (2007),1, 707
- [9] S.S.Hussaini, N.R.Dhumane, G.Rabbani,P.Karmuse, V.G.Dongre, M.D.Shirsat, *Cryst. Res. Technol.*, (2007), 42, 1110.
- [10] S. S. Hussaini, N.R. Dhumane, V.G.Dongre, and M.D. Shirsat, *Material Science-Poland.*, (2009), 27, 2.
- [11] S.S. Hussaini, N.R.Dhumane, V.G.Dongre and M.D. Shirsat, *J. Optoelect and Adv.Mat Rapid communication.*, (2008), 2, 108.
- [12] N.R. Dhumane, S. S. Hussaini, V.G.Dongre and Mahendra D. Shirsat, *Optical Material .*, (2009),31, 328.
- [13] S. Moitra, T.Kar, *opt.Mats.*, (2008) , 30,1621.