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OPTICAL AND STRUCTURAL STUDIES OF L-PHENYLALAINE, L-METHIONINE AND L-GLUTAMIC ACID DOPED KDP CRYSTALS FOR TUNED LASER APPLICATIONS

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***Abstract*— The Potassium di hydrogen phosphate (KDP) is a well-known dielectric inorganic nonlinear optical (NLO) material in tuned laser applications. Since most of the amino acids exhibit NLO property, it is of interest to dope them in KDP to increase their application. In the present study optically good quality crystal of pure and amino acid (L-phenylalaine, L-methionine and L-glutamic acid) doped KDP have been grown from low temperature solution growth technique using water as a solvent. The crystalline nature of the grown crystals is characterized by powder X-ray diffraction and single crystal X-ray analysis, it reveals that the crystal belongs to tetragonal system. The presence of various functional groups of pure and amino acids doped KDP crystals were identified by FT-IR analysis, the UV-visible spectrum shows an improvement in the optical transmittance and it is used in optical sensors. The second harmonic generation (SHG) efficiency of amino acids doped KDP crystals were found and compared with pure KDP crystals.**

***Index Terms*— Solution growth technique FT-IR, Single crystal XRD, powder XRD, UV-Visible and SHG.**

I. INTRODUCTION

In recent years, the search for new conversion materials for various device applications has lead to discovery of many organic, inorganic and semi-organic nonlinear optical (NLO) materials due to their various application such as in laser technology [1, 2] optoelectronics, second harmonic generation (SHG) The numerous applications of the nonlinear optical (NLO) crystals in the vast field of science and technology made to process of search of the new crystals for improved applications. Optical crystals with a high degree of perfection find applications in critical technology areas such as high power laser technology, amplitude and phase modulation, higher harmonic generation, fast growing development of optical communication system and optical information storage devices, switching and other signal processing. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet region and is used in the area of photonics and optoelectronics technologies. In particular, amino acids family crystals possess high NLO efficiency because they have a proton donor carboxyl acid (-COO) group and the proton acceptor amino (-NH2) groups. It is quite attracting to dope amino acids into KDP crystals to increase the second harmonic generation (SHG) efficiency fundamental laser beam. This has been successfully achieved by doping L-arginine [3], L-aspartic acid [4] L-lysine [5] some amino acids [6] and L-alianine [7] into KDP crystals which increased SHG efficiency of the crystals. In the present investigation the authors aim to dope the impurity of amino acids like namely L-phenylalaine, L-methionine, and L-glutamic acid doped into KDP crystals and investigate their properties by single crystals XRD, powder XRD, FTIR, UV-vis Spectra and SHG efficiency in terms of effect of doping.

II. CRYSTAL GROWTH

Wherever Times is specified, Times Roman or Times New Roman may be used. If neither is available on your word processor, please use the font closest in appearance to Times. Avoid using bit-mapped fonts. True Type 1 or Open Type fonts are required. Please embed all fonts, in particular symbol fonts, as well, for math, etc.

III. EASE OF USE

A. Synthesis

Potassium di hydrogen orthophosphate, KH2PO4, (KDP) (Merck) salt was taken and dissolved in 100 m L triple distilled water and saturated solution of KDP was prepared by using its solubility data at room temperature. The solution was continuously stirred for 6 h with a magnetic stirrer to ensure homogeneity of the solution. After preparation of saturated solution of pure KDP, it is separately doped with L-phenylalaine, L-methionine, L-glutamic acid continuously and stirred for half an hour then each solution was filtered using watman filter papers and filtered solution was poured into several Petri dishes, covered with porous paper and kept in a closed room where the slow evaporation was gradually done. After a period of three weeks, optically highly transparent crystals of pure and doped KDP crystals were formed. Figure nos. (1, 2, 3, 4) shows that Pure and amino acid doped grown KDP crystals.

$KH_2PO_4+C_9H_{11}NO_2$	→	**KH_2PO_4 ($C_9H_{11}NO_2$)**
KDP + L- phenylalaine		**(L** – phenylalaine doped KDP)
$KH_2PO_4+C_5H_{11}NO_2S$	→	**KH_2PO_4 ($C_5H_{11}NO_2S$)**
KDP + L- methionine		**(L** – methionine doped KDP)
$KH_2PO_4+C_5H_9NO_4$	→	**KH_2PO_4 ($C_5H_9NO_4$)**
KDP + L- glutamic acid		**(L** – glutamic acid doped KDP)

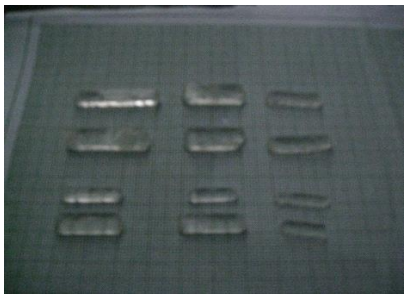

Figure 1 Photograph of as grown Pure crystals

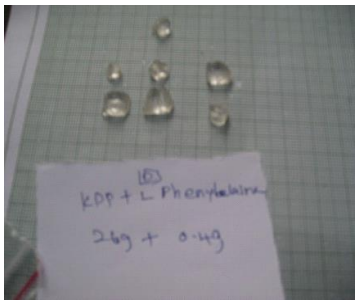

Figure 2 Photograph of L-phenylalaine doped with KDP crystals

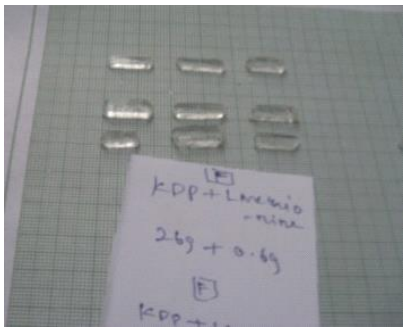

Figure 3 Photograph of L-methionine doped with KDP crystals

Figure 4 Photograph of L-glutamic acid doped with KDP crystals

IV. Result and Analysis

A. Powder X-ray diffraction technique

The grown single crystals were subjected to powder XRD analysis, using rich seifert X-ray diffarctometer with CuKα (λ=1.5406Å) radiation, The sample of LP doped KDP, LM doped KDP, LG doped KDP crystals, were scanned for 2θ values from 10o to 70o at a rate of 2o / min. The prominent peaks observed in the diffraction pattern confirm. The single crystalline, nature of LP doped KDP, LM doped KDP, LG doped KDP crystals, which the change the intensity of the peak is observed when compared to diffraction pattern of pure KDP crystals. The LP doped KDP, LM doped KDP, LG doped KDP crystals of powder X-ray shows some shift in the peaks, confirms incorporation of dopants in the pure KDP crystals. Figure nos. (5, 6, 7, 8) shows that XRD Patterns of as grown pure KDP and amino acids doped KDP crystals.

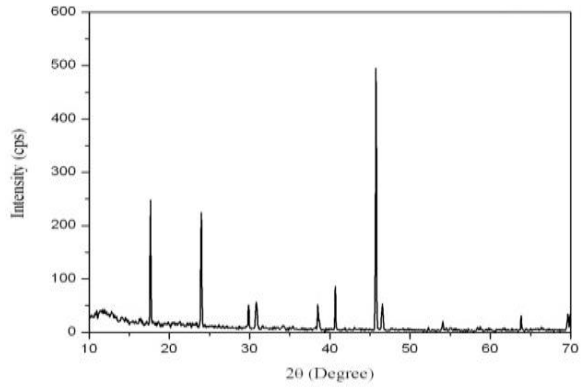

Figure 5 XRD Pattern of as grown pure KDP crystals

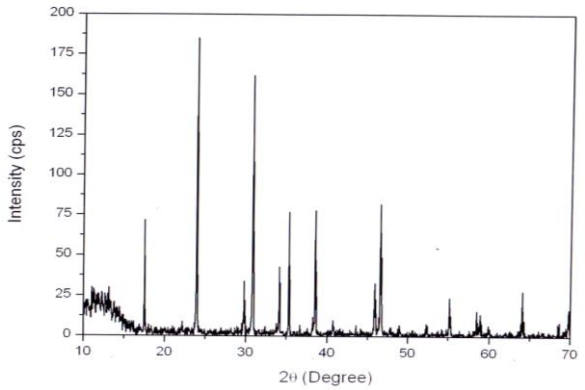

Figure 6 XRD Pattern of grown L-phenylalaine with doped KDP Crystals

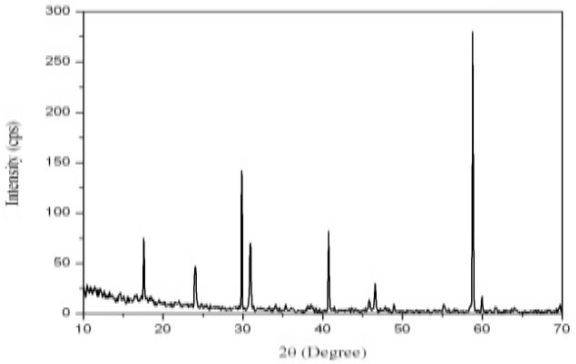

Figure 7 XRD Pattern of grown L-Methionine doped with KDP single crystals

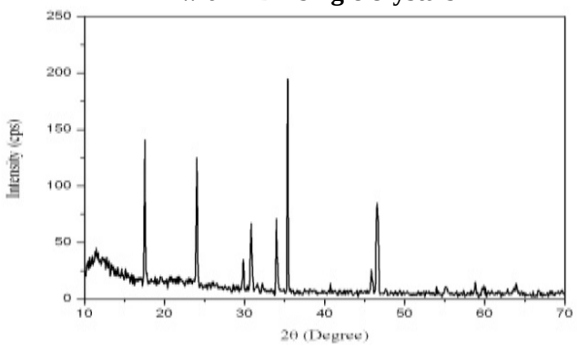

Figure 8 XRD Pattern of grown L-glutamic acid doped with KDP single crystals

B. Single crystal X- ray diffraction of study of pure and amino acids doped KDP crystals

The single crystal X-ray diffraction analysis was performed using single crystal diffractrometer CAD4/MACH3 and the data was collected using graphite mono chromate MOKα (λ=0.717Å) radiation of wavelength at room temperature 293k. The pure KDP, LP doped KDP, the LM doped KDP and LG doped KDP passes tetragonal geometry. The cell parameters value of amino acids (LP doped KDP, the LM doped KDP and LG doped KDP), is given the table 1. This clearly indicates that doping changes the cell axis and cell volume Comparison of unit cell parameters of pure and amino acid doped KDP crystal suggests that a slight distortion has occurred as a result of amino acid doped KDP crystal.

Table 1 Cell parameter of pure and LGKDP, L-MKDP and L-PKDP

Sl. No.	Samples	Lattice Parameter a=b (Aº) a = b	Lattice Parameter c (Aº)	Interfacial Angles (◦) α =β =γ	Cell Volume (A^3)
1.	Pure KDP Crystal	7.448	6.977	90º	389
2.	KDP +L Glutamic acid (0.6g)	7.47	6.99	90º	390
3.	KDP + L-Methionine (0.6g)	7.48	6.95	90º	389
4.	KDP +L Phenylalanine (0.4 g)	7.46	6.99	90º	394

C. UV-Vis NIR Spectral Analysis

Usually an NLO material must have a wide transparency window and the UV-vis –NIR spectrum gives information about the structure of molecule because the promotion of the electron in the σ and Π orbital from the ground state to higher energy states. The transmittance spectrum of the samples spectrum is shown in Fig. (no. 9, 10, 11, 12) which shows that the transmittance of pure KDP is 90%, the transmittance of LP doped KDP is 100%, the transmittance of LM doped KDP is 93% and the transmittance of LG doped KDP is 80% as compared pure and amino acid of (LP doped KDP, the LM doped KDP and LG doped KDP) the transmittance percentage is more LP doped KDP. The each sample's cut of wave length is 190Å.

Table 2 Growth period of Pure and doped KDP Crystals

Sl.No.	Crystals	Growth Period
1.	Pure KDP Crystal	10-12 days
2.	L-Phenylalainine with doped KDP Crystal	15-20 days
3.	L-Methionine with doped KDP Crystal	12-15 days
4.	L-Glutamic acid with doped KDP Crystal	20-25 days

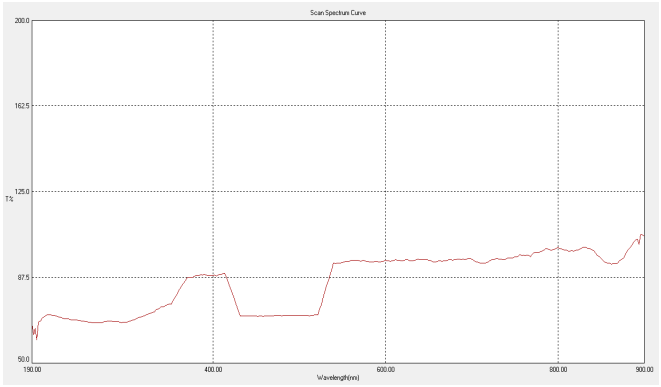

Figure 9 UV Transmittance spectrum of Pure KDP crystals

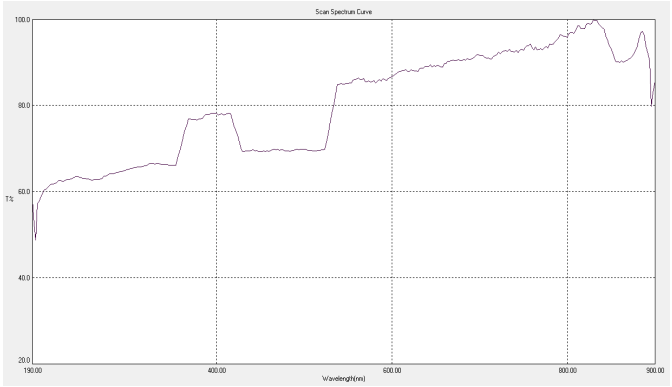

Figure 10 UV Transmittance spectrum of L-Phenylalaine (0.2g) doped KDP crystals

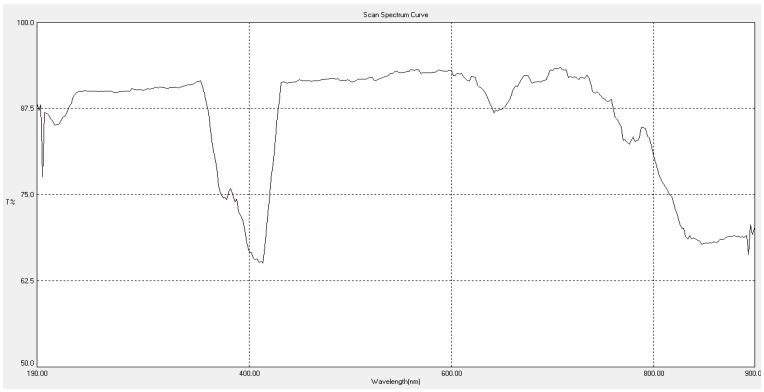

Figure 11 UV Transmittance spectrum of L-Methionine (0.2 g) doped KDP crystals

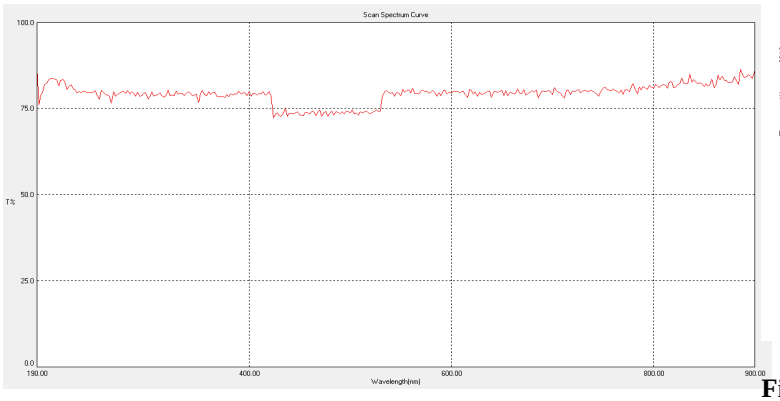

Figure 12 UV Transmittance spectrum of L-Glutomic acid (0.2g) doped KDP crystals

D. FT-IR ANALYSIS

The FT-IR spectrum of pure KDP and L-phenylalaine, L-methionine, L-glutamic acid doped KDP crystals have been recorded on perkin Elmer FT- IR spectrometer within the wave number range 400 cm-1 to 4000 cm-1. Pellets of the mixture of each sample with KBr have been prepared and used in the experiment. In the FT-IR spectra of pure KDP crystal, the observed absorption peaks correspond to the P-OH stretching, P-O-H bending. In the FT-IR spectra of amino acid (L-phenylalaine, L-methionine, L-Glutamic acid) doped KDP crystals, the same peaks have been observed with additional peaks The figure no.(13 to 20) shows the FTIR spectrum of pure KDP and different weight percentage of amino acid namely like (L-phenylalaine, L-methionine, L-Glutamic acid) doped KDP crystals.

These additional peaks correspond to the functional groups of (L-phenylalaine, L-methionine, L-glutamic acid) ,which confirms the doping of the (L-phenylalaine, L-methionine, L-glutamic acid) with KDP Crystals

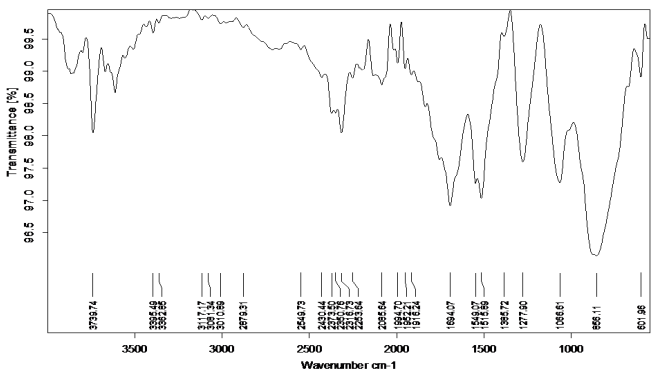

Figure 13 FTIR Spectrum of Pure KDP Crystal

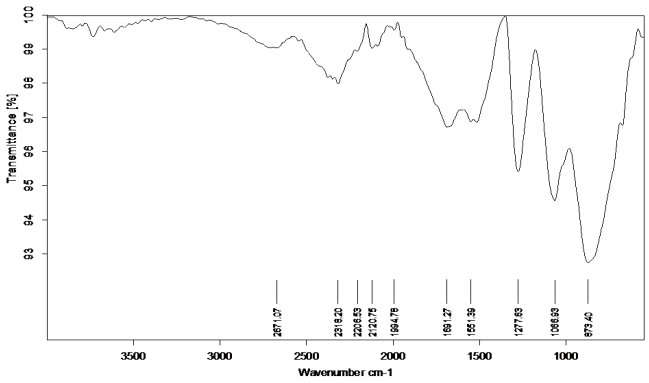

Figure 14 FTIR Spectrum of L-Phenylalaine (0.2) doped KDP Crystals

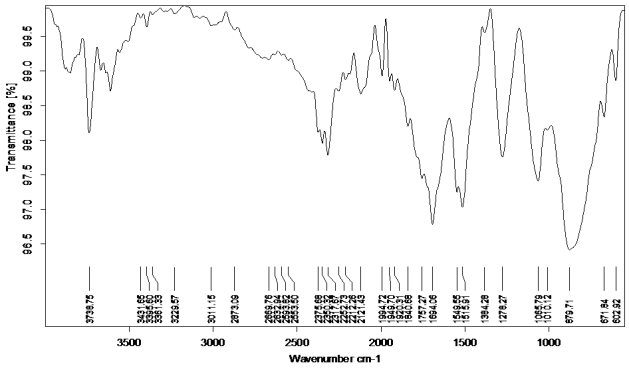

Figure 15 FTIR Spectrum of L-Methionine (0.2g) doped KDP Crystals

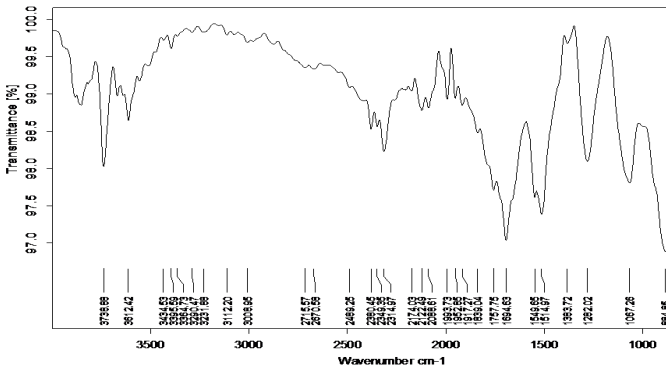

Figure 16 FTIR Spectrum of L-Methionine (0.6g) doped KDP Crystals

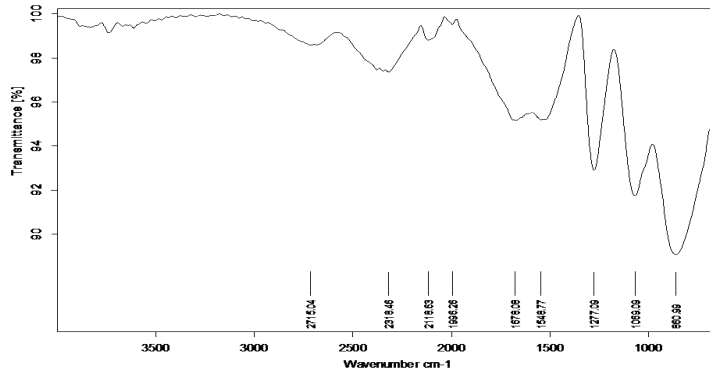

Figure 17 FTIR Spectrum of L-Methionine (0.4g) doped KDP Crystals

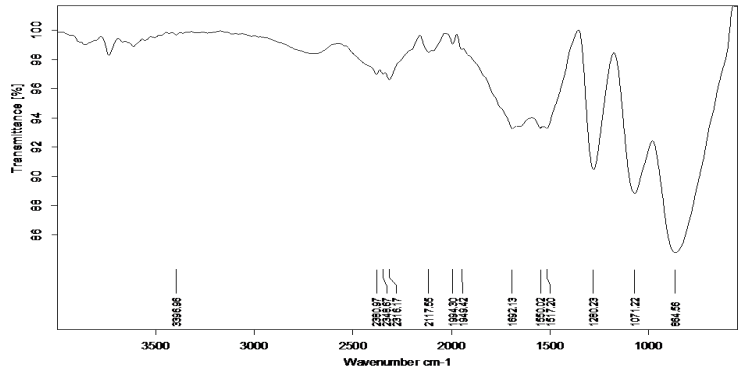

Figure 18 FTIR Spectrum of L-glutamic acid (0.2 g) doped KDP Crystals

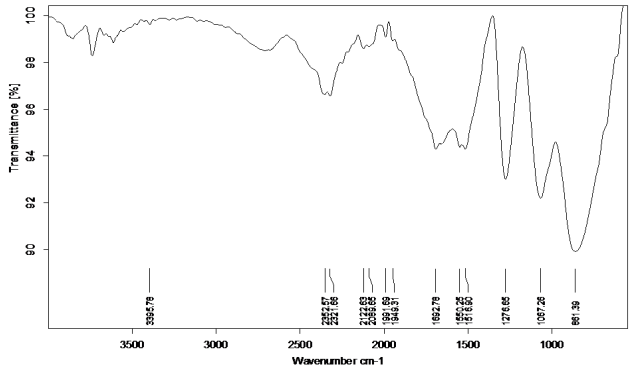

Figure 19 FTIR Spectrum of L-glutamic acid (0.4 g) doped KDP Crystals

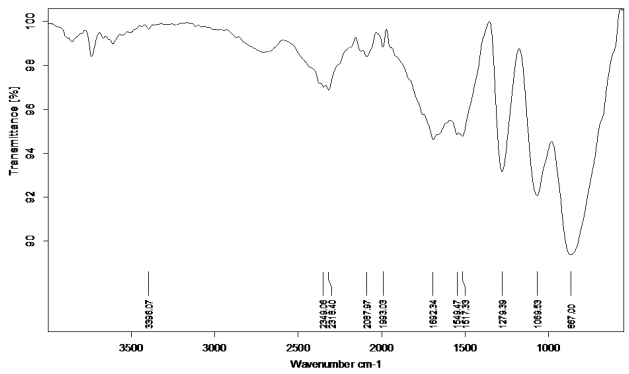

Figure 20 FTIR Spectrum of L-glutamic acid (0.6 g) doped KDP Crystals

Table No.3 FTIR Wavenumber assignments for the L-Methionine doped KDP grown crystals

Pure KDP(cm^{-1})	L-methionine doped KDP	L-methionine doped KDP	L-methionine doped KDP	Assignment
3739.74 3395.49 3362.85 3117.17 3081.34 3010.89 2879.31 2549.73 2430.44 2373.50 2350.76 2316.73 2253.64 2085.64 1994.70 1952.21 1916.24	3738.75 3431.65 3395.60 3361.33 3229.57 3011.15 2873.09 2669.76 2632.94 2593.82 2553.50 2375.68 2350.32 2317.67 2252.73 2212.26 2121.43 1994.72 1949.70 1920.31 1840.68 1757.27	3738.88 3612.42 3434.53 3395.59 3364.73 3290.47 3231.88 3112.20 3008.95 2715.57 2670.58 2489.25 2380.45 2349.35 2314.97 2174.03 2122.49 2088.61 1993.73 1952.85 1917.27 1839.04 1757.75	2715.04 2318.46 2118.63 1996.26	P-OH stretching of H_2PO_4 , O-H stretching of COOH and water of crystallization, N-H stretching of NH_3, C-H stretching of CH_2 and CH vibration C=O stretching vibration ,P-O-H bending and –C= NH_4 stretching
1694.07	1694.06	1694.63	1678.08	Asymmetrical NH_3^+ bending vibration
1549.07 1515.89	1549.55 1515.91	1549.65 1514.97	1548.77	COO^- asymmetric stretching
1385.72	1384.28	1383.72		CH_2 bending. P=O stretching of KDP, Asymmetric vibration
1277.90	1278.27	1282.O2	1277.09	C-COO^- stretching
1066.61	1065.79 1010.12	1067.26	1069.09	P-OH and C-H stretching Symmetric stretching of NO_3
856.11	879.71	884.85	860.99	P-OH deformation, C-CN scissoring of
601.96	671.84 602.92	639.22 603.72		-COO bend

Table No.4 FTIR Wave number assignments for the L-glutamic and L-phenlalanine doped KDP grown crystals

Pure KDP Peak values (cm^{-1})	L-glutamic Acid	L-glutamic Acid	L-glutamic Acid	L-phenylalanine	Assignment
3739.74 3395.49 3362.85 3117.17 3081.34 3010.89 2879.31 2549.73 2430.44 2373.50 2350.76 2316.73 2253.64 2085.64 1994.70 1952.21 1916.24	3396.96 2380.97 2348.67 2316.17 2117.55 1994.30 1949.42	3395.78 2352.57 2321.66 2122.66 2122.63 2089.65 1991.69 1949.31	3396.07 2349.06 2318.40 2087.97 1993.03	2671.07 2318.20 2206.53 2120.75 1994.78	P-OH stretching of H_2PO_4, O-H stretching of COOH and water of crystallization, N-H stretching of NH_3, C-H stretching of CH_2 and CH vibration C=O stretching vibration , P-O-H bending and –C= NH_4 stretching
1694.07	1692.13	1692.78	1692.34	1691.27	Asymmetrical NH_3^+ bending vibration
1549.07 1515.89	1550.02 1517.20	1550.25 1516.90	1549.47 1517.33	1551.39	COO^- asymmetric stretching
1385.72					CH_2 bending. P=O stretching of KDP, Asymmetric vibration
1277.90	1280.23	1276.65	1279.39	1277.63	C-COO^- stretching
1066.61	1071.22	1067.26	1069.53	1066.93	P-OH and C-H stretching Symmetric stretching of NO_3
856.11	864.56	861.39	867.00	873.40	P-OH deformation, C-CN scissoring of
601.96					-COO bend

E. Second Harmonic Generation Efficiency analysis.

To conform the NLO property, the grown crystals of pure and doped KDP were subjected to the second harmonic generation (SHG) efficiency technique by the modified version of the powder technique developed by Kurtz and Perry (15) using an ND;YAG (QUANTA RAY Model LAB-170-10) Q switched laser beam, 10ns laser with a pulse repetition rate of 10Hzworking at 1064nm. The sample was grounded into powder and tightly packed in a micro- capillary tube. It was placed in the path of the laser beam of 0.69 joule of energy. The output light was passed through a monochromatic transmitting only the second harmonic green light was registered by a photomultiplier tube converted into an electrical signal. This was displayed on the oscilloscope screen.KDP crystals grounded into samples of identical size was used as reference material in SHG measurements.

The second harmonic signal of input energy (joule) and output energy mJ, respectively were obtained for pure and amino acids doped KDP and it shows that the SHG efficiency of the doped crystals are greater than pure KDP crystals.

Table No.5. Comparison of frequency conversion efficiency for pure and doped KDP

Sl.No.	Crystal	Output Energy (mJ)	Input Energy (J)	η =(output / input) x100%	SHG Efficiency
1.	LP KDP	25.9	0.69	3.75	1.94
2.	LM KDP	22.4	0.69	3.24	1.67
3.	LG KDP	21.3	0.69	3.08	1.59
4.	Pure KDP	13.34	0.69	1.90	1.00

V. Summary and Conclusion

The transparent, colorless crystals of pure and amino acid doped potassium di-hydrogen Phosphate crystals have been successfully grown by using slow evaporation technique at room temperature. The powder X ray diffraction confirms the crystal quality of the crystal grown. The cell parameters are determined from the single crystal X ray diffraction technique and the grown crystal belong to tetragonal. Due to the variation of the lattice parameters of doped KDP, it is confirmed the doped material is in the crystal lattice of pure KDP. The transmission spectrum reveal that amino acid additives increases of the optical transparency of the crystals and have sufficient transmission in the entire UV – Visible and IR regions as compared pure and amino acid (L-phenylalaine, L-methionine,) doped KDP crystals of UV transmittance spectrum more efficiency than pure KDP crystals. The FTIR analysis confirmed presences of all functional groups in pure and (L-phenylalaine, L-methionine and L-glutamic acid) Doped KDP crystal. SHG studies confirm the nonlinearity of the grown crystal by the emission of green light and the SHG efficiency of the grown amino acid doped KDP crystals to be greater than pure KDP crystals. Hence amino acid doped KDP crystals are potential material for NLO and sensor application.

Acknowledgment

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References

[1] J. J. De Yoreo, A. K. Burnham and P. K. Whiteman, "Developing KH2PO4 and KD2PO4 crystals for the world's most powerful laser", Inst. Mater. Rev. 47, (2002) 113.

[2] R.Rajasekaran, RM.kumar, R Jayavel, P Ramasamy, Growth and characterization of zinc thiourea chloride (ZTC) a semi organic nonlinear optical crystals, Journal of crystal growth 252 (1-3), 317-327 (2003)

[3] R. S. Adhav, "Application of Non Linear Crystal, LIA Hand Book of Laser Materials Processing" Magnolia (2001).

[4] R.Krishnamurthy, R.Rajasekaran, B.S.Samuel, Growth and characterization of KDP crystals doped with L-aspartic acid, Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy 104, 310-314. (2013)

[5] K. D. Parikh, D. J. Dave, B. B. Parekh and M. J. Joshi, "Thermal, FT–IR and SHG efficiency studies of L-arginine doped KDP crystals", Bull. Mater. Sci. 30, (2007)105-112.

[6] S.Gunasekaram, S.Ponnusamy, R.Rajasekaran, "Growth and charactersation of potassium dihydrogen phosphate (KDP) crystal doped with amino acids., Indian Journal of Physics 78, 553-561 (2004)

[7] K. D. Parikh, D. J. Dave, B. B Parekh and M. J. Joshi, "Growth and characterization of L-alanine doped KDP crystals", Cryst. Res. Technol, 45 (2010) 603-610.

[8] R.Rajasekaran, Chennai. "Studies on nucleation kinetics growth and characterization of Non linear optical ZTC, ZTCP. TTCS and metal ions doped KDP crystals".

[9] G.R. Ester, R. Price, P.J. Halfpenny (1997). An atomic force microscopic investigation of surface degradation of potassium hydrogen phthalate (KAP) crystals caused by removal from solution, J. Cryst. Growth, 182, 95-102.

[10] K. Uthayarani, R. Sankar, C.K. Shashidharan Nair (2008). Growth, spectral and thermal properties of KAP single crystals in the presence of DL-Alanine and L-Methionine amino acid dopants, Cryst. Res. Technol, 43,733-739.

[11] A. Elakkina Kumaran, P. Kanchana, C. Sekar (2012). Effect of amino acid additives on the growth and physical properties of potassium acid phthalate (KAP) crystalsSpectrochim Acta A, 91, 370 374.

[12] A.C. Sajikumar, S. Vinu, C. Krishnan (2015). Studies on structural, optical and thermal properties of LHistidine doped potassium hydrogen phthalate single crystal, Int.J.Eng.Res.Technol, 4, 525-528.

[13] M.Porchelvi, R.Rajasekaran "Synthesis, Growth and charactersization of L-Histidine doped Pottassium dihydrogen Phosphate (LHKDP) crystals".

[14] C. Amuthambigai, C.K. Mahadevan, X. Sahaya Shajan (2016). Optical studies of potassium acid phthalate single crystals added with amino acids, Optik., 127, 5935-5941.

[15] J. Thomas Joseph Prakash, J. Martin Sam Gnanaraj, S. Shek Dhavud, S. Ekadevasena (2015). Effect of amino acid dopants on the spectral, optical, mechanical and thermal properties of potassium acid phthalate crystals for possible optoelectronic and frequency doubling applications, Opt Laser Technol., 72, 108-115.

[16] P. Murugakoothan, R. Mohan Kumar, P.M. Ushasree, R. Jayavel, R. Dhanasekaran, P. Ramasamy (1999). Habit

modification of potassium acid phthalate (KAP) single crystals by impurities, J. Cryst. Growth., 207, 325-329.

[17] B. Orel, D. Hadzi, F. Cabassi (1975). Infrared and Raman spectra of potassium hydrogen Phthalate, Spectrochim. Acta. A, 31, 169 – 182. 18. A.E. Newkirk, Renette Laware (1962). Thermogravimetric analysis of potassium hydrogen Phthalate, Talanta, 9, 169-173.

[18] R. Belcher, L. Erdey, F. Paulik, G. Liptay (1960). A derivatographic study of potassium hydrogen phthalate, Talanta, 5, 53-57.

[19] A.G. Kunjomana, K.A. Chandrasekharan (2005). Microhardness studies of GaTe Whiskers, Cryst. Res.Technol, 40, 782-785.

[20] K. Uthayarani, R. Sankar, C.K. Shashidharan Nair (2008). Growth, spectral and thermal properties of KAP single crystals in the presence of DL-Alanine and L-Methionine amino acid dopants, Cryst. Res. Technol, 43, 733-739. 22. S.K. Kurtz and T.T. Perry (1968). A Powder Technique for the Evaluation of Nonlinear Optical Materials, J. Appld. Phys, 39, 3798-3812