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Effect of amino acids (L-Glutamic acid, L-Histidine, L-Valine) on the performance of KDP single crystals

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Amino acids (L-Glutamic acid, L-Histidine, L-Valine)doped potassium dihydrogen phospate crystals are grown by solution growth technique. Slow cooling as well as slow evaporation methods were employed to grow these crystals .The concentration of dopants in the mother solution was varied from 0.1 mole% to 10 mole % .The solubility data for all dopants concentration were determined. There is variation in pH value and hence, there is habit modification of the grown crystals were characterized with XRD, UV - VIS, FT-IR studies, hardness, SHG trace elements and dielectric studies XRD studies reveal slight distortion of lattice parameter for the heavily doped KDP crystals. UV – Visible spectra confirm the improvement in the transparency of these crystals on doping metal ions. FT – IR spectra reveal strong absorption band between 1400 – 1600 cm^{-1} for metal ion doped crystals. The dopants increase the hardness value of the material and it also depends on the concentration of the dopants. Amino acids doping improved the NLO properties. The detailed results on the spectral parameters, habit modifications and constant values will be presented.

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1. Introduction

The impact of non-linear optics (NLO) on science and technology has been to enhance the understanding of fundamental light-matter interaction and to be a driving force in the regeneration of optical technology for several areas of science and engineering. NLO materials both organic and inorganic are important for operational characteristics of NLO devices. The growth of NLO materials for[1-5] frequency conversion, all-optical limiting etc. is important for the successful operation of these devices.

Non –linear optical materials utilize the non-linear dependence of the refraction index on the applied electric field to produce other frequencies. The results(1-5) in either harmonic generation (frequency doubling, tripling, mixing etc) or a frequency shifting (such as optical parametric oscillation). The development of the field was enhanced in parallel with the introduction of lasers, because the laser became posses the energy density necessary to produce non-linear effect. One of the obvious requirements for a non-linear crystal is that should have excellent optical quality. This means that for new materials, for which single crystal specimen are not available, it is necessary to grow single crystal specimens of optical quality. Thus in many cases the search for new and better non linear optical quality for a useful non linear optical material are more stringent that even the most exciting requirements on optical quality for materials used in linear optics. For a device to succeed, it is vital that it meets a number of other criteria and these should receive greater emphasis. The relevant issues include reliable crystal growth techniques for availability, optical non-linearity, birefringence, moderate to high transparency and optical homogeneity for high conversion efficiency mechanical strength, chemical stability polishing and coating technology for ease of fabrication, low absorption, temperature phase matching band width, fracture toughness and thermo mechanical properties for high average power, and damage threshold, non linear absorption and brittleness index for life time and system capability.

KDP is an efficient angle tuned dielectric medium for optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for an optical birefringence large enough to bracket its refractive index for even extreme wavelength over which it is transparent. An additional advantage of KDP is its ability to withstand repeated exposure to high power density laser radiation without inducing strains and subsequent in homogeneities in the refractive index. These[7-9] characteristics makes KDP a desirable material for frequency doubling and mixing experiments with many solid state and dye lasers with fundamental wavelengths between 1060 nm and 525 nm. The results for doped KDP are compared with the results of the pure KDP crystals and as well as the results available in the literature.

2. Experimental procedure

2.1 Crystal Growth

Pure KDP crystals were grown from aqueous solution by slow evaporation and also by slow cooling method

(0.5^0 C/Day). The same method is followed for doped KDP crystals (0.1 mole % of L-Glutamic acid orL-Histidine or L-Valine). The solubility of doped KDP in the solvent was measured for each dopants, it was found to be 31.5 gms/100 ml at 42 °C for L-Glutamic acid, 30.5 gms/100ml at 40 °C for Histidine and 32.75 gms/100 ml at 40 °C for L-Valine. The seed crystals are prepared at low temperature by spontaneous nucleation. The seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystals KDP and doped KDP (L-Glutamic acid, L-Histidine, L-Valine) were grown using constant temperature bath (CTB) controlled with an accuracy of 0.01^0 C. The mother solution was saturated with the initial pH values, 4.2, 4.65 and 4.75 for L-Glutamic acid, L-Histidine, L-Valine dopants respectively. The growth was carried out for more than 22 days by keeping the bath at a temperature of 39 °C.

2.2. Characterisation studies

Powder X-ray diffraction (Fig. 1) studies were carried out for the as grown crystals using Rich Seifert X-ray diffractometer with CuK á (ë = 1.5498 Å) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000 cm –1 operating at 200mW power at the samples with a spectral resolution of 2 cm –1 . The IR spectra were also recorded on Shimadzu–800, FTIR spectrometer series of Japan in the region 400 – 4000 cm^{-1}. The frequencies for all sharp bands are accurate to ± 1 cm^{-1}. The UV-VIS spectrum [Fig. 3] of KDP, doped KDP crystals were taken in the wavelength 200 nm -1200 nm range using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Kurtz SHG test was performed to find the non- linear optical property of KDP. The crystal was illuminated using spectra – physics Quanta-Ray DHS2 Nd-YAG laser using the first harmonics out put of 1064 nm with a pulse width of 8 ns.

2.2.1 FTIR Studies

The FTIR [Fig.2]of all of them were recorded from solid phase samples on a bruker IFS 66V model spectrophotometer using 1064nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000 cm^{-1} operating at 200mW power at the samples with a spectral resolution of $2cm^{-1}$. The IR spectra were also recorded on Shimadzu–800, FTIR spectrometer series of Japan in the region 400 – 4000 cm^{-1}. The frequencies[10-12] for all sharp bands are accurate to ± 1 cm^{-1}. The observed spectra of single and doped KDP shown in Fig. 1.

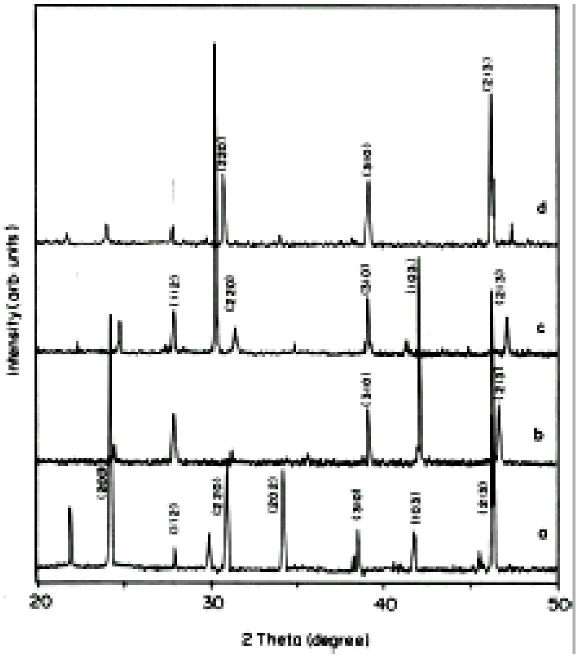


Fig. 1. XRD of amino acid doped KDP crystal.

The values of bond length and bond angles were taken from Sutton's table. Internal co-ordinates for the out of plane torsional vibrations are defined as recommended by IUPAC. The general quadratic valence force was adopted for both in plane and out of plane vibrations.

The frequencies with their relative intensities obtained in FTIR of pure and doped KDP and their most probable assignments are presented in Table 1. The observed spectra are explained on the C_3 point group symmetry for potassium dihydrogen phosphate and C_2v point group symmetry for potassium hydrogen phthalate ion. The 11 optically active fundamental vibrations belong to C_3 point groups are

$$\begin{aligned}
\Gamma &= \Gamma_{tra} + \Gamma_{rot} + \Gamma_{vib} \\
\Gamma &= 5\,A + 10\,E \\
\Gamma_{tra} &= A + E \\
\Gamma_{rot} &= A + E \\
\Gamma_{vib} &= \Gamma - \Gamma_{tra} - \Gamma_{rot} \\
&= 5\,A + 10\,E - 2\,A + 2\,E \\
\Gamma_{vib} &= 3\,A + 8\,E
\end{aligned}$$

The 42 active vibrations of C_2v point groups are distributed as

$$\begin{aligned}
\Gamma &= 16A_1 + 8A_2 + 16B_1 + 8B_2 \\
\Gamma_{rot} + \Gamma_{transl} &= A_1 + A_2 + 2B_1 + 2B_2 \\
\therefore \Gamma_{vib} &= 15A_1 + 7A_2 + 14B_1 + 6B_2
\end{aligned}$$

Table 1. Observed and calculated IR frequencies (cm^{-1}) of Pure KDP and KDP doped with L(+) Glutamic Acid, L(–) Histidine and L(+) Valine; VS – Very Strong S – Strong M – Medium W – Weak VW – Very Weak

Species	Calculated Frequencies cm^{-1}	Observed IR frequencies and intensities				Assignments
		Pure KDP	KDP doped with L(+) Glutamic Acid	KDP doped with L(–) Histidine	KDP doped with L(+) Valine	
A/E	3605	3600 VW	–	–	–	Free O–H stretching hydrogen bonded of KDP
	3333	3340 W	3350 VW	3435 M	3425 VW	O–H stretching hydrogen bonded of KDP
		–	3290 S	–	–	N–H hydrogen bonded stretching
	2919	2924 W	2950 M	2923 M	2923 M	C–H aliphatic stretching superimposed with N–H stretching
	2839	2844 VW	–	2852 VW	2853 VW	P–O–H symmetric stretching
	–	–	2762 S	–	–	NH_3^+ N–H stretching
	2461	2466 W	2418 M	2465 M	2460 M	NH_3^+ bending superimposed with P–O–H stretching
	2358	2362VW	–	–	–	P–O–H bending of KDP
	–	1725 M	–	1713 M	1713 M	C=O stretching
	1650	1655 VS	1648 VS	1641 VS	–	O || P–OH stretching of KDP
	1295	1299 S	1303 S	1303 S	1303 S	P=O stretching of KDP
	1100	1101 S	1086 S	1099 S	1099 S	P–O stretching of KDP
	904	908 S	–	908 S	907 S	P–O–H stretching of KDP
	–	–	878 M	–	–	N–H wagging
	–	–	676 M	–	–	N–H out of plane wagging
	535	539 S	–	534 S	535 S	HO–P–OH bending
	–	–	487 S	487 S	486 S	N–H torsional oscillation
	–	–	480 S	481 S	479 S	N–H torsional oscillation

All these modes are active in Infrared except A_2 mode, which is Infrared inactive for C_2v group. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data.

The bands appeared at 3600 cm^{-1} in pure KDP, KDP doped with L-Glutamic acid, L-Histidine, L-Valine were assigned to free O–H stretching. The very weak bands indicate its presence in low concentration. The absence of even such a weak band in the case of KDP doped with L-Glutamic acid indicated the strong interaction of L-Glutamic acid with O–H groups. The broad absorption band appeared at 3340, 3296, 3255 were assigned to hydrogen bonded O–H stretching frequencies in pure KDP, KDP + L-Glutamic acid and KDP + L-Histidine respectively. The absence of this peak in KDP doped with L-Valine supported again the strong interaction of L-Glutamic acid with O–H groups and the possible entry of these ions in the lattice site of KDP crystal.This lead to the decrease in the frequency of O–H stretching and confirmed the non-linear optical property of pure and doped. This property is also reflected in the P=O, P–O, P–OH stretching and HO–P–OH bending vibrations (refer Table 1).

Our present IR study on pure and doped KDP clearly indicated the effect of dopants on the crystal structure of pure KDP, which leads to the change in the absorption of IR frequencies and the non-linear optical property of both the crystals. The study also confirmed that the dopants had entered the lattice sites of tetragonal KDP.

2.2.2 NLO Properties

In order to confirm the NLO property the doped KDP crystal has been tested using the Nd-YAG laser. Small crystals of amino acids doped KDP was placed on the sample holder and the red color laser beam was made to pass through the crystal and the incoming beam passing through the crystal converted into the green light. The efficiency of doped KDP crystals were compared with pure KDP and also shows that L-Valine doped KDP crystal have higher efficiency.

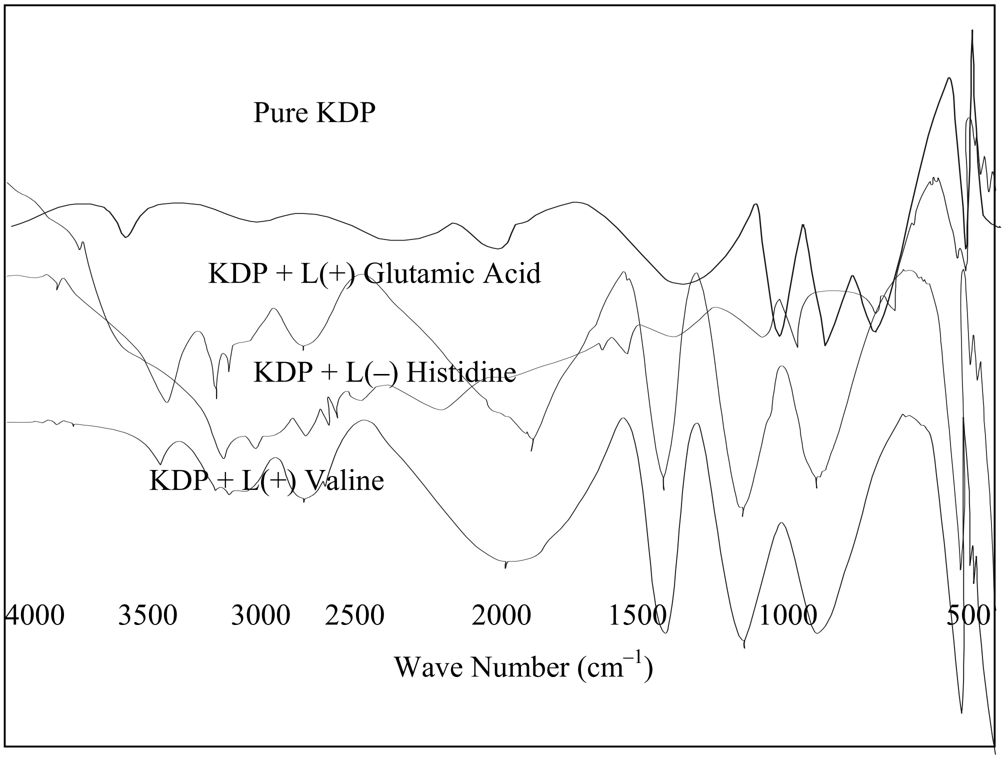


Fig. 2. Observed FTIR spectra of single and doped KDP.

3.Results and discussion

The dopants L-Glutamic acid, L-Histidine and L-Valine are expected to substitute the potassium ions in the KDP lattice due to their valency as well as proximity of ionic radius. KDP was doped with L (+) Glutamic acid and IR spectrum was recorded for the range from 4000 cm^{-1} to 400 cm^{-1}. The absorption frequencies of KDP + L (+) Glutamic acid and pure KDP are compared. The O–H stretching OH–P–OH bending vibrations appeared at 3600(vw) cm^{-1} and 539(s) cm^{-1} in pure KDP were found to be missing in the IR spectrum of KDP doped with L (+) Glutomic acid. It clearly indicated that the O–H group of KDP might have reacted with COOH group of L (+) Glutamic acid. The dopant Glutamic acid consists of two COOH and one NH$_2$ group. One of the COOH groups has been converted into COO$^-$ and NH$_3^+$ (zwitter ion) by reaction with NH$_2$ group. The second COOH group of L (+) Glutamic acid might have reacted with OH group of KDP (12). The P=O stretching usually appear at 1152 cm^{-1} and 1190 cm^{-1} in oxides of phosphorous appeared at 1299 cm^{-1} in pure KDP and at 1303 cm^{-1} in KDP doped with L (+) Glutomic acid revealed the etherification of P–O–H group of KDP with one of the COOH group of L (+) Glutamic acid. This is further confirmed by increase in the P=O stretching frequency of KDP doped with L (+) Glutamic acid. This increase is due to the electro negativity of the alkoxy group of L (+) Glutamic acid. The change in the structure of the pure KDP when it is doped with L (+) Glutamic acid results in the change in the interaction of IR radiation with sample and confirms the non-linear optical property of the KDP with dopant L (+) Glutamic acid.

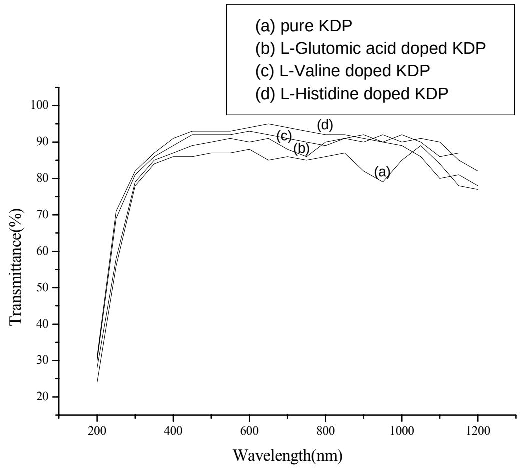


Fig. 3. UV-Visible spectra of amino acid doped KDP crystal.

The comparison of IR spectrum of pure KDP and KDP doped with L(–) Histidine and L(+) Valine revealed that no much change in the frequencies absorbed for pure

KDP and KDP doped with L(–) Histidine and L(+) Valine except some additional IR frequencies appeared at 2852 cm^{-1} and 2465 cm^{-1} due to the interaction of the N–H stretching frequency of amino acids with P–O–H symmetric stretching of KDP. The very low intensity of O–H stretching frequency in the KDP doped with L (–) Histidine revealed the involvement O–H in hydrogen bonding with ring nitrogen of L (–) Histidine. This was further confirmed by high intensity O–H stretching band at 3435 cm^{-1} in KDP doped with L (–)Histidine compared to free O–H stretching frequency band at 3600 cm^{-1} in the case of the pure KDP. Further the decrease in the O–H hydrogen bonded stretching frequency by 165 cm^{-1} in the case of KDP doped with L (–) Histidine compared to free O–H of pure KDP revealed the extend of hydrogen bonding between H^+ of KDP with ring nitrogen of L (–) Histidine and in weakening the O–H bond strength of pure KDP.

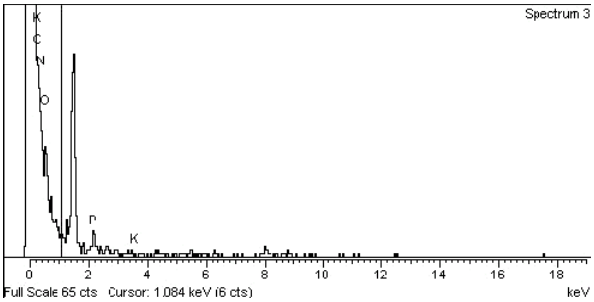


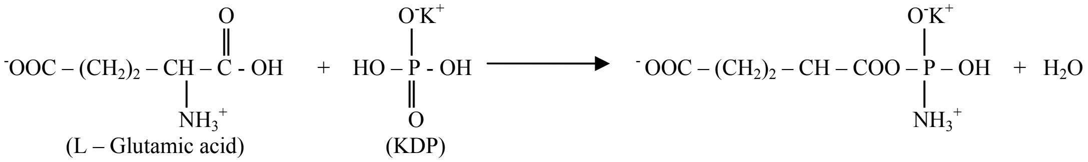
Fig. 4. Absorbance spectrum of doped (L-Valine) KDP single crystal.

It was found that the optical property of pure and doped KDP changed not only due to the weakening of the bond between O–H and C=O due to hydrogen bonding but also due to the substitution of metal ions in the crystal lattice of tetragonal KDP crystals which increased the bond strengths. It was found that the optical property of pure and doped KDP were changed not only due to the weakening of the bond between O–H and C=O due to hydrogen bonding but also due to the substitution of metal ions in the crystal lattice of tetragonal KDP crystals which increased the bond strengths. Since H + ion having the radii of only 0.3 Å is being replaced by amino acids there must be a stain in the accommodation of these ions instead of H^+. Hence, only a limited number of ions can diffuse into the lattice sites of tetragonal KDP crystals. The adsorption of impurities on prismatic faces retards the growth velocity of the prismatic face and induces many tiny imperfections. The adsorption of silica clusters under high super saturation results in growth centers, which are effectively blocked, and this causes subsequent growth of islands. This is supported by observations that inclusions including tiny ore minerals and Brazil twins [13-15]are concentrated in the growth sectors of prism and tapered faces and the impurities are riched in the prism sectors. As a result, the growth hillocks change form from rectangular to square-like on the[16-17] prismatic faces of crystals grown from solution with impurities. A large number of tiny growth islands elongated in the x-direction are formed on the tapered faces of KDP crystals.

All three amino acids used as dopant are colorless crystalline. They melt with decomposition at high temperature. They are soluble in polar solvents. They possess asymmetric carbon atom. Therefore, they are optically active.

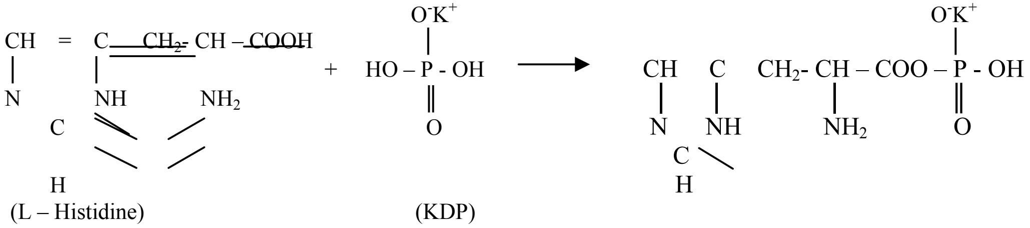
The partial substitution of potassium ions may be explained as the consequence of following chemical reactions.

KDP + L – Glutamic acid

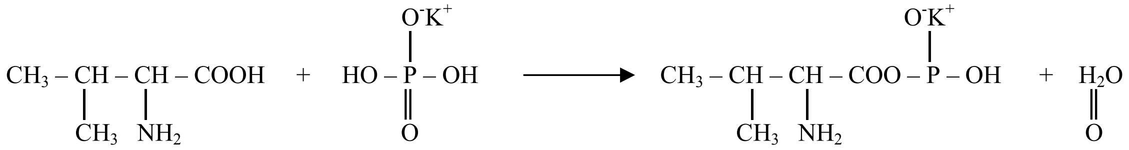


$$^{-}OOC-(CH_2)_2-CH(NH_3^+)-C(=O)-OH + HO-P(O^-K^+)(=O)-OH \longrightarrow {}^{-}OOC-(CH_2)_2-CH(NH_3^+)-COO-P(O^-K^+)-OH + H_2O$$

* KDP + L – Histidine



* KDP + L – Valine



$$CH_3-\underset{CH_3}{CH}-\underset{NH_2}{CH}-COOH + HO-\overset{O^-K^+}{\underset{O}{P}}-OH \longrightarrow CH_3-\underset{CH_3}{CH}-\underset{NH_2}{CH}-COO-\overset{O^-K^+}{P}-OH + \underset{O}{H_2O}$$

(L – Valine) (KDP)

4. Conclusions

Optically clear KDP and doped KDP crystals with dimension up to 20 × 25 × 10 mm^3 has been grown by slow evaporation technique and also by slow cooling technique.Powder XRD was taken to analysis the structures of the doped crystals. In the FTIRspectrum, the characteristic peaks due to C-O-H in plane and out of plane bands clearlydemonstrate protonation of COO – group. KDP was doped with L (+) Glutamic acid and IR spectrum was recorded for the range from 4000 cm^{-1} to 400 cm^{-1}. The absorption frequencies of KDP + L (+) Glutamic acid and pure KDP are compared. The O–H stretching OH–P–OH bending vibrations appeared at 3600(vw) cm^{-1} and 539(s) cm^{-1} in pure KDP were found to be missing in the IR spectrum of KDP doped with L (+) Glutamic acid.

The functional groups present in the grown crystals have been confirmed by FTIR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis. The study not only confirmed the strong interaction amino acids of the dopants with the –OH group of KDP but also the entry of these ions in the crystal lattice of tetragonal KDP crystal. The comparison of IR spectrum of pure KDP and KDP doped with L (–) Histidine and L (+) Valine revealed that no much change in the frequencies absorbed for pure KDP and KDP doped with L (–) Histidine and L (+) Valine except some additional IR frequencies appeared at 2852 cm^{-1} and 2465 cm^{-1} due to the interaction of the N–H stretching frequency of amino acids with P–O–H symmetric stretching of KDP. The very low intensity of O–H stretching frequency in the KDP doped with L (–) Histidine revealed the involvement O–H in hydrogen bonding with ring nitrogen of L(–) Histidine. This was further confirmed by high intensity O–H stretching band at 3435 cm^{-1} in KDP doped with L (–) Histidine compared to free O–H stretching frequency band at 3600 cm^{-1} in the case of the pure KDP. Further the decrease in the O–H hydrogen bonded stretching frequency by 165 cm^{-1} in the case of KDP doped with L (–) Histidine compared to free O–H of pure KDP revealed the extend of hydrogen bonding between H^+ of KDP with ring nitrogen of L (–) Histidine and in weakening the O–H bond strength of pure KDP.

All three amino acids used as dopatd are colourless and crystalline. They melt with decomposition at high temperature. They are soluble in polar solvents. They possess asymmetric carbon atoms. Therefore, they are optically active.

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