SYNTHESIS, GROWTH AND CHARACTERIZATION OF NEW OPTICAL, STRUCTURAL, THERMAL, Di-ELECTRIC, AND NON-LINEAR STUDIES OF L-HISTIDINE, L-VALINE, L-ARGININE DOPED KDP CRYSTALS FOR TUNED LASER APPLICATIONS

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ABSTRACT

The potassium Di hydrogen phosphate (KDP) is a well known nonlinear optical (NLO) material in the field of photonics and optoel ectronics. Since most of the amino acids exhibit NLO property, it is of interest to dope them in KDP. In the present study optically good quality crystal of pure KDP, L histidine L- valine and L- Arginine doped KDP have been grown from low temperature solution growth by slow evaporation technique using triple time deionized water as a solvent. The crystalline nature of the grown crystal was characterized by powder X-ray diffraction. The single crystal X-ray diffraction analysis reveals that the crystal belongs to tetragonal system. The presence of various functional groups of pure KDP, L histidine L- valine and L Arginine doped KDP crystals were identified by (FTIR) spectrum recorded in the wave number range 400 - 4000 cm^{1}. The UV-visible spectra were recorded to find cut off wavelength and transmittance the results show an improvement in the optical transmittance compared to pure KDP crystals. The nonlinear optical (NLO) property of the grown crystal has been confirmed by Kurtz powder technique, the second harmonic generation (SHG) efficiency of L- histidine L-valine and L- Arginine doped KDP crystals were found to be more than pure

KDP.

Keywords: *Solution growth, FT-IR, Single crystal XRD, powder XRD, UV-visible, Thermal, Dielectric and SHG.*

1 Introduction

Crystals are the unacknowledged pillars of modern technology, since the discovery of second harmonic generation of ruby laser radiation in a quartz crystal by Franken in 1961. In the recent years, the search for new crystals with good frequency conversion properties continues even today. For various device applications has lead to discovery of many organic, inorganic and semi-organic nonlinear optical (NLO) materials. Potassium Dihydrogen Phosphate (KDP, KH2PO4) single crystals attract much attention due to their wide applications in different fields of nonlinear optics, optoelectronics and photonics.

KDP group crystals possess high structure perfection ,mechanical strength, wide range of spectral transparency as well as relatively high values of laser damage threshold. Moreover, the growth technology makes it possible to obtain KDP crystals with well- developed growth sectors containing practically no defects. Crystals are widely used in the field of electronic industry, photonic industry, semi conductors, super conductors, sensors and non linear optics. Crystal using in the material science, chemical engineering, metallurgy, crystallography, mineralogy, which have potential applications in 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 known crystal is a never stopping process. The 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, and the fast growing development of optical communication system and optical information storage devices, switching and other signal processing.

One of the most important applications of NLO materials is their use for fast data transfer, combined with a very high Signal-to-Noise ratio, even over long distances. In recent years, different applications of NLO and photorefractive materials have been developed, for example, optical frequency conversion, electro-optical modulation, dynamic holography, optical writing and optical guiding of laser beams It is seen that L-proline and (4*R*)- hydroxy-L-proline derivatives, containing donor groups are chiral carriers [98]. The introduction of chirality by means of an asymmetrically substituted carbon should in addition respect the molecular features leading to a high nonlinear behaviour. Proline and its derivatives are often used as asymmetric catalysts in organic reactions. Only noncentrosymmetric alignment of the chromophores in the crystal lattice leads to an observable bulk second-order NLO response . In order to obtain the adjustment of the nonlinear efficiency/transparency, based on the molecular engineering and crystal engineering approach, it is tried to develop a new method to design organic non-linear optical second-harmonic generation materials such as organic inclusion complex .

The NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications major role in the field of photonics and optoelectronics technologies. KDP crystal is studied from various aspects and widely used NLO crystals. The non linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication. This chapter address the crystal growth technique, in particular the slow evaporation

solution growth technique. This technique is used to grow a crystal in a simple manner and provide improvements in purity. Additionally, this technique can produce organic, inorganic and semi organic NLO crystal at ambient temperature in different solvents. Hence we chose this technique in growth our crystals, to analyze of amino acid based dopants on the non linear optical property of KDP crystals, efforts were made to dope KDP with the amino acids L-histidine, L-valine and L-arginine.

The effects of impurity atoms on the quality and performance of material are analyzed. 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. In the present investigation, we studied the influence of the growth aspects of KDP crystals grown from the solution by using the low temperature solution growth technique and amino acids like namely L-histidine, L-valine and L-arginine doped KDP crystals has been studied. also the characterization such Single crystals XRD, Powder XRD, FTIR, UV-Vis Spectra, thermal, dielectric and SHG efficiency studies were carried out and the results are presented and discussed in detail.

2 EXPERIMENTAL DETAILS

2.1 CRYSTAL GROWTH

The commercially available of the Potassium Di hydrogen orthophosphate, KH_2PO_4 (KDP) (Merck), L-histidine L-valine and L-arginine have been used for synthesizing the L-histidine doped KDP (LHKDP), L-valaine doped KDP (LVKDP) and L-arginine doped KDP (LAKDP) crystals.

a) LHKDP crystal

The LHKDP crystal were thus prepared by taking the Potassium Di hydrogen

orthophosphate, KH_2PO_4 (KDP) and L- histidine weight of 0.2 gram salt were taken and dissolved in 100 ml triple time distilled water and under saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of under saturated solution of pure KDP is doped with L-histidine continuously stirred for one hour then the solution was filtered in the Whatman 20-25 μm filter paper and transferred to a Petridish. The Petridish is covered with a pourous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure and L-histidine doped KDP crystals were formed. The figure 3.1 shows as grown pure KDP crystal and LH: KDP crystals shown in the figure 3.2

$$\mathbf{KH_2PO_4 + C_6H_9N_3O_2 \longrightarrow KH_2PO_4\,(C_6H_9N_3O_2)}$$

KDP+L-histidine **L-histidine doped KDP crystal**

b) LVKDP crystal

The LVKDP crystal were thus prepared by taking the Potassium Di hydrogen orthophosphate, KH_2PO_4 (KDP) and L-valine weight of 0.2 gram salt were taken and dissolved in 100 ml triple time distilled water and saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of saturated solution of pure KDP is doped with L-valaine continuously stirred for one hour then the solution was filtered in the whatman20-25 μm filter paper and transferred to a Petridish. The Petridish is covered with a porous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure

and L-valaine doped KDP crystals were formed. The figure 33 shows as grown LV: KDP crystal.

$$KH_2PO_4 + C_5H_{11}NO_2 \longrightarrow KH_2PO_4\,(C_5H_{11}NO_2)$$

KDP+L-valine **L-valine doped KDP**

c) LA KDP crystal

The LA:KDP crystal were thus prepared by taking the Potassium Di hydrogen orthophosphate, KH_2PO_4 (KDP) and – arginine weight of 0.2 gram salt were taken and dissolved in 100 ml triple distilled water and under saturated solution of KDP was prepared. The solution continuously stirred for 6 hour with a magnetic stirrer to ensure homogeneity of the solution. After preparation of saturated solution of pure KDP is doped with L-arginine continuously stirred for one hour then the solution was filtered in the whatman 20-25 μm filter paper and transferred to a Petridish. The Petridish is covered with a porous paper tied on top with a rubber band to facilitate and kept in a closed room where the slow evaporation gradually done, at room temperature. After a period of two weeks, optically highly transparent crystals of pure and L-arginine doped KDP crystals were formed. The figure 34 shows as grown LA: KDP crystal.

$$KH_2PO_4 + C_6H_{14}N_4O_2 \longrightarrow KH_2PO_4\,(C_6H_{14}N_4O_2)$$

KDP+L-arginine **L-arginine doped KDP crystal**

Figure 1 As grown pure KDP Crystal

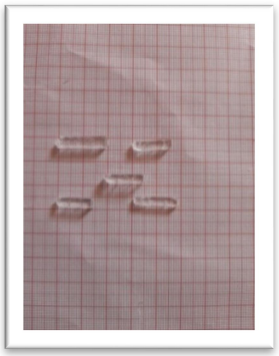


Figure 2 As grown LH KDP Crystal

Figure 3 As grown LVKDP Crystal

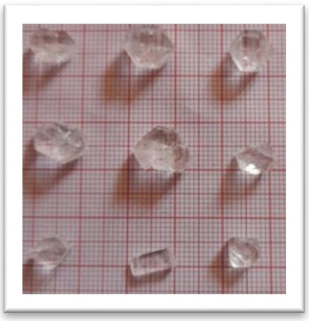


Figure 4 As grown LAKDP Crystal

3 Results and Analysis

The grown pure KDP and LHKDP, LVKDP and LAKDP crystal were characterized by different analytical methods and outcome is discussed.

3.1 Powder X-ray diffraction and single crystal analysis

The grown crystals where subjected to powder X-ray diffraction analysis using β Rigaku Minifix II-C, CuKα radiation of wavelength (1.5406Å) The powder X-Ray diffraction pattern of as grown KDP and doped L-histidine ,L-valine and L-arginine were shown in the figure 5 to 8. The Powder XRD shows the grown crystals are having good crystalline quality. The doped KDP powder XRD shows some shift in the peaks confirms the incorporation of dopants in the pure KDP crystals.

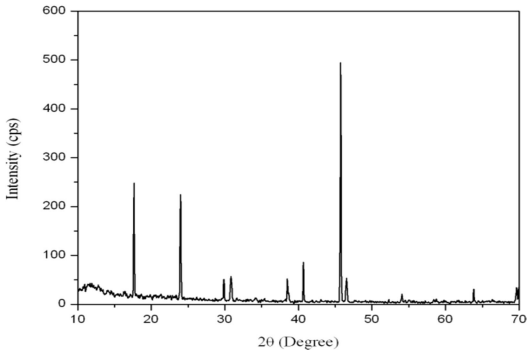


Figure 5 XRD Pattern of as grown pure KDP crystal

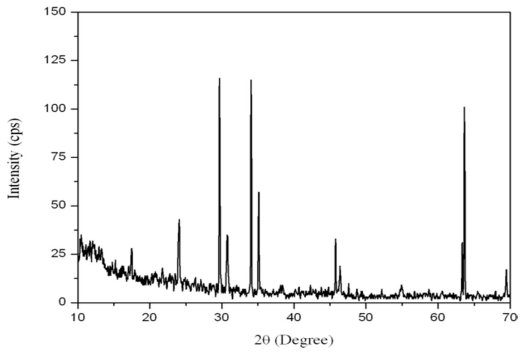


Figure 6 XRD Pattern of as grown L-histidine with doped KDP Crystal

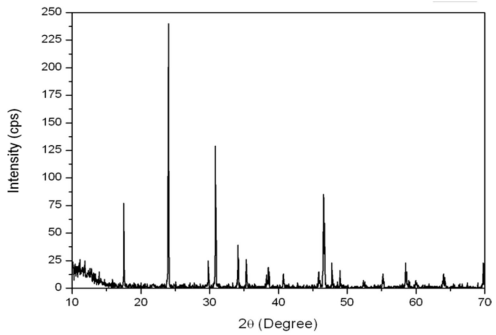


Figure 7 XRD Pattern of as grown L-valine with doped KDP Crystal

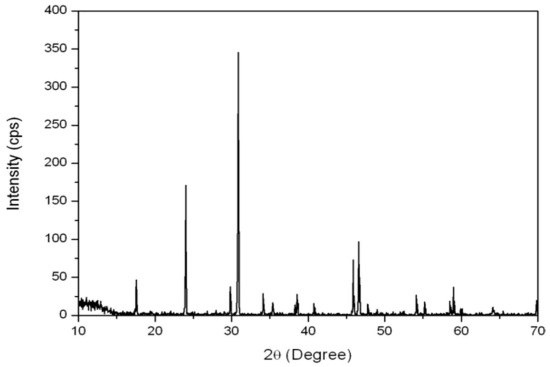


Figure 8 XRD Pattern of grown L-arginine with doped KDP Crystal

3.2 Single crystal X- ray diffraction of study of pure and amino acids doped KDP crystal

The cell parameter values of the pure KDP crystals and LHKDP, LVKDP and LAKDP crystals were studied by Single crystal X-ray single crystal diffractrometer CAD4/MACH3 and the data was collected using graphite mono chromate $M_OK\alpha$ (λ=0.717Å) radiation of wavelength at room temperature 293K. 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. The XRD data of the present work is very well agreement the reported value.

Table 3.1 Cell parameter of pure and LAKDP, LVKDP and LHKDP crystals

crystal	Lattice Parameter a = b (Å)	Lattice Parameter (Å) c	Interfacial angles (°) α=β =γ	Cell Volume (A^3)
Pure KDP Crystal	7.448	6.977	90°	389
KDP +L–arginine	7.47	6.99	90°	390
KDP +L-valine	7.48	6.95	90°	392
KDP +L-histidine	7.47	6.98	90°	394
KDP +L-arginine	7.54	7.03	90°	400

3.3 Optical Transmission Spectrum

The optical transmission spectra of the grown the pure KDP, LH KDP, LVKDP and LA KDP crystals were recorded in the wavelength range of 190-900 nm

using LABINDIA UV 3092. UV- Visible spectrometer with a grown crystal of thickness the optical spectra are very important for any NLO material due to the fact that the material can be practical use only if it has optical 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 UV-Visible NIR spectrum for growth Pure KDP, LHKDP, LV: KDP and LAKDP crystal of the transmittance spectrum are shown in Figure. 9 to 12 this spectrum shows good transparent nature of the sample L-ariginine and L-histidine doped crystal had more transmittance than pure KDP Crystals. It is interesting to more that the crystals are essential requirements for better optical quality and suitable for frequency doubling. The band gap energy E_g is calculated in eV using the planks equation as follows.

$$E_g = hc/\lambda$$

Where h is the Plancks constant c is the velosity of the light and λ is the lower cut- off wavelength. The calculated energy gap value of grown pure KDP, LHKDP, LVKDP and LAKDP crystal has 6.5 ev and cut- off wave length of each crystals has 190nm.from the energy gap values of pure KDP, LHKDP, LVKDP and LAKDP crystals belongs to the category of insulating materials. The LHKDP, LVKDP and LAKDP crystals will be very useful for nonlinear optical application.

Growth periods of pure KDP, LHKDP, LVKDP and LAKDP doped crystals are tabulated in table 3.2

Table3. 2 Growth period of Pure LHKDP, LVKDP and LAKDP doped KDP Crystals

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

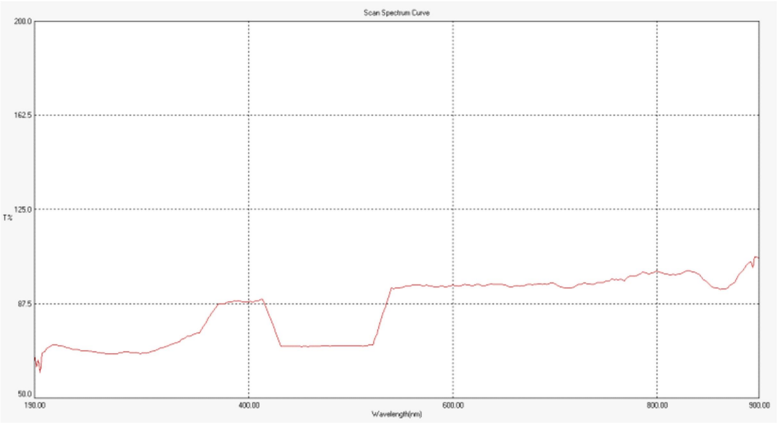


Figure 9 UV Transmittance spectrums of Pure KDP crystal

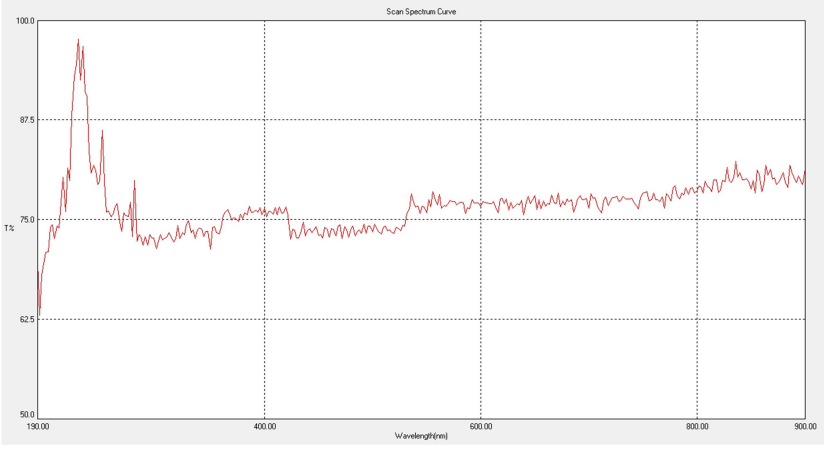


Figure 10 UV Transmittance spectrum of L-Arginine KDP crystal

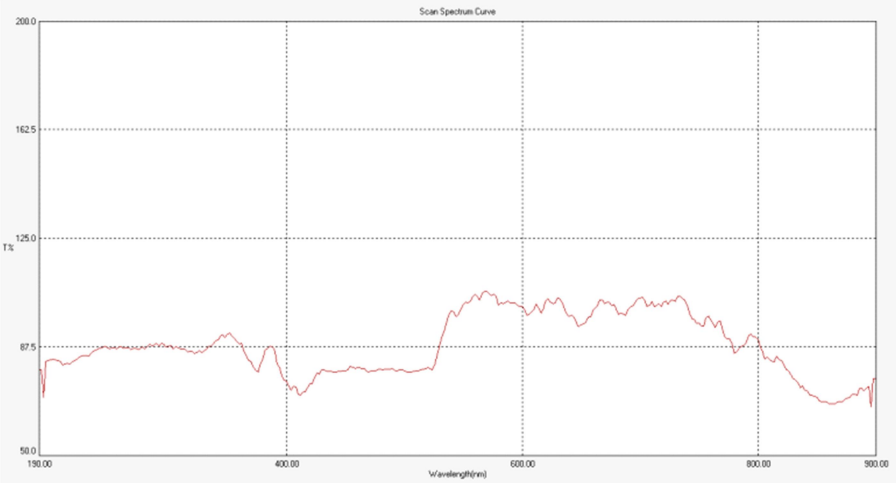


Figure 11 UV Transmittance spectrum of L-Histidine KDP crystal

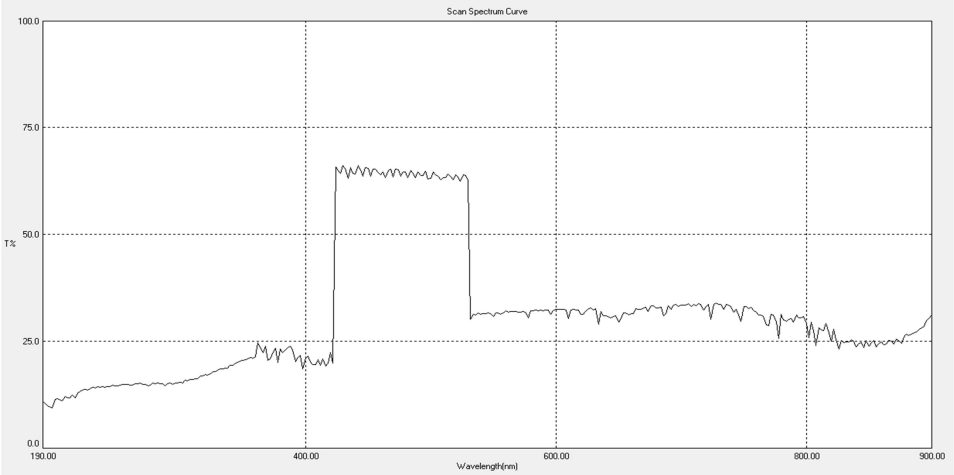


Figure 12 UV Transmittance spectrum of L-Valine KDP crystal

3.4 FT-IR ANALYSIS

The FTIR spectrum of pure KDP and L-histidine L-valine and L-arginine doped KDP crystals have been recorded on Perkin Elmer FTIR 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 is bending. In the FT-IR spectra of amino acid L-histidine L-valine and L-arginine doped KDP crystals, the same peaks have been observed with additional peaks. These

additional peaks correspond to the functional groups of L-histidine L-valine and L-arginine which confirm the doping of the L-histidine L-valine and L-arginine in the spectra of amino acids doped L-histidine L-valine and L-arginine crystals, some bands of H_2PO_4 overlap with amino acid vibration. Hence few a bands of Di hydrogen phosphate ion become broader and some of the frequencies are slightly shifted. The asymmetric stretching vibrations of NH_3^+ of amino acid appear in the region 3100-3450 cm^{-1}.

Some of them overlap with the OH stretching vibrations of Di hydrogen phosphate ion. The symmetric deformation of NH_3^+ ion appears at around 1500cm^{-1} in the spectra of all doped crystals with medium intensity. The CH_3 bending vibrations of amino acids appear around 1450 cm^{-1}. These vibrations of amino acids present in the spectra of doped crystals reveals the incorporation of impurities in the crystals. The Figure 3.13 to 3.16 show .that FTIR spectrum of pure KDP and L-histidine L-valine and L-arginine doped KDP crystals and Table No.3.3 shows that FTIR Wave number assignments for the L-histidine, L-Valine and L-arginine doped KDP grown crystals

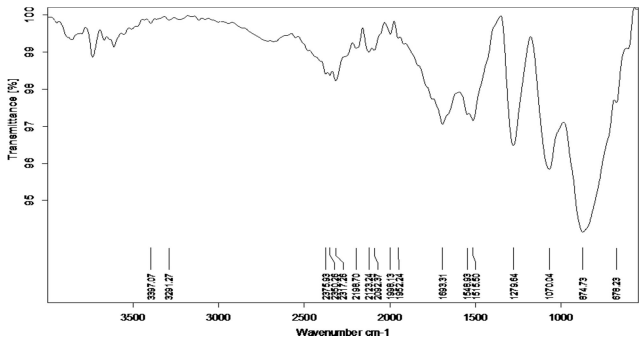


Figure 13 FTIR Spectrum of Pure KDP Crystal

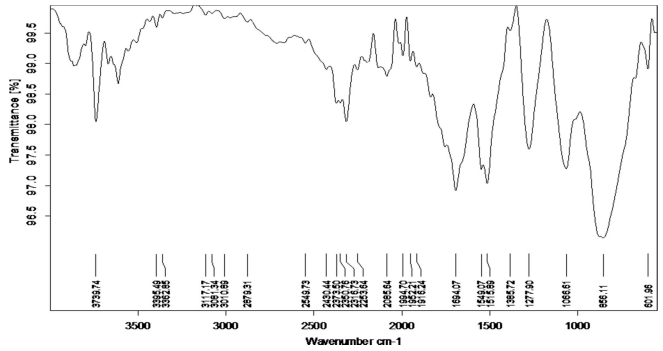


Figure 14 FTIR Spectrum of L-histidine doped KDP Crystal

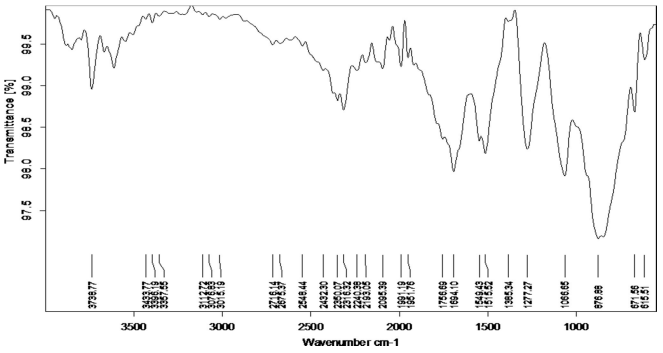


Figure 15 FTIR Spectrum of L-valine doped KDP Crystal

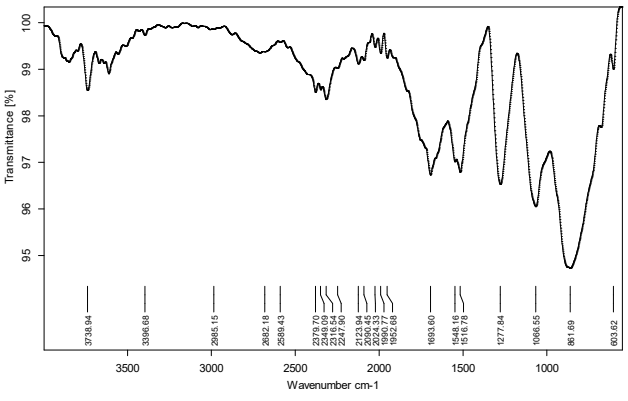


Figure 16 FTIR Spectrum of L-arginine doped KDP Crystal

Table. 3 FTIR Wave number assignments for the L-histidine, L-Valine and L-argnine doped KDP grown crystals

Pure KDP Peak values ($c\ m^{-1}$)	L-histidine doped KDP ($c\ m^{-1}$)	L-valine doped KDP ($c\ m^{-1}$)	L-argnine doped KDP ($c\ m^{-1}$)	Assignment
3739.74	3738.77	3397.07	3738.94	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
3395.49	3433.77	3291.27		
3362.85	3396.19	2375.93	3396.68	
	3357.55	2350.26	2985.15	
3117.17	3112.72	2317.26		
3081.34	3076.83	2198.70		
3010.89	3015.19	2123.24		
2879.31	2716.14	2092.37		
2549.73	2675.37	1998.13		
2430.44	2548.44	1952.24	2682.18	
2373.50	2432.30		2589.43	
2350.76	2350.07		2379.70	
2316.73	2316.32		2349.09	
2253.64	2240.38		2316.54	C=O stretching vibration, P-O-H bending and –C= NH_4 stretching
2085.64	2193.05		2247.90	
1994.70	2095.39		2123.94	
1952.21	1991.19		2090.45	
1916.24			2024.33	
	1951.76		1990.77	
			1952.68	
	1756.69			
1694.07	1694.10	1693.31	1693.60	Asymmetrical NH_3^+ bending vibration

1549.07 1515.89	1549.43 1515.52	1548.93 1515.50	1548.16 1516.78	COO^- asymmetric stretching
1385.72	1385.34			CH_2 bending. P=O stretching of KDP, Asymmetric vibration
1277.90	1277.27	1279.64	1277.84	C-COO^- stretching
1066.61	1066.65	1070.04	1066.55	P-OH and C-H stretching Symmetric stretching of NO_3
856.11	876.88	874.73	861.69	P-OH deformation , C- CN scissoring of
601.96	671.56 615.51	678.23	603.62	-COO bend

3.5 Thermal Analysis

TGA /DTA/DSC are powerful tool to investigate the melting behaviour, of the pure KDP, LHKDP, LVKDP and LAKDP crystals were carried out as follows. In order to study the thermal stability of the grown crystals, Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) have been carried out using SDT Q600 model thermal analyzer. Differential scanning clorimetry is a thermo-analytical in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function temperature. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to the sample than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. The amount of sample taken for the analysis is about 15 mg and the temperature range is about30- 800^0C with the heating rate of about

20^0C/minute. The TGA and DSC pattern of LHKDP crystal is shown in Figure 17. The DSC curve of LH: KDP shows that there is no phase transition up to 223.8**ºC** and there found two endothermic curves at 237.37 ºC and 338.73 ºC

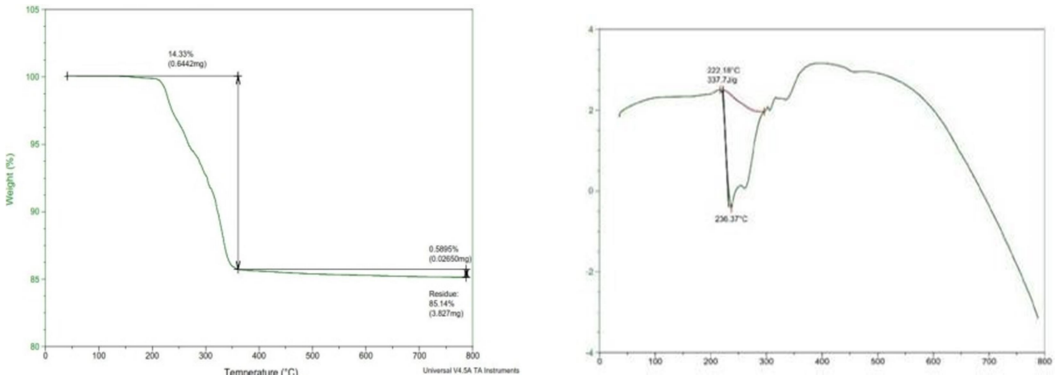
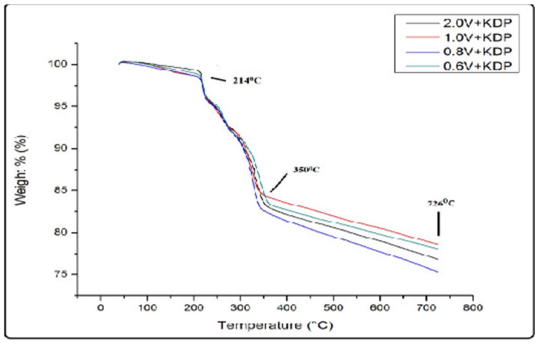


Figure 17 TGA and DSC curves of LHKDP Crystal

DTA and TGA of KDP were carried out with the help of an instrument (STA 409C) using KDP crystals as sample and alumina as reference. LV doped KDP sample was decomposed at 272.20 ^{o}C. The graphs show the peaks at 435.85^{o}C and 520^{o}C reveal exothermic reaction due to escape of oxygen atoms from the KDP crystal. TGA curve sharply decrease at temperature at 214^{o}C and 350^{o}C is most probable melting point of KDP crystal. TGA curve shows that crystals are thermally stable below 220^{o}C. This shows that the presence of l-valine appears to increase the decomposition temperature of KDP. Fig. 18 and 19 shows TGA and DTA curves for LV doped KDP crystal. The DTA curve shows an endothermic peak at 272.20^{o}C, 435.85^{o}C, 520.5^{o}C. Enthalpy changes in the endothermic reaction are 241.44 J/gm, 63.75 J/gm.



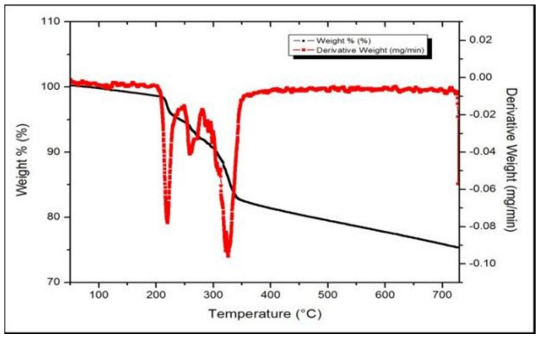
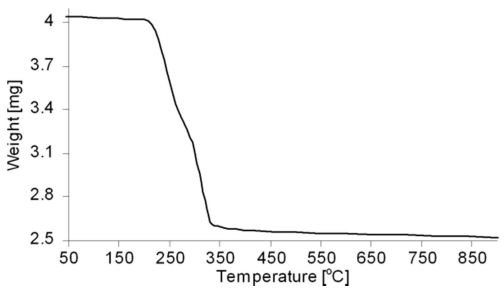


Figure 18 TGA curves of LV doped KDP **Figure 19** DTA curves of LV doped KDP

The TGA curve of L-arginine doped and pure KDP crystals have been recorded on Perkin Elmer Dimmer TGDTA at a heating rate of 20°C/min under argon atmosphere. For pure KDP crystal, after temperature about 230 °C the weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP (Fig.20) The TGA curve for 0.6 mol% L-arginine doped KDP crystal has been shown in Fig. 21. The experimental results show that the initial weight loss starts at about,



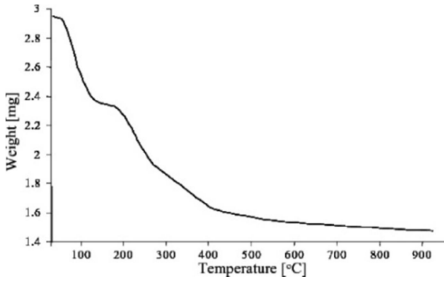


Figure 20 TGA curve of pure KDP crystal. **Figure 21.** TGA curve of LAKDP crystal.

67°C and ends at 120°C with about 18% weight loss, which corresponds to the liberation of ammonia and water molecule. Second weight loss starts at about 205°C. Rapid weight loss occurs up to 262°C and continues slowly up to 400°C, which is possibly due to the decomposition of the KDP and remaining L-arginine.

3.6 Dielectric Studies

The single crystals of pure KDP and amino acid L-histidine L-valine and L-arginine doped KDP were used for dielectric studies. The dielectric constant was calculated by relation $\varepsilon_r = Cd/\varepsilon_o A$, where, C = capacitance of sample, d = thickness of sample, A = area of sample and ε_o = absolute permittivity.

The dielectric loss is a measure of the energy absorbed by dielectric. It is known that in a capacitor, the dielectric usually has a resistance R and reactance $1/\omega C$. Which are related to the phase angle $\tan\delta = 1/\omega CR$. Here $\tan\delta$ is referred to as the dielectric loss. The dielectric constant and dielectric loss depend on frequency of applied field.

The dielectric analysis is an important characteristic feature that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed. (N.kangathara and G.Anbalagan). The dielectric constant is one of the basic properties of the solids.

The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depends on the frequencies.[S.M.dharmaprakash] Figure No.22 represents the dielectric constant and dielectric loss against log f for LHKDP crystals. From the figures, it is inferred that the value of dielectric constant is high at lower frequencies and it is lower at high frequencies. The low value of the dielectric loss at high frequency for these samples suggests that the samples possess enhanced optical quality and this parameter is very important for NLO materials in their applications [Balarew 1984].

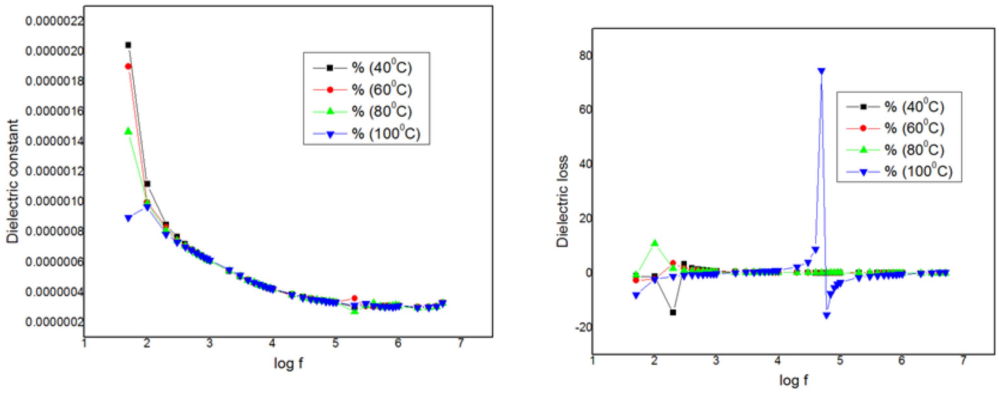


Figure 22 Dielectric constant and dielectric loss graph of LHKDP crystal.

The dielectric measurements of pure KDP and LVKDP crystals (2.5 mm) have been carried out in the temperature range of 40–120 °C at a frequency of 100 kHz using the HIOKI-3532 LCR cube meter. In order to obtain accurate results the parallel faced quality single crystals were applied by the silver paste and connected to the electrical probes. The external electric field and temperature majorly influence the dielectric constant of material as shown Fig21. It is evident that the increase in temperature leads to instability in polarization activity (ionic, electronic, dipolar and space charge) of the crystal as a consequence of which the dielectric constant of crystals increases with the increase in temperature.

The analysis confirms that the dielectric constant of KDP crystal has been reduced to a lower level after the addition of LV. The lower dielectric constant favours less power consumption and enhancement in SHG coefficient of material which are advantageous parameters for designing electrooptic modulators, photonics, and NLO and microelectronics devices. The measurement of dielectric loss enables to investigate the dissipation of electromagnetic energy through defects (solvent impurities, macro and micro cracked, grain boundaries, porosity and random crystallite orientation) in crystal medium. The variation of dielectric loss with

temperature is shown in Figure .23 and it reveals that the dopants LV effectively reduce the dielectric loss of KDP crystal demonstrating the improved optical quality and minimized electrically active defects in doped KDP crystals. The lower dielectric constant and dielectric loss of doped KDP crystals is a significant and decisive parameter for optoelectronics and NLO applications.

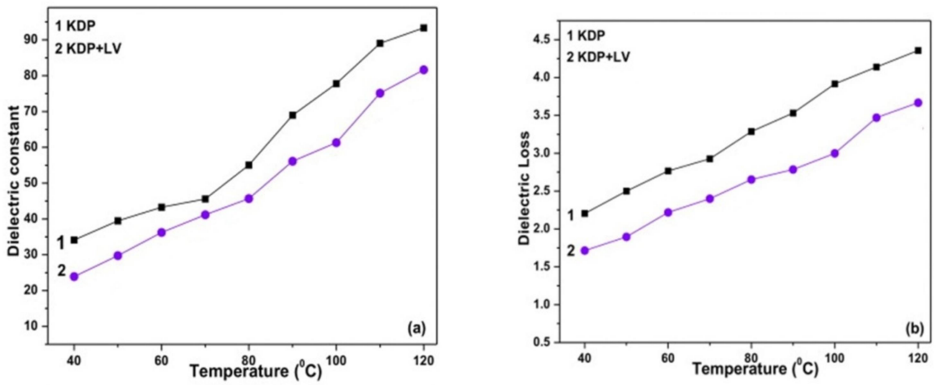
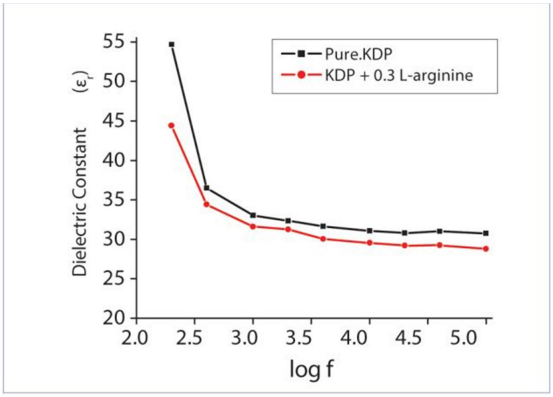


Figure 23 Di electric constant and dielectric loss graph of LVKDP crystal.

Figure-24 shows the variation of ε_r with frequency of applied field. The dielectric constant decreases rapidly as frequency increases. It is also observed that the doping concentration affects the values of dielectric constants. As the doping concentration increases the dielectric constant decreases. The rapid decreases in the values of the dielectric constant with increase in the frequency of the applied field suggest that the dipoles cannot comply with the changes in the frequency of the applied field after the certain value. More-or-less, the same type of nature is observed for the variation of dielectric loss (tanδ) with the frequency of applied field as shown in the Figure-25.



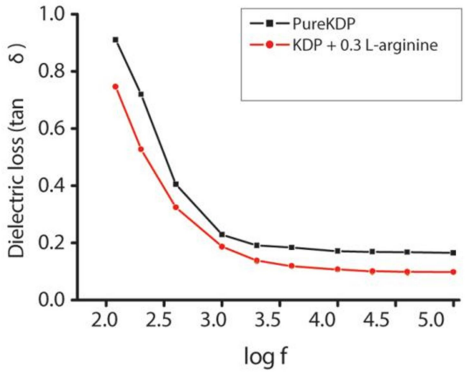


Figure 24 Plot of dielectric constant & Log f **Figure 325** Plot of dielectric loss & Log f

For pure and L-arginine doped KDP crystals for pure and L-arginine doped KDP crystals

3.7 Second Harmonic Generation efficiency analysis

To conform the NLO nature, the grown crystals of pure and doped grown pure KDP and LH KDP, LVKDP and LAKDP crystals were estimated by Kurtz and Perry powder technique. Second harmonic generation (SHG) efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry using an ND ;YAG (QUANTA RAY Model LAB -170- 10) Q switched laser beam, 10ns laser with a pulse repetition rate of 10 Hz working at 1064 nm. 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 ground 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 acid doped KDP, Thus the SHG

efficiency of LVKDP and LAKDP crystals were found to 1.07 and 1.22 times greater than pure KDP crystals. Hence LHKDP, LVKDP and LAKDP are a potential material for the second order NLO applications.

Table 4 Comparison of frequency conversion efficiency for pure LHKDP, LVKDP and LAKDP crystal

Sl. No.	Crystal	Input nergy (J)	Output Energy (m.J)	η =(output / input) x 100%	SHG Efficiency
1.	L- arginine	0.69	12.4	1.80	0.92
2.	L-valine	0.69	14.3	2.07	1.07
3.	L-histidine	0.69	16.3	2.36	1.22
4.	KDP pure	0.69	13.34	1.9	

4 Summary and Conclusion

The transparent, colorless nonlinear optical single crystals of pure and amino acid doped LHKDP, LVKDP and LAKDP crystals have been successfully grown in a period of 10-12,12-15, 15-20 and 20-25 days at room temperature by using slow evaporation solution growth technique. The tetragonal crystal system, cell parameter values of the pure and LHKDP, LV KDP and LAKDP crystals were confirms by the single crystal X- ray diffraction studies. The powder X- ray diffraction test confirms the crystalline of the nature grown pure KDP crystal and LHKDP, LV KDP and LA: KDP crystal. The transmission spectra reveal that amino acid LH KDP, LVKDP and LAKDP additives were increased the optical transparency of the crystals and have sufficient transmission in the entire UV – Visible and IR regions. The presence of

functional group in the grown pure KDP crystal, LHKDP, LVKDP and LAKDP crystal were identified by the FTIR spectroscopy analysis The thermal properties of the pure KDP and amino acids doped KDP crystals are studied by obtaining the TGA/DTA/DSC curves. The electrical properties were also studied by dielectric constant studies. The high dielectrisc constant in the doped crystal than pure crystal indicating that the doping is highly useful for NLO applications. The SHG efficiency studies is relatively confirm the nonlinearity of the grown pure KDP crystal, LHKDP, LVKDP and LAKDP crystal by the emission of green light and the SHG efficiency of the grown LVKDP and LHKDP crystals relatively 1.07 and 1.22 times greater than pure KDP crystals, and the grown crystals confirms the suitability of the materials for the SHG application and LHKDP, LVKDP and LA KDP crystals are used in tuned laser applications and sensors.

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