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Synthesis, Growth and characterization of L-Histidine doped Potassium dihydrogen Phosphate(LHKDP) crystals.

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Abstract: *L-histidine doped potassium dihydrogen phosphate (LHKDP) single crystals are grown by slow evaporation technique method. The addition of amino acid to KDP influences the characterization of pure KDP crystals. There is a slight modification in the linear and nonlinear property, mechanical hardness, SHG of pure KDP. The unit cell parameters and cell volume are determined with single crystal X-ray diffractometer. SHG studies show slight decrease in the NLO property due to doping. As the Load increases the Hardness also increases for LHKDP crystals. The Laser damage threshold value is slightly higher for LHKDP crystals when compared to pure KDP. TGA and DSC graphs of the samples are also taken.*

Keywords: *Single crystal XRD, FTIR, Optical property, SHG efficiency, Non-linear optics, Laser Damage threshold Value.*

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I. Introduction

Nonlinear optics is a new frontier of science and technology as they are the precursor of current research playing a major role in the emerging era of photonics. Non linear optical processes have applications in the field of telecommunication ,optical signal processing and optcal switching and laser technology.[1,2] (Dhanuskodi and Mary 2003; Prasad and Williams 1991). So extensive studies have been made on the synthesis and growth of NLO materials over the past decades.

An organic compound possesses a high degree of delocalization due to their weal Van der Waa'ls and hydrogen bonding which is not present in the inorganic compounds. Therefore organic compounds posses more optic nature rather than inorganic compounds [K.J.Arun(2009)]. But it is very difficult to grow large size crystals for organic compounds. In order to rectify the above mentioned drawbacks both in inorganic and organic materials properties and there to increase the desired advantages, material scientists approached a new strategy, that is to develop hybrid organic –inorganic materials with some tradeoff in their respectieve advantages. These new class of materials are nothing but a semi-organic materials[S.Gopinath et (2011)].

Potassium dihydrogen phosphate (KDP) is an excellent inorganic non-linear optical (NLO) material and has a considerable interest among the researchers due to their extraordinary qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cut off wavelength and high laser damage threshold against the high power laser.[P.V. Dhanraj et al(2009)] . Also, KDP has an efficient
supersaturation, temperature and pH of the solution. The effect of impurities on the growth rate and habit of the crystal growing in the solution has been the subject of many experimental and theoretical studies [15,16](Sangwal 1996, Kuzentsov et al 1998).

A lot of research has been undertaken to modify the properties and growth rate of KDP with the addition of suitable impurities[17,18](Anandakumari et al 2003 and Shirsat et al 2008)[19]Kumaresan et al(2007) have grown L-glutamic acid, L-Histdine and L-Valine doped KDP crystals. They have shown an improved optical transmission and NLO property and also growth habit modifications. Also they observed an increase in the mechanical hardness with respect to pH variations.(Shaikh Kalim shaik Hanif et al 2015) [20] reported Glycine doped KDP crytal with enhanced NLO property than pure KDP.[21,22,23](Parikh et al (2007,2010) and Muley et al(2009) have reported an increased SHG efficiency and optical transmission by doping L-argnine and L-alanine respectievely in KDP. Sandhya et al (2015) investigated and reported the Phenylalanine doped KDP with improved NLO property than pure KDP[24].Suresh kumar et al (2008) reported the SHG efficiency is found to increase appreciably by the addition of amino acid glycine. So there are so many reports related to doping of amino acids with KDP. With those references the present work is aimed at the doping of amino acid L-Histidine with KDP and its effect and changes in the growth of KDP have been reported.

1.2 Determination of Solubility of L-Histidine Doped Kdp

The solubility of L-Histidine doped KDP, is determined for six different temperatures starting from 30, 35,40, 45, 50, and 60 ^{o}C and were shown in fig 1.1. Initially, supersaturated solution of LHKDP is prepared separately at room temperature in an air tight container maintained at a constant temperature with continuous stirring , the solution is analyzed gravimetrically and the solubility of the doped KDP solutions of 100ml of solvent is determined. It was observed from the solubility curve that the solubility increases with temperatures. Care was taken during heating of the solution and temperatures as low as 60^{o} C was maintained to avoid any decomposition.

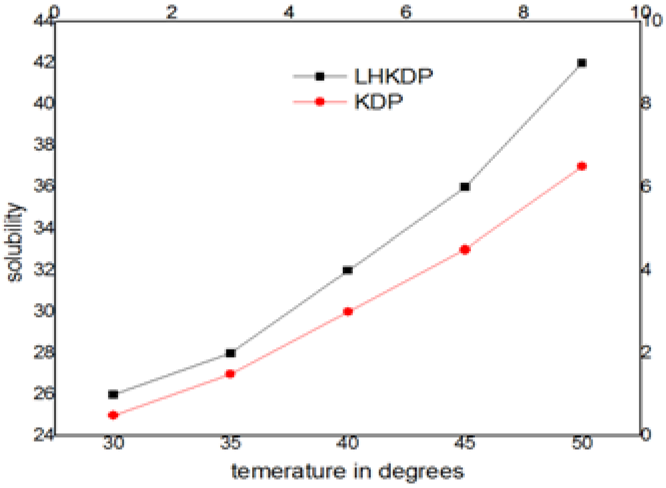


Figure1.1 Solubility graph for KDP and LHKDP

1.3 Growth and Synthesis of Amino Acid Doped KDP

First a 100ml of Pure KDP solution was prepared using analytical grade[Merck] KDP salt by dissolving it using a Millipore water whose resistivity is about 18.2 MΩ. In every 100ml of pure kdp solution 0.1 g of L-Histidine dopant is mixed. 0.1g of L- Histidine doped KDP mixture was thoroughly and uniformly mixed using a magnetic stirrer. With the help of constant stirring, a uniform and homogeneous distribution throughout the entire volume of LHKDP solution can be attained. On reaching saturation, the solution was filtered twice using Wattman filter paper and transferred to a Petri dish. Thus the solutions in the petri dishes were covered with the thick paper with fine pores in order to avoid dust to enter and to minimize the rate of evaporation. Upon complete evaporation of solvent, single crystals of sizes as shown in the figure 1.1 were harvested. The optimized growth condition LHKDP, are mentioned below in the table 1.1.

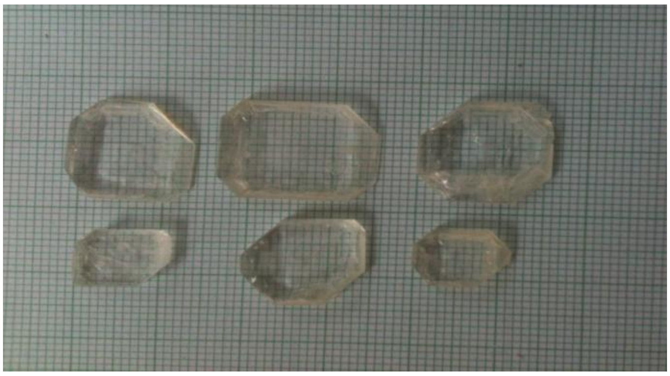


Figure 1.2 As Grown LHKDP Crystal

Table1.1 Optimized growth conditions of amino acids doped KDP crystals

Method of growth		Slow evaporation	
Solvent used/pH		Millipore water of 18.2 Mohms cm resistivity / 5	
Operating temperature		Room temperature	
Molar ratio		0.1g/100ml	
Name of the sample	Period of growth	Dimension	Growth rate
LHKDP	12 days	$18 \times 9 \times 3mm^3$	1.75mm/day

1.4. Structural Studies of LHKDP Crystals

1.4.1Single Crystal X-Ray Diffraction Studies

A fine quality of LHKDP single crystals were kept on an Xcalibur, Eos diffractometer at 293(2) K. Single crystal X-ray diffraction analyses of this single crystals have been taken out and the unit cell parameters are given in the Table1.2.

Table 1.2 Unit cell Parameters of Pure and LHKDP crystals,

CRYSTALS	UNIT CELL PARAMETERS					
	a (A)	b(A)	c (A)	α=β=γ°	Crystal system	Volume ($A^{3)}$
PUREKDP	7.45	7.45	6.97	90		386
LHKDP	7.47	7.47	6.99	90	Tetragonal	390

The doped KDP shows a trivial distortion in its cell parameters when compared to that of pure KDP. This clearly indicates that doping changes the cell axes and hence the cell volume [R.R. Saravanan et al (2013)].

1.4.2 Powder X-Ray Diffraction Studies

Powder X-ray pattern for LHKDP single crystals were recorded and shown in Figure 1.3 respectively. To identify the reflection planes and to check the crystalline perfection of the grown crystal, powder X-ray diffraction patterns of the powdered sample have been recorded using a Reich Seifert diffractometer with CuKα(λ=1.5418 A) radiation at 30 kV, 40mA. The synthesized grown crystals were scanned over the range from 10o to 50o diffraction angle at a scan rate of 2° /minute at room temperature. The inter planar spacing (d) was calculated for the prominent peaks of the grown crystals using Bragg's equation. Using the 'index' software, the prominent peak's hkl values were calculated and indexed.

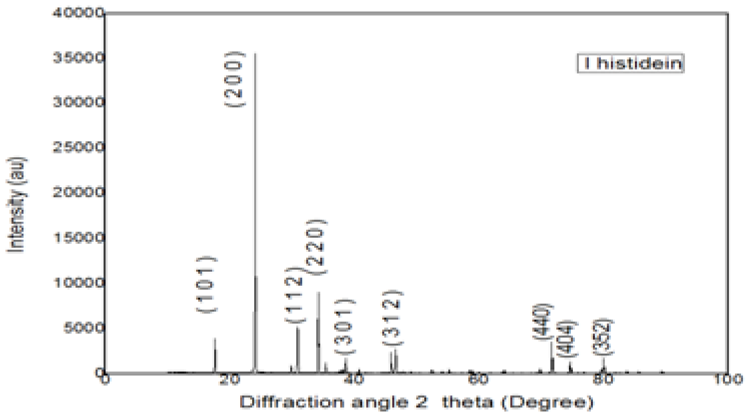
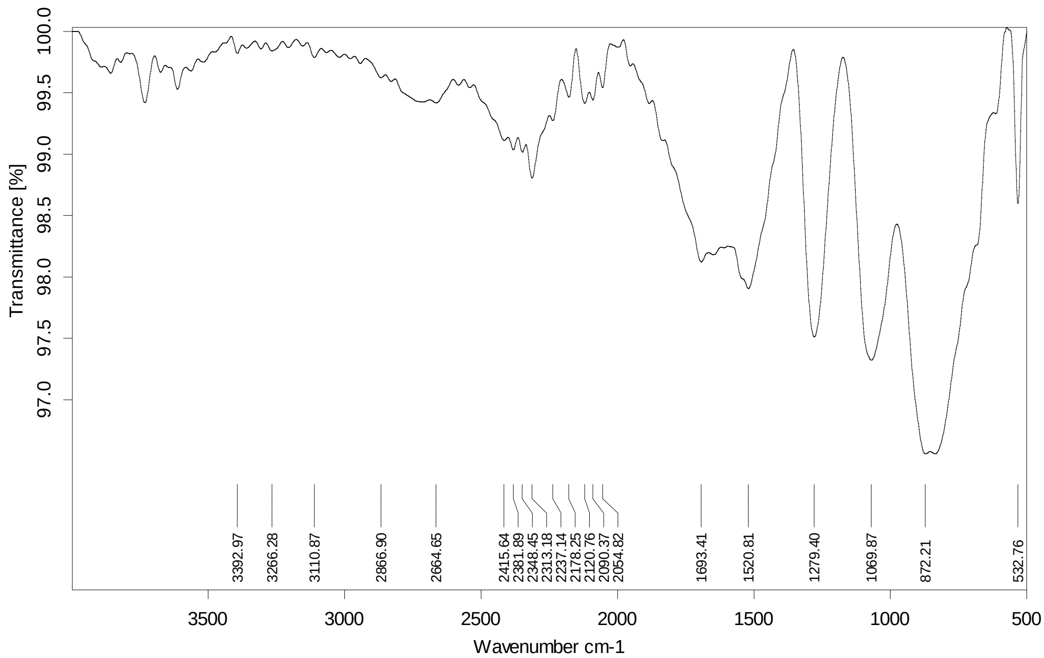


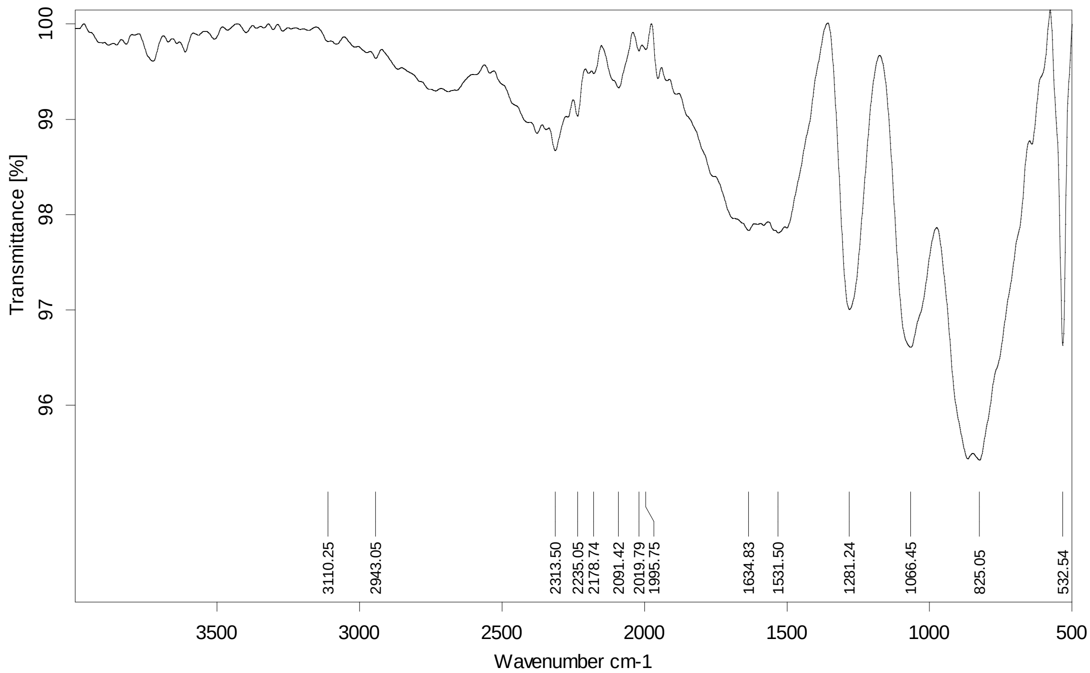
FIG : 1.3 XRD Pattern of LHKDP Crystal

The powder XRD spectra for the pure and L-Histidine doped KDP , it is clear that the structures of the doped crystals are slightly distorted when compared to the pure KDP crystal. All the prominent peaks present at lower diffraction angles were similar to that of pure KDP and the trivial distortion occurs at the peaks found for higher diffraction angles.

1.4.3 FT-IR Spectral Studies

Fourier transform infrared spectrum was recorded for the grown crystals using KBr pellet over the range 500-4000 cm^{-1} to determine the functional groups present in the doped crystal. The FT-IR spectra for,LHKDP crystals are shown in Figure 1.4.





Figure(1.4) FTIR Spectrum of KDP and LHKDP crystals.

Table`1.4 Band Assignments of FTIR- spectrum of LHKDP crystal.

PureKDP	KDP doped with L- Histidine	Assignments
3740(vw)	-	Free O-H stretching vibration
		Free N-H stretching mode
3301..01-3112.56(br)	3110.25(sh)	IntramolecularHydrogen bonded O-H stretching
2942.25(w)	2943.06(m)	P-OH symmetric stretching
-		C-H aliphatic stretching vibration superimposed with NH-stretching
2623.50		O= P-OH asymmetric stretching
2457.85		
2416.14(br)		Stretchingof PO_4
2314.35	2313.50	P-OH stretching of $H_2 PO_4$
2178.32(w)		P-OH asymmetric stretching

	2091.42	
	1995.75	C=O stretching
1840.27		
1692.61(m)	1634.83	KDP stretching
	1531.50	N^+H_3 symmetric bending
1280.78(w)	1281.24	P=O stretching of KDP
	1066	C-N stretching from amino acid
874.06		Bending modes of C-H and CH_2 groups
823.04	825.65	O=P-OH bending
610.09		
530.05	532.5	HO-P-OH bending

The frequencies for all sharp bands were accurate to ±1 cm^{-1}. 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.[Dongli Xu and Dongfeng 2006).[27]

The band appeared between 3700 cm^{-1} and 3400 cm^{-1} in pure and doped KDP was assigned to free O-H stretching. The weak bands in doped KDP assigns its presence in low concentration. The band appears slightly weak , weak, very weak or absence of the band in the case of doped KDP indicate the strong interaction of the dopants with O-H groups. The broad absorption bands appeared between 3301 cm^{-1} and 3100 cm^{-1}were assigned to Intramolecular hydrogen bonded OH stretching and N-H stretching frequencies in doped crystal which indicates the weak interaction of the dopants with one of the O-H groups of KDP and the possible entry of the dopants in the lattice sit of KDP crystal. The non-linear optical properties of pure and doped KDP crystals are confirmed with the decreasing frequency of O-H stretching. (Chernov 1990) [28]. This property was also reflected in the P=O, P-O, P-OH stretching and HO-P-OH bending vibrations [29]Kumaresan 2007. The broad absorption bands around 2900 cm^{-1} – 2800 cm^{-1} exists as the results of superimposed O-H and NH_3^+ stretching bands. The peaks found at 2450cm^{-1} and 610 cm^{-1} for Pure KDP crystals were absorbed or not present in doped Ftir graphs. The N^+H_3 Symmetric bending vibration band was found at 1531.50 cm^{-1} for LHKDP crystal The peaks near 1066cm of LHKDP, corresponds to the C-N stretching from amino acids. The band near 870 cm^{-1} corresponds to the bending modes of C-H and CH_2 groups.[Jagdish et al(2011)]. The band near 530.05 cm^{-1} corresponds to the HO-P-OH bending vibrations which is slightly shifted towards 532.50 cm^{-1} for LHKDP.

1.5 OPTICAL PROPERTIES OF LHKDP CRYSTALS

1.5.1 Linear Optical Property Studies

The optical transmission spectrum of gown crystals were recorded using Perkin Elmer Lambda 35 UV-Visible spectrophotometer in the wavelength range 200-1100 nm. The crystals should have more optical transmission percentage and lower cutoff wavelength, between 200 and 400 nm, for efficient NLO applications.

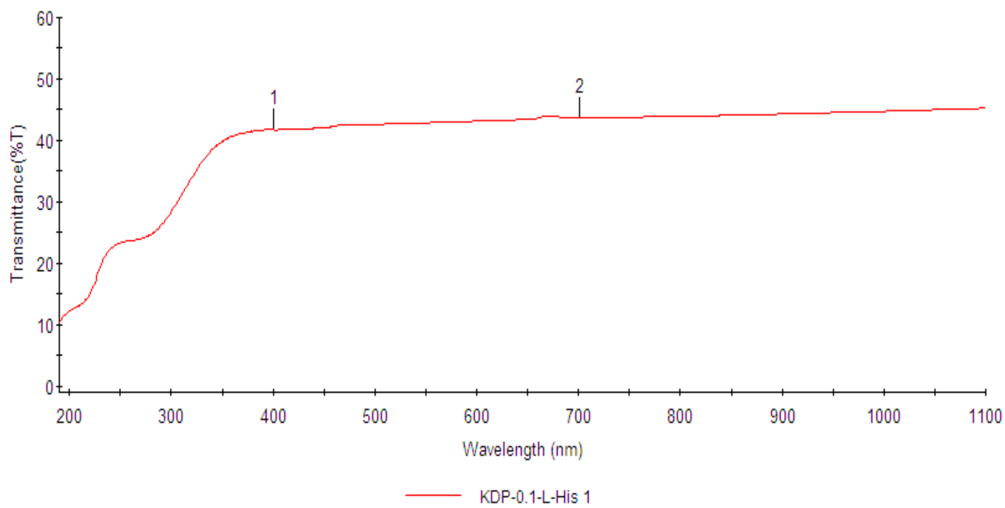


Figure1.5 UV vis Spectrum of LHKDP crystal

The figure shows the UV-Vis spectrum of LHKDP crystals. For optical applications, the crystal should be highly transparent in the considerable region of wavelength[10-N.Kangatharan LLysine doped KDP crystal]. The transparency of the LHKDP crystals are far better and the percentage of the transparency is 43.6% for LHKDP .The lower percentage of tranparency is may be due to defects in the crystal. The percentage can be improved much better growing the defect free crystals by improving the growth conditions and the criteria's that influences the growth. Transmittance percentage increases with the increase in dopant concentration.

1.5.2 Nonlinear Optical Test

Non-linear optical test is an important and popular tool to evaluate the conversion efficiency of the NLO materials. Inorder to confirm the enhancement of nonlinearity of KDP due to the addition of amino acids the sample was subjected to Kurtz and Pery technique[Madhav N.Rode] The SHG efficiency of LHKDP, is studied using a modified Kurtz and Perry powder technique. Q-switched Nd:YAG laser of wavelength 1064 nm and pulse width of 8ns with the repetition rate of 10Hz was employed The powdered sample prepared from the grown crystals were subjected to the SHG test and the efficiency of the energy(frequency) conversion is confirmed by the emission of green light.

Table 1.4 SHG efficiency of pure KDP crystal and LHKDP crystal

Samples	$I_{2\omega}$(mV)	Relative SHG Efficiency
Pure KDP	28.1	1.00
LHKDP	27.5	0.9786

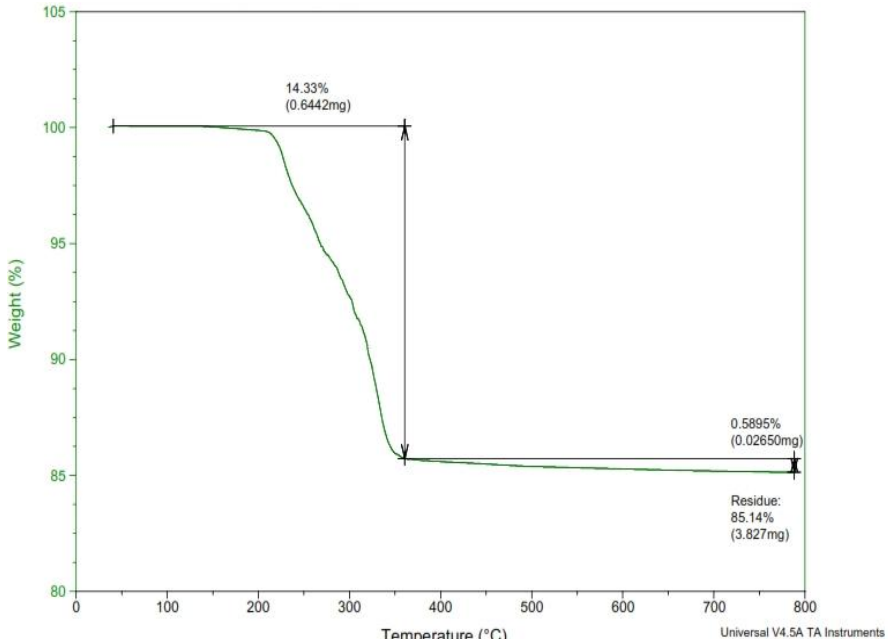
The results shows that doping with LHKDP, the NLO efficiency of KDP is slightly decreased.

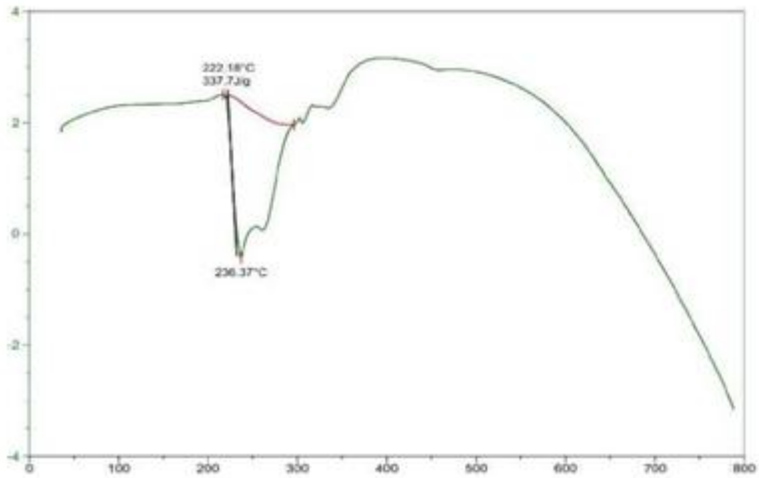
1.6 Thermal Analysis

Inorder to study the thermal stability of the grown crystals, Thermogravimetric(TGA) and Differential Scanning Calorimetry(DSC) have been carried out using SDT Q600 model thermal analyser.

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.[N.Pattanaboonmee 2012]

The amount of sample taken for the analysis is about 15 mg and the temperature range is about30-800^{0}C with the heating rate of about 20^{0}C/minute. The TGA and DSC pattern of LHKDP crystal is shown in figure5.





Figure(1.6) TGA and DSC curves of LHKDP Crystal

The DSC curve of LHKDP shows that there is no phase transition upto 222.48°C and there found two endothermic curves at 236.37°C and 337.73°C.

1.7 Microhardness Test

The microhardness testing is the simplest characterization technique that can be well suited to study the mechanical properties of the material, such as structure behaviour, field strength, brittleness index and temperature of cracking[B.R. Lawn et al (1975)]. Lattice energy, Debye temperature, heat of formation and inter- atomic spacing are the various factors that influences the hardness of the material.[L.I.Keya et al (2009), Charles (1991) J.Gong(2000)].

Vickers hardness H_v was calculated using the relation (Mot 1956)

H_v= 1.8544 X p/d^2 Kg/mm^2

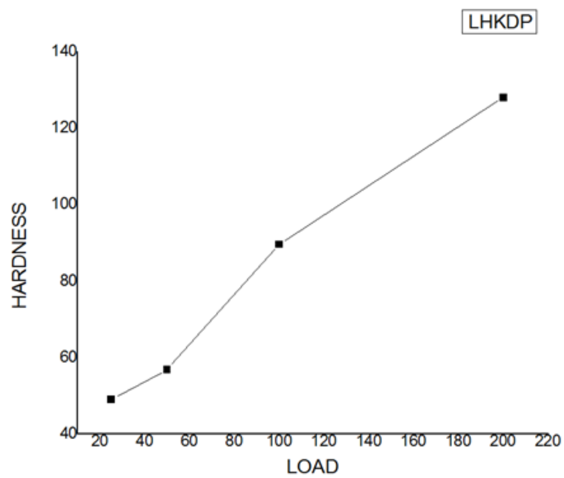
Where P is the applied load and d is the diagonal length of the indentation impression, and 1.8544 is a constant of a geometrical factor for the diamond pyramid.

The Mayer's index number or work-hardnening coefficient 'n' was calculated from the Mayer's law([Jagannanthan (2007)], which relates the load (P) and indentation diagonal length(d)

$P=kd^n$

The plots of Vickers hardness number (H_v) versus load (P) for the LHKDP, crystal is shown in Figure

From the figure it is observed that, microhardness increases with increase of load. At a load of 120, the hardness reaches saturation and beyond which the crack develops. In doped crystal the hardness number H_v value is significantly higher than pure KDP crystals.



Figure(1.7) Hardness graph of LHKDP

1.8 Dielectric Studies

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[P.V.Dhanaraj]. 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 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].

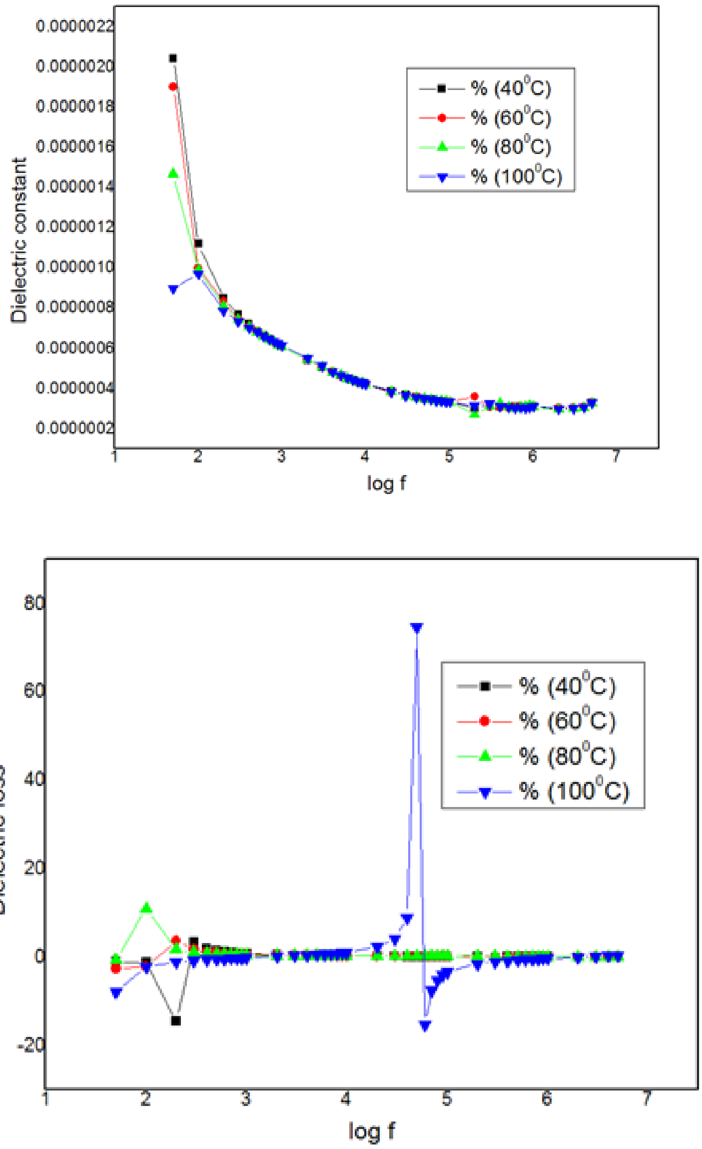


Figure (1.8) Dielelctric constant and dielectric loss graph of LHKDP crystal.

4.9 Laser Induced Damage Threshold Studies

Optical damage tolerance is one of the most important characteristic feature in the choice of a material for nonlinear optical applications. The nonlinear materials must be able to withstand high power intensities because very high optical intensities are involved in nonlinear processes. In the present study, an actievely Q-switched array side pumped Nd:YAG laser is used for the laser induced damage threshold studies. The pulse width of the laser pulses are 10 ns at 1064 nm radiation.For this measurement 1mm diameter beam is focused onto the sample with 35 cm focal length lens. The beam spot size of the LHKDP crystal is 0.701mm. Well polished samples with clean surface were chosen for the present study. The calculated laser induced damage threshold of LHKDP is 102 mJ.

II. Conclusion

Synthesis, growth and properties of LHKDP is studied. The LHKDP doped KDP crystals were grown from aqueous solution by slow evaporation solution growth technique at room temperature. Various characteristic studies were taken to characterize the properties of the sample. The single crystal XRD for the sample is recorded, that reveals LHKDP belongs to tetrahedral system. The incorporation of amino acids into LHKDP is confirmed by the FTIR studies

The powder X-ray diffraction pattern of LHKDP is recorded and indexed which reveals the high degree crystalline perfection. The peaks of amino acids doped KDP crystals are shifted towards diffraction angle side, when compared to pure KDP crystal, confirms the increase in lattice parameters due to doping, as already found in single crystal XRD. The shift, variation in number and change in intensities of the peak in the doped crystal, compared to pure KDP may be due to the incorporation of amino acids in pure KDP crystal.

The presence of functional groups in the amino acids doped KDP are confirmed by the FT-IR analysis. The optical transmission spectrum of the samples were recorded in the wavelength region between 200nm and 800 nm. The optical transmittance of LHKDP is better. The thermal properties of the sample is studied by obtaining the TGA-DSC curves.

The SHG was carried out for LHKDP crystals. The results shows that the efficiencies of the sample is about 0.9786, times as that of pure KDP crystal.

From the hardness study, the hardness number increases with the increase in the applied load which will be useful for nolinear optical applications. The electrical properties were also studied by dielectric constant studies. The high dielectric constant in the doped crystal than pure crystal indicating that the doping is highly useful for NLO applications. The Laser damage threshold study is taken to state that the tolerance of the sample against the high power laser intensities so that the sample can be used for non linear optical applications.

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