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SYNTHESIS, GROWTH AND CHARACTERIZATION OF L-PROLINE DOPED POTASSIUMDIHYDROGEN PHOSPHATE (LPKDP) CRYSTALS

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ABSTRACT

A nonlinear optical crystal of LPKDP crystal was grown at room temperature by slow evaporation technique. The size of the grown crystal is 11*7*2 mm3 at a growth rate of 0.55m/day. The single crystal X-ray diffraction analysis has been carried out to find the lattice parameters and powder x-Ray diffraction patterns has been recorded and indexed for the analysis of crystalline nature of the grown material. The FTIR spectrum of LPKDP crystal confirms the presence of functional groups. The Second Harmonic Generation efficiencies predict the non-linear property of the sample. Laser damage threshold study confirms the superiority of this crystal over conventional laser materials. Micro hardness studies of the grown crystal shows that as load increases, the hardness value also increases. The transparent nature of the material was confirmed by UV spectrum which is taken around 100-1100 nm.

KEYWORDS: Crystal growth, XRD, FTIR, UV-Visible, NLO, SHG.

INTRODUCTION

Nonlinear optics is a new frontier of science and technology and the nonlinear optic materials 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 optical switching and laser technology. So extensive studies have been made on the synthesis and growth of NLO materials over the past decades. [1,2] 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[3] KDP is an efficient angle tuned dielectric medium for optical harmonic generation in the visible region.[4]. Of all organic materials, amino acids exhibit an extraordinary nonlinear optical properties as they contain both a donor group NH_2 and acceptor COOH group and also there is a possibility to transfer intermolecular charge in amino acids.[5] .Amino acids and their compounds belong to a family of organic materiasl which have wide applications in NLO.L-Proline is an α- amino acid, and it is one of the twenty DNA-encoded amino acids. L-Proline is abundant in collagen and is exceptional among the amino acids, because it is the only one in which the amine group is part of a s. pyrolidine ring making rigid and directional in biological system[6,7].

An impurity can suppress, enhance or stop the growth of crystal completely.[8] (Sangwal 1996A lot of research has been undertaken to modify the properties and growth rate of KDP with the addition of suitable impurities.[9] 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.[10](Shaikh Kalim shaik Hanif et al 2015)[reported Glycine doped KDP crytal with enhanced NLO property than pure KDP . 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-Proline with KDP and their effect and changes in the growth of KDP have been reported.

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DETERMINATION OF SOLUBILITY OF L-PROLINE

The solubility of L-proline doped KDP is determined for six different temperatures starting from 30, 35,40, 45, 50, and 60 ^{o}C and were shown in fig 5.1. Initially, supersaturated solution of LPKDP was prepared separately at room temperature in an air tight container maintained at a constant temperature with continuous stirring , the solutions were analyzed gravimetrically and the solubility of these doped KDP solutions of 100ml of solvent were determined. It was observed from the solubility curves 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.

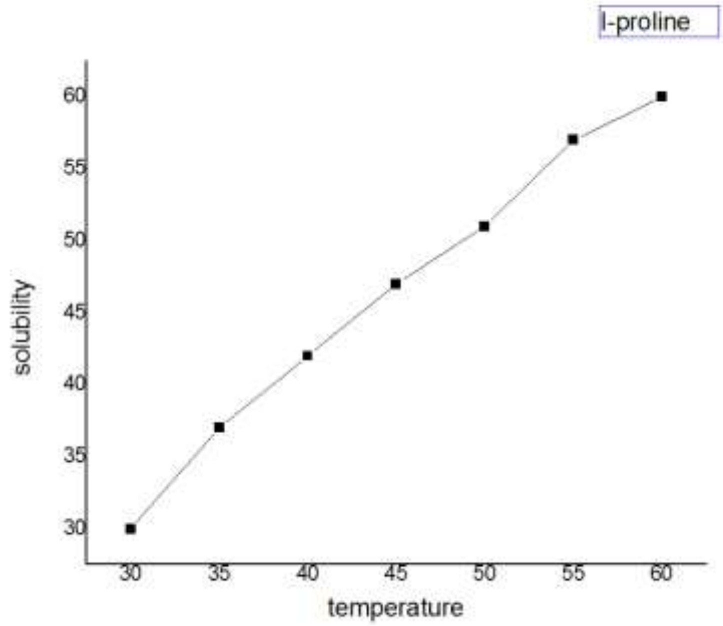

Figure.(1.1)

GROWTH AND SYNTHESIS OF L-PROLINE DOPED KDP

First a 100ml of Pure KDP solution was prepared using analytical grade KDP salt by dissolving it using a Millipore water whose resistivity is about 18.2 M. 0.1g of L-Proline 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 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 conditions of LPKDP, mentioned below in the table 1.1.

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

$KH_2PO_4 + C_5H_9NO_2 \rightarrow C_5H_9O_4NPO^{-}K^{+} + H_2O$ (1)

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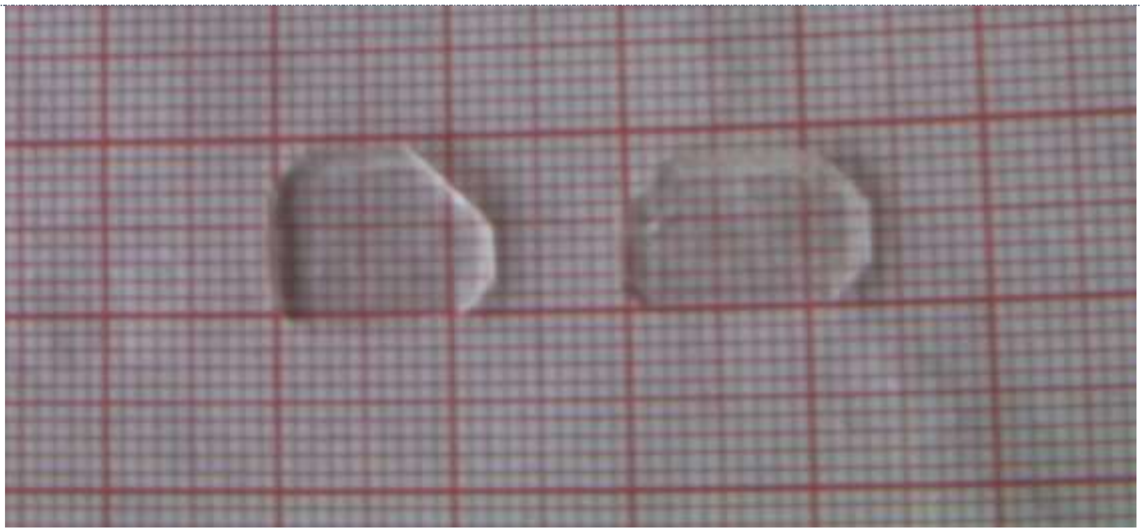

Figure (1.2) As Grown LPKDP crystal

Table 1.1 Optimized growth conditions of LPKDP doped KDP crystals

Method of growth		Slow evaporation		
Solvent used/pH		Millipore water of 18.2 M ohms cm resistivity / 5		
Operating temperature		Room temperature		
Name of the crystal	Molar ratio	Period of growth	Dimension	Growth rate
LPKDP	0.1g/100ml	7-10 days	$11\times7\times2mm^3$	1.1 mm/day

STRUCTURAL STUDIES OF LPKDP CRYSTAL

Single Crystal X-Ray Diffraction Studies

A fine quality of LPKDP single crystal is kept on an Xcalibur, Eos diffractometer at 293(2) K. Single crystal X-ray diffraction analyses of these single crystals have been taken out and the unit cell parameters are given in the Table 1.2.

Table1.2

CRYSTALS	UNIT CELL PARAMETERS					
	a (A)	b(A)	c (A)	$\alpha=\beta=\gamma°$	Crystal system	VolumeA^3
PUREKDP	7.45	7.45	6.97	90	tetragonal	386
LPKDP	7.46	7.46	6.99	90^o	tetragonal	389

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 [11].

Powder X-Ray Diffraction Studies

Powder X-ray pattern for LPKDP single crystals were recorded and shown in Figure 5.2. 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 10^o to 50^o 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.

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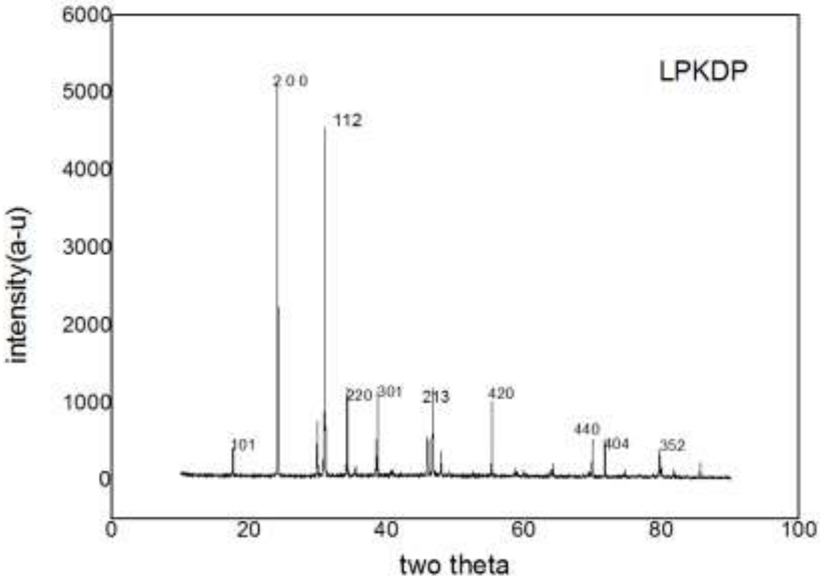

Figure 1.3 XRD pattern of LPKDP crystal

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 LPKDP, crystal are shown in Figures 5.4(a)

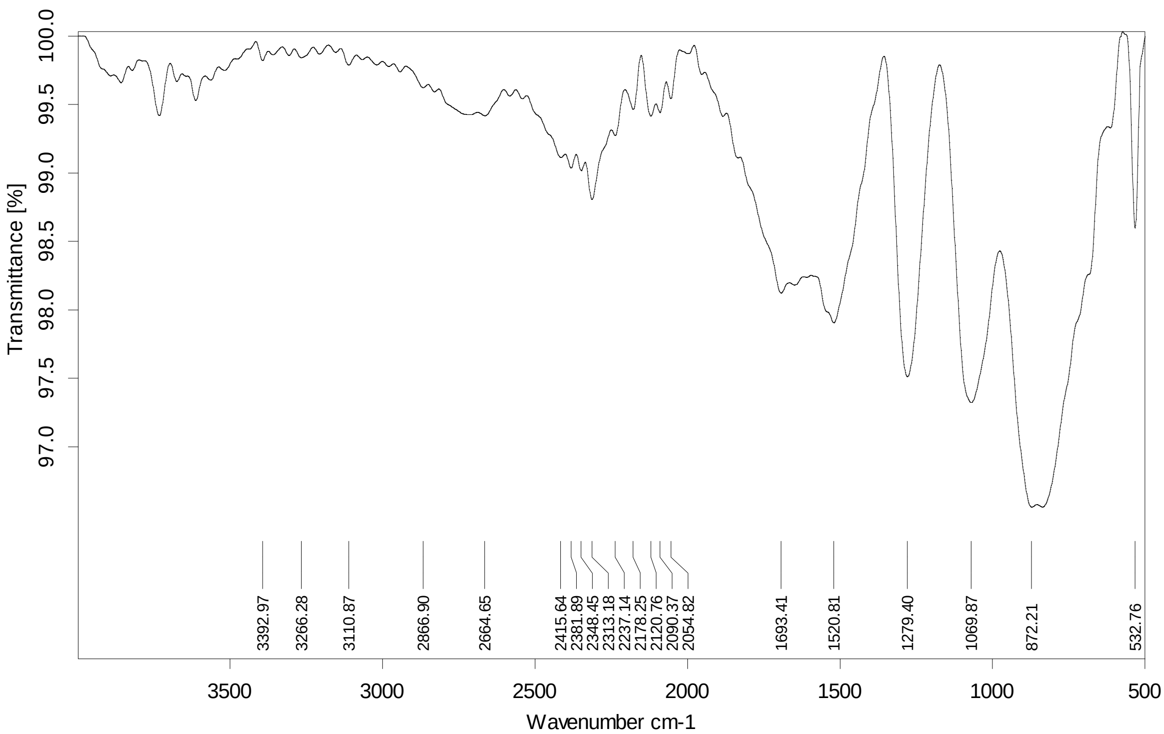

Figure 1.4 FTIR spectrum of LPKDP crystal

Table 1.3

Wavenumber in cm^{-1} (LPKDP)	Assignments
3266.28(br	IntramolecularHydrogen bonded O-H stretching
2866.80(w)	C-H aliphatic stretching vibration superimposed with NH-stretch
2664.65(br)	O= P-OH asymmetric stretching
2415.64(br)	Stretchingof PO_4
2314.35	P-OH stretching of H_2 PO_4
1693.41	KDP stretching
1520.81	N^+H_3 symmetric bending
1279.40	P=O stretching of KDP
1069.87	C-N stretching from amino acid
872.21	CH-CH_2 bending mode
532.76	O=P-OH bending

The band between 3700and 3503 in pure KDP corresponds to free O-H vibration.Very weak peak near 2800cm^{-1} corresponds to the stretching vibration of CH group of L-Proline. These bands can therefore assigned to overtones of deformation of both CH_2 and NH_2 groups. The band near 1520 cm^{-1} denotes the bending mode of NH_3. The band near 872.21 cm^{-1} is assigned to bending modes of C-H and CH_2 groups of L-Proline, which is sharp in pure KDP and undergo broadening with the addition L-Proline.[12]

OPTICAL PROPERTIES OF LPKDP CRYSTAL

Linear Optical Property Studies

The optical absorption spectrum of gown LPKDP crystal is recorded using Perkin Elmer Lambda 35 UV-Visible spectrophotometer in the wavelength range 200-800 nm. The crystals should have more optical transmission percentage and lower cutoff wavelength, between 200 and 400 nm, for efficient NLO applications.

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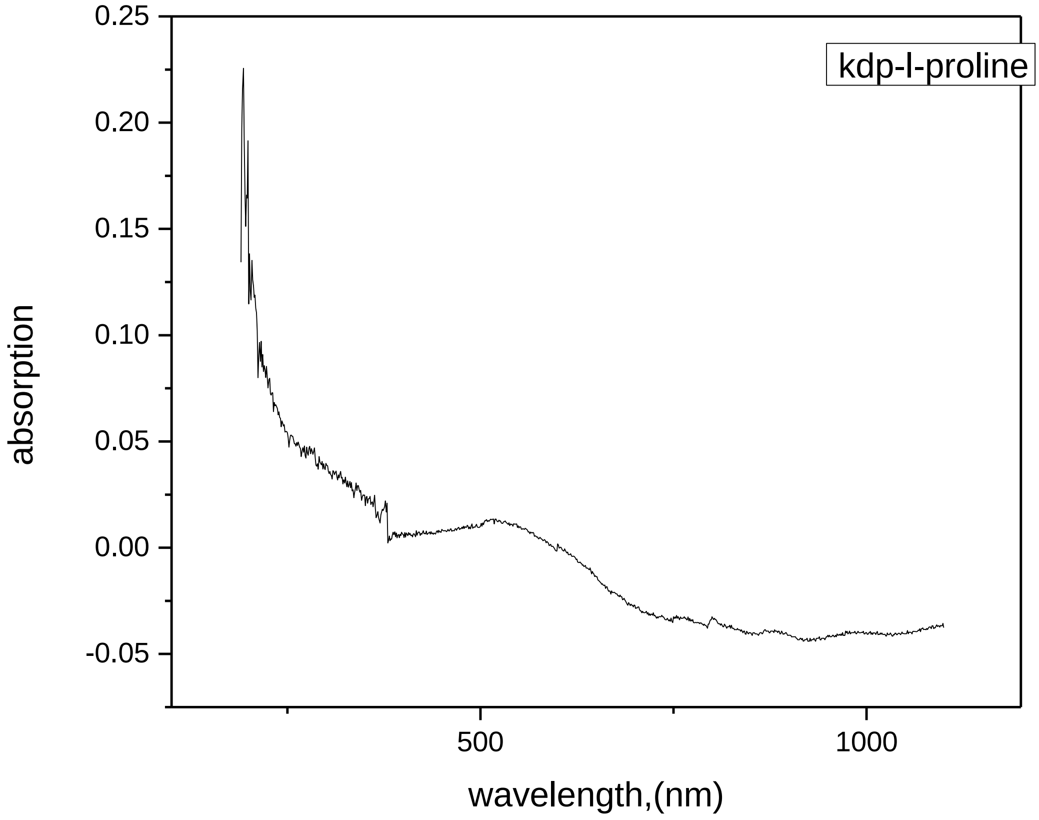

Figure 1.5 UV-absorption spectra of LPKDP crystal

Figure (5.6) shows the UV-Vis spectrum of LPKDP crystal. For optical applications, the crystal should be highly transparent in the considerable region of wavelength[13]. UV – absorption spectra of LPKDP crystal shows that the lower cutoff wavelength is around 200 (nm)..

SHG STUDIES

The SHG efficiency of LPKDP 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 crystal is subjected to the SHG test and the efficiency of the energy(frequency) conversion is confirmed by the emission of green light.

SHG efficiency of pure KDP crystal and LPKDP crystal

Table1.4

Samples	Relative SHG Efficiency
Pure KDP	1.00
LPKDP	1.24

The results shows that by doping with amino acid, the NLO efficiency of KDP can be enhanced. The Phosphate (PO_4) group of KDP makes a significant contribution to the SHG effect and hydrogen bonds help in enhancing the birefringence. The possibility of hydrogen bond formation between oxygen unit of PO_4 group of KDP and

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CODEN: IJESS7

the amino group NH_3 of the amino acid may have lead to an increase in non-linearity of KDP [14]which in turn increases the SHG efficiency. Thus the NLO efficiency of LPKDP is 1.24 times as that of pure KDP which indicates that doping enhances the SHG efficiency.

THERMAL ANALYSIS

In order to study the thermal stability of the grown crystals, thermo gravimetric (TGA) and Differential Scanning Calorimetriy (DSC) have been carried out using SDT Q600 model thermal analyzer.Differential scanning calorimetry 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 [15]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 LPKDP crystal is shown in figure(1.7a)The TGA of the LPKDP sample indicates that they are stable upto 190^{0}C and there is a slight weight loss around 200^{0}C, TGA curve exihibit a weight loss of about 13.51% between 200 till 370^{0}C. The loss of weight is probably due to the decomposition of KDP and the amino acid L-proline. Figure (1.7b) represents the DSC spectra of LPKDP sample which shows the endothermic transitions occurs at 221.22^{0}C, 235.7 and 344.7^{0}C respectievely and the decomposition temperature is about 235.7^{0}C.

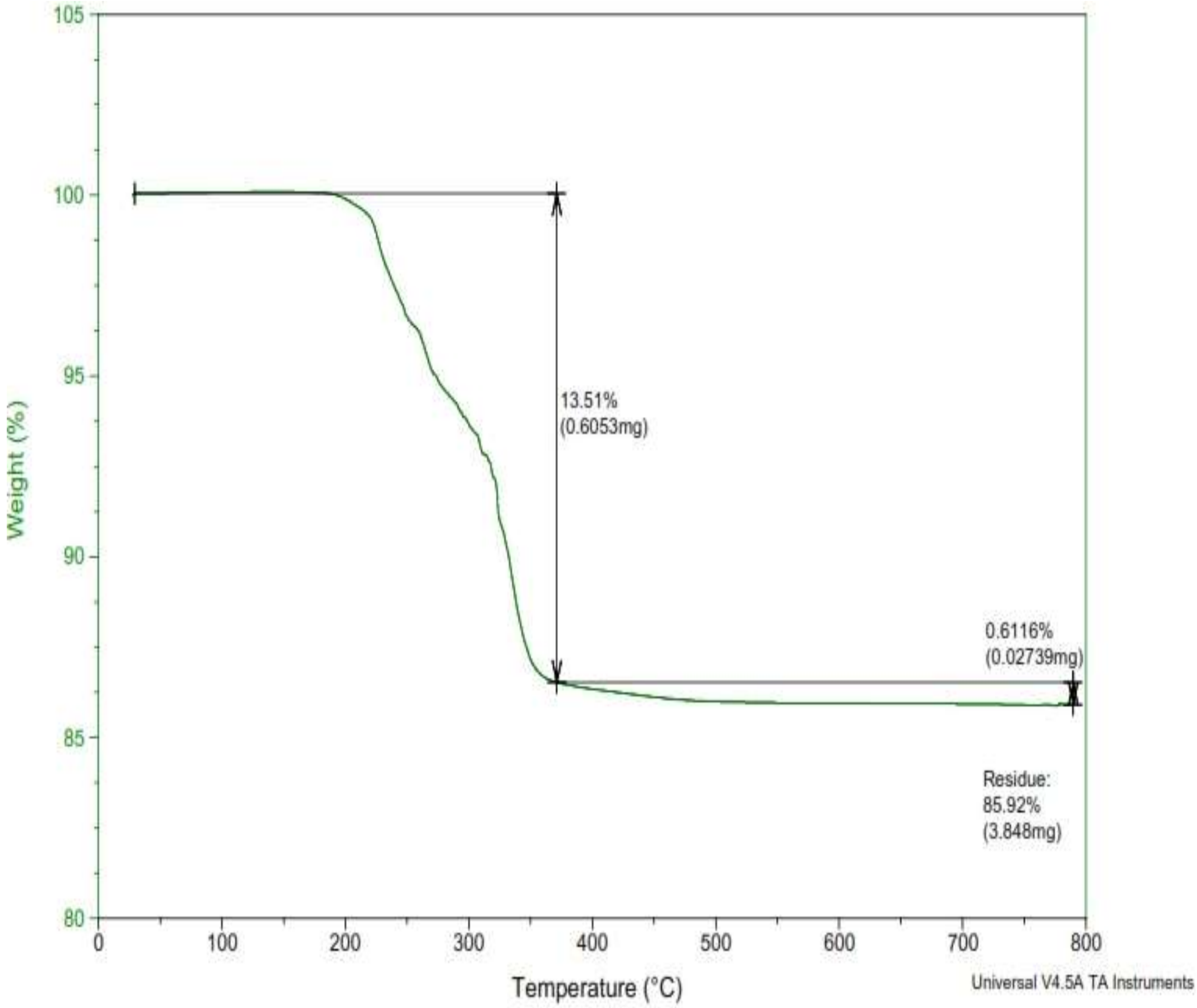

Figure 1.7(a) TGA OF LPKDP

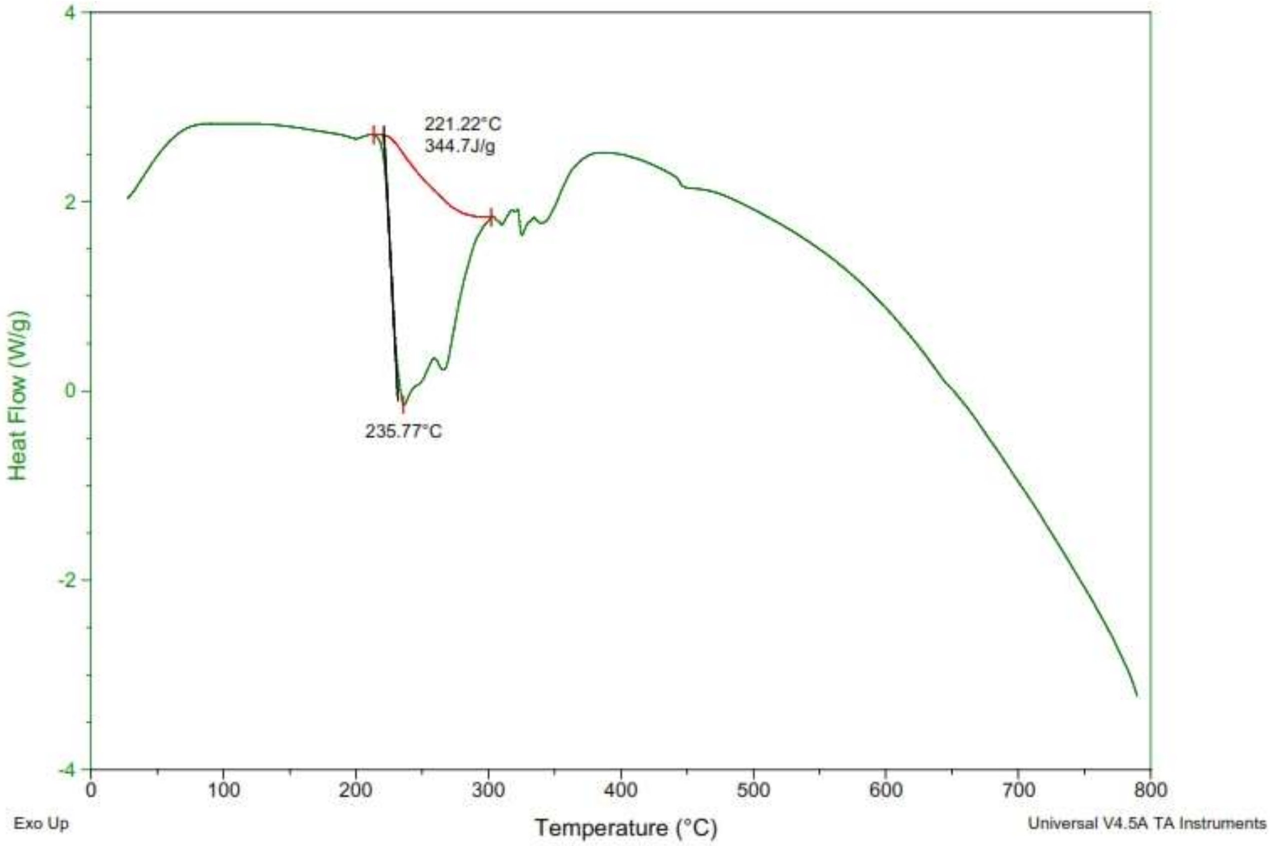

Figure 1.7(b) DSC of LPKDP

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[16] . The flat surface of the LPKDP crystal were subjected to the hardness measurements using Leitz-Weitzlar hardness tester fitted with a Vicker's diamond indenter.. Loads of different magnitudes from10g, 25g and50g were applied for duration of 5 seconds. The Vickers hardness H_v was calculated using the relation [17]

$$H_v = 1.8544 \text{ X } p/d^2 \text{ Kg/mm}^2$$

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 plots of Vickers hardness number (H_v) versus load (P) for the LPKDP crystal is shown in Figure.5.8

From the figure(5.8) it is observed that, microhardness increases with increase of load. As L- Proline possess ring structure, which is stable molecular structure and hence food mechanical hardness is observed in the doped crystal.[18] In general, L-proline has an exceptional confirmational rigidity compared to other amino acids

Table 1.5

Sample	Hardness H_v Kg/ mm^2
KDP	95.5
LPKDP	121.4

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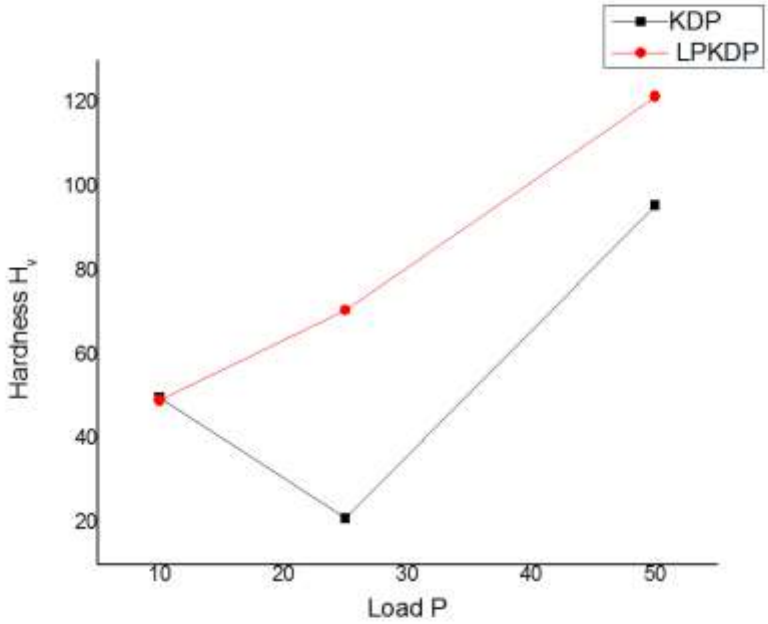

Figure 1.8 Hardness graphs of KDP and LPKDP

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.[19] From the figure dielectric loss is maximum for lower frequency region and it is minimum for high frequency region and also at lower temperatures the dielectric loss is low when compared to high temperature ranges.

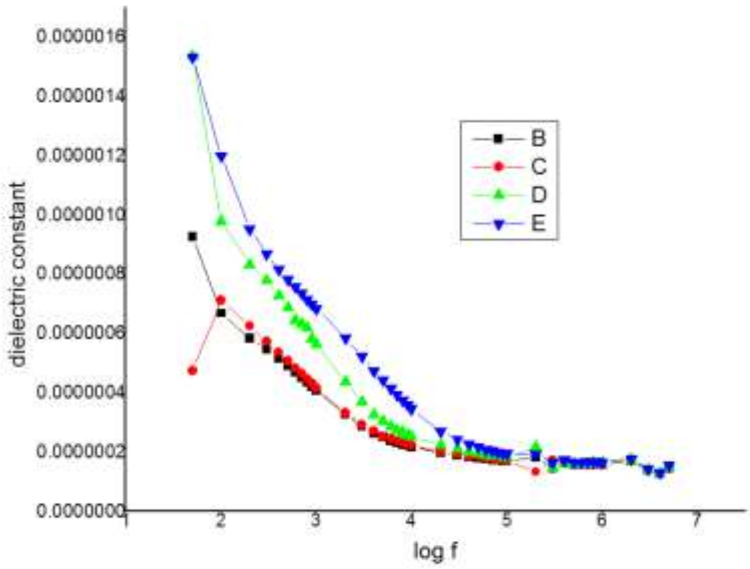

Figure 1.9(a) Frequency Vs Logf

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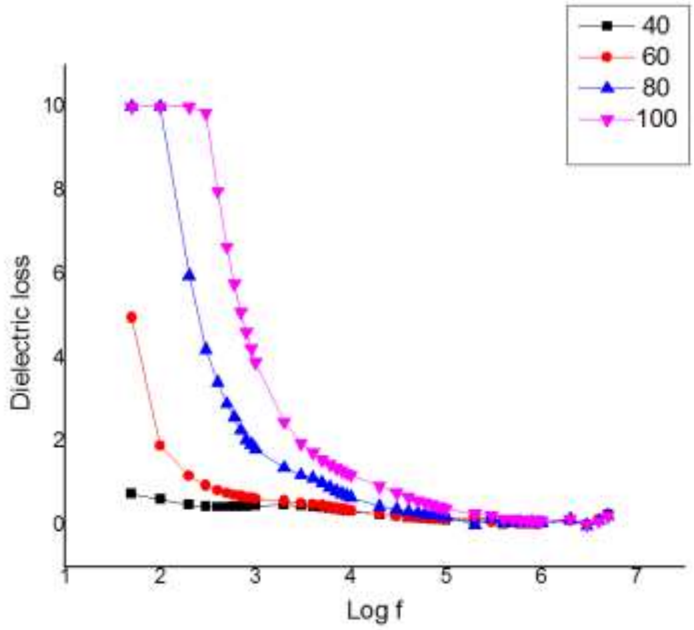

Figure 1.9(b) Dielectric Loss

From the figure dielectric loss is maximum for lower frequency region and it is minimum for high frequency region and also at lower temperatures the dielectric loss is low when compared to high temperature ranges.

LASER INDUCED DAMAGE THRESHOLD STUDIES

Optical damage tolerance is one of the most important characteristic features 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 activeely 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 LPKDP is 0.75 mm .Well polished samples with clean surface were chosen for the present study. The calculated laser induced damage threshold of the samples LPKDP is 228mJ.

CONCLUSION

Synthesis, growth and properties of LPKDP was studied.The amino acids doped KDP crystal is grown from aqueous solution by slow evaporation solution growth technique at room temperature.. The single crystal XRD for the samples was recorded, that reveals LPKDP belongs to tetrahedral system and increase in the volume proves the doping of L-Proline into KDP. The powder X-ray diffraction pattern of L-Proline doped KDP was recorded and indexed which reveals the high degree crystalline perfection. 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 LPKDP is much better but it can be increased to greater extent. The thermal properties of the samples were studied by obtaining the TGA-DSC curves revealing the thermal stability of the sample as 190°C and the decomposition temperature is about

The SHG is carried out for LPKDP crystal. The results shows that the efficiencies of the sample is about 1.2419, 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 Laser damage threshold studies were taken to state that the tolerance of the samples against the high power laser intensities so that the samples can be used for non linear optical applications.

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