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Studies on optical, mechanical, thermal, dielectric and SHG of L-Cysteine doped Potassium dihydrogen Phosphate(LCKDP) Crystals.

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ABSTRACT

Amino acid (L-Cysteine) doped potassium hydrogen phosphate crystals are grown by solution growth technique at room temperature. To identify structure and the morphology the grown crystals were subjected to characterization like powder and single crystal XRD analysis. Second harmonic generation study has been done to investigate the nonlinear optical properties of the crystal. UVvis spectrum and FTIR studies are performed there to identify the cutoff wavelength and to predict various functional groups present in the grown crystal. The microhardnessstudy reveals that the dopant increased the hardness value of the material. The electrical properties of the crystals were studied by dielectric studies.

KEYWORDS LCKDP, FTIR, Differential Scanning analysis, NLO, Hardness, thermal and dielectric studies.

1.Introduction

The prodigious success of molecular engineering in controlling NLO in last decade has provoked better wits in crystal engineering. The search for efficient NLO materials for fast and optimum processing continues to exist for the development of optical fiber communication laser based imaging and remote sensing etc. Potassium dihydrogenphosphate has been paid intense attention as an inorganic material showing the second order nonlinear optical effect because of their non-linearity. The nonlinear phenomenon which are very important in the field of optical image and optical data storage are frequency doubling, frequency mixing and electro-optic modulations [.S.R. Marder(1991),Mark J.Rosker(1996) M.Gnasekaran(2002),N.R. Dhumane(2006)].

The amino acids are the famous organic materials which plays a vital role in the field of nonlinear optical crystal growth. Since most of the amino acids exhibit NLO property it is of interest to dope them in KDP. Parikh KD (2007) Among the amino acids, L-cysteine [$C_3H_7NO_2S$] is the simplest one and it has center of chirality and is optically active. L-cysteine can exist as neutral molecule in the gas phase; it exists as a Zwitterion in solution as well as in solid state. L-cysteine crystallizes in non-Centro symmetric space group making it a potential candidate for NLO applications. Additionally, a thiol group is present in a aqueous solution of L-cysteine. The dipolar nature of L-cysteine is the root cause of high melting point. The presence of chromophores namely, amino group and carboxyl group makes L-cysteine to be transparent in the UV- Vis region)], thus more emphasis has been given by the scientists to develop non-linear optical crystals in L-cysteine and its analogs. The work done by Martin et al, Loganayaki et al, Bhagavannarayana et al. reveal the suitability of L-cysteine family crystals for their non-linear properties and applications. The present study deals with L-cysteine potassium dihydrogen phosphate, (LCKDP), growth and characterization and compares the studies. The growth of the crystal has been achieved by slow evaporation technique.

2.2 Solubility

The size of the crystal depends on the amount of the material available in the solution which decides the solubility of the material in that solvent for solvent growth technique (Christian.R) The solubility of synthesized of material in water is performed by maintaining the water at constant temperature and adding the known quantity of the solution is pipette out and its decomposition is determined gravimetrically. The variation of solubility with temperature of LCKDP.

3.GROWTH AND SYNTHESIS OF AMINO ACIDS 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 M□.In that pure solution of KDP 0.1 g of L-Cysteine dopant was mixed. 0.1g of L-Cysteine 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 LPKDP solution can be attained. On reaching saturation, the solution was filtered twice using Watt man filter paper and transferred to a Petri dish. 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 4.1 were harvested. The optimized growth conditions of LCKDP, was mentioned below in the table 3.1.

3 Materials and Methods

3.1 Crystal growth

Analytical reagent grade (AR) samples of KDP, L-cysteine along with Millipore water were used for the growth of single crystals. A supersaturated solution of KDP powder is prepared in distilled, deionized water. The amount of KDP salt to be dissolved is determined from its solubility at the average temperature of 35,40 , 45, 50 , 55°C.by dissolving the KDP salt in deionized water in an air-tight container maintained at constant temperature , The solution is stirred long enough to ensure complete dissolution of the solute, and filtered using Watt Mann filter paper to remove the residual particles. The optimized growth conditions of LCKDP were mentioned below in the table 1.1.

Table1.1 Optimized growth conditions of amino acids 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	
Molar ratio		0.1g/100ml	
Name of the sample	Period of growth (days)	Dimension (mm^3)	Growth rate mm/day
KDP	07	1883	2.5
LCKDP	09	23	2.5

Figure.1 As grown LCKDP crystal

4. RESULTS AND DISCUSSION

4.1 Single crystal X- ray diffraction

A fine quality of LCKDP 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.

CRYSTALS	UNIT CELL PARAMETERS					
	a (A)	b(A)	c (A)	α=β=γ◦	Crystal system	Volume (A3)
PUREKDP	7.45	7.45	6.97	90	Tetragonal	386
LCKDP	7.47	7.47	7.00	90	Tetragonal	391

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)].

4.2 Powder XRD Analysis

The powdered sample of LCKDP is subjected to powder X-ray diffraction studies. The X-ray diffraction analysis for LCKDP is performed 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° to 50° 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. Figure 2 represents the powder X-ray diffractogram for the grown crystal.

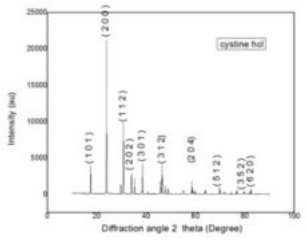


Figure 2. Powder XRD pattern of LCKDP crystal

4.3 FTIR ANALYSIS

In order to analyze the sample qualitatively for the prediction of functional groups in LCKDP , Fourier Transform Infrared (FTIR) spectrum is recorded in the range of 4000-500 cm^{-1} using KBr pellet are shown in figure 4.(a) and 4.(b) L-cysteine exists in zwitterions in which the absorption due to carboxyl group is observed at 892.8 and 1614 cm^{-1} respectively. In LCKDP, these peaks are shifted to 874.06 and 1645.90 cm^{-1}. The sharp and strong band at 1734 cm^{-1} indicates the C=O stretching of COOH group which is shifted to1840.27 cm^{-1} in LCKDP sample. Additional evidences for the zwitterion monolyser is the in-plane bending and asymmetric stretching assigned to1291cm^{-1} and 865.97 cm^{-1} region [Pavia et al (2001), Pawlukoje(2005)].

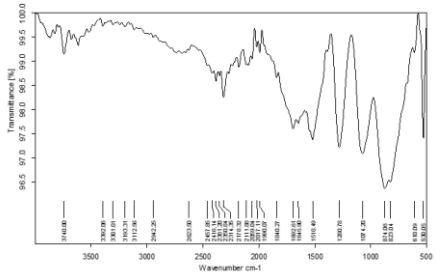


Figure 3. FTIR Spectrum of LCKDP Crystals

4.4 U V-Vis transmittance spectrum

The V-Vis transmittance spectrum of the grown 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. Also it is observed that the crystal is transparent throughout the entire region. The maximum absorption takes place around 250 nm. The absorption in the UV range is again the property of amino acids and its substituted crystals. This property is the key requirement for the NLO materials and other optoelectronic applications.[N.Vijayan et al(2002)]

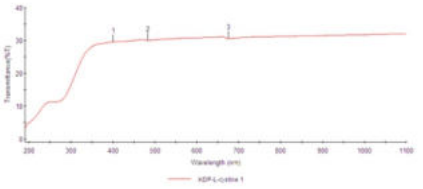


Figure 4. UV-Vis transmittance spectra of LCKDP Crystal

4.5 TGA and DSC Analysis

The thrmogravimetry analysis is employed to identify the phase transition, different stages of decomposition and melting point of the grown crystals.Gonsago(2012TGA analysis is carried out between 20°C/min using SDT Q600 V20 analyser. From TGA curve it is observed that that the sample is found to stable upto 190°C and weight loss occurs at three stages, at first stage a minor weight loss occurs around 200°C is just about 0.283% which corresponds to a small peak because of loss of water molecule. The Second stage of weight occurs between 220°Cand 390°C and the percentage of weight loss is about 14.89% and this is the major weight loss occurs in a sample and at the third stage a slight weight loss of about 1.054% occurs between 400°C and 800°C. Similarly, the DSC curve of LCKDP powdered sample is carried out between 20°C and 800°C. The resulting spectrum is shown in the figure An endothermic peak found the DSC trace assigned to the loss of weakly absorbed water. The intense endotherm above 223°C is assigned to be the decomposition temperature. The melting point of the material is determined to be 200°C. The decomposition process continuesupto 475°C Hence from this study, we can be able to state the the crystal can retain its texture and its application is retained upto 200°C only)

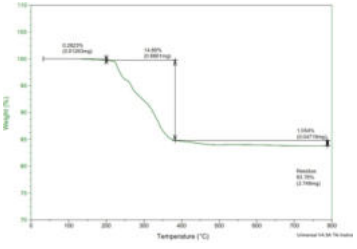


Figure 5(a). TGA curve of LCKDP Crystal

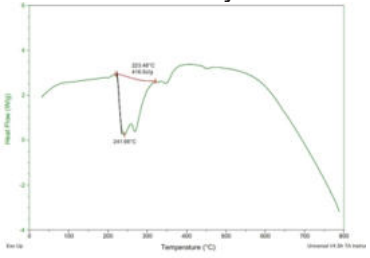


Figure 5(b) DSC curve of LCKDP Crystal

4.6 DIELECTRIC STUDIES

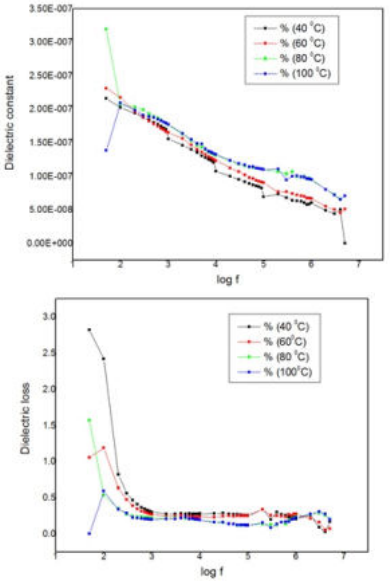
The dielectric analysis is an important characteristic feature that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed[N.kangathara and G.Anbalaganet al (2012)].

The dielectric constant is one of the basic properties of the solids[P.V.Dhanarajetal(2009)]. 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 et al (1989)]

Figures represents the dielectric constant and dielectric loss against log f for LCKDP crystals. Fro the figure one can infer that the dielectric constant is very high at lower frequencies and low at higher frequencies. The dielectric loss which is plotted against frequency shown in figure6(b) suggests that the dielectric loss is strongly dependent on the frequency of the applied fiel, similar to that of dielectric constant. The lesser the dielectric values of the sample higher is its NLO applications 916,17) [S. Sagadevan (2014), Suresh et al (2011)].

Figure 6(a) and (b). Dielectricconstant and Dielectric loss of LCKDP

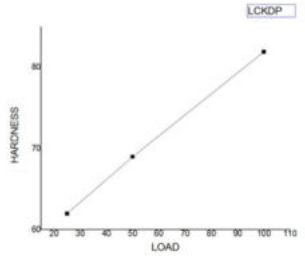


4.7 SHG STUDIES

The second harmonic generation efficiency is evaluated by Kurtz and Perry powder technique and powder sample of pure KDP is taken as reference material. The SHG efficiency of LCKDP 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. It is observed that the conversion efficiency of LCKDP is 1.1601 times as that of pure KDP crystal.

4.8 Microhardness test

The structure and molecular composition in crystals greatly influenzed the mechanical properties. Microhardness measurements have been made on as grownflat face LCKDP crystals using Leitz Weitzlar hardness tester fitted with a Vickers diamond indenter Hardness of the material is a measure of the resistance it offers to local deformation [Marylinet(2010)].The variation of Hardness Hv with Load P ranging from 25g to 100g is measuredand and the hardness number increases with the increase of the load, this type of behavior is called reverse indentation size effect.[sangwal etal 2002].



5. CONCLUSION

Bulk size LCKDP single crystals were grown by slow evaporation technique. Single crystal and Powder XRD confirmed the lattice parameters and crystal structure. The optical property of the grown material is studied by UV-Vis spectroscopy which shows the lower cut off wavelength to be 190nm. The functional groups present in the sample are confirmed by FTIR analysis. The TG-DSC analysis depicted the crystal is thermally stable upto 200°C. The dielectric constant and dielectric loss measurements are carried out at different temperatures and frequencies. The hardness study reveals that the sample exhibits reverse indentation size effect behavior. The SHG studies were done to examine the NLO property of the sample.

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