Synthesis and characterization of L-glutamic doped KDP non-linear optical crystal

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Growth of a desirable quality single crystals of L-glutamic doped potassium dihydrogen phosphate (KDP) a semi-organic nonlinear optical (NLO) material is reported. The crystals of dimensions 7 x 3 x 1 mm^3 were obtained from its aqueous solution by slow solvent evaporation technique. The harvested crystals have been characterized by XRD, dielectric and ferroelectric properties. The increase in the value of ferroelectric charge coefficient has been found 0.6 pc/N on polling the sample at 1 kV/cm, which confirm its use for a nonlinear optical material.

(Received January 16, 2014; accepted March 19, 2015)

Keywords: L-glutamic doped KDP, XRD, Dielectric constant, Nonlinear optical material, Ferroelectric material

1. Introduction

Nonlinear optical materials (NLO) are required for the generation of new frequencies as like second harmonic generation (SHG) and third harmonic generation (THG). Their study is important for photonics and optoelectronic technologies. These NLO materials are having a significant impact on laser technology, optical communication and optical data storage [1]. During the last two decades a lot of progress has been made in the development of such NLO materials [2, 3]. The technologists are always in search for a new type of material with improved quality over the earlier ones. In view of the above mentioned facts, semi-organic NLO materials have been found superior over the pure organic and inorganic crystals due to their high nonlinearity, high resistance to laser damage threshold, good mechanical strength and low angular sensitivity [4]. As, the potassium dihydrogen phosphate (KDP) crystal is well known in the field of high power lasers inspite of its modest optical nonlinearities [1]. Many researchers have carried out a lot of studies on KDP crystals. But most of the literature on KDP is available about the influence of impurities on nucleation kinetics. An improved nonlinearity of the L-arginine phosphaste monohydrate (LAP) semi-organic NLO material was discovered by Xu et. al [1,5] to replace the conventional KDP crystals for laser induced fusion experiments. Moreover, Kumaresan et.al. [6] have reported that the doping of aminoacids improved the NLO properties of KDP crystal. Jagdish et.al. [7] have reported to produce efficiency upto 1.45 times with respect to pure KDP of SHG signal at 532nm with a fundamental Nd: YAG laser in the case of L-proline doped KDP. Therefore, aminoacids have been found most suitable candidates as dopants in growing semi-organic crystals. In the present course of work, the synthesis and crystal growth of L-glutamic acid doped KDP single crystals have been reported. The grown crystals were characterized by XRD measurement. The properties of dielectric and ferroelectric have also been carried out.

2. Experimental Details

2.1 Synthesis and growth

The L-glutamic acid doped potassium dihydrogen orthophosphate (KH_2PO_4) single crystals were grown by solution growth slow evaporation technique.

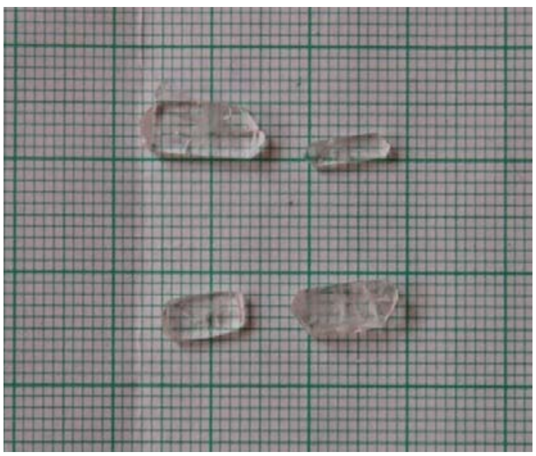
(i) Detail of L-glutamic acid

Formula	:	COOH $(CH_2)_2$ CH-(NH_2)COOH
Chemical name	:	L-2-amino-pentanedioic acid
Molecular weight	:	147.13
Colour	:	Plates
Crystalline form	:	Tetragonal
Solubility in water	:	0.89 gm per 100ml at 25°C
Polarity	:	Non-polar

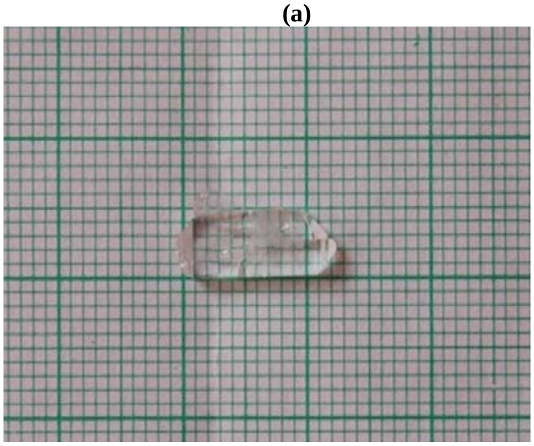
(ii) Detail of KDP material

Molecular weight	:	136.09
Crystalline structure	:	Tetrahedral
Index of refraction	:	1.51
Colour	:	Deliquescent
Melting point	:	252.6°C
Solubility in water	:	33gm per 100ml at 25°C.

For growing the crystal 0.1 mol% of L-glutamic acid doped KDP; the amount of L-glutamic acid of 0.49 gm and 45.36gm of KDP were dissolved together in 140ml of distilled water. A supersaturated solution of KDP powder was prepared in distilled and deioinized water. The amount of KDP salt to be dissolved was determined from its solubility at an average temperature of 35°C. The solution is stirred long enough to ensure the complete dissolution of the solute and then it was filtered using a Whatman filter paper to remove residual microscopic particles. Then 0.1 mol% L-glutamic acid has been doped in KDP by dissolving the KDP salt in deionised water in an air tight container maintained at a constant temperature with continuous stirring. After attaining the saturation, equilibrium concentration of the solute was analyzed gravimetrically. The solubility of the doped KDP was measured for the dopant and it was found to be 32.5g/100 ml. at 40°C for L-glutamic acid. The seed crystals were prepared by spontaneous nucleation. The crystal with perfect shapes and free from macro defects were used for growth experiments. The growth was carried out in two days. A few nuclei of doped KDP had appeared at the bottom of the beaker and grow for a day.



(a)



(b)

Fig. 1 (a) and (b): Photographs of 0.1 mol% L-glutamic doped KDP crystals.

The synthesized crystals have been found of good quality transparent crystals. In the fig. 1(a) and 1(b) the graph paper is clearly visible through the grown crystals which confirm that they are good transparent materials. The order of transparency of the doped KDP seems to be almost similar to the pure KDP like the KCl doped KDP was grown by Podder [8]. The amino acid (L-glutamic) used as dopant is a colorless crystalline. It melts with decomposition at high temperature. It is soluble in polar solvent. The grown crystal is optically active due to possession of asymmetric carbon atom.

2.2 XRD setup

The x-ray powder diffractometer of Phillips PW 3710 was used for structure determination. The CuKα (1.54A°) radiation was used for recording the crystal diffraction. A proportional counter position sensitive detector was used to record the intensity peak and it converts the signal to a count rate which is then connected to a printer or computer. The PC-APD diffraction software was used for recording the crystal diffraction. The geometry of x-ray diffractometer is such that the sample rotates in the path of the collimated x-ray beam at an angle θ while X-ray detector is mounted on an arm to collect the diffracted x-rays and it rotates at angle 2θ. The powder diffraction patterns data for the grown sample was collected at 2θ from 15° to 70°.

2.3 Impedence analyser

The Agilent's E4980A multifrequency LCR meter was used to measure capacitance (C). The dielectric constant of the sample as a function of frequency in the range 20 Hz to 2 MHz was measured. This LCR meter provides the best combination of accurate and fast measurement for a wide range of component. It has high resolution LCD display which provides clear and easy viewing. In built wide DC voltage-bias-range source provide accurate evaluation for C, L and material measurement. Furthermore, it is compact and light in weight. This versatile device has flexible PC connectivity and USB interface. The specific features are that it has DC source of ±10V and in built DC bias capability are 1.5 V and 2.0V. Moreover, it has auto-level and web browger control.

2.4 Method for ferroelectric polarization

An automatic ferroelectric (P-E) hystresis loop tracer was used to measure ferroelectric polarization of the prepared samples. It is completely under computer control and using USB inputs. It is also possible to vary and control the temperature of the unit over a range of temperature from room temperature to 200°C. Its polarization measurement system is based on a modified Sawyer-Tower circuit. The other key features are the range of sampling capacitor is 1-10 µf, output voltage range is 0 to 10 KV, voltage resolution is 1 KV to 1.0 Volt, charge resolution is 50 Pc/N, PC operating system is window XP, powder supply is a.c. of 220V at 50Hz. The sample holder can hold the sample in silicon oil to prevent the sample from arcing at high voltage. Its data display is for (i) polarization vs electric field (ii) current vs voltage and (iii) polarization vs temperature. It is also having a provision of safety devices at high voltage from dielectric breakdown of the material.

3. Results and Discussion

3.1 XRD analysis

The X-ray powder analysis was used to confirm the physical phase of the grown crystals. They were ground using an agate mortar and pestle in order to determine the crystal lattice parameters by X-ray diffraction. The fig. 1 shows XRD pattern of the grown L-glutamic acid doped KDP single crystal. The lattice constant values are found to be varied with the addition of impurities. The experimental data has been presented in the tables 1 and 2. The unit cell parameter were calculated as a=b=7.442 A^o, c=6.813 A^o and $\alpha = \beta = \gamma = 90^o$. The structure belongs to the scalenohedral (twelve faced polyhedron) class of tetragonal shape crystal. The crystal structure was obtained similar to that in the case of pure KDP [8]. As a comparison the X-ray diffraction graph of pure KDP has been refer to the earlier published work [8]. The respective experimental data of pure KDP was presented in table 1. The effect of L-glutamic acid on the growth and structure of KDP may be understood with the help of tables 1 and 2. The deviation of 2θ values suggest that the structure were slightly distorted as compared to the structure of pure KDP [8]. Furthermore, the deviation of the 2θ values may be due to the incorporation of dopant and thus causes the lattice expansion of L-
glutamic doped KDP. The values of lattice constant were found to be consistent with that of the earlier reported value of other impurities doped crystals [8]. More distortion of the lattice parameters have been reported by Kumaresan et.al. [6] for heavily doped KDP crystals with amino acids. Table 2 lists the observed d-value and intensity of doped KDP crystal rapidly grown from 0.1 M% L-glutamic acid added solution compared with those of pure KDP crystal. The X-ray powder diffraction patterns of the product were found consistent with the pure KDP crystal which indicates that there are no other impurities. Therefore, it may be predicted that additive has not deteriorated the non-linear optical properties of the pure KDP.

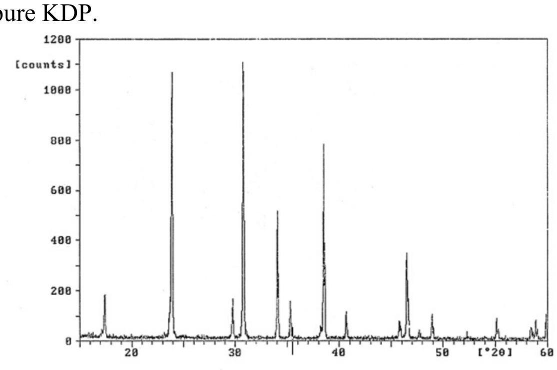


Fig. 2: The XRD diffraction pattern of L-glutamic acid doped KDP crystal

Table 1: The x-ray powder diffraction data for pure KDP and L-glutamic doped KDP crystals.

hkl	Pure KDP		L-glutamic doped KDP	
	2θ exp (°)	I/Io%	2θ exp (°)	I/Io%
101	17.501	64	17.425	15.5
200	24.199	100	23.895	95.8
112	31.102	84	30.755	100.0
301	38.804	28	38.610	34.3
312	46.612	80	46.650	11.1
332	59.105	76	59.114	16.73

Table 2: The x-ray powder diffraction data for observed d-values and intensity of KDP crystal grown from 0.1M% L-glutamic acid compared with those of pure KDP crystal.

d(0.1M% L-glutamic doped)	d (pure KDP)	I (0.1M% L-glutamic doped	I (pure KDP)
5.0852	5.1083	Weak	Weak
3.7209	3.7330	Very Strong	Very Strong
3.0030	3.0104	Weak	Weak
2.9048	2.9103	Middle	Middle
2.6308	2.6379	Weak	Weak
2.5436	2.5472	Weak	Weak
2.3364	2.3415	Weak	Weak
2.2176	2.2212	Weak	Weak
1.9808	1.9831	Weak	Weak
1.9515	1.9531	Middle	Middle

3.2 Dielectric constant

For the measurement of dielectric constant the grown sample of L-glutamic doped KDP single crystal was polished upto a proper thickness on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. Under this study the sample dimensions were taken as 7 x 3 x 1 mm^3. The silver paste electrodes on opposite sides ensure good electrical contact. Then, the crystal was put in between the probe whose ends are conducting. The wire in connection with sample holder probe are connected to the E4980A multi-frequency LCR meter to measure dielectric constant of the sample as a function of frequency.

The measurements were carried out in the temperature range 35-150°C for L-glutamic doped crystal grown at 4.2 pH value. The dielectric constant is high at low frequency and decreases with increases in frequency as shown in the fig. 3. The dielectric behavior of the grown sample agreed well with the earlier reported results by Kumaresan et.al. [6] in the case of different amino acids doped KDP crystals. At high frequency the dielectric material becomes conductive and thus dielectric loss increases.

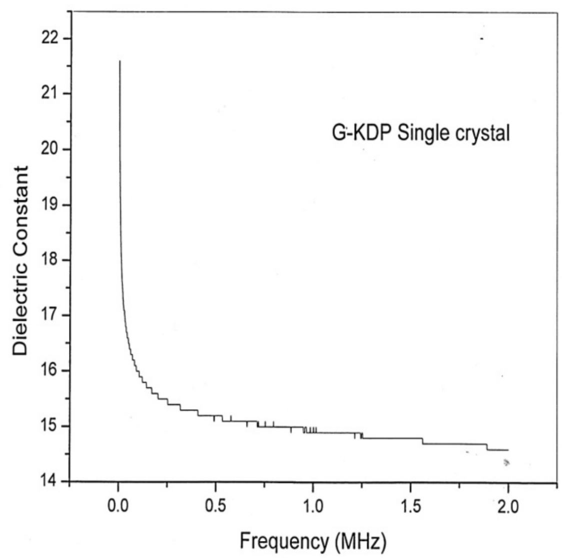


Fig. 3. Variation of dielectric loss as a function of frequency.

The dielectric constant of a material is generally composed of four types of contribution, viz. ionic, electric, orientation and space charges polarization. All of them may be active at low frequency. The nature of variations of dielectric constant with frequency indicates the types of above mentioned deferent contributions that are present in the prepared material. The dielectric parameters depend on the frequency of the a.c. voltage applied across the material. The large value of the dielectric constant at low frequency is due to the presence of space charge polarization which depends on the purity and perfection of the grown sample. The vibrations of the atoms present in the materials need characteristic time to build up an equilibrium polarization. The capacitance in parallel mode (Cp) is 2.7130 picofarad at 2MHz and the dielectric loss or dissipiation factor (D) value is 0.36684. The low value of dielectric loss indicates that L-glutamic doped KDP material possesses good crystalline quality with fewer defects. The values of dielectric constant are required for the interpretation and application of various theories of lattice dynamics when the dielectric material is under the influence of an external deriving a.c. field.

3.3 Ferroelectric – polarization

The fig. 4 is showing the ferroelectric properties of the L-glutamic doped KDP single crystals. These properties were studies by applying external electric field and at the same time polarization was measured by calculation of the charge developed across the crystal.

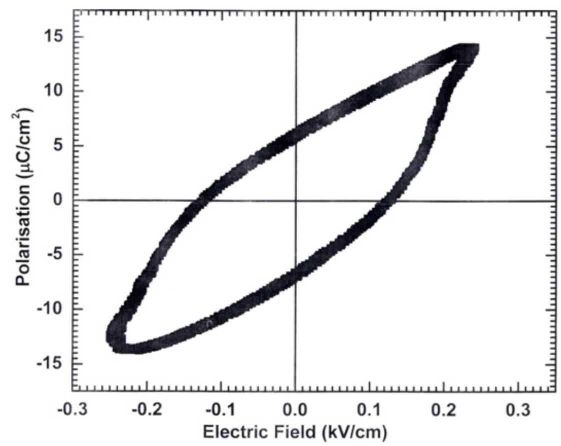


Fig. 4: The P-E loop showing ferroelectric properties of KDP crystal.

The traced loop for polarization vs electric field has been shown in the fig. 4. This figure is showing that induced polarization does not vary linearly with the applied electric field (E). The ferroelectric observations indicate that the L-glutamic doped KDP is a ferroelectric material and the crystal exhibit hysteresis phenomenon in a manner similar to the ferromagnetic materials. The observed results may be believed due to the fact that amino acids possess electron donor and acceptor groups connected through extended π-electrons and shows large hyperpolarizabilities [7]. As the electric field is applied the total polarization increases rapidly until the saturation value is reached. It is the position where all the electric domains in the material are parallel to the applied field. When the field decreases to zero, the polarization does not return to zero. The values of the spontaneous and permanent polarization and the coercive field can be measured from the hystersis loop P-E as like the B-H loop for magnetic materials.The grown ferroelectric crystal exhibit piezoelectric effect. The piezoelectric charge coefficient of L-glutamic doped KDP crystal was calculated as d_{33} = 0.22pc/N. The same coefficient was found to be 0.6pc/N after polling at 1 KV/cm. This result may be understood in the support for the increased efficiency of SHG by using a laser in the Kurtz and Perry method [9] reported earlier by other researchers [6,7]. On the basis of the results of ferroelectric properties of the grown crystal it is believed that the grown sample of L-glutamic acid doped KDP material may be utilized for optoelectronic and nonlinear optical applications.

4. Conclusion

The powder XRD results confirm tetragonal structure of the prepared crystals. The high value of dielectric constant at low frequency and low value of dielectric loss at high frequency conclude that L-glutamic doped KDP crystal possesses minor defects and it was found of good crystalline in nature. The results of ferroelectric charge coefficient indicate that the crystal is a nonlinear optical material and it has applications in modern optics. The increase in the value of ferroelectric charge coefficient upto 0.6 pc/N on polling the sample at 1 KV/cm has further confirmed it for nonlinear optical use. On the basis of the literature survey [6, 7] it may be suggested that intensive research is required for suitably doped KDP crystals.

References

[1] K. Meera, R. Muralidharan, R. Dhanasekaran, Prapun Manyum P. Ramasamy, Journal of Crystal Growth, **263**, 510 (2004).
[2] D.S. Chemla J. Zyss, Academic Press, New York, (1987).
[3] Tapati Malik, Tanusree Kar, Crystals Res. Technol. **40**(8), 778 (2005).
[4] K. Selvaraju, R. Valluvan, S. Kumararaman, Materials Letters, **60**, 3130 (2006).
[5] D. Xu, M.H. Jiang, T. Zhong-ke, Acta Chim. Sinica **41**, 570 (1983).
[6] P. Kumaresan, S. Moorthy Babu, P.M. Anbarasan, J. Nonlinear Optical Physical & Materials **16**, 255 (2007).
[7] P. Jagdish, N.P. Rajesh, J. Optoelectron. Adv. Mater. **13**(8), 962 (2011).
[8] J. Podder, J. Crystal Growth **237**, 70 (2002)
[9] S. K. Kurtz, T.T. Perry, J. Applied Physics **39**, 3798 (1968)

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