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ARTICLE

Optical, P-XRD & U-V Properties by Varying the Concentration of L-valine Amino Acid in Pure KDP

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Abstract: H_2PO_4 potassium dihydrogen phosphate crystals (KDP) were prepared for dopant L- valine amino acid. The bulk growth was reported along <011> and <101> plane by seed rotating crystal method and solution growth method. The doping concentrations in the mother solution were 0.4 mole%, 0.6 mole% and 0.8 mole% and the corresponding seed rotation rates were 30 rpm, 60 rpm and 100 rpm for 15 to 20 days. KDP crystal of dimensions 102 x 23 mm, 72 x 23 mm and 102 x 35 mm size has been grown. FTIR spectra showed the presence of functional groups in the crystal. Powder X-ray diffraction analysis of transparent bulk nonlinear optical crystal doped with LV confirms the formation of the tetragonal system. Energy Dispersive X-ray analysis (EDAX) confirms the elemental analysis of potassium and phosphate radicals in the reported crystal. Optical transmission increases with the increase of concentration of L-valine in KDP crystals.

Keywords: Crystal growth, Symmetry, FTIR, UV, EDAX.

1. Introduction

The non-linear property of a single crystal is very useful for optoelectronics, acousto-optics, laser, telecommunication technologies, medical instrumentation, … etc. KDP single crystal possesses important piezoelectric, ferroelectric, electro-optic and mainly NLO properties [1, 2]. NLO property of matter is essential for frequency conversion in laser devices. KDP is suitable for higher harmonic generation of a huge laser system of fusion experiments, because it can be grown to larger sizes and KDP has a high laser damage threshold. Some of the crystal-like KTP used in Nd: YAG laser by frequency doubling to get green light; lithium borate, potassium beryllium boro-fluoride, strontium beryllium borate, … etc. are promising for UV generation because of their wide bandgap and adequate optical nonlinearity. Many researchers have attempted to enhance the properties and growth rate of KDP crystal by varying the concentration of dopant or by changing the growth conditions [3-6]. The doping of organic impurities like amino acid improved the NLO properties of the KDP crystal [7].

In the present investigation, the kinetic mechanism of growth of prismatic faces of pure and doped KDP solutions was studied. The crystal morphology depends on the expansion rates of the various crystallographic faces. The study shows that the prismatic face (1 0 0) type is much more sensitive to some impurities than the (1 0 1) pyramidal faces [8].

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2. Methods

2.1 Solution Growth

A bulk-size transparent crystal which has high solubility and has variation in solubility with temperature when the material decomposes at the melting point and a suitable solvent are available to make a saturated solution at the desired temperature [9]. The basic concept of this method is to achieve a super-saturated solution first and then to have it crystallized. The low-temperature solution crystal growth method is extremely popular in the production of many technologically important crystals compared with high-temperature growth methods. It is the most widely used method for the growth of single crystals having solubility up to 1000C. This method is a long lived method. Most electro-optic and ferroelectric single crystals have been produced by solution growth technique [10-12].

2.2 Seed Rotating Crystal Method

In this method, seeds shown in Fig. 1a of solution method of pure KDP are used for harvesting bulk crystal by the rotating method. The mother solution was prepared under saturation condition and thoroughly stirred for 5 to 6 hours for homogenization at 40°C. The c-axis direction <101> plane of the seed crystal was selected for this method to grow a crystal. Firstly, processed seed is placed on a cylindrical platform (Fig. 1b) which was made by using an acrylic sheet. The cylindrical platform was attached with a rotating unidirectional DC motor, which was controlled by an electronic dc power supply of 12 V at about 30 rpm. The whole assembly was placed on a rectangular constant temperature bath (Fig. 2) which was made by a glass plate. In this method, seed crystal mounted on a cylindrical platform is allowed to rotate in the forward direction in an estimated time interval. The complete assembly is placed inside the crystallizer. Constant temperature bath controller is maintaining the temperature at 40°C with an accuracy of 0.01°C. The solution is prepared according to the solubility curve at a particular temperature. The amount of solute is calculated according to the solubility curves at different temperatures. The temperature of the crystallizer was reduced by 1°C per day to maintain the supersaturation level. This process increased the growth rates of the seed crystal. Good-quality transparent and bulk size of KDP crystal is harvested within two weeks, as shown in Fig. 1c. The sizes of grown crystals are 102 x 23 mm, 72 x 23 mm and 102 x 35 mm.

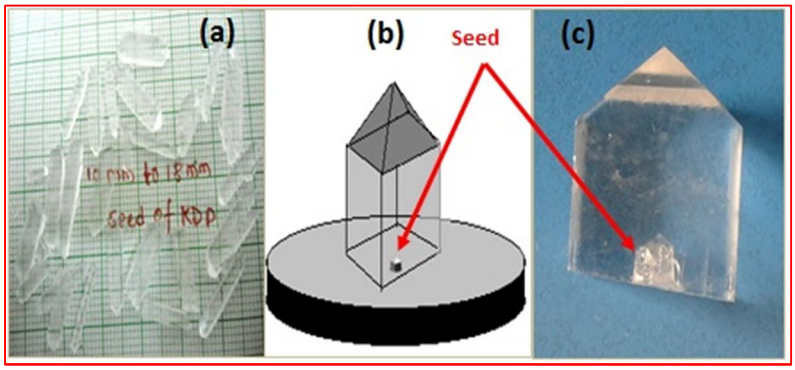

FIG. 1. (a) Seeds of pure KDP, (b) Schematic diagram of cylindrical platform and (c) Grown crystal.

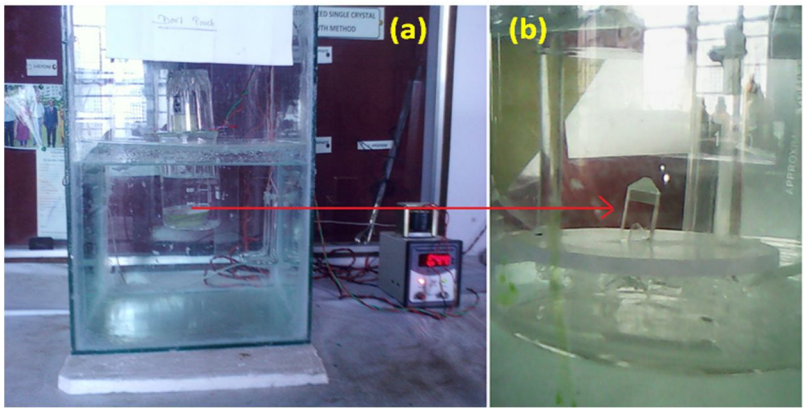

FIG. 2. (a) Constant temperature bath for seed rotating crystal method and (b) Grown crystal.

3. Results

3.1 Structural Analysis by XRD

Crystalline phase characterization of the powder samples is carried out by using a Bruker AXS D8 Advance (λ=1.5406 Å) Vertical, Theta/2 Theta geometry, X-ray diffractometer. The powder sample is scanned over the range 100-700 at a scan rate of 10/min. The XRD patterns of the single crystals are further refined by the Origin 8 SRO v8.0725 (B725) and CELREF Beta version (2000) software. The standard International Centre Diffraction Data (ICDD) and calculated ICSD diffraction file are used to match the evolving phases of the single crystals. The JCPDS card No. 35-0807 is used to compare the interplanar spacings and intensities of the powder pattern [13, 14]. The observed and calculated lattice parameters of pure and doped KDP are shown in Table 1. The single-crystal study reveals that the grown crystal belongs to the tetragonal system with space group I42d, where the number of molecules per unit cell is 4 [15]. The recorded Powder X-ray diffraction patterns of doped KDP crystals for different concentrations of L-valine dopant as 0.4 mole %, 0.6 mole % and 8.0 mole % are shown in Fig. 3.

TABLE 1. Observed and calculated lattice parameters of pure and doped KDP.

Sr. No.	Compound	Observed lattice parameters	Lattice parameters by using CELREF Beta Version	Lattice parameters by using X-powder
1	Pure KDP	a =b=7.4077 Å, c=6.9389 Å, Cell volume=380.76 Å^3	a=b =7.3977 Å, c =6.8789 Å, Cell volume= 376.45 Å^3	a=b = 7.3963 Å, c = 6.8808 Å, Cell volume=376.418 Å^3
2	0.4 mole %+ KDP	a =b=7.4098 Å, c=6.9335 Å, Cell volume=380.68 Å^3	a=b =7.3998 Å, c =6.8335 Å, Cell volume=374.182 Å^3	a=b =7.4000 Å, c =6.8356. Cell volume=374.317 Å^3
3	0.6 mole %+ KDP	a =b=7.4280 Å, c=6.8738 Å, Cell volume=379.26 Å^3	a=b =7.428 Å, c =6.934 Å, Cell volume= 382.58 Å^3	a=b = 7.4221 Å, c = 6.9599 Å, Cell volume=383.408 Å^3
4	0.8 mole %+ KDP	a =b=7.4377 Å, c=6.8356 Å, Cell volume=378.14 Å^3	a=b =7.4377 Å, c =6.9612 Å, Cell volume=385.0893 Å^3	a=b =7.444 Å, c =6.9612 Å, Cell volume= 385.74 Å^3

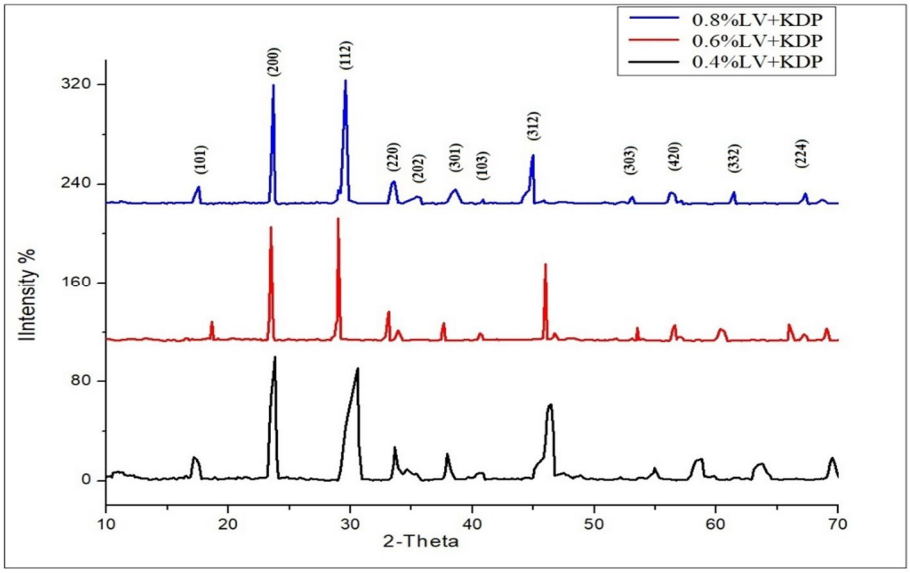

FIG. 3. Powder XRD pattern of L-valine-doped KDP crystals.

3.2 UV-Vis NIR Spectral Analysis

UV-Vis-NIR spectral transmittance was studied using a model Varian, Cary 5000 spectrophotometer with a single crystal of 5 mm thickness in the range of 200 – 1600 nm. Recorded spectrum (Fig. 4a) reveals that the percentage of optical transmission increases with the increase of concentration of L-valine in KDP

crystals about 90 % for the highest dopant concentration. The results of L-valine-doped KDP have good agreement with the results reported in [7]. The crystal has sufficient transmission within the entire visible and IR region. The lower stop wavelength is around 224 nm. The transmission spectra reveal that a higher concentration of amino acid additives has not destroyed the optical transparency of the crystals which have sufficient transmission in the entire UV- visible and IR regions [16]. Hence, it could be concluded that L-valine doping plays a vital role in improving the optical quality of KDP crystals [17-19].

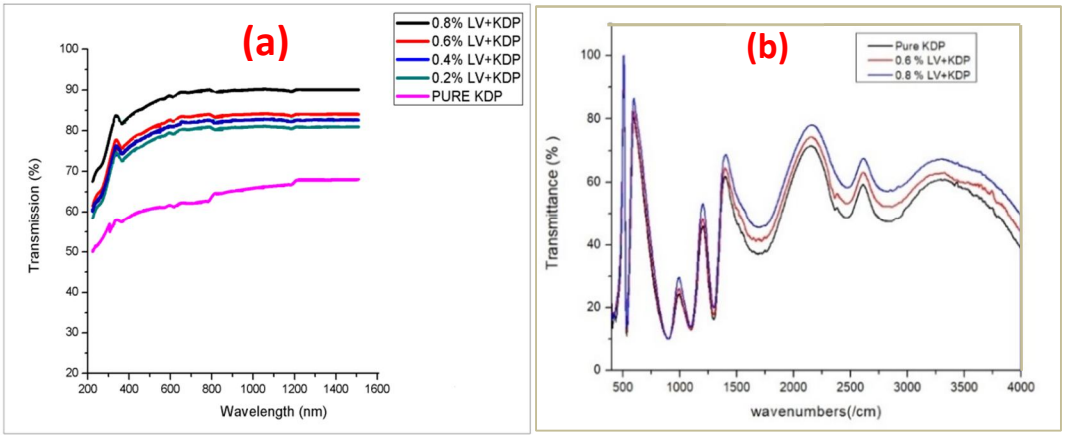

FIG. 4. (a) UV- spectra and (b) FTIR spectra of pure and doped KDP.

3.3 EDAX Analysis

Energy Dispersive X-ray analysis (EDAX) utilized in conjunction with all types of microscope has become an important tool for characterizing the weather present within the crystals. During this work, the grown crystal was subjected to EDAX analysis using the instrument JEOL Model JED - 2300 energy dispersive X-ray micro analyzer. The load percentage (wt %) of C, N, K, P and O as obtained from EDAX analysis shown in Table 2 is concurrent with the theoretical values [20-22].

TABLE 2. Weight percentage (wt %) of (a) 0.6 mole % LVKDP and (b) 0.8 mole % LVKDP.

Element	0.6 mole % LVKDP (a)				0.8 mole % LVKDP (b)			
	(keV)	Mass%	Atom%	K	(keV)	Mass%	Atom%	K
C K	0.277	5.37	12.1	2.9183	0.277	2.56	6.06	2.9183
O K	0.525	14.95	25.31	1.1103	0.525	14.5	25.81	1.1103
P K	2.013	40.81	35.68	1	2.013	40.4	37.14	1
K K	3.312	38.87	26.92	1.2645	3.312	42.54	30.98	1.2645
Total		100	100			100	100	

3.4 FTIR Spectral Analysis

The spectra were recorded in the infrared region of range 400- 4000 cm^{-1} using a Thermo Nicolet, Avatar 370 FTIR spectrometer by KBR beam splitter as shown in Fig. 4b. The vibration frequencies of functional groups of additives used in KDP crystal have been identified by FTIR spectroscopy. The values of bond length and bond angles were taken from Sutton's table (Internal coordinates for the out of plane torsional vibrations are defined as recommended by IUPAC). The spectrum confirms the interaction between KDP and organic amino acid by additional peaks corresponding to the functional groups of L-valine. There are high similarities between the spectra of pure and L-valine-doped KDP. It is found that the optical properties of pure and doped KDP changed due to the weak force of attraction of the bond between O-H and P=O. Also, low concentrations of dopant pure KDP peaks are predominant over valine peaks. Overall, the vibration spectra reveal the incorporation of impurities in the host crystals [21].

The band which appeared at 3672 cm^{-1} assigned to free O–H stretching is analogous with calculated wave number 3605 cm^{-1}, but this is absent in 0.6 and 0.8 mole % due to low concentration of dopant in pure KDP. The broad absorption bands that appeared at 3372 and 3472

cm^{-1} were assigned to hydrogen-bonded O–H stretching frequencies in 0.8 mole%-doped KDP. These peaks are absent in 0.6 mole%. This leads to a decrease in the frequency of O–H stretching and confirms the non-linear optical property of pure and doped KDP. This property is also reflected in the P=O, P–O, P– OH stretching and HO–P–OH bending vibrations shown in Table 3. The vibration assignments show that hydrogen bonding leads to stretching frequencies of the O-H group of KDP and therefore the carboxyl of L-valine molecules. This confirms the presence of L-valine in pure KDP crystal [7, 23].

TABLE 3. Assignment of vibrational wave numbers.

Sr. No.	Calculated frequencies (cm^{-1})	Pure KDP (cm^{-1})	0.6% LV+KDP (cm^{-1})	0.8% LV+KDP (cm^{-1})	Assignment
1	3605	--	--	--	Free O-H stretching; hydrogen bonding of KDP
2	3333	--	---	3472.45	O-H stretching; hydrogen bonding of KDP
4	2839	2844.65	2836.73	2824.74	P-O-H symmetric stretching
5	2461	2484.24	2464.90	2468.90	NH_3^+ bending superimposed with P–O–H stretching
6	2358		2362.94	2362.94	P-O-H bending of KDP
7		1718.49	--	--	C=O stretching
	1650		1681.25	1671.25	O=P-OH stretching of KDP
8	1295	1297.39	1301.42	1297.42	P=O stretching of KDP
9	1100	1095.92	1103.50	1097.51	P-O stretching of KDP
10	904	899.72	899.72	899.72	N-H wagging
11	535	534.66	533.76	537.76	Symmetric HO-P-OH bending
12	416	409.81	411.81	397.82	N-H torsional oscillation

3.5 Second-harmonic Generation Studies

Measurements of second-harmonic generation potency (SHG) were created by victimization of the Kurtz and Perry photography. The input ray of light was more experienced through IR reflector, so incident on the fine powder variety of the KDP specimen, that was packed in a glass tube. The resultant second-harmonic signal (532 nm) was detected once the ray of light was more matured essential amino acid-doped KDP specimen. The second-harmonic generation potency was measured with reference to KDP. From this measurement, we have a tendency to find that the relative SHG potency of essential amino acid-doped KDP slightly changes that of the standard dihydrogen phosphate. For the Nd :YAG optical device, the elemental beam of 1064 nm generates a second-harmonic signal of 532 nm. The output pulses were measured for 0.8 % and 2.0 % with relation to pure KDP (80 mV) and therefore, the results square measure is compiled in Table 4. It's determined that the essential amino acid-doped KDP crystal shows the property of SHG [23].

TABLE 4. SHG in valine-doped KDP.

Sr. No.	Sample	Second-harmonic signal output (mV)	Ratio with pure KDP
1	pure KDP	80 mV	1.00
2	0.8 mole % LV + KDP	80 mV	1.00
3	2.0 mole % LV + KDP	75 mV	0.93

4. Discussion and Conclusion

The calculated unit cell parameters of grown crystals are a = b = 7.428, c = 6.934 which are in good agreement with the results reported in the literature. Single-crystal study reveals that the grown crystal belongs to the tetragonal system with space group I42d. The number of molecules per unit cell is 4. Powder X-ray diffraction

analysis confirmed the crystalline nature of the KDP crystal. Optical absorption of KDP single crystal shows no absorption in the entire UV–visible region. The lower cut-off wavelength is around 224 nm. The transmission percentage of valine-doped KDP crystal is around 90 %. The transmission percentage of valine-doped KDP crystal for highest dopant concentration is higher. As the entire region does not bear any absorption band, it shows good transparency in the visible region. This means that the dopant increases the optical transmission of the crystal. The weight percentage (wt %) of C, N, K, P and O obtained from EDAX analysis is concurrent with the theoretical values. All elements are present in the sample and confirmed by their respective energy peak. The energy peaks were observed in the EDAX spectrum of elements as follows: Oxygen 0.525 keV, Phosphorous 2.013 keV, Potassium 3.312 keV and Carbon 0.277 keV. It was observed that 0.6 and 0.8 mole % of organic amino acid L-valine is incorporated into the crystal. The dopant L-valine is expected to substitute the potassium ions in the KDP lattice compared to pure KDP due to its valency as well as proximity of ionic radius. FT-IR spectra confirmed the presence of organic additive amino acid in potassium dihydrogen phosphate. From second-harmonic generation, the valine-doped KDP crystal shows the property of NLO.

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