Research Paper

NaCl, KCl and $SrCl_2$ Doping Effect on Linear and Nonlinear Optical Properties of KDP Crystal

ABSTRACT

The effect of NaCl, KCl and $SrCl_2$ doping on the crystal structure, optical transmission, and second harmonic generation (SHG) efficiency of the potassium dihydrogen phosphate (KDP) crystals has been investigated. The single crystals of pure and, NaCl, KCl and $SrCl_2$ doped KDP were grown by solution growth technique from aqueous solutions. The crystal structure was studied by powder X-ray diffraction. The doped crystals possess higher optical transparency than pure KDP crystals. SHG efficiency of doped crystals is found to more than pure KDP crystal. The grown crystals were subjected to the photoluminescence, atomic absorption and FT-IR spectroscopic study.

Keywords: Crystal growth, X-ray diffraction, nonlinear optical, FT-IR spectroscopy, Optical transmission, Second harmonic generation.

1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) is an important inorganic hydrogen bonded nonlinear optical (NLO) crystal exhibiting unique NLO and ferroelectric properties. It is widely used in frequency conversion and electro-optic switching applications and extensively investigated the effect of changes in growth conditions and dopants on its properties like growth rate, optical transparency, thermal and mechanical stabilities, electrical properties, and second harmonic generation (SHG) efficiency [1-7]. The NLO applications demand a crystal of large SHG efficiency, good thermal and mechanical stabilities, high laser damage threshold and easy crystal growth process [8]. The effect of urea and KCl doping on the crystal structure of KDP has been studied [9]. In the study, the increase in lattice constants in urea doped KDP, while decrease in case of KCl doping has been reported. The effect of KCl and NaCl doping on dielectric properties and electrical conductivities of KDP has been studied by Ananda Kumari and Chanrdamani [10]. They have confirmed that the electrical conductivity is due to the anions and increases with increasing concentrations of KCl and NaCl. The increases in dielectric constants has also been reported but have not studied the linear and nonlinear optical properties. Probably at a first time, $SrCl_2$ is being used as a dopant to study its effects on the properties of the KDP crystal. The effect of titanium dioxide (anatase) nanocrystals on growth process, optical and structural properties of KDP crystal have been studied by Pritula, et al. [11]. The trivalent impurity Cr(III) increases the mean growth rate along the [001] direction [12]. Owczarek and Sangwal have reported same observations in case of Fe(III) and Cr(III) doping [13]. The effect on different properties of KDP using amino acids L-alanine, L-arginine [14-16], L-glutamic acid, L-valine, L-histidine [17] and L-lysine [18] as a dopant have been studied. As amino acids possess high optical nonlinearity, it increases SHG efficiencies and optical transparencies of the KDP. Cerium [19], N'N dimethyl urea [20], and urea phosphate [21] doping modifies the growth habit and optical properties of KDP.

In the present study the effect of NaCl, KCl and $SrCl_2$ doping on the crystal structure, optical transmission, photoluminescence and second harmonic generation efficiency of KDP crystal has been investigated. The single crystals of pure and, NaCl, KCl and SrCl2 doped KDP were grown from solution at low temperature by evaporating water solvent at a constant temperature. The crystal structure was studied by powder X-ray diffraction (XRD) and the data was analysed using software PowderX [22]. In case of KCl doped crystals, the decrease in the lattice constants has been reported while for other doped crystals, all the lattice constants have been increased. The doped crystals have higher optical transparency than pure KDP crystals. SHG efficiency of doped crystals is more than pure KDP crystal. The maximum SHG efficiency of NaCl and KCl doped crystals has been observed for 2mole% doping and in case of $SrCl_2$ doped crystals, it is observed for 1mole% doping.

2. MATERIAL AND METHODS

2.1 Sample preparation and crystal growth

Analytical reagents grade KDP, NaCl, KCl and $SrCl_2$ (S D Fine-Chem Ltd. India) chemicals were used for the preparation of sample solutions. One solution of pure KDP and nine solutions of 1, 2 and 4mole% NaCl, KCl and $SrCl_2$ doped KDP were prepared in 50ml of double distilled water by taking appropriate amount of KDP, NaCl, KCl and $SrCl_2$ chemicals. The solutions were stirred continuously for four hours using magnetic stirrer at 40^{o}C, filtered and then kept for crystallisation at a constant temperature 35^{o}C to get seed crystals. The harvested seed crystals were used to grow good quality crystals of pure and doped KDP. An abbreviation; KDP is used to represent pure KDP crystal, while other doped crystals are abbreviated as first letter K represents KDP, second character is a number representing doping percentage and third and forth characters represent the compound used as a dopant. NC, KC and SC are used to represent NaCl, KCl and $SrCl_2$ respectively. For example; K1NC is an abbreviation for the crystal of KDP doped with 1mole% NaCl. Photographs of few grown crystals are shown in Fig. 1.

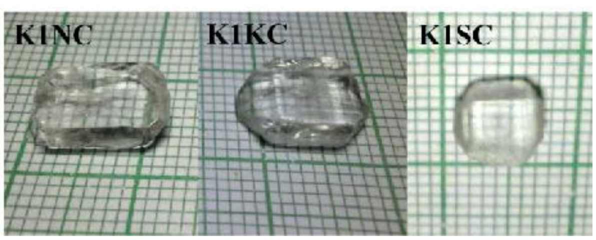

Fig. 1. Photographs of grown crystals.

2.2 Characterizations

The FT-IR spectra of all samples were recorded on instrument FT-IR spectrometer (Schimadzu, Japan). UV-visible-NIR transmission spectra of the grown crystals were recorded with UV-visible spectrophotometer (Black-Comet-SR, Stellarnet Inc. USA) over wavelength range 190-1083nm.The powder XRD patterns of pure and doped KDP crystals were recorded on Bruker D8-Advance X-ray diffractometer (Germany) in the range 2θ=20 to 80^{o} using CuKα radiation of wavelength 1.5406Å at room temperature. The powder XRD data was then analysed by using software PowderX [22]. The SHG efficiency of pure and doped KDP was measured by Kurtz and Perry method [23]. Photoluminescence study was carried out on the instrument fluorescence spectrophotometer (F-7000, Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1 Solubility

Solubility measurement of pure and doped KDP crystals was carried out gravimetrically in aqueous solutions at different temperatures, as it is important for deciding the crystal growth temperature and the crystal growth method. Pure and doped KDP compounds have moderate solubility's and increases with increasing temperature. Moreover, there is an enhancement in the solubility's of doped crystal. This increase is attributed to the presence of ionized species, which polarizes water molecule, enhances water molecule and KDP molecule interaction. It is desirable to have increased solubility of the KDP to grow good quality big size crystals with fast growth rate. Thus with addition of dopants NaCl, KCl and SrCl2, solubility can be enhanced.

3.2 Atomic absorption spectroscopy

The amount of K, Na and Sr elements present in the doped KDP crystal was determined by atomic absorption spectroscopy. 0.1g powder sample of each doped crystals was dissolved separately in 10ml of double distilled water and used in the measurement. The instrument was firstly calibrated using reference solutions of K, Na and Sr. The estimated amount of K, Na and Sr elements in solutions, added during crystal growth, and in crystals are given in Table 1. The concentration of Na and Sr in the crystals found to low as compare to the concentration in solution during crystal growth. It is expected that Na and Sr can replace some K positions and also enter in to the interstitial positions. The possibility of entering Sr atoms at interstitial position as compare to the Na atoms is less. It may be the reason behind less concentration of Sr in doped crystals. In case of KCl doping, the variation in concentration of K in doped crystals can be assigned to entering K atoms at interstitial positions.

Table 1. Amount of K, Na and Sr elements present in growth solutions and grown crystals

Crystal	Quantity present (mg/1000ml)						Weight % inclusion
	In solution			In crystal			
	Na	K	Sr	Na	K	Sr	
K1NC	16.9	--	--	4.15	--	--	24.56
K2NC	33.7	--	--	6.32	--	--	18.75
K4NC	67.3	--	--	7.25	--	--	10.77
K1KC	--	2901.8	--	--	2878.1	--	99.18 (17.71)[@]
K2KC	--	2930.5	--	--	2880.3	--	98.29 (12.70)[@]
K4KC	--	2988.0	--	--	2881.1	--	96.42 (7.04)[@]
K1SC	--	--	64.3	--	--	7.01	10.90
K2SC	--	--	128.5	--	--	8.12	6.32
K4SC	--	--	256.5	--	--	8.82	3.44

[@]The numbers in parenthesis represents weight percent inclusion of K atoms as a dopant.

3.3 FT-IR spectroscopy

The FT-IR spectra of pure and doped KDP crystals were recorded in 400-4000 cm^{-1} wavenumber range. The powdered samples of all crystals mixed with KBr placed in sample holder were used for the measurement. The absorption peaks observed in all samples, at around 2731 cm^{-1} corresponds to the P-OH stretching, 2422 cm^{-1} to O-H and P-OH stretching, 1651 and 1550 cm^{-1} to the P-O-H bending, and 1296 cm^{-1} to O-H deformation and P=O stretching. The peaks around 1095 and 902 cm^{-1} attributed to P-OH stretching and HO–P-OH bending. In doped crystal, these peaks are displaced from the position as in pure KDP. Moreover, few more peaks are apparent in the 3000-3400 cm^{-1} wavenumber range in doped crystals, which correspond to the hydrogen bonds formed with oxygen and chlorine atoms. The appearance of more peaks in this region and displacement of peaks of pure KDP in case of doped crystals confirms qualitatively the inclusion of dopant in the KDP host crystal.

3.4 UV-visible-NIR transmission study

Optical transparency of all grown crystals was studied by UV-visible-NIR spectroscopy. In the measurement, polished thin samples of thickness 2mm were used to study the transmission over wavelength range 190-1083nm. The UV-visible-NIR spectra are shown in Fig. 2. The magnified portions of transmission spectra over 80-86% transmission range are shown in incent to visualize the change in the optical transparency. All the crystals show high transmission over wide range of wavelengths. Lower cutoffs for all the crystals have found at around wavelength 195nm. 2mole% NaCl and KCl doped crystals have highest optical transparency among their respective group. In $SrCl_2$ doped crystals, 4mole% doped KDP crystal has maximum transparency. NaCl, KCl and $SrCl_2$ are ionic compounds and according to Kumari and Chanrdamani [10] the electrical conductivity is due to anions. At room temperature, also the anions can move inside the crystal due to the presence of vacancies, leaving behind cations, separated anions, and polarized molecules forms hydrogen bonds with KDP molecules and distort it in some extent. The distortion of KDP molecules due the doping may be the reason behind increasing SHG efficiency, lattice parameters, and optical transparency.

The optical absorption coefficients (α) of all crystals for wavelength range 190-1083nm were calculated by using equation;

$$\alpha = \frac{2.303}{d} \log \frac{1}{T};$$

Where, ‘T’ is the transmittance and ‘d’ is the thickness of the crystal.

The plots of variation of $(\alpha h\nu)^2$ verses photon energies ($h\nu$) are shown in Fig. 4. The values of band gap of all the crystals calculated as per procedure discussed elsewhere [24] are given in Table 3. The values of band gap found to be more for all doped crystals. The increase in the band gap is consistent with the increase in optical transparency of doped crystals.

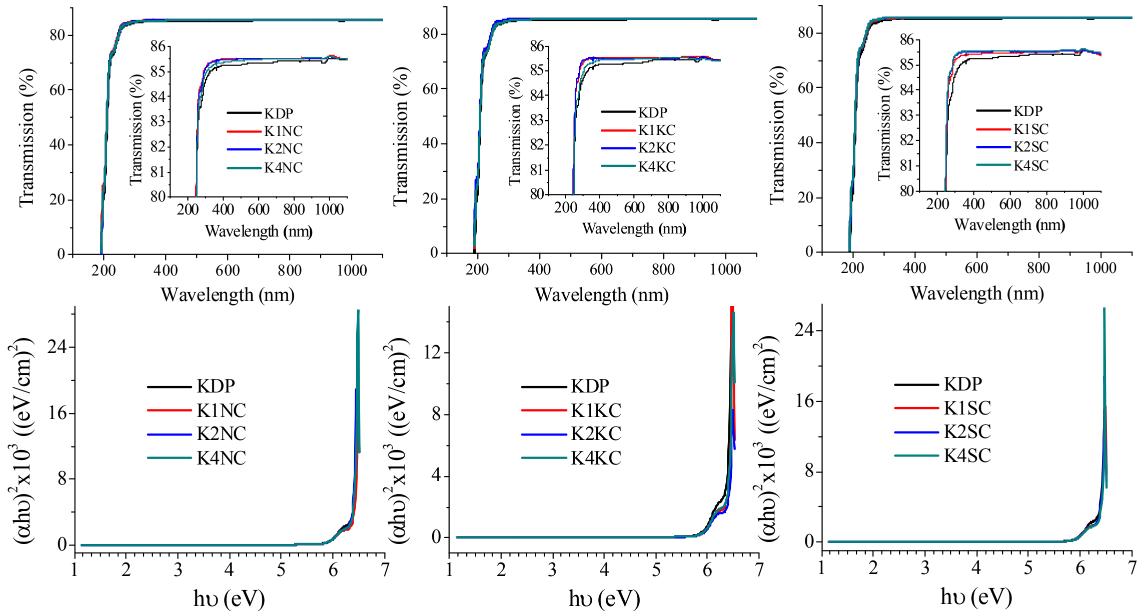

Fig. 2. UV-visible-NIR transmission spectra of pure and doped KDP crystals and plots of variation of photon energies (hv) vs. $(\alpha hv)^2$.

3.5 Powder XRD study

The recorded powder XRD patterns of pure and doped KDP crystals are shown in Fig. 3 with assigned 'hkl' values to the observed peaks. PowderX software [22] was used to analyze powder XRD data and calculate lattice parameters. Calculated lattice parameters are given in Table 2. The increase in lattice constants of NaCl and $SrCl_2$ doped crystals and decrease in lattice constants of KCl doped crystals was observed, while the crystal system and space symmetries remain same. This change in the lattice parameters confirms the incorporation of dopants in KDP crystal. The increase in lattice constants may be because of replacement of K by Na and Sr, which leads to the increase in bond lengths or inclusion in crystal lattice at interstitial positions leading to the distortion in the crystal. The observations of decrease in lattice constants of KCl doped KDP crystals confirms the report of Kumari and Chanrdamani [10].

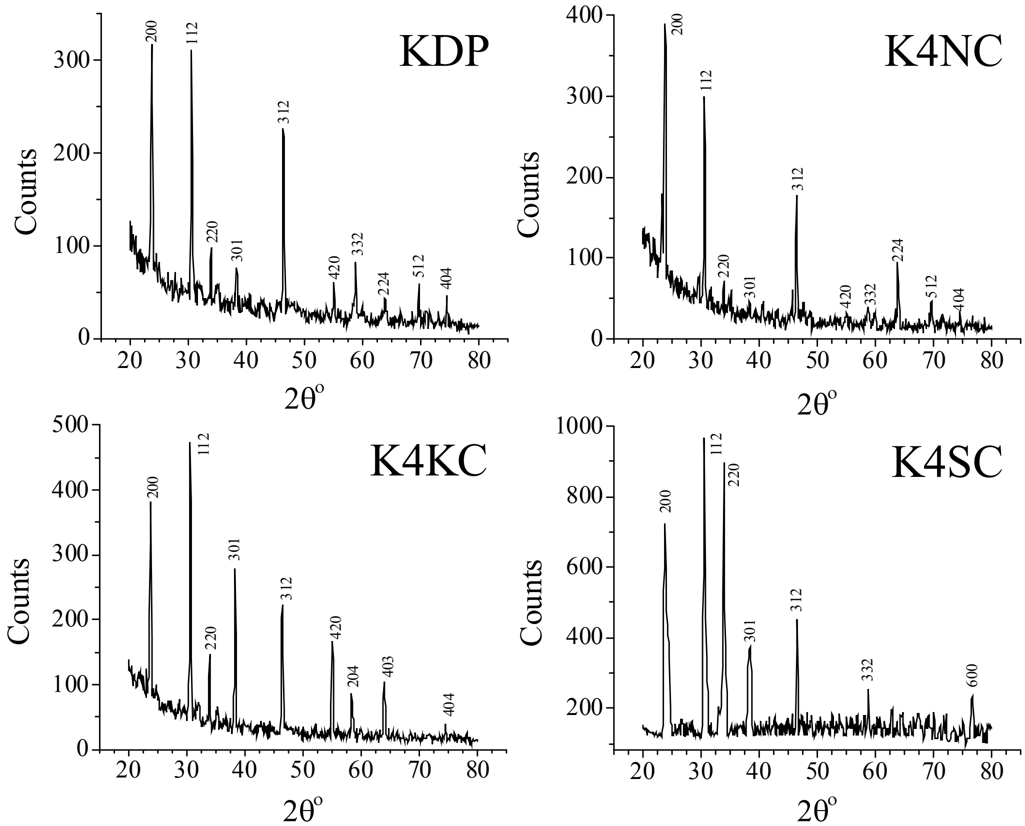

Fig. 3. Powder XRD patterns of pure and doped KDP crystals.

Table 2. Calculated lattice parameters of pure and doped KDP crystals

Crystal	**Unit cell parameters**
KDP	a= b=7.4494Å, c=6.9773Å α=β=γ=90^0 V=387.1964$Å^3$
K4NC	a=b=7.4529Å, c=6.9785Å α=β=γ=90^0 V=387.6203$Å^3$
K4KC	a=b=7.4470Å, c=6.9730Å α=β=γ=90^0 V=387.1220$Å^3$
K4SC	a=b=7.4540Å, c=6.9985Å α=β=γ=90^0 V=388.8540$Å^3$

3.6 SHG efficiency measurement

The SHG efficiency of the powdered samples was measured by Kurtz and Perry method [23] with reference to the pure KDP. Q-switched, mode locked Nd:YAG laser of wavelength 1064nm of peak power 7.1mJ, pulse duration 8 ns, beam diameter 6mm and repetition rate 10Hz was used in the SHG measurement. The power of second harmonics of 1064nm at wavelength 532nm signal was measured at output. The SHG efficiencies are tabulated in the Table 3. The SHG efficiency of 1mole% NaCl doped KDP found to be less as compare to KDP but for higher mole% doping, the SHG efficiency is more. Maximum SHG efficiency is found to be for 2mole% NaCl doping in KDP. In case of KCl doping, maximum SHG efficiency, 1.87 times KDP has been found for 2mole% doping. For all other KCl doping SHG efficiency is more than pure KDP. The $SrCl_2$ doping also enhances SHG efficiency of KDP. The maximum SHG efficiency has been found for 1mole% doping. As discussed above, the increase in SHG efficiency of doped crystals may be because of the distortion produces in KDP crystal by dopant molecules.

Table 3. SHG efficiencies of pure and doped KDP crystals

Crystal	SHG efficiency	Energy band gap (eV)
KDP	1	5.79
K1NC	0.85	5.83
K2NC	1.06	5.85
K4NC	1.03	5.82
K1KC	1.84	5.84
K2KC	1.87	5.82
K4KC	1.05	5.82
K1SC	1.29	5.80
K2SC	1.05	5.80
K4SC	1.10	5.82

3.7 Photoluminescence study

The emission spectra of pure and 2mole% NaCl, KCl and $SrCl_2$ doped KDP crystals recorded in spectral range 300-700nm using excitation wavelength 254nm are shown in Fig. 4. The curves are asymmetric; therefore each curve was deconvoluted in to two curves (not shown in figure). The peaks of deconvoluted curves and their full width at half maximum (FWHM) are given in Table 4. From Table 4, one can see that there is a red shift in the peak positions for NaCl and KCl doped crystal and blue shift for $SrCl_2$ doped crystals. FWHM is found to decrease for NaCl and $SrCl_2$ doped crystals, while it is increased for KCl doped crystal. The decrease in the FWHM may attribute to the sharp emission enhanced by doping is NaCl and $SrCl_2$. KCl doping may broaden the spectrum leading to the increase in the FWHM.

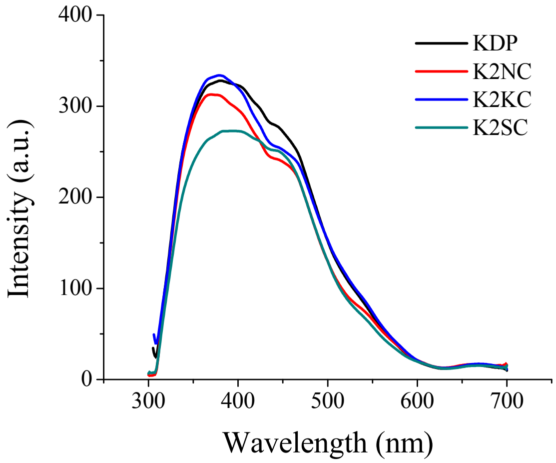

Fig. 4. Emission spectra of pure and doped KDP crystals (Excitation wavelength λ_{ex}-254nm).

Table 4. Details of emission peaks

Crystal	**Ist Peak**		**IInd Peak**	
	Position (nm)	**FWHM (nm)**	**Position (nm)**	**FWHM (nm)**
KDP	359.86	54.10	431.78	123.22
K2NC	360.79	53.48	433.94	117.45
K2KC	363.15	59.48	437.49	126.56
K2SC	358.11	49.79	431.77	115.45

4. CONCLUSION

Pure and, NaCl, KCl and $SrCl_2$ doped KDP crystals were grown by slow evaporation of solvent method at a low temperature from aqueous solution. UV-visible-NIR spectroscopy of grown crystals confirms increase in the optical transparency of doped crystals. The calculated band gaps of doped crystals are more than pure KDP crystal. NaCl, KCl and $SrCl_2$ doping in KDP affects the absorption peak positions of characteristic bondings and functional groups in FT-IR spectra, which confirm qualitatively the doping in KDP crystal. NaCl and $SrCl_2$ doping results in increases in the lattice constants of doped KDP crystals, while decrease in lattice constants has been witnessed in case of KCl doping. The SHG efficiency study shows modifications in the efficiency of doped crystals. The maximum SHG efficiency has been found for 2mole% doping of NaCl and KCl and, 1mole% doping of $SrCl_2$ in KDP crystals. Photoluminescence study confirms the red-shift in emission peaks in NaCl and $SrCl_2$ doped crystals and blue-shift in KCl doped crystals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Chunpeng Lu, Hang Gao, Jinghe Wang, Xiaoji Teng, Biling Wang. Mechanical properties of potassium dihydrogen phosphate single crystal by the nanoindentation technique. Mater Manuf Process. 2010;25:740-48.
2. Remedios CMR, Dos Santos AO, Lai X, Roberts KJ, Moreira SGC, Miranda MAR, et al. Experimental evidence for the influence of Mn^{3+} concentration on the impurity incorporation and habit modification mechanism of potassium dihydrogen phosphate. Cryst Growth Des. 2010;10:1053-58.
3. Grabovsky SV, Shnaidshtein IV, Strukov BA, Uesu Y, Fukunaga M. Dielectric dispersion in KDP crystals with complex organic and inorganic impurities. Ferroelectr. 2010;397:90-95.
4. Liang XL, Wang B, Sun X, Gu QT, Ding JX, Xu XG. Effect of Na^{+} on the growth of KDP crystals. J Synth Cryst. 2010;39:628-32.
5. Ding J, Lu Y, Wang S, Mu X, Gu Q, Wang Z, et al. Influence of SiO_3^{2-} impurity on growth habit of potassium dihydrogen phosphate crystal. Cryst Res Technol. 2010;45:800-04.
6. Ding JX, Zhang JQ, Wang SL, Mu XM, Xu XG, Gu QT, et al. Effect of typical anionic impurity on electrical conductivity of KDP crystal. J Synth Cryst. 2010;39: 1089-93.
7. Wu WJ, Li MW, Cheng M, Cao YC, Shi H. Investigation on the solution stability of KDP with EDTA and KCl double doped. J Synth Cryst. 201;40:616-23.
8. Ramasamy P, SanthanaRaghavan. Crystal growth processes and methods; KRU Publications, Kumbakonam, India, 1999.
9. Podder J, Ramalingom S, Narayana Kalkura S. An investigation on the lattice distortion in urea and KCl doped KDP crystals by X-ray diffraction studies. Cryst Res Technol. 2001;36:549-56.
10. Ananda Kumari R, Chanrdamani R. Electrical conductivity and dielectric measurement in Au^{+} doped/undoped KDP crystals with KCl and NaCl as additives. Indian J Pure Appl Phy. 2005;43:123-28.
11. Igor Pritula, Vladimir Gayvoronsky, Marina Kolybaeva, Viacheslav Puzikov, Mykhaylo Brodyn, Valentin Tkachenko, et al. Effect of incorporation of titanium dioxide nanocrystals on bulk properties of KDP crystals, Opt Mater. 2011;33;623-30.
12. Selemani Seif, Kamala Bhat, Ashok K Batra, Mohan D Aggarwal, Ravindra B. Lal. Effect of Cr(III) impurity on the growth kinetics of potassium dihydrogen phosphate and triglycine sulfate crystals grown from aqueous solutions. Mater Lett. 2004;58:991-94.
13. Owczarek I, Sangwal K. Effect of impurities on the growth of KDP crystals: Mechanism of adsorption on (101) faces. J Cryst Growth. 1990;102:574-580.
14. Muley GG, Rode MN, Pawar BH. FT-IR, thermal and NLO studies on amino acid (l-arginine and l-alanine) doped KDP crystals. Acta Phy. Polonica A. 2009;116:333-38.
15. Parikh KD, Dave DJ, Parekh BB, Joshi MJ. Growth and characterization of L-alanine doped KDP crystals. Cryst Res Technol. 2010;45:603-10.
16. Pattanaboonmee N, Ramasamy P, Manyum P. Growth and characterization of L-arginine doped potassium dihydrogen phosphate single crystals grown by sankaranarayanan-ramasamy method. Ferroelectrics. 2011;413:96-107.
17. Kumaresan P, Moorthy Babu BS, Anbarasan PM. Optical studies on pure and amino acids doped KDP crystal. J optoele Adv Mater. 2007;9:2780-86.
18. Kanagathar N, Anbalagan G. Growth, optical and dielectric studies on pure and l-lysine doped KDP crystals. Int J Opt. 2012;2012:1-6.
19. Voronov AP, Babenko GN, Puzikov VM, Roshal AD, Salo VI. Doping of KDP single crystals with cerium: growth and optical properties. Crystallogr Rep. 2008;53:708-12.

20. Muley GG, Rode MN, Pawar BH. On the growth habit of NLO N, N' dimethyl urea doped KDP crystals. Optoele Adv Mater.-Rap Commun. 2009;3:704-06.

21. Muley GG. Study on growth habit, SHG and thermal properties of urea phosphate doped KDP crystals. Sci Technol. 2012;2:109-13.

22. Dong C. PowderX: Windows-95-based program for powder X-ray diffraction data processing. J Appl Crystallogr. 1999;32:838.

23. Kurtz SK, Perry TT. A powder technique for the evaluation of nonlinear optical materials. J Appl Phy. 1968;39:3798-13.

24. Anbazhagan G, Joseph PS, Shankar G. Optical reflectance, optical refractive index and optical conductivity measurements of nonlinear optics for L-aspartic acid nickel chloride single crystal. Opt Commun. 2013;291:304-08.