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

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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~~ is 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. The SHG efficiency of doped crystals ~~is~~ was 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 optics~~al~~, FT-IR spectroscopy, Optical transmission, Second harmonic generation.

1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) is an important inorganic hydrogen bonded nonlinear optical (NLO) crystal that exhibits~~eing~~ unique NLO and ferroelectric properties. It is widely used in frequency conversion and electro-optic switching applications, and extensively investigated for 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~~ crystals of large SHG efficiency, good thermal and mechanical stability~~ies~~, 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. Ananda Kumari and Chanrdamani [10] have studied the effect of KCl and NaCl doping on dielectric properties and electrical conductivities of KDP. They have confirmed that the electrical conductivity is due to the movement of anions and it increases with increasing concentrations of KCl and NaCl. The increases in dielectric constants has also been reported in same communication but have not studied the linear and nonlinear optical properties. Probably ~~at~~ for 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

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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 crystal. Cerium [19], N'N dimethyl urea [20], and urea phosphate [21] doping modifies the growth habit and optical properties ~~of KDP~~. Potassium acetate (CH_3COOK), potassium citrate ($K_3C_6H_5O_7$) [22] and potassium carbonate (K_2CO_3) [23], potassium dichromate ($K_2Cr_2O_7$) [24] and urea [25] added into KDP results in lowering dielectric constants of the crystal. The dopants viz. potassium acetate (CH_3COOK), potassium citrate ($K_3C_6H_5O_7$) [22] and potassium carbonate (K_2CO_3) [23] improve optical transparency and SHG efficiency also. The effect of addition of potassium thiocyanate on dielectric, crystalline perfection, SHG efficiency and hardness of KDP crystals has been reported [26]. DC and AC electrical measurements carried out at various temperatures along a- and c- directions indicate an increase of the electrical parameters with the increase of temperature, which can be attributed mainly to the increase of thermally generated hydrogen bond vacancies (L- defects). L-arginine addition leads to reduction of electrical parameters of KDP and ADP single crystals, which can be attributed mainly to the decrease of L-defects due to creation of additional hydrogen bonds by the impurity in random directions [27]. NaCl and NaBr dopants have been tried to modify various properties of KDP [28, 29]. Urea and thiourea [30]; NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$, and $(NH_4)_2SO_4$ [31,32] added KDP single crystals have been grown by the gel method using silica gels and electrical conductivity measurement has been carried out to study lattice variation and thermal parameters like Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency.

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 $SrCl_2$ 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 [33~~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^oC, filtered and then kept for crystallisation at a constant temperature 35^oC 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 that represents KDP, second character is a number representing doping percentage and third and fourth 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 1mol~~e~~% NaCl. Photographs of a 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 [33~~22~~]. The SHG efficiency of pure and doped KDP was measured by Kurtz and Perry method [34~~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 it increases with increasing temperature. Moreover, there is an enhancement in the solubility~~'s~~ of doped crystals. This increase is attributed to the presence of ionized species, which polarizes water molecule, enhances interaction between 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 $SrCl_2$, 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~~ for 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 is found to be low as compared 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 compared 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 powder~~ed~~ samples of all crystals mixed with KBr placed in sample holder were used for the measurement. The absorption peaks observed in all the 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} is attributed to P-OH stretching and HO–P-OH bending. In doped crystals, these peaks are displaced from the position as in pure KDP. Moreover, a 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. The absorption band at 1621 cm^{-1} in KDP corresponding to the P-OH bending found to shifted on higher frequency side in FT-IR spectrum of K4KC (appears at 1652 cm^{-1}) and lower frequency side in spectra of K4NC and K4SC (appear at 1620 and 1618 cm^{-1}, respectively). Another peak 1296 cm^{-1} in KDP spectrum corresponding to the P=O stretching and O-H deformation found to appear at 1304 cm^{-1} in K4KC spectrum. The band centered at 928 cm^{-1} representing OH stretching in KDP appears at 903 cm^{-1} in K4NC and K4SC. The shifting in absorption bands on higher frequency side in K4KC and lower frequency side in K4NC and K4SC may be because of bond tightening in K4KC and bond weakening in K4NC and K4SC.

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 inset to visualize the change in the optical transparency. All the crystals show high transmission over wide range of wavelengths. Lower cutoff~~s~~ for all the crystals ha~~ves~~ been found at around wavelength 195nm. 2mole% NaCl and KCl doped crystals have highest optical transparency among their respective group. Lowering transparency with higher doping level may be due to the insertion of impurity levels below conduction band, which is confirmed from photoluminescence study for 2mol% KCl doping. The full width at half maximum (FWHM) of emission peaks of the sample K2KC found to increased as compare to KDP (Table 4). 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 form~~s~~ hydrogen bonds with KDP molecules and distort it in some extent. The distortion of KDP molecules due to 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 (hν) are shown in Fig. 2 4. The values of band gap of all the crystals calculated as per procedure discussed elsewhere [35 ~~24~~] are given in Table 3. The values of band gap are found to be more for all doped crystals and it may be because of reduction in width of absorption edge near cut-off wavelength. ~~The increase in the band gap is consistent with the increase in optical transparency of doped crystals.~~

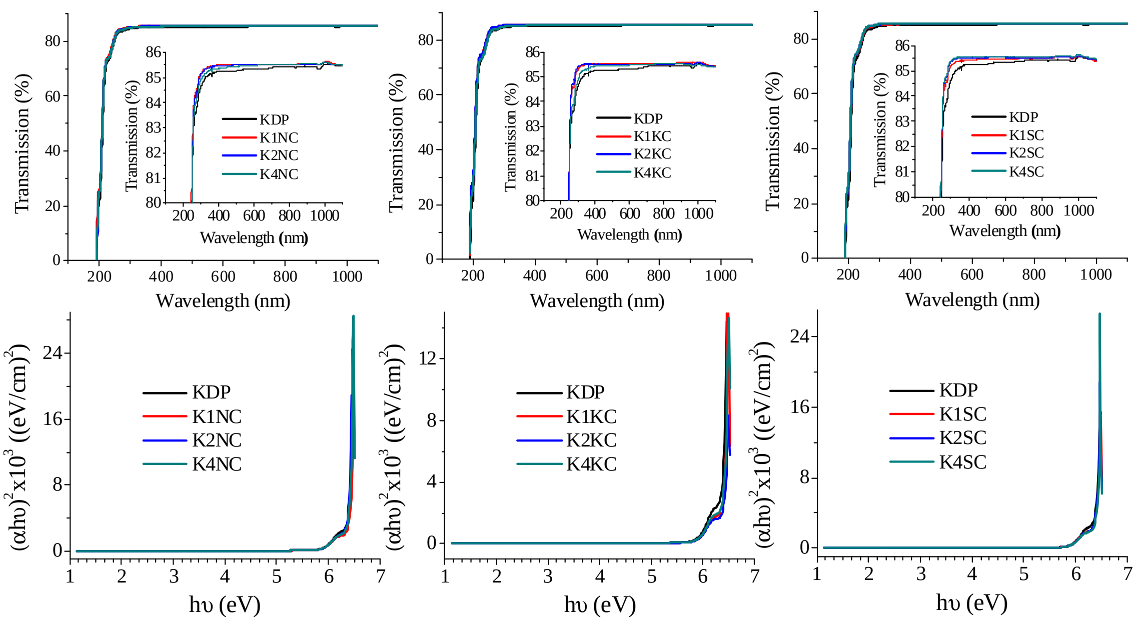

Fig. 2. UV-visible-NIR transmission spectra of pure and doped KDP crystals and plots of variation of photon energies (hv) vs. $(\alpha hv)^2$.

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 [33~~22~~] was used to analyze powder XRD data and to 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 ~~wa~~is 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, which is confirmed by FT-IR study, or inclusion in crystal lattice at interstitial positions leading to the distortion in the crystal. The observation~~s~~ of decrease in lattice constants of KCl doped KDP crystals, may be because of bond tightening, confirms the report of Kumari and Chanrdamani [10].

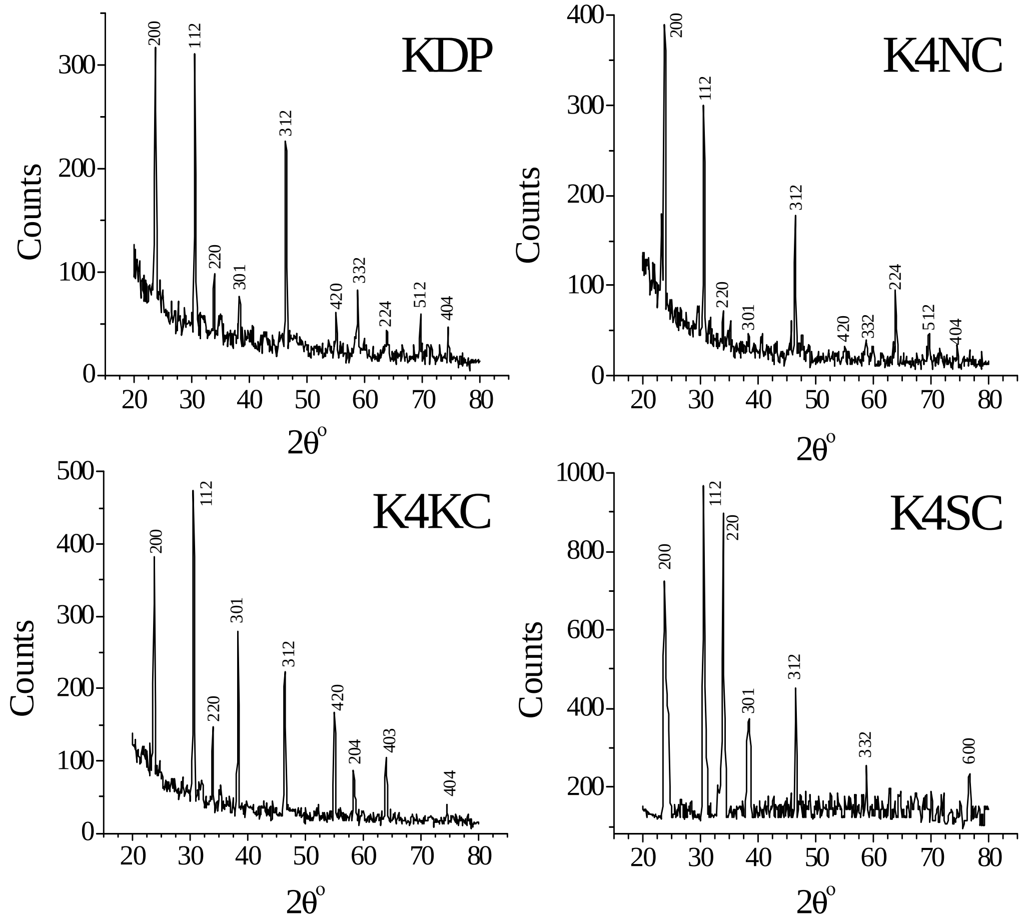

Fig. 3. Powder XRD patterns of pure and doped KDP crystals.

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

Crystal	Unit cell parameters
KDP	a= b=7.4494Å, c=6.9773Å $\alpha=\beta=\gamma=90^o$ V=387.1964$Å^3$
K4NC	a=b=7.4529Å, c=6.9785Å $\alpha=\beta=\gamma=90^o$ V=387.6203$Å^3$
K4KC	a=b=7.4470Å, c=6.9730Å $\alpha=\beta=\gamma=90^o$ V=387.1220$Å^3$
K4SC	a=b=7.4540Å, c=6.9985Å $\alpha=\beta=\gamma=90^o$ V=388.8540$Å^3$

3.6 SHG efficiency measurement

The SHG efficiency of ~~the~~ powder~~ed~~ samples was measured by Kurtz and Perry method [34~~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 the output. The SHG efficiencies are tabulated in the Table 3. The SHG efficiency of 1mole% NaCl doped KDP is found ~~to be~~ less as compared 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 produce~~s~~d in KDP crystal by dopant molecules. Nonlinear polarisation produced in the sample by fundamental wave results in SHG [36]. The dopants producing distortion in the crystal may enhance polarization, which may be in phase to the polarsation component responsible for SHG. The phase and extent of enhanced polarization may depend on nature of dopant and its concentration. The enhanced SHG efficiency of K2NC, K2KC and K1SC may be due to the additional polarisation introduced by doping produced distortion is in phase to the polarisation responsible for SHG.

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 the~~ir~~ ~~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 be attributed to the sharp emission enhanced by NaCl and $SrCl_2$ doping ~~is NaCl and SrCl~~$_2$. ~~KCl doping may broaden the spectrum leading to the increase in the FWHM.~~ KCl doping in KDP may introduce impurity levels around edge of the conduction band to form impurity band, which may results in the broadening of emission band.

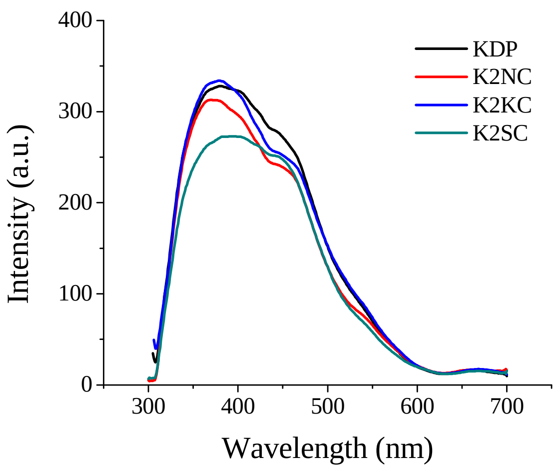

Fig. 4. Emission spectra of pure and doped KDP crystals (Excitation wavelength λ_{ex}-254nm).

Table 4. Details of emission peaks

Crystal	I[st] Peak		II[nd] 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. CONCLUSIONS

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 larger ~~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 increase~~s~~ 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, while 1mole% doping of~~ ~~$SrCl_2$ in KDP crystals.~~ The maximum SHG efficiency has been found for 2mol% doping of NaCl and KCl in KDP crystals while $SrCl_2$ doped crystals has maximum efficiency for 1mol% doping. Photoluminescence study confirms the red-shift in emission peaks in NaCl and $SrCl_2$ doped crystals and blue-shift in KCl doped crystals.

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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. Dhanaraj PV, Rajesh NP, Ramasamy P, Jeyaprakasan M, Mahadevan CK, Bhagavannarayana G. Enhancement of stability of growth, structural and NLO properties of KDP crystals due to additive along with seed rotation. Cryst Res Technol. 2009;44:54-60.
23. Dhanaraj PV, Mahadevan CK, Bhagavannarayana G, Ramasamy P, Rajesh NP. Growth and characterization of KDP crystals with potassium carbonate as additive. J Cryst Growth. 2008;310:5341-5346.
24. Priya M, Mahadevan CK. Effect of dichromate addition on the electrical properties of KDP crystals. Archives Applied Sci Res. 2011;3:233-240.
25. Goma S, Padma CM, Mahadevan CK. Dielectric parameters of KDP single crystals added with urea. Mater Lett. 2006;60:3701-3705.
26. Dhanaraj PV, Rajesh NP, Mahadevan CK, Bhagavannarayana G. Nucleation studies and characterization of potassium thiocyanate added KDP crystals grown by seed rotation technique. Physica B: Condensed Matter. 2009;404:2503-2508.
27. Meena M, Mahadevan CK. Growth and electrical characterization of L-arginine added KDP and ADP single crystals. Cryst Res Technol. 2008;43:166-172.
28. Mahadevan CK, Vincent Jerin C, Maragatha Selvi S. Lattice variation and thermal parameters of KDP crystals added with NaCl and NaBr, Indian J Phys. 2005;79:377-380.
29. Deepa G, Freeda TH, Mahadevan C. D. C. electrical conductivity measurements on KDP single crystals added with NaCl and NaBr, Indian J Phys. 2002;76A:369-372.
30. Priya M, Padma CM, Freeda TH, Mahadevan C, Balasingh C. Electrical conductivity measurements on gel grown KDP crystals added with urea and thiourea. Bull Mater Sci. 2001;24:511-514.
31. Freeda TH, Mahadevan C. Lattice variation and thermal parameters of gel grown KDP crystals added with some ammonium compounds. Pramana- J Phys. 2001;57:829-836.
32. Freeda TH, Mahadevan C. Electrical conductivity measurements on gel grown KDP crystals added with some ammonium compounds. Bull Mater Sci. 2000;23:335-340.
33. Dong C. PowderX: Windows-95-based program for powder X-ray diffraction data processing. J Appl Crystallogr. 1999;32:838.

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

35. 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.

36. Shen YR. The principles of nonlinear optics; Wiley-Interscience, 2003.