

Growth and characterization of metal ions and dye doped KDP single crystals

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The organic dyes (Amaranth, Rhodamine and Methyl Orange) were introduced in KDP crystals. Influence of supersaturation and dye concentration in the solution, on the color and crystal habit of KDP, were observed. Amaranth in the solution at low super saturation and high dye concentration colored the pyramidal section (101) of the crystals. The highly supersaturated solutions produce entirely colored crystals. Metal ions (Al^{3+} , Na^+) doped KDP crystals were also grown by solution growth technique. The concentration of dopants in the mother solution was varied from 0.1 mole% to 10-mole %. The studies on pure and doped KDP crystals clearly indicate the effect of dopants (Al^{3+} , Na^+) on the crystal structure, in the absorption of IR frequencies and the non-linear optical property. The frequencies with their relative intensities are obtained in FT-IR of pure and doped KDP. The very weak bands for dopants indicate its presence in low concentration. The absence of even such a weak band in the case of KDP doped with AlPO_4 indicates the strong interaction of Al^{3+} ion with O–H groups. The calculated IR frequency 3333 cm^{-1} for O–H stretching was in close agreement with the experimentally obtained one for pure KDP at 3340 cm^{-1} . The doped crystals show good second harmonic generation efficiency. The dopants increase the hardness value of the material, which also depends on the concentration of the dopants. Dye doping improves the NLO properties of the grown crystals. Results of the growth kinetics of KDP crystals in the presence of impurities are also discussed.

(Received January 9, 2007; accepted August 23, 2007)

Keywords: Growth from solutions, Single crystal growth, Non-linear optical materials, Dye doped KDP

1. Introduction

One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Potassium dihydrogen orthophosphate (KDP) is a model system for non-linear optical device application. Optical quality KDP (KH_2PO_4) crystals can be grown by conventional solution growth methods as well as by fast growth techniques. KDP is an efficient angle tuned dielectric medium for optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket its refractive index for even extreme wavelength range over which it is transparent. Among non-linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication [1-3].

KDP finds widespread use as a frequency doubler in laser applications and has been studied in great detail. Improvement in the quality of the KDP crystals and the performance of KDP based devices can be realized with suitable dopants. To analyse the influence of metal ions and amino acid based dopants on the non-linear optical property of KDP crystals, efforts were made to dope KDP with metal ions (Na_2CO_3 , AlPO_4) and dyes (Amaranth, Rhodamine and Methyl Orange). The effects of impurity atoms on the quality and performance of the material are analysed. In the present investigation, the growth aspects of KDP and doped KDP have been studied. Bulk crystals of KDP and doped KDP were grown by slow evaporation

and also by slow cooling techniques. The structural, chemical, optical, mechanical and non-linear optical properties of the doped crystals were studied with the characterization studies such as powder XRD, FT-IR, UV-visible, micro hardness and SHG measurements respectively. The results for doped KDP are compared with the results of the pure KDP crystals and with the results available in the literature.

2. Experimental procedure

2.1 Crystal growth

Pure KDP crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5 deg/day). The same method was followed for doped KDP crystals (0.1 mole % of Na_2CO_3 or AlPO_4 or Amaranth or Rhodamine or Methyl Orange). The solubility of doped KDP in the solvent was determined for each dopants for four different temperatures 30, 35, 40 and 45 °C by dissolving the KDP salt in deionised water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility of doped KDP was measured for each dopant and was found to be 32.5-grams/100 ml at 40 °C for sodium, 31.5 grams/100 ml at 400 °C for aluminium, 32.75-grams/100 ml at 400 °C for Amaranth, 31.5-grams/100 ml at 40 °C for Rhodamine and 32 grams/100 ml at 40 °C for Methyl Orange. The seed crystals were prepared at low temperature by spontaneous

The supersaturated solution of KDP was first prepared at 313 K in 1 litre beaker. And then, Amaranth or Rhodamine or Methyl orange in 0.1M aqueous solution was added into the super saturated solution of KDP at 313 K. The solution was kept for a few weeks at 313 K. A few nuclei of doped KDP had appeared at the bottom of the beaker and grew for a few days. The change of super saturation was greater than 15% of the critical super saturation during the growth of doped KDP crystals. Constant temperature bath were used for the bulk growth of dye doped KDP crystals. Transparent good quality crystals were obtained after 20 days Fig. 1. Dye concentrations in the prismatic and pyramidal sections of the crystals were measured. The analyzed wavelengths for Amaranth, Rhodamine & Methyl orange doped KDP were 1400, 1650 and 1570 nm respectively.

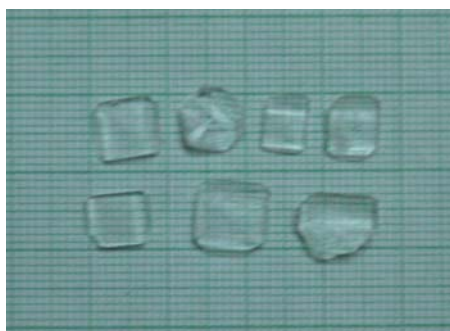


Fig. 1. Seed crystals of Amaranth doped KDP crystals.

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on Shimadzu-800, FTIR spectrometer using 1064 nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region $400\text{--}4000 \text{ cm}^{-1}$ operating at 200 mW power at the samples with a spectral resolution of 2 cm^{-1} . The frequency for all sharp bands is accurate to $\pm 1 \text{ cm}^{-1}$. The hardness measurements on the grown crystals were carried out with Vickers Pyramidal indenter and using the Leitz Metallux II microscope. The UV-VIS spectrum of KDP, doped KDP crystals were taken in the wavelength $200\text{--}1200 \text{ nm}$ range using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Kurtz

3. Results and discussion

$$\begin{aligned} 2 \text{KH}_2\text{PO}_4 + \text{Na}_2\text{CO}_3 &\rightarrow 2 \text{NaH}_2\text{PO}_4 + \text{K}_2\text{CO}_3 \\ \text{KH}_2\text{PO}_4 + (\text{CH}_2)_3\text{C}_2\text{N}_2\text{H}_3(\text{NH}_2)_2\text{COOH} &\rightarrow \\ (\text{CH}_2)_3\text{C}_2\text{N}_2\text{H}_3(\text{NH}_2)_2\text{CO-H}_2\text{PO}_4 + \text{KOH} \end{aligned}$$

Powder XRD spectra (Fig. 2) for the pure and dye doped KDP revealed that the structures of the doped crystals are slightly distorted compared to the pure KDP crystal. This may be attributed to strains on the lattice by the absorption or substitution of dyes. It is observed that the reflection lines of the doped KDP crystal correlate well with those observed in the individual parent compound [8, 9], with a slight shift in the Bragg angle.

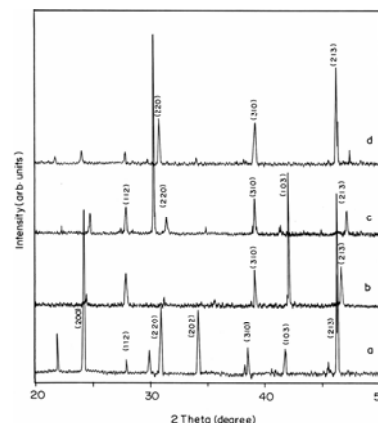


Fig. 2. XRD spectra of (a) Pure (b) Amaranth (c) Rhodamine and (d) Methyl Orange doped KDP crystal.

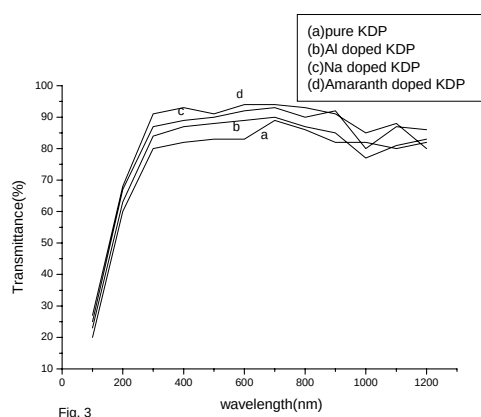


Fig. 3. UV-visible transmission spectra of (a) Pure (b) Al (c) Na (d) Amaranth doped KDP crystal.

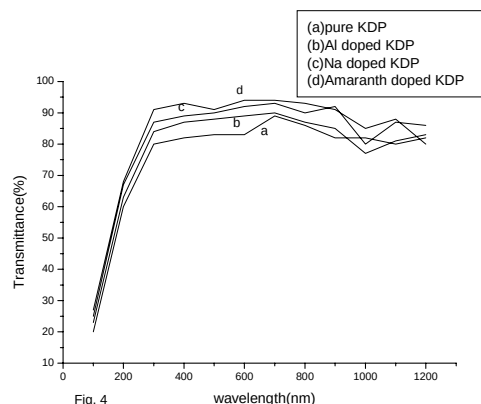


Fig. 4. UV-visible transmission spectra of (a) Pure (b) Amaranth (c) Rhodamine and (d) Methyl Orange doped KDP crystal.

The UV-visible spectra for the doped KDP crystals are as shown in Figs. 3-4. All the crystals irrespective of the dopants are transparent in the entire visible region. This transparency in the visible region is a desired property of materials [10,11] for NLO applications. The origin of some peaks (around 600 nm) in doped sample shows that the structure of KDP doped sample is altered. There is an absorption hump and extended absorption edge around 200 - 275 nm for KDP crystal doped with metal ions. The absorption edge for the Al-doped KDP is shifted to lower wavelength than the sodium- doped sample. This gives an idea of the fundamental energy gap for the doped crystals and the energy gap may be more for Al-doped KDP compared with Na doped KDP. The UV-visible spectra for dyes (Amaranth, Rhodamine, Methyl Orange) doped shows that the Methyl Orange enhances the optical property of KDP crystal. After incorporation of dyes, the UV absorption was shifted to blue region. The blue shift increases in accordance of mole fractions of dopants. The pure KDP crystal has about 70% of transmission. The Rhodamine doped crystal is invariably has higher transmission percentage compared to pure KDP crystal. In

the spectrum, transmission percentage increases due to additive of dyes in KDP crystal.

The hardness measurements were made using the Vickers pyramidal indenter for various loads. The maximum value of hardness for cleavage plane of KDP crystal is found to be 172.50 Kg/mm². Addition of impurities in KDP extensively modifies the hardness values and the doped KDP crystals much more harder than the pure crystal. The hardness values of the pure and doped KDP crystals are tabulated in Table 1.

Table 1. Micro hardness values of pure and doped KDP.

S.No	Crystal	Micro-hardness (Kg/mm ²)
1.	KDP	165.79
2.	KDP + Na ₂ CO ₃	168.67
3.	KDP+AlPO ₄	169.24
4.	KDP+Amaranth	171.54
5.	KDP+Rhodamine	169.67
6.	KDP+Methyl Orange	172.50

FT-IR spectra for the pure and doped KDP crystals are as shown in Fig. 5 and Fig. 6. The frequencies with their relative intensities obtained in FTIR of pure and doped KDP and their most probable assignments are presented in Table 2. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data [12]. The values of bond length and bond angles were taken from Sutton's table [13]. Internal co-ordinates for the out of plane torsional vibrations are defined as recommended by IUPAC. The general quadratic valence force was adopted for both in plane and out of plane vibrations. The normal co-ordinate calculations were performed using the program given by Schachtschneider [14]. The initial sets of force constants were taken from the literature for the derivatives of allied molecules. The calculated frequencies agree favourably with the observed frequencies.

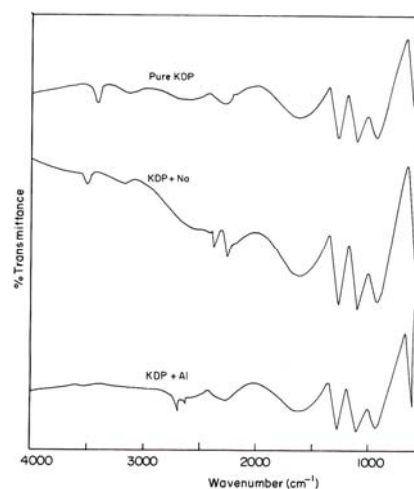


Fig. 5. FT-IR spectra recorded for the pure and metal ions doped KDP crystal.

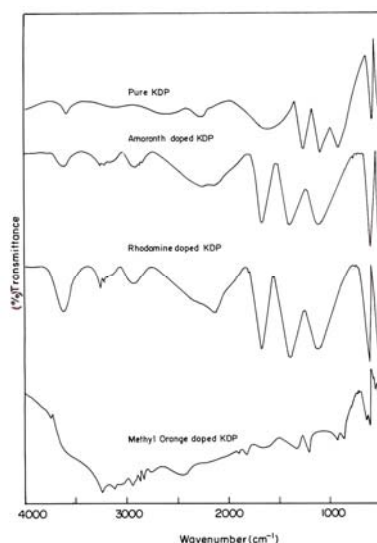


Fig. 6. FT-IR spectra recorded for the pure and dyes doped KDP.

Table 2. Observed and calculated IR frequencies (cm^{-1}) of pure KDP and KDP doped with Na_2CO_3 , AlPO_4 , Amaranth, Rhodamine and Methyl Orange.

S P E C I E S	Calculated Frequencies Cm^{-1}	Observed IR frequencies and intensities						Assignments
		Pure KDP	KDP Doped with Na_2CO_3	KDP doped with AlPO_4	KDP doped with Amaranth	KDP Doped with Rhodamine	KDP Doped with Methyl Orange	
A/E	3605	3600 (vw)	3600 (vw)	-	3500 (vw)	3345(vw)	3450 (vw)	Free O-H Stretching
	3333	3340 (w)	3296 (vw)	-	3355 (vw)	3250(vw)	3340 (w)	O-H Stretching Hydrogen bond
	2919	2924 (vw)	2924 (m)	2924 (vw)	2824 (vw)	2950(vw)	2924 (vw)	P-O-H asymmetric stretching
	2839	2844 (vw)	2844 (m)	2844 (vw)	2744 (vw)	2800(vw)	2844 (vw)	P-O-H asymmetric stretching
	2461	2466 (w)	2466 (w)	2466 (w)	2566 (cw)	2500(cw)	2466 (w)	O P - OH stretching
	2358	2362 (vw)	2362(vw)	2362 (vw)	2462 (s)	2400(s)	2362 (vw)	P-O-H bending
	1650	1655 (m)	1655 (m)	1655 (m)	1559 (vw)	1750(m)	1540(m)	O P - OH stretching
					1690	1650	1540	N-H bending of the dopant
					1501	1450	1544	C-H stretching of the dopant
	1295	1299 (s)	1300 (s)	1301 (s)	1404 (s)	1380(s)	1280(s)	P=O stretching
					1350	1300	1420	C-N-H stretching of the dopant
	1100	1101 (s)	1102 (s)	1101 (s)	1096 (s)	1022(s)	1028(s)	P=O stretching
	904	908 (s)	904 (s)	908 (s)	858 (s)	870(s)	840(s)	P-O-H stretching
					813	800		N-H wagging of dopant
	535	539 (s)	537 (s)	537 (s)	503 (s)	450(s)	447(s)	HO-P-OH bending
					445	440	400	N-H Torsional oscillation of dopant

vs - very strong s- strong m-medium w-weak vw-very weak

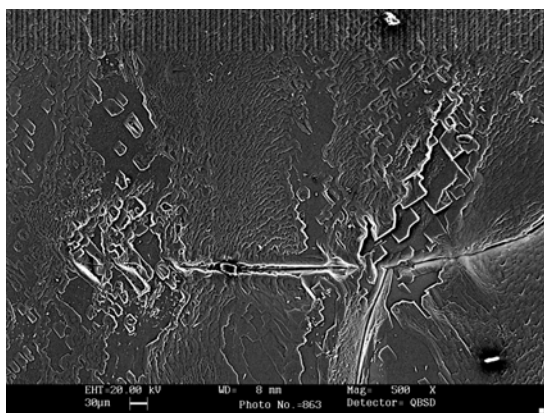


Fig. 7. SEM photograph of Amaranth doped KDP crystal.

There is a broad strong absorption between 1500 cm^{-1} and 1700 cm^{-1} resulting from hydrogen [15] bonded N - H stretching bands. Absorption in this region is characterized by fine structure on the lower wave number side of the band. The bands which appeared at 3600 cm^{-1} in pure KDP, KDP doped with Na_2CO_3 and Aluminium were assigned to free O-H stretching. The very weak bands indicate the presence of low concentration of Na and Aluminium in KDP. The absence of even such a weak band in the case of KDP doped with AlPO_4 indicated the strong interaction of Al^{3+} ion with O-H groups. The broad absorption band appeared at 3340, 3296, 3255 were assigned to hydrogen bonded O-H stretching frequencies in pure KDP, KDP + Na_2CO_3 and KDP + Aluminium respectively. The absence of this peak in KDP doped with AlPO_4 supported again the strong interaction of Al^{3+} with O-H groups and the possible entry of these ions in the lattice site of KDP crystal. The calculated IR frequency 3333 cm^{-1} for O-H stretching was in close agreement with the experimentally obtained one for pure KDP at 3340 cm^{-1} . Its deviation from pure KDP to lower frequency at 3296 cm^{-1} in KDP doped with Na_2CO_3 and at 3255 cm^{-1} in KDP doped with Aluminium indicated clearly the interaction of dopants with P-O-H group of KDP and in weakening the strength of the bond between oxygen and hydrogen. This leads to the decrease in the frequency of O-H stretching and confirmed the non-linear optical property of pure and doped KDP crystals at these sites in the crystal lattice. This property is also reflected in the P=O, P-O, P-OH stretching and HO-P-OH bending vibrations (Table 2). The present IR study on pure and doped KDP clearly indicates the effect of dopants [17-19] on the crystal structure of pure KDP, which leads to the change in the absorption of IR frequencies and the non-linear optical property of both the crystals. Its deviation from pure KDP to lower frequency at 3100 cm^{-1} in KDP doped with Amaranth and at 3350 cm^{-1} in KDP doped with Amaranth indicated clearly the interaction of dopants with P-O-H group of KDP and in weakening the strength of the bond between oxygen and hydrogen. The study also

confirmed that the dopants [20-24] had entered the lattice sites of tetragonal KDP. Rhodamine doped with KDP also changes optical properties. The second harmonic signal, generated in the crystal was confirmed from the emission of green radiation by the crystals on laser irradiation. The SEM picture (Fig. 7) confirms the formation of a layer on the surface of the crystal due to impurities. The SEM studies reveal that the Amaranth present in the solution causes to form a surface layer that prevents the entry of impurities and thereby it helps to grow the crystal with high crystalline quality.

4. Conclusions

Optically clear KDP and doped KDP (Al, Na, Amaranth, Rhodamine and Methyl Orange) crystals with dimension up to $25 \times 22 \times 10\text{ mm}^3$ have been grown by a slow evaporation technique and also by a slow cooling technique. Powder XRD was taken to analysis the structures of the doped crystals. In the FTIR spectrum, the characteristic peaks due to C-O-H in plane and out of plane bands clearly demonstrate protonation of COO-group. The functional groups present in the grown crystals have been confirmed by FTIR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis. The study not only confirmed the strong interaction of Al^{3+} and Na^+ ions of the dopants with the -OH group of KDP but also the entry of these ions into the crystal lattice of the tetragonal KDP crystal. It was found that the optical property of pure and doped KDP were changed not only due to the weakening of the bond between O-H and C=O due to hydrogen bonding but also due to the substitution of metal ions in the crystal lattice of tetragonal KDP crystals which increased the bond strengths. Since H^+ ion having the radii of only $0.3\text{ \AA}$ is being replaced by Al^{3+} ion ($0.535\text{ \AA}$) and Na^+ ($1.02\text{ \AA}$), there must be a strain in the accommodation of these ions instead of H^+ . Hence, only a limited number of ions can diffuse into the lattice sites of tetragonal KDP crystals. In the present work, pure and doped (Amaranth, Rhodamine and Methyl Orange) single crystals of KDP are grown by slow cooling method in a period of 20 – 25 days. The doped crystals of KDP undergo two – stage thermal decomposition similar to that of pure ones. The micro hardness studies of doped KDP were analyzed. The NLO studies analyzed with Nd – YAG laser technique confirm that the grown crystals are non linear in nature. Doped crystals have relatively higher hardness values than the pure crystals. Powder XRD analysis confirms the structure and change in lattice parameter values for the doped crystals. The presence of dopants in the crystal lattice has been qualitatively confirmed by FT – IR analysis.

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