OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 2, February 2007, p. 65 - 69

Effect of metal ion and amino acid doping on the optical performance of KDP single crystals

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Potassium dihydrogen orthophosphate (KDP) single crystals doped with metal ions (Al^{3+}, Na^+) and amino acid (L-Arginine) have been grown by a solution growth technique. Slow evaporation and slow cooling methods were employed to grow these crystals. The concentration of dopants in the mother solution was varied from 0.1 mole% to 10 mole %. The solubility data for all dopant concentrations were determined. Powder XRD studies revealed the distortion of lattice parameter values for the heavily doped KDP crystals. UV and visible spectra confirmed the improvement in the transparency of these crystals on doping with metal ions. FT – IR spectra revealed a strong absorption band between 1500 – 1700 cm^{-1} for metal ion doped crystals. The functional groups present in the grown crystals have been confirmed by FT-IR 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 in the crystal lattice of tetragonal KDP crystal. The dopants increase the hardness value of the material, which also depends on the concentration of the dopants. Amino acid doping improves the NLO properties of the grown crystals. The growth kinetics of KDP crystals in the presence of impurities is discussed.

(Received January 8, 2007; accepted January 15, 2007)

Keywords: Growth from solutions, Single crystal growth, Nonlinear optical materials, 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, Al PO_4) and an amino acid (L-Arginine). 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 properties of the doped crystals were studied with the characterization studies such as powder XRD, FT-IR, UV-visible, microhardness and SHG measurements respectively. The results for doped KDP are compared with the results of the pure KDP crystals and as well as 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 L-Arginine). The solubility of doped KDP in the solvent was determined for each dopants for four different temperatures 30, 35, 40 and 45 ^oC by dissolving the KDP salt in deionised water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining a 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 ^oC for sodium, 31.5 grams/100ml at 40^0 C for aluminium and 32.75-grams/100 ml at 40^0 C for L-Arginine. The seed crystals are prepared at low temperature by spontaneous nucleation. Seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystal KDP and doped KDP (Na, Al, L-Arginine) were grown using a constant temperature bath (CTB), controlled with the Indtherm temperature programmer/controller. The mother solution was saturated using the initial pH values, 4.5, 4.6 and 4.8 for sodium, aluminium and L-Arginine dopants respectively. The growth was carried out for more than 20 days by keeping the bath at a temperature of 38 ^{o}C.

Table 1. Observed and calculated IR frequencies (cm^{-1}) of pure KDP and KDP doped with Na_2CO_3, $AlPO_4$, L-Arginine.

SPECIES	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 L-Arginine	
A/E	3605	3600(vw)	3600(vw)	-	3600 (vw)	Free O-H Stretching
	3333	3340 (w)	3296(vw)	-	3255 (vw)	O-H Stretching Hydrogen bond
	2919	2924(vw)	2924 (m)	2924 (vw)	2924 (vw)	P-O-H asymmetric stretching
	2839	2844(vw)	2844 (m)	2844 (vw)	2844 (vw)	P-O-H asymmetric stretching
	2461	2466 (w)	2466 (w)	2466(w)	2466 (cw)	O ‖ P - OH stretching
	2358	2362(vw)	2362(vw)	2362 (vw)	2362 (s)	P-O-H bending
	1650	1655 (m)	1655 (m)	1655 (m)	1659 (vw)	O ‖ P - OH stretching
					1590	N-H bending of the dopant
					1401	C-H stretching of the dopant
	1295	1299 (s)	1300 (s)	1301 (s)	1304 (s)	P=O stretching
					1250	C-N-H stretching of the dopant
	1100	1101 (s)	1102 (s)	1101 (s)	1096 (s)	P=O stretching
	904	908 (s)	904 (s)	908 (s)	898 (s)	P-O-H stretching
					800	N-H wagging of dopant
	535	539 (s)	537 (s)	537 (s)	533 (s)	HO-P-OH bending
					483	N-H Torsional oscillation of dopant

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

2.2. Characterisation studies

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with CuK_{α} (λ = 1.54598 Å) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064 nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000 cm^{-1} operating at 200 mW power at the samples with a spectral resolution of 2 cm^{-1}. The IR spectra were also recorded on Shimadzu–800, FTIR spectrometer in the region 400 – 4000 cm^{-1}. The frequency for all sharp bands is accurate to ± 1 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 of 200-1200 nm range using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Kurtz SHG test was performed to find the non- linear optical property of KDP, doped KDP (doped with metal ions and amino acid). The crystal was illuminated using Spectra – Physics Quanta-Ray DHS2 Nd-YAG laser, using the first harmonics output of 1064 nm with a pulse width of 8 ns.

3. Results and discussion

The dopants sodium and L-Arginine are expected to substitute for potassium ions in KDP lattice due to their valency as well as their similarity of ionic radius. However, the aluminium ions can occupy the interstitials instead of the potassium sites. The partial substitution of potassium ions may be explained as the consequence of the following chemical reactions.

$$2\,KH_2PO_4 + Na_2CO_3 \rightarrow 2\,NaH_2PO_4 + K_2CO_3$$

$$KH_2PO_4 + (CH_2)_3C_2N_2H_3(NH_2)_2COOH \rightarrow (CH_2)_3C_2N_2H_3(NH_2)_2CO\text{-}H_2PO_4 + KOH$$

Earlier studies have reported that selective adsorptions of metallic cation suppress the growth of surfaces like the prismatic [4-7] section (100) or pyramidal section (101) of KDP crystals. The suppression is explained by the pinning effect of impurities on the step growth of the crystal and the adsorption model of impurity on the crystal. It is well known that metallic cations (Al^{3+}, Na^{+}) influence the growth of the prismatic section of KDP crystals and change the habit from the needle like towards pyramidal. $H_2PO_4^{2-}$ anions appear on the prismatic surface of the crystals. Cations play a significant role in suppressing the crystal growth of the prismatic section. In this connection, the dopants play an important role in the habit modification of the doped crystals (Fig. 1).

Powder XRD spectra for the pure and doped KDP are as shown in Fig. 2. X-ray studies revealed that the structures of the doped crystals are slightly distorted compared to the pure KDP crystal. This may be attributed to strains in the lattice by the absorption or substitution of metal ions and amino acid. 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.

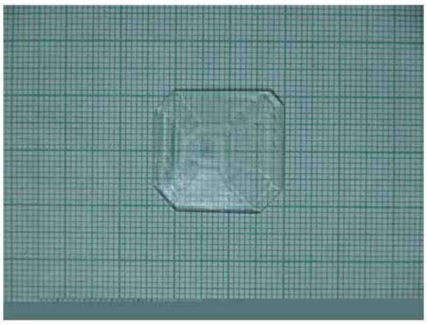

Fig. 1. L-Arginine doped KDP crystal.

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.

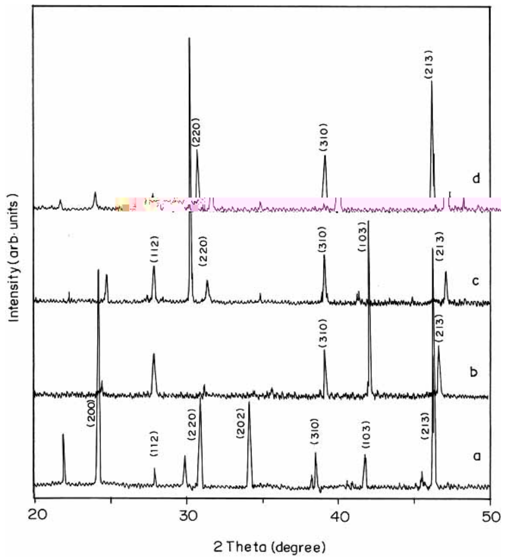

Fig. 2. Powder XRD Pattern of (a) Pure, (b) Al, (c) Na, (d) L-Arginine doped KDP single crystal.

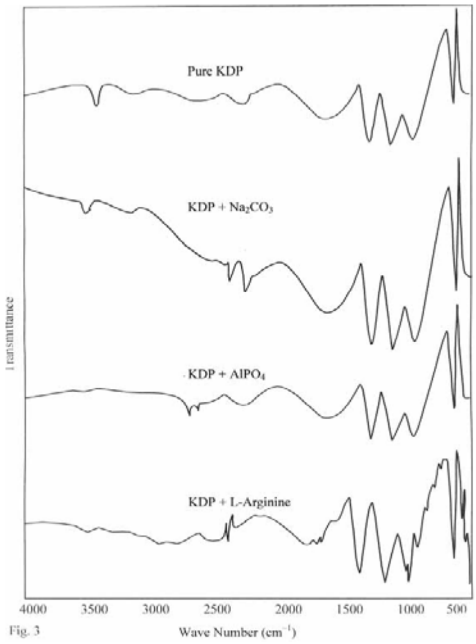

Fig. 3. FT-IR spectra recorded for the pure and doped KDP crystals.

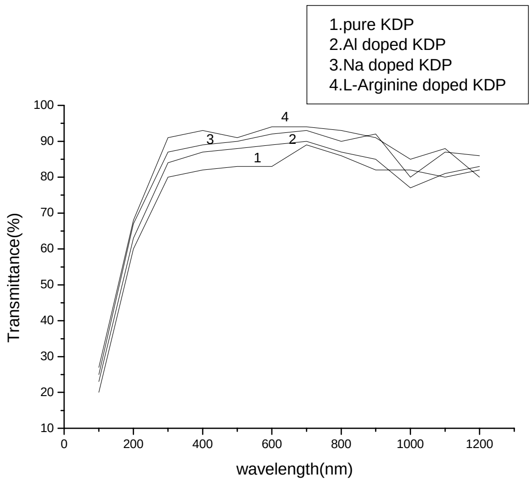

Fig. 4. UV-visible transmission spectra (a) Pure, (b) Al, (c) Na, (d) L-Arginine doped KDP single crystal.

The hardness measurements were made using the Vickers pyramidal indentor for various loads. The maximum value of hardness for cleavage plane of KDP crystal is found to be 165.79 kg/mm^2. Addition of impurities in KDP, extensively modifies the hardness values and the doped KDP crystals are much harder than the pure crystal. The hardness values of the pure and doped KDP crystals are tabulated in Table 2.

Table 2. Microhardness values of pure and doped KDP.

S.No	Crystal	Microhardness (kg/mm^2)
1.	KDP	165.79
2.	KDP +Na_2CO_3	168.67
3.	KDP+$AlPO_4$	169.24
4.	KDP+L-Arginine	171.54

FT-IR spectra for pure and doped KDP crystals are as shown in Fig. 4. The frequencies with their relative intensities obtained in FTIR of pure and doped KDP and their most probable assignments are presented in Table 1. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data [12-13]. The values of bond length and bond angles were taken from Sutton's table [12]. 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 inplane 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. There is a broad strong absorption between 1500 cm^{-1} and 1700 cm^{-1} resulting from hydrogen [4] bonded N - H stretching bands. Absorption in this region is characterized by fine structure on the lower wave number side of the band.

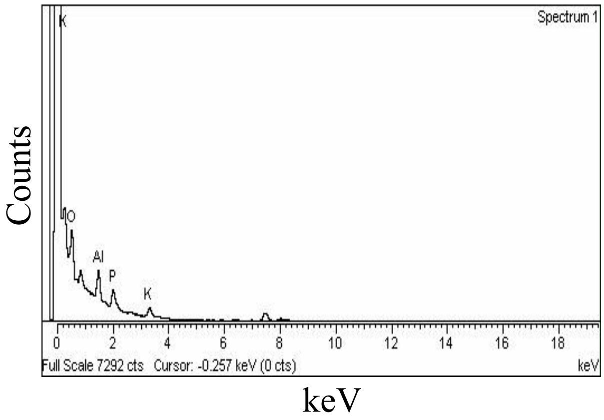

Fig. 5. EDAX of metal ions doped KDP crystals.

The bands which appeared at 3600 cm^{-1} in pure KDP, KDP doped with Na_2CO_3 and L-Arginine were assigned to free O–H stretching. The very weak bands indicate the presence of low concentration of Na and L-Arginine 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 + L-Arginine 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}(44 cm^{-1}) in KDP doped with Na_2CO_3 and at 3255 cm^{-1} (85 cm^{-1}) in KDP doped with L-Arginine 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 1). The present IR study on pure and doped KDP clearly indicates the effect of dopants 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. The study also confirmed that the dopants had entered the lattice sites of tetragonal KDP. The second harmonic signal, generated in the crystal was confirmed from the emission of green radiation by the crystals.

The EDAX data of metal ion doped KDP crystals are shown in Fig. 5.

4. Conclusions

Optically clear KDP and doped KDP (Al, Na and L-Arginine) crystals with dimension up to 25 × 22 ×10 mm^3 have been grown by a slow evaporation technique and also by a slow cooling technique. Powder XRD was used to analyse 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 Å is being replaced by Al^{3+} ion (0.535 Å) and Na^+ (1.02 Å), 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.

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