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Effect of irradiation of swift heavy ions on dyes doped potassium dihydrogen phosphate crystals for laser applications

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The organic dyes (Amaranth, Rhodamine and Methyl Orange) were introduced in Potassium Dihydrogen Phosphate (KDP) crystals. Influences of super saturation and dye concentration in the solution, on the color and crystal habit of KDP, were observed. The highly super saturated solutions produce entirely colored crystals. The concentration of dopants in the mother solution was varied from 0.1 mole/L to 10-mole/L. The studies on pure and doped KDP crystals clearly indicate the effect of dopants 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. This letter reports room temperature MeV Li^+ ion irradiation induced depletion of hydrogen from single crystalline Potassium Dihydrogen Phosphate, which has wide applications as a non linear optical material in optoelectronics technology. Irradiations have been performed using 50 MeV Li^+ ions up to a maximum dose of 2.4×10^{15} ions/cm^2. Simultaneously, by detecting the elastically recoiled Li atoms allows to recover the hydrogen profile. A possible explanation of these phenomena is suggested.

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1. Introduction

One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Potassium Dihydrogen Phosphate (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 [1-4]. The understanding of fundamental light-matter interaction has been a driving force in the several areas of optical technology.

KDP finds widespread use as frequency doublers 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 analyze 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 dyes (Amaranth, Rhodamine and Methyl Orange). The effects of impurity atoms [5-8] on the quality and performance of the material are analyzed. 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, 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 [9-10]. In the recent years, 50 MeV Li^+ ion implantation (up to dose of 10^{16} ions/cm^2) has been used to produce optical waveguides in a large number of materials like oxides (Al_2O_3, SiO_2), phosphate ($KTiOPO_4$), niobates ($LiNbO_3$, $KNbO_3$) etc., for use in the optoelectronic technology. The desired changes [11] in optical properties are brought about by several process, viz., changes in stoichiometry properties of new phases, structural changes, defects produced by the electronic and nuclear energy loss, volume expansion in the nuclear damage region, stress effects etc. occurring during implantation.

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/L 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 32.75 grams/100 ml at 40 °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 nucleation. Seed crystals (Fig. 1 and Fig. 2) with perfect shape and free from macro defects were used for growth experiments. Large single crystal of KDP and doped KDP were grown using a constant temperature bath (CTB), controlled by the Indtherm temperature programmer/controller. The mother solution was saturated using the initial pH values, 4.5, 4.6, 4.8, 4.5, and 4.25 for Amaranth, Rhodamine and Methyl orange dopants respectively. The growth was carried out for more than 20 days by keeping the bath at a temperature of 38 °C.

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 40 °C. The solution was kept for a few weeks at 40 °C. 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 was used for the bulk growth of dye doped KDP crystals. Transparent, good quality crystals were obtained after 20 days.

Fig. 1. Amaranth dye doped KDP crystal.

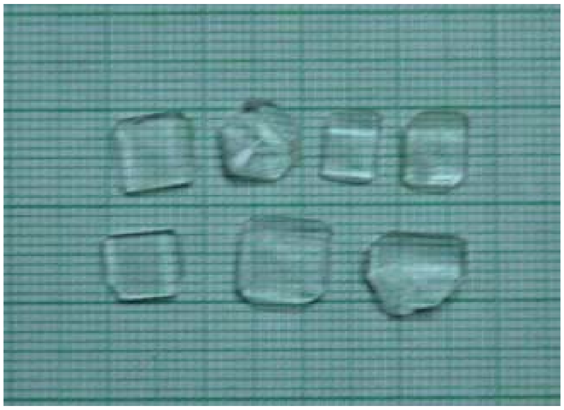

Fig. 2. Seed crystals of Rhodamine doped KDP crystal.

Well polished, transparent, single crystalline KDP samples, procured from the Crystal Growth Centre, Anna University, Chennai, India, were used for Li^+ irradiation at room temperature. The samples were irradiated with 20 MeV Li ions by using a 15 UD Pelletron Accelerator at the Inter University Accelerator Centre, New Delhi, India. These studies were performed at room temperature in an experimental chamber under vacuum better than 10^{-7} Torr. The beam was scanned a 10 mm ×10 mm area on the sample using a magnetic beam scanner. The dose of charge accumulated in the sample was measured separately in terms of the fluences and the following fluences were used: 1×10^{11}, 1×10^{12}, 1×10^{13} and 1×10^{14} ions cm^{-2}. According to the calculation of stopping and ranges of ions in matter (SRIM) [8], the projected range (Rp) of the 20 MeV Li ions in KDP is 7.5 μ m. Also the corresponding end of range lateral distribution of straggling is 4.567MeV (mg $cm^{-2})^{-1}$ and the longitudinal distribution of straggling is 7.5 MeV (mg $cm^{-2})^{-1}$. The atomic force microscopy (AFM) image was acquired using the Vecco Digital Nanoscope III AFM in the show mode.

2.2. Characterization 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 = 1.5405 Å) 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 – 4000 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 ± 1 cm^{-1} [16]. Kurtz SHG test was performed to find the non- linear optical property of KDP (doped with metal ions and dyes). 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 aluminium are expected to substitute for the potassium ions in the KDP lattice due to their valence as well as their similarity of ionic radius. X – ray diffraction pattern of the irradiated samples with the ion fluencies of 1×10^{11}, 1×10^{13} and 1×10^{14} cm^{-2} is shown in Fig. 3. It is observed that the prominent peak intensity at an angle (2θ) of 39.3°, which corresponds to bulk KDP, decreases as a function of the incident ion fluence. Further, the full width half maximum (FWHM) values of the lines increased with the fluence. Since the X – ray-probing depth depends upon the angle of incidence; we have selected the angle of incidence in a wide range. Therefore, in our case, the X – ray penetrates more than 7 micrometers in the sample. However, it might be due to creation of an extra plane of interstitials by irradiation.

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

SPECIES	Calculated Frequencies cm $^{-1}$	Observed IR frequencies and intensities				
		Pure KDP	KDP doped with Amaranth	KDP doped with Rhodamine	KDP doped with Methyl Orange	Assignments
A/E	2705	3600 (vw)	4600 (vw)	3345(vw)	3450 (vw)	Free O-H Stretching
	3333	3340 (w)	3355 (vw)	3250(vw)	3340 (w)	O-H Stretching Hydrogen bond
	2919	2924 (vw)	2524 (vw)	2950(vw)	2924 (vw)	P-O-H asymmetric stretching
	2494	2844 (vw)	2744 (vw)	2450(vw)	2844 (vw)	P-O-H asymmetric stretching
	2361	2466 (w)	2566 (cw)	2600(cw)	2466 (w)	O ‖ P - OH stretching
	2358	2162 (vw)	2462 (s)	2400(s)	2362 (vw)	P-O-H bending
	1650	1655 (m)	1459 (vw)	1750(m)	1540(m)	O ‖ P - OH stretching
	1400	943	1690	1650	1540	N-H bending of the dopant
	1095	1232	1501	1450	1544	C-H stretching of the dopant
	1295	1299 (s)	1404 (s)	1380(s)	1280(s)	P=O stretching
	1046		1350	1300	1420	C-N-H stretching of the dopant
	1100	1101 (s)	1096 (s)	1022(s)	1028(s)	P=O stretching
	904	908 (s)	858 (s)	870(s)	840(s)	P-O-H stretching
	675	879	813	800	654	N-H wagging of dopant
	535	539 (s)	503 (s)	450(s)	447(s)	HO-P-OH bending
	400	307	445	440	400	N-H Torsional oscillation of dopant

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

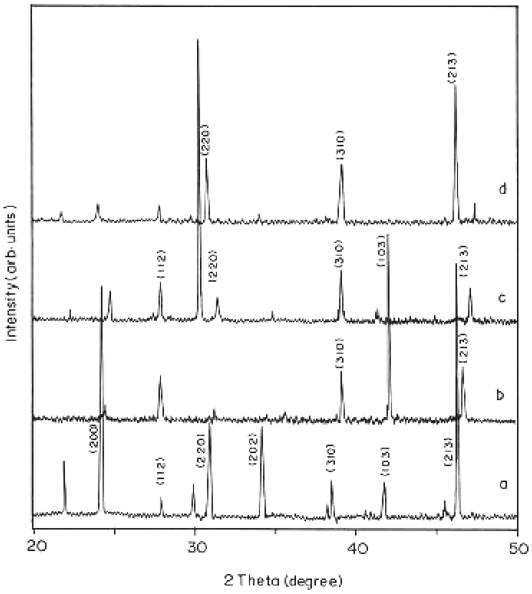

Fig. 3. XRD spectra of (a) Pure (b) Amaranth (c) Rhodamine and (d) Methyl Orange doped KDP crystal.

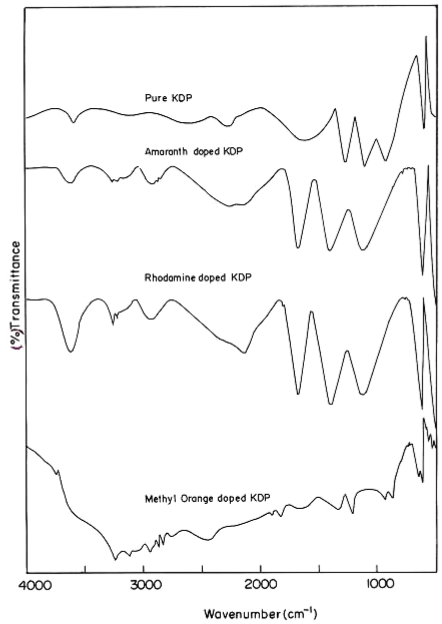

Fig. 4. FT-IR Spectra of dyes doped KDP crystal.

FT-IR spectra for the 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 [17].

There is a broad strong absorption between 1500 cm^{-1} and 1700 cm^{-1} resulting from hydrogen [18] bonded N-H stretching bands. Absorption in this region is characterized by the fine structure on the lower wave number side of the band. The very weak bands indicate the presence of low concentration of Amaranth in KDP. The absence of even such a weak band in the case of KDP doped with Rhodamine indicated the strong interaction 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 + Amaranth and KDP + Rhodamine respectively. The absence of this peak in KDP doped with Amaranth supported again the strong interaction 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 Amaranth and at 3255 cm^{-1} in KDP doped with Methyl Orange 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 [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 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 [20-22] 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.

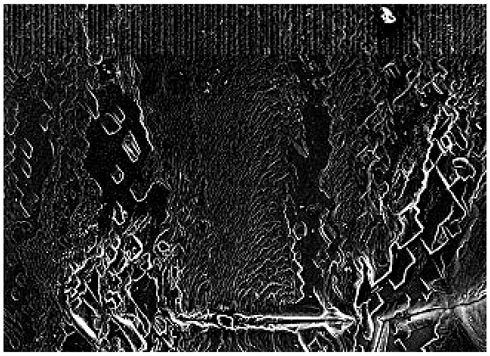

Fig. 5. SEM photograph of Amaranth doped KDP crystal.

The SEM picture (Fig. 5) 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 creates a surface layer, which prevents the entry of impurities and thereby it helps to grow the crystal with high crystalline quality. The crystal surface morphology of pure and Li^+ ion irradiated KDP sample was investigated by AFM and it is shown in Fig. 6.

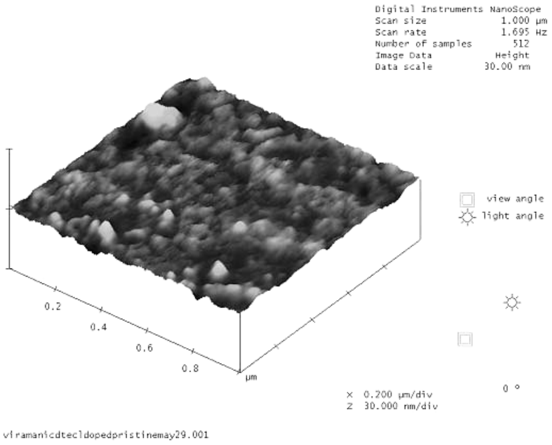

Fig. 6. AFM photograph of Amaranth doped KDP (after irradiation).

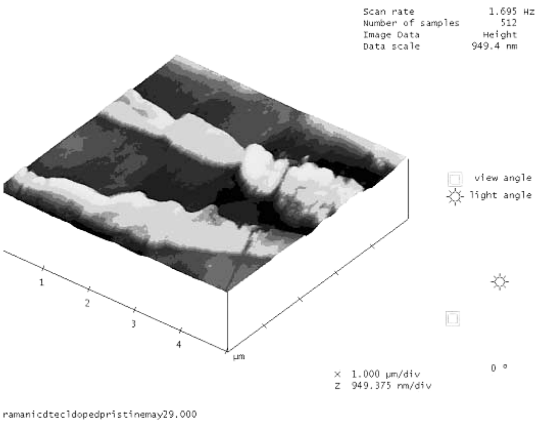

Fig. 7. AFM photograph of Amaranth doped KDP (after irradiation with supplementary magnification).

As evident, while the pristine KDP sample appears to be smooth, ordered arrangement with least dislocation and corresponding Root Mean Square (RMS) surface roughness value is 0.0114 nm, the Li^+ ion irradiated KDP sample demonstrate smoothness and ordered arrangement in their surface morphology (Fig. 7) gets distributed due to lattice disorder. It appears as twinning with minor cracks and the corresponding RMS surface roughness value increases to 6.156 nm. Similar observation was found from Scanning Electron Microscopy (SEM).

4. Conclusions

We have grown single crystals of KDP and organic dyes doped KDP and characterized them by employing FT-IR and X-Ray diffraction methods. The doped crystals show good second harmonic generation efficiency. There is a different class of non-linear optical materials, which possess important optoelectronic properties. However, to fabricate optical devices using these materials, a detailed study of ion induced stoichiometric and structural changes occurring in them are necessary. Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiations such as X-ray and UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied. In this paper, it has been shown that irradiation modifies the optical properties of KDP crystal.

Li^+ irradiation leads to the development of a well-defined surface H peak. The depletion of hydrogen from the KDP sample in terms of the possible bond-breaking mechanism occurs. Due to beam interaction, an electron moves to the conduction band leaving behind the free hole, which can get self–trapped and configurationally changes occurring in the neighbouring structural units. The irradiation determines diffusion of the dyes uniformly in the crystal.

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