Second harmonic generation and laser damage threshold studies of pure and doped potassium dihydrogen phosphate single crystals

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Single crystals of Potassium dihydrogen Phosphate (KDP) have been grown from water using slow evaporation technique at constant temperature. Good quality seed crystals were obtained. The diffraction data of the grown crystals were determined by Powder X-Ray Diffraction (XRD). The XRD data were indexed using Unit cell software and the lattice parameters were calculated. The results were in good accordance with the literature. The KDP crystals were doped with cobalt, nickel, manganese, paranitrophenol, in view of modification of the properties of KDP crystal. It is found from the Powder XRD, that the incorporation of dopants slightly alters the lattice parameters. The Second Harmonic Generation (SHG) studies were carried out using Kurtz Perry technique. The SHG efficiencies of the doped crystals were found to be 1.12, 1.08, 1.08 and 1.20 times greater than the standard KDP crystals. The laser damage thresholds were determined for the pure and doped KDP crystals using single shot laser mode. It is found that the addition of dopants increases the damage threshold of the crystals, making it suitable for applications.

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1. Introduction

Ferroelectrics due to relatively high nonlinear efficiency and dielectric permittivity, huge piezoelectric effect and pyroelectric properties, the possibility of the spontaneous polarization reorientation in a comparatively small field are used in a wide variety of optoelectronic devices and sensor technology, nonlinear optical and information optical storage, etc.

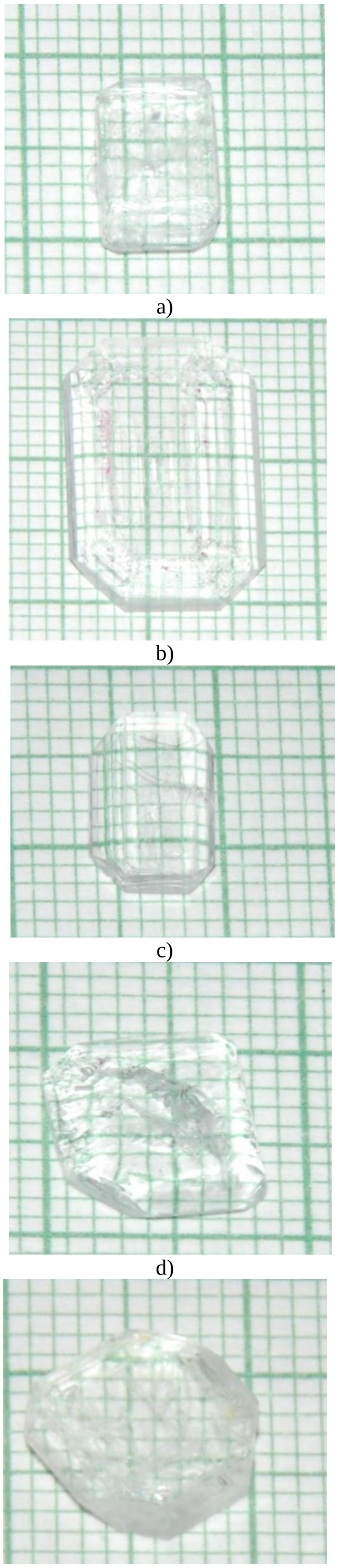
Potassium Dihydrogen Phosphate (KH_2PO_4) single crystals have good laser damage threshold, appreciable nonlinear optical coefficients, fine structural quality and mechanical properties. KDP crystals have enormously device applications. The electro-optic effect in KDP is used to obtain phase and amplitude modulations. The acousto-optic tunable filters have been developed using KDP [1-5]. Rapid growths of large size (40 - 55 cm) KDP crystals as well as rapid growth of KDP crystals with additives [6] have given way to obtain perfect KDP crystals for device application on an industrial scale. These crystals are distinguished by high efficiency of non-linear conversion and a wide optical transparency range which extends far (up to 176 nm) to the short-wavelength region of the spectrum [7].

The present investigation deals with the growth of pure, cobalt, nickel, manganese and paranitrophenol doped KDP crystals by slow solvent evaporation technique. The grown crystals have been subjected to powder XRD, laser damage threshold, second harmonic generation studies.

2. Growth of pure and doped KDP single crystals

Potassium dihydrogen phosphate (KDP) of analytical grade (AR) was procured from Loba Chemicals. Slow evaporation method was used to grow the KDP crystals. The analytical grade KDP was further purified by repeated recrystallization process using water as solvent.

The solubility of KDP crystal was determined by many researchers in many solvents like water, acetone, dimethyl formamide, acetic acid, methanol, ethanol, ethyl acetate. In the present work, water was used as the solvent for the growth of KDP crystals. The purified salt of KDP was dissolved in water and stirred continuously for 3 hours using a magnetic stirrer to obtain a homogeneous mixture. The solution was filtered twice using ultra micro pore filter paper. The resulting solution is kept in a beaker and covered for controlled evaporation. After a period of 5 days, small crystals were obtained and these crystals were suspended in the mother solution to get good quality crystals as shown in the Fig. 1. For doped crystals, the percentage of dopants was 1 mole %. The calculated amount of cobaltous chloride hydrate (0.65g), nickel chloride hexahydrate (0.64g), manganese sulphate (0.76g), paranitrophenol (0.70g) were dissolved in 50 ml of water and then mixed with the mother solution. The solutions of the doped KDP crystals were filtered and good seed crystals were obtained over a period of 5 days. These seed crystals were suspended in the mother solution to get good quality crystals. The photographs of the pure and the doped KDP crystals are presented in Fig. 1 (a) to 1 (e) respectively.



a)

b)

c)

d)

e)

Fig. 1. Photograph of (a) pure (b) cobalt (c) nickel (d) manganese and (e) paranitrophenol doped KDP crystals

3. Results and discussion

3.1. Powder X-ray diffraction studies

X-ray powder diffraction (XRD) was performed on the grown crystals, to study the effect of doping in KDP crystals with cobalt, nickel, manganese, paranitrophenol. The powder XRD pattern was recorded using powder SEIFERT
X-ray diffractometer with $CuK_{\alpha 1}$ Radiation (λ = 1.5406 Å).The powdered samples were scanned over the range 20^o - 80^o at a rate of 1^o per minute. The powder XRD data obtained were indexed with the help of UNIT CELL program.

The lattice parameters of the pure and doped crystals are shown in Table 1. The peaks in the XRD patterns which were obtained in the present work are slightly shifted due to the addition of dopants which indicates that the dopants have entered in to the lattice of the crystal. This is the cause for the change in the lattice parameters and cell volume on doping. A similar effect was observed by Prasanyaa et al., [8] by doping KDP crystal with L-arginine trifluroacetate. Parikh et al., [9-10] and Kumaresan et al., [11] have studied the powder X-ray diffraction for the doped KDP crystals. The indexed powder pattern is shown in Fig. 2.

Table 1. Lattice parameters of pure and doped KDP crystals by powder X-ray diffraction

Crystal	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**	***V*** **(Å)^3**
Pure KDP	7.436	7.436	6.979	385.92
Cobalt doped	7.427	7.427	6.936	382.65
Nickel doped	7.408	7.408	6.992	383.70
Manganese doped	7.431	7.431	6.955	384.10
Paranitrophenol doped	7.449	7.449	6.936	384.91

3.2. Second harmonic generation studies

The nonlinear optical property of the grown single crystal is tested by passing the output of Nd: YAG Quanta ray laser through the crystalline powder sample. A Q-switched, mode locked Nd: YAG laser was used to generate about 6 mJ/pulse at the 1064 nm fundamental radiation. This laser can be operated in two modes. In the single shot mode, the laser emits a single 8 ns pulse. In the multishot mode, the laser produces a continuous train of 8 ns pulses at a repetition rate of 10 Hz. In the present study, a single shot mode of 8 ns laser pulse with a spot radius of 1mm was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 6 mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm.

The photodiode detector and oscilloscope assembly measure the light emitted by the sample. Microcrystalline powder of urea or KDP is taken in a similar capillary tube sealed at one end for comparison. The intensity of the second harmonic output from the sample is compared with that of either KDP or urea. Thus, the figure of merit of SHG of the sample is estimated.

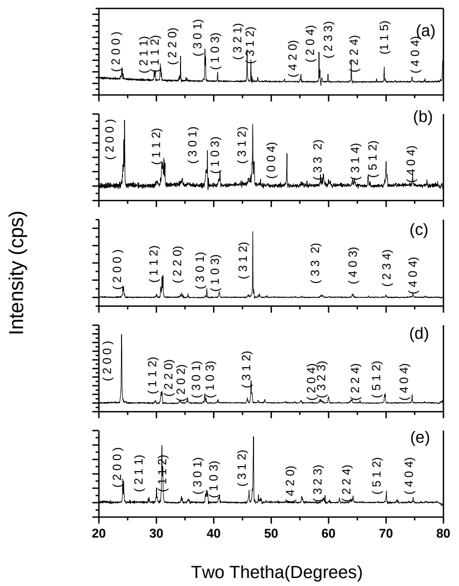


Fig. 2. Powder X-ray diffraction patterns of (a) pure (b) cobalt (c) nickel (d) manganese and (e) paranitrophenol doped KDP crystals

The pure and doped KDP crystals were made into fine powders of the size of 20 µm. The micro particles were exposed to 1064 nm laser beam from a pulsed Nd: YAG laser to test the second harmonic generation efficiency. An input pulse of 5.8 mJ/pulse was supplied. Signal amplitude in millivolts on the oscilloscope indicates the efficiency of the sample. The pure KDP crystal gave an output 24 mV whereas the doped KDP crystal showed an increase in the SHG efficiency. The cobalt, nickel, manganese and paranitrophenol doped KDP crystal gave an output of 27 mV, 26 mV, 26 mV and 29 mV respectively. It is found that the output voltage varies in the case of doped crystals, although there is no appreciable change in the lattice parameters from powder X-ray diffraction indicating the dopants have entered the lattice of the crystal. Thus, the SHG efficiencies of the doped crystals are 1.12, 1.08, 1.08 and 1.20 times greater than the standard KDP crystals respectively.

3.3. Laser damage threshold studies

Laser damage threshold is an important material parameter, the knowledge of which is essential for using the crystal as an NLO element in various applications involving large laser input power like frequency doubling, optical parametric processes, etc. In fact, laser induced damage in optical materials remains the limiting factor in the development of high power laser systems and optoelectronic devices. Although the optical damage has been studied in materials ever since the advent of high power lasers, much still remains to be learnt about the interaction of a high intensity laser beam with materials

The laser damage thresholds were determined for the pure and doped KDP crystals using single shot laser mode. A Q-switched Nd: YAG laser (pulse duration 47 ns) at 1064 nm was focused on the sample using a 10 cm focal length lens. The incident fluence was varied using neutral density filters. The spot radius ($1/e^2$ points) was estimated by measuring the transmission of the laser beam through a known aperture (Diameter 100 µm) and is 126 µm. Reflection losses (2.9 % at 20^o for KDP) were taken into account for estimating the incident fluence. The input energy was 20.5 mJ. The beam diameter used was 8 mm. The energy required to damage the crystals is given in Table 2. The laser damage photographs are shown in Fig. 3. It is found that the laser damage threshold of pure and doped KDP crystals are in the range 0.25 GW/cm^2 to 0.30 GW/cm^2 which is consistent with the already available literature for pure KDP [12]. It is also observed that doping the KDP crystals increases the laser damage threshold as reported by Pritula et al [7].

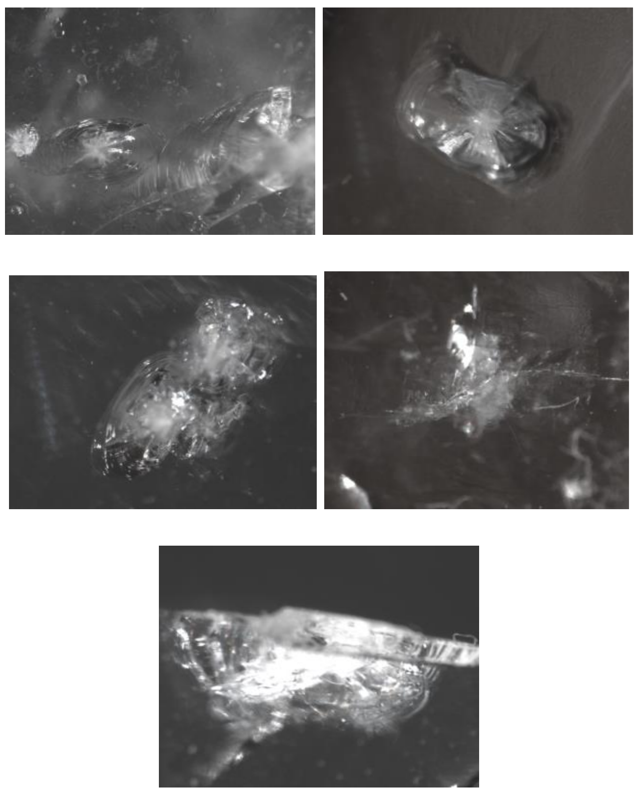


Fig. 3. Laser damage photographs of (a) pure KDP (b) cobalt (c) nickel (d) manganese and (e) paranitrophenol doped KDP crystals

Table 2. Laser Damage Energy values of Pure and doped KDP crystals

S. No	Crystal	Laser Damage Threshold (GW/cm^2)
1.	Pure KDP	0.25
2.	Cobalt doped KDP	0.27
3.	Nickel doped KDP	0.26
4.	Manganese doped KDP	0.26
5.	Paranitrophenol doped KDP	0.27

4. Conclusion

Fine crystals of pure, cobalt, nickel, manganese, paranitrophenol doped KDP have been grown by slow solvent evaporation technique. The various planes were indexed using powder XRD. The SHG studies and laser damage threshold studies indicate that doped KDP crystals have enhanced NLO efficiency and laser damage threshold values respectively Thus, the good laser damage threshold values, SHG efficiency makes the pure, doped KDP crystals, a promising candidate for NLO applications.

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