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On the growth habit of NLO N, N' dimethyl urea doped KDP crystals

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Pure and N, N' Dimethyl Urea doped Potassium Dihydrogen Phosphate (KDP) single crystals have been grown from solution by slow evaporation of the solvent technique for nonlinear optical applications. The change in growth habit of doped KDP crystals has been reported. On the grown crystals, FT-IR, UV-VIS-NIR transmission and powder X-Ray diffraction studies have been performed. The improvement in Second Harmonic Generation efficiency has also been confirmed by Kurtz and Perry method.

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1. Introduction

The Nonlinear Optical (NLO) crystals have found to be central to the numerous applications in science and technology [1-4]. Potassium Dihydrogen Phosphate (KDP) single crystals have been widely used and thoroughly studied NLO crystal. The attempts have been made to modify the properties and growth rate of the KDP crystal by either changing the growth conditions or by adding different impurities [5-11].

Urea has been reported as a NLO material. Although it's optical and mechanical properties are comparable to those of KDP, but its crystallization and handling is rather difficult as it is highly hygroscopic. Different derivatives of urea have been studied for NLO applications. Some of them found useful for NLO applications [12-17]. NLO properties of N, N' Dimethylurea (NNDMU) have been recorded [18]. In the present work, an attempt has been made to catch the properties of Urea derivative and add with KDP to investigate the effects. The growth of NNDMU doped KDP crystals and their characterizations have been reported first time. Improvement in the SHG efficiency has been reported. 2mol% NNDMU doped KDP crystal found to be 1.39 times more efficient than pure KDP. Modification in the growth habit has also been observed.

2. Experimental

2.1 Bulk crystal growth

The solubility's of the pure and 2mol%, 4mol% and 6mol% NNDMU doped KDP crystals in double distilled water in the temperature range 30-60°C were measured gravimetrically. The materials have positive solubility gradient with temperature. Thus double distilled water was used as a solvent through out the experiment.

Good quality crystals of pure and 2mol%, 4mol% and 6mol% NNDMU doped KDP were grown within 10-15 days. In doped crystals, growth rate along c-axis is found to be decreased. The pH of the solutions was ranged from 4.5 to 4.7. The photograph of some of the grown crystals has been shown in Fig. 1.

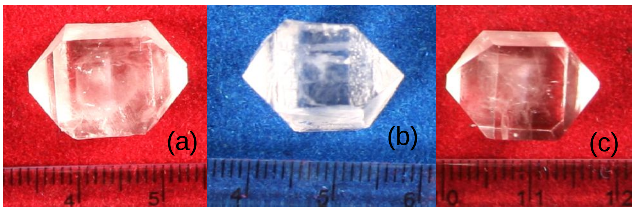

Fig. 1. Photographs of (a) 2mol%, (b) 4mol% and (c) 6mol% doped KDP crystals.

2.2 Characterization

The FTIR study was carried on the pure and doped KDP crystals to confirm the doping of the dopant in the crystals. SHG efficiency was measured by employing Kurtz and Perry method. Transparency of the crystals in the range 190-1100nm was studied by using UV-1700 SHIMADZU Spectrophotometer. Powder XRD patterns were recorded on XPERT Pro Diffractometer and analyzed. The results have been presented.

3. Results and discussion

3.1 Growth habit

During the crystal growth of the NNDMU doped KDP crystals, regular observations were taken. Growth rate along c-axis is found to be decreased and tapering of faces occurred along c-axis in the doped crystals. It has evidence that the metallic cations and dyes influence the growth of prismatic (100) section and pyramidal (101) section of KDP crystals and changes the crystal habit to the needle-like crystal toward pyramidal direction. $H_2PO_3^{2-}$ anions occupy the site on the prismatic surface of the crystals. Anion species of organic and inorganic compounds having larger size adsorb on the prismatic surface of the crystals reduces the growth rate [19-23]. In this case the decrease in the growth rate along c-axis is possibly because of accommodations of the bigger size cation $(CH_3)_2N\text{-}CO(NH_3)^+$ at the place of relatively smaller size cation K^+.

3.2 SHG efficiency measurement

Kurtz and Perry method was employed to measure the SHG efficiency of the grown doped crystals in reference with the pure KDP [24]. In the measurement, Q-switched, mode locked Nd:YAG laser of wavelength 1064nm of peak power 2.35mJ, pulse duration 8 ns and repetition rate 10Hz was used. The output was measured at wavelength 532nm. The SHG efficiencies of the doped crystals found to be more with reference to pure KDP (Table 1).

Table 1. SHG efficiencies of pure and NNDMU doped KDP crystals.

	Measured out put	SHG efficiency
Pure KDP	357mV	1
2mol% NNDMU doped KDP	496 mV	1.39
4mol% NNDMU doped KDP	464 mV	1.30
6mol% NNDMU doped KDP	411 mV	1.15

3.3 Fourier transform infrared (FT-IR) study

The FT-IR spectra of pure and NNDMU doped KDP crystals (**Fig. 2**) were recorded on Perkin Elmer FT-IR Spectrophotometer within the wavenumber range 600 to 4000cm^{-1}.

In the FTIR spectrum of pure KDP crystal, the observed absorption peak at 3734.75cm^{-1} corresponds to the P-OH stretching, 2367.30 cm^{-1} to O-H and P-OH stretching, 1753.44 cm^{-1} to the P-O-H bending, 1281.08 cm^{-1} to O-H deformation and P=O stretching and 912.19 cm^{-1} attributed to P-OH stretching and HO–P–OH bending. In the FT-IR spectra of NNDMU doped KDP crystals, same peaks with slight change in positions due to hydrogen bonding have been observed with some additional peaks. These additional peaks observed in the range 3000 cm^{-1} -2700 cm^{-1} corresponds to the C-H stretching. The peaks at 1408.16 cm^{-1} and 1457.88 cm^{-1} are attributed to the C-H deformation, C=O and N-H stretching. The peaks at 1043.39 cm^{-1} and 1017.67 cm^{-1} are assigned to the C-H, O-H Deformation and C-O stretching, which confirms the doping of the crystals with NNDMU.

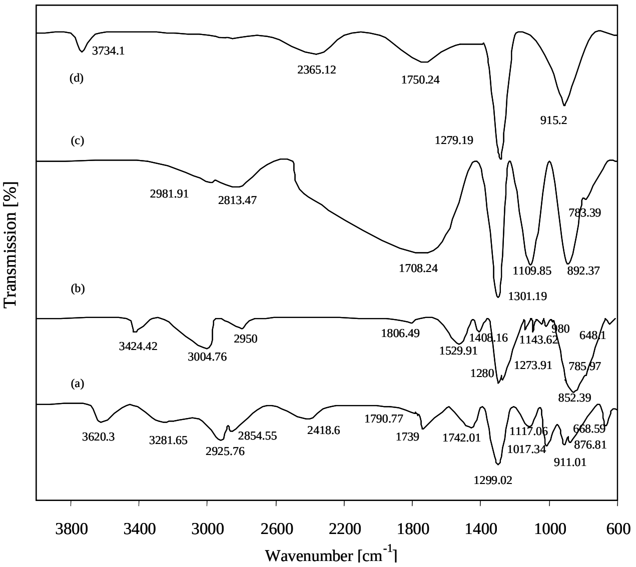

Fig. 2. FT-IR spectra of (a) 2mol%, (b) 4mol% and (c) 6mol% NNDMU doped KDP and (d) pure KDP crystals.

3.4 UV-VISIBLE-NIR Spectroscopy

The transmission of the crystals over wavelength range 190nm-1100nm was measured on UV-1700 SHIMADZU SPECTROPHOTOMETER. The increase in the transparency of the doped crystals has been observed. The increase in the doping level improves the fine cutoff at lower wavelength side but no change in the cutoff wavelength has been observed. UV-VIS-NIR spectrums of

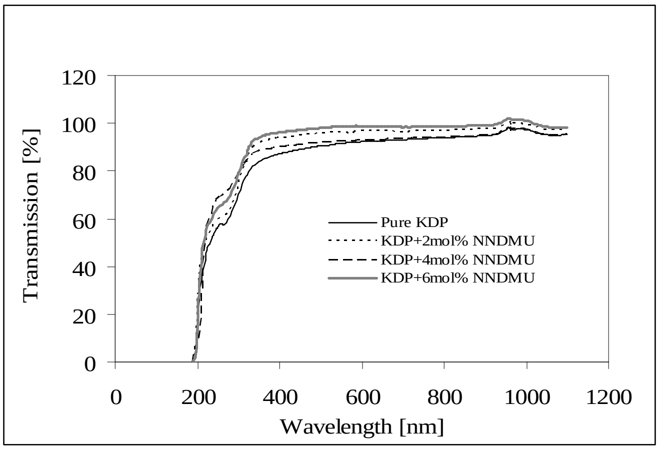

Fig. 3. UV-VIS-NIR spectra of pure and NNDMU doped KDP crystals.

3.5 XRD study

The powder XRD pattern of the pure and 6mol% NNDMU doped KDP crystals have been recorded using X-ray Diffractometer XPERT-PRO using Cu Kα radiations (1.54060Å, 40 mA, 45 kV). The powder samples were scanned in steps of 0.0170° for a time interval of 10.3359 sec over a 2θ range of 10.0144–119.9874°. The unit cell parameters have been calculated (Table 2).

Table 2. Unit cell details.

	Crystal system	Space group	Unit cell parameters
KDP	Tetragonal		a=b=7.455Å, c=6.975 Å. $\alpha=\beta=\gamma=90^0$
6mol% NNDMU doped KDP	Tetragonal		a=b=7.456Å, c=6.973 Å. $\alpha=\beta=\gamma=90^0$

4. Conclusions

The pure and NNDMU doped KDP crystals of best quality were grown from solution within two weeks. The doping in the crystals has been qualitatively confirmed by the FTIR spectroscopy.

The SHG efficiency study shows the improvement in the efficiency of the doped crystals.

Increasing transparency with concentration of dopant in the host crystal was confirmed by the UV-VIS-NIR Spectroscopy.

The XRD study of the 6mol% NNDMU crystal reveals the crystal structure and lattice parameters. Doping in the KDP crystals leads to slightly change in the lattice parameters, but the crystal system and space group of the KDP retained.

External morphology of the crystal reveals the decrease in the growth along [001] direction in NNDMU doped KDP crystals. The growth rate decreases with increasing doping level. This decrease in the growth rate is attributed to the attachment of the larger size cations on prismatic face (100).

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