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A remarkable enhancement between optical transparency and SHG efficiency on doped-KHP single crystals

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Abstract. Potassium hydrogen phthalate (KHP) single crystals are non-linear optical materials and their transmittance window are remarkably enhanced by an organic dopant such as resorcinol. The present study was mainly focused on the growth and characterization of the single-crystal KHP doped with resorcinol which was synthesized by a slow evaporation solution technique and its dimension was found to be $8 \times 7 \times 2.75$ mm^3 at ambient temperature. Vibrational assignments of the functional groups confirmed the presence of dopants. The optical behaviour of the grown crystal was explored by ultraviolet–visible–near-infrared studies which result in 99% of the transmittance with the cut-off wavelength of 250 nm. The mechanical property was analysed by the Vickers microhardness test. The apparent microhardness increases with increasing applied indentation load revealing the reverse indentation size effect behaviour. Organic impurity increases the second harmonic generation efficiency of KHP, suggesting that the molecular alignment in the presence of resorcinol results in enhanced non-linearity.

Keywords. KHP; organic dopant; FTIR; fluorescence.

1. Introduction

Materials with high second-order optical nonlinearities and optical transparency received attention from the fields such as solid state physics, fibre optic communication, optical conversion and optical data storage, etc. [1]. In semiorganic, there exists a stoichiometric bond between organic and inorganic molecules stimulating an added advantage of combined properties of both the materials [2]. Potassium hydrogen phthalate (KHP) is one of the semiorganic materials belonging to an orthorhombic system of alkali phthalate series exhibiting pyroelectric, piezoelectric, ferroelectric, elastic and nonlinear optical properties [3–5]. Hence, it has long-term stability in devices and also widely used in Q-switches for Nd:YAG and Nd:YLF, substrates for epitaxial growth of oriented polymers and a hierarchical growth of organized materials. Moreover, the organic impurities in KHP crystals will greatly influence the growth habit as well as the optical and physical properties [6]. Resorcinol is an organic compound possessing piezoelectric and pyroelectric properties. Resorcinol-based crystals revealing a variety of high-optical transmittance possibility and considerably high-second order nonlinear optics (NLO) which have been reported [7,8]. The effect of organic impurity of the meta-isomer on the characteristic properties of KHP has been analysed by a solution growth technique.

Several studies exploring the effects of the dopant on KHP have been carried out [9–11]. Hence, the present investigation is focused on elucidating the influence of the organic dopant resorcinol on structural, vibrational, optical transmittance, mechanical and nonlinear optical properties of KHP crystals which reveal the remarkable features of the adduct. An increase in the NLO property is expected due to the decrease of symmetry in the adduct compared to KHP as well as resorcinol.

2. Experimental

2.1 *Materials and methods*

The pure and resorcinol-doped crystals were synthesized by a slow evaporation technique. The laboratory chemicals such as KHP and resorcinol purchased from Loba Chemie were used after checking the physical characteristics. The homogenous solution was prepared by a slow addition of the calculated amount of dopant resorcinol into a saturated aqueous solution of KHP with continuous stirring for 3 h. The solution was maintained at a pH value of 4. The resultant homogeneous solution was allowed to evaporate under ambient conditions and transparent crystals have been harvested after a period of 10 days with dimensions up to $8 \times 7 \times 2.75$ mm^3. The purity of the crystal was attained by successive recrystallization and filtration. The photograph of a grown crystal is shown in figure 1.

3.   Results and discussion

3.1   *PXRD analysis*

Powder X-ray diffraction (PXRD) analysis was performed on a Bruker D8 advance diffractometer using a Cukα radiation source ($\lambda = 1.5406$ Å). The powder X-ray diffractograms of the doped-KHP crystal is depicted in figure 2. The sample was scanned by a diffracted beam over the range of 0–60° with a scanning rate of 0.01 s^{-1}. From the diffraction peaks, a noticeable variation was observed in the peak intensity of the doped crystal in comparison with that of pure KHP which confirms the influence of dopant ions into the KHP lattice.

The lattice parameter values of the pure and doped crystals are tabulated in table 1. A slight variation was observed in the
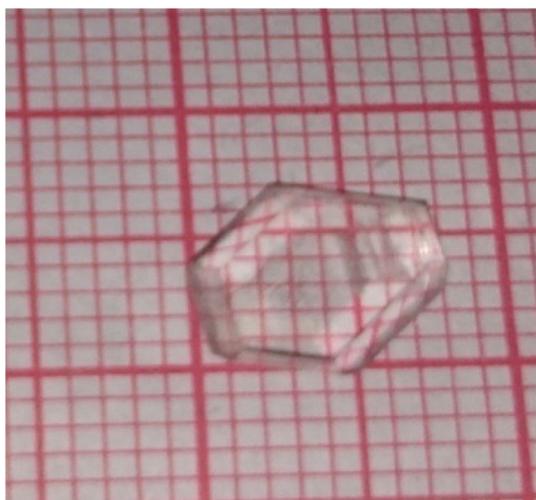
Table 1.   Lattice parameters.

Lattice parameters	Pure KHP	Doped KHP
a (Å)	9.612	9.662
b (Å)	13.312	13.264
c (Å)	6.502	6.473

lattice parameters and is due to the lattice distortion by the presence of dopant. Hence, it was confirmed that the grown crystal belongs to the orthorhombic crystal system.

3.2   *FTIR spectroscopy*

The presence of structural units in the title compound was confirmed using Fourier transform infrared (FTIR) spectroscopy by a KBr pellet technique. The FTIR spectrum of pure KHP and doped KHP in the wavelength range of 4000–400 cm^{-1} is presented in figure 3. The corresponding modes of vibrations are shown in table 2. From the spectrum, the band at 3479 cm^{-1} is the characteristic of OH stretching vibration of resorcinol. The peak at 1670 cm^{-1} assigned to carbonyl stretch of KHP. The symmetric and asymmetric stretching vibration modes of the carboxylate ion group are not much shifted in the adduct which are found at 1566 and 1386 cm^{-1}. The C–O stretching vibrations at a frequency of 1285 cm^{-1} in the pure KHP shifted to 1292 cm^{-1} in the resorcinol-doped crystal. The wagging vibrations of the C–O group yielded its peak at 691 cm^{-1}. The occurrence of C=C–C out-of-plane ring deformation is evident at 551 cm^{-1}. The above assignments are consistent well with previously reported data [12]. Thus, a corresponding broadening of the absorption band with very slight changes in the characteristic peak positions affirms the presence of dopant resorcinol in the parent lattice.
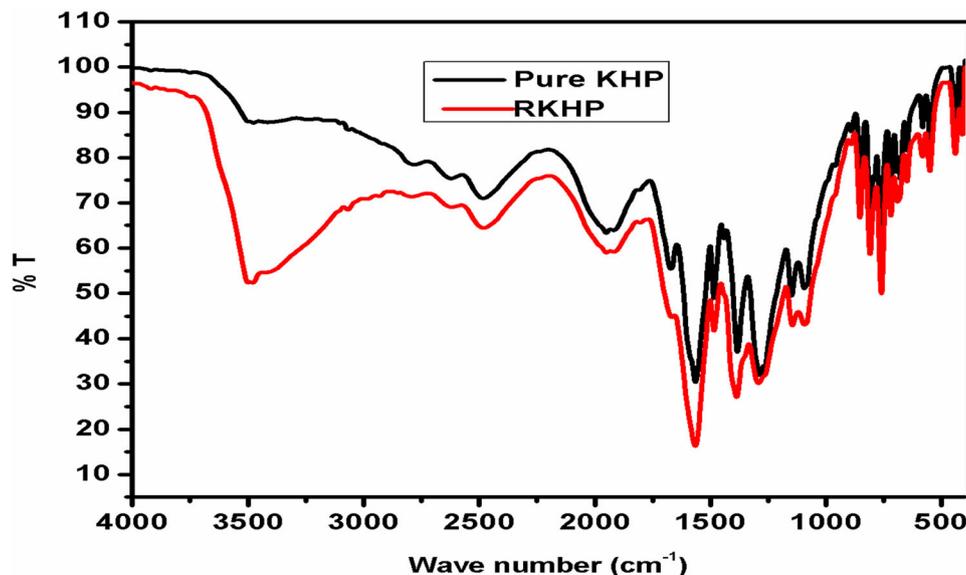

Figure 1.   Photograph of the as-grown RKHP crystal.
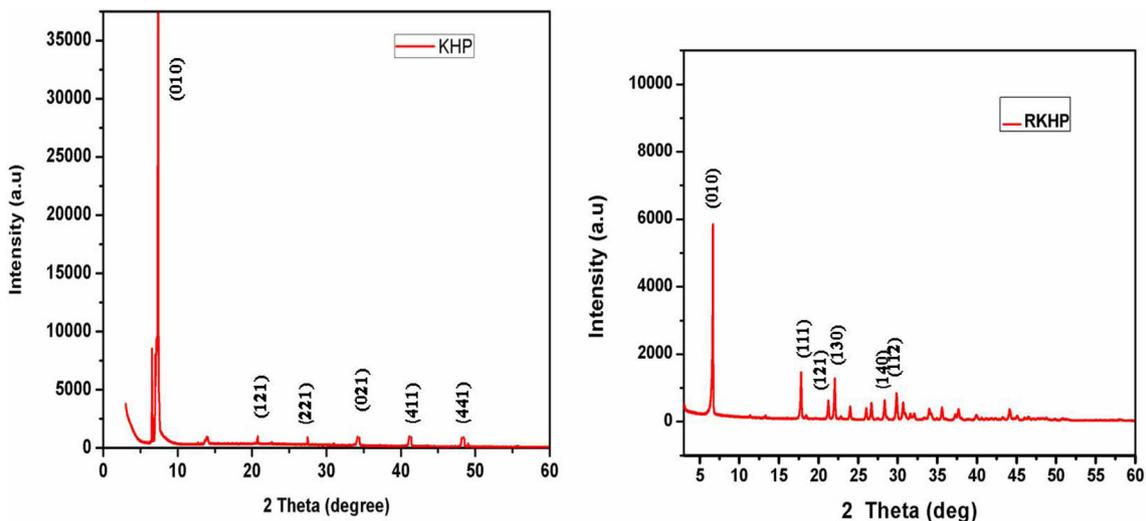
Figure 2.   PXRD patterns of pure KHP and doped RKHP.

Figure 3. FTIR spectrum in the range of 4000–400 cm^{-1}.

Table 2. Vibrational assignments.

Wavenumber (cm^{-1})		
Pure KHP	RKHP	Assignments
3476	3479	OH stretch of resorcinol
1670	1667	C=O stretch acid group
1566	1565	Asymmetric stretch of COO$^-$
1383	1387	Symmetric stretch of COO$^-$
1285	1292	C–O stretch
1094	1093	C–C–O stretching vibrations
852	853	CH out of plane bending
441	441	C–C plane bending
678	691	C–O Wagging vibration
550	551	C=C–C out of plane ring deformation

Figure 4. UV–Vis spectrum in the range of 190–1200 nm.

3.3 *UV–Vis–NIR analysis*

The assessment of optical analysis is an important factor to identify an NLO material [13]. Ultraviolet–visible–near-infrared (UV–Vis–NIR) spectral analysis of crystals with the thickness of about 1 mm was performed on a Perkin Elmer Lambda 35 spectrophotometer in the wavelength region of 190 to 1100 nm at room temperature. The optical transmittance spectrum of resorcinol-doped KHP (RKHP) is shown in figure 4. No drastic changes in the transparency were achieved, but the low concentration of the dopant does not affect the transparency of the pure KHP crystal.

It can be seen that the crystal has a UV absorption edge around 250 nm and can transmit well down to 300 nm. The crystal presents good transparency in the range of 300–1000 nm with a transmittance efficiency of about 99% facilitating the effective use for the second harmonic generation 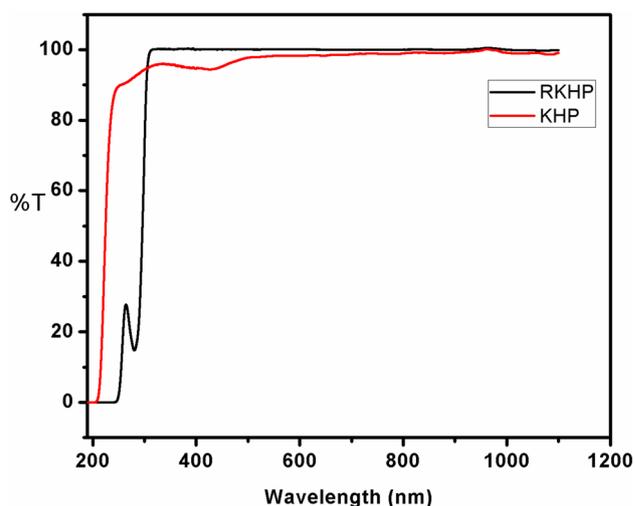(SHG) and other optical applications. A decrease in the percentage of optical absorption may be due to the absence of solvent inclusions which led to reduced-scattering centres and thereby increasing transmitting efficiency [14].

3.4 *Mechanical study*

Mechanical strength of a crystal is an important parameter for the fabrication of devices and is closely related to the structure of the material [15,16]. The transparent crystals free from inclusions or cracks were selected for hardness measurement. The crystal was mounted on the microscope and indentations were made on the crystal for all loads with a dwell time of 15 s. The average values of the diagonal length were considered to calculate hardness number by the following relation

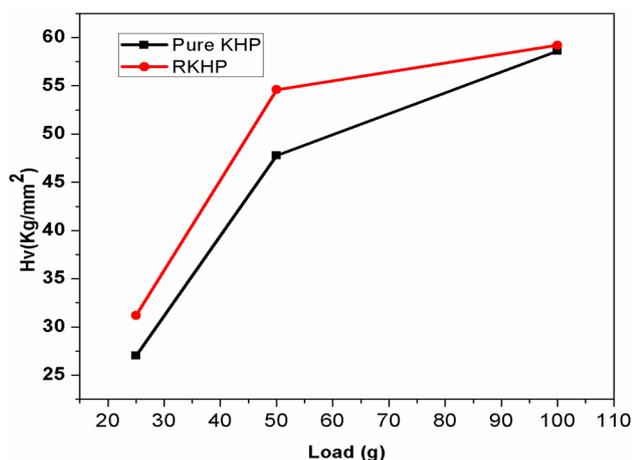$$H_v = kP/d^2 \ \text{kg mm}^{-2} \tag{1}$$

Figure 5. Load *vs.* H_v.

where P is the applied load and d is the diagonal length of indentation impression. The geometrical conversion factor (k) is 1.854 for a diamond pyramidal indenter. The variation of hardness (H_v) with load (P) ranging from 25–100 g is shown in figure 5. The variation of H_v follows a reverse indentation size effect trend. The higher value of H_v implies that greater stress is needed to create dislocations and thus confirming high-crystalline perfection [17,18]. The hardness values of resorcinol-doped crystals were high compared to pure KHP which implies good mechanical strength. The concentration of the dopant resorcinol is only 1 mol%. For such a low concentration the hardness number (H_v) does not show any decrease. Thus, the presence of dopant does not affect the mechanical strength of the grown RKHP crystals.

3.5 *SHG study*

The second order nonlinear optical response of grown crystals has been studied by using a standard Kurtz–Perry technique. The powdered sample was prepared and tightly packed in a cavity and irradiated by a Q-Switched Nd-YAG laser operating at a wavelength of 1064 nm with a repetition rate of 10 Hz. The output of the green light having a wavelength of 564 nm confirms the nonlinear behaviour of the grown crystal. The SHG efficiency of the grown crystal turns out to be 10.52 mJ with an input energy of 0.70 J. The frequency doubling efficiency of RKHP found to be 1.1 times than that of the reference material KDP. The SHG response of the pure KHP material results in an energy output of 3.2 mJ. The higher SHG response facilitates that inclusion complexation can alter the molecular alignment of the host material and thereby enhancing SHG efficiency [19,20]. An increase in the NLO property is expected due to the absence of symmetry in the adduct formed by resorcinol and KHP crystals.

4. Conclusion

Single crystals of RKHP have been synthesized by a slow solvent evaporation method. The functional group analysis of the crystal reveals the inclusion of the dopant into the material which gives a broad band at 3479 cm^{-1} through a FTIR spectrum. The UV–Vis spectrum implies that doped crystals did not affect the optical transmittance of the parent compound KHP. The mechanical properties were analysed *via* the Vickers hardness test. An enhanced SHG output in the case of RKHP is due to the absence of symmetry in the crystal. From investigation, it is concluded that the enhanced optical and NLO properties mainly rely on the presence of dopant.

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