

GROWTH, SPECTRAL, MECHANICAL AND NONLINEAR OPTICAL CHARACTERIZATION OF POTASSIUM HYDROGEN PHTHALATE CRYSTALS

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ABSTRACT

Single crystals of Potassium Hydrogen Phthalate (KHP) have been grown from aqueous solution by slow evaporation technique at 37°C. The carbon and hydrogen environment in molecular design of KHP is determined by the FT-NMR method. The mechanical strength of KHP was investigated by Vickers microhardness test. The relative SHG efficiency of KHP was measured by employing Kurtz and Perry powder technique using a Q-switched mode-locked Nd:YAG laser emitting 1064 nm. The intensity of the green emission was found to be 1.12 times greater than KDP of KHP crystal. Third-order nonlinear optical properties were determined by the Z-scan procedure by He-Ne laser. Closed aperture Z-scan study reveals the positive nonlinearity in KHP and open aperture Z-scan demonstrates the nonlinear absorption is reverse saturation absorption.

Keywords: Noncentrosymmetry; Reverse indentation size effect; Z-scan measurement; Self-focusing; Reverse saturable absorption.

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INTRODUCTION

A nonlinear optical material plays an important role in several applications such as frequency conversion, visual switching and signal refining etc¹⁻³. KHP is a semi-organic material used in the X-ray spectroscopy as an analyzer. These KHP crystals are orthorhombic crystal system with space group Pca2₁. Electro optic and NLO behaviors of KHP have been studied⁴⁻⁶.

In this work, single crystals of KHP have been grown using slow evaporation solution growth method. The grown crystals were characterized by FT-NMR spectroscopy, Vickers micro hardness test, Second harmonic generation (SHG) and third harmonic generation of the Z-scan method and the results are reported.

EXPERIMENTAL

Single crystals of KHP were grown by slow evaporation method at 37°C. KHP was dissolved in deionized water and this solution was continuously stirred for 3 hours until it becomes completely transparent. This was filtered by Whatman filter paper and sealed with a perforated top. Then the filtered solution was maintained at 37°C using constant temperature bath of accuracy ±0.1°C. Due to slow evaporation of solvent small crystals of KHP were grown at the bottom of the beaker. After 40 days transparent crystals with the dimensions 20×11×2 mm³ were obtained and are shown in Fig.-1.

RESULTS AND DISCUSSION

NMR Studies

The ¹H NMR and ¹³C NMR spectral analysis are the valuable cogent procedure used to review the design of organic compounds. The ¹H NMR (proton) and ¹³C NMR (carbon) spectra have been recorded for the KHP crystal dissolved in heavy water (D₂O) using a Bruker 300 MHz (Ultrashield)TM instrument at 23 °C (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) to confirm the molecular design.

The proton and carbon spectra of KHP crystal are presented in Fig.-2 and Fig.-3 respectively. The chemical shifts are given with assignments in Table-1.

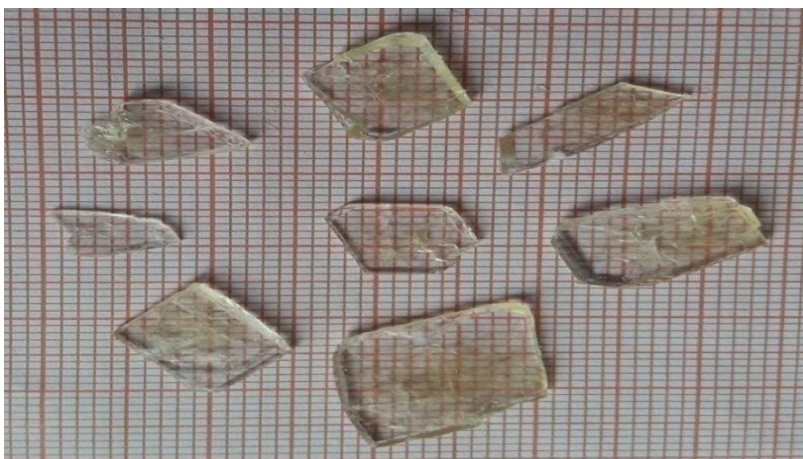


Fig.-1: Photograph of KHP crystals

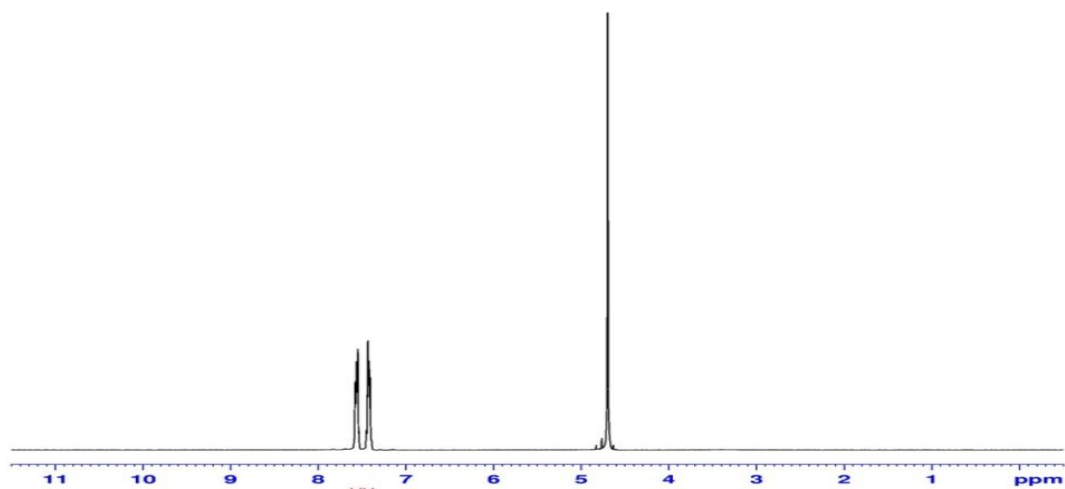


Fig. -2: ¹H NMR spectrum of KHP crystal

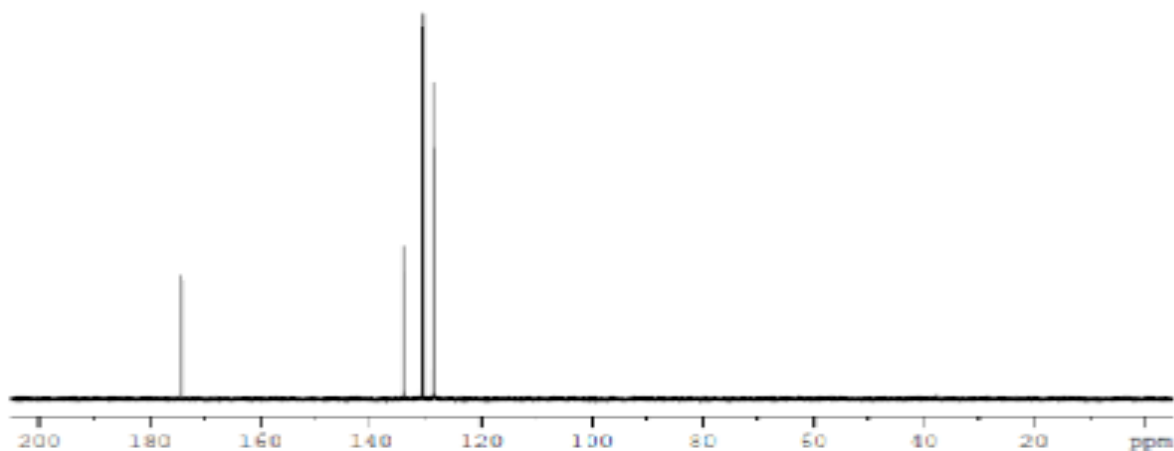


Fig.-3: ¹³C NMR spectrum of KHP crystal

In ^1H NMR peak due to C–H proton of phthalic acid is observed at 7.435 ppm and COOH proton of phthalic acid is observed at 7.579 ppm. The strong intense solvent peak appeared at 4.698 ppm⁷. The ^{13}C NMR spectrum of KHP can be understood with the help of the molecular structure shown in Fig.-4⁷.

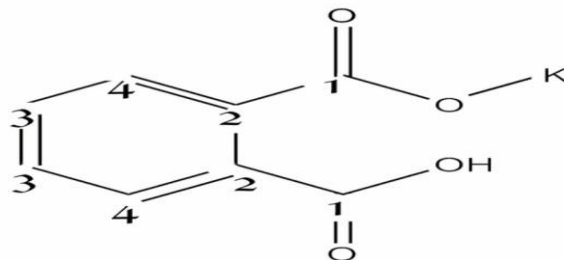


Fig.-4: Carbon atomic Numbering of KHP Crystal

The peak observed at 174.18 ppm corresponds to carbon 1 atom (COOH group of phthalic acid). The peak at 133.86 ppm is due to carbon 2. The peaks observed at 130.67 ppm and 128.58 ppm are due to carbon 3 and carbon 4 respectively (CH group). The results are in agreement with the reported values⁷.

Table-1: Chemical shifts in ^1H NMR and ^{13}C NMR spectra of KHP

| Spectra | Chemical shift (ppm) | Group identification |
|---------------------|----------------------|----------------------------------|
| ^1H NMR | 4.698 | D ₂ O |
| | 7.435 | CH proton of the Phthalic acid |
| | 7.579 | COOH proton of the Phthalic acid |
| ^{13}C NMR | 174.18 | Carbon 1 (COOH group) |
| | 133.86 | Carbon 2 |
| | 130.67 | Carbon 3 (CH group) |
| | 128.58 | Carbon 4 (CH group) |

Micro Hardness Study

The mechanical strength of crystal was measured by Shimadzu HMV-2t Vickers microhardness tester fitted with the diamond indenter. By shifting the enforced load from 25 g to 100 g the crosswise diameter was measured. Vickers Hardness number H_v was determined by the relation:

$$H_v = 1.8544P / d^2 \text{ (Kg/mm}^2\text{)}$$

Where, P is load and d is mean crosswise diameter. The plot of hardness number with load is shown in Figure 5. It is clear that hardness number is increasing with applied load. The increase in H_v with increasing load is due to the reverse indentation size effect (RISE)⁸.

Second Harmonic Generation Analysis

The Kurtz and Perry method was utilized to measure powder SHG efficiency of KHP crystals. KHP crystals were ground into very fine powder and packed in a micro capillary tube which served as the sample cell. Then it was kept in the path of Nd:YAG laser. The generation of green light confirmed the NLO property of KHP. The NLO efficiency of reference material KDP is 55mV while that of KHP is 62mV. The SHG efficiency of KHP single crystals is 1.12 times greater than the KDP crystal⁹.

Z-scan Measurement

The third-order nonlinear optical property of KHP single crystal was analyzed by Z-scan technique. The nonlinear refractive index (n_2), the nonlinear absorption coefficient (β) of KHP single crystal was

evaluated by Z-scan technique. In this method, He-Ne laser (632.8 nm) with beam radius 2 mm was used to scan the sample. n_2 was calculated by the relation,

$$n_2 = \frac{\Delta\phi}{KI_0L_{\text{eff}}}$$

Where $K = 2\pi / \lambda$, I_0 is the intensity of the laser beam at the focus ($Z=0$), L_{eff} is the effective thickness of KHP which was estimated by the formula,

$$L_{\text{eff}} = \frac{1 - \exp(-\alpha L)}{\alpha}$$

Here α represents linear absorption coefficient and L is the thickness of sample (2mm). Closed aperture Z-scan curve was shown in Fig.-6. In a closed curve, valley followed by peak reveals the positive nonlinear refractive index (n_2) of material. This suggests that crystal having self-focusing nature.

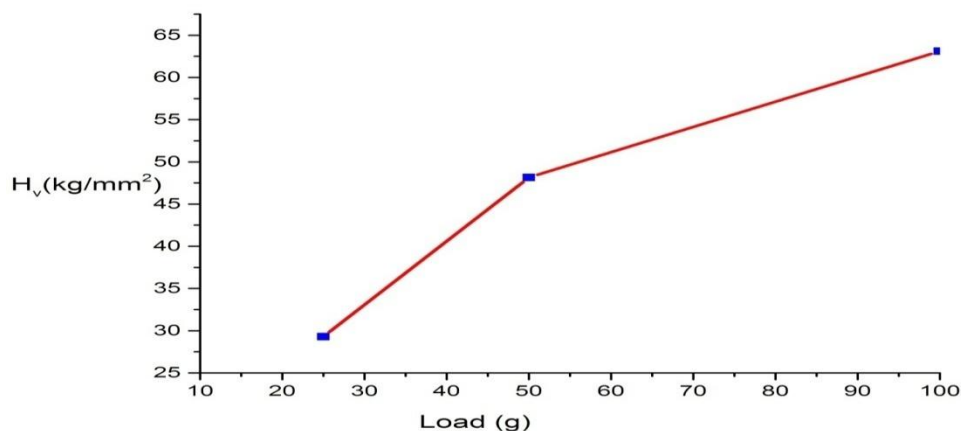


Fig. -5: Variation of H_v for various loads

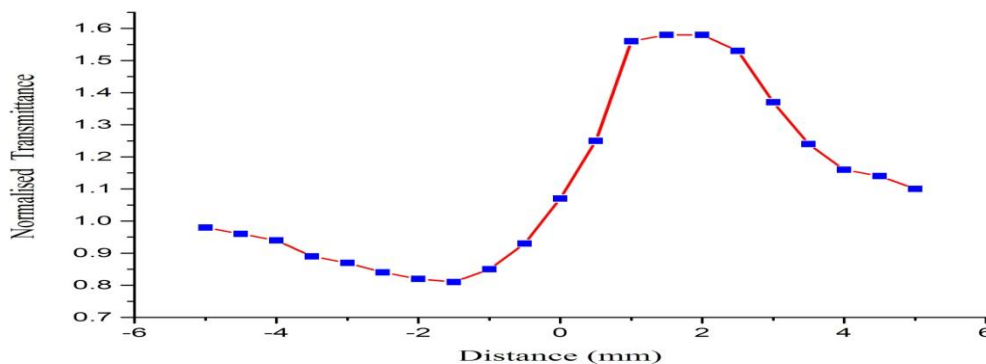


Fig. -6: Closed aperture Z-scan pattern of KHP crystal

From the open aperture Z-scan data, β is determined using the expression,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{\text{eff}}}$$

Where $\Delta T = 1 - T_v$. (T_v - valley value at the open aperture Z-scan curve) Fig.-7. Represents the open aperture Z-scan curve. In the figure, minimum transmission occurs near the focus. This is due to reverse saturable absorption of the material¹⁰.

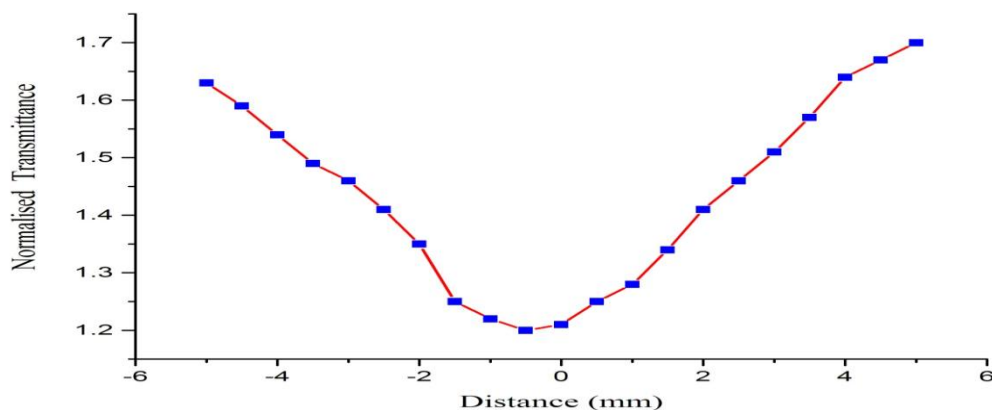


Fig.-7: Open aperture Z-scan pattern of KHP crystal

The real and imaginary parts of $\chi^{(3)}$ are defined as:

$$\begin{aligned} \text{Re } \chi^{(3)} \text{ esu} &= 10^{-4} \epsilon_0 C^2 n_0^2 n_2 / \pi \quad (\text{cm}^2 / \text{W}), \\ \text{Im } \chi^{(3)} \text{ esu} &= 10^{-2} \epsilon_0 C^2 n_0^2 \lambda \beta / 4\pi^2 \quad (\text{cm} / \text{W}), \end{aligned}$$

Where ϵ_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and C is the velocity of light in vacuum. The absolute value of $\chi^{(3)}$ is calculated from:

$$\chi^3 = \sqrt{[\text{Re}(\chi^3)]^2 + [\text{Im}(\chi^3)]^2}$$

The nonlinear parameters such as n_2 , β , and χ^3 have been evaluated and tabulated in Table-2.

Table-2: Measurement details and the results of the Z-scan technique

| | |
|--|--|
| Laser beam wavelength (λ) | 632.8 nm |
| Lens focal length (f) | 18.5 cm |
| Optical path distance (Z) | 115 cm |
| Spot-size diameter in front of the aperture (ω_a) | 1 cm |
| Aperture radius (r_a) | 2 mm |
| Incident intensity at the focus (Z=0) | 3.13 MW/cm ² |
| Nonlinear refractive index (n_2) | 3.156 x 10 ⁻¹² cm ² /W |
| Nonlinear absorption coefficient (β) | - 6.7 x 10 ⁻⁴ cm/W |
| The real part of the third-order susceptibility [Re (χ^3)] | 1.53 x 10 ⁻¹⁰ esu |
| Imaginary part of the third-order susceptibility [Im (χ^3)] | 7.71 x 10 ⁻⁶ esu |
| Third-order nonlinear optical susceptibility (χ^3) | 7.86 x 10 ⁻⁴ esu |

CONCLUSION

The single crystals of KHP were been successfully grown from low-temperature solution growth technique. The molecular structure KHP crystal was established by ¹H and ¹³C NMR techniques. From the microhardness measurement, it was informed that the hardness increased with the increase of load until saturation occurred. The SHG efficiency of KHP crystals was confirmed by green colour emission. n_2 , β , and χ^3 are calculated using Z-scan analysis.

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