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Linear and Nonlinear Optical Constants of Potassium Acid Phthalate crystal

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Abstract—Single crystals of potassium hydrogen phthalate (KAP) are grown by the solution growth technique. Linear optical constants are evaluated from the UV/VIS/NIR spectrum. The *Z* scan technique is used to elucidate the third order nonlinearity in the material. The results indicate that the compound exhibits reverse saturable absorption (RSA) and self-defocusing performance. The second harmonic generation (SHG) efficiency of the crystal evaluated by Kurtz and Perry technique is compared with that of the standard KDP crystal. An attempt is made to correlate the SHG efficiency with the crystalline perfection in the material.

Hydro phthalate crystals (XAP: C_6H_4 COOH COOX where X is a metal ion) are most useful for long wave X-ray spectroscopy. Acid phthalate crystals are organic crystals with 2d spacing of the order of 26Å. The crystals cleave along the (010) planes and have a good record for long term stability [1]. KAP is an orthorhombic crystal, crystallizing in the space group $P_{ca}2_1$ with the unit cell dimension a=9.609Å, b=13.857Å, c=6.466Å and contains 4 KAP molecules. The habitual morphology of the crystal has 14 growth faces. It has a (010) face with a high morphological importance on which spiral patterns could be easily observed due to relatively high monosteps. This material is a fine model material for studying the crystallization process, especially the mechanism of spiral growth in crystals [2-3]. Growth and structural characterization studies of this material have already been done but the nonlinear optical behaviour has not been dealt with in detail [4-5]

In the present work, KAP crystals are grown by the floating seed technique. The X-ray diffraction pattern and the morphology of the crystal is shown in Fig. 1. The optical absorption spectrum of KAP crystal is recorded from 200nm to 2000nm (Fig. 2). The variation of n, k and the real part of a dielectric constant with energy are determined. The UV/Vis/NIR spectrum plays a vital role in identifying the potential of a NLO material because a given NLO material can be of utility only if it has a wide transparency window without any absorption at the fundamental and second harmonic wavelengths [8].

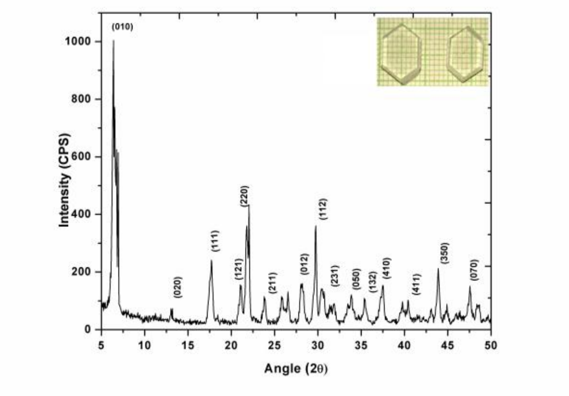

Fig. 1. Powder XRD pattern of the grown KAP crystal.

When scattering effects are neglected, the absorption coefficient may be expressed by:

$$\alpha h\upsilon = A\,(\alpha h\upsilon - E_g)^n, \tag{1}$$

where A is the constant nearly independent of photon energy and E_g is the optical band gap. The plot of $(\alpha h\upsilon)^2$ versus hν for the KAP crystal is shown in Fig. 3. The band gap of KAP crystal is found to be 4.1eV. The optical constants such as refractive index (n), extinction coefficient (k) and absorption coefficient (α) are determined from the transmission (T) and reflection (R) spectrum based on the following relations:

$$T= (1–R)^2 \exp(–\alpha t) / 1–R^2 \exp(–\alpha t), \tag{2}$$

where t is the thickness and the absorption coefficient α is related to extinction coefficient k (absorption index) by:

$$K= \alpha\, \lambda / 4\pi. \tag{3}$$

There exists a relationship between R and n (refractive index) given by:

$$R = (n - 1)^2/ (n + 1)^2. \tag{4}$$

The relationship between ε and k is given by:

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$$\varepsilon = \varepsilon_r + i\varepsilon_i = (n + ik)^2. \tag{5}$$

The real part of the dielectric constant is given by:

$$\varepsilon_r = n^2 – k^2. \tag{6}$$

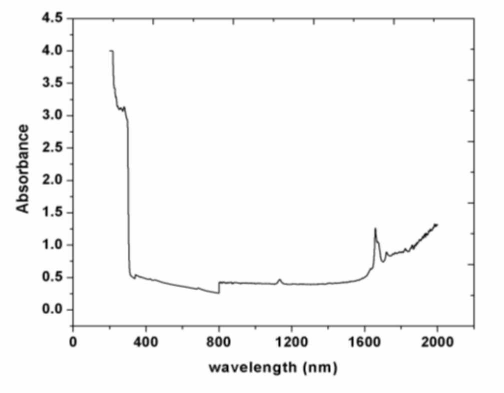

Fig. 2. UV/Vis/NIR absorption spectrum.

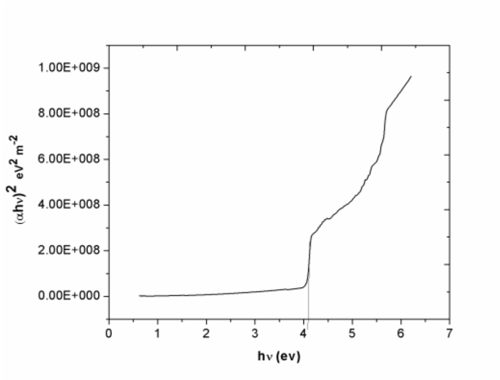

Fig. 3. Plot showing the optical band gap.

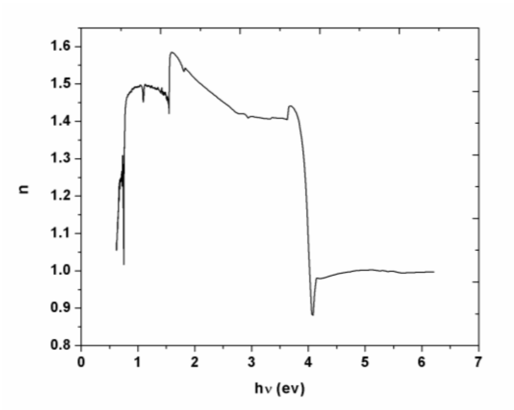

Fig. 4. Graph showing the variation of n with energy.

Figure 4 and Figure 5 show the variation of n and dielectric constant with photon energy.

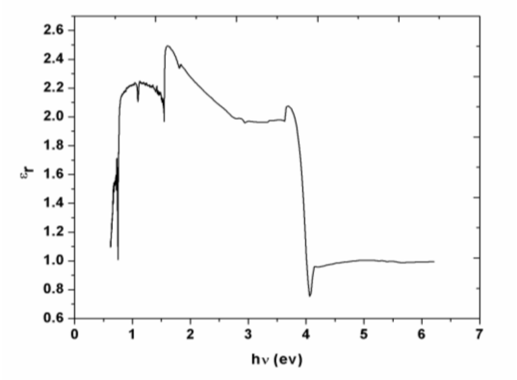

Fig. 5. Variation of dielectric constant with photon energy.

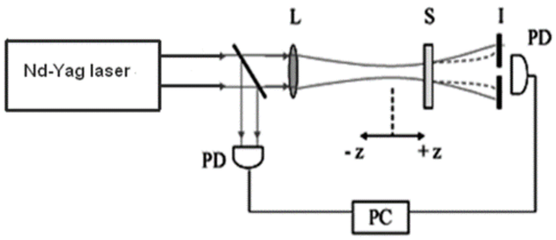

Fig. 6. Z-scan setup.

The z-scan technique shown in Fig. 6 is a method which can measure both nonlinear absorption and refraction in solids and liquid solutions and has gained rapid acceptance as a standard technique for separately determining nonlinear changes in refraction index and in absorption. The index change (Δn) and absorption change ($\Delta\alpha$) can be determined directly from the data without resorting to fitting. The laser used is 532nm, 7ns pulses from the second harmonic output of a hybrid mode-locked Nd: YAG laser. The crystal is fixed on a microprocessor controlled translation stage that has a range of 30cm. For closed aperture measurements, a suitable aperture is placed in front of the photo diode. Data acquisition is facilitated in real time by the use of a PC.

The open aperture z-scan curve is shown in Fig. 7. The reverse saturable absorption coefficient β(m/W) can be obtained from the best fitting performed on the experimental data of the OA measurement with Eqs. (8)-(9), where α and β are linear and effective third order NLO absorption coefficients, respectively, τ is the time, I(z) is the irradiance and L is the optical path length.

$$T(z) = \frac{1}{Q(z)\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln\left[1 + Q(z)\right] e^{-\tau^2} d\tau, \tag{8}$$

$$Q(z) = \beta I(z) \frac{1 - e^{-\alpha L}}{\alpha}, \tag{9}$$

where $(1–e^{-\alpha L})/\alpha$ is the effective path length L_{eff}. The value of the non linear absorption coefficient β is found to be equal to 9.089cm/GW. Figure 8 shows the closed aperture z-scan, obtained for KAP crystal indicating a negative refractive nonlinearity. The nonlinear refraction coefficient n_2 (m^2/W) is obtained through the following equation:

$$\Delta\Phi_0 = k\, n_2\, I_0 L_{eff}. \tag{10}$$

In the above equation the phase shift $\Delta\Phi_0$ is equal to $2\pi/\lambda\; n_2 I_0 L_{eff}$. The difference between the normalized transmittance at the peak and valley is related to $\Delta\Phi_0$ by the relation:

$$\Delta T_{P\to V} = 0.406\,(1–S)^{0.25}\,\Delta\Phi_0 \tag{11}$$

The value of n_2 is calculated to be equal to -53.651×10^{-14} m^2/W. The molecular second hyperpolarizability γ may be obtained to be 14.97×10^{-24} esu with the equation below.

$$\gamma = 40\pi\, n_2/ cn_0. \tag{12}$$

The real and imaginary parts of the $\chi^{(3)}$ of the sample can also be calculated by the following equations:

$$\mathrm{Re}\,\chi^3\,(\mathrm{esu}) = (cn_0^2/ 120\pi^2)\, n_2, \tag{13}$$

$$\mathrm{Im}\,\chi^3\,(\mathrm{esu}) = (cn_0^2\varepsilon_0\lambda /2\pi)\,\beta. \tag{14}$$

The value of the real part of nonlinear susceptibility $\mathrm{Re}\chi^{(3)}$ (esu) and imaginary part $\mathrm{Im}\chi^{(3)}$ (esu) is found to be equal to -3.057×10^{-11} esu and 0.4391×10^{-11} esu respectively. The value of the coupling factor ρ, which is the ratio of an imaginary part to a real part of third-order nonlinear susceptibility, is found to be equal to 0.143 indicating that the nonlinearity is electronic in origin. The characteristic pattern of the open aperture curve shows that the nonlinear absorption is reverse saturation absorption implying that the crystal can be effectively used for optical limiting applications. The peak-to-valley configuration of the closed aperture curve suggests that the refractive index change is negative, exhibiting, self-defocusing effect.

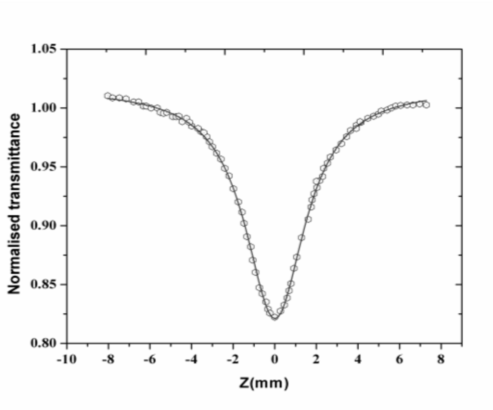

Fig. 7. Open aperture z-scan curve.

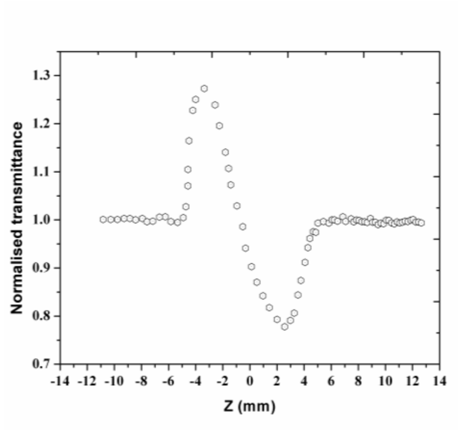

Fig. 8. Closed aperture z-scan curve.

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