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Third order Non- Linear optical properties of Vanillin Single Crystals by Z-Scan Technique

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ABSTRACT

Single crystals of vanillin were grown by the solution growth method using methanol as a solvent. Crystal up to the size of $1 \times 0.6 \times 1.4 cm^3$ *were grown for optical characterization. Optical quality of crystal was observed to be good. Vanillin has a higher figure of merit when compared to other crystals suitable for non-linear optical applications in the visible to near-infrared region. The crystal structure was studied by X-ray diffraction. The UV–Visual absorption spectra indicate a good transparency between 200 and 800 nm. The nonlinear refractive index* n_2 *and susceptibility* $\chi^{(3)}$ *have been measured through the Z-scan technique. Vanillin exhibits saturation absorption and self-focusing performance. Non-linear absorption Co-efficient* β *is determined as* $7.6518 \times 10^{-4} cm/W$. *Non-linear refractive index* n_2 *measured at the wavelength of 632.8 nm is calculated as* $1.6369 \times 10^{-8} cm^2/W$. *The real and imaginary parts of* $\chi^{(3)}$ *have been measured at 632.8 nm and were found to be* $1.1915 \times 10^{-7} esu$ *and* $2.8062 \times 10^{-6} esu$ *respectively. Also, the absolute value of the third order Non-linear optical susceptibility* $\chi^{(3)}$ *is* $2.8088 \times 10^{-6} esu$.

Keywords: Growth from solution, vanillin, single XRD, U-V Spectrum, Z-Scan)

INTRODUCTION

The Z-Scan technique [1-3] is a popular method for the measurement of optical non-linearity of the material. It has the advantage of high sensitivity and simplicity. One can simultaneously measure the magnitude and sign of the non-linear refraction and non-linear absorption, which are associated with the real part $\chi_R^{(3)}$ and imaginary part $\chi_I^{(3)}$ of the third order non-linear susceptibilities. The Z-Scan technique has been used to measure the non-linear optical properties of semiconductors [4,5], dielectrics [6,7] organic or carbon-based molecules [8,9] and liquid crystals [10,11]. In this work, we present the growth of vanillin single crystals by the solution growth method using methanol as a solvent. Single X-ray diffraction, optical absorption spectrum Z-Scan measurements were carried out. Z-Scan results reveal that it is a potential candidate for the optical switching [12] and optical limiting [13]. The experimental setup used to measure the nonlinear refractive index and absorption of our crystal sample in this work as depicted in the Figure 1.

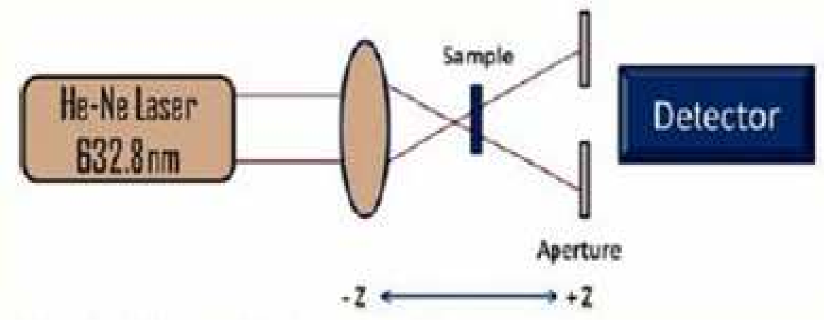


Figure 1 Schematic diagram of Z-scan technique

MATERIALS AND METHODS

Crystal Growth

Vanillin single crystals were grown using AR grade chemical and methanol as a solvent by slow evaporation technique. By repeated re crystallization, water-clear plate like crystals of $1\times0.6\times1.4\,cm^3$ are obtained within 5 days. The grown crystals present good optical transparency. Grown crystals were as shown in the figure 2.

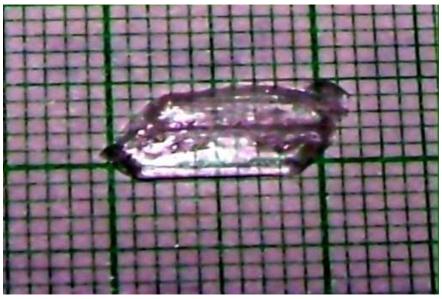
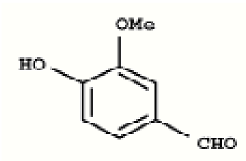


Figure 2 Grown Crystal of Vanillin.

RESULTS AND DISCUSSION

Molecular Formula : $C_8H_8O_3$ Structural formula :



Molecular Weight = 152.16 gm. Anisotropic, linear refractive index n = 1.694

Crystal Structure: Monoclinic.

3.1 Single Crystal XRD

Single crystal X-ray diffraction analysis for the grown crystals has been carried out using ENRAF NONIUS CAD4 X-Ray diffractometer to confirm the lattice parameters of vanillin. The single crystal data of Vanillin is given in Table 1.

Table 1. The single crystal X-ray data for Vanillin single crystal

System	Monoclinic		
Lattice parameter	$a = 7.88\ \AA$	$b = 13.976\ \AA$	$c = 13.592\ \AA$
	$\alpha = 90°$	$\beta = 113.20°$	$\gamma = 90°$
Volume (V)	$1496.89\ \AA^3$		
Space group	$P2_1$		

3.2 UV –VIS-NIR Spectra of Vanillin

The UV-VIS-NIR absorption spectra are very useful tool in the transmission range of the crystal for the study of NLO behaviour. Absorption spectra of the grown single crystals of Vanillin were recorded using Varian Cary 5E UV spectrophotometer in the range 200-800 nm. Small crystal of thickness 5 mm was used for study. The spectra reveal a low UV cut off value at 350 nm for vanillin. The absorption is found to be low in range 340 to 800 nm for vanillin. Figure 3 shows the UV-Vis-NIR spectra of Vanillin.

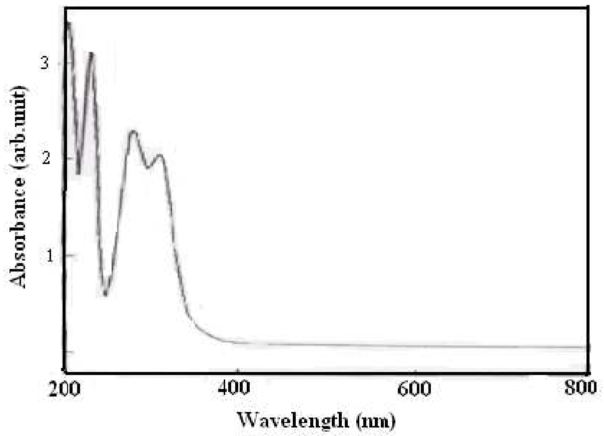


Figure 3. UV-Vis-NIR Spectra of Vanillin

3.3 NLO MEASUREMENTS

3.3.1. SHG Measurement

Powder SHG studies for Vanillin single crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry [14]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm and pulse width of 8 ns with a repetition rate 10 Hz was used. The vanillin single crystals were powdered with a particle size of around 150 µm and placed in a micro capillary tube and exposed to laser radiation. The second harmonic signal was present for this sample confirms the nonlinear optical (SHG) nature of this crystal. Its SHG efficiency is greater than Urea, KDP and L-Arginine etc.

3.3.2. Refractive Index Measurement

The refractive index of the Vanillin Single crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal is mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal is perfecty perpendicular to the intra-cavity beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster's angle (θ_P) for Vanillin single crystal is measured to be 55.59 degrees. The refractive index has been calculated using the equation $n = \tan\theta_P$, where θ_P is the polarizing angle and it is found to be 1.5697.

3.3.3. Third Order Non-Linear Optical Measurement

A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam. The difference between the peak and valley transmission (ΔT_{P-V}) is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}|\Delta\Phi_0| \quad \text{.................. (1)}$$

where, nonlinear phase shift with the sample at focus (Z=0)

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff} \quad \text{.................. (2)}$$

The nonlinear refractive index is given by

$$n_2 = \frac{\Delta\Phi_0}{K\, I_0\, L_{eff}} \quad \text{.................. (3)}$$

where, $\Delta\Phi_0$ is the phase shift with the sample at focus (Z=0), $K = \frac{2\pi}{\lambda}$ (λ is the laser wavelength), 'L_{eff}' is the effective thickness of the sample $= \frac{(1-e^{-\alpha L})}{\alpha}$ 'L' is the thickness of the sample. 'I_0' is the intensity of the laser beam at the focus (Z=0) .

"S" is the transmittance of the aperture in the absence of a sample and calculated using the relation

$$S = 1 - \exp\left(\frac{-2\, r_a^2}{\omega_a^2}\right) \quad \text{.................. (4)}$$

where, "r_a" is the aperture and ω_a is the beam radius at the aperture.

From open aperture Z-scan data, the non-linear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad \text{...................... (5)}$$

where, ΔT is the one valley value at the open aperture Z-scan curve.

The value of β will be positive for saturable absorption and negative for two photon absorption. The real and imaginary parts of the third order Non-linear optical susceptibility $\chi^{(3)}$ are defined as

$$\text{Re}\ \chi^{(3)} = \frac{10^{-4} \times (\varepsilon_0 c^2 n_0^2 n_2)}{\pi} \quad (esu)$$

$$\text{Im}\ \chi^{(3)} = \frac{10^{-2} \times (\varepsilon_0 c^2 n_0^2 \lambda\, \beta)}{4\pi^2} \quad (esu)$$

.... (6)

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 the third order Non-linear optical susceptibility $\chi^{(3)}$ is calculated from the formula

$$\chi^{(3)} = \sqrt{\left(\mathrm{Im}\,\chi^{(3)}\right)^2 + \left(\mathrm{Re}\,\chi^{(3)}\right)^2}\quad (esu) \qquad (7)$$

Figure 4 shows the normalized transmittance for the Open Aperture (OA) curve of Vanillin. The transmission is symmetric with respect to the focus (Z = 0), where it has a maximum transmission. This indicates that the materials exhibit Saturation Absorption (SA).

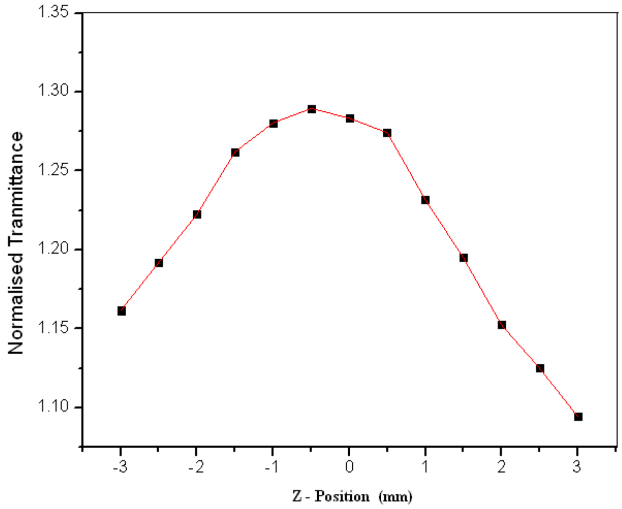


Figure 4 Open Aperture curve of Vanillin

Figure 5 shows the normalized transmittance for the Closed Aperture (CA) curve of vanillin. The valley to peak configuration of the curve (Figure 5) suggests that the refractive index change is positive, exhibiting a self focusing effect. This may be an advantage for the application in protection of optical sensors. As seen from the closed aperture Z-scan curve, the prefocal transmittance valley is followed by the post focal peak which is the signature of positive nonlinearity [15].

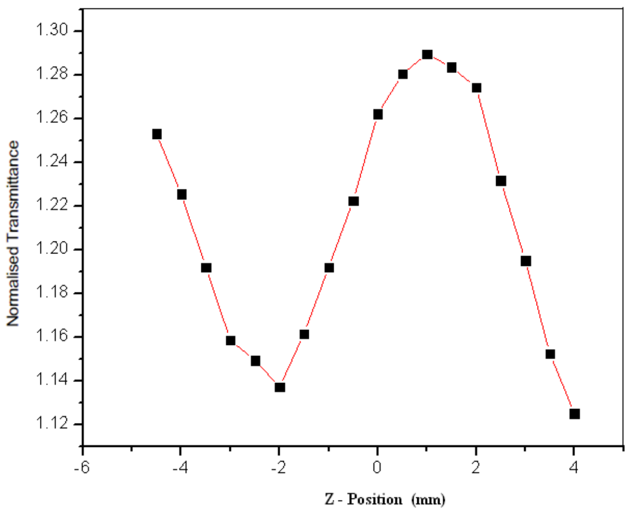


Figure 5 Closed Aperture Curve of Vanillin

The calculated the value of the nonlinear refractive index n_2 is found to be $1.6369\times10^{-8}cm^2/W$. As the material has a positive refractive index, it results in self – focusing nature of the material. From the open aperture Z-scan curve, it can be concluded that the nonlinear absorption is regarded as saturation absorption. The nonlinear absorption coefficient (β) is found to be $7.6518\times10^{-4}cm/W$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and were found to be $1.1915\times10^{-7}esu$ and $2.8062\times10^{-6}esu$ respectively. Also, the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is $2.8088\times10^{-6}esu$. The value of $\chi^{(3)}$ is found to be larger than the other well known compounds [16] and it is due to the p-electron cloud movement from the donor to acceptor which makes the molecule highly polarized. The value of the $\chi^{(3)}$ of Vanillin single crystals reported here is of the same order of the magnitude of the materials such as Chaclogenide glasses [17] and C60 etc.

CONCLUSION

We have reported here the optical properties of Vanillin single crystal. The SHG efficiency confirms vanillin as a potential candidate for non-linear optical applications. Vanillin's SHG efficiency is greater than that of UREA, KDP and L-Arginine single crystals etc. The Z-Scan measurement with 632.8 nm laser revealed that non-linear refractive index of the crystal is in the range of $10^{-8}cm^2/W$. The measured third order non-linear properties confirm its suitability for non-linear optical devices such as optical switching device.

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