Investigations on the nonlinear optical properties of glycinium oxalate single crystals

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Single crystals of glycinium oxalate (GLO) are grown by solution growth technique. 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. Attempt is made to correlate the SHG efficiency with the crystalline perfection in the material.

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There is considerable interest in finding materials with large yet fast nonlinearity. This interest is driven primarily by the search for materials for all-optical switching and sensor protection applications, and both nonlinear absorption (NLA) and nonlinear refraction (NLR) are concerned. The *Z*-scan technique is a method which can measure both NLA and NLR in solids particularly in liquids and liquid solutions[1,2], and has gained rapid acceptance as a standard technique for separately determining the nonlinear changes in index of refraction and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. The index change Δn and the absorption change $\Delta\alpha$ can be determined directly from the data without resorting to fitting.

Amino acid crystals with delocalized π electrons usually display large nonlinear optical (NLO) response and are potential candidates for applications in the emerging areas of photonics[3]. Most of such crystals are composed of dipolar aromatic molecules, which exhibit intramolecular charge transfer. Molecules, which show asymmetric polarization induced by electron donor and acceptor groups, are responsible for electro-optic and NLO properties[4,5]. The charge transfer compound of glycine and oxalic acid-glycinium oxalate (GLO) is a potential NLO material[6]. In this work, the glycinium oxalate (GLO) is synthesized from aqueous solutions of γ glycine and oxalic acid taken in 1:1 molar ratio. The seed crystal prepared using the synthesized powder is top seeded in its saturated solution at 28^{0}C, which yields good optical quality in three weeks (Fig.1), with an optimum size of 10 mm × 10 mm × 3 mm.

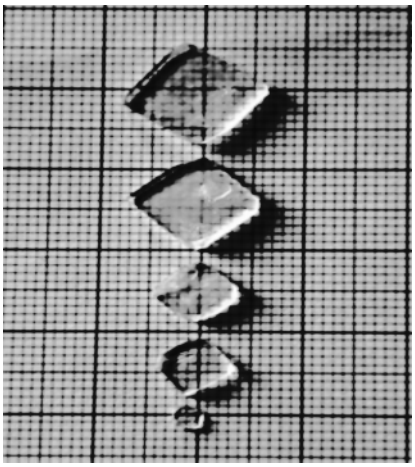

Fig.1 Glycinium oxalate single crystals

In a typical *Z*-scan experimental setup (Fig.2), a laser beam with a Gaussian profile is initially focused by a lens. The sample is then moved along the axial direction of the focused beam in such a way that it is moved away from the lens, passing through the focal point. At the focal point, the sample experiences the maximum pump intensity, and the intensity will progressively decrease in either direction of motion from the focus. If a light detector is placed in the far field and the transmitted intensity is measured as a function of the position of the sample, one obtains an ‘‘open aper-

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ture'' *Z*-scan curve, the shape of which will reveal the presence of any absorptive nonlinearity in the sample. On the other hand, if a properly chosen aperture is placed in front of the detector, a ''closed aperture'' *Z*-scan curve is obtained which will reflect the occurrence of refractive nonlinearities. The used laser is 532 nm, 7 ns plane polarized pulses from the second harmonic output of a hybrid mode-locked Nd: YAG laser operating at 10 Hz repetition rate. The crystal is fixed on a microprocessor controlled translation stage that has a moving range of 30 cm and a resolution of 2 μm, so that it can be accurately moved through the focal region of the laser beam. A fast photodiode monitors the input laser energy, and a large-area photodiode collects the transmitted beam. For the closed aperture measurements, a suitable aperture is placed in front of the photodiode. Data acquisition is facilitated in real time by the use of a PC.

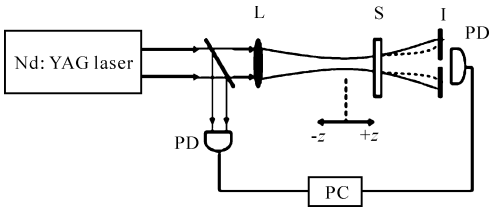

Fig.2 *Z* scan experimental setup

The second harmonic generation behavior is tested by the Kurtz powder technique[7] using *Q* switched Nd: YAG laser as source. The powder sample of GLO is illuminated by the laser source (λ = 1064 nm, 7 ns, 10 Hz). A bright green emission is observed from the sample. The second harmonic signal (532 nm) generated in the sample is collected by the lens and is filtered by an IR filter to remove the fundamental signal detected by the monochromator, which is coupled with the New Port 818UV-photodiode with a spectral range from 190 nm to 900 nm. The powdered KDP sample with the same particle size is used as the reference material, and the output power intensity of GLO is compared with that of KDP.

The dielectric loss in the material is found by microwave cavity perturbation technique[8]. Dislocation density in the material is measured by chemical etching studies[9].

In the open aperture *Z* scan, the open aperture transmission normalized to the linear transmission of the sample is plotted against the sample position measured relative to the beam focus as shown in Fig.3. Nonlinear absorption in the present study is indicated by a smooth valley-shaped curve, symmetric about the focal position (z= 0). The RSA coefficient β (m/W) can be obtained from a best fitting performed on the experimental data of the OA measurement with Eqs. (1) and (2)[10], where α and β are the 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.

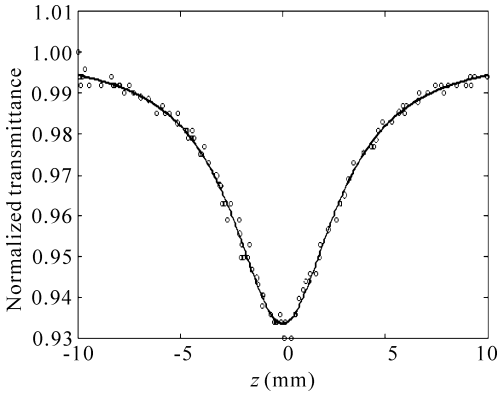

Fig.3 Open aperture *Z* scan curve of GLO crystal at 18 μJ

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

$$Q(z)=\beta I(z)\frac{1-\mathrm{e}^{-\alpha L}}{\alpha} \quad , \tag{2}$$

where $(1\text{-}e^{-\alpha L})/\alpha$ is the effective path length L_{eff}. The value of the nonlinear absorption coefficient β is found to be equal to 7.429 cm/ GW.

Fig.4 shows a typical closed aperture *Z* scan curve obtained for glycinium oxalate crystal. The peak-valley structure of the curve is a clear indication of a negative refractive nonlinearity exhibited by the medium[2]. The nonlinear refraction coefficient n_2 (m^2/W) is obtained through the following equation

$$\Delta\Phi_0 = kn_2 I_0 L_{\mathrm{eff}}, (\kappa = 2\pi/\lambda) \quad . \tag{3}$$

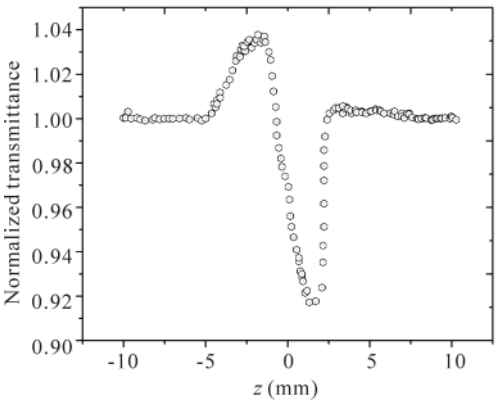

Fig.4 Closed aperture *Z* scan curve of GLO crystal

The difference between the normalized transmittances at the peak and valley is related to $\Delta\Phi_0$ by the relation

$$\Delta T_{\mathrm{P\to V}} = 0.406\,(1\text{-}S)^{0.25}\,\Delta\Phi_0 \quad . \tag{4}$$

The value of n_2 is calculated to be equal to -1.689×10^{-13} m^2/W. The molecular second hyperpolarizability, γ, may be

obtained to be 4.0424×10^{-24} esu with the equation below[11],

$$\gamma = 40\delta n_2 / cn_0 \ . \quad (5)$$

The real and imaginary parts of the $\chi^{(3)}$ of the sample can also be calculated by the following equations[12,13]

$$\mathrm{Re}\ \chi^{(3)}(\mathrm{esu}) = (cn_0^2/120\ \delta^2)\ n_2 \ , \quad (6)$$

$$\mathrm{Im}\ \chi^{(3)}(\mathrm{esu}) = (cn_0^2\ \varepsilon_0 \lambda / 2\delta)\ \beta \ . \quad (7)$$

The values of the real part of nonlinear susceptibility Re $\chi^{(3)}$ (esu) and the imaginary part Im $\chi^{(3)}$ (esu) are found to be equal to 1.474×10^{-11} esu and 0.40854×10^{-11} esu, respectively.

Introducing the coupling factor ρ, the ratio of imaginary part to real part of third-order nonlinear susceptibility is

$$\rho = \mathrm{Im}\ \chi^{(3)} / \mathrm{Re}\chi^{(3)} \ . \quad (8)$$

The value of ρ in this case is found to be equal to 0.27. The observed value of coupling factor is seen to be less than 1/3, which indicates that the nonlinearity is electronic in origin[14].

The SHG efficiency of GLO crystal is compared with that of the standard KDP. The second harmonic signal of 110 mV is obtained for the input energy of 3.0 mJ/ pulse, while KDP gives a SHG signal of 120 mV for the same input energy. SHG efficiency will vary with the size of the powdered crystalline aggregates[15]. It is found that the defects and dislocations presented in the crystal influence the NLO property especially the second harmonic generation[16]. The measured dielectric loss shown in Fig.5 is very small, which signifies the good crystalline perfection of the grown crystal. Very small dielectric loss is quite useful for device applications. Dislocation density measured by chemical etching studies is at the order of 10^4 /cm^2, which is small compared with that in semiconductors[17], implying better crystallinity.

The open aperture curve demonstrates a nonlinear absorption, and the characteristic pattern of the curve shows

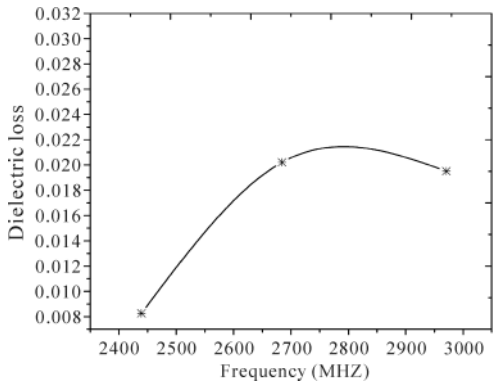

Fig.5 Variation of dielectric loss with microwave frequency (*S* band)

that the nonlinear absorption is the reverse saturation absorption (RSA), implying that the crystal can be effectively used for optical limiting applications. The peak-valley configuration of the closed aperture curve suggests that the refractive index change is negative, exhibiting a self defocusing effect. The experimental results show that the GLO crystal possesses great third-order NLO properties. The reason for the large value of RSA coefficient may be the delocalization from the protonation of amino group, which leads to the formation of glycinium oxalate molecule[9].

Since a large molecular hyperpolarizability γ is the basis of a strong second harmonic generation (SHG) response, organic molecules with large γ values are certain candidate for NLO applications. The better SHG efficiency of GLO compared with the standard KDP is due to the better crystalline perfection in the material.

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