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ARTICLE

Growth and Characterization of Mono-Urea Oxalic Acid Crystals

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ABSTRACT

An organic NLO material *viz.*, mono-urea oxalic acid (MUOA) crystal was synthesized and grown as the single crystal by slow evaporation technique using the double distilled water as the solvent. The grown crystal was transparent, colourless and the size of the crystal was about 14 mm × 17 mm × 7 mm obtained within a period of 30 days. The grown crystal was subjected to various studies like XRD, microhardness, linear optical studies, SHG studies and Z-scan studies. The mono-urea oxalic acid crystals crystallize in monoclinic structure with a centrosymmetric space group. This crystal gives out SHG emission even though it is a centrosymmetric crystal. The mechanical parameters like hardness, work hardening coefficient, yield strength and stiffness constant were evaluated. UV-visible spectrum was recorded in the wavelength range of 190-1100 nm to find the linear optical parameters like transmittance, band gap, absorption coefficient and extinction coefficient. Third order NLO studies were carried out by Z-scan technique to find non-linear absorption coefficient, non-linear refractive index and non-linear susceptibility.

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KEYWORDS

Crystal growth, Single crystal, XRD, NLO, Transmittance, Hardness, Z-scan, Extinction coefficient, Stiffness constant.

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INTRODUCTION

The significance of non-linear optics (NLO) is to understand the non-linear behaviour in the induced polarization and to analyze the propagation of light in the materials. To create the non-linear behaviour, high intense laser light is necessary. Recently, the understanding of the non-linear polarization mechanisms and their relation to the structural characteristics of the materials has been improved and novel NLO materials are being synthesized and grown in the form of single crystals using various growth techniques [1-3]. There are mainly three types of NLO materials *viz.*, organic NLO, inorganic NLO and semi-organic NLO materials. Organic NLO crystals are found to possess high non-linear optical efficiencies and additionally offer large number of design possibilities. Some of them show extremely fast optical non-linearities and have high laser damage threshold compared to that of inorganic NLO crystals and they have high figures of merit for operation as linear and non-linear devices [4,5]. Usually, centrosymmetric NLO crystals produce third order non-linearity and non-centrosymmetric

NLO crystals produce second order non-linearity. But it is reported that some centrosymmetric NLO crystals also show second order non-linearity and hence they give out second harmonic emission [6-8]. Third order NLO materials have applications in optical switching, modulating and computing devices and optical signal processing devices [9,10].

Urea is hydrogen bonded, which leads to enough delocalization, yet it has strong localized features such as *p* electrons in the carbonyl groups which contribute significantly to non-linear response. It has high a non-linear coefficient, a high biref-ringence and a high laser damage threshold [11,12]. It is reported that urea molecule forms an extensively hydrogen bonded host structure and the phase diagram of urea dicarboxylic acid has been reported in the literature [13-15]. Urea is observed to be combining with L-malic acid and L-tartaric acid to form interesting NLO materials [16,17]. Krishnan *et al.* [18] have reported about the growth and studies of urea succinic acid crystal. It is reported that urea can be combined with oxalic acid in two ways forming two compounds *viz.*, mono-urea oxalic acid and di-urea oxalic acid. The crystal structure of mono-urea oxalic acid and di-urea oxalic acid crystals have been solved and reported in the literature [19,20]. Dhivya *et al.* [21] have reported the nucleation kinetics and ferroelectric properties of urea oxalic acid crystals prepared by taking urea and oxalic acid in 2:1 molar ratio. Since no studies of mono-urea oxalic acid crystals are found in the literature, it is decided to carry out the various characterization studies of mono-urea oxalic acid crystals prepared by taking urea and oxalic acid in 1:1 molar ratio.

EXPERIMENTAL

Synthesis and growth: Good quality (AR grade from Merck India) chemicals of urea and oxalic acid were purchased commercially and they are taken in molar ratio of 1:1. The calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 4 h using a hot magnetic stirrer to ensure homogeneous concentration over entire volume of the solution and at the same time the solution was heated at 50 °C. Then, the solution filtered was filtered to remove unsoluble impurities if any and it was kept for evaporation. The synthesized salt was obtained after 3 days and it was re-crystallized twice to improve the purity of the salt of mono-urea oxalic acid (MUOA). Single crystals of MOUA were grown using the synthesized salt dissolving in double distilled water. Aqueous saturated solution of the sample was prepared, stirred well and filtered and this solution was taken in a growth vessel covered with perforated sheet for slow evaporation. To control the temperature of the solution constant, a constant temperature bath (accuracy: ± 0.01 °C) was used. After 3 to 4 days, the saturated solution was changed into supersaturated solution and then tiny crystals are formed in the solution. Bulk crystals of mono-urea oxalic acid were harvested after a growth period of 30 days. The obtained optically transparent crystal is shown in the Fig. 1.

Fig. 1. Grown crystal of mono-urea oxalic acid

Characterization techniques: A grown of mono-urea oxalic acid crystal was subjected to single crystal X-ray diffraction using ENRAF NONIUS CAD-4 diffractometer with MoK_{α} (λ = 0.71073 Å) radiation at room temperature to find the lattice parameters. UV-visible transmittance spectrum of mono-urea oxalic acid crystal was recorded using Perkin Elmer lambda 35 UV-visible spectrophotometer in the range of 190-1100 nm to find the linear optical parameters. Second harmonic generation efficiency was measured using Kurtz and Perry powder technique using Nd:YAG laser. Z-scan measurement was performed in both the modes like open aperture mode and closed aperture mode using the He–Ne laser (λ = 632.8 nm) focused by a lens of 30 mm focal length to find the third order NLO parameters. Mechanical parameters of the grown crystal was evaluated using a Vickers microhardness tester with a diamond indenter.

RESULTS AND DISCUSSION

Structural analysis: Single crystal XRD data were collected using an X-ray diffractometer and from the data it is confirmed that the grown mono-urea oxalic acid crystal belongs to monoclinic system. The obtained values of lattice parameters of the sample are provided in the Table-1 and these values are found to be in good agreement with the reported values [19]. The number of molecular units per unit cell is observed to be 4 and the volume of the unit cell is found using the relation V = a b c sin b. The space group of mono-urea oxalic acid crystal is observed to be C2/c. This space group is identified as the centrosymmetric space group and hence according to the theory of NLO, mono-urea oxalic acid crystal should not give out emission of green laser light when it is irradiated with Nd:YAG laser. But experimentally it is found that it emits green laser light under the irradiation of Nd:YAG laser.

TABLE-1
THE REPORTED AND OBTAINED VALUES OF LATTICE PARAMETERS OF MONO-UREA OXALIC ACID CRYSTAL

Crystal parameters	Present work	Reported work [19]
a	13.066(5) Å	13.0625 (7) Å
b	6.647(4) Å	6.6437 (2) Å
c	6.853(2) Å	6.8478 (3) Å
α	90°	90°
β	93.28°	92.474 (6)°
γ	90°	90°
V	594.21(2) Å^3	593.72 (6) Å^3
Z	4	4

Mechanical studies: Mechanical studies were carried out to find the mechanical parameters like hardness, yield strength, stiffness constant *etc*. Since the grown mono-urea oxalic acid crystal is soft, low loads are applied onto the crystal to find hardness parameters and this kind of study is known as micro-hardness study. Microhardness of the grown crystal was measured using a Vickers microhardness tester with diamond indenter. A well polished crystal was used in this method. The loads used to find the microhardness are 25, 50, 75 and 100 g. When a load is applied, the diamond indenter will make an impression on the crystal and the average diagonal length of impression formed on the crystal was measured as d. The micro-hardness number (H_v) can be calculated using the formula $H_v = 1.8544\ P/d^2$ where P is the load applied in g and d is the diagonal length of the indentation impression in millimetre. Since the microhardness tester is a computerized one, the values of d and H_v are directly obtained from the hardness studies. The obtained values of H_v for different applied loads are presented in Fig. 2. The results indicate that the hardness increases with increase of the applied load upto 75 g and then the crystal seems to be not withstanding when the load is more than 75 g. The small crack is formed when the crystal is subjected to more than 100 g. According to the normal indentation size effect, the microhardness of crystal decreases with increasing load and in reverse indentation size effect (RISE), the hardness increases with increase of the applied load [22,23]. Hence, mono-urea oxalic acid crystal has the behaviour of RISE upto 75 g and beyond 75 g, the crystal shows normal indentation size effect. To find the work hardening coefficient (n), the Meyer's relation $P = ad^n$ is used. Here P is the load and 'a' is a constant [24]. By plotting a graph of log (P) against log (d) as given in the Fig. 3, the slope is obtained and this is equal to the work hardening coefficient for mono-urea oxalic acid crystal. The work hardening coefficient for the sample is obtained as 2.6257. Since this value is more than 1.6, the mechanical strength of mono-urea oxalic acid crystal is low and the grown crystal is a soft material.

The non-linear behaviour of mono-urea oxalic acid crystal can be analytically explained by using the relation $P = W + Ad^2$ where P is the applied load, d is the average diagonal indentation length, W is the minimum load to initiate plastic deformation in gram (g) or resistance pressure, A is the load-independent constant. This kind of approach is called as the Hays-Kendall's approach [25]. The values of W and A are obtained from the plot drawn between P *versus* d^2 as shown in the Fig. 4. The resultant value of W becomes negative and hence the sample exhibits behaviour of reverse indentation size effect. The corrected indentation size independent hardness (H_o) is determined using the relation $H_o = 1.8544\ A$. The obtained values of W and H_o for mono-urea oxalic acid crystal are -7.394 g and 0.0985 g/mm^2 respectively.

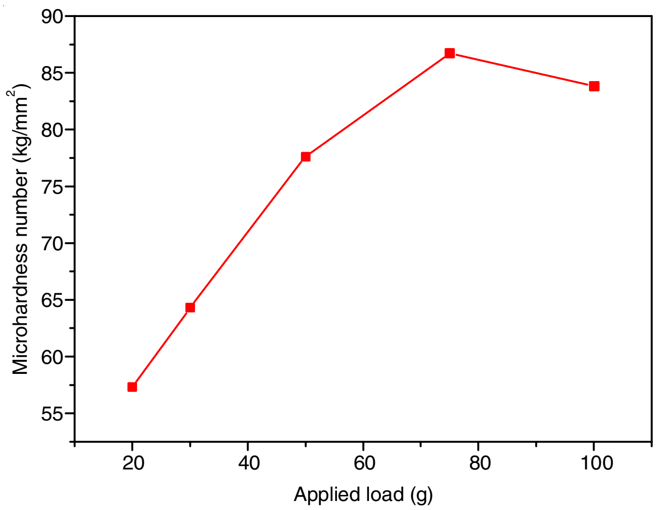

Fig. 2. Variation of microhardness number with applied load for mono-urea oxalic acid crystal

Fig. 3. Meyer's plot for mono-urea oxalic acid crystal

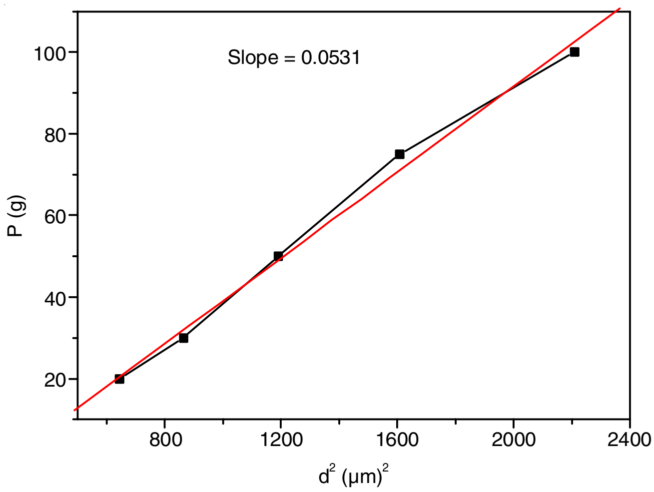

Fig. 4. Plot of P *versus* d^2 for mono-urea oxalic acid crystal

Other mechanical parameters like yield strength and stiffness constant of mono-urea oxalic acid crystal were determined using the values of microhardness number (H_v). Yield strength (σ_y) of the crystal is found out using the relation $\sigma_y = (H_v/3)(0.1)^{n-2}$ where n is the work hardening coefficient. The elastic stiffness constant (C_{11}) can be calculated using Wooster's empirical relation given by $C_{11} = H_v^{7/4}$. The yield strength and stiffness constant depend on the hardness and type of the material [26,27]. The obtained values of yield strength and stiffness constant of mono-urea oxalic crystal are presented in the Table-2. From the results, it is observed that the yield strength and stiffness constant for mono-urea oxalic crystal increases with

TABLE-2
VALUES OF YIELD STRENGTH AND STIFFNESS CONSTANT FOR MONO-UREA OXALIC ACID CRYSTAL

Applied load (g)	Yield strength $\times 10^9$ (N/m^2)	Stiffness constant $\times 10^{14}$ (N/m^2)
20	0.1085	20.484
30	0.1217	25.062
50	0.1468	34.826
75	0.1641	42.284
100	0.1586	39.840

increase of load upto 75 g and then these values decrease slightly and this indicates that there is a reduction of mechanical strength slightly when the load is applied beyond 75 g to the crystal.

Linear optical studies: The linear optical studies were carried out for mono-urea oxalic acid crystal by recording transmittace/absorbance spectra in the wavelength range of 190-1100 nm using Lamda 35 model spectrophotometer. Using the values of transmittance, the linear absorption coefficient of the sample was evaluated using the relation $\alpha = [2.303 \log_{10}(1/T)]/d$ where T is the transmittance and d is the thickness of the crystal. Here the thickness of the crystal is taken as 1.2 mm. The variation of absorption coefficient with wavelength for mono-urea oxalic acid crystal is shown in the Fig. 5. It is observed that the transmittance is high and hence the absorbance and absorption coefficient are low in the visible region of the spectrum. Low absorption in the entire visible region and near infrared region with lower UV cut-off wave length at 247 nm is suggesting that mono-urea oxalic acid crystal could be used for second harmonic generation applications (Fig. 6). Using the Tauc's equation, the correct value of optical band gap is obtained and the Tauc's equation for direct band gap material is given by $(\alpha h\nu)^2 = A(hn-E_g)$ where E_g is the optical band gap of the crystal, h is the Planck's constant, n is the frequency of light, a is the linear absorption coefficient and A is a constant [28]. The optical energy gap (E_g) is determined from the plot of $(\alpha h\nu)^2$ *versus* hν and extrapolated line with the photon energy axis and the plot is shown in the Fig. 7. The obtained value of optical band gap for mono-urea oxalic acid crystal is 5.03 eV. Extinction coefficient (K) of the sample was determined using the relation

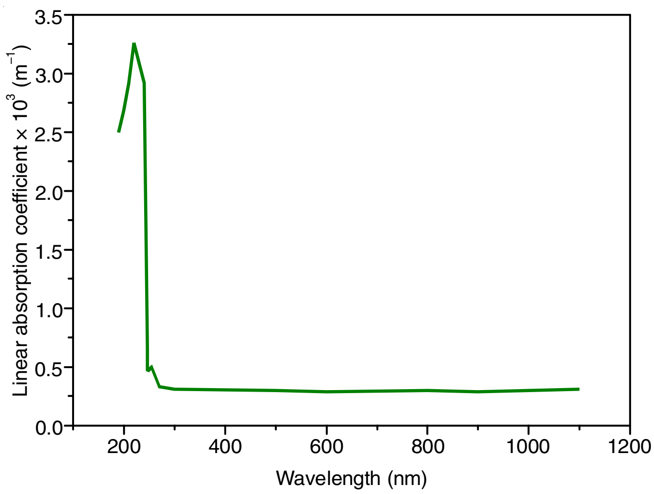

Fig. 5. Plot of linear absorption coefficient *versus* wavelength for mono-urea oxalic acid crystal

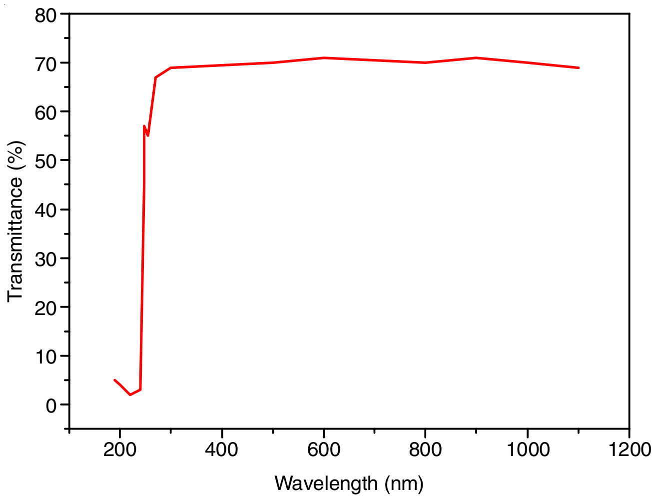

Fig. 6. UV-visible-NIR transmittance spectrum of mono-urea oxalic acid crystal

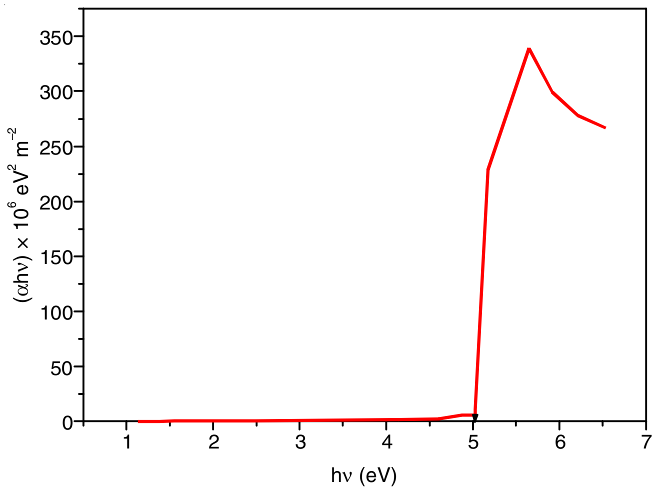

Fig. 7. Tauc's plot for mono-urea oxalic acid crystal

$K = \alpha\lambda/4\pi$ where α is the absorption coefficient and l is the wavelength of the light [29]. The wavelength dependence of the extinction coefficient for mono-urea oxalic acid crystal is presented in Fig. 8. The extinction coefficient is found to be low of the order of 10^{-5} for the grown crystal and it increases with increase of wavelength in the visible region. At UV cut-off wavelength, the extinction coefficient is observed to be maximum for the sample. The high transmittance and low extinction coefficient of the grown crystal of mono-urea oxalic acid indicate that this crystal is suitable for NLO applications [30].

SHG studies: The non-linear optical property of powdered material of mono-urea oxalic acid was tested by the Kurtz-Perry powder method [31]. The sample was tested using Q-switched and Nd:YAG laser (1064 nm, Quanta ray series). The crystal was grounded into powder and densely packed between two transparent glass slides. An Nd:YAG laser producing pulse width of 6 ns at a repetition of 10 Hz was used. This laser beam is fall normally on the sample cell and sample converts the 1064 nm radiation into green light of wavelength 532 nm. The emission of green radiation from the crystal confirms the second harmonic generation. The second harmonic signal was detected by a photomultiplier tube and displayed

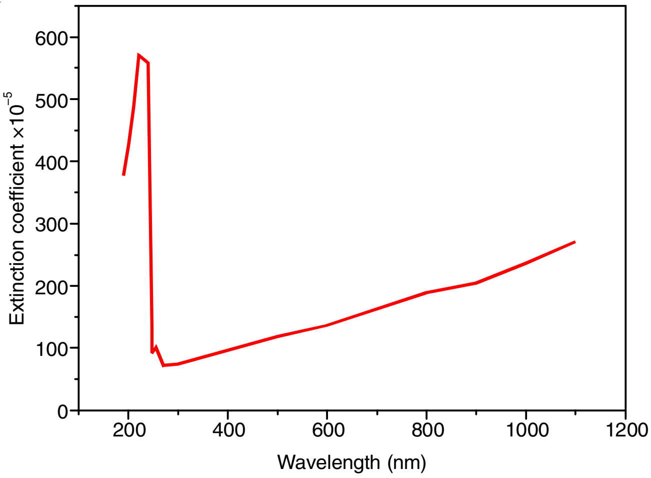

Fig. 8. Variation of extinction coefficient *versus* wavelength for mono-urea oxalic acid crystal

on the storage oscilloscope. This value is compared to potassium dihydrogen phosphate (KDP) crystal. From the SHG measurement, it is observed that the relative SHG efficiency of mono-urea oxalic acid crystal is 0.84 times that of potassium dihydrogen phosphate. Hence, experimentally it is proved that a centrosymmetric crystal like mono-urea oxalic acid crystal gives out SHG emission like other centrosymmetric crystals [6-8].

Third order NLO studies: Third order NLO studies were carried out by Z-scan technique using a He-Ne laser of wavelength 632.8 nm, power of the laser is 5 mW. Z-scan technique is a simple and sensitive single beam technique for measuring the change in phase induced on a laser beam upon propagation through a non-linear material. This technique helps to determine non-linear absorption coefficient, non-linear optical refraction and non-linear susceptibility for optical materials. In this technique, the laser beam was changed to a Gaussian beam using a Gaussian filer and the beam was focused by a convex lens of focal length of 30 mm. The beam waist radius (ω_o) at the focus (Z = 0) can be calculated using the relation:

$$\omega_o = f\lambda/D$$

where f is the focal length of the lens (f = 30 mm), D is the beam radius at the lens (D = 1.12 mm) and the obtained value of ω_o is 16.95 μm. Rayleigh length of the Gaussian laser beam can be determined using following the relation:

$$Z_R = \pi\, \omega_o^2/\lambda$$

The calculated value of Rayleigh length (Z_R) of the beam is 1.43 mm. Using the screw gauge, the thickness (L) of the polished crystal is found to be 1.12 mm. Since L is less than Z_R, the condition of Rayleigh length factor is satisfied here for the Z-scan experiment. The sample was moved along +Z and –Z direction using a stepper motor and the transmitted intensity was measured using a digital power meter. The relative or normalized transmittance of the crystal was measured at different positions with respect to focus of the beam (Z = 0). There are two modes in the Z-scan analysis namely, open and closed aperture modes. In the closed aperture method, an aperture is placed in front of the detector to prevent some of the light from reaching the detector. Hence, only the central region of the cone of light reaches the detector. The detector is now sensitive to any focusing or defocusing that a sample may induce. In the open aperture method, the aperture is removed to allow all the light to reach the detector and hence sets the normalized transmittance and this method is used to determine the non-linear absorption coefficient of the crystal. The closed aperture method is used non-linear refractive index and non-linear susceptibility of the sample [32-35]. The open aperture and closed aperture Z-scan curves for mono-urea oxalic acid crystal are shown in the Figs. 9 and 10. The closed Z-scan curve is characterized by a pre-focal transmittance peak followed by a post-focal transmittance valley intensity. The transmittance difference between peak and valley (ΔT_{p-v}), linear transmittance aperture (S), third order non-linear refractive index (n_2) of the crystal, non-linear absorption coefficient (β) and third order non-linear optical susceptibility (χ^3) were determined using the following procedure and the equations.

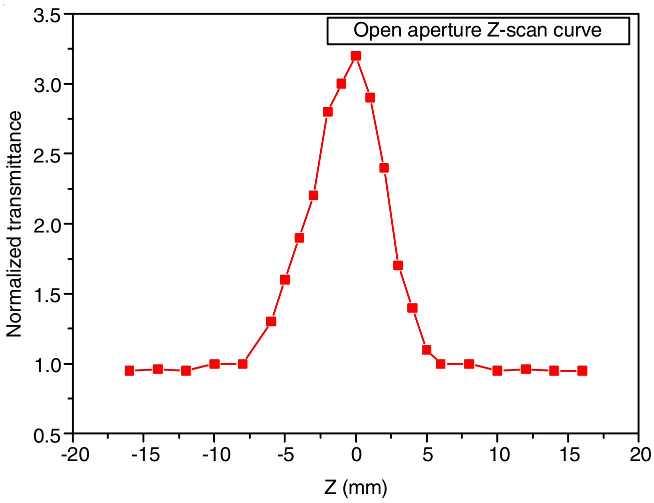

Fig. 9. Open aperture Z-scan curve for mono-urea oxalic acid crystal

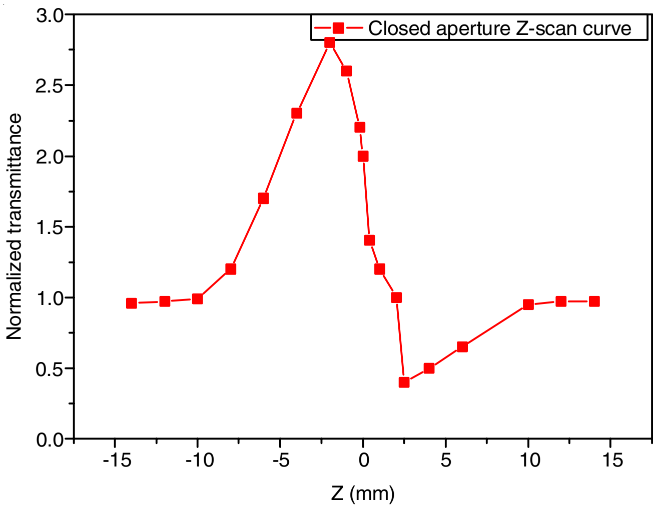

Fig. 10. Closed aperture Z-scan curve for mono-urea oxalic acid crystal

The transmission difference between peak and valley (ΔT_{p-v}) is written in terms of phase shift (Δϕ).

$$\Delta T_{p-v} = 0.406\,(1 - \sigma)^{0.25}\,|\Delta\phi|$$

Linear transmittance aperture (S) is calculated using the relation:

$$S = 1\text{-}\exp[(-2r_a^2)/(\omega_a^2)]$$

where r_a is the radius of the aperture and ω_a is the beam radius at the aperture. The third order non-linear refractive index (n_2) of the crystal was calculated by the relation.

$$n_2 = \Delta\phi/(K\, I_o\, L_{eff}) \quad m^2/W$$

where I_o is the intensity of the laser beam at the focus and $K = 2\pi/\lambda$ (λ is the wavelength of laser beam).

The effective thickness of the sample can be calculated using the relation:

$$L_{eff} = [1\text{-}\exp(-\alpha L)]/\alpha$$

where α is the linear absorption coefficient and L is the thickness of the sample. The non-linear absorption coefficient (β) can be calculated using the following relation:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_o L_{eff}} \quad m/W$$

where ΔT is the peak value or valley value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for two photon absorption process. The real and imaginary parts of the third order non-linear optical suceptibility ($\chi^{(3)}$) are defined as

$$\text{Real part of } \chi^{(3)} = (10^{-4}\varepsilon_o\, c^2\, n_o^2\, n_2)/\pi \quad \text{(esu)}$$

$$\text{Imaginary part of } \chi^{(3)} = (10^{-2}\varepsilon_o\, c^2\, n_o^2 \lambda\, \beta)/4\pi^2 \quad \text{(esu)}$$

$$\text{Absolute value of } \chi^{(3)} = [\{\text{Real part of } \chi^{(3)}\}^2 + \{\text{Imaginary part of } \chi^{(3)}\}^2]^{1/2} \quad \text{(esu)}$$

Here ε_o is the vacuum permitivity, n_o is the linear refractive index of the sample and c is the velocity of the light in vacuum. The calculated values of third order NLO parameters of mono-urea oxalic acid crystal and the relevant data are provided in Table-3. The negative value of non-linear refractive index indicates that the sample has self-defocussing nature and this property is useful in the protection of optical sensors such as night vision devices. When self-defocusing occurs in the sample, it tends to diverge the beam at the aperture and hence it causes a decrease of the transmittance at the aperture. The scan usually is seen linear at the normalized transmittance T = 1 initially and a peak and a valley are formed in the case of self-defocusing sample and the scan is finished when the transmittance becomes linear again (T = 1). The closed Z-scan curve is not the sensitive to non-linear refraction and hence the closed aperture curve is symmetric with respect to focus. Using the closed aperture Z-scan curve, the non-linear refractive index of mono-urea oxalic acid crystal is found to be -5.281×10^{-11} m^2/W and using the open aperture Z-scan curve, the non-linear absorption coefficient is found to be 1.825×10^{-4} m/W. Using the values of both non-liner refractive index and non-linear absorption coefficient, the third order non-linear susceptibility of mono-urea oxalic acid crystal is obtained to be 4.761×10^{-7} esu. It is observed that the value of third order non-linear susceptibility of mono-urea oxalic acid crystal is more than the values of non-linear susceptibiliy of other crystals [36-38]. The large value of third order susceptiblity of mono-urea oxalic acid crystal is due to electron density transfer and large third order non-linearity in the sample.

TABLE-3
RELEVANT DATA USED AND OBTAINED VALUES FROM Z-SCAN MEASUREMENT

Parameters in connection with Z-scan measurement	Values
Wavelength of laser	532.8 nm
Power of the laser	5 mW
Focal length of convex lens used	30 mm
The beam waist radius (ω_o) at the focus	16.95 µm
Rayleigh length (Z_R) of the Gaussian beam	1.43 mm
Spot size diameter at the aperture (ω_a)	3.5 mm
Aperture radius (r_a)	2 mm
Effective length (L_{eff})	0.96 mm
Linear absorption coefficient (α)	303.35 m^{-1}
Non-linear absorption coefficient (β)	1.825×10^{-4} m/W
Non-linear refractive index (n_2)	-5.281×10^{-11} m^2/W
Real part of non-linear susceptibility	3.226×10^{-8} esu
Imaginary part of non-linear susceptibility	4.732×10^{-7} esu
Absolute value of non-linear susceptibility	4.761×10^{-7} esu

Conclusion

Single crystals of mono-urea oxalic acid were successfully grown using urea and oxalic acid in the aqueous solution at room temperature. The unit cell parameters of the grown crystal were found out by XRD method and it is noticed that mono-urea oxalic acid crystal is a centrosymmetric crystal. The UV-visible-NIR transmittance study reveals the cut-off wavelength of 247 nm and the band gap energy 5.03 eV. The absorption coefficient is observed to be low and transmittance is high in the visible region. The hardness studies show that hardness number of mono-urea oxalic acid crystal increases with increase of load and this indicates that the sample has reverse indentation size effect. Meyer's index number of the sample is found to be 2.6257. The relative SHG efficiency of mono-urea oxalic acid crytal is calculated to be 0.84 times that of potassium dikhydrogen phosphate crystal. According to theory of XRD, mono-urea oxalic acid crystal is a centrosymmetric crystal, but it shows experimentally the SHG behaviour. Using the closed aperture Z-scan curve, the non-linear refractive index of mono-urea oxalic acid crystal is found and using the open aperture Z-scan curve, the non-linear absorption coefficient is found. The third order non-linear susceptibility of mono-urea oxalic acid crystal is obtained to be 4.761×10^{-7} esu and this value is observed to be more compared to those of other NLO crystals.

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