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Third order non-linear optical properties of L-arginine hydrochloride monohydrate single crystals by Z-Scan technique

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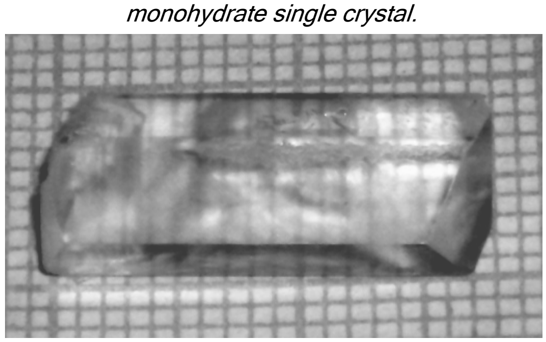
Abstract
L-arginine hydrochloride monohydrate (L-arginine hydrochloride monohydrate) was synthesized by the reaction between hydrochloric acid and the strongly basic amino acid, L-arginine taken in the ratio of 1:1. The crystal structure of the sample was studied by single X-ray diffraction. The UV transmittance spectra of the grown crystals indicate a good transparency between 200 and 1000 nm. The nonlinear refractive index n_2 and susceptibility $\chi^{(3)}$ have been measured through the Z-scan technique. The results indicate that the compound exhibits reverse saturation absorption and self-defocusing performance. Non-linear absorption co-efficient is determined as 9.2194×10^{-4} cm/w. The non-linear refractive index of the L-arginine hydrochloride single crystals were found to be 1.7129×10^{-7}cm ^{2}/w. The real and imaginary pars of non-linear susceptibility $\chi^{(3)}$ have been measured at 632.8 nm and found to be 1.1573×10^{-05} esu and 3.1382×10^{-05} esu, respectively.

Keywords: Growth from solution, single XRD, UV spectrum, Z-scan

Introduction
L-arginine hydrochloride monohydrate is one of the new semi organic NLO materials by Monaco *et al.* (1987). Use of these crystals for NLO devices demands large size single crystals of extremely high quality. Here we present the third order non-linear optical properties of L-arginine hydrochloride monohydrate by Z-scan technique. The Z-scan technique (Zhao *et al.,* 1993; Yin *et al*. 2000; Natarajan *et al*., 2010; Sivanesan *et al*., 2010) is a popular method for the measurement of optical non-linearities of materials. 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 (Krauss & Wise, 1994), dielectrics (Gomes & De Araujo, 1992; Rangel-Rojo, *et al.,* 1994) organic or carbon-based molecules (Wei *et al*., 1992; Zhang *et al.,* 1993) and liquid crystals (Paparo *et al.,* 1994; Li *et al.,* 1994). In this work we present the growth of L-arginine hydrochloride monohydrate single crystals from aqueous solution. Single X-ray diffraction, optical absorption spectrum Z-scan measurements were carried out. Z-scan results reveal that L-arginine hydrochloride monohydrate single crystal is a potential candidate for the optical switching (Lee *et al.,* 1993) and optical limiting (Fryad *et al.,* 1993).

Fig. 1. L-arginine hydrochloride monohydrate single crystal.



Crystal growth
Synthesis of L-arginine molecule $NH_2CNHNH\ (CH_2)_3\ CH\ (NH_2)\ COOH$ has two groups namely guanidyl and amino groups, which can be protonated. L-arginine hydrochloride monohydrate single crystal was synthesized by the reaction between hydrochloric acid and the strongly basic amino acid, L-arginine taken in the ratio of 1:1 (higher ratios like two or more yields highly viscous solution). The required amount of hydrochloric acid was added to the double distilled water. Then the calculated amount of L-arginine was added and dissolved in dilute hydrochloric acid. The following reaction takes place in this process

$$NH_2CNHNH\ (CH_2)_3\,CH\ (NH_2)\ COOH + HCl + H_2O \rightarrow (H_2N)_2^{+}CNH\ (CH_2)_3\,CH\ (NH_3)^{+}COO^{-}\,Cl^{-}\,H_2O.$$

The synthesized salt was purified by repeated re-crystallization process until optically clear crystals of size 1.9 x 0.9 x 0.4 mm^3 was obtained as shown in Fig. 1. Then it was grounded to around 2 mm thickness.

Results and discussion
Single crystal XRD
Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters. This study reveals that the grown crystal belongs to monoclinic system with the space group P_{21}. The calculated lattice parameter values are listed in Table 1. The single crystal XRD results are in good agreement with the reported values and thus confirm the structure of the grown crystal.

Optical measurements
Optical absorption spectrum: The

optical absorption spectrum analysis of the grown crystal was carried out between 200 nm to 900 nm using Varian Cary 5E spectrophotometer. The recorded spectrum is as shown in the Fig. 2. The crystal is transparent in the entire visible region and shows maximum UV transmission. The L-arginine hydrochloride monohydrate possesses a good transparency of 74% with the lower cut-off wavelength at 220 nm. The material can find application as windows in spectral instruments in this region.

Table1. Single XRD data of L-arginine hydrochloride monohydrate single crystals

Empirical formula $C_6H_{15}N_4O_6Cl$	Formula wt. 274.66
Crystal system orthorhombic	Space group P_{21}
a = 11.07 Å	
b = 8.50 Å	
c = 11.22 Å	
β= 91.37^0	
Volume = 1056 (Å^3)	

Refractive index measurement: The refractive index of the L-arginine hydrochloride monohydrate crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal of L-arginine hydrochloride monohydrate was mounted on a rotating mount at an angle varied from 0 to 90°. The angular reading on the rotary stage was observed, when the crystal is perfectly perpendicular to the incident beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster's angle (θp) for L-arginine hydrochloride monohydrate is measured to be 58.5°. The refractive index has been calculated using the equation n = tan θp; where θp is the polarizing angle and it is found to be 1.632.

Non-linear optical measurements

SHG measurements: The second harmonic generation efficiency of the grown crystals was carried out using the Kurtz powder technique (Kurtz & Perry *et al.,* 1968). The sample is irradiated at 1064 nm Nd: YAG pulsed laser. The crystal of L- arginine hydrochloride monohydrate single crystals were powdered with a particle size of 100-150 µm and then placed in a micro capillary and exposed to laser radiation. The output from the sample was monochromatic to collect the intensity of 532 nm component, and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. The generation of the second harmonic was confirmed by the emission of green light. Urea crystal was powdered to the same particle size as the experimental sample and it was used as a reference material for this measurement. The SHG conversion efficiency of L-arginine hydrochloride monohydrate single crystal was found to be 0.17 with respect to Urea and 0.38 times that of KDP it is comparable with the reported values (Meera *et al.*, 2004; Kalaiselvi *et al.,* 2008). Thus, п-п* transitions occurs in the carboxylate and guanidyl groups which give rise to the NLO properties in of L- arginine hydrochloride monohydrate single crystal.

Z-scan method: The third order optical non-linearities of L-arginine hydrochloride monohydrate single crystals were investigated with the Z-scan method as outlined earlier (Sivanesan *et al.*, 2010). A CW He-Ne laser of wavelength of 632.8 nm was used in the experiment. The laser beam was focused to a waist of 45 µm with the help of a convex lens of focal length 12 cm to give the intensity at the focus 6.25 x 10^7 W/m^2. The sample is moved along the (beam direction) optic axis (Z-direction) through the focus of the lens. The energy transmitted through an aperture is recorded as a function of the sample position. The Rayleigh length of Z_0 was calculated is greater than the thickness of the sample. Fig. 3 shows the normalized transmission for the open aperture (OA).

The transmission is symmetric with respect to the focus (Z = 0) where it has a minimum transmission. This indicates that the sample exhibits resonance saturation absorption (RSA/two photon absorption). Phase shift at the focus is calculated using the relation

$$\Delta\Phi_0 = \beta I_0 L_{eff} /Z \quad (1)$$

$_{Leff}$ = [1-exp (-αd)/α] where α is the linear absorption co-efficient at 632.8 nm and "d" is the thickness of the sample. Ll_{eff} is the effective thickness of the sample I_0 is the intensity of the beam focused at the focus and β is non-linear absorption co-efficient. β is calculated from the formula:

$$\beta = 2\sqrt{2}\Delta T / I_o L_{eff} \quad (2)$$

The calculated value of β = 9.2194 x 10^{-4} cm/W. The imaginary part of the third order non-linearity $\chi_I^{(3)}$ is related to the non-linear absorption co-efficient β by the relation

$$\chi_I^{(3)} = 10^{-2} \epsilon_0 c^2 n_o^2 \lambda \beta / 4 \Pi^2 \quad (3)$$

Where n is the linear refractive index (n=1.453 at λ = 632.8 nm) ε_0 is the permittivity of free space and c is the velocity of light. The experimentally determined value of $\chi_I^{(3)}$ at 632 nm was found to be 3.1382 x 10^{-05} esu. The normalized transmittance for closed aperture (CA) is observed in Fig. 4.

The non-linear refractive index of the said crystal is calculated using the relation

$$n_2 = \Delta\Phi_0 / K I_0 L_{eff} \quad (4)$$

The peak to valley configuration of the curve suggests that the refractive index change is negative, exhibiting a self defocusing effect. This may be an advantage for the application in protection of optical sensors. The value for non-linear refractive index "n_2" calculated by z-scan method is found to be 1.7129 x 10^{-7}cm^2/W.

The real part of the third order non-linear susceptibility

$$\chi_R^{(3)} = 2 n_0^2 \varepsilon_0 c \gamma \quad (5)$$

The value of of $\chi_R^{(3)}$ at 632 nm is found to be 1.1573 x 10^{-05} esu. By comparing the values of imaginary and real non-linearities, one can come to the conclusion that the $\chi_I^{(3)} > \chi_R^{(3)}$, i.e. $\chi_I^{(3)}$ which gives rise to the absorption change, is dominant, and this can be seen from Fig. (3) where the valley is much larger than the peak. The absolute value of $|\chi^{(3)}|$ was calculated from the formula:

$$|\chi_R^{(3)}| = \sqrt{(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2}$$

gives 3.3448 x 10^{-05} esu. The value of the $\chi_I^{(3)}$ and $\chi_R^{(3)}$ of L-arginine hydrochloride monohydrate reported here is of the same order of the magnitude of the materials such as Chalogenide glasses (Sheik-Bahe *et al.,* 1990) and C_{60} (Fryad *et al.*, 1993) etc.

Fig. 2. UV absorption spectra of L-arginine hydrochloride monohydrate single crystals

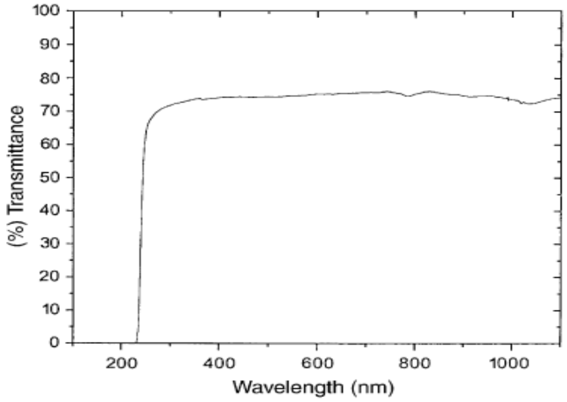


Fig. 3. Open aperture curve of L-arginine hydrochloride monohydrate single crystals

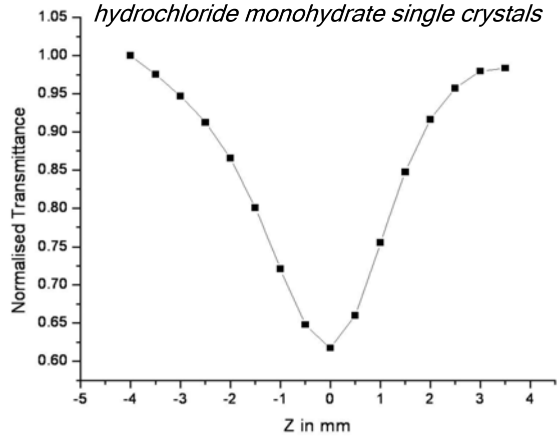
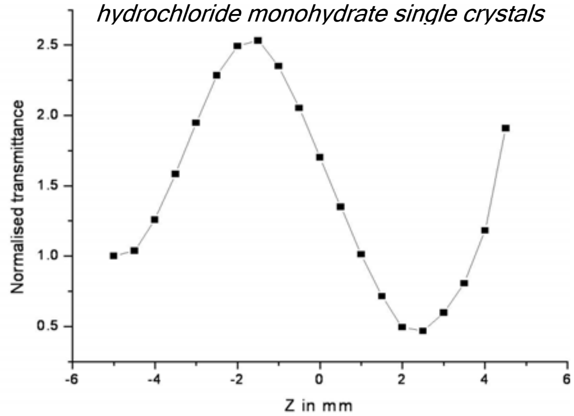


Fig. 4. Closed Aperture curve of L-arginine hydrochloride monohydrate single crystals



Conclusion

We have reported the optical properties of L-arginine hydrochloride monohydrate single crystal. The Z-scan measurement with 632.8 nm laser pulses revealed that non-linear refractive index of the crystal is in the range of 10^{-7} cm^2/W. The measured 3^{rd} order non-linear properties confirm its suitability for non-linear optical devices such as optical limiting (Lee *et al.,* 1993) and optical switching (Fryad *et al.,* 1993).

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