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Growth, SHG, THG and Impedance Analysis of Urea Admixtured L-Alanine (ULA) Single Crystals

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Abstract : Urea admixtured L-alanine (ULA) is an organic, NLO crystal and that was grown by solution method with slow evaporation technique. The structure of the grown crystal was determined by single crystal XRD study. Second harmonic generation of the grown crystal was confirmed by Kurtz–Perry powder technique. The third order nonlinear optical property of ULA crystal was analysed by Z-scan experiment and nonlinear absorption coefficient, nonlinear refractive index, third order nonlinear susceptibility etc were calculated. The real and imaginary parts of impedance were investigated for the ULA crystal as a function of frequency. Bulk resistance and dc conductivity of the grown crystal were determined from Nyquist plot. The storage energy in a capacitor with ULA crystal has been calculated as a function of frequency.
Key words: single crystal; Z-scan; SHG; Impedance.

Introduction

Nonlinear optical (NLO) materials play an important role in the fields like photonics and optoelectronics such as frequency conversion, optical switches, optical modulators, optical storage, optical computing, electro optical devices etc[1,2]. The organic NLO materials with small organic molecules have a large dipole moment, chiral structure, high nonlinear figure of merit for frequency conversion, high laser damage threshold and fast optical response time as compared with inorganic NLO materials[3]. The amino acid crystals are of great interest due to their attractive nonlinear optical properties. Most of natural amino acids are individually exhibiting the NLO properties and predominantly zwitter ions rather than unionized molecules[4]. L-alanine is an alpha amino acid with the chemical formula CH_3CHNH_2COOH and it belongs to the orthorhombic crystal system and it is an important source of energy for muscle tissue, the brain and central nervous system[5]. Crystals of L-alanine complexes have been studied by many researchers and reported in the literature[6-8]. Urea (carbamide) is an organic compound, the molecule has two amide groups joined by a carbonyl functional group and it is highly soluble in water and non-toxic. Urea and its derivatives are extensively used in crystal engineering and supramolecular chemistry. Many researchers have reported on the growth and studies of various urea type crystals in the literature[9,10]. In this work, L-alanine is combined with urea to form urea admixtured L-alanine (ULA) bulk crystal by slow evaporation technique using optimized growth conditions. Here we report the studies on second-order, third-order NLO activity and impedance properties of the grown ULA crystals for the first time.

Experimental

Urea admixtured L-alanine (ULA) was synthesized by taking analytical grade L-alanine and urea in the equimolar ratio and the calculated amount of the materials was dissolved in double distilled water. The saturated solution was prepared and allowed to dry at 45°C in the constant temperature water bath (CTB with accuracy ±0.01°C) and the salt was obtained. The purity of the synthesized salt was further increased by successive recrystallization process. From the optimized nucleation critical parameters, the supersaturated solution (supersaturation ratio S= 1.05) of purified salt of ULA has been prepared at room temperature (31°C) and the solution was stirred well for 2 hours to get the homogeneous solution using a hot plate magnetic stirrer. Then the solution was filtered using 4 micro Whatmann filter paper. The filtered solution was taken in a beaker and covered by a perforated cover and the beaker was put inside the constant temperature water bath for slow evaporation technique. After few days, small sized crystals were formed at the bottom of the container due to spontaneous nucleation and seed immersed technique was used to grow big-sized crystals in about 30 days. The grown crystal was stable, colourless and non-hygroscopic. The photograph of the harvested crystals is shown in the fig. 1.

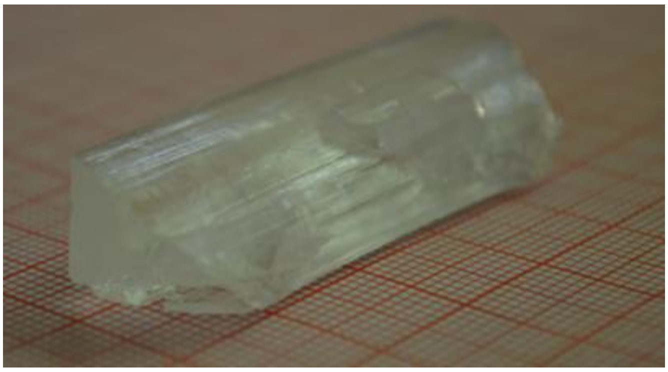

Figure 1: Photograph of the grown ULA crystal.

Results and Discussion

Single crystal X-ray diffraction analysis was used to determine the structure of the crystals. This study for ULA crystal was carried out using a single crystal X-ray diffractometer (Model: ENRAF NONIUS CAD-4) with MoK_{α} (λ= 0.71069 Å) radiation. It is observed that the ULA crystal belongs to orthorhombic structure with non centrosymmetric space group $P2_12_12_1$ and the space group is satisfying one of the basic and material requirements for the SHG activity of the crystal[11]. The obtained unit cell parameters are a= 5.799 (10) Å, b= 6.031 (11) Å, and c= 12.341 ± (20) Å; α=β=γ=90° and the volume of the material is found to be 431.61 (1) Å3. The slight change of lattice parameters is observed for the ULA crystal compared to pure L-alanine crystal. The changes in the lattice parameters may be attributed to the presence of urea in the interstitials of lattice of the L-alanine crystal. From the results, it is confirmed that the grown crystal is the L-alanine crystal added with urea.

A high intensity Nd:YAG laser (l=1064 nm) with an input power of 0.68 J and a pulse duration of 6 ns at a repetition rate of 10 Hz was passed through the powdered ULA sample to measure SHG. The SHG signal generated in the sample was confirmed from the emission of green light from the sample. KDP crystal was powdered to the identical size and used as reference material in the SHG measurement. It is observed that the SHG relative efficiency of ULA sample was found to be 0.75 times higher than that of KDP and 2.3 times that of L-alanine[5].

Z-scan technique was originally introduced by Sheik Bahae et al.[12]. This is a simple and sensitive single beam technique to measure the sign and magnitude of both real and imaginary part of third order nonlinear susceptibility. There are two Z-scan methods namely open and closed aperture used for the measurement of nonlinear absorption coefficient and nonlinear optical refraction for optical materials. The beam was focused using a convex lens and the focal point has been taken as Z = 0. By placing the sample in different positions with respect to the focus of the beam, the corresponding normalized transmission to the crystal was measured. The optically transparent ULA crystal of 1cm of length, 1 cm of breadth and 1 mm of thickness and He-Ne laser of wavelength 632.8 nm were used in this experiment. The transmission difference [13] between peak and valley (ΔT_{p-v}) is

$$\Delta T_{p-v} = 0.406(1-s)^{0.25}|\Delta\varphi|$$

where s is the linear aperture transmittance and $|\Delta\varphi|$ is the on axis phase shift.

$$s = 1 - exp\left(\frac{-2r_a^2}{\omega_a^2}\right)$$

where r_a, ω_a are the aperture radius and beam radius respectively.
The third-order nonlinear refractive index is calculated using the following relation

$$n_2 = \frac{\Delta\varphi\lambda}{2\pi I_o L_{eff}}$$

The effective thickness of the sample is

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

where L, α are the thickness of the sample and linear absorption coefficient respectively and the nonlinear absorption coefficient is given by

$$\beta = \frac{2\sqrt{2}\,\Delta T}{I_o L_{eff}}$$

The real and imaginary parts of the third-order nonlinear optical susceptibility is determined using the following relations

$$Re\,\chi^{(3)} = \frac{10^{-4}\varepsilon_o C^2 n_o^2 \; n_2}{\pi}$$

$$Im\,\chi^{(3)} = \frac{10^{-2}\varepsilon_o C^2 n_o^2 \; \lambda\beta}{4\pi^2}$$

The absolute value of third-order nonlinear optical susceptibility is calculated using

$$|\chi| = \sqrt{(Re\,\chi^{(3)})^2 + (Im\,\chi^{(3)})^2}$$

The diagrams for open aperture and closed aperture Z-scan curves are presented in the figures 2 (a) and 2 (b).

The nonlinear absorption coefficient, nonlinear refractive index and the absolute third order nonlinear susceptibility are 2.179 $\times 10^{-5}$ cm/W, 0.647 $\times 10^{-10}$ cm^2/W and 3.274 $\times 10^{-5}$ respectively.

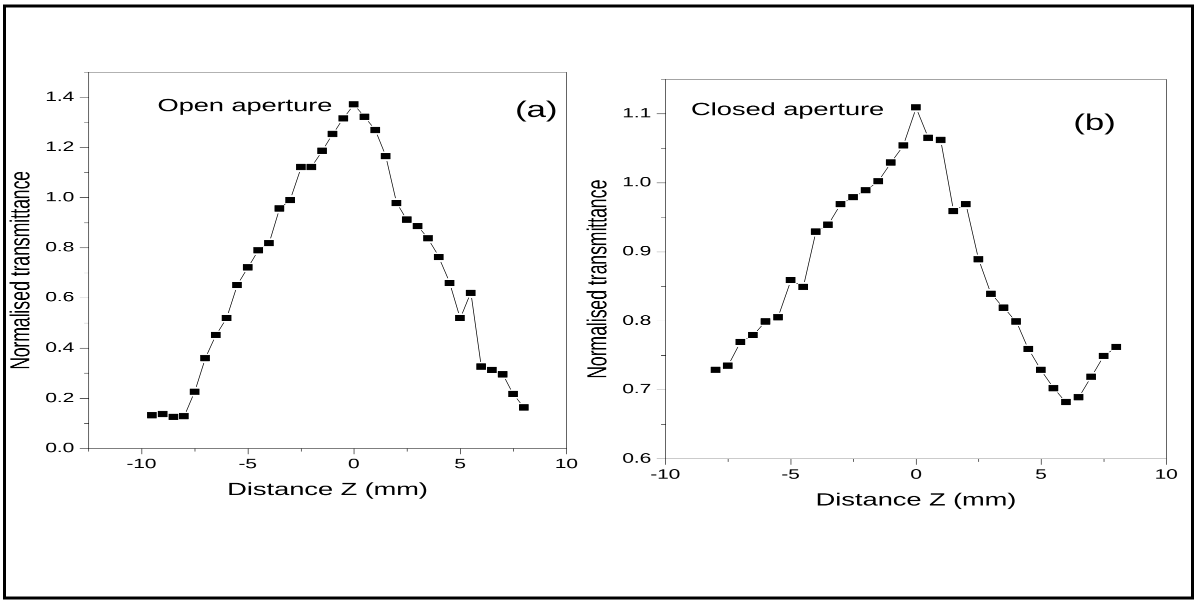

Figure 2: Z-scan curves (a) open aperture (b) closed aperture

Impedance spectroscopy (IS) is used to study the ionic conductivity, electrical and dielectric properties of the materials. This technique is also useful to study the contributions of bulk and electrode polarization effect on impedance and other related parameters along with their equivalent circuits. Electrical impedances were measured in a frequency ranging from 1 Hz to 1 MHz using an impedance analyzer (Model: Versa STAT MC) and silver paste electroded ULA crystal was placed in the two probe arrangement. The complex impedance Z* measurement [14] can be expressed as a function of resistance R and capacitance C using the equation

$$Z^{*} = Z' - jZ''$$

where Z', Z" are the real and imaginary parts of the impedance respectively. Figure 3 and its inset show the variation of real and imaginary parts of impedance of the grown ULA crystal as a function of frequency at 30^{o}C. The results indicate that the real part of impedance decreases with rise in frequency and provides an indication of increasing conduction with frequency. Inset (figure 3) shows the variation of imaginary part of impedance with frequency at room temperature and it is observed that imaginary part of impedance decreases with frequency.

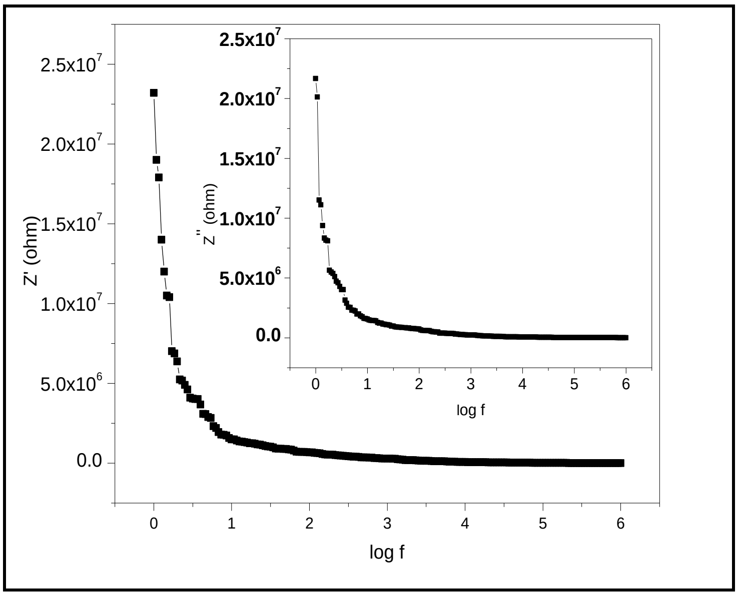

Figure 3: Plot of real part of impedance versus frequency for ULA crystal.

Inset: Variation of imaginary part of impedance of the ULA crystal with frequency.

The Nyquist plot between Z' and Z" of the ULA crystal is shown in figure 4 and this graph explains the transport response function. From the graph, one partial semicircular arc has been observed and this depicts the bulk effect. This bulk effect arises due to the parallel combination of bulk resistance (R_b). The value of bulk resistance is found to be 6.857x10^{6} ohm and the observed value is typical for an insulating material. The dc conductivity (σ_{dc}) of the crystal is calculated using the formula $\sigma_{dc}= d/R_bA$, where A is the area of crystal surface and d is the thickness of the crystal. The dc conductivity of the ULA crystal was found to be 8.334 x10^{-6} m^{-1}mho at 30^{o}C. The low dc conductivity suggests that the number of defects or impurities present in the grown ULA crystal is low.

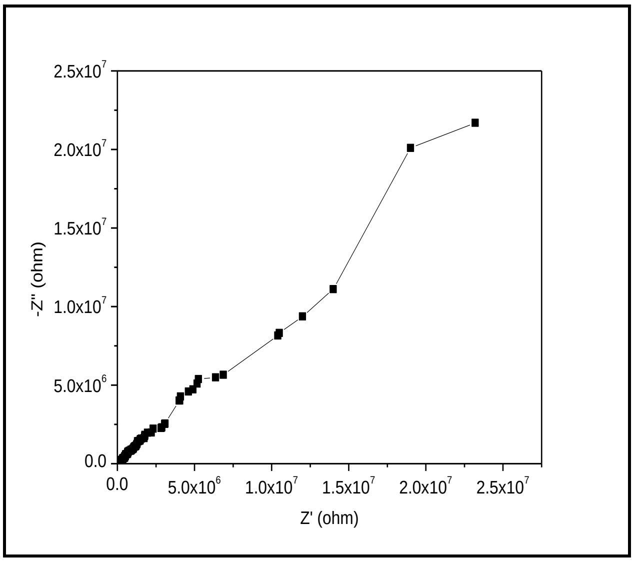

Figure 4: Nyquist plot for ULA crystal

When the ULA crystal is placed between the plates of a capacitor, the charge storage and capacitance increase in the capacitor. This is due to dielectric constant of the sample. The energy storage in the capacitor is calculated using the formula $E=1/2\ CV^2$. The variation of energy storage with frequency for ULA crystal is given in the figure 5. From the results, it is observed that the energy storage decrease with frequency and this is due to the decreases of dielectric constant of the sample with frequency.

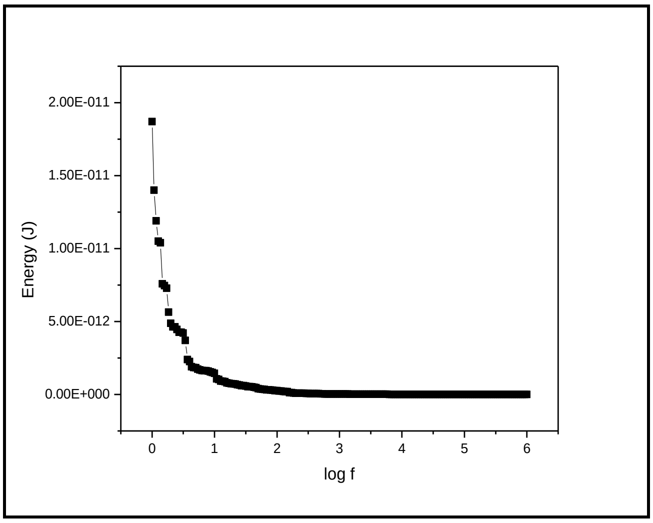

Figure 5: The variation of storage energy with frequency for ULA crystal

Conclusion

Good quality bulk single crystal ULA has been grown by solution method with slow evaporation technique. The crystal system of the ULA was identified by single crystal XRD. The real and imaginary parts of the impedance are found to be decreasing with increase of frequency for ULA crystal. From the Nyquist plot, the dc conductivity of the ULA crystal was calculated. The energy storage in the capacitor is observed to be decreasing with increase of frequency. The third order NLO parameters were determined for ULA crystal.

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References

1. Munn R. W. and Ironside C. N., Principles and Applications of Nonlinear Optical Materials, Chapman and Hall, London, UK, 1993.
2. Shaokang Gao, Weijun Chen, Guimei Wang, Jianzhong Chen, Synthesis, crystal growth and characterization of organic NLO material: N-(4-nitrophenyl)-N-methyl-2-aminoacetonitrile, J. Cryst. Growth, 2006, 297, 361-365.
3. Nalwa H. S. and Miyata S., Nonlinear Optics of Organic Molecules and Polymers, CRS Press, New York, 1996.
4. MohanKumar R., RajanBabu D., Jayaraman D., Jayaval R., Kitmura K., Studies on the growth aspects of semi-organic L-alanine acetate: a promising NLO crystal, J. Cryst. Growth, 2005, 275, e1935 – e1939.
5. Hema Durga K.K., Selvarajan P., Shanthi D., Nucleation Kinetics, XRD and SHG studies of L-alanine single crystals grown at different supersaturation levels, Inter. J. Curr. Res. Rev., 2012, 4, 68-77.
6. Razzetti C., Ardoino M., Zanotti L., Zha M., Parorici C., Solution growth and characterization of L-alanine single crystals, Cryst. Res. Technol., 2002, 37, 456-465.
7. Vijayan N., Bhagavannarayana G., Maurya K.K., Sharma S.N., Gopalakrishnan R.,Jayabharathi J., Ramasamy P., Synthesis, growth of single crystals and their characterization : L-alaninium maleate, Optik, 2012, 123, 604-608.
8. Shanthi D., Selvarajan P. and Jothi Mani R., Nucleation kinetics, Growth and Hardness parameters of L-alanine alaninium picrate (LAAP) single crystals, optik, 2014, 125, 2531-2537.
9. Krishnan S., Justin Raj C., Jerome Das S., Growth and Characterization of novel ferroelectric urea – succinic acid single crystals, J. Cryst. Growth, 2008, 310, 3313–3317.
10. Rajalakshmi T., Qhalid Fareed R.S., Dhanasekaran R., Ramasamy P., Jacob Thomas, Srinivasan K., Characterization of Urea single crystals, Mater. Sci. Eng., 1996, 39, 111–115.
11. Dhanuskodi S., Vasantha K., Angeli Mary P.A., Structural and thermal characterization of a semiorganic NLO material: L-alanine cadmium chloride, Spectrochim. Acta A, 2007, 66 637- 642.
12. Bahae M S., Said A. A. and Van Stryland E .W., High sensitivity single beam n_2 measurements, optics Opt. Lett., 1989, 14, 955-957.
13. Peramaiyan G., Pandi P., Jayaramakrishnan V., Subhasis Das, Mohan Kumar R., Investigation on second and third order nonlinear optical, phase matching and birefringence properties of Gamma–glycine single crystals, optical Mater., 2012, 35, 307-309.
14. Banarji Behera, Nayak P., Choudhary R.N.P., Impedance spectroscopy study of $NaBa_2V_5O_{15}$ ceramic, J. Alloys Comp., 2006, 436, 226 -232.

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