International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.11, pp 4702-4708, Oct-Nov 2014

Nucleation Kinetics, Growth, Nlo Studies, Hardness Parameters And Etching Analysis Of Phosphoric Acid Added L-Alanine Single Crystals (Pla)

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Abstract: Phosphoric acid added L-alanine (PLA) single crystals were grown successfully by slow evaporation technique at room temperature by taking 2:1 molar ratio of L-alanine and phosphoric acid. Solubility and nucleation kinetic measurements were carried out for the PLA sample. Critical nucleation parameters have been calculated. Structural analysis reveals that PLA crystal crystallizes in orthorhombic system. Grown crystals have been characterized by XRD, second harmonic generation analysis, hardness measurement, Z-scan analysis, laser damage threshold (LDT) and etching analysis.
Key words: Solution growth; single crystal; XRD; etching; Z-scan; SHG; NLO

1. Introduction

In recent years, many significant achievements have been occurred in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic type [1-2].The need for nonlinear optical materials is much more than other materials because of their significant impact on laser technology, optical communication and optical data storage technology [3]. Amino acids are the organic materials which contain proton donor carboxylic acid (COOH) group and the proton acceptor amine (NH_2) group in them and they are used to prepare novel derivatives and give the direction for searching new second-order and third-order NLO materials [4-6]. L-alanine is an efficient organic NLO compound under the amino acid category and exhibits optical isomerism. So efforts have been made on L-alanine to get mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and nonlinear optical properties. If L-alanine is mixed with different organic, inorganic acids and salts to form novel materials, it is expected to get novel properties [7]. Keeping this in mind L-alanine is mixed with phosphoric acid to form PLA crystal by slow evaporation method.

Already growth and characterization of PLA crystals was reported in literature [8]. We report here for the first time the investigations on nucleation parameters, third harmonic generation analysis, laser damage threshold measurement, hardness measurement and etching studies of phosphoric acid added L-alanine single crystals (PLA).

2. Experimental For Growth And Nucleation

2.1 Synthesis, solubility and growth

PLA salt was synthesized by taking L-alanine (99% purity) and analar grade phosphoric acid (98% purity) in the molar ratio of 2:1 in double distilled water. The dissolved solution was heated at 50 ^oC for the synthesis of PLA salt. Solubility test was carried out by gravimetric method [9] at various temperatures viz. 30 ^oC, 35 ^oC, 40 ^oC, 45 ^oC and 50 ^oC and the corresponding solubility values for 100 ml is 17.8, 18.6, 19.3, 20.1

and 21 grams respectively and the values show that PLA sample possesses positive temperature coefficient of solubility. According to solubility data the calculated amount of PLA salt was dissolved in double distilled water using magnetic stirrer about 3 hours and then the solution was allowed for crystal growth by slow evaporation method. The transparent and colourless harvested crystal is shown in figure 1.

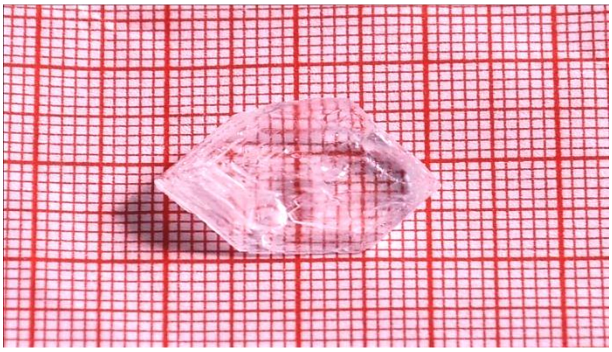

Figure 1: A harvested crystal of PLA

2.2 Nucleation kinetic parameters

To attain the crystal growth, nucleation is the important phenomenon. When few atoms or molecules are joined together in a supersaturated solution, then a cluster of nucleus is formed. The Gibbs free energy change is given by [10].

$$\Delta G=4\pi r^2\sigma+\frac{4}{3}\pi r^2\Delta G_v$$

Where ΔG_v = - (kT/v) ln S. Here the Gibbs free energy is the sum of the surface free energy and volume free energy. Here σ is the surface energy per unit area, v is the volume of one molecule and r is the radius of the nuclei, ΔG_v is the free energy per unit volume. This energy is maximum for a certain value of r is called critical radius (r^*). Using the classical theory of nucleation, the equations for the nucleation parameters have been derived [11] and are given here. The interfacial tension (σ) is $\sigma = kT\{3\ m/16\pi v^2\}^{1/3.}$ Here the slope 'm' is determined from the plot of $1/(\ln S)^2$ against ln τ. The size of the critical nucleus is given by $r^* = \frac{-2\sigma}{\Delta G_V}$. . Using the value of critical radius, the number of molecules in a critical nucleus is found using n = (4/3) (π/v) r^{*3}. The nucleation rate (J) can be calculated using the equation J = A exp [-ΔG*/(kT)] where A is the pre-exponential factor, ΔG* is the critical free energy of the nucleus which is determined by using $\Delta G^* = mkT/(\ln S)^2$ where k is the Boltzmann constant and T is the absolute temperature of the solution. The calculated nucleation parameters are presented in table 1. It is noticed from the results that the values of ΔG*, n and r* decrease with increase in supersaturation ratio (S). The studies on induction period, interfacial tension, nucleation rate and other nucleation parameters give ideas for the controlled growth of PLA crystals by slow evaporation method.

Table 1: Nucleation parameters for phosphoric acid added L-alanine sample

S	σ x10^{-3} (J/m^2)	r* (10^{-9}m)	n	ΔG^*x10^{-21} (kJ/mole)	Jx10^{24} (Nuclei/sec/vol.)
1.05		1.3370	20.45	9.4325	0.1043
1.1	1.261	0.6855	12.45	2.4717	0.5524
1.15		0.4675	3.952	1.1494	0.7588
1.2		0.3583	2.779	0.6754	0.8503

3. Characterization

3. 1 Structural analysis

The obtained lattice parameters for PLA crystal from a single crystal X-ray diffractometer are a=5.805 Å, b=6.036 Å, c=12.356 Å, α=β=γ=90° and V = 432.94 $Å^3$. The structure of the sample is orthorhombic crystal system. The obtained structure of grown crystal is almost coincided with those of L-alanine crystal. The obtained lattice parameters for PLA crystal in this work are found to be in agreement with the data reported in the literature [8]. Slight changes in lattice parameters may be due to incorporation of phosphoric acid.

3.2 Second harmonic generation analysis

The nonlinear optical property of the grown PLA crystal was studied by Kurtz and Perry technique using Nd: YAG laser with fundamental wavelength of 1064 nm [12]. The laser beam was passed through an IR reflector and then directed to the sample holder. The SHG efficiency was confirmed by bright green light emission which is collected by a photomultiplier tube (PMT) (Philips photonics 8563). The incident optical signal in PMT was converted into voltage output at the CRO (Tektronix TDS 305213). The SHG efficiency of PLA is found to be 0.93 times greater than KDP material. Comparing to SHG efficiency of L-alanine crystals grown from water (0.33), PLA sample shows improved NLO efficiency.

3.3. Z-scan analysis

The *Z*-scan technique has been widely used over the past decade as a sensitive method for measuring the third order nonlinear optical parameters. The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for determining the nonlinear changes in index and changes in absorption. Third-order nonlinear optical studies were performed using Z-scan technique for the grown PLA crystal in order to estimate the intensity dependence of nonlinear absorption and nonlinear refraction process. The theory part and experimental part for Z-scan technique was reported already [13]. And also this technique is useful to find the sign of nonlinear refractive index (n_2). The negative nonlinear refractive index of the sample shows transmittance peak followed by transmittance valley, similarly the positive nonlinear refractive index shows the transmittance valley followed by transmittance peak. The nonlinear absorption coefficient (β), nonlinear refractive index (n_2) and third-order susceptibility of the grown crystal have been measured in open and closed aperture modes (figure 2 and figure 3) and the obtained third-order nonlinear parameters are $n_2=1.49\times10^{-10}$ cm^2/W, $\beta=2.08\times10^{-5}$ cm/W and third-order nonlinear susceptibility($\chi^{(3)}$ = 0.8842×10^{-6} esu. Negative absorption was observed in figure 2.

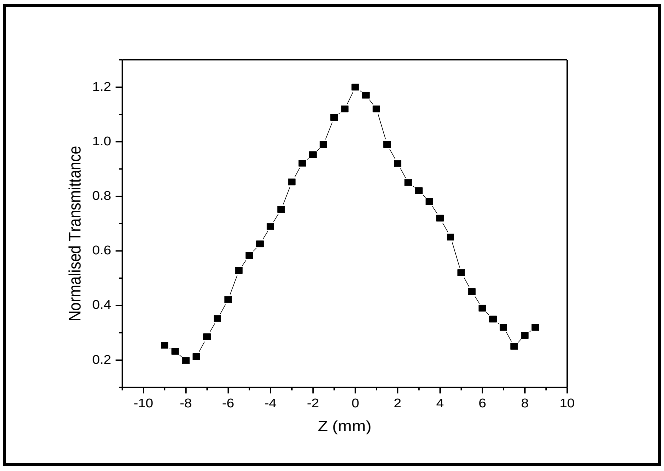

Figure 2: Open aperture Z-scan curve for PLA sample

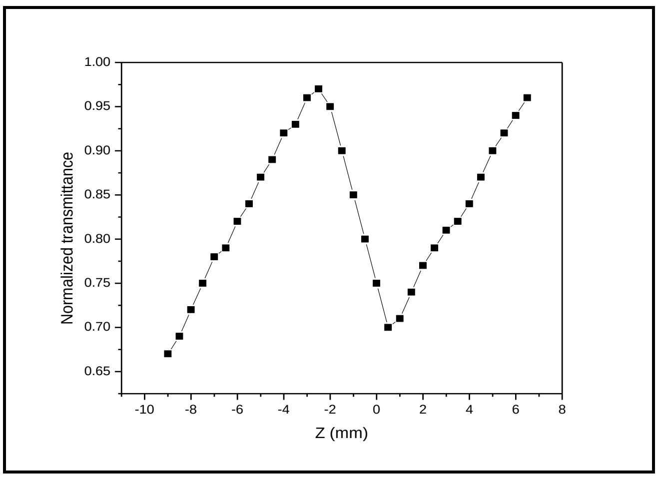

Figure 3: Closed aperture Z-scan curve for PLA sample

3.4 Laser damage threshold measurement

The laser damage threshold (LDT) was measured by coherent energy/power meter (Model No. EPM 200) and it is an important factor which affects the application of optical materials. If the material has low damage threshold it severely limits its application even though it has excellent properties like high SHG [14]. The LDT value was determined using the formula $P = E / \tau\pi r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm. The PLA crystal was exposed to a laser for a time period of 30 s. The damage was observed and the energy of the laser beam was measured by coherent energy/power meter and the obtained LDT value is 0.52 GW/cm^2. The value of LDT for PLA sample is observed to be better than that of KDP (0.21 GW/cm^2) crystal.

3.5 Etching analysis

Etching property is used as the most convenient method for visualization of defects and these studies were carried out using a computerized optical microscope attached with a camera (Olympus make). In the present work, water was used as etchant. Etch pattern of the grown PLA crystal with water is shown in figure 4. When water used as an etchant for 10 seconds, it is observed that whiskers type pits are noticed. The shape of the etch pits varies with the type of etchants because the morphology of etch pits is connected with the nature of chemical complexes present in the solution.

Figure 4: Etch pattern of PLA crystal when water was used as etchant

3.6 Hardness measurement

Hardness of a material is the measure of resistance it offers to local deformation. In the case of crystals, it can be understood in terms of resistance offered to dislocation motion. In general, it comes from the intrinsic resistance of crystals and resistance caused by imperfection in the crystal [15]. The mechanical properties of crystalline materials are closely related with their physical properties, and determine the performance of devices prepared from the solids. Hardness measurements were made on PLA sample at room temperature using a Leitz Wetzler microhardness tester with Vickers pyramidal diamond indenter. Loads ranging from 25 to 100 g were used for making indentations. The hardness value was estimated from the relationship $Hv = 1.8544\ P/d^2$ kg/mm^2 where load (P) is in kilogram, diagonal length of indentation (d) is measured in millimeter and 1.8544 is a geometrical factor. A plot between hardness number and load is depicted in figure 5. As load increases, hardness value increases. It exhibits the reverse indentation size effect. A plot shown in Fig. 6 obtained between log P and log d gives more or less a straight line. The relation connecting applied load and diagonal length d of the indenter is given by Meyer's law $P = bd^n$. Here, n is the Meyer's index or work hardening coefficient, which has been calculated from the slope of the straight line and b is a constant. The work hardening coefficient 'n' is found to be 2.62, which indicates that PLA has a soft material. As per the concept put forward by Onitsch [16], hardness increases with load when the hardness coefficient 'n' is greater than 2.

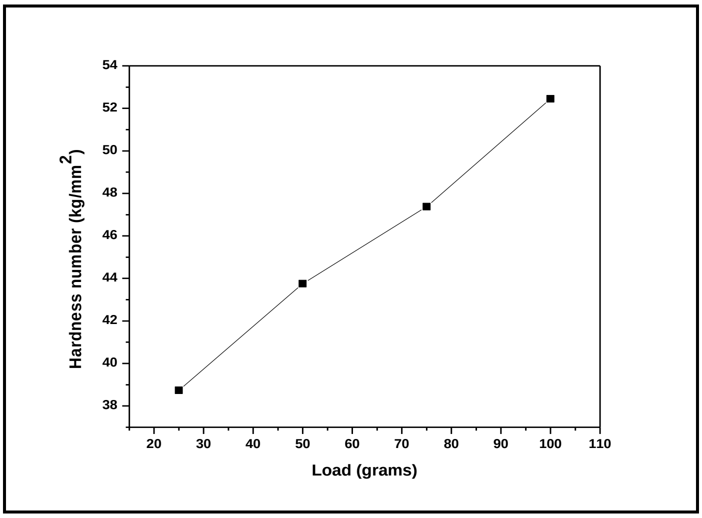

Figure 5: Variation of hardness with load for PLA sample

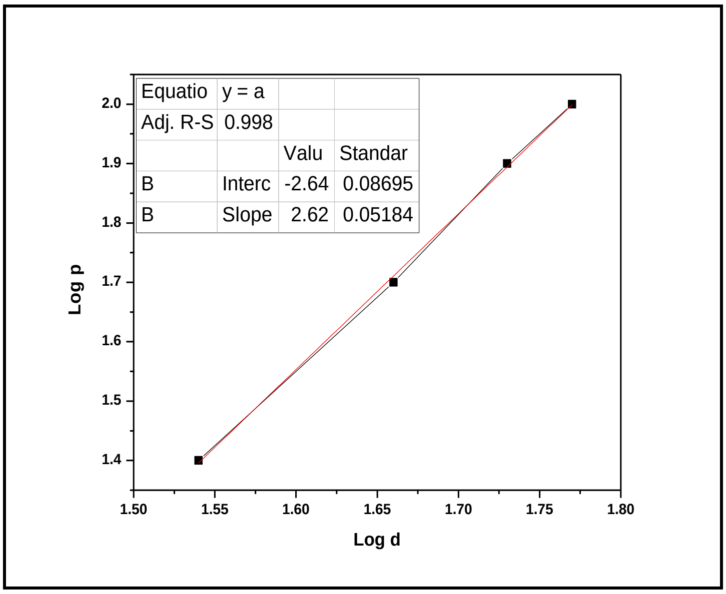

Figure 6: Log d versus Log P curve for PLA sample

The yield strength is defined as the stress at which a predetermined amount of permanent deformation occurs. Since n is found to be more than 2, yield strength of the material can be found out using the relation, Yield strength (σ_y) = (H_v/3) $(0.1)^{n-2}$ where σ_y is the yield strength and H_v is the hardness of the material. A graph is drawn between yield strength and load as shown in the figure 7. It is observed that yield strength increases with increase of load and hence the grown PLA crystal has relatively high mechanical strength. The elastic stiffness constant (C_{11}) for different loads was calculated [17] using Wooster's empirical formula $C_{11} = H_v^{7/4}$. And variation of stiffness constant with the load is given in figure 8 which gives an idea about the measure of resistance of plastic to bending and tightness of bonding between neighboring atoms. From the Fig.8, it is observed that the stiffness constant increases with increase of load. High values of C_{11} indicate that the binding forces between the ions are strong in the PLA crystal.

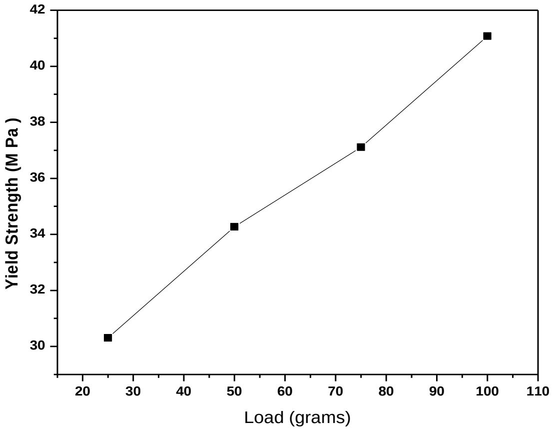

Figure 7: Variation of yield strength with load for PLA sample

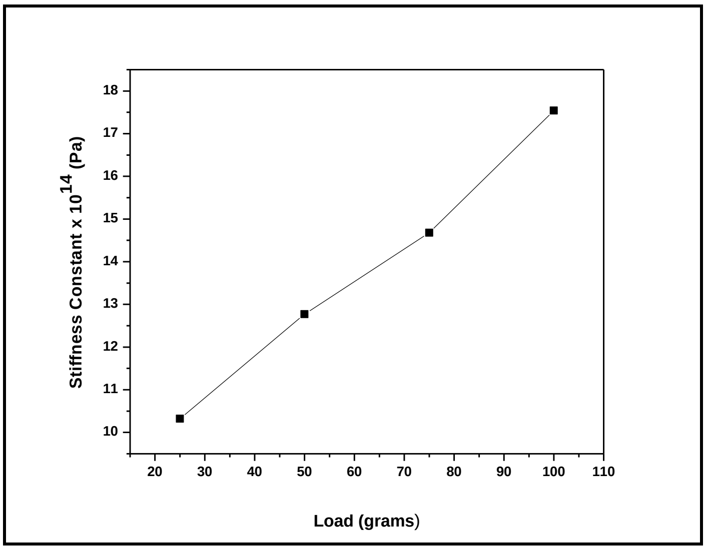

Figure 8: Variation of stiffness constant with load for PLA sample

4. Conclusion

The good quality transparent single crystals of PLA were grown by slow evaporation solution method. XRD analysis confirms its orthorhombic structure. The improved NLO efficiency of this material enables it to be a good candidate for optoelectronic applications. The third-order NLO parameters for the sample have been evaluated by Z-scan technique. Open and closed aperture curves shows negative photon absorption nature and self-defocusing effect of the PLA sample. Etching studies reveal circular and whisker shaped etch pits in the grown crystal. LDT value was measured for the grown sample and it was found to be good. Mechanical properties reveal that PLA is a highly promising material for photonics device fabrication.

Acknowledgement

The authors are grateful to Department of Science and Technology (DST), Government of India for the financial support to carry out this work. The authors thank the management of Aditanar college of Arts and science, Tiruchendur for providing the excellent research facilities. Research supports given by STIC, Cochin University, Crescent Engineering College, Chennai, St.Joseph College, Trichy and VIT, Vellore are gratefully acknowledged.

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