# Nucleation Kinetic and other studies of L-alanine alaninium nitrate (LAAN) single crystals

R.Jothi Mani*, Dr.P.Selvarajan, Dr.H.Alex Devadoss and D.Shanthi
Department of Physics, Aditanar college of Arts and Science,
Tiruchendur-628216, Tamilnadu, India.
Department of Physics, St.John's College, Tirunelveli

**Abstract**

L-alanine alaninium nitrate (LAAN) crystal is a semi-organic nonlinear optical material which was synthesized and measurement of solubility in distilled water was carried out. Using the solubility data of LAAN sample, nucleation kinetic studies were performed and various nucleation parameters were determined based on the classical theory of nucleation. It is observed from the studies that the values of induction period, Gibbs free energy change, radius of critical nucleus, number of molecules in the critical nucleus decrease with supersaturation ratio and interfacial tension was also calculated. Single crystals of LAAN sample were grown by slow cooling technique. The grown crystals of LAAN were subjected to single crystal X-ray diffraction studies, microhardness studies, etching studies and dielectric studies and the results are discussed in this paper.

**Keywords**: L-alanine complex; solubility; nucleation; induction period; X-ray diffraction; etching; microhardness; dielectric constant; conductivity; work hardening coefficient

*Corresponding author
Telephone: +91 09962646724
Fax: +91 04639 245247

## 1.Introduction

Amino acids and their complexes are the organic or semi-organic materials that have attracted great attention due to their ability in ease of processing in the assembly of optical devices. Amino acids are generally soluble in water and insoluble in non-polar organic solvents such as hydrocarbons [1, 2]. L-alanine is an organic alpha-amino acid with the chemical formula $CH_3CHNH_2COOH$ and it is a white odorless crystal powder and easily dissolves in water. L-alanine is an essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system. L-alanine crystallizes in a non-centrosymmetric crystal system and it possess nonlinear optical (NLO) activity and it may find applications in the areas of laser technology, optical communication and optical data computing technologies [3,4]. It is reported that L-alanine has second harmonic generation (SHG) efficiency of about one-third times that of the reference potassium dihydrogen phosphate (KDP) [5]. L-alanine complex crystals have been grown and studied by many researchers [6-9]. In the present work, a 2:1 nitrate salt of L-alanine was synthesized from aqueous solution and an attempt has been made to determine the critical nucleation parameters, solubility and induction period of the sample of LAAN. Growth of bulk crystal of LAAN was carried out using the optimized growth parameters obtained from nucleation kinetic studies by slow cooling technique and grown crystals were subjected to single XRD, SHG, mechanical, dielectric and etching studies.

## 2.Experimental details and results

### 2.1 Solubility measurement

L-alanine alaninium nitrate (LAAN) salt was synthesized by taking L-alanine and nitric acid in 2:1 molar ratio and the reactants were dissolved in double distilled water to prepare saturated solution. The solution was stirred and heated at 60 $^{o}$C to form LAAN salt. Then the purity of the salt was improved by re-crystallization process. The solubility of the re-crystllized salt of LAAN was carried out by gravimetrical method [10]. Fig.1 shows the solubility curve for LAAN crystal. From the graph, it is observed that the solubility of LAAN sample in water increases linearly with temperature, exhibiting a high solubility gradient and it has positive temperature coefficient of solubility.

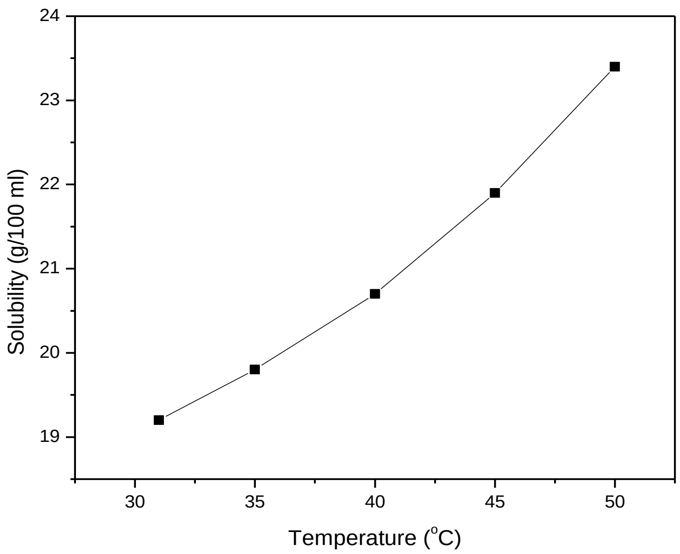


Figure 1: Solubility of LAAN crystal

### 2.2 Measurement of induction period and critical nucleation parameters

Nucleation is the precursor and the most important phenomenon for crystal growth. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval between the creation of supersaturation and the formation of critical nuclei is called as the induction period ($\tau$) and it is influenced by supersaturation, type of solvent, purity of the sample, temperature, pH value of the solution etc. To calculate the nucleation parameters, induction period is necessary and the experiment for measuring induction period for LAAN sample was performed at selected degrees of supersaturation (S), viz. 1.1, 1.15, 1.2, 1.25 and 1.3 at room temperature (30 $^{o}$C) by isothermal method [5]. The variation of induction period with supersaturation ratio (S) is depicted in the figure 2 and it is observed that the induction period decreases with increase of supersaturation ratio. Figure 2 gives the plot of $1/(\ln S)^2$ against $\ln \tau$ and the slope (m) is obtained by considering the best linear fit. The critical nucleation parameters such as (i) radius of the critical nucleus, (ii) Gibbs free energy change, (iii) interfacial tension and (iv) the number of .molecules in the critical nucleus were determined using following equations [5, 11].

Interfacial tension $\sigma = (RT/N)\,[3m/16\pi v^2]^{1/3}$

Radius of critical nucleus $r^* = 2\,\sigma v\, N / RT\, \mathit{ln}\, S$

Gibbs free energy change $\Delta G^* = mRT / [N\,(\mathit{ln}\, S)^2\,]$

Number of molecules in the critical nucleus $n = (4/3)\,(\pi/v)\, r^{*3}$

Where R is the universal gas constant, v is the specific volume of a molecule (v = volume of unit cell / number of molecules per unit cell), N is the Avogadro's number, k is the Boltzmann's constant, T is the absolute temperature and S is the supersaturation ratio which is calculated from $S = C/C_{o,\ \mathrm{where}}$ C is the supersaturated concentration and $C_o$ is the saturated concentration. The calculated values of critical nucleation parameters are provided in the table 1. It is observed from the results that the values of $\tau$, $\Delta G^*$ , n, r* decrease with increase in supersaturation ratio (S). That means the number of critical nuclei formed will be increased which will lead to spurious nucleation at higher supersaturation ratio. Hence formation of multinuclei in the supersaturated solution could be avoided when low supersaturation ratio is used for the growth of LAAN crystals. Interfacial tension is low for the aqueous solution of LAAN and hence water could be used to grow bulk crystals. By controlling superaturatuion and nucleation rate, good quality crystals of LAAN could be grown.

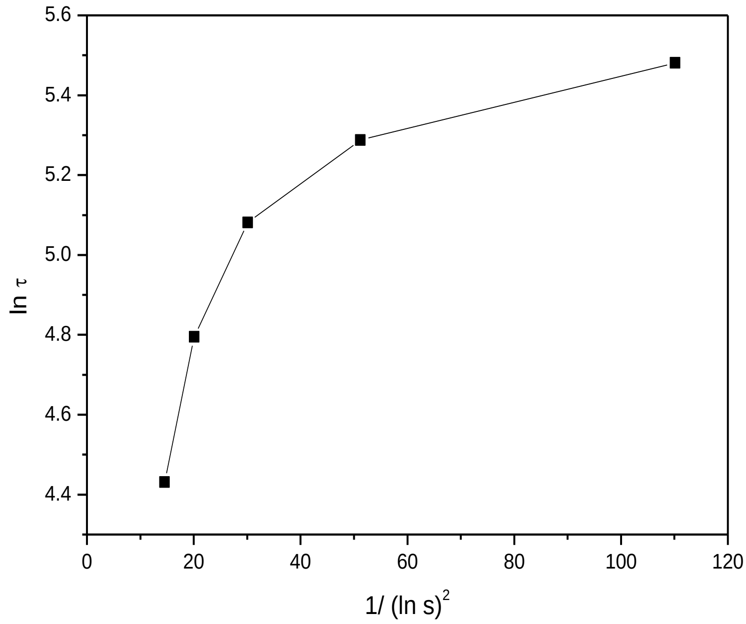


Figure 2: A plot of ln τ and $1/(\ln S)^2$ for LAAN sample

Table 1: Values of interfacial tension, Gibbs free energy change,Critical radius and number of molecules in the critical nucleus for LAAN sample

| S | $\sigma$ x$10^{-3}$ (J/m$^2$) | r* ($10^{-9}$ m) | n | ΔG* (kJ/mole) |
|---|---|---|---|---|
| 1.1 | | 1.155 | 35 | 1.853 |
| 1.15 | 0.813 | 1.116 | 20 | 1.156 |
| 1.2 | | 0.853 | 15 | 0.736 |
| 1.25 | | 0.562 | 11 | 0.615 |
| 1.3 | | 0.427 | 8 | 0.393 |

**2.3. Crystal growth**

Using the solubility data and keeping the supersaturation ratio at 1.1, the supersaturated solution of LAAN was prepared. The solution was stirred well using a hot plate magnetic stirrer for about 2 hours at 40 $^o$C to get homogeneous solution. Then the solution was loaded into a constant temperature bath (CTB) and initially the temperature was set at 35 $^o$C. The temperature of the solution was reduced at the rate of 0.5 $^o$C per day and the growth was carried out by slow cooling technique. Some seeds obtained from spontaneous nucleation have also been kept in the crystal growing container during the growth. It took about 20 days to get the crystals of LAAN. The photograph of the grown crystals is shown in figs. 3 and 4.

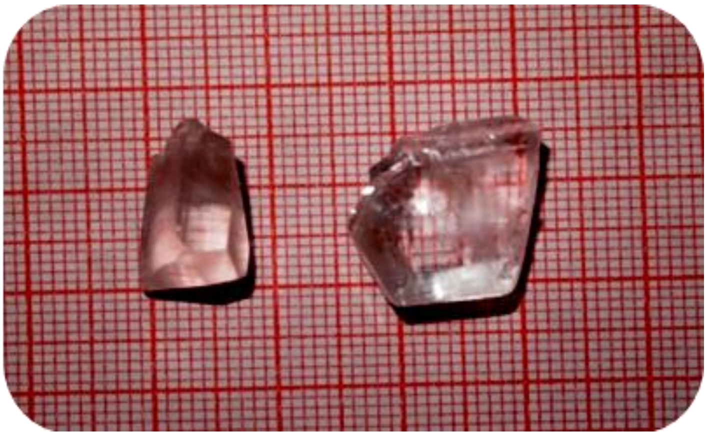

Figure 3: Grown LAAN single crystals

**2.4. Single crystal XRD Studies**

The X-ray diffraction analysis on the grown LAAN crystal was used to confirm the crystallinity and identification of the unit cell parameters. The grown LAAN crystal has been subjected to single crystal X-ray diffraction study to obtain the crystallographic data which reveals that LAAN crystal crystallizes in monoclinic structure. The space group and the number of molecules per unit cell are observed to be $P2_12_12_1$ and 2, respectively. It is reported that the space group $P2_12_12_1$ is recognized as a non-centrosymmetric and thus satisfying one of the basic and essential material requirements for the SHG activity of the crystal. The lattice parameters are found to be a=7.846(3)Å, b=5.431(4)Å, c=12.806(2) Å, β=94.65° and V=543.8.$Å^3$.

**2.5. Second harmonic generation (SHG) studies**

The second harmonic generation behavior of the powdered material was tested using the Kurtz and Perry method [12]. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered LAAN sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm) and it is a potential material for frequency conversion. It is observed that LAAN powder sample has the relative SHG efficiency of 2.1 times that of the KDP crystalline powder. It is to be mentioned here that SHG efficiency of L-alanine powdered sample is 0.33 times that of KDP crystal. Thus, the grown LAAN sample has improved NLO properties compared to L-alanine crystal.

## 2.6. Etching Studies

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 and diluted nitric acid were used as etchants. Etching of the (100) plane of the grown LAAN crystal with water as etchant for 5 seconds produces a circle shaped etch pits as in figure 5(a). When the nitric acid is used as an etchant for 5 seconds, it is observed that whiskers type pits are noticed as in figure 5(b). The shape of the etch pits varies with the type of etchants because of the morphology of etch pits is connected with the nature of chemical complexes present in the solution.


Fig.5 (a) – water as etchant Fig.5(b) – nitric acid as etchant

Fig.5: Etch patterns for LAAN crystal

## 2.7 Microhardness studies

Microhardness indentations were carried out using Vickers indenter for varying loads (P = 10-50 g). For each load, several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness. Vickers microhardness number was determined using the relation $H_v = 1.8544\ P/d^2$ where P is applied load and d is diagonal length of indentation impression [13]. The plot $H_v$ versus P is shown in the figure 6. It is observed from the results that the hardness number was found to increase with the load. This can be explained qualitatively on the basis of depth of penetration of the indenter. For small loads, only a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of this layer and $H_v$ increases with load in this region. With increase in load, the overall effect is due to surface as well as inner layers of the sample.

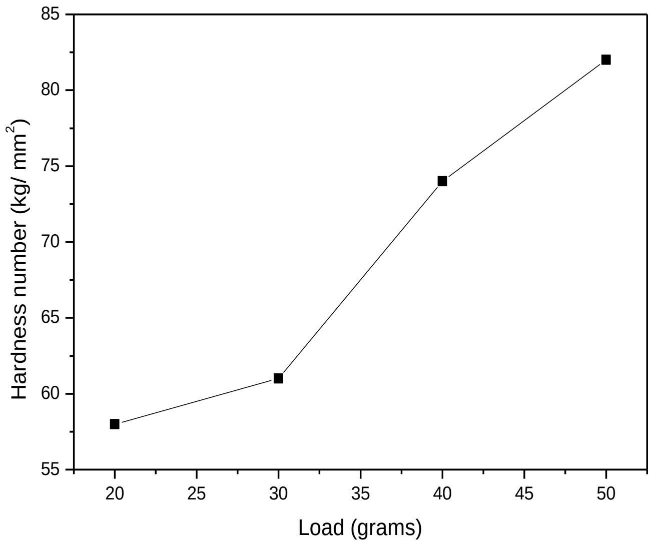


Figure 6: Variation of hardness number with the load for LAAN crystal

## 2.8 Dielectric characterization

For the measurement of dielectric constant and dielectric loss, the crystal was cut and polished. Good quality graphite paint was coated on the faces of crystal for the good ohmic contact. Then the crystal was placed between the electrodes in the two-probe arrangement. An LCR meter was used to measure capacity of the sample and hence dielectric constant was calculated using relation $K = C/C_o$ where $C_o$ is the capacity of the condenser without sample and C is the capacity of the condenser with sample. The dielectric loss (tan $\delta$) was measured directly from the LCR meter. The variations of dielectric constant (K) and dielectric loss (tan $\delta$ ) of the grown crystals with different temperatures at frequency of 1000 Hz are displayed in the figures 7 and 8 . It is noticed from the figures that dielectric constant and loss increase with increase in temperature. The dielectric constant of a solid is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is established that the space charge polarization is very predominant at lower frequency (1000 Hz in the present study). This polarization is known to arise from the charged defects or impurities present and also due to the creation and distribution of dipoles either within the bulk or at the surface of the crystal. Practically, the presence of a dielectric between the plates of a condenser enhances the capacitance. Essentially, dielectric constant is the measure of how easily a material is polarized in an external electric field. Low value of dielectric loss indicates that the grown crystals are of good quality i.e. the grown crystals are good-quality dielectric materials [14,15].

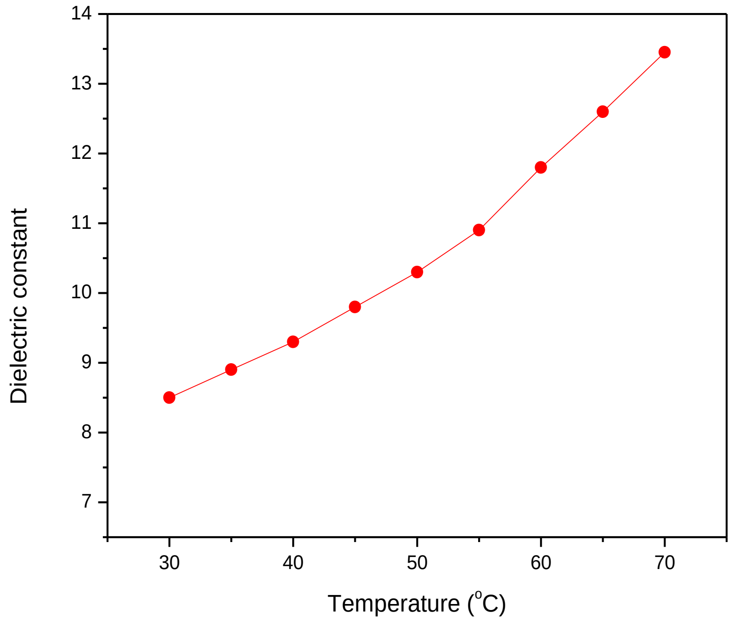


Figure 7: Variation of dielectric constant with the temperature at the frequency of 1000 Hz for LAAN sample

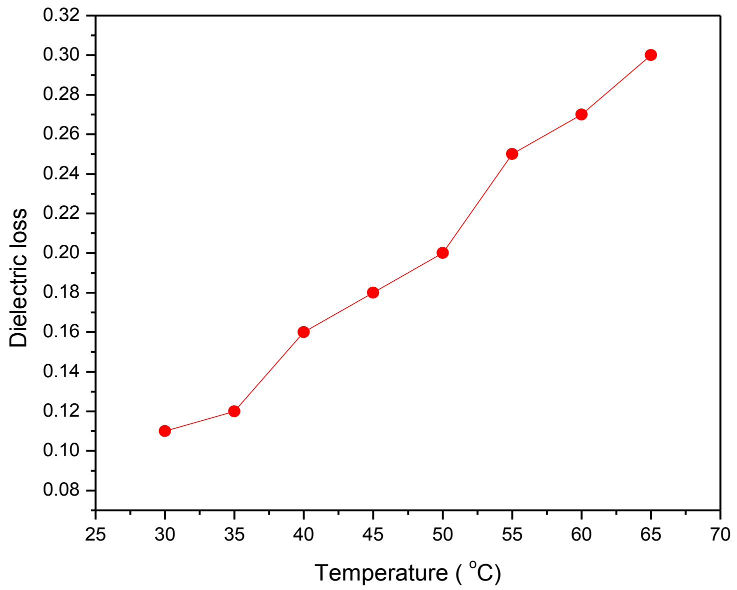


Figure 8: Variation of dielectric loss with the temperature at the frequency of 1000 Hz for LAAN sample

The AC conductivity ($\sigma_{ac}$) of the sample for different frequencies can be determined using the relation $\sigma_{ac} = 2\pi f\, K\, K_o \tan\delta$ where f is the frequency of a.c. supply, K is the dielectric constant, $K_o$ is the permitivity of free space and tan $\delta$ is the dielectric loss.

AC conductivity of a crystal can be calculated using the data of dielectric constant and dielectric loss. Temperature dependence of AC conductivity of pure LAAN crystals is shown in the figure 9. It is noticed from the results that AC conductivity increases with temperature. According to the relation, AC conductivity is directly proportional to dielectric constant and dielectric loss and hence when dielectric constant and dielectric loss increase with temperature, AC conductivity also increases with temperature.

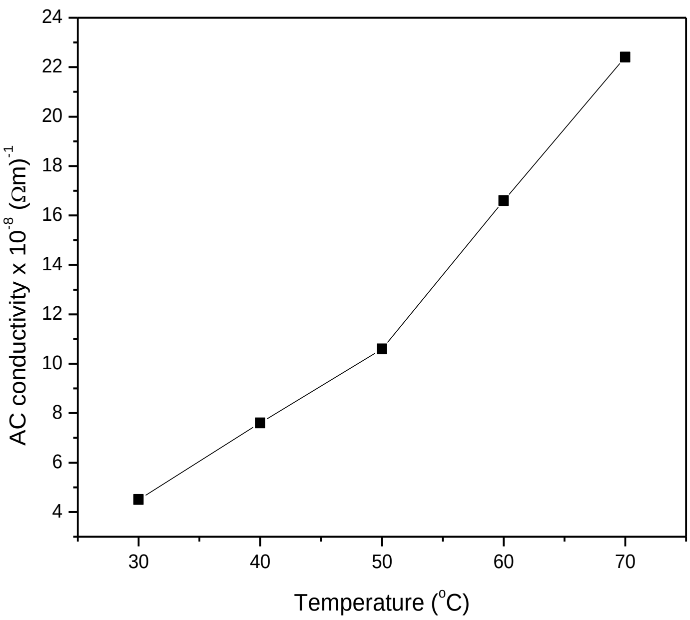


Figure 9: Temperature dependence of AC conductivity for LAAN crystal

## 3. Conclusion

L-alanine alaninium nitrate (LAAN) salt was synthesized by solution method and the purity of the sample was improved by re-crystallization process. Solubility of LAAN sample was measured and it is observed that it increases with temperature. Induction period was measured for LAAN sample and it decreases with the supersaturation level. Critical nucleation parameters such as interfacial tension, radius of critical nucleus, Gibbs free energy change and number of molecules in the critical nucleus were calculated. Growth of bulk single crystals of LAAN was performed by solution method with the slow cooling technique. Single crystal XRD study reveals the monoclinic structure of the grown crystals. The measured SHG efficiency of the grown LAAN sample was found to be 2.1 times that of KDP crystal. Etching studies reveal circular and whisker shaped etch pits in the grown crystals. The micro hardness study confirms mechanical strength of the layers of the sample.

Dielectric characterization shows that the LAAN sample is polarized in an external electric field and dielectric loss indicates that the grown LAAN crystals are of good quality and AC conductivity increases with temperature indicating the dielectric nature of the sample.

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