

Investigations on the Nucleation Kinetics of Urea Admixture L-alanine Crystals

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Abstract: Investigations on nucleation kinetic parameters are very important tools for the successful growth of good quality, transparent and big-sized single crystals. Urea admixture L-alanine (ULA) salt was synthesized and solubility studies have been carried out by gravimetric method in the temperature range of 31-50 °C. The induction period of the ULA salt for the selected supersaturation ratios at room temperature was measured. The fundamental nucleation parameters such as Gibbs free energy change, interfacial tension, critical radius, number of molecules in the critical nucleus and nucleation rate were calculated of ULA sample for the first time based on the classical theory of nucleation. Bulk size single crystal of urea admixture L-alanine was successfully grown by solution method with slow evaporation technique from the optimized growth parameters. The grown crystals were characterized by X-ray diffraction and optical studies.

Keywords: Nucleation kinetics, Solution growth, XRD, Transmittance.

1. Introduction

Crystal growth plays a vital role in the development of many solid state devices for technological applications. Amino acid family crystals also exhibit excellent electro-optic and nonlinear optical properties [1], [2]. In the recent years, there have been extensive effort to develop new inorganic, organic and semi organic nonlinear optical crystals. An organic nonlinear optical (NLO) materials have considerable attention due to their potential application in high frequency electro-optic modulation, different frequency conversion, broad band terahertz wave generation and detection [3], [4] etc. L-alanine is the smallest, naturally occurring chiral amino acid and it belongs to the orthorhombic crystal system and it is optically active molecule [5], [6]. L-alanine complexes have been studied by many researchers and reported in the literature [7]-[9]. Urea or carbamide is an organic compound with the chemical formula $(\text{NH}_2)_2\text{CO}$. The molecule has two amide groups joined by a carbonyl functional group. It has an interesting property for nonlinear optical applications. It forms crystalline complexes with organic and inorganic acids or salts [10], [11]. In this work, L-alanine is mixed with urea to form urea admixture L-alanine (ULA) salt and the nucleation parameters of ULA, which are essential for the growth of bulk crystals have been investigated. The solubility and induction period have been determined experimentally. The induction period was measured for various supersaturation ratios at room temperature. The grown crystals were characterized by single crystal XRD and optical studies are reported and discussed.

2. Synthesis and solubility

ULA salt was synthesized by dissolving equimolar ratio of L-alanine and urea in double distilled water. The saturated solution of the ULA was prepared and allowed to dry at 45°C in the constant temperature water bath (CTB with

accuracy $\pm 0.01^\circ\text{C}$) and the synthesized salt was obtained. The purity of the synthesized salt was improved by successive recrystallization process. Solubility is defined as the amount of solute in grams present in 100 ml of saturated solution at a particular temperature and provides a driving force for both nucleation and crystal growth. The solubility study was carried out for the ULA salt in double distilled water by gravimetric method [12]. Initially, solubility was determined at 31°C by dissolving the solute in 25 ml of double distilled water in an airtight container maintained at a constant temperature with continuous stirring using CTB and magnetic stirrer. ULA salt was added in small amount at successive stages and then the solute was added till a small precipitate was formed. This gave a confirmation of the super saturated condition. Then the 5 ml of the saturated solution was pipetted out and taken into a petri dish of known weight and it was heated till the solvent was evaporated. The amount of the salt present in 5 ml of the solution was measured by subtracting the empty petri dish's weight. From the above value, the amount of the salt present in 100 ml of the solution was found out. The same procedure was followed for the temperatures 35, 40, 45 and 50°C. The solubility diagram of the ULA salt is shown in figure 1.

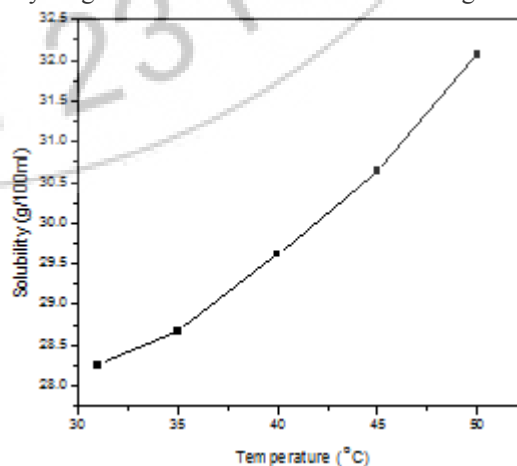


Figure 1: Solubility curve of ULA sample

3. Induction Period

Induction period is defined as the time elapsed between the achievement of a supersaturated solution and the observation of first speck or tiny crystal. Induction period of the ULA salt was measured by using isothermal method and direct vision observation method [13] for the different supersaturation ratios. The ratio of the supersaturation concentration (C) to the saturated concentration (C_o) at the particular temperature is known as supersaturation ratio (S) and is given by

$$s = \frac{C}{C_o} \tag{1}$$

From the above relation, we can find the supersaturation concentration for the selected supersaturation ratio. For S=1.05, the induction period was measured when the appearance of first visible speck at the bottom of the container is noticed. The volume of the solution was taken as 10 ml in the experiment. The consistency of the reading was verified by repeating the experiment two or three times. Similarly the induction period was carried out for S=1.1, 1.15 and 1.2. Figure 2 shows the variation of induction period with supersaturation ratio for ULA. It is observed that as the supersaturation increases induction period decreases [14]. The study of induction period against supersaturation gives an idea of optimized induction period in order to have controlled nucleation rate to grow good quality single crystals.

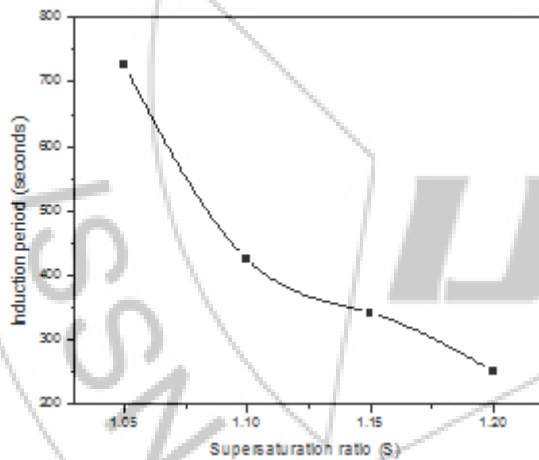


Figure 2: Induction period versus supersaturation ratio for ULA sample

4. Nucleation theory and determination of nucleation parameters

Crystallization involves two distinct processes containing nucleation which is the birth of a nucleus and crystal growth which involves the subsequent growth of the existing nucleus. Nucleation is defined as the series of atomic or molecular processes by which the atoms or molecules of a reactant phase rearrange into a cluster of the product phase large enough as to have the ability to grow irreversibly to a macroscopically larger size. Nucleation can be classified into two types namely primary nucleation and secondary nucleation. Primary nucleation is further classified into homogeneous, in the absence of foreign particles such as ions, impurity molecules, dust particles or surface of the container and heterogeneous, in the presence of foreign

particles in the supersaturated solution. Secondary nucleation takes place when nucleation is induced by the presence of crystals of the same substance.

Nucleation kinetics depends on the thermodynamic driving force, which in turn depends on the supersaturation, temperature and impurities present in the system. According to classical nucleation theory (CNT), the free energy barrier to nucleation is called the Gibbs free energy change which consists of surface free energy and volume free energy is

$$\Delta G = \Delta G_s + \Delta G_v \tag{2}$$

Let the shape of the nucleus be spherical,

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

where r is the radius of the nucleus and σ is the interfacial tension or interfacial energy. The induction period in terms of Gibbs free energy is given by

$$\ln \tau = -B + \frac{\Delta G}{kT} \tag{4}$$

where B is a constant, k is the Boltzmann's constant and T is the absolute temperature. According to Thomson-Gibbs equation, the volume excess free energy is given by

$$\Delta G_v = -\frac{kT}{v} \ln S \tag{5}$$

and it is calculated for the different supersaturation ratios. The Gibbs free energy will be maximum for a certain value of radius (r*) of nucleus, which is known as critical radius. A plot of 1/(ln S)² against ln τ forms a straight line as shown in figure 3 and interfacial energy is calculated from the slope using the equation

$$\sigma = kT \left(\frac{3m}{16\pi v^2} \right)^{1/3} \tag{6}$$

and the interfacial energy of ULA is 0.3806x10⁻³ J/m². The interfacial energy σ of the interface between the growing crystal and the surrounding mother phase plays an important role in the nucleation of crystals.

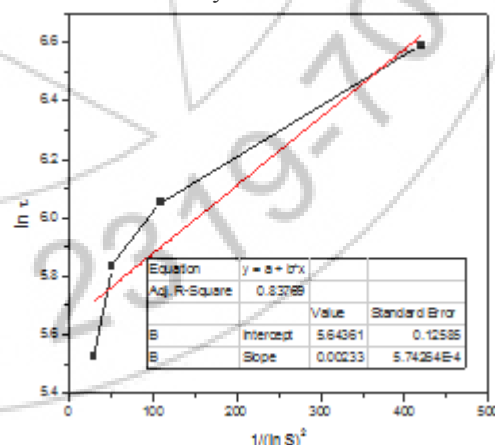


Figure 3: Plot of ln τ versus 1/(ln S)² for ULA sample

At the critical state the free energy formation obeys the condition

$$d\left(\frac{\Delta G}{dr}\right) = 0 \tag{7}$$

Hence the radius of the critical nucleus (r^*), Gibbs critical free energy change (ΔG^*) and number of molecules in the critical nucleus (n^*) can be expressed as

$$r^* = -\frac{2\sigma}{\Delta G^*} \quad (8)$$

$$\Delta G^* = \frac{mkT}{(\ln S)^2} \quad (9)$$

$$n^* = \frac{4\pi(r^*)^3}{3v} \quad (10)$$

The derivations for equations of critical nucleation parameters such as r^* , σ , ΔG^* and n are given in the literature [16]. The number of crystals produced in the supersaturated solution is expressed as nucleation rate (J). It is defined as the number of crystals produced per unit volume per unit time and given by

$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (11)$$

Where A is the pre-exponential factor and is equal to 1×10^{24} for solution [17]. Using the interfacial tension value, the radius of the critical nucleus, the Gibbs free energy change and nucleation rate were calculated at different temperature for ULA salt and presented in Table 1. From the table, it was noted that with the increase in super saturation, the values of r^* , ΔG^* and n except J decreases. Therefore the formation of multinuclei in the supersaturated solution could be avoided when low supersaturation ratio is used for the growth of ULA crystals and by controlling nucleation rate good quality and big- sized crystals could be grown.

Table 1: Nucleation kinetics parameters for ULA

S	$\Delta G^* \times 10^{-21} J$	$r^* \times 10^{-9} nm$	$J \times 10^{19} (nuclei/second/volume)$
1.05	4.106	0.401	0.375
1.1	1.076	0.205	0.773
1.15	0.500	0.140	0.887
1.2	0.294	0.107	0.932

5. Growth of bulk ULA crystal

Growth of big size crystals for device application requires a better knowledge on the nucleation parameters. From the solubility and nucleation kinetic data, 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 for 30 days. The grown crystal was stable, colourless and non-hygroscopic. The photograph of the harvested crystals is shown in the figure 4.



Figure 4: Growth ULA single crystal

6. Single crystal X-ray diffraction study

Single crystal X-ray diffraction analysis for the grown ULA crystal was carried out using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_{α} ($\lambda= 0.71069\text{\AA}$) radiation. It is observed that the ULA crystal belongs to orthorhombic structure with non centrosymmetric space group $P2_12_12_1$. The unit cell parameters obtained are $a= 5.799$ (10) \AA , $b= 6.031$ (11) \AA , and $c= 12.341 \pm$ (20) \AA ; $\alpha=\beta=\gamma=90^\circ$ and the volume of the material is found to be 431.61 (1) \AA^3 . From the results, it is confirmed that the grown crystal is the L-alanine crystal added with urea.

7. UV-vis-NIR spectrum analysis

The optical properties of the crystals are important which provide the information on the electronic band structures, localized states and types of optical transitions. The UV-visible transmittance spectrum of the grown crystal was recorded in the wavelength range 190-1100 nm using Perkin Elmer Lambda 35 spectrometer is shown in figure 5. For this study, optically transparent, cut and polished single crystal of thickness 1 mm was used. From the graph, the ULA crystal should be highly transparent in the entire visible region suggests its suitability for second harmonic generation and also this crystal is used to optoelectronic devices [17]. The cut off wavelength for ULA crystal is 249 nm.

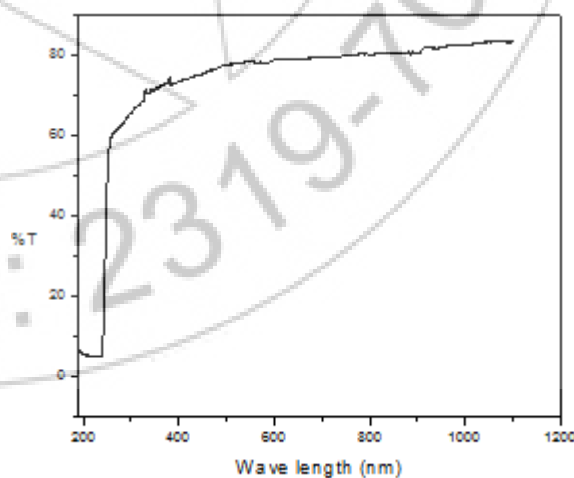


Figure 5: Optical Transmittance spectrum of ULA crystal

8. Conclusion

Solubility, induction period and the critical nucleation parameters for the ULA salt were determined by classical

nucleation theory. From the optimized nucleation parameters good quality, colourless, transparent and big-sized single crystals of urea admixed L-alanine have been grown from the supersaturated aqueous solution by slow evaporation technique. The grown single crystals have been characterized by single crystal XRD and it is confirmed that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. The optical property studies reveal that ULA crystals possess 82% transmittance and show that ULA crystal and it will be useful in electro-optical applications.

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Author Profile

D. Shanthi received M.Sc. and M.Phil. degrees in Physics from Manonmaniam Sundaranar University, Tirunelveli. She got three years of teaching experience and at present she is working as a Project Fellow in the UGC-Major Research Project under the guidance of Dr. P.Selvarajan at Aditanar College of Arts and Science, Tiruchendur. She has published five papers in the International Journals.



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Dr. S. Perumal, the present Principal of S.T.Hindu College, Nagercoil assumed charges of office on 1st June 2013. He completed M.Sc. in Physics from Madras University and Ph.D. in Physics in Manonmaniam Sundaranar University and B.Ed degree from Madurai Kamarajar University. He has a creditable teaching experience of 28 years and Research experience of 15 years. He has produced 10 Ph.D and 50 M.Phil in Physics. He has published 35 articles in International Journals. He has completed one minor project in Physics and received Rs. 12 lacs from UG for Major Research Project in the field of Crystal Growth and characterization.