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Metastable Zone Width, Growth, XRD and SHG Studies of L-alanine Alaninium Picrate (LAAP) Single Crystals

KEYWORDS: L-alanine complex; metastable zone width; induction period; Nucleation rate; SHG

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ABSTRACT *L-alanine is an amino acid which dissolves in water and it can react with other acids to form new compounds. In this work, L-alanine is mixed with picric acid to prepare L-alanine alaninium picrate (LAAP) salt. Solubility, metastable zone width and induction period for LAAP salt were measured at different supersaturation ratios. The critical nucleation parameters were evaluated based on the classical theory of homogeneous nucleation. Using the optimized nucleation parameters, single crystals of LAAP salt were grown by slow evaporation technique. XRD and SHG studies were carried out for the grown crystals of LAAP and the results are discussed.*

1. Introduction

Amino acids exhibit specific features such as molecular chirality, absence of strongly conjugated bonds, zwitterionic nature of molecules and the basis for synthesizing organic and inorganic compounds [1,2]. Amino acids 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 NLO materials. L-alanine is an alpha and L-type amino acid with the chemical formula CH_3CHNH_2COOH with the molecular weight of 89.09. L-alanine is a conditionally essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system [3,4]. Crystals of L-alanine complexes have been studied by many researchers and reported in the literature [5-9]. In this work, L-alanine is mixed with picric acid to form L-alanine alaninium picrate (LAAP) crystal and the studies on nucleation kinetics, XRD and SHG of the grown crystals are reported.

2. Nucleation and relevant equations

There are two steps to form a crystal from supersaturated solution and they are (i) formation of a nucleus and (ii) the growth of this nucleus into a crystal. The first step gives an idea of thermodynamics of nucleation and growth, whereas the second step deals with the kinetics of these processes. Crystallization starts with nucleation and control of nucleation is crucial for the control of the number, size, perfection, polymorphism and other characteristics of crystalline materials. When few atoms, ions or molecules join together in a supersaturated solution, a cluster or nucleus is formed and the overall excess free energy change (DG) between the nucleus and solute in the supersaturated solution is the Gibbs free energy change. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval in which the observation of the first sparkling particle in the undisturbed supersaturated solution is called the induction period (t). The expression for the induction period in terms of Gibbs free energy is given by ln t =-B +DG / kT where B is a constant, k is the Boltzmann's constant and T is the absolute temperature. The Gibbs free energy will be maximum for a certain value of radius (r^*) of nucleus, which is known as critical radius. Supersaturation ratio S is given by $S = C/C_o$ where C is the supersaturated concentration and C_o is the saturated concentration [10,11].The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The nucleation rate (J) can be calculated using the equation $J = A \exp[-DG^*/(kT)]$ where A is the pre-exponential factor and it is given by

$$A = \nu^* Z N$$

where ν^* is the frequency of attachment ($\nu^* \sim 300\ s^{-1}$), Z is Zeldovich factor (Z= 0.01),

N is the concentration of molecules ($n = 10^{18}\ cm^{-3}\ s^{-1}$) and approximately $A = 1 \times 10^{24}$ for solution [12]. The derivations for equations of critical nucleation parameters such as r^*, σ, ΔG^* and n are given in the literature [13].

3. Experimental and Results

3.1 Synthesis and metastable zone width

In the present study, the commercially available Analar Reagent (AR) grade salts of L-alanine and picric acid were dissolved in double distilled water in 1.5:1 molar ratio and the LAAP salt was obtained by conventional chemical reaction method. Here the reactants of solution was heated at 60 °C and the synthesized salt of LAAP was purified by re-crystallization process twice. Solubility study was carried out using a hot-plate magnetic stirrer and a constant temperature bath by gravimetrical method [14].

Metastable zone width (MSZW) is a basic and an important parameter in terms of temperature for growing a crystal by solution growth technique. In the present work, the metastable zone width of LAAP was measured by means of the conventional polythermal method [15]. Saturated solution of LAAP has been prepared in accordance with the presently determined solubility data. The studies were carried out in a constant temperature bath controlled to an accuracy of $\pm$ 0.01 °C provided with a cryostat for cooling below room temperatures. A constant volume of 10 ml of solution was used in all experiments. The solution was preheated to 5 °C above the saturated temperature for homogenization and left at the superheated temperature for 1 h before cooling. The equilibrium saturated solution is cooled from the overheated temperature and the temperature at which the first visible crystal nucleus in the solution is noted and this is the nucleation temperature. This experiment was carried out for the solution saturated at 30, 35, 40, 45 and 50 °C. Repeated trials were performed to ascertain the correctness of the observed results. The solubility curve and the nucleation curve for LAAP sample are given in the figure 1.

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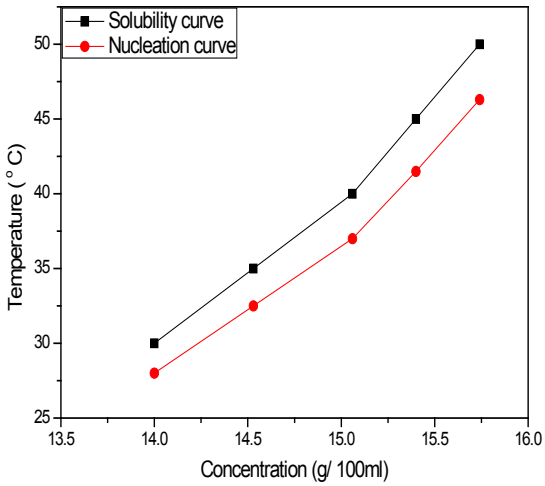


Figure 1 : Metastable zone width of LAAP crystal

From the results (Fig.1), the solubility of LAAP sample in water increases with increase in temperature and hence the sample has positive temperature coefficient of solubility. The difference between the saturation temperature and nucleation temperature in the nucleation curve is called the metastable zone width. It is evident from the plots that the metastable zone width is slightly broader in the higher temperature region whereas in the lower temperature region the width is tending to become narrow. For the maximum yield, uncontrolled nucleation should be avoided and the growth of a crystal occurs from a solution maintained in the metastable condition.

3.2 Induction period

When the solution attains supersaturation, embryos are formed by single molecular addition starting from the monomer at the beginning and it takes some time for the formation of critical nucleus from the monomers. The time taken between the achievement of supersaturation and the appearance of crystal nucleus in a supersaturated solution is known as induction period. In the present work, the direct vision observation method was used to measure the induction period. For the measurement of induction period, isothermal method was used for the selected supersaturation ratios viz. 1.1, 1.15, 1.2 , 1.25 and 1.3 at room temperature (30 °C). The plot of ln t versus supersaturation ratio (S) is depicted in the figure 2. The plot shows that the induction period decreases with increase of supersaturation (S) which suggests that the nucleation rate increases. 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.

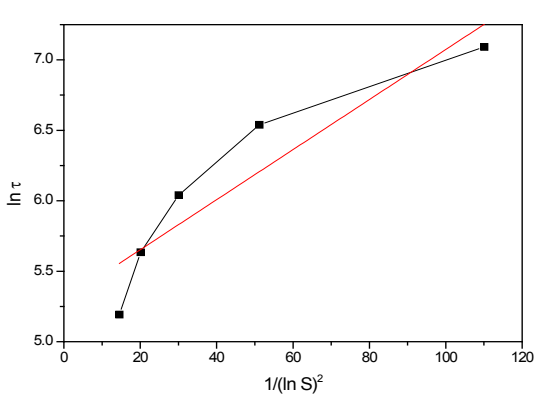
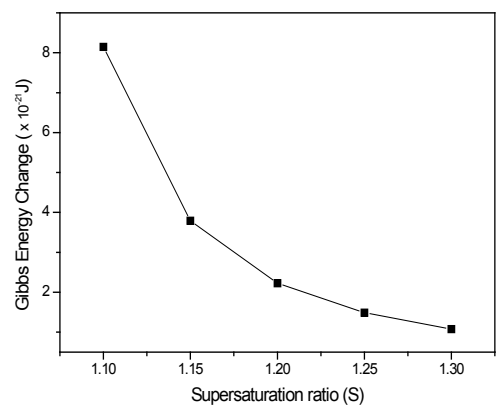


Figure 2: The plot of ln τ versus 1/ (ln S)² for LAAP sample

3.3 Determination of critical nucleation parameters

Using linear fit method, the slope (m) value was obtained from the plot of figure 2 and the critical nucleation parameters such as Gibbs free energy change, interfacial tension, the radius of critical nucleus, the number of molecules in the critical nucleus and the nucleation rate were determined. The variations of Gibbs free energy change (ΔG^*) and radius of critical nucleus (r^*) with the supersaturation ratio (S) for LAAP sample are shown in the figures 3 and 4. It is noticed from the results that the values of ΔG^* and r^* are found to be decreasing with increase of supersaturation ratio and the similar result was obtained for number of molecules in the critical nucleus (n). The interfacial energy value obtained from the experimental results is 0.7113 x 10^{-3} J/m^2 for LAAP crystal. Another important parameter is the nucleation rate and its variation with supersaturation ratio for LAAP crystal is presented in figure 5 and it observed that the nucleation rate increases with supersaturation ratio. Based on the data obtained from the nucleation kinetic studies, the optimized conditions such as formation of multinuclei could be avoided when low supersaturation is used, interfacial tension of LAAP sample is low for the aqueous solution and these conditions can be used for the bulk growth of LAAP sample [16].



3.4 Growth of crystals

Using the solubility and nucleation kinetic data, the supersaturated solution (keeping supersaturation ratio at 1.1) of re-crystallized salt of LAAP has been prepared at room temperature (30 °C) and the solution was stirred well using a hot plate magnetic stirrer for 2 hours and then it was filtered using a Whatmann filter paper. The filtered solution in a container was loaded into a constant temperature bath (CTB) and growth of crystals was carried out by slow evaporation. Tiny crystals were formed at the bottom of the container due to spontaneous nucleation and then it took about 18 days to grow big-sized crystals.

3.5 XRD studies

The grown LAAP crystal was subjected to single crystal X-ray diffraction study to obtain the lattice parameters and hence the crystal structure was identified. The crystal data obtained from single crystal XRD studies are a (Å) = 8.263(3), b(Å) = 7.515(2), c (Å) = 15.536(4), β =106.15° and hence volume ($Å^3$) = 926.65 and hence LAAP crystal crystallizes in monoclinic structure. The obtained single crystal XRD data are found to be in good agreement with the data available in the literature [17].

3.6 Second Harmonic Generation (SHG) studies

The second harmonic generation (SHG) behavior of the powdered material was tested using the Kurtz and Perry method [18]. A Q switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 0.68 J/pulse, pulse width of 6 ns and repetition rate of 10 Hz was directed on the sample. The SHG output of wavelength 532 nm (green light) was finally detected by the photomultiplier tube (PMT). The powdered

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material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. It is noticed that the SHG efficiency of the LAAP sample is 1.47 times that of the standard KDP crystal.

4. Conclusion

L-alanine alaninium picrate (LAAP) salt was synthesized and the solubility studies were carried out for various temperatures in the range 30-50 °C and it is observed that solubility increases with temperature. Metastable zone width and nucleation parameters were determined and using the optimized conditions, single crystals of LAAP were grown by slow evaporation technique. The grown crystals were subjected to XRD study and SHG studies. The crystal structure of the grown LAAP crystal was found to be monoclinic with a non-centrosymmetric space group. The NLO activity of LAAP crystal was confirmed by measuring SHG efficiency.

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