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Studies on the nucleation kinetics of nonlinear optical L-vallinium picrate crystal

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Nucleation and growth kinetics reveal valuable information about the crystal growth process, which can be employed in the growth of large size crystals. Since nucleation is the first step towards phase transition, a detailed knowledge about nucleation is of major importance for better control of crystallization or solidification. Investigations on nucleation thermodynamical parameters are very important for the successful growth of good quality single crystals. The metastable zone-width studies at different temperatures were carried out for L-Vallinium Picrate (LVP) crystal for different temperature range. The induction period and the critical nucleation parameters were calculated based on the classical theory of homogenous nucleation. The interfacial energy values for LVP crystal were calculated for different super saturation ratio. The growth parameters of LVP crystal were optimized.

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1. Introduction

Nonlinear optical (NLO) crystals are the key material for the development of laser science and technology because of their change frequency of laser beam and modulate it in amplitude and phase. It may be said that lasers could not be used so widely in modern science and technology as they have been today, without NLO crystals. Nonlinear optical (NLO) crystals has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting and optical data storage for the developing technologies in telecommunication and in efficient signal processing [1-3]. Among the materials producing NLO effects, organic molecules possess large second order non-linearity are sought for potential applications in information storage also [4]. The basic structure of organic NLO is based on the π bond system, which leads to a high mobility of electron density. Functionalization of both ends of the π bond system with appropriate electron donor and acceptor groups can enhance the asymmetric electron distribution on either or both ground and excited states, thus leading to an increased optical non linearity [5]. The development of NLO crystals with better linear optics (LO) and NLO properties, wider spectral transmission, and phase-matching range in particular is obviously essential for further widening the application field of lasers, particularly in the UV, far -IR, and even THz spectral regions.

Since nucleation is the first step towards phase transition, a detailed knowledge about nucleation is of major importance for better control of crystallization or solidification. It is an important parameter for growing a crystal by low temperature solution technique. For the growth of the crystal, it is necessary to find out the working limits of metastability. The uncontrolled nucleation should be avoided to have a maximum yield. The metastable state is thermodynamically stable only with respect to small perturbations and its relaxation occurs, when a nucleus of a new phase is formed. In the present work, nucleation parameters such as metastable zone width, interfacial energy and critical radius are determined for LVP crystal.

2. Experimental procedure

The experiments were carried out in a constant temperature bath controlled to an accuracy of ± 0.01 ºC and it is provided with a cryostat for cooling below room temperature. Single crystals of L-Valinium picrate (LVP) were grown, from aqueous solution [6]. The solution was prepared by dissolving equimolar amounts of picric acid and L-Valine in deionized water at room temperature and stirred well for a period of 3Hrs to yield a homogenous mixture of solution. The solution was then filtered. The solution was taken in a beaker which is closed tightly with a tissue paper. Saturated solution was prepared under different temperature conditions by making use of the solubility data determined already. In all the experiments, a constant volume of 100 ml of solution were used. The solution was transferred into a transparent air tight nucleation cell and then it was saturated by heating it to at least 5 ºC above room temperature. It was left at this temperature in a stirred condition using a motorized stirrer to ensure homogeneous concentration for one hour, cooling was carried out at appropriate cooling rates until the formation of first nucleus was visually observed. Since the time taken for the formation of first visible nucleus after attainment of critical nucleus is very short, the first nucleus observed may be taken as the critical nucleus. The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zone width of the system. The consistency of the results has been verified after making several trials.

3. Single-crystal x-ray diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray Diffractometer. Single crystal XRD data confirms that the crystal belongs to monoclinic crystal system and the calculated lattice parameters are a = 9.98 Å, b = 6.24 Å, c = 12.64 Å, $\alpha = \gamma = 90°$ and $\beta = 110.40°$ and which agree well with the available reported literature values [6].

4. Induction period

As soon as the solution attains supersaturation, embryos are formed by single molecular addition starting from the monomer at the beginning. Thus it takes some time for the formation of critical nucleus from the monomers. In the present investigation, the direct vision observation method was employed to measure the induction period. The saturated solution was cooled to the desired temperature and maintained at that temperature and the time taken for the formation of the first speck was measured. The critical nucleus can be observed only after the nucleus reaches a sufficient size with time. The appearance of first visible speck of nucleus was noticed at the bottom of the container and hence the induction period was recorded. The consistency of the reading was verified by repeating the experiment three or four times.

5. Interfacial energy

Interfacial energy at the solution-crystal interface is a crucial parameter involved in theories of nucleation and crystal growth. However, certain difficulties were encountered in the nucleation experiments such as the requirement of a solution free from foreign particles, volume of the solution etc. Theoretical attempts have been made by several researchers to estimate the interfacial energy using solubility data. The interfacial energy (γ) determined by conducting nucleation experiments has been used for the kinetics study. The change in the Gibb's free energy (ΔG) between the crystalline phase and the surrounding mother liquor results in a driving force, which stimulates crystallization. The Gibb's free energy is represented as the sum of surface free energy and volume free energy.

6. Measurements of metastable zone width and induction period

Saturated solution of LVP was prepared in accordance with the presently determined solubility data for the nucleation experiments. A constant volume of 100 ml of the solution was used for all the experiments. The solution was heated 5°C above the supersaturation temperature for homogenization. It was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature throughout the entire volume of the solution. The metastable zone width was measured by the conventional method [7] in which the equilibrium saturated solution is cooled from the superheated temperature until the first visible crystal is observed (Fig. 1). The induction period of LVP solution was measured using isothermal method [8]. The saturated solution was cooled to the desired temperature and the time taken for the formation of the first crystal was measured (Fig. 2). Repeated trials were carried out to ensure reproducibility.

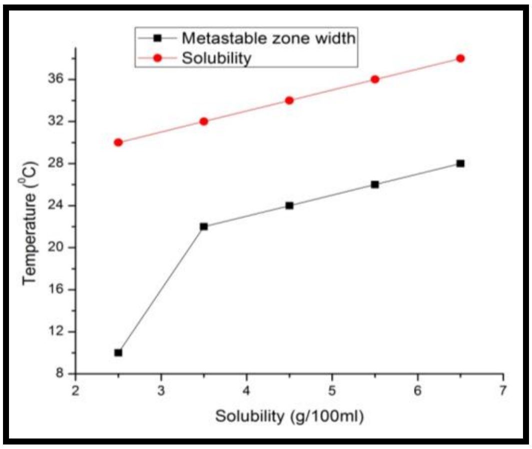

Fig. 1. Metastable zone width of LVP as a function of temperature.

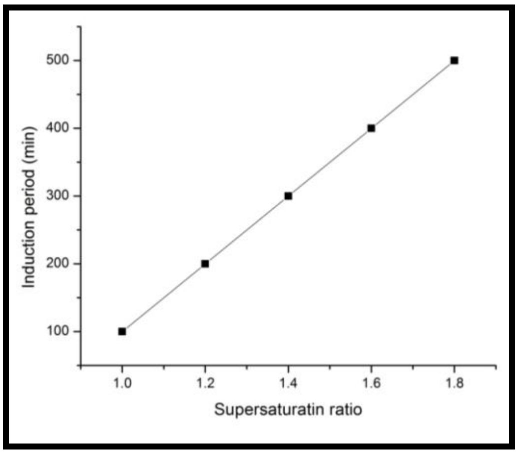

Fig. 2. Induction period vs supersaturation of LVP.

7. Interfacial tension

Interfacial tension of the crystal–solution interface is an important parameter involved in the theory of nucleation and growth kinetics. The classical homogeneous nucleation theory has been successfully tested for the nucleation of liquid solution and for crystal formation in melts [9]. Interfacial tension in the present investigation has been calculated on the basis of the classical theory of homogeneous formation of spherical nuclei [10].

$$\ln \Gamma = -\ln B + \frac{16\pi\gamma^3 V^2 N}{3R^3 T^2 (\ln S)^2} \qquad (1)$$

where V is the molar volume of the crystal. N is the Avogardo's number, R is the gas constant; γ-induction period of LVP solution at temperature T and B is constant. S is the supersaturaion ($S=C/C^*$), where C is the actual concentration and C^* is the equilibrium concentration. Eq. (1) suggests a straight line for ln Γ against $1/(\ln S)^2$ and therefore is given by

$$m = \frac{16\pi\gamma^3 V^2 N}{3R^3 T^3} \qquad (2)$$

Since ln B weakly depends on temperature therefore, the interfacial tension is evaluated from

$$\gamma^3 = \frac{3R^3 T^3 m}{16\pi\gamma^3 V^2 N} \qquad (3)$$

8. Nucleation parameters

In the present work, the nucleation parameters of the LVP crystals have been evaluated. According to classical nucleation theory, the free energy required to form a spherical nucleus is given by

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (4)$$

where ΔGv is the energy per unit volume, γ is the interfacial tension and r is the radius of the nucleus. At critical state, the free energy formation obeys the condition d $(\Delta G)/\mathrm{d}r = 0$. Hence, the radius of the critical nucleus is expressed as

$$\Delta G_v = -\frac{kT \ln S}{V}; S = C / C^* \qquad (5)$$

The critical free energy barrier

$$\Delta G^* = \frac{16\pi\gamma^3 V^3}{3(\Delta G_v)} \qquad (6)$$

The number of molecules in the critical nucleus is expressed as

$$i^* = \frac{4\pi(r^*)^3}{3V} \qquad (7)$$

The nucleation rate J has been calculated using the equation

$$J = A \exp\left[\frac{-\Delta G^*}{kT}\right] \qquad (8)$$

9. Results and discussion

The solubility, metastable zone width of LVP crystal as a function of temperature is shown in Fig. 1. The induction period as a function of supersaturation ratio is shown in Fig. 2, the figure reveals that the induction period decreases with increase of supersaturation which infers the increase in nucleation rate. That means the number of critical nuclei formed will be increased which will lead to spurious nucleation. 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. Table 1 gives the nucleation parameters such as Gibbs free energy per unit volume, critical radius of nucleus, critical energy barrier, number of molecules in the critical nucleus and nucleation rate of the grow LVP crystals for various supersaturations.

Table 1. Nucleation parameters for LVP.

S	ΔG_v	r*	ΔG_*	i*	J
1.2	4.0902	1.3421	25.3423	42.7523	4.5263×10^{27}
1.3	6.7270	1.2452	21.2976	36.87654	3.0895×10^{28}
1.4	8.1432	1.1543	19.3781	25.5435	5.0589×10^{28}
1.5	10.0432	1.0456	17.4356	21.9876	6.4587×10^{28}
1.6	12.1432	0.9876	15.3678	20.4564	7.1258×10^{28}

10. Conclusion

Single crystals of L-Valinium picrate were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system. The evaluated nucleation parameters are found to be feasible for the growth of bulk LVP crystal. The nucleation parameters such as; solubility, metastable zone width, induction period, interfacial energy and critical radius of LVP have been studied. Solubility studies revealed that the solubility of LVP increases with increase in temperature. The solubility, metastable zone width and induction period values of LVP have been determined. The interfacial tension values have been calculated using the experimentally determined induction period values. Nucleation kinetics and fundamental growth parameters have also been investigated. Thus, the performed nucleation studies offer a very good platform to identify and improve the experimental conditions favourable to grow bulk size crystals.

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