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Effect of EDTA on Growth Kinetics and Enhancement of Optical Properties of Organic Nonlinear Optical Crystal

T. Arumanayagam[1], S. Ananth[2] and P. Murugakoothan[1*]

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Abstract

The study of nucleation understands and predicts the growth time before the crystal appears. The solubility and nucleation parameters of pure and ethylenediamine tetra acetic acid (EDTA) doped guanidinium p-nitrobenzoate crystals have been determined. The lattice parameters and the crystal system were identified from single crystal X-ray diffraction technique. Solubility of the compounds was analyzed gravimetrically at different temperatures. In order to optimize the growth parameters, metastable zone width, induction-period, interfacial tension, radius of the critical nucleus and energy of nucleus formation were analyzed based on the classical theory of nucleation. Structural and optical properties of thr grown crystals have been assessed.

Keywords: Solubility; Induction period; Optical properties

1 Introduction

Crystal growth process incorporates with many factors such as dispersion, super- saturation, crystal size, mixtures, temperature, pH etc. The physico-chemical properties of crystal have influenced by the preliminary stage of crystallization such as nucleation process. In technological applications, the crystallization process comprises the rate of phase transition and the morphology of the crystal. In solution growth, faster cooling rate depends on the metastable zone width, which is extremely an important parameter in the design and optimization of crystallization processes. The stability og growth raises with increase of metastable zone width [1]. Srinivasan et al has introduced a novel method to enhance the metastable zone width by adding the chelating agent ethylenediamine tetra acetic acid (EDTA) [2-4]. Recent research reveals that the guanidinium compounds seems to be easy to obtain and is cheaper than complicated amino acids [5]. But quite often they lacking transparency, optical quality and inability to grow large size single crystals for nonlinear optical (NLO) device applications. Hence, in the present work, the experimental study of growth kinetics of guanidinium p-nitrobenzoate (GuNB) single crystal has been attempted. The crystal has been subjected to single crystal X-ray diffraction and UV-vis-NIR analyses.

2 Experimental

2.1. Synthesis and solubility of GuNB

The guanidinium p-nitrobenzoate (GuNB) was synthesized from calculated amount of guanidinium carbonate and p-nitrobenzoic acid in the ratio 1:2 and was dissolved in water-ethanol (1:1) solvent. This solution was slightly heated up to 50°C and kept for slow evaporation to dryness at room temperature for 10 days. The solubility study of GuNB was carried out in a constant temperature water bath with cryostat facility and temperature controller with an accuracy of ± 0.01˚C. The solubility was analyzed gravimetrically for different temperatures such as 30, 35, 40, 45 and 50 ˚C [6]. The same process was repeated for various solutions of GuNB added with 0.5 mol% and 1.0 mol% of EDTA. The solubility curve of pure and doped GuNB for different temperatures in water-ethanol (1:1) solvent is depicted in fig. 1.

2.2. Metastable zone width and induction period of GuNB

The metastable zone width was determined by the conventional polythermal method [7]. A constant volume of 100 mL solution was heated to 5˚C above the saturation temperature for before cooling. The solution was continuously stirred to ensure homogeneous concentration throughout the entire volume of solution. Then the the bath temperature was reduced at a rate of 0.5˚C per minute until the formation of first nuclei (speck of particle) was visually observed and the temperature was taken as the nucleation temperature. The difference between saturation temperature and the nucleation temperature is taken to be the metastable zone width [8]. The plot of metastable zone width for pure and EDTA

* Corresponding author e-mail: murugakoothan03@yahoo.co.in,
Phone: +91 9444 447 586,
[1]PG and Research Department of Physics, Pachaiyappa's College, Chennai-600030, India.
[2]Department of Physics, KPR Institute of Engineering and Technology, Coimbatore-641407, India

doped GuNB is presented in fig. 2.

Induction period (τ) is the time taken between the achievement of supersaturation and the appearance of crystal nuclei in the solution. In the present investigation, we employed direct vision method to measure the induction period. Experiments were performed at selected degrees of supersaturation (S), viz., 1.1, 1.2, 1.3 and 1.4 at constant temperature of 50°C. The results of the induction period study is presented in fig. 3(a).

2.3. Interfacial energy and nucleation kinetics

Interfacial energy at the solution-crystal interface is an important parameter involved in the theories of nucleation and growth kinetics. In the present work, the interfacial tension was calculated based on the classical theory of homogeneous nucleation [9, 10]. The relation between induction period and supersaturation ratio are given by

$$ln\tau = -\ln B + \frac{16\pi v^2\gamma^3 N}{3k^3T^3(\ln S)^2} \quad (1)$$

where v is the molar volume of the crystal, S is the supersaturation ratio, τ is the induction period of the solution at absolute temperature T and B is a constant. The value of γ has been determined using the equation (2),

$$\gamma^3 = \frac{3mk^3T^3}{16\pi V^2 N} \quad (2)$$

where the slope (m) was calculated from the straight line fit of ln τ versus $1/(\ln S)^2$ at constant temperature, shown in fig. 3(b).

Nucleation theory states that, the work done to form a cluster of n molecules is the sum of the difference in free energy between final and initial states and the formation of an interface between nucleus and solution. The free energy required to form a spherical nucleus is given by [11]:

$$\Delta G = -n\Delta\mu + 4\pi r^2\gamma \quad (3)$$

where r is the radius of the nucleus. If V be the volume of each molecule, then the above equation (3) will take the following form:

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

where ΔG_V is the volume free energy change per unit volume and is given by $\Delta G_V = -\Delta\mu/V$. At the critical state, the free energy of formation obeys the condition $d(\Delta G)/dr = 0$. Hence, the radius of critical nucleus is expressed as

$$r^* = \frac{-2\gamma}{\Delta G_V} \quad (5)$$

The above equation clearly shows that the value of r^* increases with decrease of supersaturation. That is the probability of formation of nucleation in this system will be higher at higher supersaturation. The number of nuclei formed per unit time per unit volume, i.e., the rate of nucleation can be expressed as

$$J = A\exp\left(\frac{-\Delta G^*}{kT}\right) \quad (6)$$

Here, the pre-exponential component A for the solution is nearly equal to 10^{30} [12]. The number of molecules in the critical nucleus is expressed by

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

A typical plot of J as a function of $\Delta\mu$ is depicted in fig. 4. It is evident that the nucleation rate of 0.5 wt% and 1.0 wt% of EDTA added GuNB is very low until a critical value of supersaturation is achieved, after that the rate increases exponentially. This critical supersaturation ($\Delta\mu_c$) defines the so-called metastable zone for pure GuNB which is lower than that of EDTA doped GuNB.

3 Results and Discussion

The structure of the grown GuNB single crystals were identified by single crystal X-ray diffraction analysis. The unit cell parameters obtained are a=11.13 (2) Å, b=6.64 (2) Å, c=6.94 (2) Å, β=107.97°, and v = 512.92 (3) Å^3. The grown crystal belongs to monoclinic crystal system with the space group $P2_1$. The obtained parameters are in good agreement with the reported values [13]. Solubility curve, as shown in fig. 1, show that the solubility of EDTA doped GuNB is higher than that of pure one and also found that the solubility increases with increase of temperature.

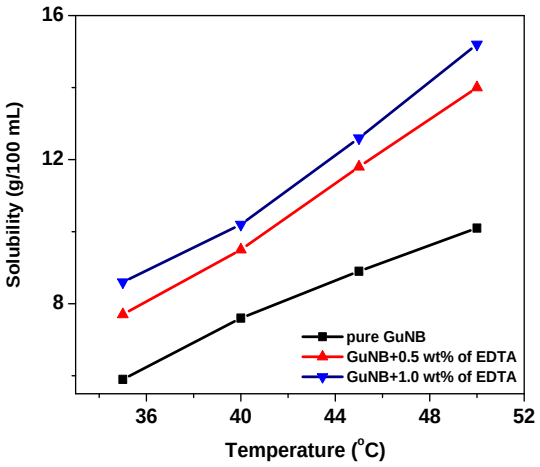

Fig. 1. Solubility of Pure and EDTA added GuNB in water-ethanol (1:1) solution.

Fig. 2 confirm that the metastable zone width increases with increase of additive concentration and clearly evident that the stability of the solution is more for higher EDTA concentration. The fig. 3 (a) shows that the value of induction period decreases with increase of supersaturation concentration and hence the nucleation rate increases [11, 14]. It is clear that the optimized induction period with controlled nucleation rate lead to

grow good quality single crystals. The slope obtained from the plot of ln τ against $1/(\ln S)^2$ noticed that the induction period increases with increase in additive concentration. Using the interfacial tension value, the nucleation parameters have been evaluated for the controlled nucleation condition. The values of critical nucleation parameters are summarized in the table 1. From the table 1, it is clear that the value of critical size of the nucleus decreases with increase of supersaturation and consequently the nucleation rate (J) increases with increase of supersaturation [15,16].

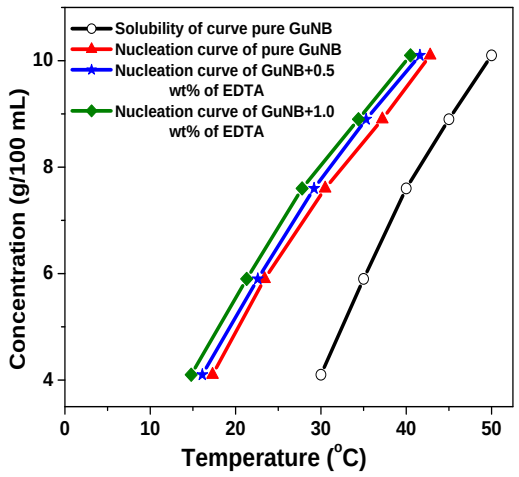

Fig. 2. Metastable zone width of pure and EDTA dopped GuNB.

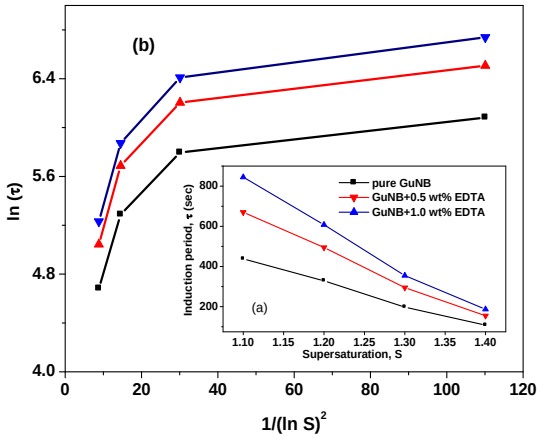

Fig. 3(a). Plot of induction period vs super saturation.
3(b). Plot of ln τ vs $1/(\ln S)^2$.

Fig. 4 clearly shows that above the critical supersaturation the nucleation rate increases exponentially, and the value of $\Delta\mu_c$ is evaluated as 79.88, 85.78 and 92.33 for pure, 0.5 wt% and 1.0 wt% of EDTA. Transparency of GuNB and EDTA added crystals was recorded using the Perkin-Elmer 35 spectrometer in the range of 200-1200 nm for the crystal thickness of 2 mm of each. The recorded spectrum is shown in fig. 5 and it is very much clear that the transmittance of GuNB crystals has enhanced by the addition of chelating agent EDTA.

Table 1
Summary of nucleation data of pure and EDTA added GuNB system

System	S	ΔG^* x 10^{-20} J	r^* x 10^{-10} m	J x10^{27} nuclei/s/V	i^*
Pure GuNB	1.1	2.711	14.37	2.283	23.98
	1.2	2.583	7.52	3.039	3.43
	1.3	2.357	5.23	5.052	1.15
	1.4	2.087	4.07	9.261	0.55
GuNB+0.5 wt% EDTA	1.1	2.901	14.55	2.493	24.89
	1.2	2.765	7.61	2.021	3.56
	1.3	2.535	5.29	3.389	1.25
	1.4	2.248	4.13	4.505	0.57
GuNB+1.0 wt% EDTA	1.1	3.003	14.75	1.184	25.83
	1.2	2.857	7.71	1.645	3.69
	1.3	2.617	5.36	2.817	1.34
	1.4	2.332	4.17	5.348	0.59

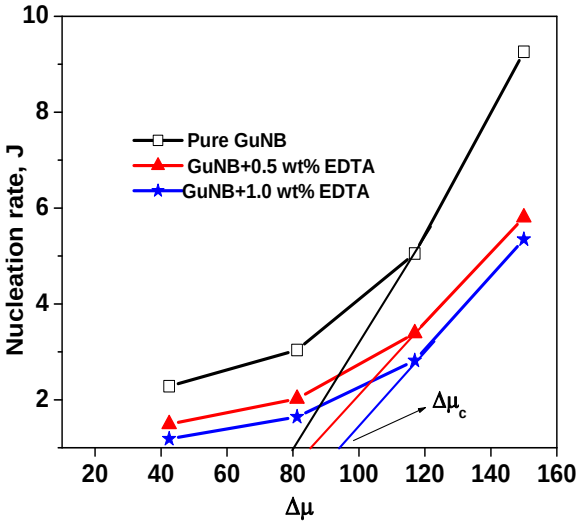

Fig. 4. Plot of nucleation rate as a function of supersaturation.

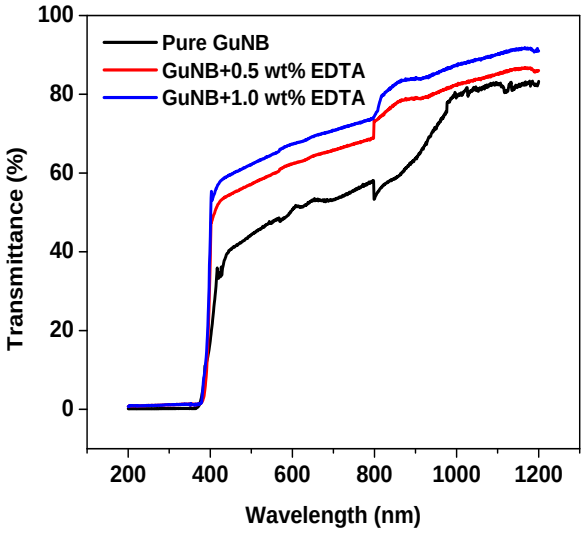

Fig. 5. Transmittance spectra of pure and EDTA added GuNB crystals.

4 Conclusions

nucleation kinetics of GuNB crystallization was carried out using constant temperature bath with microscope. The fundamental growth parameters of grown crystals have been evaluated. The experimental solubility data shows that the addition of EDTA enhances the meta-stable zone width, which is suitable for bulk growth. The induction period increases with increase of EDTA additive concentration. The UV-vis-NIR spectral analysis confirms that the optical transparency has enhanced considerably by the addition of EDTA. We hope that these studies will inspire interest to achieve good optical quality bulk crystals for device applications.

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