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Growth and Investigations on the Nucleation kinetics of Zinc succinate NLO single crystals

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Abstract : Single crystals of Zinc Succinate (ZS) were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system with the space group C2. The solubility, metastable zone width and induction period have been determined for the ZS solution. Interfacial energy has been estimated using the experimentally determined induction period values. Nucleation parameters such as Gibbs free energy, radius of critical nucleus, critical free energy barrier and number of molecules in the critical nucleus and nucleation rate have also been investigated. It is observed that the nucleation rate increases with the increase of supersaturation. The growth parameters of zinc succinate were optimized for the growth of large size crystals.
Key words: Nucleation, Metastable zone width, Interfacial energy, NLO single crystal.

1. INTRODUCTION

In organometallics, the diversity of central metals, oxidation sates and ligands fosters in optimization of the charge-transfer iteractions; a central metal atom can coordinate two different ligands. A wide variety of central metal atoms as well as the size and nature of the ligands, provide architectural flexibility to tailor NLO properties up to a maximum. Coordination of a central metal ion with different ligands could introduce a chiral centre in an organometallic molecule and therefore a high percentage of organometallic compounds are expected to have acentric crystal structures. Organometallics may have a wide range of applications in opto-electronics including, integrated optics, optical switching, telecommunications, bistability and modulation [1, 2]. The low temperature solution growth technique requires the knowledge of the essential nucleation parameters like interfacial energy (γ), metastable zone width, volume of free energy (ΔG_v), Gibbs free energy (ΔG^*) and radius of critical nucleus (r^*) for the growth of good-quality bulk single crystal. Metastable zone width provides a direct measure of the stability of the solution in the supersaturated region [3]. Hence, we have investigated the various nucleation parameters of ZS for the first time.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis and solubility

Zinc Succinate (ZS) was synthesized by dissolving hexahydrate zinc nitrate and succinic acid (AR grade) in the molar ratio of 1:1 in double distilled water. The required amounts of hexahydrate zinc nitrate and succinic acid in accordance are dissolved in double distilled water with a continuous stirring. To ensure high purity, the synthesized material was purified by successive recrystallization for several times in double distilled water. A volume of 100 ml of water was taken in an airtight container and recrystallized salt was added. The experiment was carried out in a constant temperature bath with

temperature accuracy ±0.01 °C. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was carried out for various temperature ranges as 30, 35, 40, 45 and 50 °C (Figure 1).

2.2 Crystal growth

The growths of ZS single crystals were carried out by low temperature solution growth technique. According to the solubility data of ZS in millipore water, the saturated solution of ZS was prepared using recrystallised material. The solution was filtered to remove any insoluble impurities and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to the spontaneous nucleation. Among them, defect free seed crystal was kept immersed in the mother solution, which was allowed to evaporate at room temperature. Good quality single crystals of dimension 10×5×3 mm^3 were obtained after 20 days at room temperature. The grown crystal is shown in figure 2.

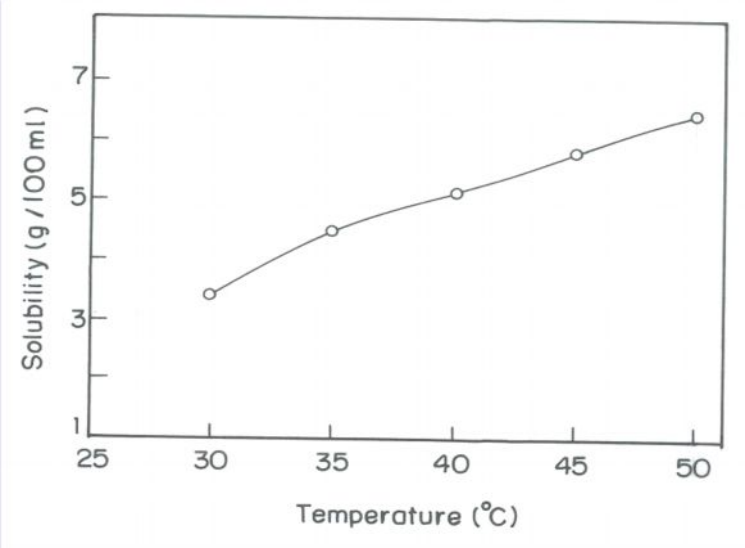

Figure 1. The solubility of ZS

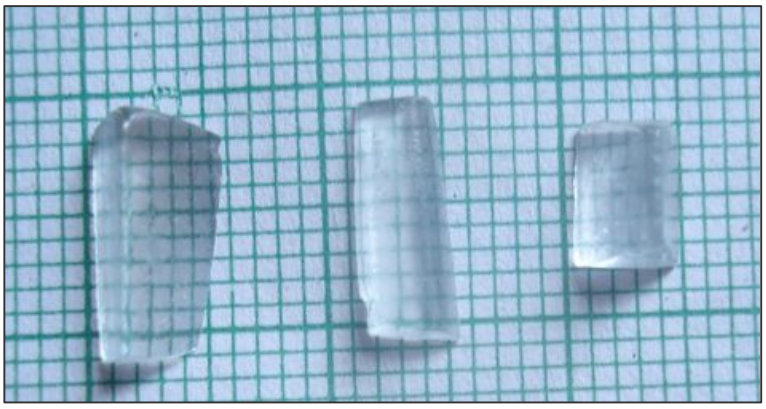

Figure 2. Photograph of ZS single crystals

2.3 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 CAD4 automatic X-ray diffractometer**.** Calculated lattice parameters are: a = 7.579 Å, b = 5.976 Å, c = 6.265 Å, β = 108.451° and the crystals belongs to monoclinic system with space group is C2. These values are found to agree with the reported values [4].

2.4 Measurements of Metastable zone width and Induction period

Saturated solution of ZS 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 [5] in which the equilibrium-saturated solution is cooled from the superheated temperature until the first visible crystal is observed (Figure 3). The induction period of ZS solution was measured using isothermal method [6]. The saturated solution was cooled to the desired temperature and the time taken for the formation of the first crystal was measured (Figure 4). Repeated trials were carried out to ensure reproducibility.

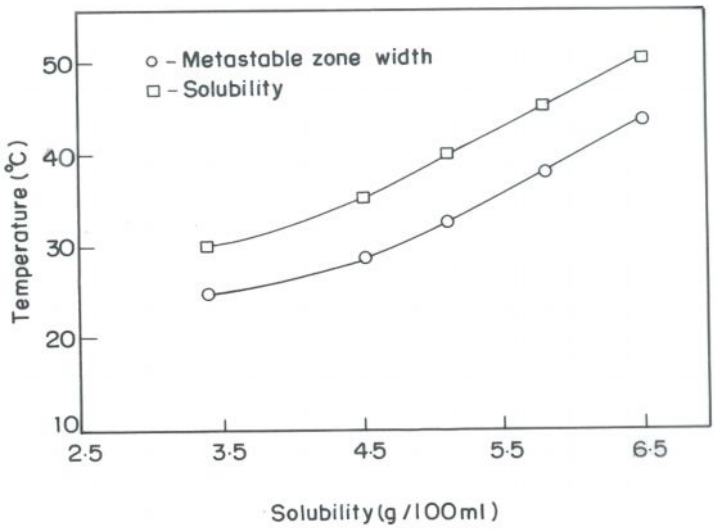

Figure 3. The metastable zone width vs temperature of ZS

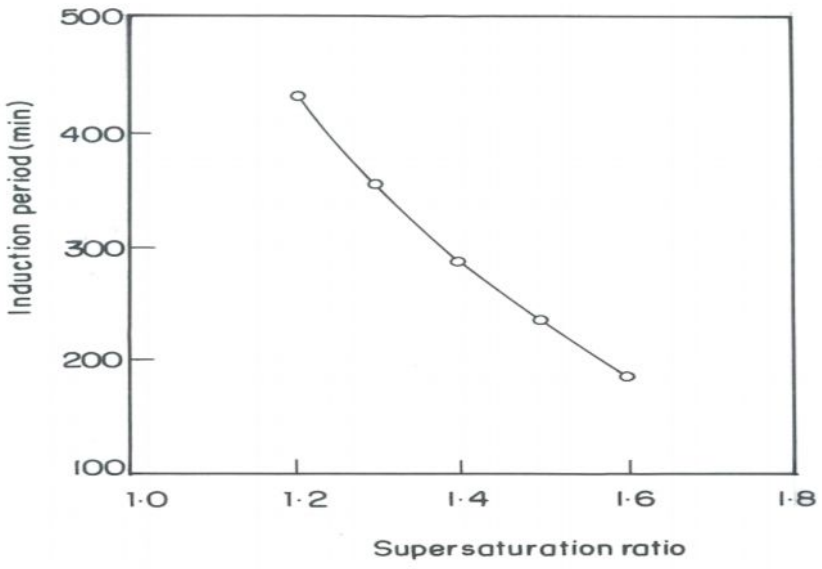

Figure 4. Induction period vs supersaturation ratio

2.5 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 [7]. Interfacial tension in the present investigation has been calculated on the basis of the classical theory of homogeneous formation of spherical nuclei [8]

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

where V is the molar volume of the crystal. N is the Avogardo's number, R is the gas constant, γ-induction period of ZS 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

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

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

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

2.6 Nucleation parameters

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

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

where ΔG_v 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 (ΔG)/dr =0. Hence, the radius of the critical nucleus is expressed as

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

where

$$\Delta G_v = -\frac{kT \ln S}{V}; \quad S = C/C^*$$

The critical free energy barrier

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

The number of molecules in the critical nucleus is expressed as

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

The nucleation rate J has been calculated using the equation

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

3. RESULTS AND DISCUSSIONS

The solubility, metastable zone width of ZS as a function of temperature is shown in figures 1 and 3. The induction period as a function of supersaturation ratio is shown in figure 4, 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 ZS crystals for various supersaturations.

Table 1. Nucleation parameters of ZS

S	ΔG_v	***r**** (nm)	**Δ*G****	***i****	***J***
1.3	5.0902	1.2374	30.6341	52.7613	5.1042 x10^{27}
1.4	7.7570	1.1224	25.3232	36.0201	2.0362 x10^{28}
1.5	9.1230	1.0247	21.6727	25.8291	5.0217 x 10^{28}
1.6	10.0517	0.9852	19.9826	20.3142	8.8325 x 10^{28}

4. CONCLUSION

Good quality single crystals of ZS were grown by slow evaporation technique. Single-crystal XRD analysis confirms that the crystals belong to monoclinic system with the space group C2. The solubility, metastable zone width and induction period values of ZS 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. The evaluated nucleation parameters are found to be feasible for the growth of bulk ZS crystals.

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