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Investigations on the nucleation kinetics and growth of organometallic non linear optical ZCTC crystal

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ABSTRACT

The solubility, metastable zone width and induction period have been determined for the zinc cadmium thiyocyanate (ZCTC) solution. 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. Interfacial energy has been estimated using the experimentally determined induction period values. It is observed that the nucleation rate increases with the increase of supersaturation. The growth parameters of ZCTC were optimized for the growth of large size crystals.

Key words: SCN ligand; Metastable zone; Interfacial energy; NLO crystal; Nucleation.

INTRODUCTION

The organometallic complexes of thiocyanate are desirable nonlinear optical materials for realizing blue-violet light by frequency doubling of laser radiation. The experiments conducted by Chinese and Indian research groups strongly favour the possible use of this class of materials for various nonlinear optical applications and photonics device fabrications [1-3]. An important aspect of utilizing organometallic structures for nonlinear optics is in their unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal. An important aspect of utilizing organometallic structures for nonlinear optics lies in their unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal [1]. 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 [4,5].

Growth of organometallic single crystals has been a subject of perennial concern in order to use these materials for device application. In these crystals, a central metal ion is surrounded by a number of organic and/or inorganic ligands. The organic ligand is usually more dominant in the NLO effect. As for organic ligands, they can be small π-electrons systems such as thiocyanate SCN^-, urea $OC(NH_2)_2$ and thiourea $SC(NH_2)_2$. Many metal-organic coordination materials with good NLO effect have been designed and synthesized using thiourea (TU), allylthiourea (AT) and thiocyanate (SCN) in the recent past [6]. Hong Zhang et al [7] have systematically explained the various coordination modes of thiocyanate and the formation of metal thiocyanate structures. SCN^- is a highly versatile ambidentate ligand with modes of coordination: two terminal modes and thirteen multidentate bridging modes. Though the growth of ZCTC crystals has been achieved, there are challenges pertaining to the growth of large size single crystals free from defects. For crystal growers, an in-depth understanding about the growth mechanism and surface morphology of crystals is needed, which can do much help in accelerating the growth rate, enhancing the crystal quality and thereby expediting the crystal development [8]. 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^*), chemical potential 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 [9]. Hence, we have investigated the various nucleation parameters of ZCTC for the first time. The grown crystals are confirmed by single crystal XRD.

MATERIALS AND METHODS

Synthesis and solubility

High purity starting materials of ammonium thiocyanate (NH_4SCN), mercury chloride ($HgCl_2$) and Zinc chloride ($ZnCl_2$) were purchased (E-Merck, AR grade). zinc cadmium thiocyanate ($ZnCd(SCN)_4$) was synthesized using aqueous solution. The following reaction formula was used to synthesis the compound:

$$4NH_4SCN + ZnCl_2 + CdCl_2 \rightarrow ZnHg(SCN)_4 + 4NH_4Cl$$

To ensure high purity, the synthesized material was purified by successive recrystallization (typically 3 to 4 times) in double distilled water.

Solubility corresponds to saturation i.e. to equilibrium between a solid and its solution at a given temperature and pressure. Thermodynamically, this means that the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. Solubility factors define the supersaturation which is the driving force for the rate of crystal growth. Hence for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion.

Three different solvents such as water, water with 8% ammonium chloride and water with acetone (1:1) were used to determine the solubility of ZCTC. As per the available data, the growth of ZCTC crystal of large size is limited due to its low level of solubility. Hence, an attempt has been made to investigate the growth of ZCTC in various solvents so as to improve the solubility level and identify the best solvent.

The synthesized salts were used to measure the solubility in Milli-Q water. Knowledge of the solubility of the material to be grown and stability of the solution in the vicinity of the equilibrium point are the key factors for the successful development, optimization, and scale up of a crystallization process. A 100 ml beaker containing 50 ml of Milli-Q water was placed in a cryostat (accuracy ±0.01˚ C). Initially, the temperature was set at a particular value and the beaker was closed with an acrylic sheet containing a hole at the center through which the stirrer was dipped into the solution. The addition of the powdered sample of ZCTC to the solution in small amounts and subsequent stirring of the solution by a motorized stirrer was continued till the excess salt was deposited at the bottom of the beaker. The stirring was further continued, to ensure homogeneous temperature and concentration throughout the entire volume of the solution. After confirming the saturation, the content of the solution was analyzed gravimetrically. A known quantity (20 ml) of the saturated solution of the sample was taken in a warmed pipette and then poured into a clean Petri dish, it was slowly allowed to evaporate and then dried. The mass of the obtained crystalline powder of ZCTC in 20 ml of solution was determined by weighing the Petri dish with salt and hence the solubility i.e., the quantity of ZCTC salt (in gram) dissolved in a given volume of water was determined. The solubility of ZCTC was determined for four different temperatures 30, 40, 50 and 60 °C. Fig.1shows the solubility curves for ZCTC at different temperatures. Among the three salts, ZCTC has the minimum solubility and it has the positive solubility like the other two salts. The solubility slope for water, water with ammonium chloride and water with acetone are 0.165, 0.17 and 0.1735 respectively. The solubility of ZCTC is found to be higher with acetone-water mixed solvent than the other solvents used.

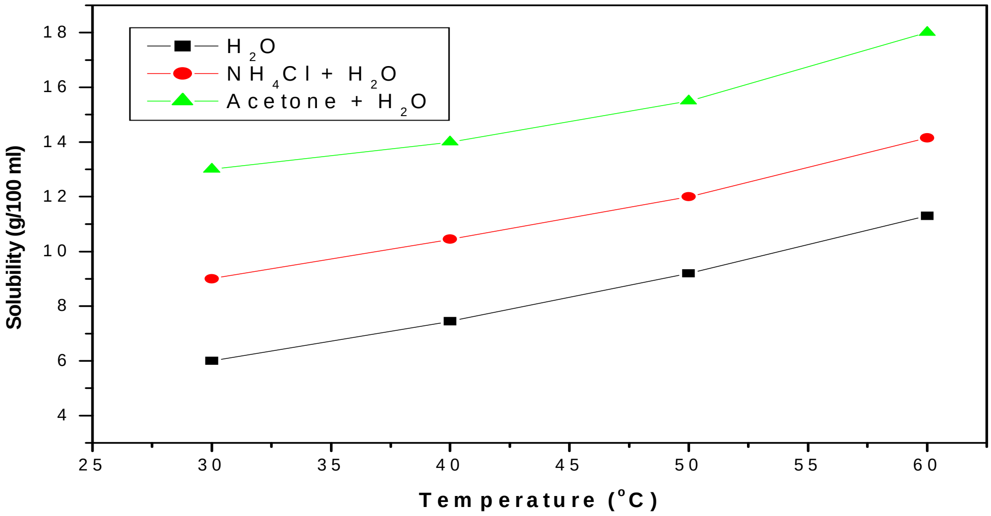

Fig. 1. Solubility curve of ZCTC

Measurements of nucleation parameters

2.2.1 Metastable zone width

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. The metastable zone width of ZCTC was measured by means of the conventional polythermal method [10,11]. The nucleation studies were performed in a constant temperature bath kept in a cryostat, which has the provision to operate from 0 ˚C to 80˚ C with a controlling accuracy of ± 0.01˚ C. Saturated solution of ZCTC was prepared at four different temperatures (30, 40, 50, and 60 °C) by making use of the solubility data determined in the present study. In all our experiments, a constant volume of 50 ml of solution was used. The solution was transferred in to a transparent air tight nucleation cell and then it was undersaturated by heating it at least 5 °C above saturated temperature and it was left at this temperature in a stirred condition. The solution was stirred continuously using an immersible Teflon coated magnetic stirrer to ensure homogeneous concentration and temperature for the entire volume of the content. After a lapse of one hour, cooling was carried out at appropriate cooling rates until the formation of first nuclei was visually observed. Since the time taken for the formation of first visible nucleus after attainment of critical nucleus is very small, the first nucleus observed may be taken as 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.

2.2.2 Induction period

When 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. The time taken between the achievement of supersaturation and the appearance of crystal nucleus in a supersaturated solution is known as induction period. Different methods are used for the measurement of induction period. Conductivity and turbidity methods are more suitable for materials having low solubility whereas; dilatometer and direct vision methods are suitable for materials having high solubility. In the present investigation, we have employed the direct vision observation method 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 crystal 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.

2.2.3 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 researches to estimate the interfacial energy using solubility data.

2.3 Nucleation kinetics of ZCTC crystal

The interfacial energy (γ) determined by conducting nucleation experiments has been used for the kinetics study. The change in the Gibbs free energy (ΔG) between the crystalline phase and the surrounding mother liquor results in a driving force, which stimulates crystallization. The Gibbs free energy is represented as the sum of surface free energy and volume free energy.

$$\Delta G = \Delta G_s + \Delta G_v \qquad (1)$$

For a spherical nucleus

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

Where, r is the radius of nucleus, γ is the interfacial energy and ΔG_v is the free energy change per unit volume. The free energy formation obeys the condition d (ΔG)/dr = 0. Hence the radius of the critical nucleus is expressed as

$$r^* = -\,2\gamma/\ \Delta G_v \qquad (3)$$

and the interfacial energy

$$\gamma = kT/d^2\ \ (0.174 - 0.247*\ln S) \qquad (4)$$

Where, k is the Boltzmann's constant ($1.38\text{x}10^{-23}$ J/ K)

The bulk energy change per unit volume is represented as

$$\Delta G_v = -(kT \ln S)/V \qquad (5)$$

The corresponding critical free energy barrier is

$$\Delta G^* = 16\ \pi\gamma^3\ /3\Delta G_v^{\ 2} \qquad (6)$$

The number of molecules in the critical nucleus is given as

$$i^* = 4\pi(r^*)^3\ /3V \qquad (7)$$

2.4 Crystal growth

The success of growing large and high quality single crystals with low defect density is highly dependent on the purity of the starting materials. Hence, the synthesized product of ZCTC was purified by recrystallization and dissolved in mixed solvent of acetone and water (4:1). Since acetone is very volatile, ZCTC can be easily recrystallized and purified by the mixed solvent [1]. In addition with the solubility data, saturated solution of 200 ml of ZCTC was prepared. The prepared solution of ZCTC was allowed to evaporate at room temperature (303 K). In a period of 5–7 days, tiny, transparent and needle shape crystals were obtained. Among them defect free seed crystals were taken and kept immersed into the reactant mother solution. Within a period of 15-20 days ZCTC crystals of sizes up to 7 x 5 x 3 mm^3 were formed (Fig.2). The crystals appear colourless and are non-hygroscopic in nature. During the growth of ZCTC, the control of multi nucleation is more tedious process. Hence, it is difficult to grow bulk size ZCTC from slow evaporation method.

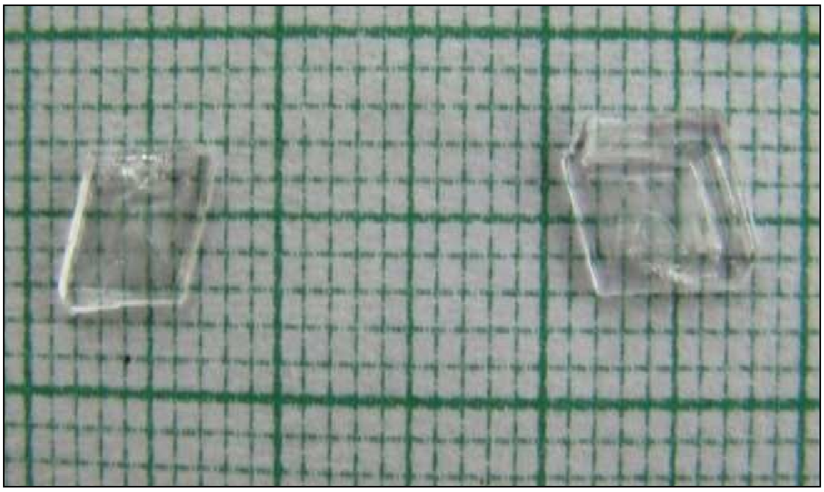

Fig. 2. Photograph of ZCTC single crystals

RESULTS AND DISCUSSION

Fig.3 shows the plot of metastable zonewidth at different temperatures for ZCTC. From the curve, it is obvious that the metastable zonewidth decreases slightly with the increase in temperature, which is the most important aspect for growing bulk size crystals. Fig.4 presents the variation of the induction period with respect to different supersaturation ratios of the solution. The induction period is found to decrease when the supersaturation is increased, which infers the increase in nucleation rate. The variation of interfacial energy with supersaturation is shown in Fig. 5, it is observed that the interfacial energy decreases gradually with increase in the supersaturation of the solution. The measured average interfacial energy values vary in the range of 1.013–2.268 10^{-3}J/m^2. The evaluated value of critical radius is plotted in Fig.6 as a function of supersaturation, which suggests that the free energy changes exponentially with supersaturation. Based on the equations given in the discussion on nucleation kinetics (2.3), nucleation parameters like number of molecules in the critical nucleus (i*), Gibbs free energy per unit volume (ΔG_v) and critical free energy barrier (ΔG^*), were determined. It is evident from the table as the level of supersaturation increases, both the radius of critical nucleus and the critical energy barrier decrease. It is worth to note that the minimum nucleation barrier occurs at the interfacial energy of 2.268 10^{-3}J/m^2. The interfacial energy plays a vital role in the nucleation mechanism. The stability and velocity of crystal growth depends on several of crucial parameters such as temperature, the degree of supersaturation, concentration of impurities existing in the solution, the pH value of the solution etc. In order to achieve this, one needs to accurately control the growth temperatures and supersaturation as well as to purify the growth solutions. The present study confirms that the evaluated nucleation parameters are feasible for the growth of bulk ZCTC single crystal.

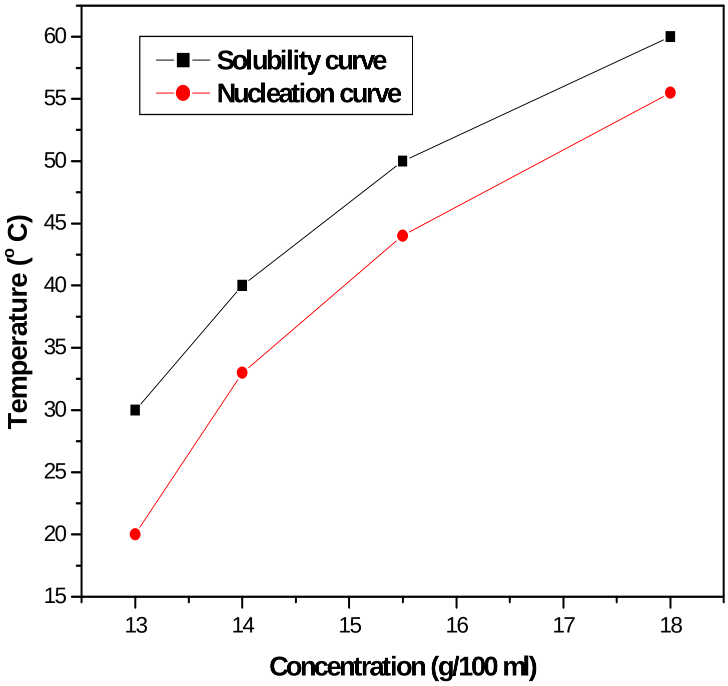

Fig.3. Metastable zonewidth of ZCTC

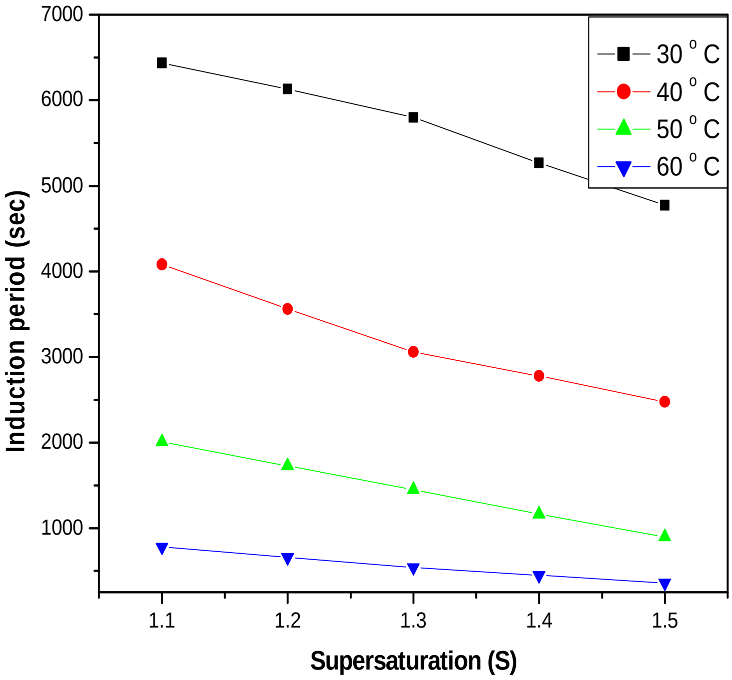

Fig. 4. Induction period Vs supersaturation

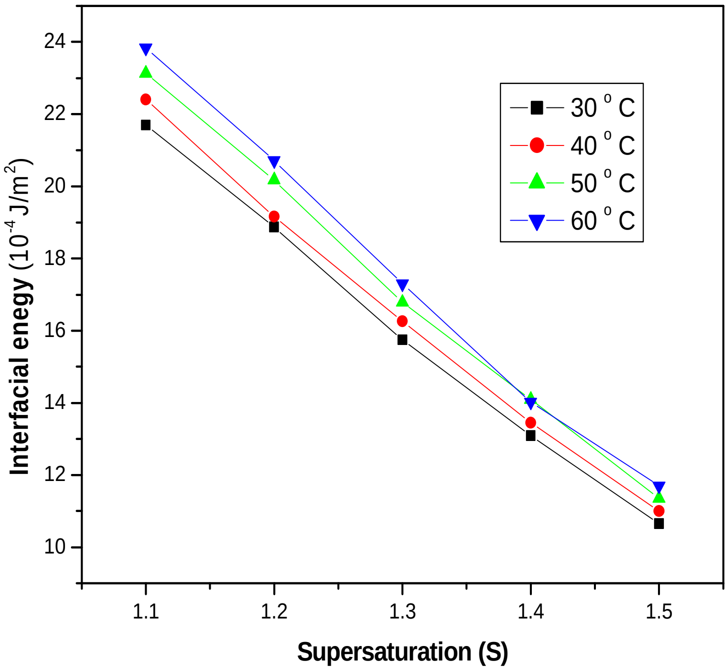

Fig. 5. Interfacial energy Vs supersaturation

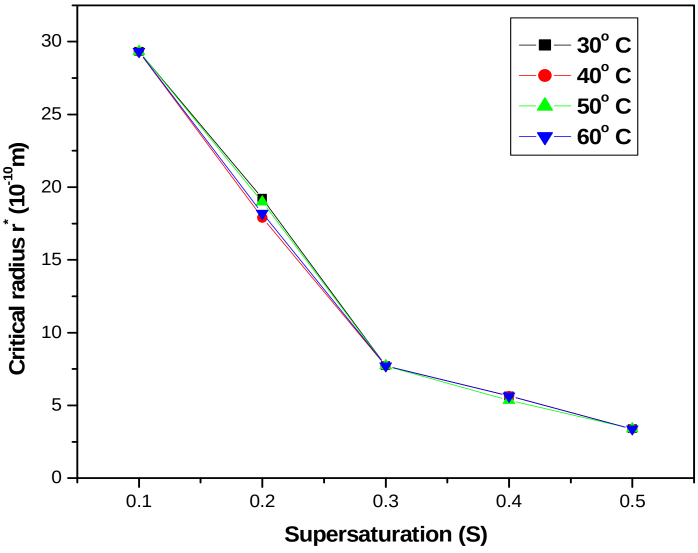

Fig. 6. Critical radius Vs supersaturation

CONCLUSION

An attempt has been made to understand the nucleation kinetics of bimetallic non linear optical crystals of zinc mercury thiyocyanate and metastable zonewidth and induction period are evaluated experimentally for crystallization. In addition, the fundamental growth parameters such as critical radius, volume free energy change, and critical free energy barrier have been estimated. The experimental results show that the critical radius of nucleus and the critical energy barrier decrease with supersaturation. On the basis of the obtained nucleation data, single crystals were successfully grown. Though the growth of bulk size ZCTC crystal has been achieved by carrying out the nucleation studies, there are challenges in further improving the crystalline perfection of the material, which will determine the chances of direct utility of the material for non linear applications.

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