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Studies on the nucleation kinetics and growth of tu-SCN ligand based NLO crystal of TMTZ

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ABSTRACT

Investigations on nucleation thermodynamical parameters are very essential for the successful growth of good quality single crystals. The metastable zone-width studies have been carried out for organometallic crystals of Tetrathiourea mercury (II) tetrathiocyanato zincate (II) (TMTZ) for different temperature range. The induction period measurements were done and the critical nucleation parameters were evaluated based on the classical theory of homogenous nucleation and the results will be discussed. The interfacial energy values for TMTZ were determined for different super saturation ratio. The growth parameters of TMTZ were optimized for the growth of large size crystals.

Keywords: Nucleation, tu-SCN ligand, Nonlinear optical crystal, Metastable zone, Interfacial energy.

INTRODUCTION

The search for new frequency conversion materials over the past decades has led to the discovery of many organic NLO materials with high nonlinear susceptibilities. However, their often inadequate transparency, poor optical quality, and lack of robustness, low laser damage threshold and inability to grow in large size have impeded the use of organic material in device applications. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganics has been found to be overwhelmingly successful in the recent past. Hence, current search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [1-3]. An important aspect of utilizing organometallic structures for nonlinear optics is their unique charge transfer transitions either from metal to ligand or ligand to metal. A reasonable number of metal-organic coordination materials with good NLO effect have been designed and synthesized using Thiourea (tu), Allylthiourea (AT) and Thiocyanate (SCN) [4-6].

Metal thiourea and thiocyanate co-ordination complexes are potential NLO materials. If the bidenate ligands of thiourea and thiocyanate are made available as organic chromophores in the metal complex, then these complexes could possess good NLO property. Hence, attempt has been made to combine thiocyanate ion and thiourea molecules with metals to improve the performance of optical second order nonlinear devices. In this connection, the crystal structure of tetrathiourea mercury (II) tetrathiocyanato zinc (II) (TMTZ) was first reported by Jiang et al [7]. Synthesis of TMTZ was reported with crystals of micron size only [8]. However, Rajarajan et al [9] have grown bulk size of TMTZ crystal by employing ethanol-water mixed solvent. This article deals with our attempt to further improve the size of the TMTZ crystals by careful optimization of growth parameters. Nucleation parameters such as metastable zone width, interfacial energy and critical radius are determined.

MATERIALS AND METHODS

Synthesis and solubility

High purity starting materials of thiourea (N_2H_4CS), potassium thiocyanate (KSCN), mercury chloride ($HgCl_2$) and zinc chloride ($ZnCl_2$) were used as purchased (E-Merck, AR grade, 99 % purity) to synthesize Tetrathiourea mercury (II) tetrathiocyanato zincate (II) (abbreviated as TMTZ).

$$4(N_2H_4CS) + 4(KSCN) + HgCl_2 + ZnCl_2 \longrightarrow Hg\,(N_2H_4CS)_4\,Zn\,(SCN)_4 \downarrow + 4KCl$$

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.

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 250 ml beaker containing 100 ml of the solvent was placed in a cryostat (accuracy ±0.01 ºC). 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 TMTZ to the solution in small amounts and subsequent stirring of the solution by a motorized stirrer were 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 TMTZ in 20 ml of solution was determined by weighing the Petri dish with salt and hence the solubility i.e., the quantity of

TMTZ salt (in gram) dissolved in 100 ml of solvent was determined. The solubility of TMTZ salt (Figure 1) was determined at five different temperatures 30, 35, 40, 45 and 50 °C in mixed solvent of ethanol-water taken in3:1 ratio.

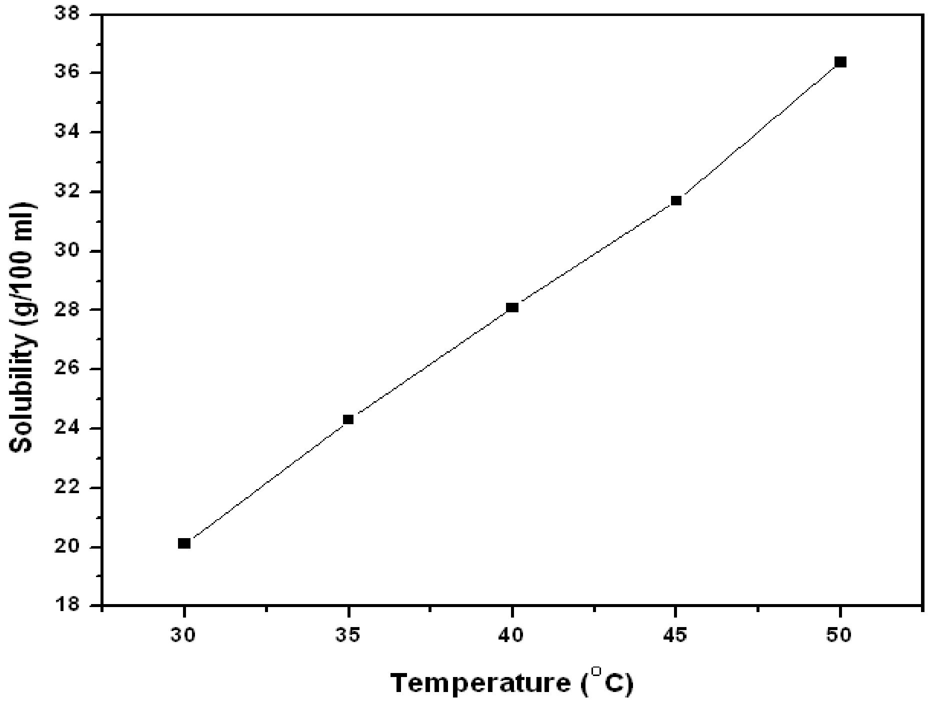

Figure 1 Solubility of TMTZ in ethanol - water (3:1)

Measurement of nucleation parameters

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.

Metastable zone width is a basic and an important parameter in terms of temperature for growing a crystal by low temperature solution growth technique. For the growth of the crystal, it is essential to determine the working limits of metastability. By all means, uncontrolled nucleation should be avoided to have a maximum yield. The growth of a crystal occurs from a solution maintained in the metastable condition. The metastable state is thermodynamically stable only with respect to small perturbations and its relaxation into a thermodynamically stable state occurs, when a nucleus of a new phase is formed.

In the present work, the metastable zone width of TMTZ was measured by means of the conventional polythermal method [10, 11]. 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. Saturated solution was prepared at different temperatures by making use of the solubility data determined already. In all the experiments, a constant volume of 100 ml of solution was used. The solution was transferred into a transparent air tight nucleation cell and then it was undersaturated by heating it to at least 5 ºC above saturated temperature and it was left at this temperature in a stirred condition. The solution was stirred continuously using a motorized 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 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. The metastable zone width of TMTZ as a function of temperature is shown in Figures 3. It is evident from the plots that in general, the metastable zone width is slightly broader in the lower temperature region whereas, in the higher temperature region the width is tending to become narrow. Hence, the choice of the temperature for carrying out the growth of the crystal must be carefully done based on the available facility and the control as well as accuracy of the constant temperature bath/cryostat.

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. The time taken between the achievement of supersaturation or supercooling and the appearance of crystal nucleus in a supersaturated solution is known as induction period.

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. Figure 4 shows the variation of induction period with supersaturation at 40 ºC for TMTZ.

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.

$$\Delta G = \Delta G_s + \Delta G_v \qquad \text{(i)}$$

For a spherical nucleus

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

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

$$r^* = -\ 2\gamma/\ \Delta G_v \qquad \text{(iii)}$$

and the interfacial energy

$$\gamma = kT/d^2\ [0.174 - 0.247 \ln S] \qquad \text{(iv)}$$

where, k is the Boltzmann’s constant (1.38×10^{-23} J/ K), d is the interionic distance.

The value of d is estimated using the expression

$d= (abc)^3$, where a,b,c are lattice parameters of the crystal.

The bulk energy change per unit volume is represented as

$$\Delta G_v = -(kT \ln S)/V \qquad \text{(v)}$$

The corresponding free energy barrier is

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

The number of molecules in the critical nucleus is given as

$$i^* = 4\pi(r^*)^3\ /3V \qquad \text{(vii)}$$

Crystal growth

To synthesize TMTZ, in the early stages X. Q Wang et al (2004) [8] have employed two different types of reaction schemes. However, Rajarajan et al (2006) [9] have used a much simpler and direct reaction scheme. The main differences between these two approaches lie in the choice of starting material for the ligands, appropriate solvent, and the number of stages involved in the reaction. The source material for SCN ligand was chosen as ammonium thiocyanate by X. Q Wang et al (2004) [8] whereas; potassium thiocyanate was used by Rajarajan et al (2006) [9]. In the present work, KSCN has been taken as the source material for SCN ligand.

Based on the solubility data, TMTZ was synthesized and the product was filtered from the mother solution and then dried. To ensure high purity, the material was purified by successive recrystallization in the mixed solvent of ethanol-water. Since TMTZ is sparingly soluble in water, it is very difficult to grow large size single crystals from water [8]. However, in the present study, good size crystal was successfully grown by using a mixed solvent of ethanol and water taken in the ratio of 3:1. To achieve single crystals of good optical quality and relatively large size, many growth attempts were made. The easiest method is to form tiny crystals by spontaneous nucleation, among them optically clear and defect free crystals with perfect shapes were chosen as seeds to carry out further growth experiments. The seeds were hung in the mother solution with nylon thread and the growth was achieved by slow solvent evaporation technique at a constant temperature of 305 K. Optically transparent and well defined single crystals of dimensions 5x5x4 mm^3 were grown in a period of 40-45 days. Figure 2 shows the photograph of as grown single crystals of TMTZ, which indicates that the grown crystals are highly transparent and water white in colour and the resulting morphology is nearly a square or a rectangle with sharp edges.

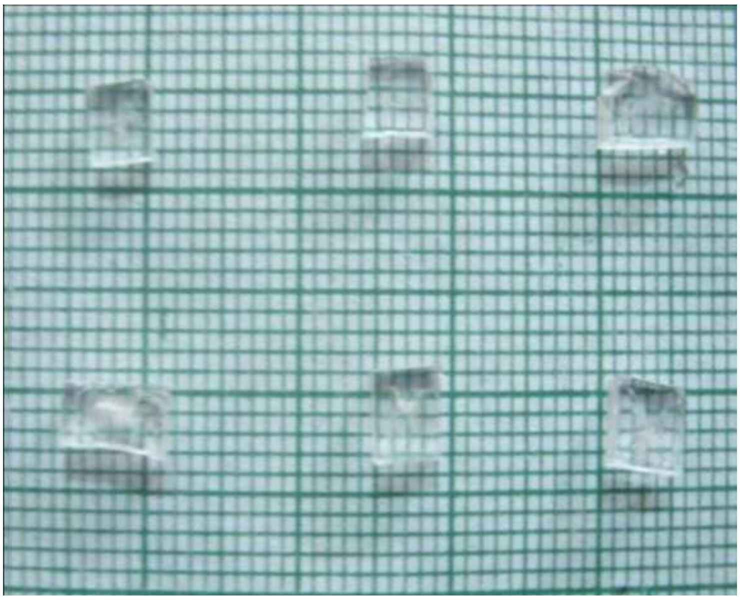

Figure 2 Photograph of TMTZ crystals grown by slow evaporation method

RESULTS AND DISCUSSION

The solubility curves for TMTZ in the mixed solvent of ethanol-water are shown in Figure 1. It is evident from the solubility plot that TMTZ has positive solubility coefficient. The value of the solubility slope is 0.80. Figure 3 represents the variation of metastable zonewidth with temperature for the salt of TMTZ. From the plots, it is obvious that the metastable zone width of these material decrease slightly with the increase in the temperature. This is the most important aspect for growing bulk size crystals. Such minute variations always favour the growth of crystals by slow cooling / slow evaporation method.

The variations of induction period with supersaturation measured at 40 ºC for TMTZ sample is presented in Figure 4. The induction period is found to decrease with increase in supersaturation, which indicates the increase in the nucleation rate. Thus the level of supersaturation plays a major role in controlling the nucleation rate. The variation of interfacial energy with supersaturation at a temperature of 40 °C is depicted in Figure 5. It is observed from the plot that the interfacial energy decrease gradually with increase in supersaturation of the solution. The measured average interfacial energy values vary in the range of 1.969-4.012x10^{-8} J/m^2 for TMTZ.

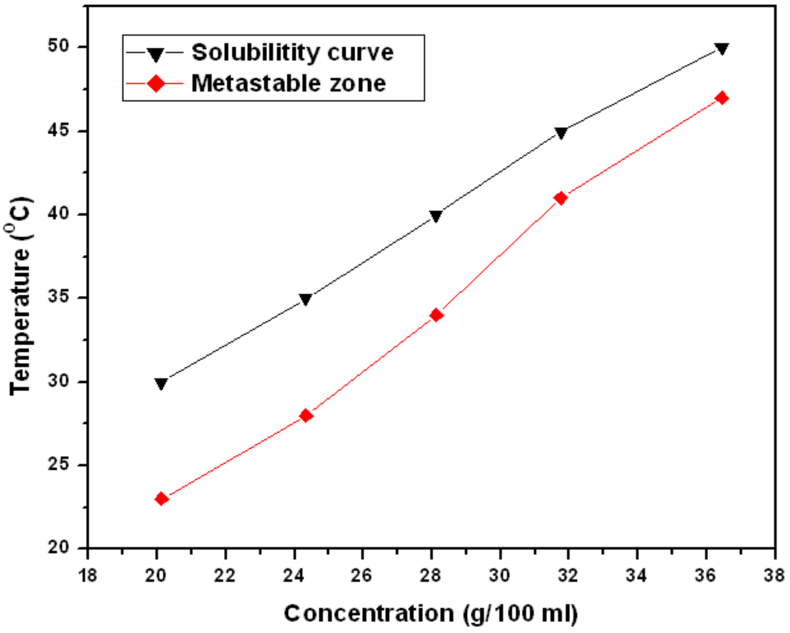

Figure 3 Metastable zonewidth of TMTZ

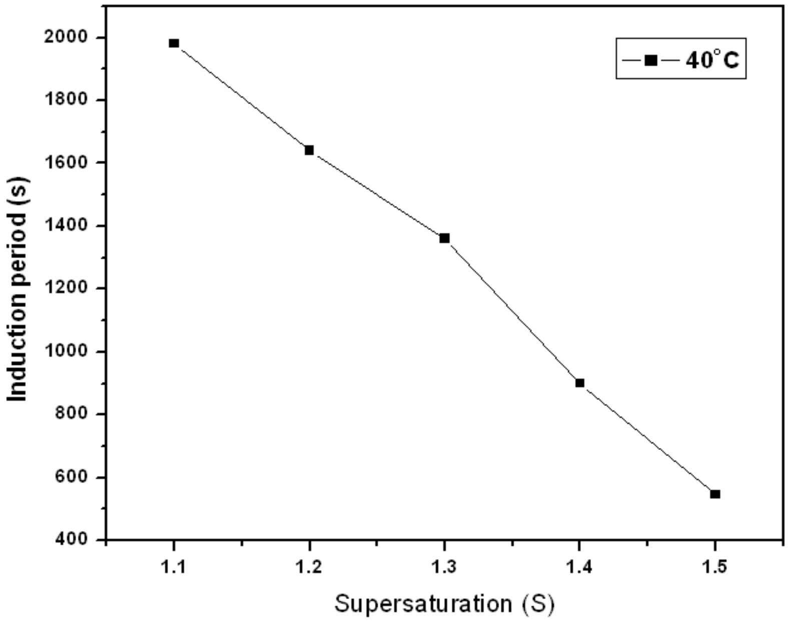

Figure 4 Induction period *vs* supersaturation for TMTZ

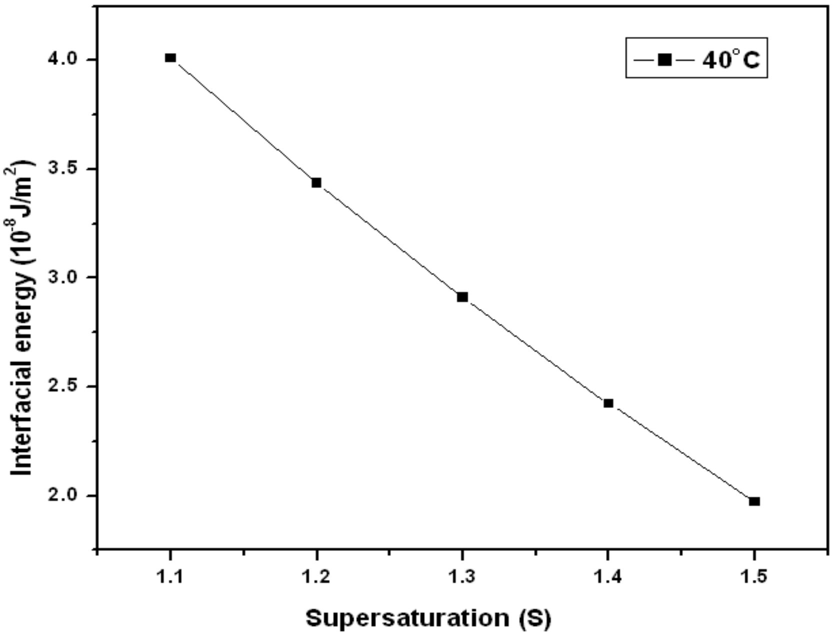

Figure 5 Interfacial energy *vs* supersaturation for TMTZ

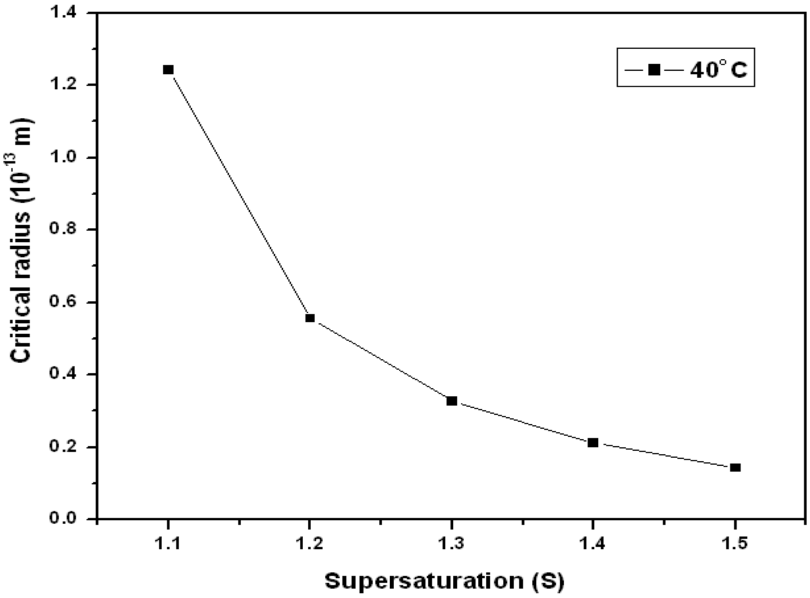

Figure 6 Critical radius *vs* supersaturation for TMTZ

The variations of critical radius with the supersaturation at a temperature of 40 ºC are given in Figure 6. It is evident from graph that as the level of supersaturation increase, the radius of critical nucleus decrease. The interfacial energy plays a vital role in the nucleation mechanism. The stability and velocity of crystal growth depends on several crucial parameters such as; temperature, the degree of supersaturation, concentration of impurities existing in the solution etc. In order to achieve this, one needs to accurately control the growth temperatures and supersaturation and maintain high purity level of the growth solution. The present study confirms that the evaluated nucleation parameters are feasible for the growth of bulk size single crystal of TMTZ.

CONCLUSION

The nucleation parameters such as; solubility, metastable zonewidth, induction period, interfacial energy and critical radius of TMTZ has been studied. Solubility studies revealed that the solubility of TMTZ increases with increase in temperature. Metastable zonewidth is found to decrease slightly with increase in temperature. The induction period is found to decrease with increase in the level of supersaturation. Thus, enhanced nucleation rate is observed under the higher level of supersaturation. Interfacial energy and critical radius are found to decrease with supersaturation. 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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