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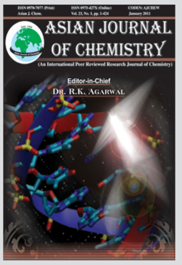

Investigation on Nucleation Kinetics of Bimetallic Non-linear Optical $CdHg(SCN)_4$ Single Crystals

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The metastable zone width and the nucleation parameters such as interfacial energy, radius of the critical nucleus and volume of free energy have been carried out for an efficient thiocyanate ligand based bimetallic non linear optical cadmium mercury thiocyanate single crystal. Cadmium mercury thiocyanate was synthesized and the solubility of the synthesized salt was determined in two different solvents at varying temperatures. The metastable zone width study was carried out for different supersaturation levels. The induction period measurements have been carried out and the critical nucleation parameters are evaluated based on the classical theory of homogeneous nucleation. Using the experimentally determined induction period values, the interfacial energy was estimated. Bulk single crystals of cadmium mercury thiocyanate have been grown in ethanol: water mixed solvent by employing slow cooling method. The grown crystals were characterized by single crystal XRD and UV-Vis spectroscopic techniques.

Key Words: Cadmium mercury thiocyanate, Nucleation, Kinetics, NLO.

INTRODUCTION

The search for new frequency conversion materials over the past five decades has led to the discovery of many organic non-linear optical (NLO) materials with high non-linear 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 single crystal organic material in practical device applications.

The approach of combining the high non-linear optical coefficients of the organic molecules with the excellent physico-chemical properties of the inorganics has been found to be overwhelmingly successful in the recent past. Hence, current research is concentrated on semiorganic materials due to their large non-linearity, high resistance to laser induced damage, low angular sensitivity, good mechanical hardness and better thermal and environmental stability[1-3].

An important aspect of utilizing organometallic structures for non-linear optics lies in their unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal[4]. 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[5,6].

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 and thiourea. Many metal-organic coordination materials with good NLO effect have been designed and synthesized using thiourea, allylthiourea and thiocyanate in the recent past[3-6]. Zhang *et al.*[7] have systematically explained the various coordination modes of thiocyanate and the formation of metal thiocyanate structures. Thiocyanate is a highly versatile ambidentate ligand with modes of coordination: two terminal modes and thirteen multidentate bridging modes.

The II (B) group metal (Zn, Cd, Hg) compounds usually have a high transparency in the UV region because of their closed d^{10} shell[6]. These complexes have all the good characteristics, such as crystallizing in a noncentrosymmetric space group $I\bar{4}$, pale colours and high thermal stability[8]. These crystals possess favourable environmental stability. Their aqueous solution can retain in stable states without decomposition and hydrolysis at atmospheric pressure and room temperature for a long time. Based on the above considerations, coordination complex material, $CdHg(SCN)_4$ (CMTC) has been investigated in this work.

The growth of CMTC crystals dates back to 1968 by Masakatsu Lizuka and Toshio Sudo by the lowering temperature method. In 1970, Bell Laboratories, USA confirmed the NLO property of the crystal[6]. Due to severe growth difficulties, poor crystal size and inadequate crystal quality, the application of CMTC was neglected for many years. In the early stages, attempts to grow this crystal from solution generally gave poor results in terms of crystal quality and reproducibility[9,10]. This has been traced to the low aqueous solubility values of the salt. The gel growth technique, on the other hand, appeared quite attractive for growing crystals of such compound on account of its unique advantages in terms of both the quality of the crystals produced and the simplicity of the process. Experiments relating to the gel growth of cadmium mercury thiocyanate (CMTC) were described by Blank[10]. CMTC crystals of 2-3 mm in size have been successfully grown in silica gels at near ambient temperature, within 7-10 days. However, in order to obtain large single crystals of CMTC with adequate size for non-linear optical application, a systematic investigation has been carried out by Chinese researchers. Duan *et al.*[11] have reported on the suitable conditions and key factors needed for achieving the growth of CMTC crystal. Jiang *et al.*[12] have reported on the growth mechanisms of CMTC by atomic force microscopy (AFM). Cadmium mercury thiocyanate crystal belongs to the tetragonal system, space group, with the unit cell parameters: a = 11.487(3) Å, c = 4.218(1)Å, D = 3.54g/cm^3, V = 556.6(2)Å^3, z = 2. The crystal has versatile good properties such as; highly efficient non-linear optical response, chemical stability below 247 °C, no cleavage and Mhos hardness of 2.9[13].

The present article deals with our attempts to improve the size of the crystals by performing the solubility and nucleation studies. 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. For the first time, a two-step procedure has been employed using gel and solution growth techniques for achieving the growth of good quality single crystals of CMTC. The grown crystal is characterized by single crystal XRD and optical absorption studies.

EXPERIMENTAL

Synthesis: High purity starting materials of ammonium thiocyanate (NH_4SCN), mercury chloride ($HgCl_2$) and cadmium chloride ($CdCl_2$) were used as purchased (E-Merck, AR grade). Cadmium mercury thiocyanate was synthesized separately in two different solvents [8 % KCl mixed with water and ethanol mixed with water (1:1)].

The following reaction is expected to take place:

$$4NH_4SCN + CdCl_2 + HgCl_2 \rightarrow CdHg(SCN)_4 + 4NH_4Cl$$

The obtained product appeared as white powder and its purity was further improved by repeated recrystallization.

Solubility studies: 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. The synthesized salt was used to measure the solubility in the solvents of KCl with water and ethanol mixed with 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. The purity of the synthesized salt was checked before performing the solubility study. Different solutions were prepared separately with two solvents *i.e.* 8 % KCl mixed with water and ethanol mixed with water (1:1). A 100 mL beaker containing 50 mL of the solvent 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 CMTC 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 CMTC in 20 mL of solution was determined by weighing the Petri dish with salt and hence the solubility *i.e.*, the quantity of CMTC salt (in gram) dissolved in a given volume of the solvent was determined. The solubility of CMTC salt in the two solvents was estimated for four different temperatures (30, 40, 50 and 60 °C) by adopting the same procedure.

Fig. 1 shows the solubility curves for CMTC. It is evident from the solubility plot that CMTC has positive solubility coefficient. The estimated slope for 8 % KCl mixed with water and ethanol mixed with water solvents are 0.73 and 0.2963, respectively. It is further noticed from Fig. 1 that the solubility is 2-3 times higher for ethanol-water mixed solvent than the KCl-water mixed solvent. On the basis of the quality of the harvested crystals, the mixed solvent of ethanol-water showed better results than the KCl-water mixed solvent. Hence, for nucleation studies followed by the growth of crystals (on the basis of the measured nucleation parameters) the ethanol-water mixed solvent was chosen as the appropriate solvent for achieving growth of bulk crystal.

Nucleation studies: Nucleation is an important phenomenon in crystal growth. In a supersaturated (or supercooled) system when a few atoms or molecules join together, a change in energy takes place in the process of formation of the clusters.

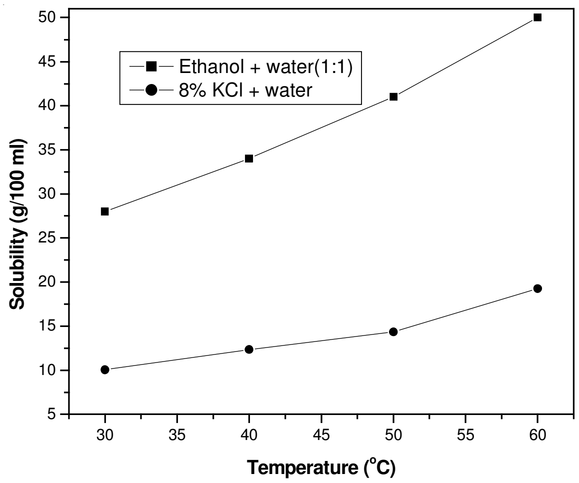

Fig. 1. Solubility curves of CMTC

The cluster consisting of such atoms or molecules is normally termed as embryo. An embryo may grow or disintegrate and disappear completely. If the embryo grows to a particular size (known as critical nucleus), then there is greater probability for the nucleus to grow. Thus the birth of the critical nucleus is an important event in crystal growth.

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 avoid 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 CMTC was measured by means of the conventional polythermal method[14,15]. The experiments were carried out in a constant temperature bath controlled to an accuracy of ± 0.01 °C and it is provided with a cryostat for cooling below room temperature. Saturated solution was prepared for different temperatures by making use of the solubility data determined already. In all the 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 under-saturated 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 1 h, 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 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. For nucleation studies, only one solvent was used, the solvent was chosen on the basics of the results obtained in each case. Best results were obtained with ethanol-water mixed solution for CMTC.

Induction period measurement: 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, 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 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.

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.

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.

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

For a spherical nucleus

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

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:

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

and the interfacial energy,

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

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

The bulk energy change per unit volume is represented as:

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

The corresponding free energy barrier is:

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

The number of molecules in the critical nucleus is given as:

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

Growth of cadmium mercury thiocyanate (CMTC) crystal: Crystal defects are highly minimized in gel grown crystals as the growth takes place due to the process of diffusion of the reactants at a slow rate without convection. Hence, a two-step procedure was employed for achieving CMTC crystal growth. In the first stage, high purity CMTC was synthesized by gel method and the synthesized product was used for further growth experiments by slow cooling techniques.

Single crystals of CMTC have been obtained from silica gel, by single diffusion method. Stock solution of sodium meta silicate was prepared by adding 48.8 g of sodium meta silicate ($Na_2SiO_3 \cdot 9H_2O$) to 100 mL of Milli-Q water. By adjusting the pH of the stock solution to 4 with AR grade glacial acetic acid of purity 99.8 %. The stock solution was mixed with a mixture of 32 mL aqueous solution of 0.2 M $HgCl_2$ and 16 mL aqueous solution of 4 M NH_4SCN and then allowed to settle in the U-tube. It took nearly 48 h for the gelation to be completed. Then the outer reagent of 16 mL aqueous solution of 3 M $CdCl_2$ was added slowly over the set gel, to initiate the growth of crystals. Due to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagents, tiny crystals started growing within 2-3 days, colourless transparent crystals of moderate size were obtained within 20 days at room temperature. Fig. 2 shows CMTC crystals grown in U-Tube.

Fig. 2. Cadmium mercury thiocyanate crystals grown in a U-tube by gel method

The crystals harvested from gel method were washed with ethanol and water and then dried for few hours. The crystals were then made into a fine powder and used to prepare the saturated solution for growth by slow cooling method. Cadmium mercury thiocyanate showed a relatively high solubility in the mixture of water and ethanol (1:1), the homogenized solution was covered with airtight sheet, which controls the evaporation of ethanol from the mixed solution and then kept in a constant temperature bath. The temperature was then reduced from 45 °C at a temperature lowering rate of 0.1-0.2 °C per day and crystals of dimension up to 10 mm × 9 mm × 3 mm were obtained in 30 days (Fig. 3).

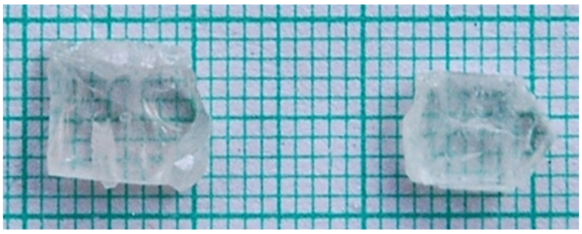

Fig. 3. Crystals of CMTC grown by slow cooling method

Single crystal X-ray diffraction analysis: The single crystal X-ray diffraction analysis was performed for the single crystal of CMTC. Nonius MACH-3/CAD4 single crystal X-ray diffractometer with MoK$_\alpha$ (λ = 0.71073 Å) radiation was used for single crystal XRD analysis. Since the crystal was transparent, the single crystalinity was studied with Leica polarizing microscope. Single crystal of suitable size (0.3 mm × 0.3 mm × 0.3 mm) was cut and mounted on the X-ray goniometer. The crystal was optically centered at the sphere of confusion using the built in tele-microscope. Twenty five reflections were collected from different zones of the reciprocal lattice using random search procedure. The reflections were indexed using method of short vectors followed by least square refinements. The unit cell parameters thus obtained were transformed to correct Bravais cell.

UV-Visible absorption study: The UV-Vis optical spectrum of the sample was recorded in the range of 200-900 nm covering the entire near ultraviolet and visible regions using the Shimadzu 2410 UV spectrophotometer. The absorption coefficient 'α' of CMTC single crystal of thickness 2 mm was determined from the optical transmittance measurements. The value of 'α' was estimated using the following expression:

$$\alpha = - (1/t) \ln (T) \quad (8)$$

where, T is the transmittance, t is the thickness of the specimen. These absorption coefficient values were used to determine optical energy gap.

RESULTS AND DISCUSSION

The plot of metastable zone width at different temperatures for cadmium mercury thiocyanate (CMTC) salt is shown in Fig. 4. From the curve, it is obvious that the metastable zone width of the salt decrease slightly with the increase in temperature, which is the most important aspect for growing bulk size crystals. Such variation always favours the growth of crystals by slow cooling method. Fig. 5 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. Thus the level of supersaturation has a major role in controlling the nucleation rate. The variation of interfacial energy with corresponding supersaturation is shown in Fig. 6. It is observed that the interfacial energy decrease 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 values of critical radii for CMTC are plotted in Fig. 7 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, nucleation parameters like number of

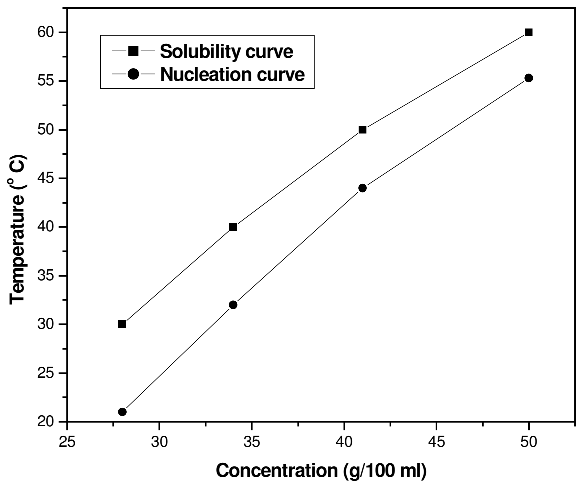

Fig. 4. Metastable zone width of CMTC

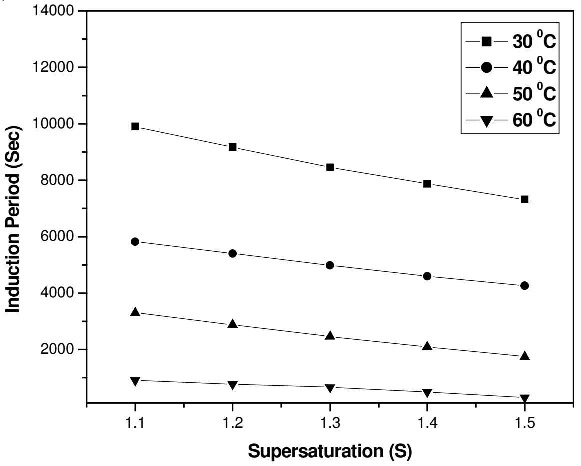

Fig. 5. Induction period *vs.* supersaturation for CMTC

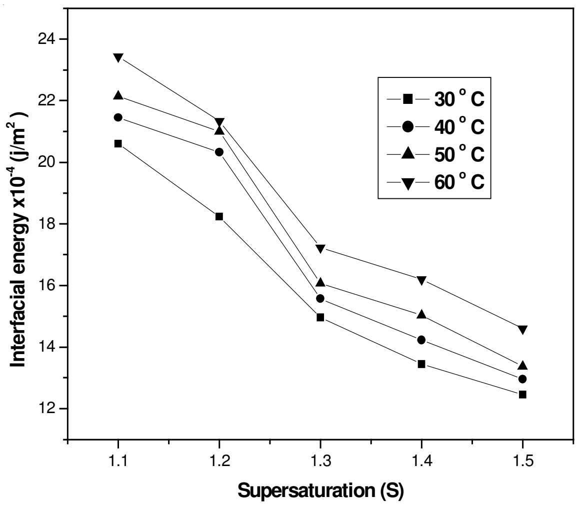

Fig. 6. Interfacial energy *vs.* supersaturation for CMTC

molecules in the critical nucleus (i*), Gibbs free energy per unit volume (ΔGv) and critical free energy barrier (ΔG*), were determined and presented in Table-1. It is evident from the table that as the level of supersaturation increases, both the radius of critical nucleus and the critical energy barrier decrease.

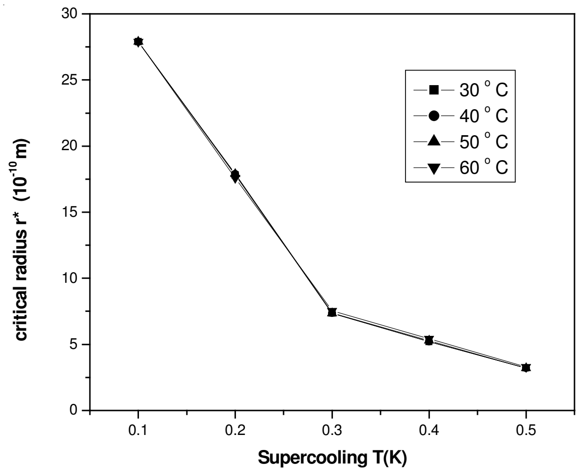

Fig. 7. Critical radius *vs.* supersaturation for CMTC

TABLE-1
NUCLEATION PARAMETERS OF CMTC

T (°C)	S	γ (10^{-4} J/m^2)	ΔG$_v$ (10^6 ergs/cm^3)	r* (10^{-10} m)	i*
30	1.1	20.6389	-1.4801	27.8885	329.01220
	1.3	14.9788	-4.0740	7.3553	6.03310
	1.4	10.1302	-6.2967	3.2176	0.50540
40	1.1	21.3200	-1.4950	27.8890	329.15400
	1.3	15.4731	-4.2089	7.3525	6.03120
	1.4	10.4646	-6.5046	3.2175	0.50540
50	1.1	22.0012	-1.5430	27.8840	329.13300
	1.3	15.9675	-4.2490	7.3532	6.03290
	1.4	10.7989	-5.4490	3.2175	0.50542
60	1.1	22.6813	-1.5430	27.8800	329.15000
	1.3	16.4618	-4.2490	7.5359	6.49390
	1.4	11.1332	-5.4490	3.2982	0.54440

The interfacial energy plays a vital role in the nucleation mechanism. The stability and velocity of crystal growth depends on several parameters such as temperature, 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 as well as maintain high purity level of the growth solutions. The present study confirms that the evaluated nucleation parameters are feasible for the growth of bulk size single crystals of CMTC.

From single crystals diffraction, it is observed that the lattice parameter values of CMTC are a = 11.445(3) Å and c = 4.202(1) Å, volume V = 550.4 Å^3. The XRD data obtained in the present study is in fair agreement with the earlier reports[10,11]. The determined unit cell parameter values and density of the crystal are presented in Table-2.

The UV optical absorption spectrum (Fig. 8) recorded for CMTC shows its wide optical transmission window (378-800 nm). Fig. 9 shows the plot of $(\alpha h\nu)^2$ *versus* hν, where α is the optical absorption coefficient and hν is the energy of the incident photon. The direct energy gap (E_{gd}) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. From this drawing, E_{gd} is found to be 2.3 eV.

Conclusion

An attempt has been made to understand the nucleation kinetics of organometallic crystal of cadmium mercury thiocyanate.

TABLE-2
XRD DATA FOR CMTC CRYSTAL

Empirical formula	$CdHg(SCN)_4$
Crystal system	Tetragonal
Space group	$I\bar{4}$
a (Å)	11.445(3)
b (Å)	11.446(3)
c (Å)	4.202(1)
α (°)	90
β (°)	90
γ (°)	90
Volume $(Å)^3$	550.4(3)
Molecules per unit cell (Z)	2
Calculated density (mg/cm^3)	3.214

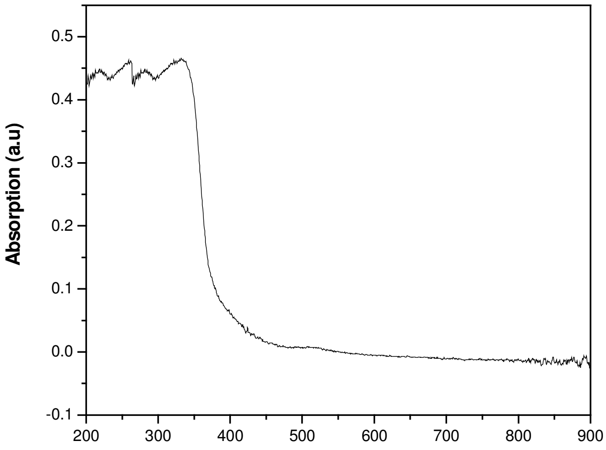

Fig. 8. UV-Vis spectrum of CMTC

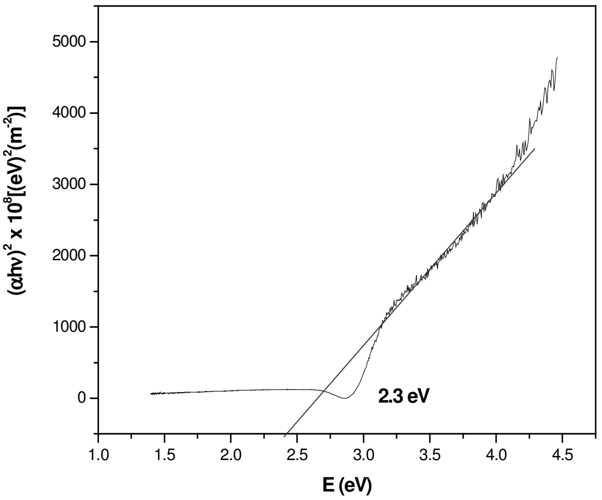

Fig. 9. Tauc's plot for CMTC

The metastable zone width and induction period were evaluated experimentally for optimizing the crystallization. In addition, the fundamental growth parameters such as critical radius, volume free energy change and critical free energy barrier were 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 of dimensions 10 mm × 9 mm × 3 mm were successfully grown in a period of 30 days. The single crystal XRD data confirms the structure and space group of the harvested crystal. Using the Tauc's plot the optical direct band gap of the sample was found to be 2.3 eV. Thus the present nucleation study is helpful for further improving the growth characteristics of cadmium mercury thiocyanate crystal.

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