

Nucleation kinetics and theoretical calculation of anorgano-metallic cadmium thiosemicarbazide bromide Hydrate (TSCCB) nonlinear optical single crystal

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Abstract - An organo-metallic compound, cadmium thiosemicarbazide bromide hydrate grown from slow evaporation solution growth technique at room temperature. The cell dimensions were obtained by single X ray diffraction study and crystal system was confirmed as Triclinic. Nucleation parameters such as radius of critical nucleus, critical free energy change and interfacial tension were evaluated for the title compound and its growth condition was optimized. The dielectric studies of the sample were carried out at different temperatures in the frequency range from 50 Hz to 5 MHz. The nonlinear optical property was tested using Kurtz Perry powder technique and SHG efficiency was measured nearly same as that of KDP.

Keywords: Crystal growth, Nucleation Kinetics, Slow evaporation solution growth technique, Thiosemicarbazide and Kurtz Perry powder technique

1. INTRODUCTION

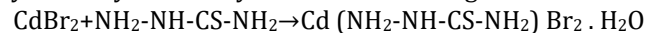
The search for new frequency conversion materials over the past decades has led to discovery of new class of semiorganic materials. Semiorganics include organic-inorganic salts and metal-organic coordination compounds. In the case of metal-organic coordination complexes, the organic ligand is usually more dominant in the NLO effect. As for the metallic part, focus is on the group (II B) metals, (Zn, Cd and Hg) as these compounds usually have a high transparency in the UV region, because of their closed d10 shell. Regarding the organic ligands, small-electron systems such as thiocyanate (SCN)⁻, urea [OC(NH₂)₂], and thiourea [SC(NH₂)₂] have been used with remarkable success [1-3].

Potential NLO materials like bis (thiourea) cadmium chloride (BTCC) [4], triallyl-thiourea cadmium chloride (ATCC) [4], thiosemicarbazide cadmium chloride Cd(NH₂NHCSNH₂)Cl₂·H₂O (TSCCC) [5,6] thiosemicarbazide

cadmium bromide Cd(NH₂NHCSNH₂)Br₂·H₂O (TSCCB) exhibits a very significant SHG efficiency that of KDP by Kurtz Perry powder technique. TSCCB has been characterized by Wang et al. [7] and is shown to display an SHG efficiency, six times that of KDP. In this paper the results of dielectric studies and nucleation parameters such as radius of critical nucleus, critical free energy change and interfacial tension were evaluated for the title compound and its growth condition was optimized and discussed in detail.

2. SYNTHESIS AND GROWTH TECHNIQUE

The cadmium thiosemicarbazide bromide has been synthesized by taking cadmium bromide and thiosemicarbazide in a 1:1 stoichiometric ratio. The calculated amount of cadmium bromide was first dissolved in deionized water. Then thiosemicarbazide was added to the solution slowly. Cadmium thiosemicarbazide bromide Hydrate crystal was synthesized according to the reaction.



The priority of the synthesized crystal was improved by recrystallization processes. Photograph of grown TSCCB crystal is shown in Figure 1: (Inset).

3. SINGLE CRYSTAL XRD ANALYSIS

The single crystal X-ray diffraction of the grown cadmium thiosemicarbazide bromide crystals were analyzed using ENRAF NONIUS CAD-4 diffractometer (graphite - monochromated, MoK α = 0.71073 Å). The title material TSCCB crystallizes in monoclinic system with space group I_a, the lattice parameter values are a=7.058 Å, b=14.21 Å, c=8.68 Å, β =100.20°, V=879 Å³ well matches with the reported one [7]. semicarbazide bromide (TSCCB) single crystal has been

4. NUCLEATION KINETICS

4.1 Classical nucleation theory (CNT)

When a crystal nucleus of TSCCB is formed in the mother solution due to supersaturation, The change in Gibbs free energy (ΔG) is written as

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

Where ΔG_s is the surface excess free energy and ΔG_v is the volume excess free energy. When the crystal nucleus is formed well within the mother phase, the type of nucleation is termed as homogeneous nucleation. For homogeneous nucleation, the shape of the nucleus is reasonably assumed to be spherical since the nucleus contains few molecules in the initial stage. For the spherical nucleus,

$$\Delta G = 4\pi r^2 \sigma_0 + \frac{4}{3}\pi r^3 \Delta G_v \quad (2)$$

Where σ_0 is the interfacial or surface energy per unit area ΔG_v is the volume excess free energy change per unit volume and it is a negative quantity. According to classical nucleation theory, the surface energy σ_0 is assumed to be same throughout nucleation for simplicity. This is called capillarity approximation. As the nucleus grows in size, ΔG increases, attains maximum and then starts decreasing. The size corresponding to maximum free energy change is called critical nucleus. At the critical stage, the condition $d(\Delta G)/dr = 0$ is applied to obtain the radius of the critical nucleus (r^*) and critical Gibbs free energy change (ΔG^*). The expressions for nucleation parameters are thus obtained as G_v

$$r^* = \frac{-2\sigma_0}{\Delta G_v} \quad (3)$$

and

$$\Delta G^* = \frac{16\pi\sigma_0^3}{3\Delta G_v^2} \quad (4)$$

The nucleation rate, according to Zeldovich and Frenkel [8] is given as

$$J = Z\beta S(i^*)C(i^*) \quad (5)$$

where Z is Zeldovich factor or non-equilibrium factor, β is the impingement flux, $S(i^*)$ is the syrface area of the critical nucleus and $C(i^*)$ is the concentration of the critical

nuclei. The nucleation rate is now written as

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

where the pre-exponential factor

$$A = \frac{Zv}{d^2} \exp\left(\frac{-\Delta G_{diff}}{kT}\right) 4\pi r^{*2} C(i) \quad (7)$$

The Zeldovich factor for a spherical nucleus was calculated using the following expression given by Turnbull and Fisher [9].

$$Z = \left(\frac{\Delta G^*}{4\pi kT}\right)^{\frac{1}{2}} \quad (8)$$

ΔG^*_{diff} is of the order $2kT$ and v is of the order 10^{13} Hz. $C(i)^0$ was calculated from unit cell volume of TSCCB.

4.2 Induction period measurement - Evaluation of surface energy σ_0

The induction periods were measured at temperature 308K for the supersaturation range 1.03 - 1.07 using constant temperature bath with an accuracy of $\pm 0.001^\circ\text{C}$. The induction period (τ) is related to the steady state nucleation rate (J) as at a particular temperature T . Since the nucleation J is defined as the number of critical nuclei per unit time in a unit volume. We know

$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (9)$$

And

$$\tau = \frac{1}{A \exp\left(\frac{-\Delta G^*}{kT}\right)} \quad (10)$$

$$\tau = B \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (11)$$

where B is a constant. Taking logarithms n both sides of equation (9)

$$\tau = \ln B + \left(\frac{\Delta G^*}{kT}\right) \quad (12)$$

Substituting the value of ΔG^* ,

$$\ln \tau = \ln B + \left(\frac{16\pi\sigma_0^3 v^2}{3k^2 T^2 (\ln S)^2}\right) \quad (13)$$

where v is the specific volume of the crystal, σ_0 is the

surface energy per unit area, S is the supersaturation ratio and B is a constant.

The surface energy per unit area was also calculated from the following expression given by Nelson et al [10].

$$\sigma_o = \frac{kT}{a_1^2} [0.173 - 0.248(X_m)] \quad (14)$$

where k is Boltzmann constant, T is the temperature, a_1 is the inter-ionoc distance and X_m is the mole fraction of the solute at temperature T .

The inter-ionoc distance a_1 was estimated from the lattice parameters of the crystal.

$$a_1 = (abc)^{\frac{1}{3}} \quad (15)$$

Using the value σ_o , the nucleation parameters ΔG_v , r^* and ΔG^* were calculated.

4.3 Modified classical nucleation theory (MCNT)

The classical nucleation theory makes use of the capillarity approximation in which the surface energy σ_o is assumed to be same throughout nucleation for mathematical simplicity. In real situation, the surface energy and other properties will change in the micro level stage. Rasmussen et al [11] developed a theory for the nucleation kinetic equation incorporating the dependence of interfacial energy on the size of the cluster. After that, Jayaraman et al [12] have obtained the following expression for the surface energy as a function of size of the nucleus using the concept of thermodynamics.

$$\sigma = \sigma_o \left[1 - \frac{\delta}{r} \right] \quad (16)$$

Where δ is the size of the monomer. When is replaced by in the Gibbs free energy change equation (2), the capillarity approximation is corrected. After this correction, the expressions for nucleation parameters were modified.

Using classical nucleation theory and modified classical nucleation theory, the nucleation parameters have been calculated for the TSCCB crystal at different supersaturations. Table - 1 presents the values of ΔG_v , r^* and ΔG^* using the above theories. It is observed that the volume free energy change per unit volume decreases with supersaturation at a fixed temperature. Consequently, the

critical radius (r^*) and critical free energy change (ΔG^*) decrease with increase of supersaturation. As a result, the nucleation rate increases considerably with increase of supersaturation at a fixed temperature. The supersaturation for which nucleation rate $J = 1$ is called critical supersaturation (S_c). The predicted critical supersaturations are found to be 1.058 and 1.56 at room temperature 308 K using the classical nucleation theories and modified classical nucleation theories.

Table 1: Nucleation parameters of TSCCB single crystal

Temperature (K)	Surface energy σ_o (mJ/m ²)	S	$-\Delta G_v$ (J/m ³) $\times 10^6$ J/m ³	r^* (nm)		ΔG^* ($\times 10^{-19}$ J)		$(\Delta G^*/KT)$	
				CNT	MCNT	CNT	MCNT	CNT	MCNT
				308	2.353	1.03	0.581	9.48	9.44
		1.04	0.771	7.15	7.11	5.90	4.59	138.97	131.17
		1.05	0.959	5.74	5.69	3.81	2.51	89.80	82.63
		1.06	1.14	4.69	4.65	2.67	2.36	62.92	55.76
		1.07	1.330	4.14	4.11	1.98	1.63	46.69	39.58

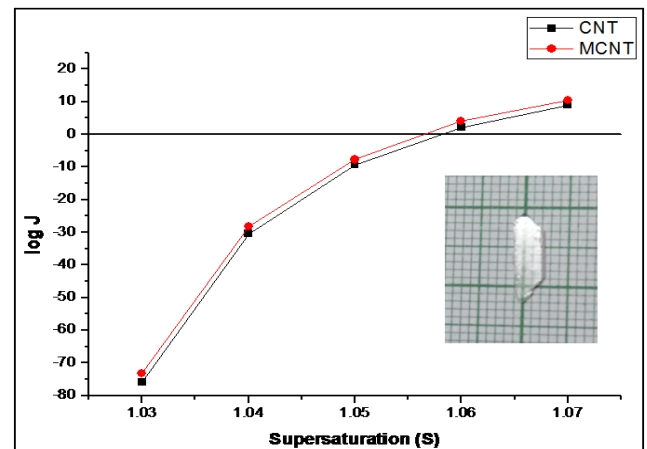


Figure - 1: Plot of nucleation rate versus supersaturation, Inset: Photograph of grown TSCCB crystal

5. DIELECTRIC STUDIES

Dielectric studies were carried out using a HIOKI LCR HITESTER in the frequency range from 50 Hz to 5 MHz. Both the dielectric constant and dielectric loss decrease with increase in frequency and shown in Fig. 2 (a). The high value of the dielectric constant at low frequency is due to the presence of electronic, ionic, dipolar and space charge polarizations [13]. In accordance with the Miller rule, the lower value of the dielectric constant at higher frequencies is a suitable parameter for the enhancement of the SHG coefficient [14]. The variation of the dielectric loss with frequency is shown in Fig. 2 (b). The characteristic of a low dielectric loss with high frequency for the crystal suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role in the fabrication of nonlinear optical devices [15].

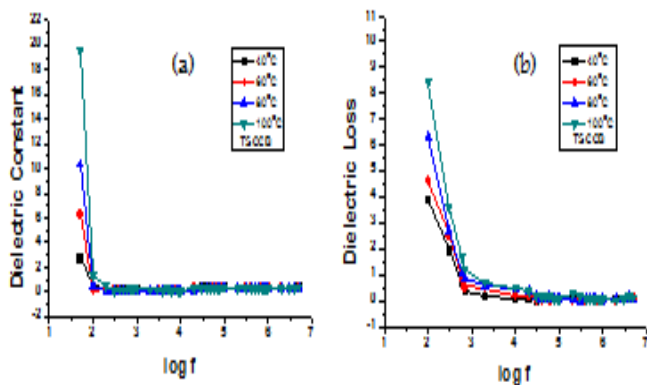


Figure - 2: (a) Dielectric constant and (b) loss vs log f

CONCLUSION

The cadmium thiosemicarbazide bromide hydrate single crystal was grown by slow evaporation technique. From XRD data, it is observed that the grown crystal belongs to monoclinic system with non-centrosymmetric space group I_a . The values of nucleation parameters critical radius (r^*), the free energy of formation of critical nucleus, the number of molecules in the nucleus (i^*) and nucleation rate (J) have been evaluated. Dielectric studies establish the dielectric behavior of the grown material.

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