

Nucleation kinetics and dielectric study on acetophenone thiosemicarbazone (APTSC) single crystals

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Abstract - Single crystals of acetophenone thiosemicarbazone (APTSC) is the potential organic nonlinear optical material, which belongs to the ketone group of compound was grown from slow cooling solution grown technique. The growth condition was optimized using nucleation kinetics. The grown crystal was subjected to XRD study to determine the cell parameters and space group. Dielectric studies on the grown crystal estimate the dielectric constant and dielectric loss with respect to frequency.

Key Words: Crystal growth, Nucleation Kinetics, Solution growth, Slow cooling technique and Dielectric properties.

1. INTRODUCTION

Semiorganic materials have been attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response time and good optical properties. When compared with the inorganic, organic materials. Recently there has been considerable interest in the co-ordination chemistry of aryl hydrazones such as semicarbazones, thiosemicarbazones and guanyl hydrazones because of their importance for drug design [1] organocatalysis and for the preparation of hetero cyclic rings [2]. Further extensive electron delocalization reported in these types of structures helps the thiosemicarbazone complexes to acquire second harmonic generation (SHG) efficiency [3,4]. Single crystals of acetophenone thiosemicarbazone (APTSC) is the potential organic nonlinear optical materials, which belongs to the ketone group of compound.

2. SYNTHESIS AND GROWTH TECHNIQUE

APTSC was synthesized by reacting analytical grade acetophenone (C₈H₈O) and thiosemicarbazide (CH₅N₃S) in 1:1 molar ratio in the distilled water. The prepared

solution was stirred well using magnetic stirrer and gently warmed until a clear solution was obtained. Filtered it and allow it to grow crystal in slow cooling solution grown technique.



Figure - 1: Photograph of grown crystal

3. SINGLE CRYSTAL XRD ANALYSIS

The title material APTSC crystallizes in the orthorhombic space group Pbc_a agreed well with reported [5]. The cell parameter values are a=15.429 Å, b=7.127 Å, c=8.340 Å.

4. NUCLEATION KINETICS

4.1 Classical nucleation theory (CNT)

When a crystal nucleus of APTSC 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

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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,

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

Where σ_o 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_o 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

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

and

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

The nucleation rate, according to Zeldovich and Frenkel [6] 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 surface 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

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

The Zeldovich factor for a spherical nucleus was calculated using the following expression given by Turnbull and Fisher [7].

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

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

3.2 Induction period measurement - Evaluation of surface energy σ_o

The induction periods were measured at temperature 308K for the supersaturation range 1.05 - 1.09 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 on both sides of equation (9)

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

Substituting the value of ΔG^* ,

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

where v is the specific volume of the crystal, σ_o 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 [8].

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

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-ionic distance a_1 was estimated from the lattice parameters of the crystal.

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

Using the value σ_0 , the nucleation parameters ΔG_v , r^* and ΔG^* were calculated.

The predicted critical supersaturations are found to be 1.065 at room temperature 308 K using the classical nucleation theories.

Table 1: Nucleation parameters of APTSC single crystal

Temperature (K)	Surface energy (σ_0) (mJ/m ²)	S	$-\Delta G_v$ (J/m ³) 10 ⁶ /m ³	r^* (nm)	ΔG^* ($\times 10^{-19}$ J)	($\Delta G^*/KT$)
308	2.353	1.05	0.522	7.55	4.71	110.70
		1.06	0.623	6.32	3.30	77.61
		1.07	0.724	5.44	2.45	57.56
		1.08	0.823	4.79	1.89	44.49
		1.09	0.922	4.27	1.51	35.48

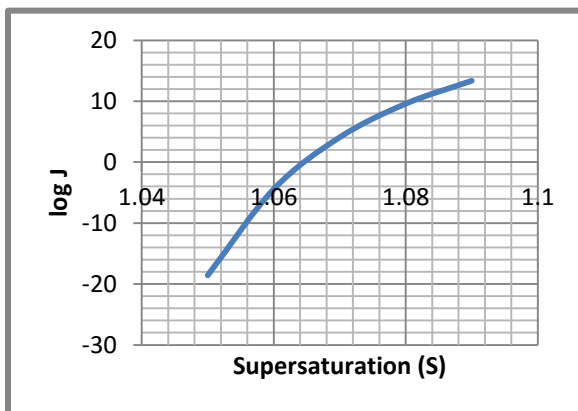


Figure - 2: Plot of nucleation rate versus supersaturation

5. DIELECTRIC STUDIES

The dielectric property of the APTSC crystals was studied at room temperature using HIOKI 3532 LCR HITESTER in the frequency region 50Hz - 5MHz. The variation of dielectric constant and loss with frequency is shown by Fig. 3 (a) and (b) respectively. The presence of electronic, ionic, dipolar and space charge polarizations in the material are the reasons for the high value of dielectric constant at low frequency. In accordance with Miller rule, the lower value of dielectric constant at higher frequency is a suitable parameter for the enhancement of SHG coefficient [9]. The crystal possesses enhanced optical

quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices because of low dielectric loss with high frequency for the samples (Fig. 3 (b) [10]).

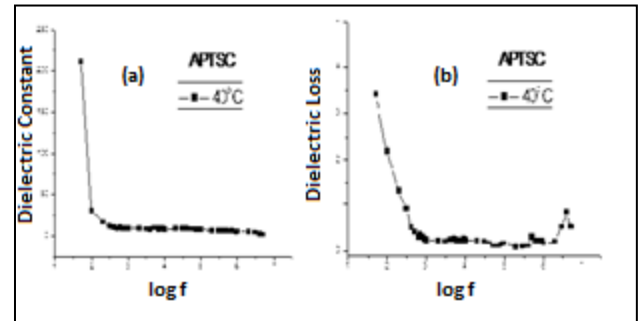


Figure - 3: (a) Dielectric constant and (b) loss vs log f

6. CONCLUSION

The APTSC single crystal was grown by slow evaporation technique. From XRD data, it is observed that the grown crystal belongs to orthorhombic system with space group Pbc_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 by classical nucleation theories. Dielectric studies on the grown crystal estimate the dielectric constant and dielectric loss with respect to frequency.

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