

A Theoretical Study of Primary Nucleation Kinetics of L-Histidine Bromide: Semi Organic Optical Single Crystal

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ABSTRACT: L-histidine bromide (LHB), semi organic non linear optical (NLO) crystals having good optical transmission in the entire visible region and hence it is a potential material for non linear frequency conversion. LHB is Biaxial crystal which crystallizes in the orthorhombic structure with space group $P2_12_12_1$ with lattice parameter value $a = 7.0530$, $b = 9.0409$, $C=15.2758$. In the present study , both classical nucleation theory and the modified classical nucleation theory have been employed to study the nucleation parameters of LHB crystal. A comparative study has been made and the result are analyzed. From the study of nucleation parameters the critical super saturation S_c is fixed in order to grow good quality single crystals.

KEYWORDS: Solubility, nucleation parameters, interfacial energy, critical nucleus, critical energy barriers, nucleation rate.

I.INTRODUCTION

Nonlinear optical (NLO)frequency conversion material have significant impact in laser technology, optical communication and optical storage technology. The search for frequency conversion materials over the past decade has led to the discovery of many organic NLO

Estimation of nucleation parameter for LHB

1. Interfacial energy:

The surface energy of the interface between a solid crystal and the surrounding saturated solution is a critical parameter which plays a major role in determining the rate of nucleation and growth of the crystal. Based on regular solution theory, Sangwal has derived an expression for the interfacial tension as

$$\sigma = \frac{kT}{8d^2} [3 - \ln(x_m)] \quad \text{-----(1)}$$

Where d is the interionic distance $(6\gamma/\pi)^{1/3}$, γ is specific volume x_m is the mole fraction of the solute, T is the absolute temperature in Kelvin and k is the Boltzmann constant. The above expression is used in the present study to calculate the value of interfacial energy from the knowledge of the existing solubility data.

2. Nucleation kinetics

The total free energy of a crystal in equilibrium with its surrounding at constant temperature and pressure would be minimum for a given volume. Since the volume free energy per unit volume is constant, then

$$\sum_1^n a_1 \gamma_1 = \text{minimum} \quad \text{-----(2)}$$

Where a_1 the area of the i th is face and γ_1 is its surface energy per unit area. The critical nucleus will not have a regular morphology of the crystal since it normally contains few tens of atoms or molecules, under such condition the spherical is assigned to the nucleus.

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(An ISO 3297: 2007 Certified Organization)

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3. Classical nucleation theory :

When the crystal nucleus form due to super saturation of the solution a certain quantity of energy is spent for the creation of new phase. The free energy change associated with the formation of the nucleus can be written as

$$\Delta G = \Delta G_s + \Delta G_v \quad \text{----- (3)}$$

Where ΔG_s the excess surface is free energy and ΔG_v is the excess volume free energy

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

Where ΔG_v is a negative quantity. The expression for ΔG_v is given for the nucleation from solution using Gibbs-Thomson equation as

$$\Delta G_v = \frac{-KT}{v} \ln S \quad \text{-----(5)}$$

Where $S = \frac{c}{c^*}$ is the super saturation ratio

The size corresponding to the maximum free energy change is called critical nucleus. At the critical state, the free energy formation obeys the condition $\frac{d(\Delta G)}{dr} = 0$ -----(6)

Hence, by setting the condition $\frac{d(\Delta G)}{dr} = 0$

The expression for radius and free energy change of the critical nucleus are obtained as

$$r^* = -\frac{2\sigma}{\Delta G_v}$$

$$\text{and } \Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} \quad \text{-----(7)}$$

Based on the classical homogeneous nucleation theory, the nucleation rate can be calculated using the relation [8]

$$J = A \exp\left[-\frac{\Delta G^*}{KT}\right] \quad \text{-----(8)}$$

J = nucleation rate rep. the no of nuclei formed per unit cell.

Where A is known as the pre-exponential factor and its value is estimated as 10^{28} .

4. Modified classical nucleation theory:

The properties of nucleus in the micro level are different from those in macro level. The interfacial energy is an important parameter to control nucleation rate and growth rate. An expression for the interfacial energy has been derived and this is incorporated in the nucleation kinetics for capillarity approximation.

Let σ & σ_0 be the interfacial energies corresponding to the crystal nucleus of micro and macro level respectively.

The interfacial energy of the nucleus of radius r is written as

$$\sigma = \sigma_0 - \left[\frac{d\sigma}{dr}\right] r \quad \text{-----(9)}$$

Equation (9) is modified as

$$\left[\frac{d\sigma}{\sigma_0 - \sigma}\right] = \frac{dr}{r} \quad \text{-----(11)}$$

Integrating the above expression we get

$$-\ln(\sigma_0 - \sigma) = \ln r + D \quad \text{-----(12)}$$

Where D- integration constant

When the first monomer is formed, it is still in the mother phase and there is no interface between mother phase and new phase. Hence the initial condition is $\sigma = 0$ where $r = \delta$, the radius of the first monomer. Applying

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(An ISO 3297: 2007 Certified Organization)

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the initial condition in eq(9), D is evaluated as $-\ln(\sigma_0\delta)$. Substituting the value of D in Eq (10) and rearranging the terms, the expression for interfacial energy is obtained as

$$\sigma = \sigma_0 \left[1 - \frac{\delta}{r}\right] \text{-----(13)}$$

The free energy associated with the formation of nucleus in the modified form can be written as

$$\Delta G = 4\pi r^2 \sigma(r) + \frac{4}{3}\pi r^3 \Delta G_v \text{-----(14)}$$

Where $\sigma = \sigma_0 \left[1 - \frac{\delta}{r}\right]$

By maximizing the equation (12), the nucleation parameters are obtained as

$$r^* = -\frac{\sigma_0}{\Delta G_v} \left[1 \pm \sqrt{1 + \frac{\delta}{\sigma_0} \Delta G_v}\right]$$

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

Substituting (r) in equal of ΔG , were

$$\Delta G^* = 4\pi r^* (\sigma_0(r^* - \delta) + \frac{1}{3}(r^{*2})\Delta G_v) \text{-----(15)}$$

The nucleation parameter of LHB crystal have been estimated using the classical and modified expression

II. RESULT AND DISCUSSION

Table presents the nucleation parameter of LHB for various super saturation using classical nucleation and modified theory at different temperatures. Interfacial energy has been calculated using the expression given by Sangwal [5].

The interfacial energy of LHB solution crystal interface to decrease with increase of temperature. It is observed that the critical size and the critical energy barrier for the formation of nucleus is considerably reduced and constantly the nucleation rate is enhanced as super saturation is increased. After applying correction to classical theory, r^* and ΔG^* are found to decrease which result in the enhancement of nucleation rate. The super saturation corresponding to $J=1$ is defined as critical super saturation (S_c). The critical super saturation is found to decrease with increase of temperature. The critical super saturation lies between 1.08 and 1.1 for the temperature range 303-323K as shown in fig. hence it is theoretically predicated that if LHB crystal is grown with the above super saturation value at particular temperature, the optical quality of the bulk crystal can be improved.

III. CONCLUSION

The nucleation kinetics of LHB has been studied. Using classical nucleation theory and the modified theory, the result obtained in the present study reveals that the nucleation parameters depends on the degree of super saturation of the system which are necessary for controlling the growth of crystal.

Critical radius, Critical free energy change and nucleation rate of L-Histidine bromide

	Classical theory				Modified classical theory			
	$S = C/C^*$	ΔG_v	r^* (nm)	$\Delta G^*/kT$	J nuclei/cm ³ /S	r^* (nm)	$\Delta G^*/kT$	J nuclei/cm ³ /S
$T = 303K$	1.08	-1.321	4.894	77.58	2.015×10^{-12}	4.843	72.80	2.287×10^{-10}

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$X_m = 0.49$	1.09	-1.479	4.371	61.87	1.335×10^{-5}	4.312	57.65	9.128×10^{-4}
	1.10	-1.636	3.952	50.58	1.071	3.901	46.77	48.62
$\sigma = 3.232$ mJ/m ²	1.11	-1.791	3.609	42.19	4.729×10^3	3.558	38.71	1.539×10^5
	1.12	-1.945	3.323	35.78	2.880×10^6	3.276	32.57	7.100×10^7
$T = 308K$	1.08	-1.343	4.791	72.77	2.487×10^{-10}	4.739	68.24	2.314×10^{-8}
$X_m = 0.53$	1.09	-1.504	4.278	58.04	6.224×10^{-4}	4.227	53.99	0.0356
	1.10	-1.663	3.868	47.44	24.73	3.816	43.79	357.132
	1.11	-1.821	3.533	39.57	6.489×10^4	3.482	36.24	1.825×10^6
	1.12	-1.977	3.253	33.56	2.660×10^7	3.202	30.48	5.736×10^7
$T = 313K$	1.08	-1.365	4.694	68.49	1.802×10^{-8}	4.644	64.14	1.401×10^{-6}
$X_m = 0.57$	1.09	-1.528	4.193	54.62	0.0190	4.142	50.73	0.9228
	1.10	-1.690	3.791	44.65	403.72	3.740	41.14	1.351×10^4
	1.11	-1.851	3.462	37.25	6.660×10^5	3.411	34.04	1.642×10^7
	1.12	-2.001	3.188	31.58	1.918×10^8	3.137	28.64	3.659×10^9
$\sigma = 3.203$ mJ/m ²								

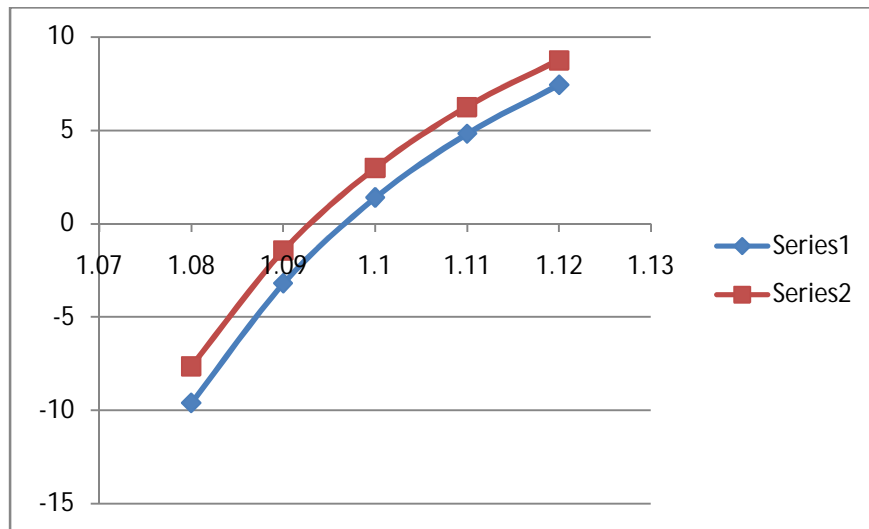
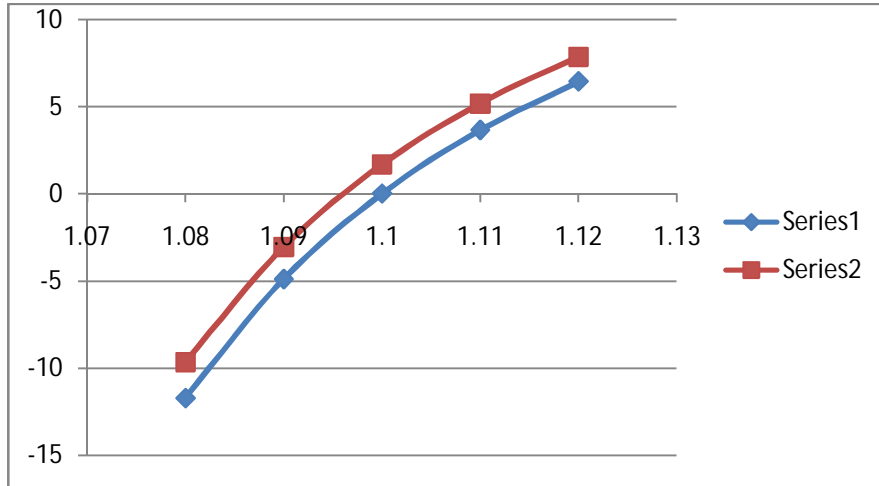
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