

Investigations on Nucleation Kinetics of a semi organic non linear optical single crystal: L-Tyrosine hydrobromide

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Abstract:

L-Tyrosine hydrobromide (LTHB), an efficient semi organic non linear optical material crystallizes in monoclinic crystal system with space group $P2_1$ and the lattice parameters are $a= 11.392 \text{ \AA}$, $b= 9.110 \text{ \AA}$, $c= 5.167 \text{ \AA}$, $\alpha=\gamma= 90^\circ$, $\beta=91.20^\circ$. In the present work the nucleation parameters of LTHB single crystal was studied based on classical nucleation theory and modified classical nucleation theory. Nucleation kinetics and fundamental growth parameters such as solubility, critical radius, critical free energy and nucleation rate were calculated to optimize the growth condition of LTHB single crystals.

Keywords: Nucleation parameter, Solubility, L-Tyrosine hydrobromide

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1. Introduction

The search for new materials with high optical nonlinearities is an important task because of their practical applications in harmonic generation, amplitude and phase modulation, laser technology, switching and other signal processing devices. Non linear optical (NLO) crystals find wide range of applications in the field of telecommunication for efficient signal processing and optical information storage devices. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [1-3]. Semi organic crystals have high non linearity, high resistance, low angular sensitivity and good mechanical hardness [4]. The complex of organic – inorganic gives semi organic material, which possess higher mechanical strength compared to organic materials. The research on the synthesis of organic and inorganic complexes increased enormously in the last few years [5, 6]. Specifically, amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals because amino acid crystals are having good optical properties [7]. L-Tyrosine is one of the essential amino acid and its hydrogen halides possess efficient NLO property. The crystal structure of L-Tyrosine hydrobromide was reported by Srinivasan (1959) [8]. Sangwal [9] has applied the regular solution theory to determine the interfacial energy from aqueous solution. The study of primary nucleation parameters of LTHB grown by low temperature solution growth technique will be more useful in order to understand the growth mechanism of crystal. The solubility of LTHB has been determined using water as a solvent with different normality, helps to study the nucleation kinetics of the grown material. In this work, an attempt has been made to apply the correction in interfacial energy. An expression for the interfacial energy as a function of size of the nucleus has been derived using the first principle [10]. The corrected interfacial energy is used to calculate the nucleation parameters of LTHB crystal and comparison is made between the classical and present modified theory. In the present study, the nucleation parameters like solubility, critical radius, critical free energy and nucleation rate of LTHB was studied based on classical nucleation theory and modified classical nucleation theory to optimize the growth condition of LTHB single crystals.

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2. Estimation of Nucleation parameter for L-Tyrosine hydrobromide (LTHB)

2.1 Interfacial energy

The surface energy of the interface between a solid crystal and the surrounding saturated solution is a crucial 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 the expression for the interfacial energy (σ) as,

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

Where d is the interionic distance $(6v/\pi)^{1/3}$, v is specific volume, x_m is the mole fraction of the solute, T is the 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.

2.2 Nucleation kinetics

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

$$\sum_i^n a_i \gamma_i = \text{minimum} \quad (2)$$

Where a_i is the area of the i^{th} face and γ_i is its surface energy per unit area. The critical nucleus will not have a regular morphology of a crystal since it normally contains few tens of atoms or molecules. Under such conditions, the spherical shape is assigned to the nucleus [11].

3. Classical Nucleation theory

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

$$\Delta G = \Delta G_s + \Delta G_v \quad (3)$$

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

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

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

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

Where, $S = \frac{C}{C^*}$ is the super saturation ratio. C is the actual concentration, C^* is the equilibrium concentration.

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

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

The expression for radius (r^*) and free energy change (ΔG^*) of the critical nucleus are obtained as

$$r^* = -\frac{2\sigma}{\Delta G_v} \quad (6)$$

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

Based on the classical homogenous nucleation theory, the nucleation rate (J) can be calculated by using the relation [12],

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

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

4. Modified classical nucleation theory

The properties of the nucleus in the micro level are different from those in the 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 and σ_0 be the interfacial energy corresponding to the crystal nucleus of micro and macro levels respectively. The interfacial energy of a nucleus corresponding to a size is written as

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

$$\left[\frac{d\sigma}{\sigma_0 - \sigma}\right] = \frac{dr}{r} \quad (10)$$

$$-\ln(\sigma_0 - \sigma) = \ln r + D$$

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

$$\sigma = \sigma_0 \left[1 - \frac{\delta}{r}\right] \quad (11)$$

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

$$\Delta G = 4\pi r^2 \sigma(r) + \frac{4}{3}\pi r^3 \Delta G_v \quad (12)$$

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

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

$$r^* = -\frac{\sigma_0}{\Delta G_v} \left[1 \pm \sqrt{1 + \frac{\delta}{\sigma_0} \Delta G_v} \right] \quad (13)$$

$$\Delta G^* = 4\pi r^* \left[\sigma_0 (r^* - \delta) + \frac{1}{3} (r^*)^2 \Delta G_v \right] \quad (14)$$

The nucleation parameters of LTHB crystal have been calculated using the classical and modified expression.

5. Results and discussion

Fig.1 shows the comparison of solubility of L-THB for various normality. It is observed that the solubility is maximum for normality 3N which can provide better conditions for the formation of a new phase. The surface energy for water solvent is the lowest when compared with other solvents (Fig.2) which means that the interface can be easily created to form the new crystalline phase. The new phase will now grow under favorable conditions in order to obtain single crystals of LTHB. Fig.3 & 4 shows that the variation of critical size and critical free energy change with super saturation for the normality 1N, 2N, 3N and 4N. It is observed that the critical nucleus is born at lower super saturation for normality 3N due to higher solubility. Fig.5 shows the plot of nucleation rate against super saturation. The level of super saturation is achieved within the optimum evaporation time for better growth conditions in the case of normality 3N. In the case of other normality, the time interval for achieving super saturation is large which may induce secondary nucleation which prohibits the growth of the primary nucleation leading to polycrystalline material. It is observed that the critical size and critical energy barrier are reduced at higher super saturation. It is found that 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 the corrections to the classical theory, r^* and ΔG^* are found to decrease which result in the enhancement of nucleation rate. Hence it is theoretically predicted that if LTHB is grown with the above super saturation value at a particular temperature, the optical quality of the bulk crystal can be improved.

6. Conclusion

Nucleation kinetics and fundamental growth parameters such as solubility, critical radius, critical free energy and nucleation rate were calculated to optimize the growth condition of LTHB single crystals. Using classical nucleation theory and modified theory, the result obtained in the present work reveal that the nucleation parameter depend on the degree of super saturation of the system which are necessary for controlling the growth of crystal.

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Table 1. Critical radius, critical free energy change and nucleation rate of L – THB in normality 1N

| | Classical theory | | | | Present theory | | |
|-------------------|------------------|-----------|-----------------|-----------------------------------|----------------|-----------------|-----------------------------------|
| | S=C/C* | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s |
| T = 313 K | 1.09 | 5.022 | 82.02 | 2.393×10^{-14} | 4.971 | 77.14 | 3.134×10^{-12} |
| $x_m = 0.34$ | 1.10 | 4.541 | 67.05 | 7.556×10^{-8} | 4.490 | 62.65 | 6.186×10^{-6} |
| $\sigma = 3.352$ | 1.11 | 4.147 | 55.92 | 0.0051 | 4.096 | 51.90 | 0.2860 |
| mJ/m ² | 1.12 | 3.819 | 47.77 | 25.26 | 3.768 | 43.72 | 1.022×10^3 |
| | 1.1 | 3.541 | 40.77 | 40.77 | 3.490 | 37.34 | 6.014×10^5 |
| | 1.14 | 3.303 | 35.47 | 3.902×10^6 | 3.252 | 32.28 | 9.550×10^7 |

Table 2. Critical radius, critical free energy change and nucleation rate of L – THB in normality 2N

| | Classical theory | | | | Present theory | | |
|-------------------|------------------|-----------|-----------------|-----------------------------------|----------------|-----------------|-----------------------------------|
| | S=C/C* | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s |
| T = 313 K | 1.08 | 5.148 | 78.90 | 5.418×10^{-13} | 5.097 | 74.32 | 5.257×10^{-11} |
| $x_m = 0.48$ | 1.09 | 4.597 | 62.92 | 4.692×10^{-6} | 4.547 | 58.84 | 2.784×10^{-4} |
| $\sigma = 3.068$ | 1.10 | 4.157 | 51.44 | 0.4546 | 4.106 | 47.75 | 18.204 |
| mJ/m ² | 1.11 | 3.796 | 42.90 | 2.315×10^3 | 3.746 | 39.54 | 6.718×10^4 |
| | 1.12 | 3.496 | 36.38 | 1.575×10^6 | 3.445 | 33.28 | 3.496×10^7 |
| | 1.13 | 3.242 | 31.28 | 2.585×10^8 | 3.191 | 28.41 | 4.571×10^9 |

Table 3. Critical radius, critical free energy change and nucleation rate of L – THB in normality 3N

| | Classical theory | | | | Present theory | | |
|-------------------|------------------|-----------|-----------------|-----------------------------------|----------------|-----------------|-----------------------------------|
| | S=C/C* | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s |
| T = 313 K | 1.08 | 4.795 | 63.76 | 2.032×10^{-6} | 4.745 | 59.79 | 1.074×10^{-4} |
| $x_m = 0.62$ | 1.09 | 4.282 | 50.86 | 0.8213 | 4.232 | 47.31 | 28.34 |
| $\sigma = 2.857$ | 1.10 | 3.872 | 41.57 | 8.792×10^3 | 3.821 | 38.37 | 2.157×10^5 |
| mJ/m ² | 1.11 | 3.536 | 34.67 | 8.707×10^6 | 3.485 | 31.75 | 1.615×10^8 |
| | 1.12 | 3.256 | 29.40 | 1.675×10^9 | 3.205 | 26.71 | 2.491×10^{10} |

Table 4. Critical radius, critical free energy change and nucleation rate of L – THB in normality 4N

| | Classical theory | | | | Present theory | | |
|-------------------|------------------|-----------|-----------------|-----------------------------------|----------------|-----------------|-----------------------------------|
| | S=C/C* | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s | r* (nm) | $\Delta G^*/kT$ | J nuclei / cm ³ / s |
| T = 313 K | 1.08 | 5.891 | 118.23 | 4.465×10^{-30} | 5.841 | 112.24 | 1.792×10^{-27} |
| $x_m = 0.28$ | 1.09 | 5.261 | 94.29 | 1.112×10^{-19} | 5.211 | 88.94 | 2.345×10^{-17} |
| $\sigma = 3.511$ | 1.10 | 4.757 | 77.09 | 3.300×10^{-12} | 4.706 | 72.25 | 4.156×10^{-10} |
| mJ/m ² | 1.11 | 4.344 | 64.30 | 1.184×10^{-6} | 4.294 | 59.88 | 9.787×10^{-5} |
| | 1.12 | 4.001 | 54.32 | 0.0208 | 3.950 | 50.46 | 1.211 |
| | 1.13 | 3.710 | 46.88 | 43.47 | 3.659 | 43.11 | 1.877×10^3 |

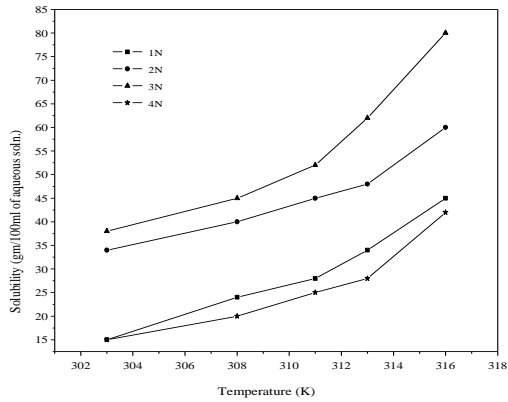


Fig.1. Solubility study of LTHB using different normality

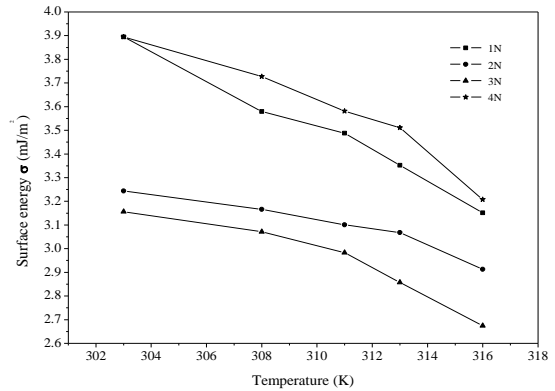


Fig.2. Surface energy vs. Temperature of LTHB crystal in different normality.

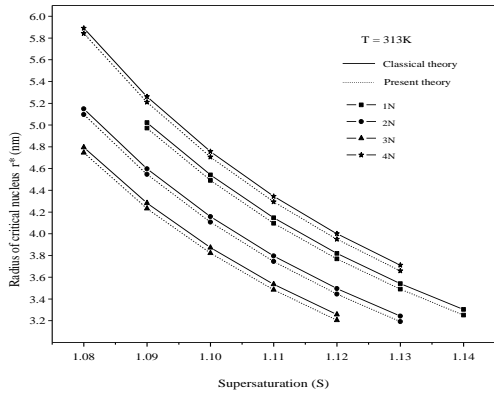


Fig.3. Radius of critical size (r^*) vs. super saturation (S) of LTHB crystal in different normality.

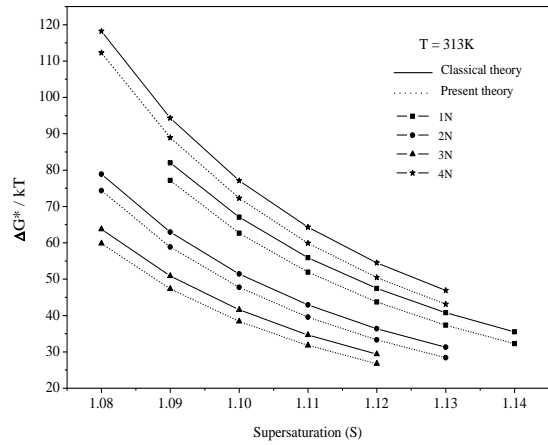


Fig.4. Critical free energy change ($\Delta G^*/kT$) vs. Supersaturation (S)

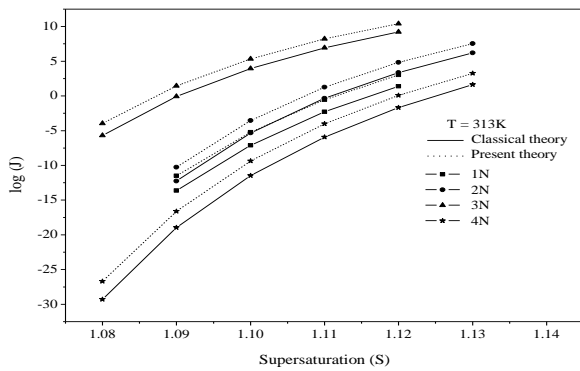


Fig.5. $\log (J)$ vs. Supersaturation (S)