

Nucleation kinetics of L-Alanine acetate

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ABSTRACT: L-Alanine acetate is one of the NLO materials which find applications in the field of optoelectronics. This material possesses attractive properties such as high damage threshold, wide transparent range, less deliquescence and high nonlinear coefficient which are the requirements for frequency doubling. This material has been grown recently by Mohan Kumar et al, using low temperature solution growth technique. It belongs to orthorhombic structure with lattice parameter $a = 5.81 \text{ \AA}$, $b = 6.07 \text{ \AA}$ & $c = 12.39 \text{ \AA}$. A nucleation parameter of this material has been computed using classical nucleation theory. From the result of the study, the proper supersaturation can be fixed in order to obtain good quality crystals. The capillarity in the classical nucleation theory is rectified by incorporating correction in the interfacial energy and the revised results of nucleation kinetics are presented.

I. INTRODUCTION

Classical nucleation theory:

When the crystal nucleus forms 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

$$\Delta G = \Delta G_s + \Delta G_v \quad \text{-----(1)}$$

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

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

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

$$\Delta G_v = \frac{-kT}{v} \ln S \quad \text{-----(3)}$$

Where $S = \frac{c}{c^*}$ is the super saturation ratio -----(4)

The size corresponding to the maximum free energy change is called critical nucleus. At the critical state, the free energy formation obeys the condition

$$\frac{d(\Delta G)}{dr} = 0 \quad \text{-----(5)}$$

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

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

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

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

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

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

II. 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

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

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 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

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

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

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

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

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

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

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

III. 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 L-Alanine acetate 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 1.10 and 1.11 for the temperature range 308-318K 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.

IV. CONCLUSION

The nucleation kinetics of L-Alanine Acetate 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-Alanine Acetate

	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
$T = 308K$	1.10	-1.65	3.88	48.52	25.2	3.82	42.12	9.8×10^2
$X_m = 0.49$	1.11	-1.83	3.56	40.21	6.52×10^4	3.44	35.21	1.6×10^7
$\sigma = 3.232$ mJ/m ²	1.12	-1.96	3.27	32.812	2.72×10^7	3.18	29.52	3.72×10^8
$T = 313K$	1.10	-1.70	3.82	45.21	405.81	3.76	42.12	1.42×10^5
$X_m = 0.53$	1.11	-1.86	3.48	38.18	6.71×10^5	3.42	33.93	1.66×10^8
$\sigma = 3.216$ mJ/m ²	1.12	-2.01	3.21	32.41	1.94×10^8	3.12	29.02	3.72×10^{10}
$T = 318K$	1.10	-1.72	3.71	41.02	1.59×10^4	3.62	37.82	4.52×10^6
$X_m = 0.57$	1.11	-1.90	3.40	33.96	1.46×10^7	3.33	31.31	3.15×10^9
$\sigma = 3.203$ mJ/m ²	1.12	-2.06	3.10	29.02	2.62×10^9	3.04	26.43	4.22×10^{11}

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