Nucleation Kinetics of L-Arginine Tetra Fluroborate Grown Using Different Solvents

Dr.Mukunthan

Department of Physics, Bharath Institute of Higher Education And Research, Chennai – 600073, India

ABSTRACT: Theoritical investigations have been made to calculate the nucleatiion thermodynamical parameters like interfacial energy,critical energy barriers and nucleation rate of L-Arginine tetrafluroborate using the solubility data and applying the classical nucleation theory . in the present study both classical nucleation theory and modified classical nucleation theory have been employed to study the nucleation parameters of L-AFB crystal using various solvents water, acetone & ethanol. A comparative study has been made with respect to the solvents and the results are analyzed the successful growth of large size crystals of good quality L-AFBby gradual temperature lowering technique using suitable solvent, requires knowledghe of fundamental nucleation parameters that influence the growth in super saturation. In other words optimum crystallization processes can only be accomplished if proper super saturation level and suitable solvent chosen during the growth technique is decided by the theoretical estimation of nucleation parameters based on the classical and present theory. Results are dissussed to understand the growth kinetics of L-AFB crystals from low temperature solution growth .

KEYWORDS:L-AFB, nucleation parameters, NLO materials, interfacial energy, solubility data, low temperature growth.

I.INTRODUCTION

Recent research has concentrated on semi organic materials due to their large nonlinearity high resistance to laser induced damage ,low angular sensitivity and good mechanical hardness .L-AFB is an organic –inorganic NLO material which not only possess the high optical non-linearity of a purely organic compound but also the favorable thermal and mechanical properties of an inorganic compound. L-AFB crystallizes in orthorhombic space group $P2_12_12_1$ with Z=4. The molecular formula of L-AFB is $C_6H_{13}N_4O_2BF_4$. The unit cell lattice parameter a=13.728,b=16.447,c=5.062,c=5.062 and $\alpha = 90^0, \beta = 90^0, \gamma = 90^0$ and cell volume 1143. Th ebulk single crystal of L-AFBis one of the potential material through out the visilble and UV spectral region. The dipolar nature exhibits peculiar physical and chemicl p0roperties in amino acids, thus making it ideal candidate for NLO applications. L-AFB is a new semi organic NLO material grown from solution by temperature lowering method. The solubility curve of L-AFB has been determined using different solvents to study the nucleation kinetics of this semiorganic material. The two kinetics steps, nucleation and crystal growth dominate the production process of crystalline material. With regards to characteristics of the material , nucleation is the first of the two kinetic steps usually has a strongly predetermined influence on the second step crystal growth .in the present study, the interfacial energy of the crystal –solution system has been calculated based on the regular solution theory. The nucleation is assumed to occur well within the mother phase and therefore the theory of homogeneous nucleation is applied in which the nuclei of the condensed phase in solution are considered to have spherical shape. The classical nucleation theory makes use of capillarity approximation in which the physical properties such as interfacial energy density chemical potential etc., are assumed to be constant throughout the process from micro to macro level.

II.METHODOLOGY

In the present work an attempt has been made to apply correction in the interfacial energy . an expression for the interfacial energy as function of size of the nucleus has been derived using the first principle. The corrected interfacial energy is used to calculate the nucleation parameters of L-AFB nucleus for various solvents and comparative study has been made a view to achieve good quality product of crystallization processes.

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

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

   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

$$\sum_{1}^{n} a_1\gamma_1 = minimum$$

   Where $a_1$the area of the ith is face and $\gamma_1$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.

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

$$\Delta G = \Delta G_s + \Delta G_v$$

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

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

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

   $\Delta G_v = \frac{-KT}{v}\ln S$

   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 $\frac{d(\Delta G)}{dr} = 0$

   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

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

and $\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2}$

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

$$J = A exp[-\frac{\Delta G^*}{KT}]$$

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

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

Equation (9) is modified as

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

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

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

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

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

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

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

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

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

Critical radius critical free energy and nucleation rate of L-AFB in solvents.
1. **Water**

	Classical theory				Present theory		
$T = 313K$ $X_m = 1.05$ $\sigma = 2.386 \; mJ/m^3$	$S = C/C^*$	r^*(nm)	$\Delta G^*/KT$	J $nuclei/Cm^2/S$	r^*	$\Delta G^*/KT$	J $nuclei/Cm^2/S$
	1.06	5.418	67.92	3.172×10^{-6}	5.367	64.18	1.341×10^{-6}
	1.07	4.666	50.38	1.321	4.615	47.16	33.13
	1.08	4.102	38.94	1.232×10^{-5}	4.051	36.10	2.087×10^{6}
	1.09	3.663	31.05	3.266×10^{-8}	3.612	28.53	4.082×10^{9}
	1.10	3.312	25.39	9.432×10^{10}	3.261	23.11	9.239×10^{11}

2. Acetone

	Classical theory				Present theory		
$T = 313K$ $X_m = 0.01$ $\sigma = 6.147 \; mJ/m^3$	$S = C/C^*$	r^*(nm)	$\Delta G^*/KT$	J $nuclei/Cm^2/S$	r^*	$\Delta G^*/KT$	J $nuclei/Cm^2/S$
	1.25	3.645	79.26	3.787×10^{-20}	3.595	72.78	2.463×10^{-10}
	1.30	3.101	57.33	0.0013	3.049	51.83	0.3091
	1.35	2.711	43.82	931.78	2.659	39.02	1.137×10^{5}
	1.40	2.418	34.86	7.258×10^{6}	2.367	30.58	5.244×10^{8}

3. Ethanol

	Classical theory				Present theory		
$T = 313K$	$S = C/C^*$	r^*(nm)	$\Delta G^*/KT$	J $nuclei/Cm^2/S$	r^*	$\Delta G^*/KT$	J $nuclei/Cm^2/S$
	1.25	3.784	88.59	3.330×10^{-17}	3.733	81.62	3.574×10^{-14}

$X_m = 0.0075$	1.30	3.218	64.09	1.468×10^{-6}	3.167	58.16	5.510×10^{-4}
$\sigma = 6.380\, mJ/m^3$	1.35	2.813	48.98	5.333	2.762	43.81	944.31
	1.40	2.509	38.97	1.194×10^5	2.458	34.35	1.202×10^8

III.CONCLUSION

The nucleation is assumed to occur well within the mother phase and therefore the theory of homogeneous nucleation is applied in which the nuclei of the condensed phase in solution are considered to have spherical shape. The classical nucleation theory makes use of capillarity approximation in which the physical properties such as interfacial energy density chemical potential etc., are assumed to be constant throughout the process from micro to macro level.

REFERENCE

1. M.H.Jiang, D. Xu, G.C.Xing , Z.S.Zhao, Synth. Cryst.3-4(1985)I.
2. W.B.Hoi, M.H. Jiang, D.R.Yuan, D. Xu,N,Zhang, M.G.Liu, X.T. Tau, Mater.Res Bull.28(1993)645.
3. S.G.Bhat, S.M.Dharmaprakash, J.Crystal Growth 81(1997)390.
4. H.O.Marey,   M.I.Rosker,   L.F.Warren,   P.H.Cunningham,   C.A.Thomas,   L.A.DeLoach, S.P.Velsko,C.A.Ebbers,J.H.Liao,M.G.Kanatzidis.Opt. Lett.20(3)(1995)252.
5. G.R.Meredith,in:D.J. Williams   Ed,Nonlinear optical properties of organic and polymeric materials,ACS Symposium Series 233,Wasington D.C.,1982,P.27.
6. D.Jayaraman, C.subramanian, P.Ramaswamy, J.Mater.Sci.Lett.8(1989)1399.