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Investigation on Nucleation Kinetics and Photoluminescence Characterization of a Nonlinear Optical L-arginine Maleate dihydrate Single Crystal

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Abstract: Nucleation parameters such as surface energy per unit area, energy per unit volume, radius of critical nucleus, critical free energy barrier, number of molecules in the critical nucleus and nucleation rate have been evaluated for L-arginine maleate dihydrate single crystals. The theoretical predictions of optimized growth conditions were confirmed by growing the crystal using solution growth technique and can grow bulk crystal with good optical quality with less poor. Unit cell parameters are confirmed by single crystal X-ray diffraction studies. Photoluminescence study is carried for the grown crystal and the result reveals that violet fluorescence emission occurs at 395 nm. Second harmonic generation efficiency of the crystal was determined by Kurtz and Perry powder technique.
Keywords: Solubility, Nucleation kinetics, Photoluminescence, Nonlinear optical crystal.

1. Introduction

Amino acid family based nonlinear optical crystals are considerable interest towards the researchers due to its peculiar features such as weak Vander Waals and hydrogen bonds, wide transparency range in the visible region and zwitterionic nature of the molecules. These materials are finding a number of applications like frequency conversion, optical switching, light modulation and optical memory storage [1]. Belongs to that L-arginine maleate dihydrate single crystal is recently discovered organic nonlinear optical material and characterized. Thus LAMD single crystal was found to crystallizes in triclinic system and non-centrosymmetric space group P_1. Cell parameters were found to be a = 5.27 Å, b = 8.04 Å and c = 9.79 Å; α = 106.15º, β = 97.26º and γ = 101.64º with unit cell volume V= 383.42 Å^3. Recently, T. Baraniraj et al reported that second harmonic generation efficiency of the crystal is 1.5 times that of standard material KDP. Even though several reports are available for the growth and characterization of LAMD [2-6], there is no report is available on the nucleation kinetics at various temperatures of the title compound. However, the grown crystals have some defects and transparency was poor. In order to grow crystals with optical qualities for NLO applications, a systematic investigation is necessary. Hence, in the present investigation the nucleation parameters at various temperatures of the LAMD were investigated. Moreover, optical materials are required photoluminescence study, is also carried out in this paper.

2. Solubility data

The solubility data of the material are very essential for analysing the growth conditions.The solubility data of LAMD were obtained using gravimetric analysis at temperaures 303, 308, 313, 318 K. The solubility

curve of LAMD is shown in Fig. 1. It is found that the solubility of the material increases linearly with increase of temperature. The solubility data provide information to prepare saturated solutions at different temperatures and to estimate the interfacial energy of the solution-crystal interface.

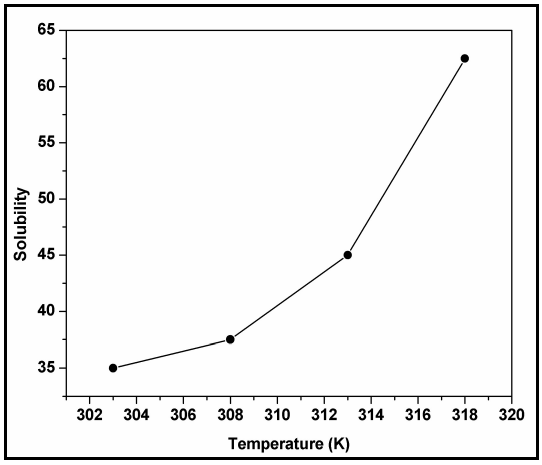

Fig. 1 Solubility curve of LAMD crystal

3. Nucleation kinetics

In the present investigation, LAMD was grown using slow evaporation of the solution. During the crystal growth from the mother solution, a nucleus is formed in the initial stage. The change in Gibbs free energy (ΔG) associated with the formation of the nucleus is written as

$$\Delta G = \Delta Gs + \Delta G_V \quad (1)$$

where ΔGs 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 homogeneous nucleation, the nucleus is assumed to the spherical. For the spherical nucleus,

$$\Delta G = 4\pi r^2 \sigma_o \pm 4 \pi r^3 \Delta Gv \quad (2)$$

where σ_o is the interfacial or surface energy per unit area and ΔGv is the volume free energy change per unit volume and it is a negative quantity. According to classical nucleation theory (CNT) the surface energy σ_o is assumed to be same throughout nucleation. 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 conditioned (ΔG)/dr = 0 is applied to obtain the radius of the critical nucleus (r^*) and critical Gibbs free energy change (ΔG^*). The expression for nucleation parameters are thus obtained as,

$$r^* = - 2 \sigma_o / \Delta Gv \quad (3)$$

and $$\Delta G^* = 16\pi \sigma_o^3 / 3 \Delta Gv^2 \quad (4)$$

The value of σ_o is estimated from the following expression [7] given by-

$$\sigma_o = (kT/a^2) [0.173 – 0.248\ln (x_m)] \quad (5)$$

where k is the Boltzmann constant , T is the temperature, a is the inter-ionic distance and x_m is the mole fraction of the solute at equilibrium. The volume excess free energy is calculated using the expression

$$\Delta Gv = - (kT/v) \ln S \quad (6)$$

where v is the specific volume and S (= C/C^*) is the supersaturation. Here, C is the actual concentration of the solution and C^* is the equilibrium concentration. The number of critical nuclei formed per unit time per unit volume is known as nucleation rate which is given by the Arrhenius reaction velocity equation. The nucleation rate (J) is given by Becker and Doring [8] as,

$$J = A \exp\{ - \Delta G^*/kT\} \quad (7)$$

where A is the pre-exponential factor and its value is 10^{30} for nucleation from solution [9]. Hence the unit of J is number of critical nuclei per cm^3 per sec. Since $\Delta G^*/kT$ is a dimensionless quantity, the unit of A is same as that of J.

The classical nucleation theory makes use of the capillarity approximation in which the surface energy σ_o is assumed to be same throughout nucleation for mathematical simplicity. In real situation, the surface energy and other properties will change in the micro level stage. Jayaraman et al [10] have derived an expression for the surface energy as a function of size of the nucleus and the expression is written as

$$\sigma = \sigma_o [\ 1- \delta/r] \qquad (8)$$

where δ is the size of the monomer.

When σ_o is replaced by σ in the Gibbs free energy change equation (2), the capillarity approximation is corrected. After this correction, the expression for nucleation parameters are modified as

$$r^* = (\sigma_{o/} \Delta Gv) [\ 1+(1- \Delta Gv/ \sigma_o)^{1/2}] \qquad (9)$$

and $$\Delta G^* = 4\pi r^* [\sigma_o (r^* - \delta)- (1/3) r^{*2} \Delta Gv] \qquad (10)$$

Using the classical nucleation theory (CNT) and modified classical nucleation theory (MCNT), the nucleation parameters have been calculated for LAMD at different supersaturation and temperatures. Table 1 presents the nucleation parameters of LAMD calculated using the equations (3), (4), (5), (7), (8), (9) and (10) with $A = 10^{30}$ for CNT and MCNT. The surface energy σ_o is found to decrease with increase of temperature. It is observed that the volume free energy change per unit volume increases with supersaturation at a fixed temperature. Consequently, the critical radius (r^*) and critical free energy change (ΔG^*) decrease with increase of supersaturation. As a result, the nucleation rate increases considerably with increase of supersaturation at a fixed temperature. Hence, it is a sensitive factor which controls the growth of the crystal. The supersaturation for which nucleation rate J=1 is called critical supersaturation (S_c). Figs.2 and 3 show the plots of supersaturation against nucleation rate at different temperatures 303, 308, 313 and 318 K using CNT and MCNT. The predicted critical supersaturations are found to be 1.73, 1.72, 1.67 and 1.58 and 1.69, 1.68, 1.63 and 1.54 at different temperatures 303, 308, 313 and 318 K using CNT and MCNT respectively. Fig.4 shows the plot of crititical supersaturation against temperature using CNT and MCNT.

4. Experimental

Analytical grade of L-arginine and maleic acid were dissolved in double distilled water and stirred continuously using magnetic stirrer to get a saturated solution. Then the prepared solution was filtered and allowed to evaporate by slow evaporation at room temperature. After the period of 30 days, good quality of single crystals harvested.

Single crystal XRD studies were carried out using Bruker Kappa APE XII single X-ray diffractometer to confirm the grown crystal. Fluorescence spectra were recorded with the help of Perkin Elmer LS45UV fluorescence spectrophotometer. Nonlinear properties of LAMD crystals was confirmed by Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10).

5. Results and Discussion

5.1 Single crystal XRD

Single crystal XRD data of the grown crystal is found out by using Bruker Kappa APE XII single X-ray diffractometer with MoK_α (λ = 0.71073Å). In order to obtain the crystal data of LAMD single crystals were collected by subjecting the samples to single crystal XRD. It is observed from the single crystal XRD data that LAMD crystallize into triclinic system and belong to the space group of P_1. The lattice parameters are: a = 5.27 Å, b = 8.04 Å and c = 9.79 Å; α = 106.15º, β = 97.26º and γ = 101.64º with unit cell volume V = 383.42 $Å^3$. These values agreed well with the reported values [11].

Table 1 Nucleation parameters of LAMD

Temperature (K)	Surface energy(σ_o) mJ/m^2	S	$\Delta Gv \times 10^7$ mJ/m^3	r^* (Å)		$\Delta G^* \times 10^{-12}$mJ		$\Delta G^*/kT$	
				CNT	MCNT	CNT	MCNT	CNT	MCNT
303 K	8.7	1.58	5	34.9	34.4	4.43	4.06	105.9	97.1
		1.6	5.1	33.9	33.4	4.19	3.83	100.3	91.7
		1.62	5.3	33.1	32.6	3.98	3.63	95.2	86.8
		1.64	5.4	32.3	31.7	3.78	3.44	90.6	82.4
		1.66	5.5	31.5	31.0	3.60	3.27	86.3	78.3
		1.68	5.7	30.8	30.2	3.44	3.11	82.3	74.5
		1.7	5.8	30.1	29.6	3.29	2.97	78.7	71.1
		1.72	5.9	29.4	28.9	3.15	2.84	75.3	67.9
		1.74	6	28.8	28.3	3.02	2.71	72.2	64.9
		1.76	6.2	28.2	27.7	2.90	2.60	69.3	62.2
		1.78	6.3	27.7	27.2	2.78	2.49	66.6	59.6
308 K	8.719	1.56	4.9	35.4	34.9	4.56	4.16	107.4	97.9
		1.58	5.1	34.4	33.9	4.31	3.92	101.5	92.3
		1.6	5.2	33.5	33	4.08	3.70	96.1	87.2
		1.62	5.3	32.6	32.1	3.88	3.51	91.3	82.5
		1.64	5.5	31.8	31.3	3.69	3.33	86.8	78.3
		1.66	5.6	31	30.5	3.51	3.16	82.7	74.4
		1.68	5.8	30.3	29.8	3.35	3.01	78.9	70.8
		1.7	5.9	29.6	29.1	3.20	2.87	75.4	67.5
		1.72	6	29	28.5	3.07	2.74	72.2	64.5
		1.74	6.1	28.4	27.9	2.94	2.62	69.2	61.7
		1.76	6.3	27.8	27.3	2.82	2.51	66.4	59.1
313 K	8.512	1.52	4.7	36.1	35.6	4.64	4.26	107.4	98.7
		1.54	4.9	35	34.5	4.36	4.00	101.0	92.6
		1.56	5	34	33.5	4.11	3.76	95.2	87.1
		1.58	5.2	33	32.5	3.88	3.54	90.0	82.0
		1.6	5.3	32.2	31.6	3.68	3.35	85.2	77.5
		1.62	5.4	31.3	30.8	3.49	3.17	80.9	73.4
		1.64	5.6	30.5	30	3.32	3.00	76.9	69.6
		1.66	5.7	29.8	29.3	3.16	2.85	73.3	66.1
		1.68	5.8	29.1	28.6	3.02	2.72	69.9	62.9
		1.7	6	28.5	28	2.89	2.59	66.9	60.0
		1.72	6.1	27.9	27.4	2.76	2.47	64.0	57.3
318 K	8.012	1.46	4.3	37	36.5	4.59	4.23	104.6	96.3
		1.48	4.5	35.7	35.2	4.27	3.92	97.4	89.5
		1.5	4.6	34.5	34	3.99	3.66	91.1	83.4
		1.52	4.8	33.4	32.9	3.75	3.42	85.4	78.0
		1.54	4.9	32.4	31.9	3.52	3.20	80.3	73.1
		1.56	5.1	31.5	31	3.32	3.01	75.7	68.7
		1.58	5.2	30.6	30.1	3.14	2.84	71.5	64.7
		1.6	5.4	29.8	29.3	2.97	2.68	67.8	61.1
		1.62	5.5	29	28.5	2.82	2.54	64.3	57.8

5.2 Photoluminescence studies

Photoluminescence study is a non-destructive tool to carry out the luminescence behaviour of the grown optical material. The emission spectrum of LAMD crystal was recorded in the range from 300 to 550 nm is shown in Fig. 5, after exciting the sample at 325 nm. From the emission spectrum, a broad peak was observed at 395 nm. The result indicates that the LAMD crystal has violet fluorescence emission. The maximum intensity peak at 395 nm is ascribed to n-π^* transition of carbonyl group. The presence of carbonyl group is thus confirmed.

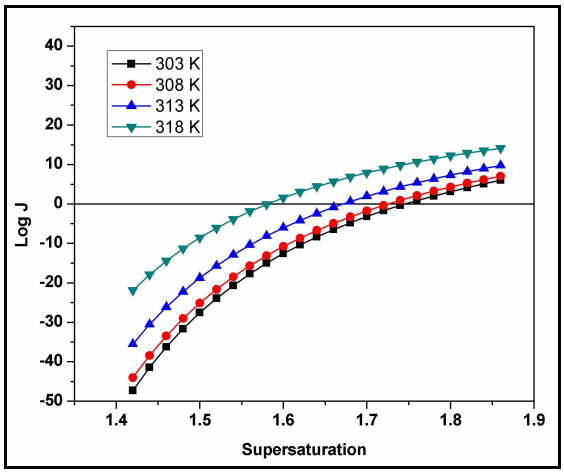

Fig. 2 Plot of nucleation rate vs supersaturation (CNT)

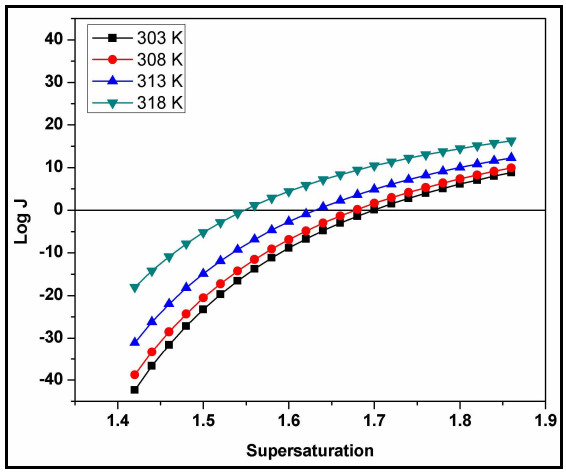

Fig. 3 Plot of nucleation rate vs supersaturation (MCNT

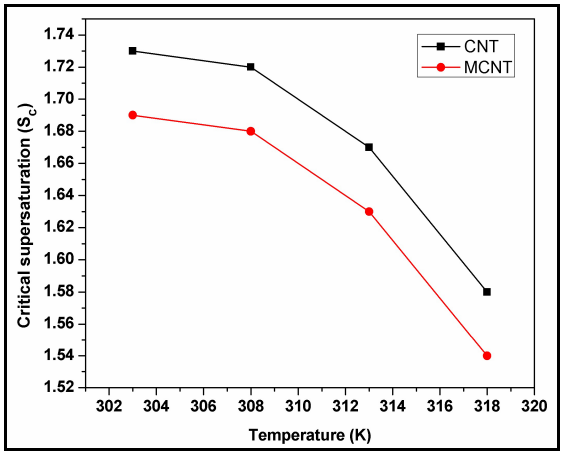

Fig. 4 Plot of critical supersaturation vs temperature

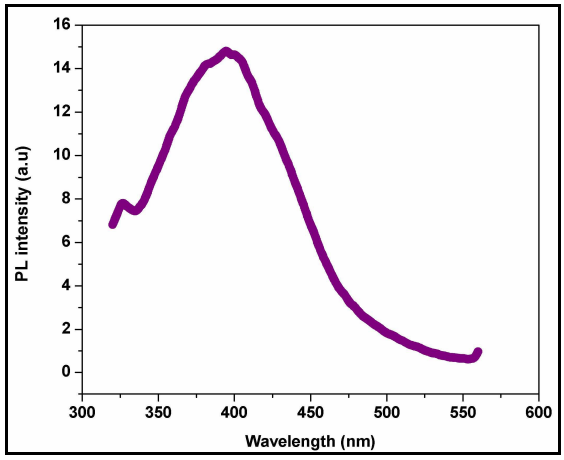

Fig. 5 Fluorescence emission spectrum of LAMD

5.3 NLO test

Nonlinear optical test was carried out for the grown crystal of LAMD and reference material KDP. The signal amplitude of both in milli-volts indicates the second harmonic generation efficiency and it was found to be 1.5 times that of KDP. This result agrees well with earlier report [6]. Therefore, NLO test reveals that the grown crystal LAMD is a potential nonlinear optical crystal and SHG efficiency is higher than that of standard crystal KDP.

6. Conclusion

In the present work, the solubility curve of LAMD crystal was determined experimentally. It is found that solubility increases with increase of temperature. The critical supersaturation were predicted in the solution growth technique at different temperatures 303, 308, 313 and 318 K using nucleation theories to optimize the growth conditions. The theoretical prediction was confirmed by growing the crystal at room temperature. Single crystal XRD studies confirm that the grown crystal belongs to triclinic system and space group P_1.The fluorescence studies indicate that L-arginine maleate dihydrate single crystals have a violet fluorescence emission. Kurtz and Perry powder technique confirms the second harmonic generation efficiency of the grown crystal.

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