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Nucleation studies of ZTC doped with L-arginine in supersaturated aqueous solutions

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ABSTRACT

The metastable zonewidth studies are carried out for various temperatures for supersaturated aqueous solutions of zinc thiourea chloride added with 1 mole % of L-arginine. The metastable zonewidth is increased with the addition of L-arginine. The induction period is experimentally determined and various critical nucleation parameters such as radius of critical nucleus, number of molecules in the critical nucleus, critical free energy of nucleus and interfacial tension are also calculated based on the classical theory for homogeneous crystal nucleation. The induction period is increased with the increase of L-arginine addition. The critical nucleation parameters vary with increase in doping concentration. It is also observed that the nucleation rate increases with the increase of supersaturation. The second harmonic generation (SHG) efficiency measurements are carried out with different doping concentration of L-arginine reveal that nonlinear optical (NLO) property is enhanced by L-arginine dopant.

1. Introduction

Nonlinear optical materials posses wide range of applications in the field of telecommunication and optical information storage devices. The search for new and efficient NLO materials has resulted in the development of a new class of materials called semiorganics. These materials have large nonlinearity, high resistance, too large induced damage, low angular sensitivity and good mechanical hardness [1–3]. Recently metal complexes of thiourea have been explored. Some of the potential thiourea complexes are zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), cadmium thiourea chloride (BTCC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA) and cadmium thiourea acetate (BTCA). These crystals have better nonlinearity optical property than KDP [4–8]. ZTC is a potential semiorganic NLO material and crystallizes in the noncentrosymmetric orthorhombic space group Pnma with lattice parameters $a = 13.012$ Å, $b = 12.768$ Å, $c = 5.890$ Å and $V = 978.64$ Å^3 [9]. Growth of ZTC single crystals using slow cooling technique has already been attempted [10]. Influence of solution pH on the growth and characteristics of ZTC has also been reported by Rajasekar et al. [11]. Hitherto no attempt has been made to study the nucleation kinetics of ZTC doped with L-arginine in supersaturated aqueous solutions. In the present study, the nucleation parameters of pure ZTC crystals and the effect of amino acid L-arginine as an added additive (additive concentration is 1–5 mole%) on the nucleation of these crystals are investigated.

In this report, in order to optimize the growth parameters for the growth of bulk crystals with improved growth rates, the solubility, metastable zonewidth and induction periods have been determined experimentally. Metastable zonewidth is an essential parameter for the growth of good crystals from solution, since it is the direct measurement of the stability of the solution in its supersaturated region [12]. The control of crystallization habit is clearly linked to the additives added to the system and the internal parameters like pH. Various critical nucleation parameters of pure and L-arginine doped ZTC crystals for the effect of supersaturation and on different doping concentration are calculated.

2. Experimental

2.1. Synthesis and solubility of ZTC

Zinc thiourea chloride (ZTC) was synthesized using analar grade zinc chloride and thiourea in a stoichiometric ratio 1:2.

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The required quantity of zinc chloride and thiourea were estimated from the following reaction:

$$ZnCl_2 + 2[CS(NH_2)_2] \rightarrow Zn[CS(NH_2)_2]_2Cl_2$$

The required quantities of the component salts were very well dissolved in double distilled water and thoroughly mixed using a magnetic stirrer and the mixture was heated at 50 °C till a white crystalline salt of ZTC was obtained. The synthesized salt was purified by repeated recrystallization process.

The solubility of ZTC at a pH value of 3.4 has been determined for four different temperatures, i.e., 30, 35, 40 and 45 °C. The solubility was determined by dissolving the solute in water in air tight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analysed gravimetrically [13]. The solubility of ZTC as a function of temperature is shown in Fig. 1.

2.2. Metastable zonewidth studies

Two hundred milliliters of ZTC solution saturated at 30 °C was prepared in accordance with the solubility diagram. Then the solution was taken in two beakers each containing 100 ml. In one beaker, 1 mole% of L-arginine was added. The solutions were filtered using a whatman filter paper. These beakers were loaded in a constant temperature bath and controlled to an accuracy of 0.01 °C provided with a cryostat for cooling below room temperature. The solution was preheated to 5 °C above the saturation temperature for 1 h before cooling. It was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature throughout the entire volume of the solution. Metastable zone width of pure and L-arginine doped ZTC was measured by polythermal method [14]. In this method, the equilibrium saturated solution was cooled at the rate of $4\,^{\circ}\mathrm{C\,h^{-1}}$ from the overheated temperature until the first visible crystal nucleus was observed. Since the time taken for the formation of first visible nucleus after attainment of critical nucleus is very small, the first nucleus observed may be taken as critical nucleus. The direct vision method is adopted for studying the nucleation temperature. The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zone width of the system. The experiment was repeated for solutions saturated at the temperatures 30, 35, 40 and 45 °C. The metastable zonewidth for different saturation temperatures for pure and L-arginine added ZTC solutions are shown in Fig. 2. There was no remarkable change in pH with the addition of L-arginine (1–5 mole%).

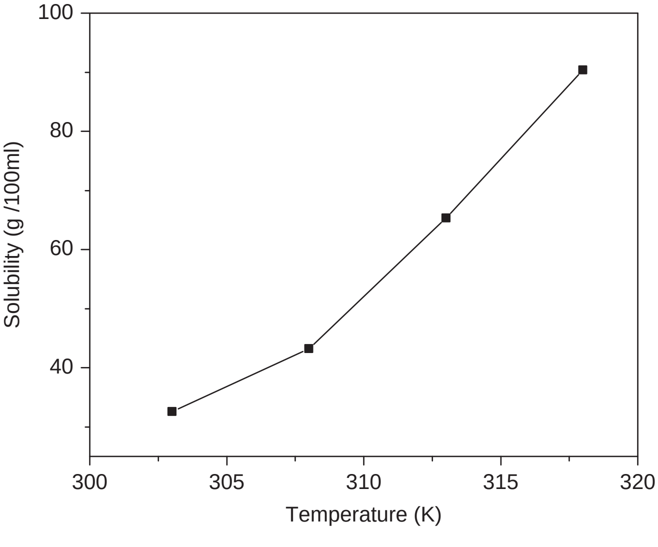

Fig. 1. Solubility of ZTC at pH of 3.4.

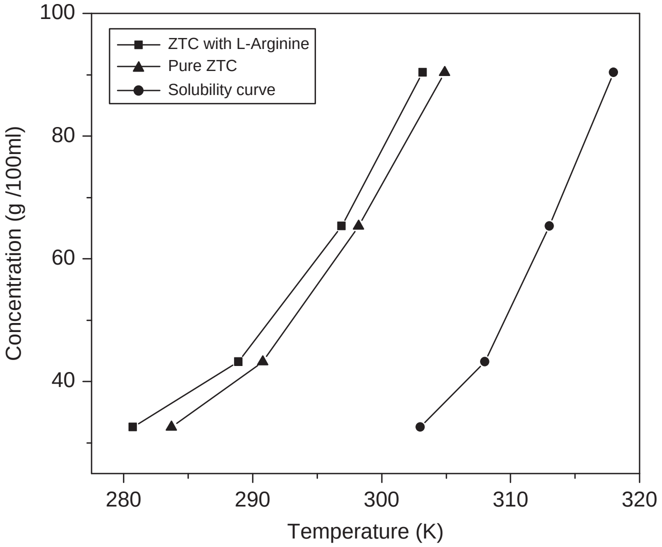

Fig. 2. Metastable zonewidth of pure and L-arginine added ZTC.

2.3. Induction period measurements and interfacial tension

Induction periods of pure and L-arginine doped ZTC solutions were measured by means of the isothermal method [15]. A solution with supersaturation ratio 1.25 was prepared and placed in a constant temperature bath (accuracy ±0.01 °C) at 34 °C. The time required for the growth of critical nucleus to a detectable size is negligibly small compared with the time needed between the attainment of supersaturation and the appearance of a crystal of detectable size and hence this can be taken as induction period. The appearance of first speck of the nucleus was seen at the bottom of the container. Induction periods were recorded for different supersaturation ratios 1.25, 1.3, 1.35, 1.4 and 1.45. Repeated trials were performed to ascertain the correctness of the observed results. Results are presented in Fig. 3. The plot of $\ln\tau$ against $1/(\ln S)^2$ is shown in Fig. 4. The induction period is written as

$$\tau \propto \exp\left[\frac{\Delta G^*}{kT}\right], \tag{1}$$

where ΔG^* is the critical free energy of the nucleus, k is the Boltzmann constant and T is the constant temperature of the solution.

$$\ln\tau = \ln B + \frac{\Delta G^*}{kT}, \tag{2}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G v^2}, \tag{3}$$

where B is a constant, γ is the interfacial tension and ΔG_v is the bulk energy change per unit volume and is given by

$$\Delta G_v = -\Delta\mu/V, \tag{4}$$

where

$$\Delta\mu = kT\ \ln S. \tag{5}$$

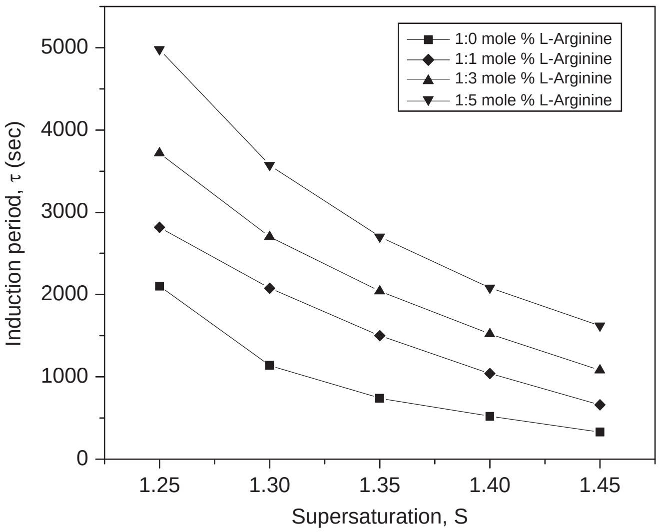

Fig. 3. Plot of S versus τ.

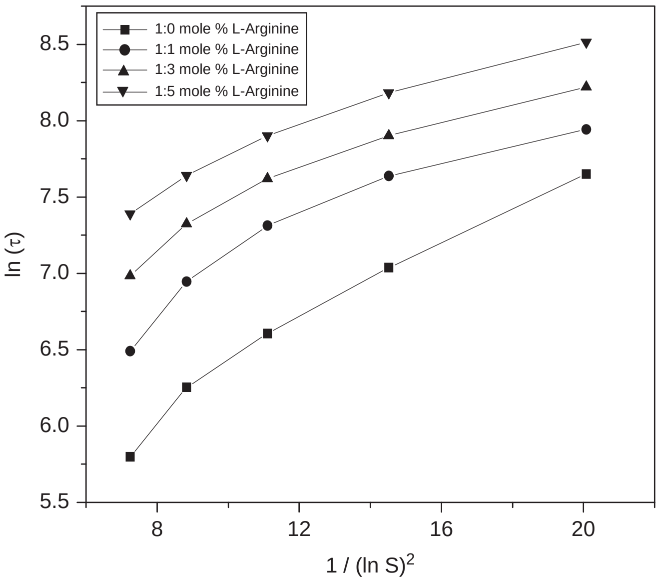

Fig. 4. Plot of $1/(\ln S)^2$ versus $\ln(\tau)$.

In the above expression, V is the molar volume of the crystal and is obtained from the expression

$$V = \frac{\text{Molecular weight}}{\text{density} \times N_A}, \tag{6}$$

and the supersaturation ratio $S = C/C^*$, C is the actual concentration of the solution and C^* is the equilibrium concentration of the solution.

The critical parameters involved in between the growing crystals and the surrounding mother liquor is the interfacial tension. In the present study, in order to estimate the critical nucleation parameters, the interfacial tension γ has been calculated using experimentally determined induction period values. According to the classical theory for homogeneous formation of spherical nuclei,

$$\ln \tau = \ln B + \frac{16\pi\gamma^3 V^2 N_A^3}{3R^3T^3(\ln S)^2}, \tag{7}$$

and

$$k = R/N_A, \tag{8}$$

where N_A is the Avogadro's number, R is the gas constant and τ is the induction period at temperature T and supersaturation ratio S. According to Eq. (7) the plot of $\ln \tau$ against $1/(\ln S)^2$ is a straight line with a slope given by

$$m = \frac{16\pi\gamma^3 V^2 N_A^3}{3R^3T^3}. \tag{9}$$

Since $\ln B$ weakly depends on the temperature, the interfacial tension γ of the solid relative to the solution has been calculated from the slope of the line as

$$\gamma^3 = \frac{3R^3T^3 m}{16\pi V^2 N_A^3}. \tag{10}$$

2.4. Evaluation of nucleation parameters

The change in Gibbs free energy (ΔG) between the crystalline phase and the surrounding mother liquor results in a driving force, which stimulates crystallization. For a rapid crystallization, $\Delta G<0$, the free energy required to form a spherical nucleus is given by [16]

$$\Delta G = \tfrac{1}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma, \tag{11}$$

where ΔG_V is the energy change per unit volume and r is the radius of the nucleus. The first term expresses the formation of the new surface and the second term represents the difference in the chemical potential between the crystalline phase (μ) and the surrounding mother liquor (μ_0). At the critical state, the free energy formation obeys the condition $d(\Delta G)/dr = 0$. Hence the radius of the critical nucleus [17,18] has been computed as

$$r^* = -2\gamma/\Delta G_v. \tag{12}$$

The nucleation rate J which is the number of critical nuclei formed per unit time and per unit volume has been calculated using the equation

$$J = A \exp\left[\frac{-\Delta G^*}{kT}\right], \tag{13}$$

where A is the pre-exponential factor ($\sim 10^{30}$ for solution) [19]. The number of molecules in the critical nucleus [20] is expressed as

$$i^* = \frac{4\pi(r^*)^3}{3V}. \tag{14}$$

Using the interfacial tension value γ, the nucleation parameters such as r^*, ΔG^* and i^* were calculated.

2.5. Second harmonic generation efficiency measurements

The first and the most widely used technique for confirming the SHG from prospective second order NLO materials is the Kurtz powder technique [21] to identify the materials with noncentrosymmetric crystal structures. The SHG conversion efficiency of L-arginine doped ZTC crystals grown at an optimized pH of 3.4 was studied using a 1064 nm Nd:YAG laser. The schematic of the experimental set- up is shown in Fig. 5. The crystalline samples were powdered into particle sizes in the range 125–150 μm. To make relevant comparisons with known SHG materials, KDP was also ground and sieved into the same particle size range. The powdered samples were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter. A Q-switched, mode-locked Nd:YAG laser was used to generate about

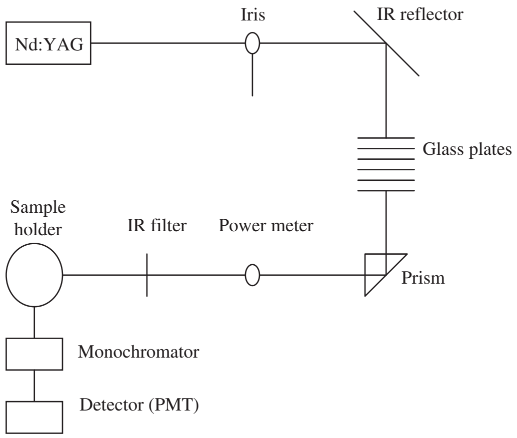

Fig. 5. Schematic arrangement of the experimental setup used for measuring the SHG efficiency.

5.7 mJ/pulse at 1064 nm as fundamental radiation. This laser device can be operated in two different-modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multi-shot mode of 8 ns laser pulse with a spot radius of 1 mm was used. This experimental set-up was used as a mirror and $\frac{50}{50}$ beam splitter to generate a beam with pulse energies of about 5.7 mJ. The input laser beam was allowed to pass though an IR reflector and then directed on the micro-crystalline powdered samples packed in a capillary tube. The photodiode detector and oscilloscope arrangements were measured the light emitted in the sample. The SHG radiations of 532 nm (green light) emitted were collected by a photomultiplier tube (PMT-Hamamatsu-model R 2059). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 305213).

3. Results and discussion

The solubility of ZTC at a pH value of 3.4 as a function of temperature is shown in Fig. 1. From the graph it is found that the solubility increases with temperature. Results of metastable zonewidth measurement and induction period measurement are presented in Figs. 2 and 3. It is found that the addition of L-arginine slightly enhances the metastable zonewidth. It is also found from the graph that the zonewidth decreases with increase in temperature. The kinetics of nucleation depends on the thermodynamic driving force, which in turn depends on the supersaturation, temperature and impurities present in the system. The induction period, a measure of nucleation rate, is determined experimentally for ZTC solution with and without the presence of L-arginine at different supersaturations. The induction period decreases exponentially with supersaturation which suggests that the nucleation rate increases exponentially. Therefore, the number of critical nuclei formed will be increased which lead to spurious nucleation. Similar results have been obtained by us for ADP admixtured TGS crystals [22] and other researchers for their systems such as deuterated L-arginine phosphate (dLAP), potassium fluoride mixed dLAP and sodium azide mixed dLAP single crystals [23], m-Nitroaniline crystals [24] and L-histidine tetrafluoro borate (L-HFB) single crystals [25]. The study of induction period against supersaturation gives an idea of optimized induction period in order to control the nucleation rate and to grow good quality of single crystals. It is observed that the number of tiny crystals formed by the spontaneous nucleation was very low compared with the pure system. This is because L-arginine suppresses the activities of heterogeneous nucleation. Plot of $\ln\tau$ against $1/(\ln S)^2$ is shown in Fig. 4. In order to reduce the effect of heterogeneous nucleation on the nucleation parameters, the results were obtained using the slopes determined by a linear fit for $\ln\tau$ against $1/(\ln S)^2$. It can be noticed that the induction period increases with increase in additive concentration. The interfacial tension has been calculated at constant temperature ($T = 307$ K) for pure ZTC and L-arginine doped ZTC crystals from the graph drawn between $\ln\tau$ and $1/(\ln S)^2$. The measured interfacial tension varies from 1.845 to 2.165 mJ/m^2. Using the interfacial tension value, the nucleation parameters such as the radius of critical nucleus (r^*), the free energy for the formation of the critical nucleus (ΔG^*) and the number of molecules in the critical nucleus (i^*) have been calculated for the controlled nucleation condition. From the plot made between the calculated critical radius r^* and supersaturation (Fig. 6), we observe that the value of r^* decreases with the increase of

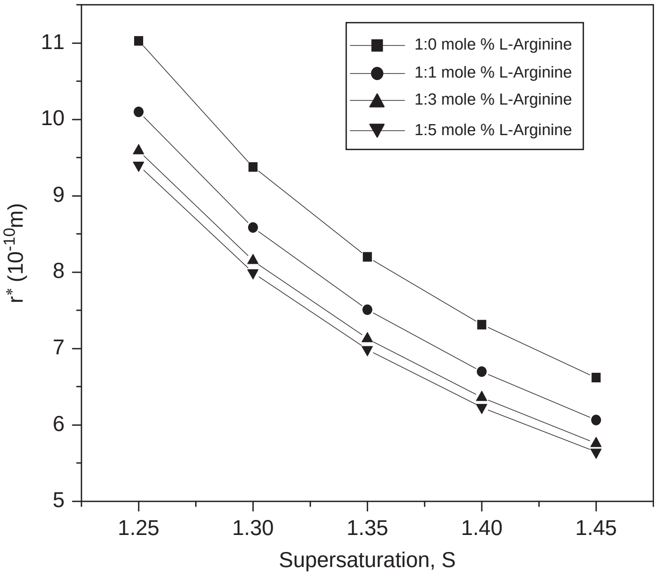

Fig. 6. Plot of S versus r^*.

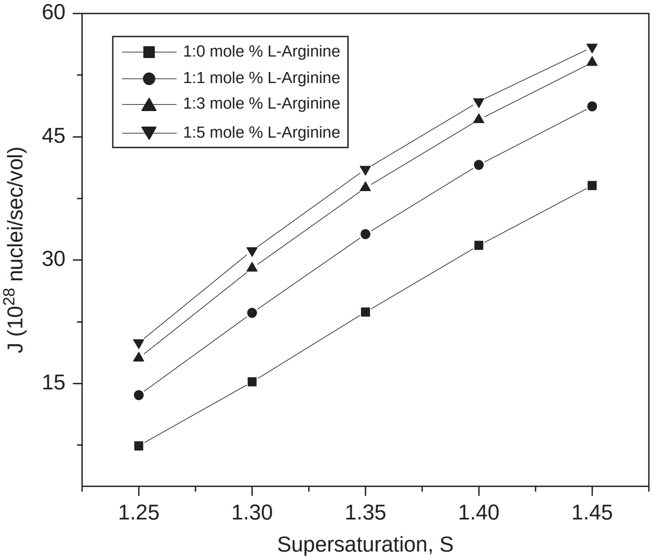

Fig. 7. Plot of S versus J.

Table 1
Summary of nucleation data for pure and L-arginine doped ZTC systems.

System	$S=C/C^*$	$\Delta G^* \times 10^{-21} J$	$J \times 10^{28}$ nuclei/s/vol	$r^* \times 10^{-10}$ m	i^*
Pure ZTC	1.25	11.03	7.40	11.024	23.298
	1.3	7.98	15.20	9.376	14.334
	1.35	6.10	23.69	8.197	9.578
	1.4	4.85	31.83	7.311	6.796
	1.45	3.98	39.09	6.621	5.047
ZTC+1 mole% L-arginine	1.25	8.46	13.58	10.097	17.901
	1.3	6.12	23.57	8.587	11.011
	1.35	4.68	33.14	7.507	7.357
	1.4	3.72	41.56	6.696	5.221
	1.45	3.05	48.68	6.064	3.878
ZTC+3 mole% L-arginine	1.25	7.25	18.07	9.588	15.328
	1.3	5.24	29.03	8.1543	9.429
	1.35	4.01	38.81	7.129	6.301
	1.4	3.19	47.09	6.358	4.469
	1.45	2.61	54.01	5.758	3.319
ZTC+5 mole% L-arginine	1.25	6.83	19.95	9.398	14.435
	1.3	4.94	31.16	7.993	8.880
	1.35	3.77	41.07	6.988	5.934
	1.4	3.00	49.26	6.232	4.209
	1.45	2.46	55.93	5.644	3.127

Table 2
SHG output of pure and L-arginine doped ZTC.

Samples	SH signal output (mV)
Pure KDP	194
Pure ZTC	121.2
ZTC+1 mole% L-arg	126.7
ZTC+3 mole% L-arg	138.2
ZTC+5 mole% L-arg	146.8

Input power = 5.7 mJ/pulse.

supersaturation and consequently the nucleation rate (J) increases with increase of supersaturation (Fig. 7). It is noted from Table 1 that the value of i^* and ΔG^* decreases with the increase of supersaturation and also varies with different doping concentrations.

The second harmonic generation output for all the specimens of undoped and doped ZTC is given in Table. 2. Output intensity of SHG gives relative values of NLO efficiency of the material. From the table, one can see that the second harmonic signal strength and the second harmonic generation efficiency increases slightly as the doping concentration of L-arginine increases. Similar results were obtained for L-arginine doped KDP crystals [26]. Although many materials have been identified with higher molecular nonlinearities, the attainment of second order effects requires favourable alignment of the molecule within the crystal structure [27]. To elaborate, the SHG demands specific molecular alignment of the crystal to be achieved facilitating nonlinearity in the presence of a dopant. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation [28].

4. Conclusion

The metastable zonewidth and induction period values of pure and L-arginine added ZTC crystals have been determined. The interfacial tension has been calculated by using the experimentally determined induction period values. Nucleation kinetics and fundamental growth parameters have also been investigated for different supersaturation and different doping concentration. The growth rate is found to be increase with supersaturation ratio for pure and L-arginine doped ZTC. Also, the growth rate of L-arginine doped ZTC (1–5 mole%) is found to be greater than the pure ZTC for same supersaturation ratio. Improvement of SHG efficiency due to L-arginine doping was observed and is comparable with that of KDP.

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References

[1] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Catella, Appl. Opt. 31 (1992) 5051.
[2] G. Xing, M. Jiang, X. Zishao, D. Xu, Chin. J. Lasers 14 (1987) 357.
[3] L.F. Warren, Electronic materials our future, in: R.E. Allred, R.J. Martinez, K.B. Wischmann (Eds.), Proceedings of the Fourth International Sample Electronics Society for the Advancement of Materials and Process Engineering, vol. 4, Covina, CA, 1990, p. 388.
[4] J. Ramajothi, S. Dhanuskodi, K. Nagarajan, Cryst. Res. Technol. 39 (2004) 414.
[5] R. Sankar, C.M. Raghavan, R. Jayavel, Cryst. Res. Technol. 41 (2006) 924.
[6] V. Kannan, N.P. Rajesh, R.B. Ganesh, P. Ramasamy, J. Cryst. Growth 269 (2004) 565.
[7] P.M. Ushasree, R. Muralidharan, R. Jeyavel, P. Ramasamy, J. Cryst. Growth 218 (2000) 365.
[8] N.P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P.S. Raghavan, P. Ramasamy, J. Cryst. Growth 262 (2004) 561.
[9] R. Rajasekaran, P.M. Ushasree, R. Jeyavel, P. Ramasamy, J. Cryst. Growth 229 (2001) 563.
[10] N.R. Kuncher, M.R. Truter, J. Chem. Soc. (1958) 3478.
[11] R. Rajasekaran, R. Mohankumar, R. Jeyavel, P. Ramasamy, J. Cryst. Growth 252 (2003) 317.
[12] H.E. Buckly (Ed.), Crystal Growth, Wiley, New York, 1951.
[13] W.S. Wang, K. Sutter, Ch. Bosshard, Z. Pan, H. Arend, P. Gunter, G. Chapuis, F. Nicolo, J. Appl. Phys. 27 (1998) 1138.
[14] J. Nyvlt, R. Rychy, J. Gottfried, V. Warzelova, J. Cryst. Growth. 6 (1970) 151.
[15] N.P. Zaitseva, L.N. Rashkovich, S.V. Bagatyacva, J. Cryst. Growth 148 (1995) 278.
[16] A.E. Nielsen, S. Sarig, J. Cryst. Growth 8 (1971) 1.
[17] N.P. Rajesh, V. Kannan, P.S. Raghavan, P. Ramasamy, C.W. Lan, Mater. Chem. Phys. 76 (2002) 181.

[18] F. Joseph Kumar, D. Jayaraman, C. Subramanian, P. Ramasamy, J. Cryst. Growth 137 (1994) 535.
[19] A.C. Zattlemoyer, Dekker, New York, 1969.
[20] S. Boomadevi, R. Dhanasekaran, P. Ramasamy, Cryst. Res. Technol. 37 (2002) 159.
[21] S.K. Kurtz, J.J. Perry, J. Appl. Phys. 39 (1968) 3798.
[22] T. Balu, T.R. Rajasekaran, N.P. Rajesh, P. Murugakoothan, Mater. Lett. 61 (2007) 4824.
[23] A.S. Haja Hameed, G. Ravi, R. Jeyavel, P. Ramasamy, J. Cryst. Growth 250 (2003) 129.
[24] T. Kanagasekaran, M. Gunasekaran, P. Srinivasan, D. Jeyaraman, R. Gopalakrishnan, P. Ramasamy, Cryst. Res. Technol. 12 (2005) 1131.
[25] K.V. Rajendran, R. Rajasekaran, D. Jeyaraman, R. Jeyavel, P. Ramasamy, Mat. Chem. Phys. 81 (2003) 50.
[26] K.D. Parikh, D.J. Dave, B.B. Parekh, M.J. Joshi, Bull. Mater. Sci. 30 (2007) 105.
[27] S.R. Hall, P.V. Kolinsky, R. Jones, S. Allen, P. Gordon, B. Boshwell, D. Bloor, P.A. Norman, M. Hursthouse, A. Karaulov, J. Baldwin, J. Cryst. Growth 79 (1986) 745.
[28] Y. Wang, D.F. Eaton, Chem. Phys. Lett. 120 (1985) 441.