IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861,
PP 39-45
www.iosrjournals.org

Studies on Nucleation, Growth and Characterization of L-Leucine Doped ZTS Crystals

N.Balasundari [1], P.Selvarajan[2]
[1]*Physics department , Sri K.G.S arts college , srivaikundam- 628619. Tamilnadu,*
enbalasundari@yahoo.co.in
[2] *Department of Physics, Aditanar college of Arts and science,*
Tiruchendur-628216, Tamilnadu.

Abstract: *Nucleation parameters such as solubility, induction period, interfacial energy and nucleation rate and critical radius, Gibbs free energy change, number of molecules in the critical nucleus have been investigated for the aqueous solution growth of a semi-organic nonlinear optical (NLO) material of L-Leucine doped Zinc Tris-thiourea sulfate (ZTS). From the results, it was observed that the induction period increases with increase in additive concentration L-leucine into ZTS solutions. The critical nucleation parameters such as radius of critical nucleus, Gibbs free energy change and number of molecules (n) in the critical nucleus decrease with supersaturation ratio and these parameters decrease when concentration of the dopant is increased. Growth of crystals were done by solution method. Characterization studies were carried out for the grown crystals by EDAX spectroscopy.*
Keywords: *Nucleation, solution growth, single crystal, NLO, doping, solubility, characterization*

I. 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. Nonlinear 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]. Within the last decade much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients. However, weak Vander Walls and hydrogen bonds with conjugated electrons constitute most of the organic NLO crystals. So they are soft in nature and difficult to polish and these materials also have intense absorption in UV region. In view of these problems, new types of hybrid NLO materials have been explored from organic-inorganic complexes with stronger ionic bond. Recent interest is centered on semi organic crystals, which have the combined properties of both inorganic and organic crystals. Semi organic crystals have large nonlinearity, high resistance, low angular sensitivity and good mechanical hardness [4-6]. These crystals have better non-linear optical property than KDP. One of the essential requirements for a material to exhibit second order optical susceptibilities described by third rank polar tensor is that the crystal should have non-centrosymmetric space group. In amino acids, except glycine, all the other possess non-centro symmetric space group. The complex of organic-inorganic gives semiorganic material, which possesses higher mechanical strength compared to organic materials. The research on the synthesis of organic and inorganic complexes increased enormously in last few years [7,8]. 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 [9]. The material ZTS is a promising semi-organic nonlinear optical material for second harmonic generation (SGH) from metal complexes of thiourea. The SHG efficiency of ZTS is 1.2 times more than that of KDP [10-13]. In the report, in order to optimize the growth parameters for the growth of bulk crystals with improved growth rates, the nucleation parameters like solubility, induction period, the critical radius, and number of molecules in the critical nucleus of pure and L-Leucine doped ZTS crystal have been investigated. Based on the nucleation parameters, bulk crystals have been grown and the grown crystals have been characterized.

II. Solubility

The solubility of pure and L-Leucine doped ZTS was determined for different temperatures namely 30, 35, 40 45 and 50°C. The measurement was performed dissolving the ZTS salt in deionized water in an airtight container maintained at 30°C with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analysed gravimetrically. The procedure was repeated for other temperatures and also for the L-Leucine doped ZTS. For comparison purpose, the solubility curves of undoped ZTS salt was drawn along with the solubility curves of the doped salt. The solubility of ZTS crystal at 30 ^{o}C is reported to be 4.3 g/100 ml (for the pH value 3.1) [14, 15] and similar results were obtained in this work. It was observed from the result (figure 1) that solubility of the sample in water increases with temperature and it is found to be more for doped sample than the pure sample. It is clear that in the case of doped samples, the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature. Since the solubility increases with temperature, the samples have positive temperature coefficient of solubility. The increase in solubility by addition of dopants may lead to change of thermodynamic parameters such as surface concentration of growth species and the surface energy and hence it may be responsible for the change in the morphology of crystals [16].

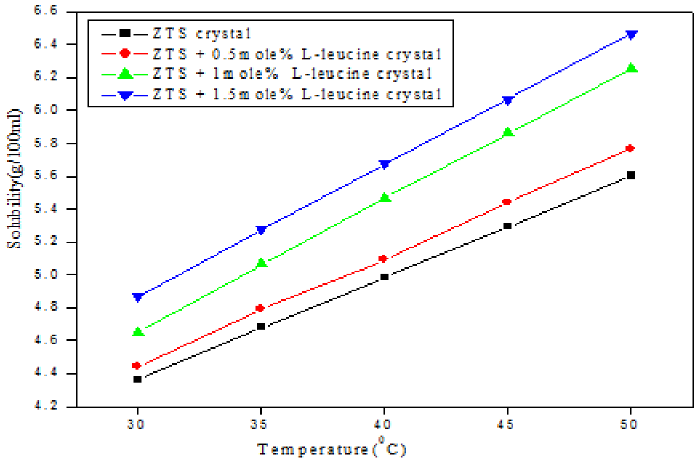

Fig.1. Solubility curves for undoped and L-leucine doped ZTS crystals

3.Nucleation kinetic studies

Nucleation is an important phenomenon in crystal growth. The critical nucleation parameters of the synthesized undoped (pure) and L-Leucine doped ZTS salts have been calculated using the values of induction period (τ).

(a) Induction period (□)

A solution with supersaturation ratio 1.1 was prepared at 30°C and placed in a constant temperature bath. The time required for the growth of critical nucleus to detectable size is negligibly small compared with the time needed between the attainment of supersaturation and the appearance of nucleus 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. For the measurement of induction period, isothermal method [16, 17] used at the selected supersaturation ratios or levels (S) such as 1.2, 1.25, 1.3, 1.35 and 1.4. The variations of induction period with supersaturation ratio for the samples are presented in the figure 2.

Department of Physics, St. John's College, Palayamkottai-627 002, Tamilnadu, India. DOI 10.9790/4861-17002033945

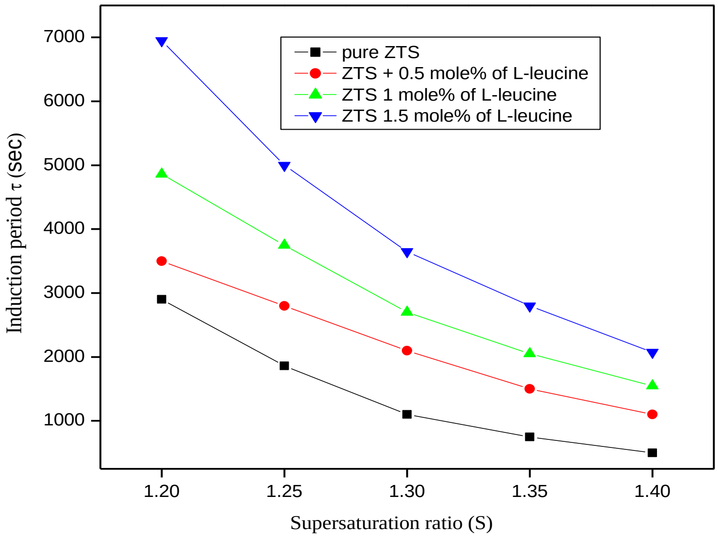

Fig. 2: Variation of induction period as a function of supersaturation ratio for the samples

(b) Interfacial tension

Interfacial tension of the crystal and solution interface is an important parameter involved in the theory of nucleation and growth kinetics. In the present study, interfacial tension has been calculated on the basis of the classical theory of homogeneous nucleation [18,19]. In order to estimate the critical nucleation parameters, the interfacial tension has been calculated using the experimentally measured induction period values by the relation

$$ln\tau = -lnB + \frac{16\pi\sigma^3 v^2 N}{3R^3T^3\,(lnS)^2} \quad \text{.........(2)}$$

where σ is the interfacial tension, v is the molar volume of the crystal, N is the Avogadro's number, R is the gas constant and S is the relative supersaturation ($S = \frac{C}{C^*}$) where C is the actual concentration and C* is the equilibrium concentration. The function ln B weakly depends on temperature and hence there is a linear dependence between $\ln\tau$ and $(\ln S)^2$.The interfacial tension of the solid related to this solution has been calculated from the relation

$$\sigma^3 = \frac{3ln\tau R^3T^3\,(lnS)^2}{16\pi v^2 N} \quad \text{.................(3)}$$

The graphs of ln τ versus 1/ $(\ln S)^2$ for the pure and L-leucine doped ZTS samples are presented in the figure 3. Plot of ln τ against 1 / $(\ln S)^2$ is almost linear. By linear fit, the slope is found and using the values of slope and the following equations, the critical nucleation parameters such as radius of critical nucleus (r^*), Gibbs free energy change (ΔG^*), interfacial tension (σ) and number of molecules in the critical nucleus (n) have been determined and the obtained values are tabulated in table 1.

c) Critical free energy, critical radius and nucleation rate

The free energy required to form a spherical nucleus is given by,

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

where ΔG_v is the energy change per unit volume, r is the radius of the nucleus. At the critical state, the free energy of formation obeys the condition that $d\left(\frac{\Delta G}{dr}\right)$= 0. Hence the radius of the critical nucleus is expressed as

$$r^* = \frac{2\sigma V}{kTlnS} \quad \text{.......................(5)}$$

The critical free energy is given by

Department of Physics, St. John's College, Palayamkottai-627 002, Tamilnadu, India. DOI 10.9790/4861-17002033945

$$\Delta G^{*} = \frac{16\pi\sigma^{3}v^{2}}{3(\Delta G_{v})^{2}} \text{ ....(6)}$$

The number of molecules in the critical nucleus is expressed by

$$n = \frac{4\pi r^{*3}}{3V} \text{ ... .(7)}$$

The rate of nucleation (i.e., the number of nuclei formed per unit time per unit volume) can be expressed by an Arrhenius-type equation

$$J = A \exp(-\Delta G^{*} / k T) \text{ ....(8)}$$

The calculated values of interfacial tension vary from 1.348 to 1.362. Using these values, the other critical nucleation parameters were determined. From the results, it was observed that induction period decreases as the supersaturation ratio increases and hence the nucleation rate increases. The induction period increases with increase in additive concentration of L-leucine into ZTS solutions. The critical nucleation parameters such as radius of critical nucleus, Gibbs free energy change and number of molecules (n) in the critical nucleus decrease with supersaturation ratio (S) and these parameters decrease when concentration of dopants is increased. The obtained results of this work were the same as observed by other authors for their systems [20-23].

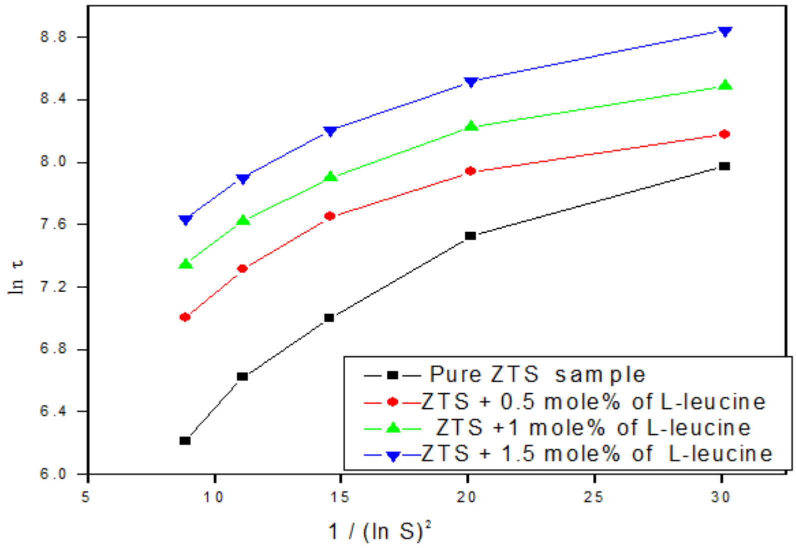

Fig.3 Graph of ln τ versus 1/ (ln S) ^{2} for the samples

Table 1: Summary of nucleation parameters for pure and L-leucine doped ZTS samples

Sample	S	ΔG^{*} x 10^{-20} (joules)	J x 10^{29} nuclei/ s/vol	r^{*} x 10^{-10} m	n
Pure ZTS	1.2 1.25 1.3 1.35 1.4	1.012 0.674 0.487 0.372 0.296	0.975 2.016 3.144 4.132 4.949	12.9 10.6 8.98 7.85 7.01	26.18 14.52 8.83 5.89 4.20
ZTS + 0.5 mole% of L-leucine	1.2 1.25 1.3 1.35 1.4	0.662 0.441 0.319 0.243 0.194	2.084 3.507 4.686 5.613 6.307	11.1 9.09 7.73 6.76 6.03	17.11 9.40 5.78 3.86 2.74
ZTS + 1 mole% of L-leucine	1.2 1.25 1.3 1.35 1.4	0.653 0.435 0.315 0.241 0.191	2.119 3.557 4.731 5.640 6.352	11.1 9.04 7.69 6.72 6.0	17.18 9.28 5.71 3.81 2.71
ZTS + 1.5 mole% of L-leucine	1.2 1.25 1.3 1.35 1.4	0.693 0.463 0.335 0.256 0.203	2.927 3.328 4.511 5.443 6.173	11.3 9.22 7.84 6.86 6.11	18.15 9.86 6.06 4.06 2.86

4. Crystal growth

In accordance with the solubility data, saturated solutions of the synthesized salts of pure and L-leucine doped ZTS were prepared separately. The solutions were constantly stirred for about 2 hours using a hot plate magnetic stirrer and were filtered using 4-micro Whatmann filter papers. Then the filtered solutions were kept in beakers covered with porous papers and kept in a dust-free atmosphere. To grow big size crystals, seed technique has been used. During the growth, very small crystals appeared at first which then grew bigger on slow evaporation. Constant temperature bath was also used to maintain the temperature constant. Several trials were tried to get good quality crystals. The grown crystals are displayed in the figures 4 (a-c).

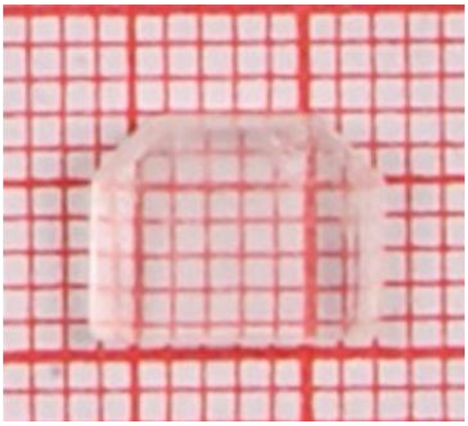

Figure 4(a): ZTS crystal doped with L-leucine (0.5 mole%)

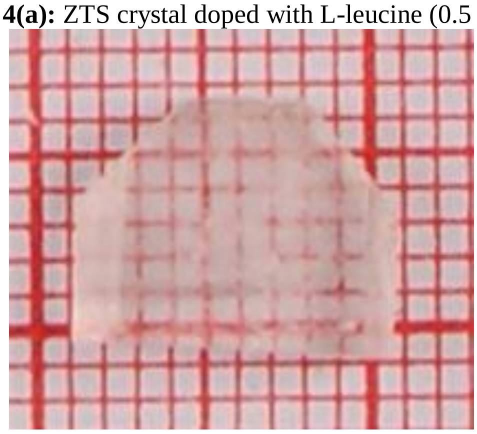

Figure 4(b): ZTS crystal doped with L-leucine (1 mole%)

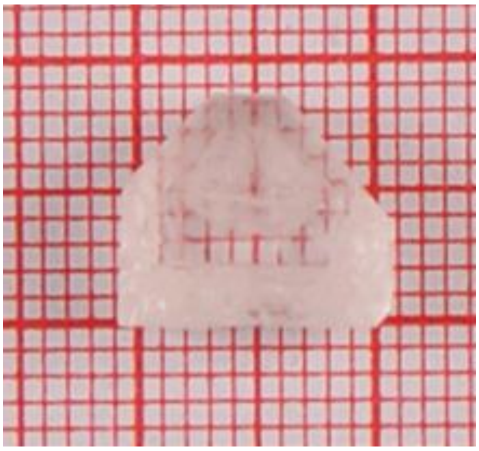

Figure 4(c): ZTS crystal doped with L-leucine (1.5 mole%)

5. EDAX spectral studies

Department of Physics, St. John's College, Palayamkottai-627 002, Tamilnadu, India. DOI 10.9790/4861-17002033945

Energy dispersive X-ray spectroscopy (EDS or EDAX) is an analytical technique used for the elemental analysis of the sample. The data generated by EDS analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the specimen being analysed. The energy dispersive spectrum analysis used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystal. In order to confirm the presence of the elements in the grown crystals, the samples were subjected to Energy Dispersive spectrum analysis using EDS detector (Hitachi model S-3000H scanning electron microscope). The obtained spectra (Fig.5) show the chemical composition of the undoped and L-leucine doped ZTS crystals thereby confirming the presence of the elements in the grown crystals. The peaks show the presence of carbon, nitrogen, zinc, sulphur, oxygen in the grown samples.

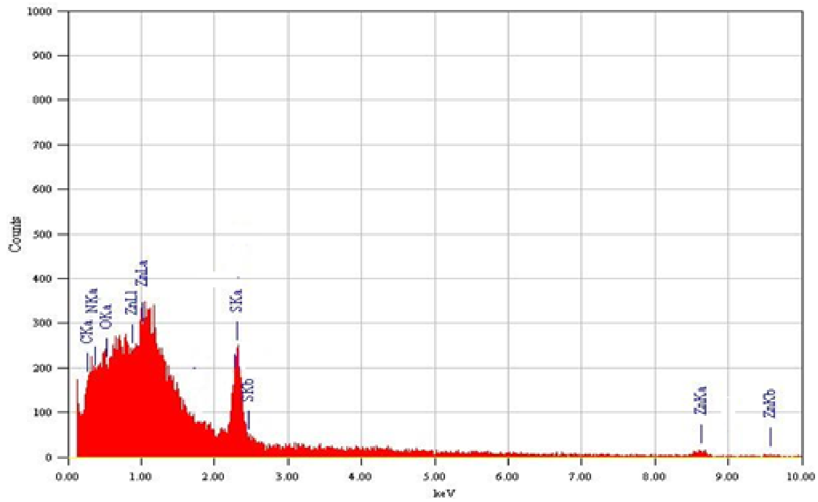

Fig.5 (a): EDAX spectrum of L-leucine added ZTS crystal (0.5 mole%)

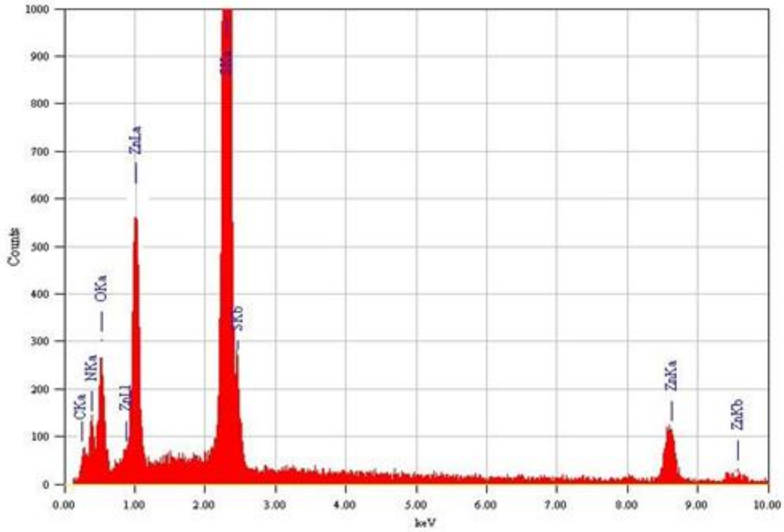

Fig.5 (b): EDAX spectrum of L-leucine added ZTS crystal (1.5 mole%)

III. Conclusion

Single crystals of undoped and L- Leucine doped ZTS crystals have been grown from aqueous solutions. Solubility was estimated for different temperatures. It was clearly observed that the induction period decreases with increase of supersaturation ratio and hence there is an increase of nucleation rate. The growth parameters were optimized for the growth of large size crystals. The nucleation parameters such as Gibbs free energy change, the radius of critical nucleus, the nucleation rate, and also the number of molecules present in the critical nuclei were evaluated in terms of the classical nucleation theory. EDAX spectra have been recorded for the samples and hence the elements present in the samples have confirmed.

Acknowledgement

The authors are grateful to the staff members of Cochin University for helping us to record EDAX spectra of the samples.

References

[1]. R. F. Belt, G. Gashurov, and Y. S. Liu, Laser Focus 10, 110 (1985).
[2]. R. S. Calark, Photonics Spectra 22, 135 (1988).
[3]. R. J. Gambino, Bull. Mater. Res. Soc. 15, 20 (1990).
[4]. G. Xing, M. Jiang, X. Zishao, and D. Xu, Chin. J. Lasers 14, 357 (1987).
[5]. S. Versko, Laser program Annual Report, Lawrence UCRL-JC 105000, Lawrence Livermore National Laboratory, Livermore, CA, (1990).
[6]. 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 of Materials and Process Engineering, Covina, CA 4, 388 (1990).
[7]. H. Koshima, M. Hamada, I. Yagi, and K. Uosaki, Cryst. Growth Des. 1, 467 (2001).
[8]. P. Anwar, S. Okada, H. Oikawa, and H. Nakanishi, Chem. Mater. 12, 1162 (2000).
[9]. C. Razzetti, M. Ardoino, L. Zanotti, M. Zha, and C. Paorici, Cryst. Res. Technol. 37, 456 (2002).
[10]. C. Krishnan, P. Selvarajan, S. Pari, Curr. Appl.Phys.10 (2010) 664.
[11]. P.M. Ushasree, R. Jayavel, P.Ramasamy,Mater.Sci.Eng. B65(1999),153
[12]. M. Oussaid, P. Becker, M. Kemiche, C. Carabatos - Nedelec, phys. Stat. Sol. (b) 207 (1998), 103.
[13]. G.d.Andreeti, L.Cavalca, and A.Musatti., Acta Cryst.Sect.B 24, 683(1968).
[14]. K.Byrappa, T.Ohachi, "Crystal Growth Technology", William Andrew Publishing (Springer), Norwich, New York (2003) .
[15]. P. M. Ushasree. R. Muralidharan, R. Jayavel, and P. Ramasamy, J. Cryst. Growth 210, 741(2000).
[16]. Dhanaraj P.V., Santheep K., Mathew N., Rejesh P., J. Crystal Growth, 310 (2008) 2532.
[17]. Zaitseva N.P., Rashkovich L.N., Bagatyareva S.V., J.Crystal Growth, 148 (1995)276.
[18]. A. E. Nielson and S. Aig, J. Cryst. Growth 8, 1 (1971).
[19]. M. Volmer and A. Weber, J. Phys. Chem. 119, 277 (1926).
[20]. Jayalakshmi D., Kumar J., J. Crystal Growth 292 (2006) 528.
[21]. Haja Hameed A.S., Ravi G., Jeyavel R., Ramasamy P., J. Cryst. Growth, 250 (2003) 129.
[22]. Kanagasekaran T., Gunasekaran M., Srinivasan P., Jeyaraman D., Gopalakrishnan R., Ramasamy P., Cryst. Res. Technol., 12 (2005) 1131.
[23]. Arunmozhi G., de M. Gomes E., Ganesamoorthy E. S., Cryst. Res. and Technol., 2004, 39 (2004) 408.