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RESEARCH ARTICLE

NUCLEATION KINETICS, GROWTH AND STUDIES OF L-ALANINE CADMIUM CHLORIDE (LACC) CRYSTALS DOPED WITH GLYCINE

[1]Malathi, M., [2]Rayar, S. L. and [3]*Selvarajan, P.

[1]Department of Physics, Research centre, Scott Christian College (Autonomous), Nagercoil-629003, Tamilnadu, India
[2]Department of Physcis, St.Jude's College, Thoothoor-629176, Tamilnadu, India
[3]Department of Physics, Aditanar College of Arts and Science, Tiruchendur- 628 216, Tamilnadu, India

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ABSTRACT

Undoped and glycine-doped L-alanine cadmium chloride (LACC) crystals were grown by slow evaporation technique. Solubility was measured for the samples at different temperatures from 30 ^{o}C to 50 ^{o}C. Nucleation kinetic studies were performed at different supersaturation ratio to understand the nucleation processes that are taking place in the aqueous solutions of the samples. XRD studies have been carried out to identify the crystal structure. UV-visible transmittance and microhardness were measured to find the suitability of the grown crystals for device fabrication. SHG efficiency and laser damage threshold (LDT) values were determined for the samples and the results are discussed in the paper.

INTRODUCTION

Amino acids are a group of organic compounds containing two functional groups such as amino group and carboxylic group. Most of the amino acids and their complexes belong to the family of organic and semiorganic nonlinear optical (NLO) materials that have potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing (Monaco *et al.,* 1987; Arun and Jayalekshmi 2008; Geetha *et al.,* 2011). Among the amino acids, L-alanine is the simplest acentric crystal and it is a naturally occurring chiral amino acid (Razzetti *et al.,* 2002). Efforts have been made on the amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and nonlinear optical properties. Amino acid based organometallic crystals like L-alanine cadmium chloride, L-arginine phosphate, L-histidine tetra fluroborate etc have been studied and they have large nonlinearity, high resistance to LASER induced damage, low angular sensitivity and good mechanical hardness (Kathleen I. Schaffers and Douglas A. Keszler 1993; Dhanuskodi and Ramajothi 2004; Eimerl *et al.,* 1989). L-alanine cadmium chloride (LACC) crystals were grown and some of its properties have been studied by the researchers (Dhanuskodi *et al.,* 2007; Bright 2010; Kalaiselvi *et al.,* 2013). To improve the various physical and chemical properties of LACC crystals, glylcine has been added as the dopant in this work. The aim of the work is to grow undoped and glycine doped L-alanine cadmium chloride (LACC) crystals and to subject the grown crystals to various studies such as nucleation kinetic studies, XRD studies, UV-visible transmittance studies, SHG studies, laser damage threshold (LDT) studies and microhardness studies.

***Corresponding author: Selvarajan, P.**
Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628 216, Tamilnadu, India.

Synthesis and growth

The salt of undoped L-alanine cadmium chloride (LACC) was synthesized by taking L-alanine (99% purity) and analar grade cadmium chloride monohydrate in the molar ratio of 1:1 and dissolved in double distilled water. The dissolved saturated solution was heated at 55 ^{o}C for the synthesis of LACC salt. To obtain the glycine doped LACC salts, 5 wt%, 10 wt% and 15 wt% of glycine was added into the solutions of L-alanine separately. The purity of the synthesized salts was further improved by re-crystallization process. Single crystals of undoped and glycine doped LACC were grown by solution method with slow evaporation technique using the saturated solutions of the relevant synthesized salts. The saturated solutions of the salts were stirred well and were filtered and taken in four beakers separately for crystallization. Over a period of 20-25 days, well faceted optically transparent seed crystals of various dimensions were collected. Good quality seed crystals were selected and were placed at the bottom of the beakers containing the solutions. The beakers were covered with perforated polythene papers and they were kept in a vibration free platform at room temperature ($30^{\circ}C$) and the seed crystals grew into big-sized crystals. The grown crystals are non-hygroscopic, stable, colourless and transparent. The external appearance of glycine doped LACC crystals seems to be different when compared to that of the undoped LACC crystal.

RESULTS AND DISCUSSION

Solubility and nucleation kinetic studies

The solubility of the crystals was measured by gravimetrical method (Selvarajan *et al.,* 2009). Fig.1 shows the solubility curves for undoped and glycine doped LACC samples and it is observed that the solubility of samples in water increases with temperature, exhibiting a positive temperature coefficient of solubility. Nucleation kinetic studies have been carried out by measuring the induction period and it is a nucleation parameter and it is defined as the amount of time elapsed between the achievement of a supersaturated solution and the observation of nuclei. The critical nucleation parameters were determined using the following relations (Kanagadurai *et al.,* 2010; Siva Dhas *et al.,* 2009; Mohan Kumar *et al.,* 1999). The expression of the induction time (τ) can be written for critical nucleus in terms of interfacial tension as $\ln \tau = -B + (16 \pi\sigma^3 v^2 N^3 / (3R^3 T^3 (\ln S)^2)$ where B is a constant, R is the universal gas constant, S is the super saturation ratio, v is the volume of unit cell, T is absolute temperature of the solution, σ is the interfacial tension and N is the Avogadro's number. The slope (m) of the plot of $1 / (\ln S)^2$ against $\ln \tau$ is given by $m = (16 \pi\sigma^3 v^2 N^3 / (3R^3 T^3)$. The Gibbs free energy change for critical nucleus is $\triangle G^* = mRT / (N (\ln S)^2)$ and the expression for interfacial tension is $\sigma = (RT/N) (3m/(16\pi v^2))^{1/3}$. The number of molecules in a critical nucleus is found using the equation $n = (4/3) (\pi/v) r^{*3}$. The nucleation rate (J) can be calculated using the equation $J = A \exp(-\Delta G^* / (kT))$ where A is the pre-exponential factor (approximately $A= 1 \times 10^{24}$ for solution) and k is the Boltzmann's constant.

Experimentally the induction period was measured by isothermal method and it can be used to evaluate the interfacial tension, Gibbs free energy change, critical radius and other nucleation parameters. Results of induction period for undoped and glycine added aqueous solutions of L-alanine cadmium chloride (LACC) at different supersaturation ratios (S) such as 1.3, 1.35, 1.4, 1.45 and 1.5 are presented in the Figure 2. It is observed that the induction period decreases with increase of super saturation ratio. The induction period is found to be increasing when glycine is added into the aqueous solutions of LACC. The variations of Gibbs' free energy change, radius of critical nucleus, number of molecules in the critical nucleus and nucleation rate with the super saturation ratio are displayed in Figures 3-6. It is noticed from the results that the nucleation parameters such as radius of critical nucleus, Gibbs' free energy change, and number of molecules in the critical nucleus decrease with super saturation and they increase when concentration of glycine is increased in the solutions of LACC. It is reported that super saturation and presence of glycine in the solution have an important role in controlling the nucleation rate and nucleation parameters during the growth of crystals. The nucleation rate is observed to be increasesing with the super saturation ratio and it decreases when LACC sample is doped with glycine. If the nucleation rate is low, the formation of multi-nuclei in the solution will be less and hence big-sized crystals could be grown.

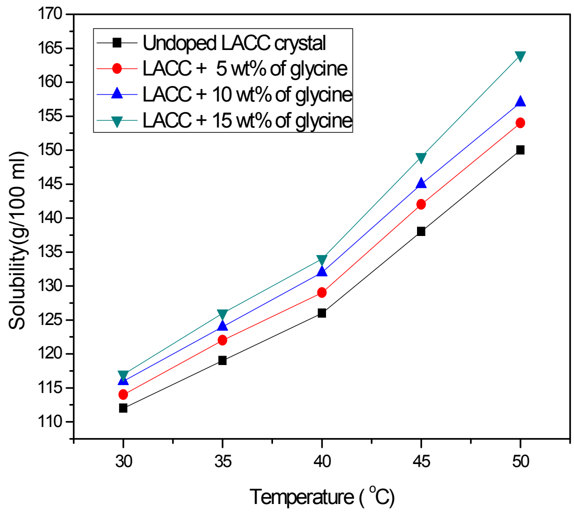

Fig.1. Solubility curves of undoped and glycine doped L-alanine cadmium chloride (LACC) samples

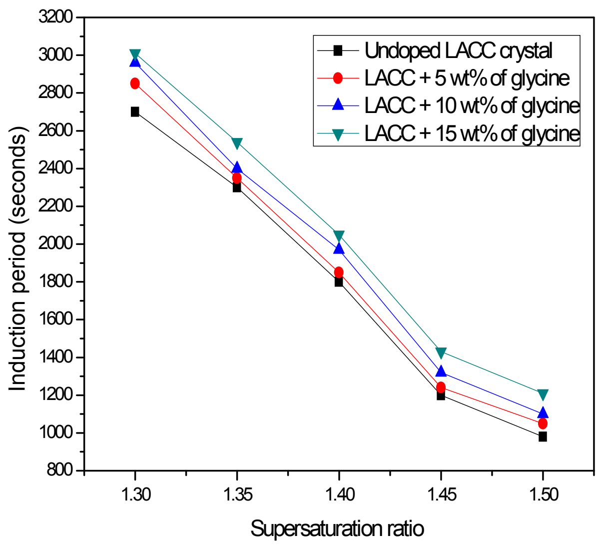

Fig.2. Variation of induction period with supersaturation ratio for undoped and glycine doped LACC samples

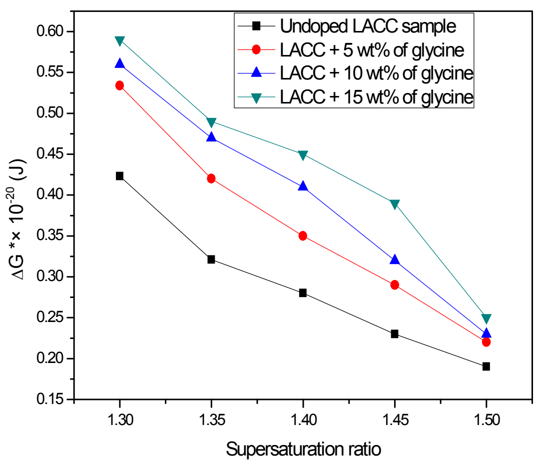

Fig.3. Plots of Gibbs free energy change with supersaturation ratio for glycine doped LACC samples

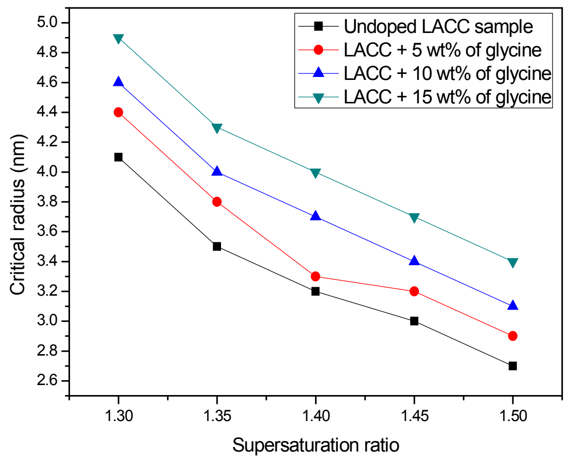

Fig.4. Plots of critical radius with supersaturation ratio for glycine doped LACC samples

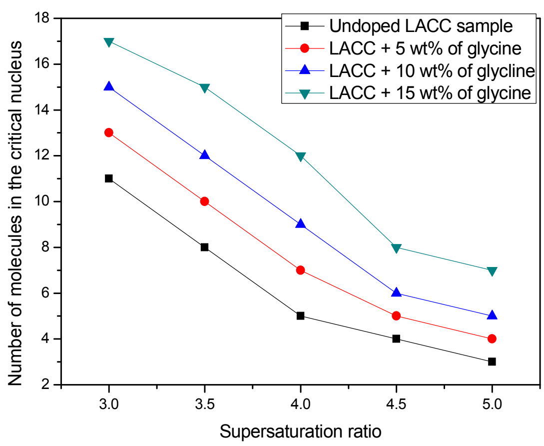

Fig.5. Variation of number of molecules in the critical nucleus with supersaturation ratio for undoped and glycine doped LACC samples

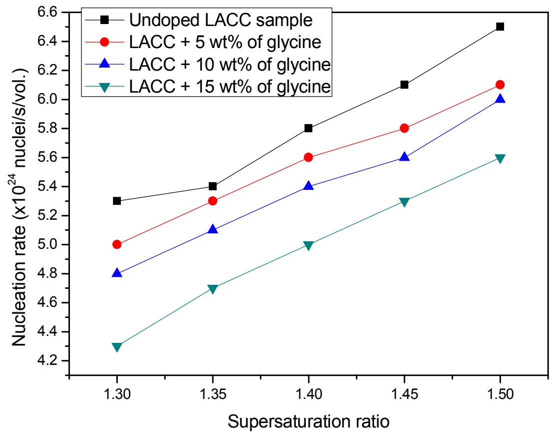

Fig.6. Plots of nucleation rate with supersaturation ratio for glycine doped LACC samples

Single crystal XRD studies

The grown crystals were subjected to single crystal XRD studies using a single X-ray diffractometer (Bruker-Nonius MACH3/CAD4) and the lattice constants were obtained. The obtained lattice parameters of the samples are provided in the Table 1. From the XRD data, it is observed that undoped and glycine doped LACC crystals crystallize in monoclinic structure. The crystal structure of the undoped LACC crystal is found to be in good agreement with the reported literature (Kathleen *et al.,* 1993). It is noticed from the results that glycine doped LACC crystals crystallize in same structure with slight changes in the values of lattice parameters and it may be due to the incorporation glycine into the host LACC crystals.

Table 1. Unit cell constants for undoped and glycine doped LACC crystals

Sample	Unit cell constants	Volume of unit cell (Å)^3
Undoped LACC crystal	a = 16.242 (3) Å b = 7.274 (3) Å c = 7.987 (2) Å α = 90 °, β= 115.55° γ =90°	851.35
LACC crystal doped with 5 wt% of glycine	a = 16.258 (1) Å b = 7.301 (4) Å c = 7.957 (3) Å α = 90 °, β= 116.26° γ =90°	847.02
LACC crystal doped with 10 wt% of glycine	a = 16.254 (2) Å b = 7.268 (4) Å c = 7.979 (3) Å α = 90 °, β= 116.32° γ =90°	844.87
LACC crystal doped with 15 wt% of glycine	a = 16.249 (2) Å b =7.273 (1) Å c = 7.892 (2) Å α = 90 °, β= 115.87° γ =90°	839.21

SHG studies

Second harmonic generation (SHG) is an important phenomenon in non-centrosymmetric crystals and it is a second-order NLO activity. The Kurtz-Perry powder technique was used to find the SHG efficiency of the samples (Kurtz 1968). A laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. The technique is crude in the sense that it detects a convolution of all the tensor components of $\chi^{(2)}$and makes little attempt to account for the propagation characteristic of the beams. SHG is confirmed by emission of green light from the sample (λ= 532 nm) when the fundamental wavelength (1064 nm) from Nd:YAG laser is used. The relative SHG efficiency for undoped and glycine dopd LACC samples are given in the Table 2. From the results, it is observed that when LACC crystals are doped with glycine, a centrosymmetric material, the values of SHG efficiency decrease.

Table 2. Values of SHG efficiency for undoped and glycine doped LACC samples

Sample	Relative SHG efficiency Ref.: KDP
Undoped LACC crystal	0.87
LACC crystal doped with 5 wt% of glycine	0.80
LACC crystal doped with 10 wt% of glycine	0.74
LACC crystal doped with 15 wt% of glycine	0.68

Mechanical studies

Mechanical property of the samples was studied by measuring micro hardness number with various loads. The hardness of a material is a measure of its resistance to plastic deformation. The mechanical studies of the samples were made by Vickers hardness measurement at room temperature. Crystals, free from cracks, with flat and smooth surfaces were chosen for the static indentation tests. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 25 to100 g for a period of 10 s using Vickers diamond indenter attached to an incident ray research microscope. The length of the two diagonals of diamond indenter was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average was found out. For a particular load, at least three well defined indentations were considered and the average value (d) was selected. The Vickers hardness (H_v) numbers at different loads were calculated using the following relation H_v= 1.8544 P/d^2 where, 'P' is the applied load in kilogram and 'd' is the average diagonal length of the indentation marks in millimetre (Jothi mani *et al.,* 2013). The obtained results are plotted in the diagram 7. The undoped and glycine doped LACC crystals exhibit the reverse indentation size effect (RISE), in which the hardness value increases with the increasing load. From the results, it is observed that the hardness of LACC crystal increases when it is doped with glycine. This increase in the hardness value of doped sample can be attributed to the incorporation of glycine in the lattice of LACC crystal and hence the glycine doped LACC crystals have more mechanical strength.

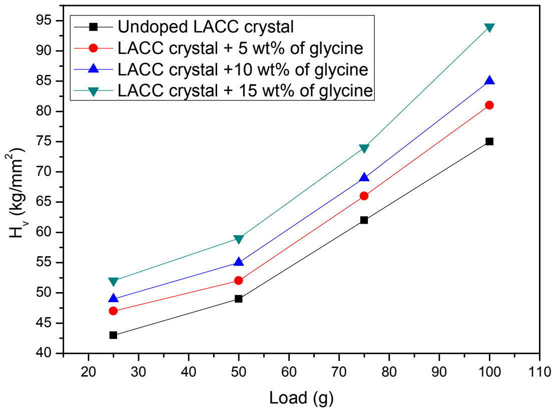

Fig.7. Variation of microhardness number (H_v) with the load for undoped and glycine doped LACC crystals

UV-visible spectral studies

UV-visible transmittance spectra are attributed to a process in which the outer electrons of atoms or molecules absorb radiant energy and undergo transitions to higher energy levels. The wavelength at which ultraviolet absorbance maximum is found and it depends upon the magnitude of the energy involved for a specific electronic transition. UV-visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm. A crystal of thickness 1.5 mm has been used in this study. The recorded UV-visible transmittance spectra of undoped and glycine doped LACC crystals are shown in Figure 8.

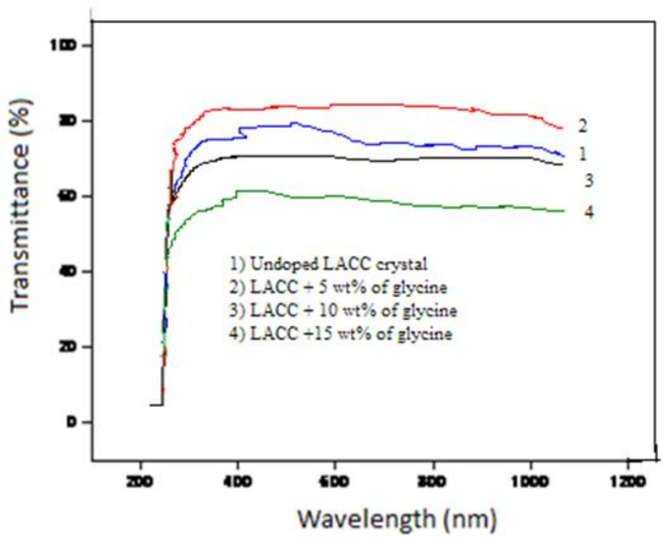

Figure 8. UV-visible transmittance spectra of undopd and glycine doped LACC crystals

From the transmittance spectra, it is noticed that pure LACC crystal has a transmittance of about 70% in the visible region and when LACC crystal is doped with 5 wt% of glycine, its transmittance seems to be increased. The transmittance is noticed to be decreased when LACC crystals are doped with 10 wt% and 15 wt% of glycine. A strong absorption is observed at

238 nm for undoped and glycine doped LACC crystals and this corresponds to the fundamental absorption and UV cut-off wavelength. From the results, it is clear that samples have good optical transparency in the complete visible region and it could be used for opto-electronic applications.

Laser damage threshold (LDT) studies

Laser damage threshold (LDT) studies for the samples were carried out using an Nd:YAG laser (1064 nm, 18 ns pulse width). The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). LDT value is determined using the formula $P = E/\pi r^2$ where E is the energy in mJ, r is radius of the spot in mm. The LDT value is one of the important device related properties of NLO crystals. LDT value is the maximum permissible power that can withstand in a particular crystal. The obtained values of LDT of the undoped and glycine doped LACC crystals are provided in the Table 3. From the results, it is observed that the values of laser damage threshold are more for the glycine doped LACC crystals than that of undoped LACC crystal.

Table 3. Values of LDT for undoped and glycine doped LACC samples

Sample	Values of LDT (GW/cm^2)
Undoped LACC crystal	0.25
LACC crystal doped with 5 wt% of glycine	0.28
LACC crystal doped with 10 wt% of glycine	0.32
LACC crystal doped with 15 wt% of glycine	0.37

Conclusion

Glycine doped L-alanine cadmium chloride crystals were successfully grown by solution method at room temperature using L-alanine, glycine and cadmium chloride as reactants. The grown samples have positive temperature coefficient of solubility and the nucleation kinetic parameters were determined. The grown crystals are observed to be crystallizing in orthorhombic structure. The hardness of L-alanine cadmium chloride (LACC) crystals are observed to be increased when glycine is added as the dopant into LACC crystal. The cut-off wavelength found for the grown crystals is at 238 nm and laser damage threshold value for LACC crystal is found to be increased when LACC crystal is doped with glycine. The SHG efficiency of glycine doped LACC crystals is measured with reference to that of KDP crystal.

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REFERENCES

Arun K.J., S. Jayalekshmi, 2008. Growth and Characterization of glycinium oxalate crystals for nonlinear optical applications, Optoelectron. *Adv. Mater. RapidCommun,* 2 (11), 701–706.

Bright K.C., T. H. Freeda, 2010. Growth and characterization of organomentallic L-alanine cadmium chloride single crystal by slow evaporation technique, *Physica*, B, 405, 3857–3861.

Dhanuskodi S., J. Ramajothi, 1993. Crystal Growth, thermal and optical studies of L-histidine Tetrafluoroborate-a Semiorganic NLO material, *Cryst. Res. Technol.,* 39 (2004) 592.

Dhanuskodi S., K. Vasantha, P.A. Angeli Mary, 2007. Structural and thermal characterization of semiorganic NLO material: L-alanine cadmium chloride, *Spectrochim. Acta. Part,* A 66, 637.

Eimerl D., S. Velsko, L. Davis, F. Wang, G. Loicono, G. Kennedy, 1989. Deuterated *L*-arginine phosphate: a new efficient nonlinear crystal, *IEEE J. Quantum Electron*. 25, 179.

Geetha D., M. Prakash, M.L. Caroline, P.S. Ramesh, 2011. Growth and characterization of the nonlinear optical single crystal: L-phenylalanine-benzoic acid, *Adv. Appl.Sci. Res.,* 2 (2) 86–92.

Jothi Mani R., P. Selvarajan, H. Alex Devadoss, D. Shanthi, 2013. Metastable Zone Width, Nucleation Parameters and other Studies of L-alanine Hydrogen Chloride (LAHC) Crystals Grown by Slow Cooling Technique, *Advances in Optoelectronic Materials* 1, 67-73.

Kalaiselvi P., S. Alfred Cecil Raja, N. Vijayan, 2013. Growth structural, spectral, optical and mechanical studies of gamma bis glycinium oxalate (GBGOx) new NLO single crystal by SEST method, Optik 124, 6978– 6982.

Kanagadurai R., R. Durairajan, R. Sankar, G. Sivanesan, S. P. Elangovan, R. Jayavel, 2010. Determination of Metastable Zone Width, Induction Period and Interfacial Energy of a Ferroelectric Crystal - Potassium Ferrocyanide Trihydrate (KFCT), *E-Journal of Chemistry* 7(1) 137-142.

Kathleen I. Schaffers, Douglas A. Keszler, 1993. Structure of CdCl2.C3H7NO2, Acta Cryst. C 49, 1156.

Kurtz S.K., T.T. Perry, 1968. A Powder Technique for the Evaluation of Nonlinear. Optical Materials,*J. Appl. Phys.,* 39, 3798–3813.

Mohan Kumar R., N. Gopalakrishnan, R. Jayavel, P. Ramasamy, 1999**.** Investigations on the Nucleation Kinetics of L-Arginine Phosphate single crystals, *Cryst. Res. Technol*. 341265.

Monaco S.B., L.E. Davis, S.P. Velso, F.T. Wang, D. Eimerl, A. 1987. Synthesis and Characterization of Chemical Analogs of l-Arginine Phosphate, *J.Cryst. Growth,* 85, 252.

Razzetti C., M. Ardoino, L. Zanotti, M. Zha, C. Parorici, 2002. Solution Growth and Characterisation of L-alanine Single Crystals, *Cryst. Res. Technol*., 37, 456-465.

Selvarajan P., J. Glorium Arul Raj, S. Perumal, 2009. Characterization of pure and urea doped gamma glycine crystals, *J. Cryst. Growth,* 311, 3835–3840.

Siva Dhas A., P. Selvarajan, T. H. Freeda, 2009. Nucleation Kinetics, Growth and XRD Studies of undoped and Zinc Sulfate-doped Triglycine Sulpho-Phosphate (TGSP) Crystals, *J. Mater.Manufact. Process*, 24, 584.

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