International Journal of Innovative Research in Advanced Engineering (IJIRAE) ISSN: 2349-2163
Issue 1, Volume 2 (January 2015) www.ijirae.com

Characterization of thiourea doped L-alanine Cadmium Chloride (LACC) crystals grown by slow evaporation technique

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***Abstract*— Thiourea doped L-alanine cadmium chloride (LACC) crystals were grown by slow evaporation technique. Solubility was measured for the samples at different temperatures from 30 °C to 50 °C and found that it decreases with temperature. Nucleation kinetic studies and metastable zone width of the samples were carried out to understand the nucleation processes. XRD studies have been carried out to identify the crystal structure. Microhardness was measured to find the suitability of the grown crystals for device fabrication. SHG efficiency, laser damage threshold (LDT) values and impedance analysis was performed for the samples and the results are discussed in the paper.**

***Key words-* L-alanine complex; doping; characterization; XRD; SHG; laser damage; hardness; impedance**

I. INTRODUCTION

Nonlinear Optics (NLO) is a study of interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude. New nonlinear optical frequency conversion materials have a significant impact on optical computing, laser technology, optical communication, data storage technology, signal processing and instrumentation [1,2]. Most of the amino acids and their complexes belong to the family of organic and semiorganic nonlinear optical (NLO) materials. L-alanine is a naturally occurring chiral amino acid and amino acid based organometallic crystals like L-alanine cadmium chloride, L-arginine phosphate, L-histidine tetra fluroborate, L-alanine hydrogen chloride etc have been studied and they have large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [3-5]. Thiourea is a nonlinear optical material and it is used to improve the various physical and chemical properties of organo-metallic crystals like L-alanine cadmium chloride. The aim of the work is to grow undoped and thiourea doped L-alanine cadmium chloride (LACC) crystals and to subject the grown crystals to various studies such as solubility, nucleation kinetic studies, XRD studies, SHG studies, hardness studies, laser damage threshold (LDT) studies and impedance studies.

II. EXPERIMENTAL

L-alanine (99% purity) and analar grade cadmium chloride monohydrate were purchased commercially and they were taken in 1:1 molar ratio to prepare L-alanine cadmium chloride (LACC) salt. The solvent used here is double distilled water. The dissolved saturated solution was heated at 55 °C for the synthesis of LACC salt. To obtain the thiourea doped LACC salts, 5 wt%, 10 wt% and 15 wt% of thiourea was added into the solutions of L-alanine cadmium chloride separately. Single crystals of undoped and thiourea 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. After a period of 30-35 days, crystals were harvested and used for characterization 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. Mechanical property was studied by measuring micro hardness of the grown crystal and this was carried out using Vickers microhardness tester of Shimadzu Model HMV 2T fitted with a diamond indenter. Indentations were made for various loads from 25 g to 100 g. SHG efficiency of the grown crystal was measured by Kurtz and Perry Powder technique [6]. The fundamental beam of 1064 nm from a laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. 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. Laser damage threshold (LDT) values for the samples were measured 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).

III. RESULTS AND DISCUSSION

3.1 Measurement of solubility and nucleation kinetic parameters

Solubility of the grown samples was measured by gravimetrical method. Fig.1 shows the solubility curves for undoped and thiourea doped L-alanine cadmium chloride samples and it is observed that the solubility of samples in water increases with temperature. Nucleation kinetic studies have been carried out by measuring the induction period. 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 supersaturation 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. 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 [7]. Results of induction period for undoped and thiourea 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 table 1. It is observed that the induction period decreases with increase of supersaturation ratio. 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 supersaturation and they decrease when concentration of thiourea is increased in the solutions of LACC. The nucleation rate is observed to be increasing with the supersaturation ratio and it increases when LACC sample is doped with thiourea.

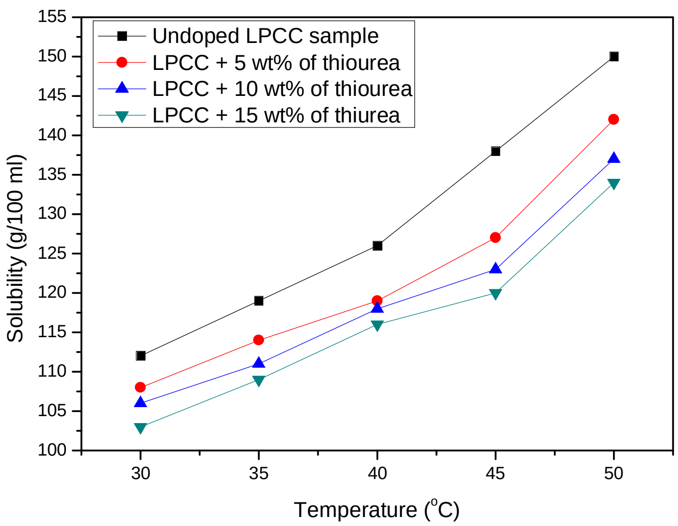

Fig.1: Solubility curves of undoped and thiourea doped L-alanine cadmium chloride (LACC) samples

Table 1: Values of nucleation kinetic parameters for pure and thiourea doped LACC samples

Sample	S	$\sigma \times 10^{-3}$ (J /m^2)	r^* (10^{-9} m)	n	$\Delta G^* \times 10^{-20}$ (kJ/mole)	$J \times 10^{23}$ (nuclei/ s/volume)
LACC added with 5 wt% of thiourea	1.3	2.67	3.92	18	0.392	3.93
	1.35		3.82	14	0.371	4.12
	1.4		3.34	11	0.352	4.32
	1.45		3.02	9	0.316	4.70
	1.5		2.63	8	0.297	4.92
LACC added with 10 wt% of thiourea	1.3	2.24	3.85	16	0.362	4.17
	1.35		3.72	12	0.346	4.53
	1.4		3.12	10	0.312	4.74
	1.45		2.84	8	0.283	4.98
	1.5		2.72	6	0.264	5.32
LACC added with 15 wt% of thiourea	1.3	1.95	3.64	14	0.332	4.42
	1.35		3.56	10	0.304	4.68
	1.4		3.02	9	0.273	4.90
	1.45		2.74	7	0.252	5.24
	1.5		2.56	5	0.224	5.85

3.2 Crystal structure and SHG efficiency

Crystal structure of the grown samples was obtained by using a single crystal X-ray diffractometer and the obtained values of undoped LACC crystal are a = 16.242 (3) , b = 7.274 (3) , c = 7.987 (2) , □□□□□□□□□□□α = 90 ^{o}, β= 115.55^o and □□□□□□□□□□□□□□□□γ□=90^o. The obtained values for 10 wt% of thiourea added LACC crystal are a = 16.310 (2) , b = 7.285 (1) , c = 7.992 (3) , □□□□□□□□□□□α = 90 ^{o}, β= 113.47^o and □□□□□□□□□□□□□□□□γ□=90^o. From the XRD data, it is observed that undoped and thiourea doped LACC crystals crystallize in monoclinic structure. It is noticed from the results that thiourea doped LACC crystals crystallize in same structure with slight changes in the values of lattice parameters.

For measuring Second Harmonic Generation (SHG) efficiency, Nd:YAG laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. 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 thiourea doped LACC samples are given in the table 2. From the results, it is observed that when LACC crystals are doped with thiourea, the values of SHG efficiency increase and found that thiourea doped LACC crystals are the better candidates for NLO applications.

Table 2: Values of SHG efficiency of the samples

Sample	Relative SHG efficiency Reference: KDP
Undoped LACC crystal	0.87
LACC crystal doped with 5 wt% of thiourea	0.95
LACC crystal doped with 10 wt% of thiourea	1.10
LACC crystal doped with 15 wt% of thiourea	1.22

3.3 Impedance studies

Electrical impedance describes a measure of opposition to alternating current (AC). And it extends the concept of resistance to AC circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. Complex impedance Z^* is given by $Z^* = Z' - jZ''$ where Z' is the real part of impedance, Z'' is the imaginary part of impedance [8]. The plots of real part of impedance (Z') with frequency for undoped and thiourea doped L-alanine cadmium chloride samples at 40 ^{o}C are given in the figure 2. It is observed that the values of Z' decrease with frequency. The higher values of Z' at lower frequencies and low temperatures means the polarization is larger. The frequency dependence of the imaginary part of impedance (Z'') is plotted for the thiourea doped LACC samples is shown in the figure 3. From the results, it is noticed that both the real part and imaginary part of impedance decrease when LACC crystals doped with thiourea. When thiourea is added as the dopant into the interstitial positions of the lattice of LACC crystals, the conductivity of the samples increases and hence the impedance decreases.

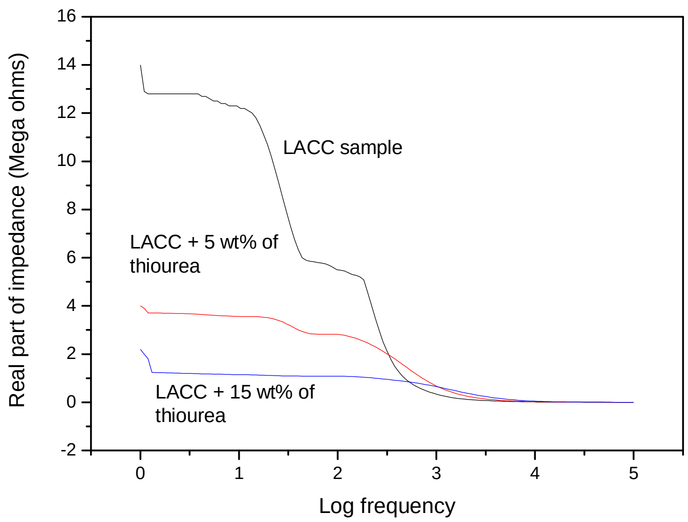

Fig.2: Variation of real part of impedance with frequency for undoped and thiourea doped LACC samples at 40 ^{o}C.

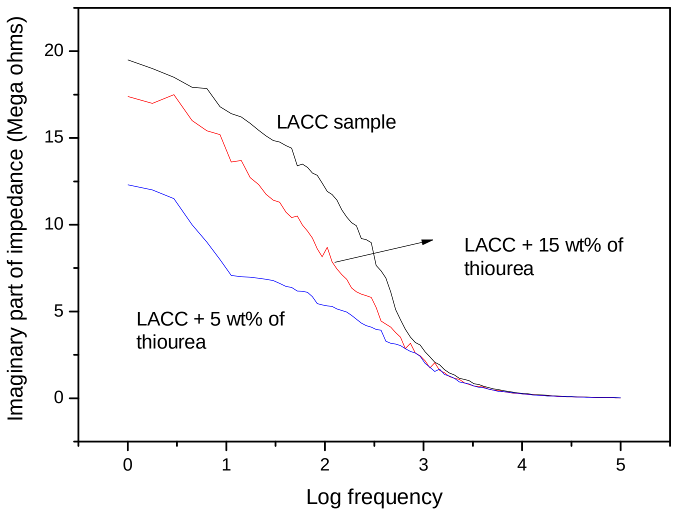

Fig.3: Variation of imaginary part of impedance with frequency for undoped and thiourea doped LACC samples at 40 °C

3.4 LDT measurement

Laser damage threshold (LDT) measurement for the samples was done 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). The LDT value (power density) was determined using the formula $P = E/\pi\tau r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm. The obtained values of LDT of the undoped and thiourea doped LACC crystals are given in the table 3. From the results, it is observed that the values of laser damage threshold are low for the thiourea doped LACC crystals than that of undoped LACC crystal. The values of LDT for grown crystals are observed to be close to that of KDP (0.2 GW/cm^2) crystal.

Table 3: Values of laser damage threshold for thiourea doped L-alanine cadmium chloride samples

Sample	Values of LDT (GW/cm^2)
Undoped LACC crystal	0.25
LACC crystal doped with 5 wt% of thiourea	0.22
LACC crystal doped with 10 wt% of thiourea	0.20
LACC crystal doped with 15 wt% of thiourea	0.17

3.5 Measurement of microhardness

The hardness of a material is a measure of its resistance to plastic deformation. The microhardness is the hardness when a crystalline sample is subjected to low applied loads. Vickers hardness measurement at room temperature was carried out using a Vickers hardness tester. Crystals, free from cracks, with flat and smooth surfaces were chosen for the static indentation tests. The selected face of crystal was indented gently by loads varying from 25 to100 g for a period of 10 s using Vickers diamond indenter. 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 value of indentation (d) was found out. The Vickers hardness (H_v) number was determined using the formula $H_v = 1.8544\ P/d^2$ where, 'P' is the applied load in kilogram and 'd' is the average diagonal length of the indentation marks in millimetre [9]. The variation of microhardness with the applied load for thiourea doped LACC crystals are shown in the figure 4. The results show that the hardness increases with increase in the applied load showing the reverse indentation size effect. Hardness is observed to be decreasing when LACC crystals are doped with thiourea and it is due to loosening of bond strength of the samples [10].

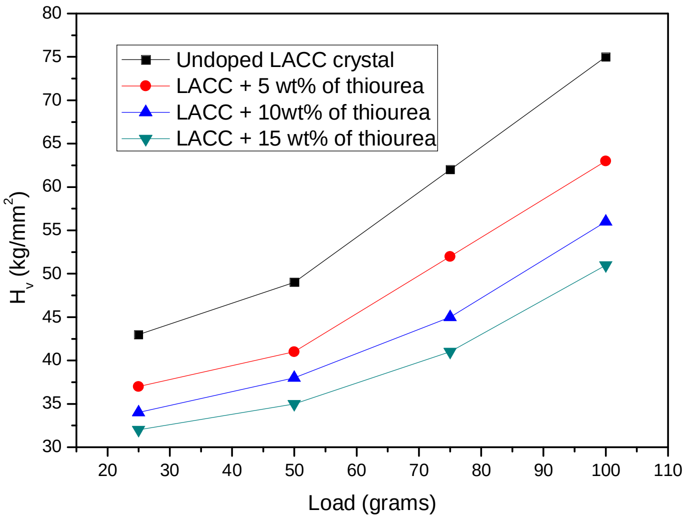

Fig.4: Plots of microhardness number (H_v) with the load for undoped and thiourea doped LACC crystals

IV.CONCLUSIONS

Pure and thiourea doped L-alanine cadmium chloride salts were synthesized and solubility measurement was measured at different temperatures. Single crystals of the synthesized salts were grown by slow evaporation technique. Nucleation kinetic parameters of the samples were evaluated by measuring the induction period by isothermal method. The crystal structure of the samples is found to be orthorhombic structure. Real and imaginary part of the samples have been measured at various frequencies and found that these parameters decrease with increase of frequency. The hardness and LDT values of L-alanine cadmium chloride crystals are observed to be decreased when LACC crystals are doped with thiourea. The undoped and thiourea doped LACC crystals are found to be second harmonic generators and visible laser light generating crystals.

ACKNOWLEDGEMENT

The authors like to thank the supported works from various research centers such as M.K. University (Madurai), PSN College of Engineering, Tirunelveli, St. Joseph College (Trichy), VIT, Vellore and Crescent Engineering College (Chennai). Also the authors are thankful to the management of Aditanar College of Arts and Science, Tiruchendur, St.Jude's College, Thoothoor and Scott Christian College, Nagercoil for the encouragement given to us to carry out the research work.

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