

Growth, Spectroscopic, Dielectric and Non Linear Optical Studies of Strontium Metal Ion Doped Novel Semi-Organic L-Alanine Cadmium Chloride

T. Retnakumar, R. Ilangoan*

Department of Nanoscience and Technology,
Alagappa University, Karaikudi – 630 004, India.

K. Sankaranarayan

School of Physics, Alagappa University
Karaikudi – 630 004, India

K. C. Bright

Department of Physics, St. John's College,
Anchal, Kollam – 691 306, India.

T. H. Freeda

Crystal Research Centre, S.T. Hindu College,
Nagercoil – 629 00 , India.

S. Vinu

Department of Physics,
Kamarajar Government Arts College,
Surandai, Tirunelveli – 627 859, India

Abstract— The single crystals of pure and strontium metal ion doped L-alanine cadmium chloride, a semi-organic compound was grown by slow evaporation solution growth technique at room temperature. The grown crystals were subjected to various characterization techniques such as single crystal and powder XRD, scanning electron microscopy (SEM), energy dispersive X-ray spectrum (EDX), FT-IR and UV-Visible spectroscopy. The presence of various functional groups has been identified by FT-IR spectral analysis ranging between 4000 and 400 cm^{-1} and the UV-vis-NIR spectroscopic study revealed that the grown crystal has good optical transmittance. Its nonlinear optical property has been studied by Kurtz powder method. Electrical parameters such as dielectric constant and dielectric loss have also been studied from 100 to 1 MHz. The low dielectric constant and dielectric loss suggested that this material is a good candidate for opto-electronic applications.

Keywords: Sr doped L-alanine, Single crystal XRD, Dielectric constant, NLO.

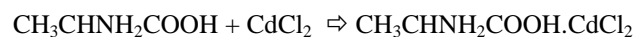
I. INTRODUCTION

Semi-organic crystals attracted the scientific community very much due to their large nonlinear optical coefficients, high resistance to laser induced damage, low angular sensitivity and excellent mechanical hardness. Also advanced opto-electronic technology requires nonlinear optical (NLO) materials for frequency conversion, optical modulation and optical switching [1]. The recent development in optical fiber communication has motivated the scientists to search for new NLO materials that are capable of fast and efficient processing of optical signals and hence the researchers are always in search for new NLO materials [2]. Recently, amino-acid based materials have been proved to be attractive materials for NLO applications,

because they contain a proton donating carboxyl group as well as proton accepting amino group in them. Owing to the excellent results of amino acid based semi-organic materials such as l-alanine cadmium chloride [3], l-asparagine thiourea monohydrate [4] and l-valine cadmium chloride [5], they are considered as best materials for NLO applications. Inspired by these results, in this present work Sr^{2+} ion doped LACC crystals were grown and subjected to different characterization in order to know its suitability for NLO applications.

II. EXPERIMENT

The strontium ion doped LACC was synthesized using L-alanine, cadmium chloride and one mole percent of strontium chloride. At first the parent LACC compound was synthesized from the equimolar ratio of L-alanine and cadmium chloride, according to the following reaction:



Along with the compound solution, one mole percentage of strontium chloride was added to get the Sr^{2+} ion doped LACC crystal. The calculated amount of the reactants were thoroughly dissolved in double distilled water and stirred well for 2 hours using a magnetic stirrer to obtain a homogeneous mixture. Then the mixture was evaporated to dry the material. The temperature was kept to below an optimum temperature of 60 $^\circ\text{C}$, to prevent the possible decomposition. It was then dissolved thoroughly in double distilled water to form a saturated solution. The solution was filtered well to remove the suspended impurities and allowed to crystallize by slow evaporation of solvent at room

temperature of about 30 °C for four weeks. Well defined single crystals (size up to 20 x 15 x 4 mm³) with good transparency were collected in four weeks. The size of the pure crystal is about 12 x 7 x 2 mm³ [Figure 1].

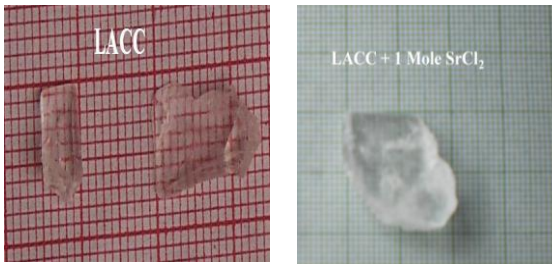


Figure 1: The single crystals of undoped and Strontium ion doped L-alanine cadmium chloride single crystal.

The LACC crystal was subjected to single crystal XRD using a computer controlled Enraf Nonius-CAD4 single crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) to determine the unit cell dimensions and morphology.

Phase analysis of the grown crystals has been done using powder XRD (*Philips X'pert Pro*) equipped with an *X'celerator* and a mono-chromator at the diffracted beam side. The X-ray scans were made in 2θ and at 0.01 degree/step for all the samples. Scans were done using CuK α radiation with a tube voltage of 40 kV and current 30 mA by exposing a constant area of the sample. The phase identification of the samples was performed using *X'pert High score* software in support with the *ICDD-PDF-2* data base.

The surface morphology of the samples have been observed using a scanning electron microscope (SEM) JEOL-JSM 5600 LV model, in back scattered mode and is operated at 20 kV. The elemental analyses of the samples were carried out using JEOL JSM 5600 LV equipped with EDAX.

The FTIR spectrum of the sample was recorded with a Fourier transform infrared spectrometer in the range of 400–4000 cm⁻¹ by KBr pellet technique. The optical transmittance range determine the suitability of strontium ion doped LACC single crystals for optical applications, the UV-Vis-NIR spectrum was recorded with a Varian Cary 100 Bio UV-Vis spectrophotometer in the range 200-2500 nm. The powder SHG measurements were performed using the Kurtz and Perry powder technique. The fine powdered sample was densely packed between two transparent glass slides. A fundamental laser beam of 1064 nm wavelength (8 ns pulse width with 10 Hz pulse rate) from an Nd-YAG LASER was made to fall normally on the sample cell and the incident beam was measured using a power meter. The input laser energy incident on the capillary tube was 5.3 mJ per pulse, an energy level optimized not to cause any chemical decomposition in the sample. The KDP crystal was used as the reference material in the SHG measurement. The well grown crystals were polished in proper size and the graphite coating was applied on the opposite faces of the samples for good electrical contact. Agilent 4284 A, Precision LCR meter was used for the measurement of the capacitance and dielectric loss in the frequency range of 100 Hz -1MHz at the temperature range of 30 – 110 °C along the b-axis of the crystal.

III. RESULTS AND DISCUSSION

There are lot of reports on growth and characterization of LACC single crystals with some dopants. The statues of dopants are still dispute [6]. In order to reveal the dopants, the single crystal XRD was carried out. The unit cell dimensions of pure LACC obtained from single crystal X-ray diffraction analysis are $a = 16.33$, $b = 7.31$, $c = 8.00 \text{ \AA}$, cell volume $V = 854 \text{ \AA}^3$, $\alpha = \gamma = 90^\circ$ and $\beta = 116.44^\circ$. Similarly for strontium doped LACC crystals, the unit cell parameters obtained from the single crystal X-ray diffraction analysis are $a = 16.352 (\pm 0.011) \text{ \AA}$, $b = 7.303 (\pm 0.005) \text{ \AA}$, $c = 7.978 (\pm .006) \text{ \AA}$, cell volume $V = 851.7 (\pm 1.7) \text{ \AA}^3$, $\alpha = \gamma = 90^\circ$ and $\beta = 116.62 (\pm 0.03)^\circ$. The powder XRD pattern of pure and strontium doped LACC crystals are shown in Figure 2 (a) and (b), which consists of peaks, corresponds to LACC, and no other peaks of other phase or element are detected within the detection limit of the instrument. The unit cell dimensions calculated from the powder XRD data for pure LACC are $a = 16.275 (\pm 0.002)$, $b = 7.265 (\pm 0.002)$ and $c = 7.97 (\pm 0.002) \text{ \AA}$, cell volume $V = 843.786 (\pm 0.002) \text{ \AA}^3$, $\alpha = \gamma = 90^\circ$ and $\beta = 116.44^\circ$. For strontium doped LACC, $a = 16.325 (\pm 0.004)$, $b = 7.331 (\pm 0.002)$ and $c = 7.947 (\pm .005) \text{ \AA}$, cell volume $V = 850.26 (\pm .05) \text{ \AA}^3$. It agrees with the reported values [7]. The grown crystal belongs to the monoclinic system with space group C2 and the number of molecules per unit cell (Z) is 4. It shows that the dopant Sr²⁺ ion does not alter the crystal structure, but it enters into the crystal lattice of pure LACC.

Figure 3 shows the SEM images of pure and strontium chloride doped LACC crystals. From the SEM images it was observed that due to strontium chloride doping there is a slight improvement in the alignment of grains and it may be due to the bunching of small grains around the impurity atom. Figure 4 shows the EDX images of pure and strontium chloride doped LACC crystals. From the EDX analysis it was observed that the Sr²⁺ ions are successfully doped into the crystal lattice of LACC.

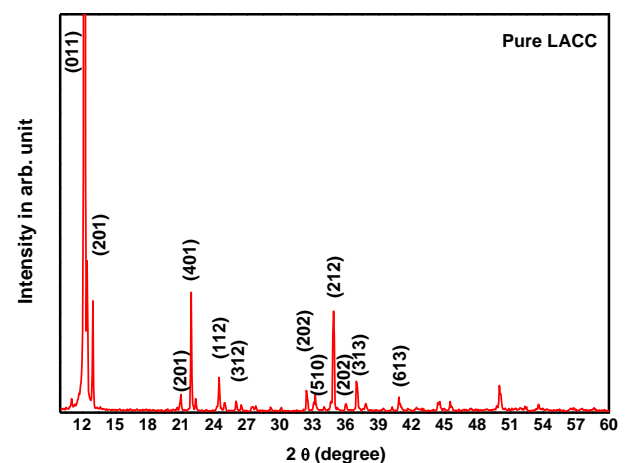


Figure 2: (a) The powder X-ray diffraction pattern of pure

strontium chloride doped crystal increases with respect to pure LACC single crystals. The results are given in Table 1.

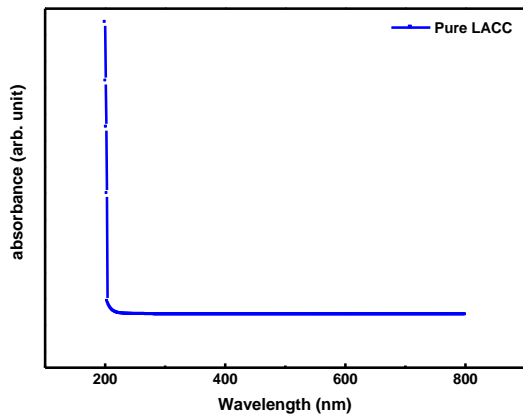


Figure 6: (a) The UV - Vis - NIR spectrum of pure L-alanine cadmium chloride

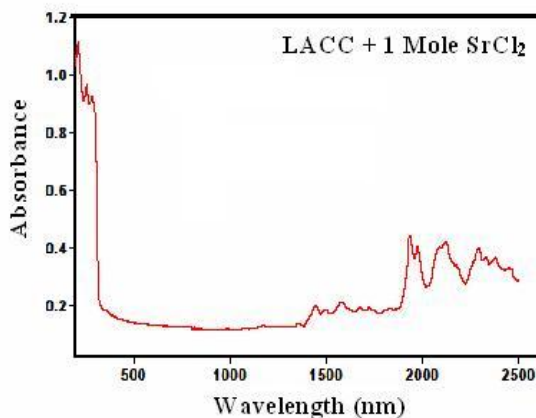


Figure 6: (b) The UV - Vis - NIR spectrum of one mole percentage strontium ion doped L-alanine cadmium chloride

Input power mJ/pulse	KDP mV	LACC mV	LACC + 1 Mole SrCl ₂ mV
5.3	17	9.7	14

Table 1: Comparison of SHG signals energy output.

Figure 7 (a) and (b) shows the variation of dielectric constant with respect to frequencies at different temperature for undoped and strontium ion doped LACC single crystals respectively. The dielectric constant increases with decrease of frequency and increase of temperature. The variations of dielectric constant with frequency suggest the presence of higher space charge polarization of the material decreases with increase of frequency, which leads to the reduction of dielectric constant [10]. Also the increase of dielectric constant with increase of temperature was due to the presence of space charge polarization near the grain boundary interfaces which depends on the purity of the sample. Again as compared with pure LACC single crystals, a slight increase of dielectric constant in the doped crystals is due to

the increase of polarisability of the dipoles caused as a result of the improvement in grain alignment.

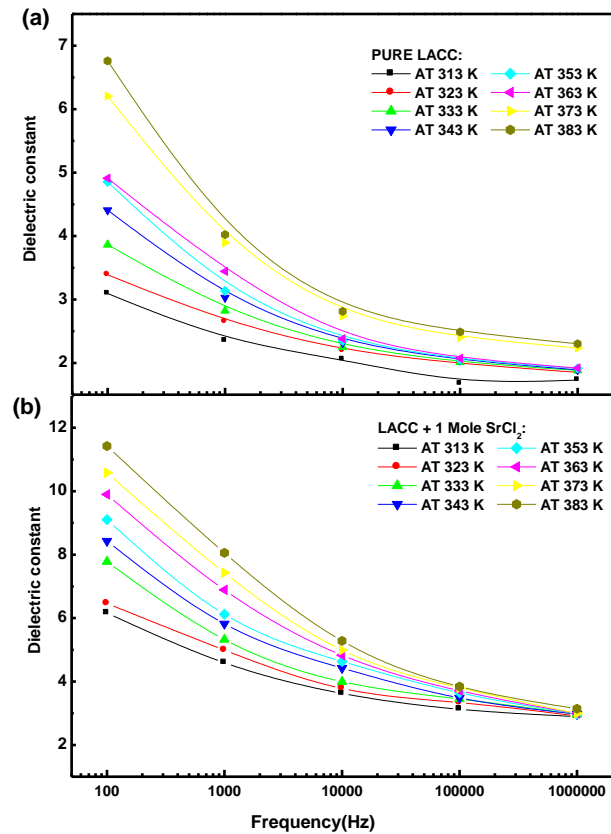


Figure 7: (a) Variation of dielectric constant with frequencies for different temperature of pure and (b) Strontium ion doped L-alanine cadmium chloride.

Figure 8 (a) and (b) shows the variation of dielectric loss with respect to frequencies at different temperature for undoped and one mole percentage strontium chloride doped LACC single crystals respectively. The nature of the curves show that the dielectric loss decreases with increase of frequency and decrease of temperature. Generally dielectric crystal can be represented by the circuit analog of resistance in parallel with capacitor. At higher frequency the capacitor offers low reactance to the sinusoidal signal, which minimizes the conduction losses in the resistor. Hence the value of dielectric loss decreases at higher frequencies. Again the material with low dielectric constant will have less number of dipoles per unit volume. As a result it will have minimum loss as compared to the material with high dielectric constant [11]. It suggests that the dielectric loss strongly depends on the frequency of the applied field which is similar to the dielectric loss in the ionic system. Again, figure 8 (a) and (b) shows that the dielectric loss of doped crystal increases slightly at lower frequencies. It may be due to higher relaxation time of the dipoles at lower frequencies and hence consume much power than that at higher frequencies.

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REFERENCES

1. H.O. Marcy, L. F. Warren, M. S. Webb, C. A. Ebberts, S. P. Velsko, G. C. Catella, Second harmonic generation in zinc tris(thiourea) sulfate, *Appl. Opt.* 31(1992) 5051-5060.
2. H. Nalwa, S. Miyata, *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, New York, 1997.
3. S. Dhanuskodi, K. Vasantha, Mary, P. A. Angeli, Structural and thermal characterization of a semiorganic NLO material: l-alanine cadmium chloride, *Spectrochim. Acta Mol. Biomol. Spectrosc* 66 (2007) 637-642.
4. Prakash, J. Thomas Joseph, S. Kumararaman, Growth and characterization of l-proline cadmium chloride monohydrate single crystals, *Mater. Lett.* 62 (2008) 4097-4099.
5. P. Maadeswaran, J. Chandrasekaran, Synthesis, growth and characterization of l-valine cadmium chloride monohydrate-A novel semiorganic nonlinear optical crystal, *Optik* 122 (2011) 1128-1131.
6. A. M. Petrosyan, V. V. Ghazaryan, M. Fleck, On the existence of "l-threonine formate", "l-alanine lithium chloride" and "bis l-alanine lithium chloride" crystals, *Spectrochim. Acta Mol. Biomol. Spectrosc* 105 (2013) 623-625.
7. I. Kathleen. Schaffers, A. Douglas. Keszler, *Acta Cryst. C* 49 (1993) 1156 - 1158.
8. K. Nagamoto, *IR Spectra of Organic and Coordination Compounds*, 2nd ed., Wiley Interscience, New York, (1978).
9. R. Silverstein, G. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, (1981).
10. S. K. Aroa, V. Patel, B. Amin, A. Kothari, Dielectric behavior of strontium tartrate single crystals, *Bull. Mater. Sci.* 27 (2004) 141-147.
11. S. Sohma, H. Takashashi, T. Taniuchi, H. Ito, Organic nonlinear optical crystal DAST growth and its device applications, *Chem. Phys.* 245 (1999) 359-364.

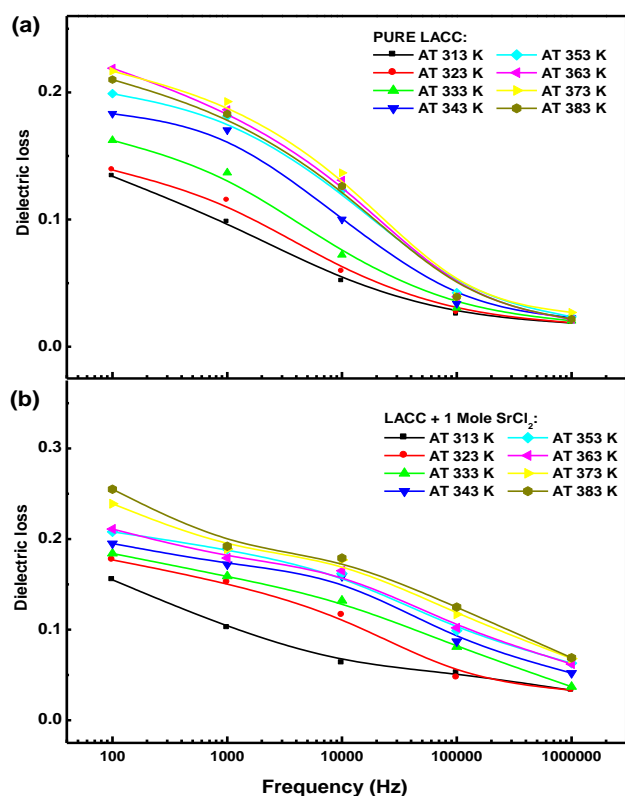


Figure 8: (a) Variation of dielectric loss with frequencies for different temperature of pure and (b) one mole percentage strontium ion doped L-alanine cadmium chloride.

CONCLUSIONS

The single crystals of pure and strontium chloride doped L-alanine cadmium chloride were grown by slow evaporation technique and characterized by both single crystal and powder X-ray diffraction studies, which showed the presence of Sr in the LACC single crystals. SEM study shows that the alignments of grains are improved in strontium doped single crystals and the presences of strontium ions in the crystal lattice of LACC crystals are also confirmed by EDS analysis. The FT-IR spectral analysis confirms the presence of functional groups in the compound. The material has good optical transparency in the entire visible region with a lower cut of wave length at 200 nm. The higher space charge polarization present in lower frequency region increases the dielectric constant at lower frequency and it is further increased due to the incorporation of Sr^{2+} ion into the lattice of pure LACC. The NLO property is confirmed by SHG measurement and its value is 0.82 times the value of KDP where as for pure LACC single crystals it is only 0.57 times. The second harmonic efficiency is remarkably enhanced by the Sr^{2+} ions and hence the strontium ion doped LACC crystals are used along with laser devices for frequency conversion and also the low values of dielectric constant and dielectric loss at higher frequency suggests that this material is a good candidate for opto electronic applications.