Asian Journal of Chemistry Vol. 22, No. 1 (2010), 109-114

Synthesis, Structural, FT-IR and Non-Linear Optical Studies of Pure and Lanthanum Doped L-Arginine Acetate Single Crystals

P. GNANASEKARAN† and J. MADHAVAN*
Department of Physics, Loyola College, Chennai-600 034, India
Fax: (91)(44)28175566; Tel: (91)(44)28178200
E-mail: jmadhavang@yahoo.com

Single crystals of pure and La^{3+} doped L-arginine acetate have been successfully grown from aqueous solution by slow evaporation technique. The grown crystals were confirmed by powder X-ray diffraction studies. The optical properties of the crystals were studied by FT-IR and UV-Vis-NIR spectral techniques and the influence of the La^{3+} is reported. The second harmonic generation efficiencies of the crystals were confirmed by Kurtz and Perry powder technique.

Key Words: Organic, Non-linear optics, Single crystal, Rare earth dopants.

INTRODUCTION

Recent studies reveal that L-arginine acetate possesses excellent optical, properties, which make it a strong candidate material for photonic device fabrications[1]. L-arginine acetate is one of the recently developed members of the L-arginine phosphate (LAP) family and it has been identified as a promising organic nonlinear material[2]. The powder SHG efficiency of L-arginine acetate was found to be three times that of potassium dihydrogen phosphate (KDP)[3]. The present investigation deals with the growth of pure L-arginine acetate and metal (La^{3+}) doped L-arginine acetate crystals by slow solvent evaporation technique. The grown crystals are subjected to powder X-ray diffraction to estimate the crystal structure and space group. The presence of La^{3+} ions were confirmed by inductive coupled plasma (ICP) studies. The optical properties of L-arginine acetate were studied using UV-Vis-NIR spectral studies. The FT-IR and NLO studies of the sample were also carried out.

EXPERIMENTAL

Equimolar quantity AR grade L-arginine and acetic acid were taken and dissolved in double distilled water to prepare the aqueous solution of LAA. The reaction that takes place between L-arginine and acetic acid in water medium is as follows:

$$(NH_2)NHCNH(CH_2)_3CH(NH_2)COOH + CH_3COOH \longrightarrow$$
$$(NH_2)_2{}^+ CNH(CH_2)_3CH(NH_3)^+ COO^- CH_3COO^-$$

†Department of Physics, C. Kandaswami Naidu College for Men, Chennai-600 102, India.

The synthesized salt of pure and doped LAA was utilized for the growth of the crystals. Pure and doped LAA single crystals were grown using slow solvent evaporation technique at 30 ºC. The growth of metal substituted crystal is achieved using the same procedure by adding dopant of 2 mole % concentration of La^{3+} to the L-arginine acetate solution. The pH of the solution was carefully noted and adjusted using HCl. Well developed and optically good quality single crystals were grown from the supersaturated L-arginine acetate solution of pH value 4.5. Transparent and defect free single crystals of pure and doped L-arginine acetate single crystals were grown in a period of 40-50 days. Fig. 1 shows the photographs of grown single crystal of both pure and doped L-arginine acetate.

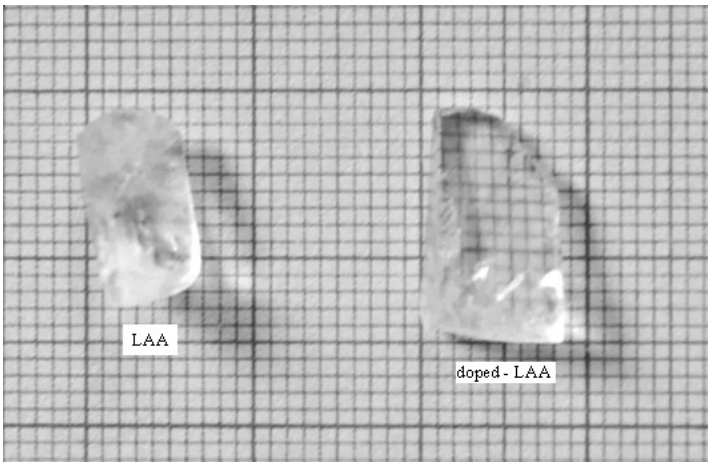

Fig. 1. As grown photographs of pure and lanthanum doped crystals

RESULTS AND DISCUSSION

Powder X-ray diffraction studies: The unit cell parameters of pure L-arginine acetate and doped L-arginine acetate single crystals were collected by subjecting the samples to powder XRD analysis using RICH SEIFERT, XRD 3000P with monochromatic nickel filtered CuK_α ($\lambda = 0.15406$ nm) radiation X-ray diffractometer and it is shown in Figs. 2 and 3, respectively. The calculated lattice parameter value of both the samples indicates that both the pure and doped L-arginine acetate crystallize into monoclinic system and belong to the space group of P21 and they are presented in Table-1. The results agree well with the reported values[3].

ICP analysis: The result of the ICP analysis show that 11 ppm of lanthanum entered into the L-arginine acetate. Hence it follows that the amount of dopant ions in the crystal is far below the concentration of dopant in the mother solution. The low incorporation of dopant may be due to the difference in ionic radii of acetate in L-arginine acetate and rare-earth ions.

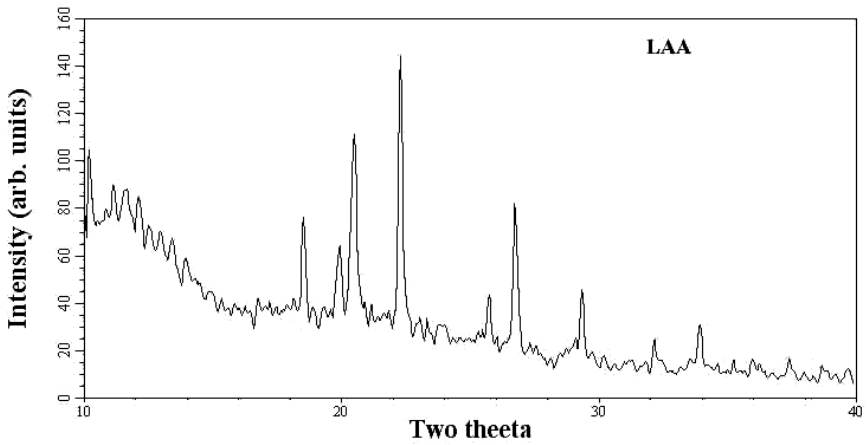

Fig. 2. Powder XRD pattern of L-arginine acetate (LAA)

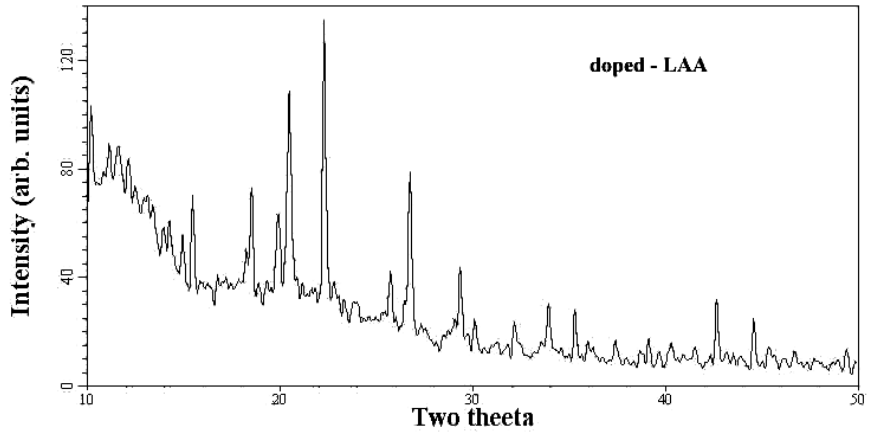

Fig. 3. Powder XRD pattern of La^{3+} doped L-arginine acetate (LAA)

TABLE-1
POWDER XRD DATA OF PURE AND DOPED LAA CRYSTALS

Lattice parameters	LAA	Doped-LAA
a (Å)	9.311	9.111
b (Å)	5.201	5.310
c (Å)	13.111	12.701
α°	90	90
β°	109	107
γ°	90	90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Volume (Å^3)	587.09	571.13

FT-IR Studies: The middle infrared spectrum of L-arginine acetate is shown in Fig. 4. The spectrum shows a broad envelope between 2100 and 3500 cm^{-1}. It is due to overlapping of peaks of NH(NH_3^+) vibrations, OH(COOH) and CH(CH_2 and CH_3). The C=O stretch of COO^- gives its peak at 1689 cm^{-1} whereas the asymmetric NH bend of NH_3^+ shows its peak at 1639 cm^{-1}. The corresponding symmetrical NH bend is assigned to the peak at 1532 cm^{-1}. All these peaks overlap and produce broad intense envelope. In this envelope, the peak due to asymmetric CO_2 stretch is observed at 1400 cm^{-1}. All the other peaks below 1400 cm^{-1} are due to COO^- and other bending modes. The torsional NH oscillations of NH_3^+ give its peak at 543 cm^{-1}. The FT-IR spectra of La^{3+} doped L-arginine acetate are shown in Fig. 5. This spectrum appears almost similar to that of pure L-arginine acetate. There is no significant change in the spectrum of L-arginine acetate as a result of La^{3+} loading. But the ICP analysis clearly indicates the presence of this metal in the lattice of L-arginine acetate as discussed earlier. The presence of La^{3+} ions do not produce any characteristic change in the IR spectrum.

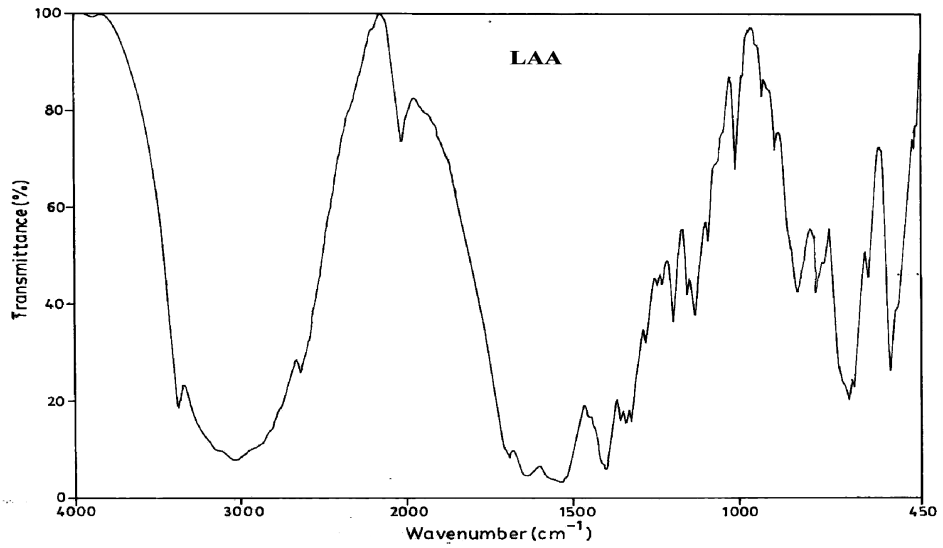

Fig. 4. FT-IR spectrum of L-arginine acetate (LAA)

UV-Vis-NIR studies: The UV-Vis-NIR spectrum of pure L-arginine acetate crystal is recorded in the range 200 to 2000 nm using VARIAN CARY 5E spectrophotometer. The spectra of pure and La^{3+} doped L-arginine acetate are shown in Fig. 6. It is observed that the optical transparency of pure L-arginine acetate is maximum over a wide range from 270-1600 nm. The presence of La^{3+} dopant has increased the percentage of transmission in L-arginine acetate. The increase in transmission enables the possibility of the material to be utilized in fabrication of optical devices[4].

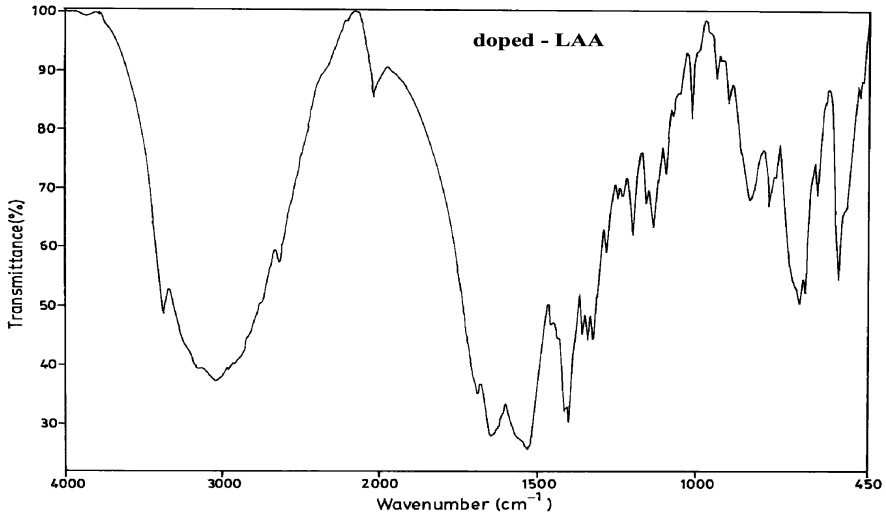

Fig. 5. FT-IR spectrum of La^{3+} doped L-arginine acetate (LAA)

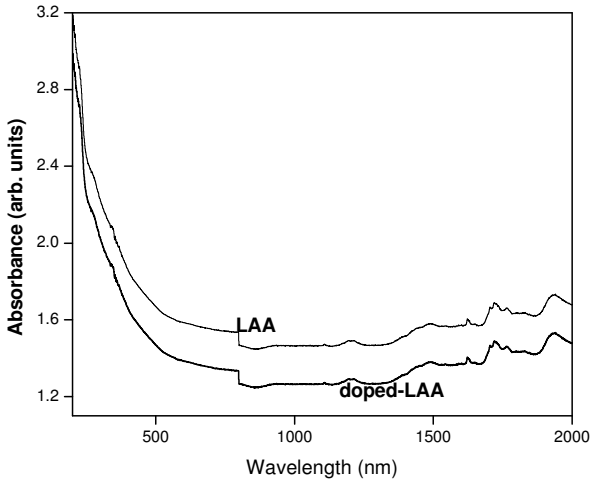

Fig. 6. Optical absorption spectra of pure and La^{3+} doped L-arginine acetate (LAA) single crystals

NLO test: Kurtz and Perry powder SHG5 test was carried out on pure and doped L-arginine acetate single crystals to study its NLO properties. The sample was illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ. The emission of green radiation from the crystal confirmed the second harmonic signal generation in the crystal. The second harmonic signal of 830 mW and 1.2 W, respectively were obtained for pure and La^{3+} doped L-arginine acetate with reference to KDP (275 mW). Thus, the SHG efficiency of pure and lanthanum doped L-arginine acetate crystals is 3 and 3.7 times that of KDP.

Conclusion

In the present study, the growth of organic NLO crystal of both pure and La^{3+} doped L-arginine acetate single crystals were achieved by slow evaporation technique. The UV-Vis-NIR spectra of the pure and La^{3+} doped L-arginine acetate, indicate a good optical transmittance in the entire visible region and the dopant have increased the percentage of transmission in L-arginine acetate. The various functional groups of pure and doped L-arginine acetate were identified by FTIR studies. The SHG efficiency of doped L-arginine acetate was found to be higher than that of pure L-arginine acetate.

ACKNOWLEDGEMENT

The authors acknowledge University Grants Commision (UGC), India for funding this research project - F.No. 33-11/2007 (SR).

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(*Received*: 15 November 2008; *Accepted*: 3 September 2009) AJC-7811