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Structural, Optical and Microhardness Properties of Lanthanum Doped Single Crystals of L-Alanine Acetate

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Single crystals of pure and lanthanum doped L-alanine acetate were grown successfully by slow evaporation technique. The grown crystals were confirmed by X-ray powder diffraction studies. The pure and doped crystals were characterized by Fourier transform infrared (FT-IR) and UV-Vis-NIR studies. It was found that the optical properties were enhanced by the incorporation of the dopant. Hardness studies were also carried out for the grown crystals. Non-linear optical studies reveal that the dopant has increased the efficiency of the L-alanine acetate crystal.

Key Words: Non-linear optical, Solution growth, L-Alanine acetate crystal, Microhardness studies.

INTRODUCTION

In the recent past, the development of science in many areas has been achieved through the growth of single crystals. Non-linear optical (NLO) materials are expected to play a major role in the technology of photonics including optical information processing[1-4]. Amino acid based L-alanine acetate crystal (LAlA) has been reported as a promising NLO material by Kumar *et al.*[5]. In the present investigation, a systematic study has been carried out on the growth of pure and lanthanum doped L-alanine acetate crystals. The grown crystals were subjected to powder X-ray diffraction analysis. The presence of lanthanum was confirmed by inductively coupled plasma (ICP) studies. FT-IR, UV-Vis-NIR, second harmonic generation (SHG) and microhardness studies were carried out for the grown single crystals.

EXPERIMENTAL

The pure and lanthanum doped L-alanine acetate crystals where grown from the aqueous solution by slow evaporation method. L-alanine acetate was synthesized by the stoichiometric incorporation of pure L-alanine and acetic acid in the ratio (1:1). The calculated amount of salts were dissolved in double distilled water and kept for slow evaporation at room temperature. The resultant product L-alanine acetate was found to be homogeneous and the purity of the same was increased by successive recrystallization. Transparent good quality seed crystals free from macro

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defects were used for growth experiments. The crystal size obtained was 13 mm × 8 mm × 8 mm in 28 d. Lanthanum doped L-alanine acetate was synthesized separately at room temperature and purified by recrystallization. Lanthanum doped crystals of size 14 mm × 5 mm × 5 mm were also successfully grown. Fig. 1 shows the photographs of grown crystals.

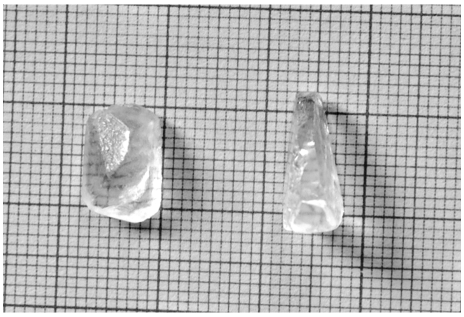

Fig. 1. Photograph of pure and lanthanum doped L-alanine acetate

RESULTS AND DISCUSSION

Powder XRD studies: Finely crushed samples of pure and doped crystals were subjected to powder diffraction analysis using an X-ray diffractometer, model Rich Seifert, XRD 3000P with monochromatic nickel filtered CuK_α (λ = 0.15406 nm) radiation. The samples were scanned over the range 10-50° at the rate of 1°/min. The diffractograms of pure and lanthanum doped L-alanine acetate crystals were shown in the Figs. 2 and 3, respectively. The results obtained from the spectra reveals that the incorporation of metal ions in the crystal lattice does not change the structure (orthorhombic) of the parent crystal. But there is a significant difference in the peak intensity between the spectra of pure and doped samples which may be attributed to the incorporation of metal ions in the crystal lattice, different sizes and orientation of the powdered grains.

The X-ray powder data were analyzed using the program XRDA and the lattice parameters were calculated and presented in the Table-1. The lattice parameters were found to be in good agreement with the reported values. A slight difference between the lattice parameters of pure and doped crystals were observed due to the presence of dopants. It reveals that the crystal structure (orthorhombic) is not changing by the incorporation of metal ions in the crystal lattice.

ICP Analysis: The exact percentage of the lanthanum metal present in the doped crystal is determined by ICP analysis. 10 mg of fine powder of the lanthanum doped L-alanine acetate crystal was dissolved in 100 mL of triple distilled water and the prepared solution was subjected to ICP analysis. The result shows that 15 ppm of lanthanum entered into the crystal lattice of the crystal. It is seen that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution.

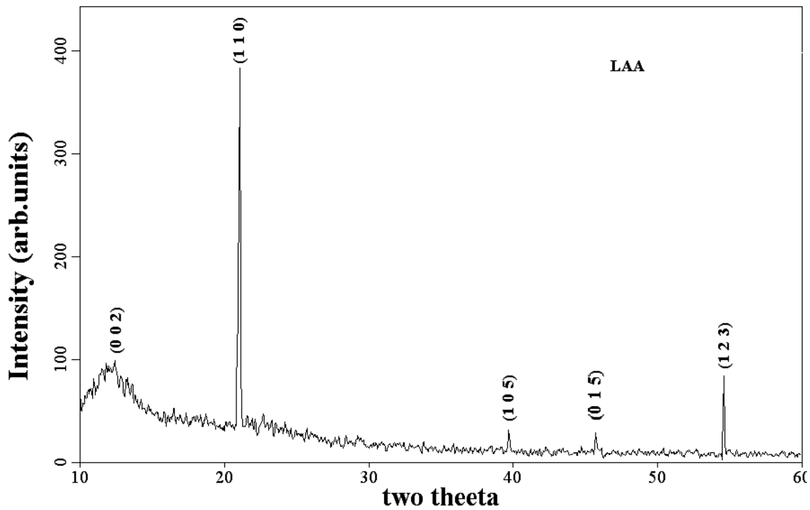

Fig. 2. Powder X-ray diffraction of L-alanine acetate (LAlA)

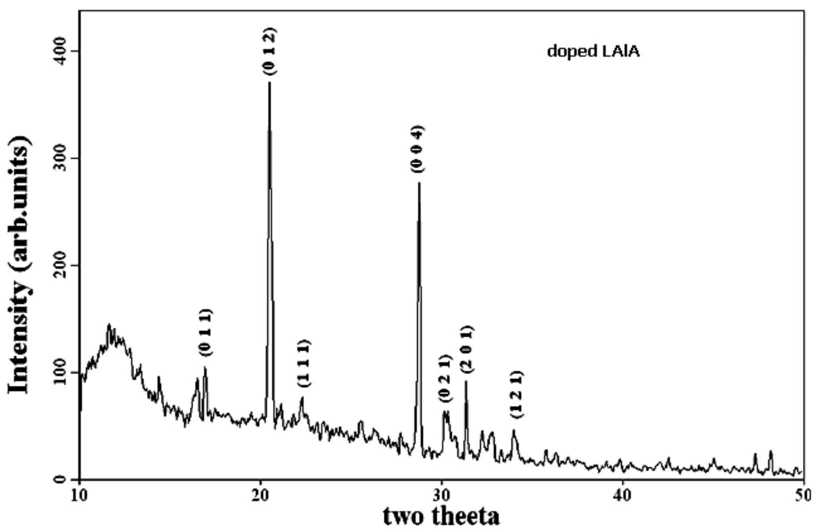

Fig. 3. Powder X-ray diffraction of lanthanum doped L-alanine acetate (LAlA)

FT-IR Spectra: In order to qualitatively analyze the presence of functional groups in L-alanine acetate, FT-IR spectra of the metal doped L-alanine acetate crystal was recorded in the range 400 to 4000 cm^{-1}, using KBr pellet on Bruker IFS FT-IR spectrometer. The FT-IR spectra of L-alanine acetate and doped L-alanine acetate crystals are shown in Figs. 4 and 5, respectively. The NH_3^+ stretching frequencies are found for both the pure and metal doped L-alanine acetate compounds between 3083 and 2603 cm^{-1} in the form of a broad strong band with multiple peaks on the low frequency wing. Lanthanum doped compound show strong absorption

TABLE-1
LATTICE PARAMETERS OF PURE AND DOPED L-ALANINE ACETATE

Crystals	LA*l*A		Doped - LA*l*A
	Present work	Reported work[5]	Present work
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	5.164(1)	5.809(1)	5.871(0.2)
b (Å)	4.306(1)	6.075(2)	6.032(0.1)
c (Å)	14.174(1)	12.391(2)	12.393(0.3)
α	90	90	90
β	90	90	90
γ	90	90	90

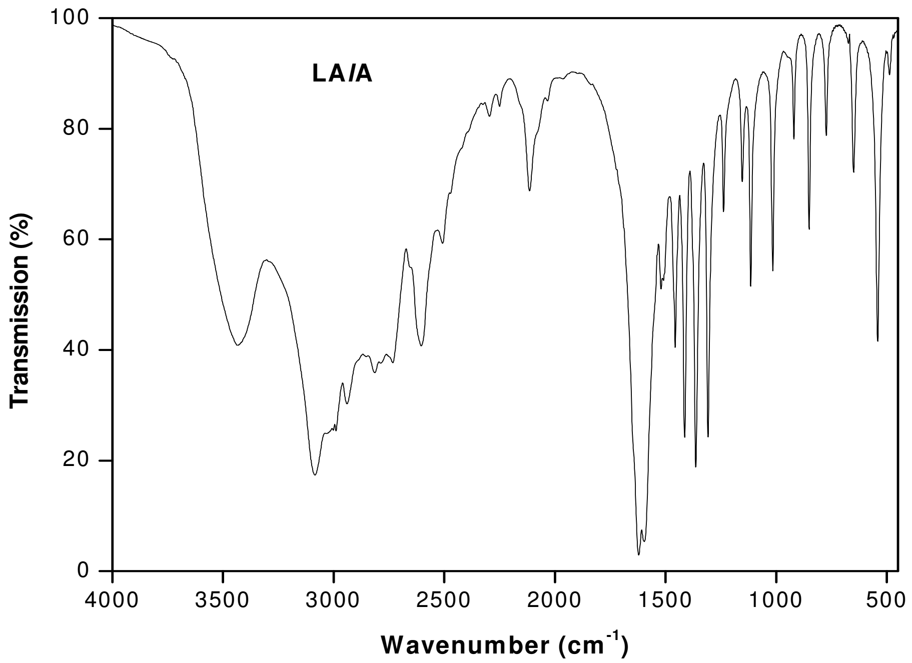

Fig. 4. FT-IR spectrum of L-alanine acetate (LAlA)

at 1620 cm^{-1} indicating the presence of primary amino group. The characteristic absorption at 1519 cm^{-1} is due to symmetric NH_3 deformation. The symmetric CO_2 stretch shows a strong absorption at 1362 cm^{-1}. The absorption at 1306 cm^{-1} is due to CH deformation. The FT-IR spectra of the crystals confirm the structural aspects of pure compounds. Absorption pattern do not show any significance change from the pure L-alanine acetate[6] due to the addition of metal dopant into the crystal lattice. The percentage change of transmittance especially, at 3434 cm^{-1} may be due to weak linkage of metal ions in the interstices of the crystal.

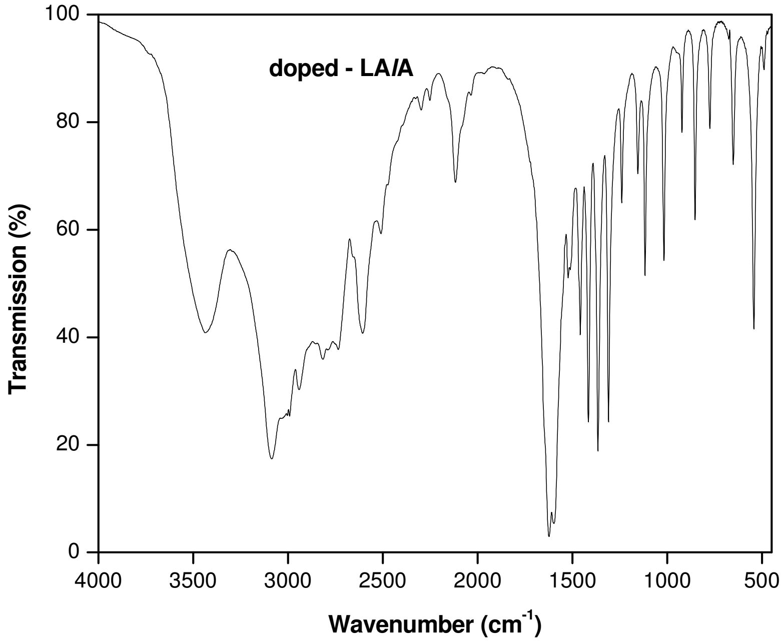

Fig. 5 FT-IR spectrum of lanthanum doped L-alanine acetate (LAlA)

UV-Vis-NIR spectra: Optical absorption data was taken on the pure and doped L-alanine acetate polished crystal samples of *ca.* 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200-1200 nm. The spectra (Fig. 5) indicate that both pure and doped L-alanine acetate crystals have minimum absorption in the region between 270-1200 nm. From the spectra, it is also seen that the doped L-alanine acetate crystal have better lower cut-off wavelength. The required key properties for NLO activity are minimum absorption and low cut-off wavelength. These properties are enhanced in the doped crystal.

NLO Studies: The SHG efficiency was measured for the grown crystal using the standard Kurtz and Perry powder technique[7]. The fundamental beam of a Q-switched Nd:YAG laser with a wavelength of 1064 nm, input energy of 6 mJ, pulse duration of 8 ns, a repetition rate of 10 Hz and a spot size of 1 mm diameter was used. When a laser input pulse of 1064 nm was passed, the second harmonic signal (532 nm) of 91.3, 296.73 and 342.37 mW, respectively were observed through KDP, L-alanine acetate and doped L-alanine acetate. The powder SHG efficiency of pure and doped L-alanine acetate L-alanine was thus found to be 3.25 and 3.75 times with respect to KDP.

Microhardness measurement: Microhardness studies have been carried out in (1 0 0) plane on pure and doped L-alanine acetate single crystals using HMV Shimadzu microhardness tester filled with diamond Vickers pyramidal indenter to estimate the mechanical properties. The static indentations were made at room temperature with a constant indentation time of 15 s for all indentations. Measurements were taken by varying the applied loads from 10 to 100 g only. The plots of variation of Vickers hardness number (Hv) with applied load (P) for pure and doped L-alanine acetate were shown in Fig. 7. The decrease of microhardness with the increasing load is in agreement with the normal indentation size effect (ISE).

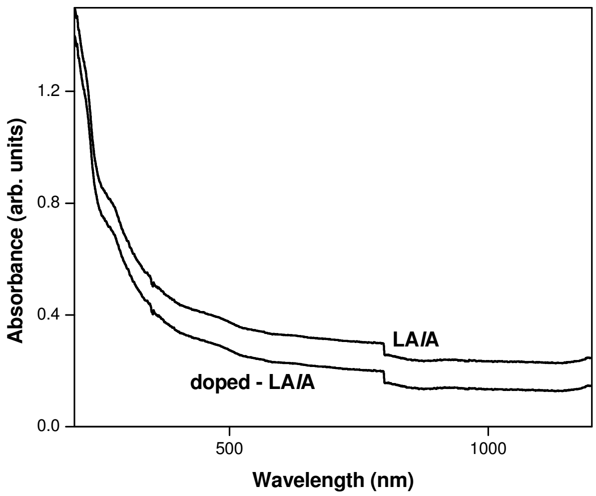

Fig. 6. Optical absorption spectra

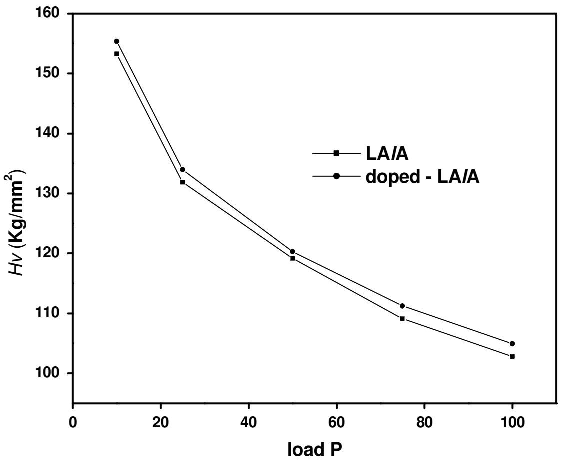

Fig. 7. Variation of hardness with applied load for the plane (011)

Conclusion

Good quality single crystals of pure and lanthanum doped L-Alanine acetate (LAlA) were grown successfully by slow evaporation technique. Powder X-ray diffraction studies were carried out to confirm the crystal structure. ICP Analysis of the doped crystals shows that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the solution. It is seen that the incorporation of dopant into the parent solution has promoted the growth rate and improved the quality of the crystals. The doped L-alanine acetate crystal possess low cut off wavelength than that of the pure one. The presences of functional groups in the grown crystals were identified by FT-IR studies. The mechanical properties were also studied. NLO studies proved that the dopant have increased the efficiency of pure L-alanine acetate. The presence of dopant had also improved the optical and non-linear optical (NLO) properties of the grown crystals and these crystals can be promising materials for nonlinear device fabrication.

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