ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Synthesis, growth & characterization of pure and doped L-Histidine acetate crystals

A.Senthamizhan[1*], Dr.T.Panchatsaram[2]
[1]Department of Physics, VRS college of Engineering & Technology, Arasur-607 107,
[2]Department of Physics, TKGA College, Tamil Nadu, India
***Corresponding author: E-Mail: senthamizhan_pa@yahoo.co.in**

ABSTRACT

The work deals with synthesis, growth and characterization of pure and sulphate of La doped NLO active L-Histidine acetate single crystals. The crystals were grown by slow evaporation technique at room temperature. The grown crystals were characterized by XRD, FTIR and other studies. The results will be discussed in detail.

KEY WORDS: Characterization, crystals, growth.

1. INTRODUCTION

The emergence of new materials with superior quality is often responsible for major advances in new technologies. The high speed, high degree of parallelism of optics will lead gradually to optoelectronic systems where an increasing number of functions will be implemented optically. However, the development of photonic technology relies largely on the progress achieved in fabricating new optical materials with better performance. In that respect, materials with a nonlinear optical (NLO) response are expected to play a major role in enabling optoelectronic and photonic technologies. Many NLO single crystals have been identified as potential candidates in optical and electro-optical devices. Nonlinear optical materials have acquired new significance with the advent of a large number of devices utilizing solid-state laser sources. NLO materials are essential for the fabrication of electro-optic modulators, which convert an electric signal to an optic one for transmission on a fiber optic cable. The exchange and processing of information is growing rapidly and more powerful data-systems including larger networks, faster processors and mass storage devices are under intensive research and development.

2. MATERIALS AND METHODS

LHA single crystals (pure and doped) were grown by slow evaporation technique at room temperature. Good quality, transparent and defect free tiny crystals formed due to spontaneous nucleation were used as seeds to grow bulk crystals shown in fig 1.

2.1. Synthesis and solubility: The pure and doped compound L-His.$CH_3COOH.2H_2O$ was synthesized by reacting equimolar proportion of L-histidine (Kemphasol 98%) and acetic acid (AR grade) in deionized water. The solubility studies of both pure and doped LHA were performed at six different temperatures (30, 35, 40, 45, 50 and 55°C). The variation of solubility (LHA/100 ml H_2O) with temperature is shown in Figure 2. The pure and doped LHA crystals were grown by slow evaporation technique at room temperature (30°C). The reaction that takes place between L-histidine and acetic acid in water medium is as follows:

$$C_6H_9N_3O_2 + CH_3COOH \longrightarrow C_6N_3O_2H_{10}{}^{+}CH_3COO^{-}$$

Within a week time, transparent seed crystals were formed due to spontaneous nucleation and among them tiny crystals with perfect shapes were used for growth experiments. Figure: 1 shows the photograph of grown pure and doped crystals of LHA with dimensions of 21x13x9mm^3 and 12x7x5mm^3, grown in a period of 35 and 30 days respectively. The crystals are found to be highly transparent, free from visible inclusions and non-hygroscopic in nature. Interestingly, microbial growth was not observed during the entire growth period and even after two months.

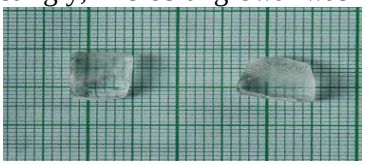

Figure.1.Photograph of pure & La^{3+} doped LHA crystal

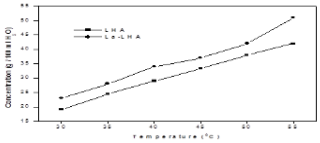

Figure.2.Solubility curves for pure& $La3^{+}$ doped LHA crystal

3. RESULTS AND DISCUSSION

3.1. Characterization techniques & discussion: The lattice parameters (Shown in Table.1) values for the pure and doped LHA crystals have been calculated, from the powder X-ray diffraction pattern (shown in Fig.3). Both the pure and doped LHA crystals crystallize in triclinic P1 space group. The FT-IR Spectra of both the pure and doped LHA confirm the structural aspects of pure compounds. The FT-Raman spectra were recorded for the pure and doped LHA in order to qualitatively analyze the presence of functional groups in LHA. FT-Raman analysis of doped crystals confirmed the presence of metal dopants in the crystal lattice. Optical absorption spectra were recorded on these polished crystal samples between 200–2500nm. Kurtz SHG tests were carried out on the pure and doped LHA samples. The SHG efficiency of doped crystal is found to be higher than that of pure crystal and KDP. The TGA and DTG analysis of pure and doped LHA crystals were done at a heating rate of 20 K/min. There is a reduction in the decomposition temperature for doped crystals. The values of work hardening coefficient of the pure and doped

crystals were found. Dielectric studies were carried out for the pure and doped LHA crystals. The dielectric nature of the pure LHA is marginally altered by the presence of dopant metals. Photoconductivity studies confirm that these materials exhibit positive photoconductivity.

Table.1.Lattice parameters for the pure and La^{3+} doped LHA crystal

Lattice parameters	Pure LHA	La^{3+}-LHA	LHA
a (Å)	8.611	8.810	8.520
b (Å)	9.101	9.712	9.059
c (Å)	9.011	9.891	9.023
α(°)	62.01	61.72	61.70
β(°)	86.78	86.91	86.60
γ(°)	86.13	85.99	86.30
Crystal System	triclinic	triclinic	Triclinic
Space group	P1	P1	P1
Volume ($Å^3$)	611.6	613.4	611.6

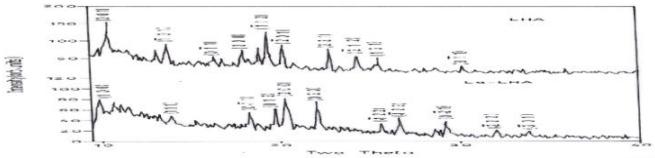

Figure.3.Powder XRD pattern of pure and La^{3+} doped LHA crystal

3.2. FT- IR analysis: FT-IR spectra of the pure and La^{3+} doped LHA crystals were recorded in the range 400 cm^{-1} to 4000 cm^{-1}, using KBr pellet on BRUKER IFS FT-IR Spectrometer. The presence of functional groups in pure and doped LHA is qualitatively analyzed. The FT-IR Spectra of the LHA crystals are shown in Figure 4. The FT-IR spectra of doped LHA appear almost similar to that of pure LHA N-H stretching frequencies of amino group are found between 3168 and 2874 cm^{-1} for both pure and doped crystals. The absorption at 3026 cm^{-1} is due to O-H stretching vibration of carboxylic group. Both the pure and metal doped compounds show strong absorption at 1626 cm^{-1} indicating the presence of primary amino group. The characteristic absorption at 1479 cm^{-1} is due to symmetric N-H deformation. The peak at 1418 cm^{-1} corresponds to the symmetric COO^- stretch. The CH deformation is found by the peak at 1319 cm^{-1}. An absorption band at 935 cm^{-1} is due to the CC stretching. The wagging of COO^- gives rise to a band at 702 cm^{-1}. Doping of metal ions into the crystal lattices does not show any significant change in absorption pattern. The frequency assignments of these crystals are presented in Table.2.

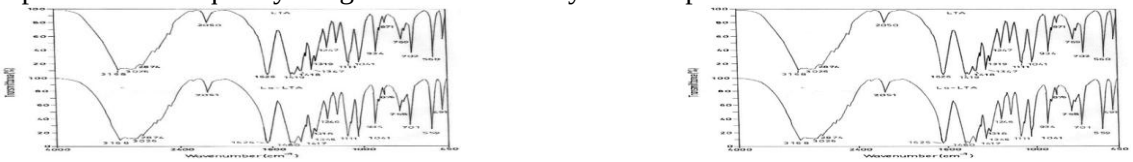

Fig.4.FT-IR spectra for pure & La 3+ doped LHA crystals

Table.2.FT-IR spectral assignments of pure and La^{3+} doped LHA crystal

Wave number (cm^{-1})		Assignments
Pure LHA	La^{3+} - LHA	
3168 - 2874	3168 - 2874	N-H stretching frequencies
3026	3026	O-H stretching vibration
1626	1626	Presence of primary amino group
1479	1479	symmetric NH_2 deformation
1418	1418	symmetric COO^-stretch
1319	1319	C-H deformation
935	934	C-C stretching
702	702	Wagging of COO^-

3.3. FT- Raman spectra: In order to qualitatively analyze the presence of functional groups in LHA, polarized FT-Raman spectra were recorded for the pure and doped LHA in the range 50 cm^{-1} – 3500 cm^{-1}. Figure 5 shows the recorded spectra of the pure and doped LHA. The O-H stretching gives a peak at 2988.9 cm^{-1}. The bands at 2938.4 cm^{-1} and 2873.5 cm^{-1} are due to aliphatic CH_2 and CH_3 stretching. The less intense peak at 1481.2 is due to the CH_2 deformation. The peak at 1337.9 cm^{-1} is due to the C=O stretching. The weak absorption at 3100 cm^{-1} is due to the N-H stretching of amino group. The absence of peaks at 3019.2 cm^{-1}, 2938.6 cm^{-1}, 1450.2 cm^{-1} and 698.2 cm^{-1} in the La-LTA spectrum which are present in the pure LTA, indicates the probable metal linkage with the N of amino group. The FT-Raman frequency assignments of these crystals are presented in Table.3.

3.4. UV-Vis-NIR spectrum: Optical absorption data were taken on the polished pure and doped LHA crystals of about 4mm thickness using a Varian carry 5E model dual beam spectro- photometer between 200nm –2500nm. The spectra (Fig.5) indicates that the pure and doped LHA crystals have minimum absorption in the region between 250 nm – 1588nm and 260nm - 1580nm. The required key properties for NLO activity are minimum absorption and low cut-off wavelengths for pure and doped LHA are 250nm and 260nm respectively. LHA crystals are found to possess these properties.

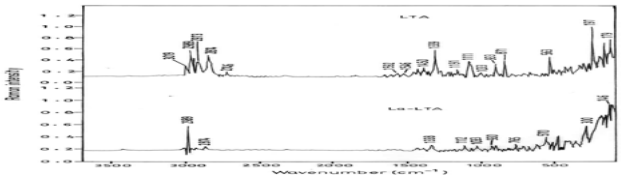

Figure.5. Absorption of pure and doped LHA crystals

Table.3.FT-Raman spectral assignments of pure and La^{3+} doped LHA crystal

Wave number (cm^{-1})		Assignments
Pure LHA	La^{3+} - LHA	
3019	-	Asymmetric NH stretching
2989	2988	O-H stretching
2938	2938	CH_2 stretching
2874	2873	CH_3 stretching
1481	1481	CH_2 deformation
1450	-	NH_2 deformation
1339	1337	C=O stretching

3.5. Microhardness studies: Microhardness studies have been carried out in (1 0 0) plane on pure and doped LHA 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 seconds for all indentations. Measurements were taken by varying the applied loads from 10g to 50g only.

3.6. Thermal Studies: Single crystals of pure and doped LHA crystals were subjected to thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) simultaneously using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 10 K/min. Figure 6 shows the resulting TGA and DTG traces of the pure and doped crystals. The decomposition of the material starts at 262º C. The material is found to be thermally stable up to 230º C. There is a reduction in the decomposition temperature of the doped crystals compared to the pure LHA crystals, which is attributed to the presence of the metal dopant La^{3+}.

Figure.6.Absorption spectrum of pure and La^{3+} doped LHA crystal

4. CONCLUSION

Good quality single crystals of pure and doped L-Histidine Acetate (LHA) were grown successfully by slow evaporation technique. Powder X-ray diffraction studies were carried out, and the lattice parameters are calculated. Inductively coupled plasma studies shows that the amount of dopant incorporated into the doped crystal is less than the concentration of the dopant in the corresponding solution. The pure and doped LHA crystals are transparent in the entire visible region, and have minimum absorption. The TGA and DTG studies show that the metal dopants have not altered the thermal stability of the molecules. From the dielectric studies it is seen that the dielectric constant and dielectric loss decreases with frequency. Photoconductivity studies reveal that the pure and doped LHA have positive photoconductivity. Hardness studies show that pure and doped LHA crystals are soft materials. NLO studies proved that the metal dopant have increased the efficiency of pure LHA. The presence of dopant has improved the Nonlinear optical (NLO) properties of the grown crystals and these crystals can be promising material for nonlinear device fabrication.

REFERENCES

Boyd R.W, Nonlinear optics, Academic press, San Diego, 1992.

Eimerl D, Velsko S, Davis L, Wang F, Lolacono G and Kennedy G, Deuterated L-arginine phosphate: a new efficient nonlinear crystal, Journal of Quantum Electronics, 25 (2), 1989.

Saleh B.E, Teich M.C, Fundamentals of Photonics, Wiley, New York, 1991.