Materials Chemistry and Physics 147 (2014) 433–438

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Synthesis and characterization of pure, urea and thiourea doped organic NLO L-arginine trifluoroacetate single crystals

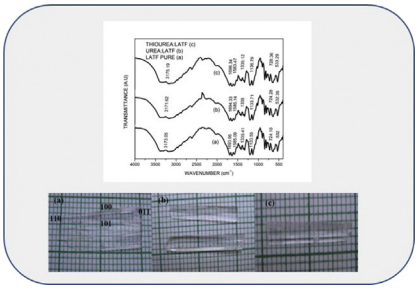
T. Prasanyaa [a], M. Haris [a,*], V. Mathivanan [a,b], M. Senthilkumar [a], T. Mahalingam [c], V. Jayaramakrishnan [d]

[a] Department of Physics, Karunya University, Coimbatore 641 114, Tamilnadu, India
[b] Department of Physics, United Institute of Technology, Coimbatore, India
[c] Department of Electrical and Computer Engineering, Ajou University, Suwon 443-749, South Korea
[d] Department of Physics, P.S.G. College of Arts and Science, Coimbatore 641 014, Tamilnadu, India

HIGHLIGHTS

- Urea doped LATF crystals enhances the structural and crystalline quality.
- Urea doping enhances optical transparency and thermal stability.
- Urea and thiourea doping in LATF improves the hardness.
- SHG efficiency of urea, thiourea doped LATF are 2.2 and 2.07 times greater than KDP.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 December 2012
Received in revised form
27 April 2014
Accepted 6 May 2014
Available online 2 June 2014

Keywords:
B. Crystal growth
A. Optical materials
A. Organic compounds
C. Mechanical testing
C. Powder diffraction

ABSTRACT

Optically transparent L-arginine trifluoroacetate (LATF) single crystals by doping with organic materials urea and thiourea were grown by slow solvent evaporation technique. Powder X-ray diffraction confirms improvement in the crystalline quality for urea doped crystals. Urea doping in LATF also improves the percentage of transmittance. The vibrational frequencies of the grown crystals were assigned by Fourier Transform infrared spectroscopy. The thermal analysis (TG/DTA) indicated the better thermal stability for urea doped LATF crystals. EDAX analysis was carried out to calculate the percentage of elements present in doped and pure LATF. The hardness has been remarkably improved on urea and thiourea doped LATF crystals. The second harmonic generation (SHG) analysis showed 2.5 times than standard KDP for pure LATF and 2.2, 2.07 times than KDP for urea and thiourea doped LATF.

1. Introduction

Recently, nonlinear optics (NLO) is at the foremost of prevalent research due to its applications in frequency shifting, optical switching, optical memory and optical modulation for the technological areas such as telecommunications, optical interconnection and signal processing [1]. Amino acids and their salts belong to a family of organic materials have wider NLO applications in this respect [2]. Organic amino acids are fascinating stuffs formed by weak vanderwaal's, hydrogen bonds and as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino ($-NH_2$) group in them and due to this dipolar nature, amino acid have substantial properties make them supreme candidates for NLO applications. They also offers an occasion for theoretical simulation, modeling and synthetic stretchability to

* Corresponding author. Tel.: +91 422 2614004; fax: +91 422 2615615.
E-mail addresses: mharis8@yahoo.com, hariscgc@yahoo.com (M. Haris).

http://dx.doi.org/10.1016/j.matchemphys.2014.05.011
0254-0584/

design and produce novel materials [3,4]. In the organic class, α-amino acids unveil some specific features such as absence of firmly conjugated bonds and molecular chirality, broad transparency ranges, zwitterionic nature of the molecule and high damage thresholds which favors crystal hardness [5–7]. In L-arginine, $NH_2C(NH)NH(CH_2)CH(NH_2)(COOH)$ the optically active amino acid has two groups α- amino acid and guanidyl which are easily protonated. In LATF salts, the α- amino group is protonated owing to hydrogen of CF_3COOH (the L-arg anion is bonded with TF cation with high valence bond) to produce this new type of crystal [8].

In recent years, the NLO properties with relatively modest optical nonlinearities were produced with complexes of organic- organic and semi- organic products. The impurity molecules present even at reduced concentration in the solution, may have remarkable reaction on their chemical properties [9]. Urea (N_2H_4CO) and Thiourea (N_2H_4CS) are simple organic molecules with immense dipole moment and have the ability to form a large scale network of hydrogen bonds. Dopant is added to occupy the interstitial positions in the lattice and in turn this may lead to distinctive changes in the physical properties of LATF [10–12]. In the present work, an attempt has been made to synthesize pure, urea and thiourea doped LATF crystals. These grown crystals are characterized for their mechanical, optical, structural and thermal behavior.

2. Experimental details

2.1. Synthesis and crystal growth

Pure LATF salt was synthesized using AR grade of Trifluoroacetic acid (TFA) and L-Arginine. De-ionized water was used as a solvent and the calculated amounts of L-Arginine and TFA were dissolved and stirred well using magnetic stirrer. Recrystallization process was repeatedly done four times for obtaining pure LATF and the reaction mechanism is given below.

$$(NH_2)NHCNH(CH_2)_3CH(NH_2)COOH + CF_3COOH \rightarrow (NH_2)_2^+CNH(CH_2)_3CH(NH_3)COO^-CF_3COO^-$$

The recrystallized pure LATF was made to saturate in 100 mL of de-ionized water. To grow single crystals of doped LATF, 1 mol% of urea and thiourea were added to the saturated solution of the synthesized salts. The crystals were grown by solution method typically the simplest slow evaporation technique at room temperature. The crystals were harvested after a period of 20–25 days and shown in Fig. 1. After several trails and optimization, well defined single crystals of good transparency were collected. Powder X-ray diffraction was taken using a SEIFERT diffractometer. FTIR spectra were measured using Perkin Elmer BX spectrometer in the range from 4000 to 400 cm^{-1} using KBr pellets. The UV–VIS–NIR transmittance spectrum was recorded with an SHIMADZU spectrometer in the range 200–800 nm. Mechanical property was studied by performing microhardness measurement on the grown crystals and it was done using a Leitz Weitzler hardness tester fitted with a diamond indenter. Second harmonic generation (SHG) efficiency analysis for the grown crystals was carried out by powder technique of Kurtz and Perry. The identification of elements in the pure and doped crystals were detected by using an energy dispersive analysis spectrometer Oxford INCA Penta FET- X3. The thermal analysis for the samples was recorded using a Perkin–Elemer TG/DTA analyzer.

3. Results and discussion

3.1. X-ray diffraction analysis

To test the crystallinity of the samples, powder X-ray diffraction patterns were obtained at room temperature using an X-ray diffractometer. The grown crystals were of high degree of crystallinity which can be revealed from the sharp and high intensity peaks. The peaks were indexed using TREOR program for corresponding 2θ values and the estimated lattice parameter values for pure LATF $a = 10.581$Å, $b = 5.710$Å, $c = 10.861$Å and crystallized in $P2_1$ space group, shows that there is no change in the crystal structure [8]. The calculated lattice parameters of urea: LATF and thiourea: LATF are estimated to be $a = 10.589$Å, $b = 5.714$Å, $c = 10.862$Å and $a = 10.579$Å, $b = 5.708$Å, $c = 10.859$Å, respectively. The unit cell parameters of the doped and pure crystals show a slight change, due to the interstitial or substitutional addition of dopant atoms. The change in intensity of peaks as well as reduction in number of peaks for urea doped LATF in the X-ray diffraction pattern shown in Fig. 2 reveals that the urea dopant has enhanced the structural and crystalline perfection in crystal lattice of pure LATF. The sharp and well defined Bragg's peak at specific 2θ angles in the pattern attest the proper orientation of the crystallite, purity and perfection of the grown crystal, this manifests that the grown pure and doped crystals belongs to single crystal class. Crystals of urea doped LATF were structurally perfect than pure LATF and this might due to the fact that the doping entered the lattice of pure LATF which led to decrease in number of nucleation centers [13].

3.2. UV–VIS–NIR analysis

Optically transparent single crystals of about (4 mm × 2 mm × 5 mm) were selected. The optical study of LATF was recorded in the range of 200–800 nm and shown in Fig. 3. The spectrum shows that pure and doped crystals have wide transparency window. LATF crystals have UV cutoff below 300 nm and the percentage of transmission of light has been observed to be nearly or more than 80% for pure and urea doped LATF crystals in the visible range. However a slight decrease in transparency (75%) is also observed for thiourea doped LATF crystal. The energy gap decreases with the increase in the conjugation length and narrows down the transparency window [14]. The high energy band shows that optical band gap is high with a lower cut- off. Hence, the doped

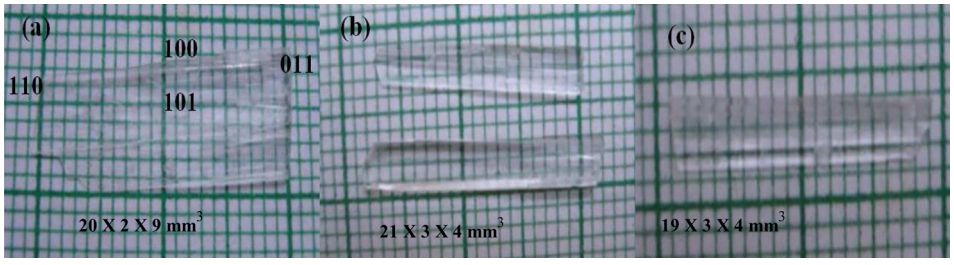


Fig. 1. Typical photographs of (a) Pure LATF (b) Urea: LATF (c) Thiourea: LATF.