Indian Journal of Science and Technology, *Vol 7(7), 1014–1017, July 2014*
ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

Studies on the Growth and Characterization of Organic L-Arginine Semicarbazone Dihydrate NLO Single Crystal

B. Anitha[1], S. Rathakrishnan[2], R. Umamaheswari[3] and A. Joseph Arul Pragasam[3*]

[1]Department of Physics, SRR Engineering College, Chennai, Tamil Nadu, India
[2]Department of Chemistry, SRR Engineering College, Chennai, Tamil Nadu, India
[3]Department of Physics, Sathyabama University, Chennai, Tamil Nadu, India; drjosephsu@gmail.com

Abstract

This paper reports an organic crystal of a New Nonlinear Optical (NLO) material, L-Arginine Semicarbazone dihydrate (abbreviated as LASC). The crystals were grown by slow evaporation from an aqueous solution and crystallize in monoclinic form which is confirmed by single crystal x-ray diffraction analysis. The molecular weight of the grown crystal was estimated by mass spectrometry. The FTIR spectra con-firm the presence of the functional groups in the crystal while The UV–vis–NIR spectrum of grown crystal LASC reveals its transparent nature. The optical absorption in the grown crystal is almost negligible in the UV and visible spectral regions with the lower cut off wavelength at around 350 nm. Minimum amount of optical absorption suggests that the LASC crystal is highly transparent in the UV–visible spectral region and is useful for nonlinear optical applications. The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be 0.51 times that of KDP crystal. The photoconductivity study shows that the grown crystal exhibit negative photoconductivity. Primary studies show that the grown crystals are appropriate for optoelectronics applications and Second Harmonic Generations.

Keywords: FTIR, NLO, Optical Absorption, Photoconductivity Study, Solution Growth

1. Introduction

An optical communication device uses nonlinear optical (NLO) materials. Inorganic, semiorganic and organic crystals have nonlinear optical property. Inorganic crystals like ADP, KDP are promising NLO crystals, but they have less nonlinear activity; also synthesizing crystals are somewhat difficult.

Among organic, semiorganic and inorganic crystals, organic NLO materials are found to have large NLO coefficients. A series of organic NLO crystals with high nonlinear susceptibility have been synthesized and characterized[1–10]. If we take organic materials, Amino acid family crystals are found to have NLO materials. Amino acid contain dual functional group which has a carboxyl group (-COOH) and an amino group(-NH_2). They exist as zwitter ions. Because of this reason, amino acids possess many unusual properties (Both physical and chemical) which make researchers to think more on amino acids. The concrete form of all amino acids (except glycine) have Centrosymmetric space group which is the major criteria for NLO applications. L-Arginine crystals such as L-Arginine Acetate, L-Arginine Phosphate and semi organic crystals such as L-Arginine Phosphate, L-Arginine Di Phosphate, L-Arginine hydrochloride etc.[11–14]. In this paper, new L-Arginine Semicarbazone dihydrate NLO single crystal is grown by slow solvent evaporation technique is reported. The grown crystal has been given for various characterizations.

**Author for correspondence*

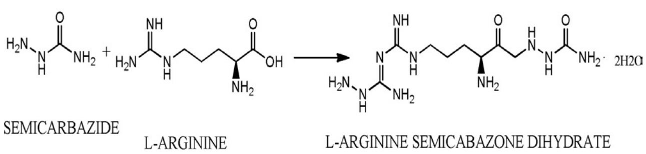
2. Experiment

The preparatory material was synthesized by taking L-Arginine and semicarbazone (Loba chemie) in the stoichiometric ratio and dissolved in double distilled water and stirred well for about five hours. Then the solution was found to be transparent and homogenous. The resultant solution is filtered using filter paper. The filtered solution is kept undisturbed at room temperature. Within 20 days good quality seed crystals were got. The grown crystal is shown in Figure 1. The pattern of reaction is shown below

3. Characterization

3.1 Single Crystal XRD

Single crystal X-ray diffraction analysis was carried out to find the lattice parameters. This study reveals that the grown crystal LASC belongs to the monoclinic system. The calculated lattice parameters are listed in Table 1.



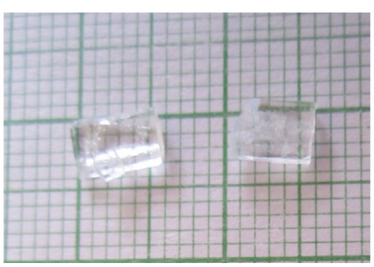


Figure 1. Grown crystal of LASC.

Table 1. Single crystal XRD data for LASC crystal.

a(Å)	11.05
b(Å)	8.49
c(Å)	11.27
α˚	90
β˚	91.31
γ˚	90
Volume(Å^3)	1057
Crystal system	monoclinic

3.2 Mass Spectral Analysis

Mass spectrometry is an analytical method that measures the mass to charge ratio of charged particles. It is used for defining masses of particles, fundamental composition of a sample or a molecule and for elucidating the chemical structure of molecules such as peptides and other chemical compounds. The mass spectrum of LASC was recorded using a thermo-electron JEOL GC mate Direct Probe ion trap mass spectrometer and is shown in Figure 2.

The source voltage was 5 kV at the capillary temperature 375 ˚C with an ionization mode EI+. Nitrogen was used both as a cover and supplementary gas crystal. The mass (m) to charge (z) ratio of the sample was scanned and the investigational molecular weight 343.04amu was found to be in good agreement with theoretical value 338.21amu). The slight deviation from the proposed molecular weight of the crystalline compound can be attributed to the existence of fractional impurities in the crystal. The spectrum of LASC showed a protonated molecular ion peak at m/z = 343.04 (C9H26N10O4). The loss of (NH-NH–CO-NH2) moiety from the molecular ion (74amu) gives the peak at m/z 365amu. The loss of [NH2-NH-CN-NH2]- moiety gives the peak at m/z 207. Thus, the formation of title compound was recognized.

3.3 FTIR Analysis

Fourier transform spectroscopy is a modest precise technique to resolve a complex wave into its frequency components. Fourier Transform Infrared (FTIR) has made the mid IR region more useful. Conventional spectroscopy called the frequency domain spectroscopy, records the changes in radiant power as a function of frequency. In the time domain spectroscopy, the changes in radiant power are recorded as a function of time. In the

Figure 2. Mass spectrum of LASC.

Fourier transform of such systems is done by means of high –speed computers. The functional group associated with wave number is shown in Figure 3 and is tabulated in Table 2.

3.4 UV-VIS Spectrum Analysis

In order to identify the effectiveness of the grown crystal LASC for nonlinear application in the visible and blue regions, UV-visible absorption study was performed. The UV-visible absorption spectrum was recorded in the wavelength region 200–800 nm using a Varian Carry-5E UV–Vis Spectrophotometer. The recorded absorption spectrum of the sample is shown in Figure 4. From the absorption spectrum, it is detected that the optical absorption in the grown crystal is almost negligible in the UV and visible spectral regions with the lower cut off wavelength at around 350 nm. Minimum amount of optical absorption suggests that the LASC crystal is highly transparent in the UV–visible spectral region and is useful for nonlinear optical applications.

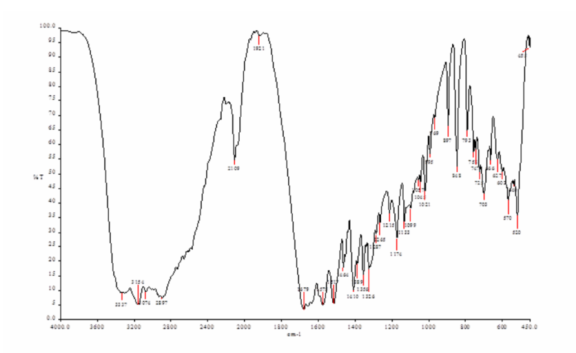


Figure 3. FTIR spectrum of LASC

Table 2. FTIR assignment table for LASC crystal

Wavenumber (cm^{-1})	Assignments
3337-2109	NH and CH stretching vibration
1679	NH_3^+ asymmetric deformation
1517	COO^- asymmetric stretching
1464	CH_2 in plane deformation
1410	COO^- symmetric stretching
1326	C-N stretching
1174	NH_3^+ rocking
1099	C-N stretching
1021	C-O stretching
995	CH_2 rocking
897	C-C stretching
848	C-C stretching
793	COO^- scissoring

4. NLO Studies

Second harmonic generation of the grown crystal LASC was proved using Kurtz and Perry powder technique[15]. An intense beam of laser wavelength 1064nm and input power 0.68J was used to illuminate the powdered sample. The emission of green radiation from the sample approves that the material exhibits nonlinear optical property. The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be 0.51 times that of KDP crystal.

5. Photoconductivity Studies

Photoconductivity measurements were taken using Keithley 485 picoammeter. The dark current was recorded by keeping the sample unexposed to any radiation. Figure 5 shows that the dark current increases with

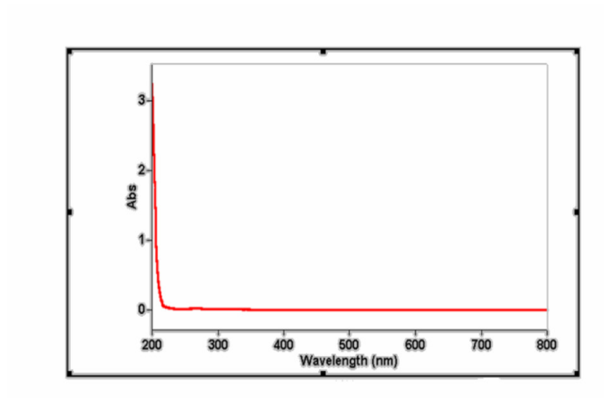


Figure 4. UV-VIS spectrum of LASC.

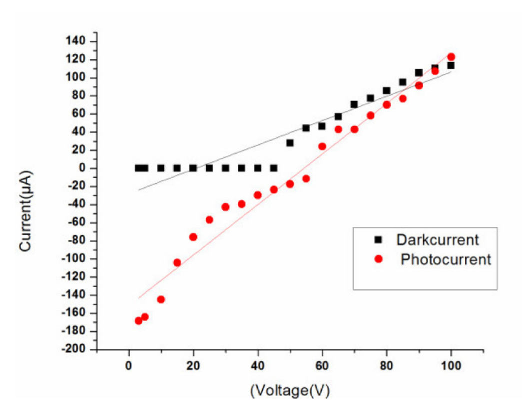


Figure 5. Photoconductivity graph of LASC crystal.

increase in voltage. But the photo current increases as the applied field increases. It is seen from the plots that both dark current and photocurrent of the sample (LASC) increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photo current, thus confirming the negative photoconductivity. The phenomenon of negative photoconductivity is explained by Stockmann model[16]. The negative photoconductivity in a solid is due to the decrease in the number of charge carriers or their lifetime, in the presence of radiation[17].

6. Conclusion

An organic NLO crystal of L-Arginine Semicarbazide (LASC) is grown by slow evaporation method . Single crystal XRD results shows that it belongs to monoclinic system. Also it has wide range of transparency in UV-Vis region and it is a promising NLO material. It is interesting to note that the NLO efficiency of the grown crystal is comparable to KDP. The photoconductivity study ascertains the negative photoconductivity nature of the grown crystal. In view of the good optical properties, better SHG efficiency, LASC crystal can be used for nonlinear optical device applications.

7. References

1. Woodford JN, Wang CH, AlexK-Y J. Dispersion of the first molecular hyperpolarizability of charge-transfer chromophores studied by hyper-Rayleigh scattering. Chem Phys. 2001; 271:137–43.
2. Singh OP, Singh VP, Singh N, Singh NB. Growth of vanillin crystals for Second Harmonic Generation (SHG) applications in the near-IR wavelength region. J Cryst Growth. 2001; 225:470–73.
3. AlosiousGonsago C, Albert HM, Malliga P, Pragasam AJA. Crystallization, spectral, and thermal characterization of L-Histidinemethyl Ester Dihydrochloride (LHMED). J Therm Anal Calorim. 2012; 107:1231–35.
4. Bahar GS,Chaloner PA, Dutta LM, Healy W, Hitchcock PB. Crystal growth and Hydration effects in morpholinium 4-hydroxybenzoate (M4HB). J Cryst Growth. 2001; 225: 474–78.
5. Zhengdong L, Baichang W, Genbo S. Nonlinear-optical, optical, and crystallographic properties of methyl p-hydroxybenzoate. J Cryst Growth. 1997; 178:539–44.
6. VasudevanV, Babu RR, ReicherNelcy A, Bhagavannarayana G, Ramamurthi K. Synthesis, growth, optical, mechanical and electrical properties of L-lysine L-lysinium dichloride nitrate (L-LLDN) single crystal. Bulletin of Materials Science. 2011; 34:469–75.
7. Bhat HL. Growth and characterization of some novel crystals for nonlinear optical Applications. Bull Mater Sci. 1994; 17:1233–49.
8. Kumar PP, Manivannan V, Sagayaraj P, Madhavan J. Growth and characterization of pure and doped NLO L-arginine acetate single crystals. Bull Mater Sci.2009; 32:431–35.
9. Manoharan AJJ, John NJ, Revathi V, Rajendran KV, Andavan PM. Effect of amino acid doping on the dielectric properties of Triglycinesulphate (TGS) crystals. Indian J Sci Technol. 2011; 4(6):688–91.
10. Jothi L, Ramamurthi K. Growth and characterization of an organic NLO crystal:4-chloro- 4-methyl benzylidene aniline. Indian J Sci Technol. 2011; 4(6):666–69.
11. Muralidharan R, Kumar RM, Jayavel R, Ramasamy P. (2003)Growth and characterization of L-arginine acetate single crystals: a new NLO material. J. Cryst. Growth. 2003; 259:321–25.
12. Meena M, Mahadevan CK. Growth and dielectric properties of l-arginine acetate and l-arginine oxalate single crystals. Mater Lett. 2008; 62:3742–44.
13. Pragasam AJA, Madhavan J, GulamMohammed M, Selvakumar S, Ambujam K, Sagayaraj P. Growth and characterization of amino acid (glycine and valine) substituted LADP single crystals. Optical Materials. 2006; 29:173–79.
14. Meera K, Muralidharan R, Dhanasekaran R, PrapunManyum, Ramasamy P. Growth of nonlinear optical material: L-arginine hydrochloride and its characterisation. J Cryst Growth; 2004; 263:510–16.
15. Kurtz SK, Perry TT. A powder technique for the evaluation of non-linear optical materials. J Appl Phys. 1968; 39: 3798–13.
16. Joshi VN. Photoconductivity. Marcel Dekker, Newyork; 1990.
17. Bube RH. Photoconductivity of solids, Wiley Interscience, Newyork; 1981.