Optik 125 (2014) 4265–4269

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Studies on growth and characterization of L-alanine strontium chloride trihydrate single crystals for optical applications

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ARTICLE INFO

Article history:
Received 23 August 2013
Accepted 1 April 2014

Keywords:
L-Alanine strontium chloride trihydrate
Growth from solution
Infrared spectrum
Second harmonic generation

ABSTRACT

The optically transparent nonlinear optical single crystals of L-alanine strontium chloride trihydrate (LASCT) were grown by slow evaporation solution growth method using water as solvent. The purity of the crystals was increased by the method of recrystallization. The grown crystals were analyzed by the single crystal X-ray diffraction pattern which proved that LASCT belongs to monoclinic crystal system. The presence of various functional groups and modes of vibrations were identified by FTIR spectroscopy. The optical absorption study confirms the suitability of the crystal for device applications. The thermal strength and the decomposition of the grown crystals were studied using TG/DTA analyses. The dielectric constant and dielectric loss measurements of the grown crystals at different frequencies of the applied field were measured and reported. The mechanical strength of the crystal is estimated by Vicker's hardness test. The nonlinear optical properties of the grown crystals were confirmed by second harmonic generation test which shows the suitability of NLO applications.

1. Introduction

The second order nonlinear optical (NLO) materials are widely used for their practical applications such as high speed information processing, laser based imaging, optical communications, remote sensing, optical parametric amplifier, optoelectronics and optical data storage [1–4]. Optically active amino acids show high efficient optical second harmonic generation (SHG) and are promising candidates for laser and optical communication technology. The complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation, as they tend to combine the advantages of the organic amino acid with that of the inorganic acid. The amino acids are interesting materials for NLO applications exist as zwitterions as they contain a proton donor carboxyl acid (—COO) group and the proton acceptor amino (—NH_2) group in them. This dipolar nature gives some specific features [5] of amino acids such as, molecular chirality, which secures acentric crystallographic structures, absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions and zwitterionic nature of the molecule, which favors crystal hardness [6]. A series of amino acid compounds such as L-arginine, L-histidine, L-threonine, L-alanine, L-valine, L-proline and glycine has been grown and tested for NLO applications [7–16]. The crystal structure of the title compound has already been reported [17]. The NLO properties of the title compound are reported for the first time in the literature.

In the present investigations deals with the growth of a semiorganic NLO crystal of L-alanine strontium chloride trihydrate (LASCT) which were grown by slow evaporation solution growth using deionized water as the solvent. The grown LASCT crystals were studied various characterization techniques such as the crystal system was identified by single crystal X-ray diffraction technique. The functional groups were identified by FTIR analyses. The transparency of LASCT crystals were depicted by UV–vis–NIR spectrum. The nonlinear optical property of this grown crystals were confirmed by second harmonic generation using Nd:YAG laser.

2. Experimental

2.1. Synthesis

The commercially available AR-grade of L-alanine ($C_3H_7NO_2$) and strontium chloride trihydrate ($SrCl_2{\cdot}3H_2O$) (Loba) in 1:1 molar

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http://dx.doi.org/10.1016/j.ijleo.2014.04.011
0030-4026/

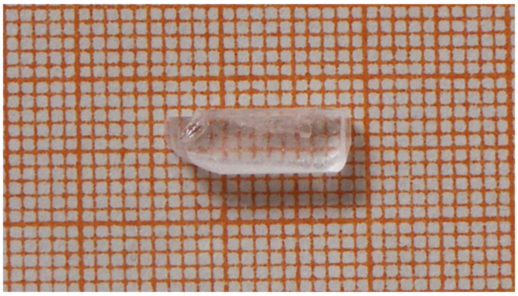

Fig. 1. As-grown LASCT crystals.

ratio were used to synthesize L-alanine strontium chloride trihydrate (LASCT). The required amount of starting materials for the synthesis of LASCT was calculated according to the following chemical reaction:

$$\underset{\text{L-alanine}}{C_3H_7NO_2} + \underset{\text{Strontium chloride trihdrate}}{SrCl_2 \cdot 3H_2O} \rightarrow \underset{\text{L-alanine strontium chloride trihydrate}}{C_3H_7Cl_2NO_2Sr \cdot 3H_2O}$$

The calculated amount of L-alanine was dissolved in solvent of deionised water and then strontium chloride trihydrate was added to the solution slowly by stirring. The mother solution was thoroughly stirred using magnetic stirrer to yield a homogenous mixture of solution. The prepared mother solution was filtered using fine porosity of filter paper. The filtered solution was transferred to crystal growth vessels and allowed to dry at room temperature, the salts were obtained by slow evaporation technique. The purity of the synthesized salt was further improved by successive recrystallization process.

2.2. Crystal growth

The solvent evaporation technique was employed for the growth of LASCT crystal at room temperature. The recrystallized salt was taken as the raw material for growth. The solvent of deionised water was taken in a beaker and the synthesized material of LASCT was added gradually in order to get the saturation. The saturated solution was further purified by filtering the filter paper provided with fine pores of size 1 μm porosity. The filtered solution was tightly closed with perforated sheets so that the rate of evaporation could be minimized and kept in dust free environment. Optically transparent single crystals of dimension 13 mm × 5 mm × 3 mm were obtained after 30 days. Fig. 1 shows the photograph of as grown LASCT crystal.

3. Characterization

In order to confirm the crystal structure of LASCT crystals, single crystal X-ray diffraction studies have been carried out using Enraf Nonius CAD4 diffractometer. Fourier transform infrared (FTIR) spectrum was obtained using Perkin Elmer spectrometer in the 450–4000 cm^{-1} to study the various functional groups present in the grown crystal. Linear optical properties of the crystals were studied using a Perkin Elmer Lambda 35 UV–vis spectrometer in the region 200–1100 nm. The thermal stability was identified by thermo gravimetric (TG) and differential thermal analyses (DTA). The thermal analyses were carried out using STA1500 thermal analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. Microhardness measurements for LASCT crystal were carried out using Vickers microhardness tester. To confirm the nonlinear optical property, the Kurtz and Perry powder second harmonic generation (SHG) test was performed on the grown crystals using a Q-switched Nd:YAG laser as source.

Table 1
Lattice parameter values of L-alanine strontium chloride trihydrate.

Lattice parameters	Present work	Reported work [18]
a	8.597 Å	8.540 Å
b	7.069 Å	7.1670 Å
c	8.725 Å	8.769 Å
β	96.65°	95.02°
Volume	526.66 $Å^3$	534.7 $Å^3$
System	Monoclinic	Monoclinic
Space group	–	$P2_1$
Z	–	2

4. Results and discussion

4.1. Single crystal X-ray diffraction studies

The single crystal X-ray diffraction of LASCT crystal was carried out using an Enraf Nonius CAD4 diffractometer with MoKα (λ = 0.7170 Å). Reflections from few planes were collected and indexed. The crystal is monoclinic with unit cell parameters a = 8.540 Å, b = 7.1670 Å, c = 8.769 Å, β = 95.02° and V = 534.7 $Å^3$; and assigned to $P2_1$ space group which is recognized as noncentrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystal [18]. The single XRD data of the present work is in good agreement with the reported literature values [17] and shown in Table 1.

4.2. FTIR analysis

In the FTIR spectral analysis was carried out in the middle infrared region extending from 450 to 4000 cm^{-1} using Perkin Elmer spectrometer. The spectrum is shown in Fig. 2. The sample was prepared by mixing it with KBr. In the higher energy region, there is a broad intense band due to the N—H stretch of NH_3^+ symmetric stretching mode of vibration is appeared at 3428 cm^{-1}. The C—H stretching and C—N stretching mode of vibrations is observed at 2603 cm^{-1} and 995 cm^{-1} respectively. The assignments of the fundamental vibrational modes due to COO^-, NH_3^+, CH_2, CH groups were made. The carboxylic group is found to exist as the COO^-, in the crystal, and it is well known that an ionized carboxylic group has identified in the regions 1303, 1203 1378 cm^{-1} respectively. The O—C—O bending mode at 773 cm^{-1} has been identified. The COO^- rocking mode of vibrations is observed at 535 cm^{-1}. In amino acids containing NH_3^+ group, the stretching and bending vibrational wave numbers are expected [19,20] in the regions 1660–1610 cm^{-1}

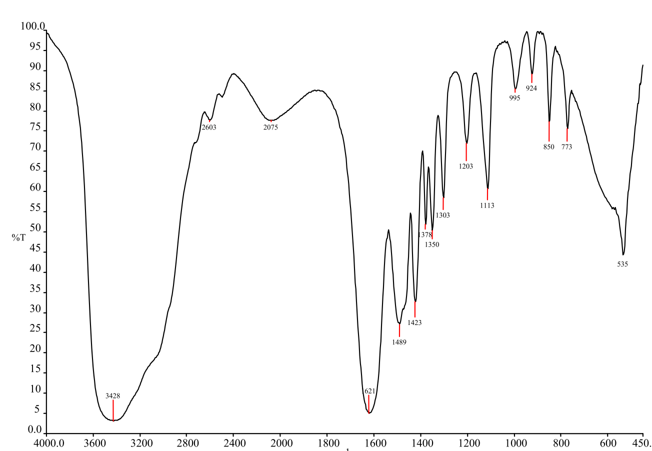

Fig. 2. FTIR spectrum of LASCT.