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Crystal growth and optical studies on a semi organic nonlinear optical material for laser blue-green generation

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ABSTRACT

In recent days amino acid single crystals are gaining importance due to good optical behavior. The title compound L-alanine lithium chloride (LAL), a semi-organic nonlinear optical material has been grown by slow evaporation technique. The material was characterized by single crystal XRD and FT-IR spectroscopic analysis. The growth mechanism and surface features are investigated by optical microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). The etching study indicates the occurrence of different types of etch pit patterns like striations, triangular etch pits and step like pattern. The UV–Vis transmittance spectrum shows that it has a good transmittance in the entire visible region with the lower cutoff wavelength at 252 nm. Fluorescence spectral studies were carried out for LAL crystal. The SHG conversion efficiency and laser damage threshold were measured using an Nd:YAG laser (1064 nm).

1. Introduction

Second order nonlinear optical materials have gained considerable attention due to their practical application in the field of optoelectronics [1]. In recent years many significant achievements have been occurred in the field of nonlinear optics because of the development of new nonlinear optical crystals of both organic and inorganic type [2]. Organic nonlinear materials have advantages such as large NLO coefficients and structural flexibility compare to inorganic counterparts [3]. The main drawbacks in organic nonlinear optical materials comes to low mechanical strength and poor physico-chemical stability. To overcome these drawbacks an attempt has been made to grow semi-organic nonlinear optical crystals include organic acids and inorganic salts and metal-organic coordination compounds [4] which makes the material to be nonlinear and good mechanical strength. Organic compounds having amino acid groups attract researches for the investigation of nonlinear optical materials offer a rich choice [5,6]. Amino acids are organic molecules that contain a carboxyl group (—COOH) as well as amino group ($—NH_2$). In the solid state, amino acids contain a protonated amino group (NH_3^+) and de-protonated carboxylic group as well as amino group (NH_2). This dipolar nature exhibits a peculiar physical and chemical properties in amino acid which makes them an ideal candidate for NLO application. As a result very good semi-organic materials such as L-histidine tetrafluoroborate (LHFB) [7], L-arginine phosphate monohydrate [LAP] [8] have been developed successfully which are found to be suitable in a number of NLO applications such as laser fusion experiments. In this series, we have grown successfully potential semi organic L-alanine lithium chloride single crystal that has NLO properties and could be used in optoelectronics.

In the present work the title compound has been synthesized by slow evaporation method. The surface features on the grown crystal has been investigated by employing atomic force microscopy (AFM), scanning electron microscopy (SEM), and etching and surface laser damage threshold (LDT) studies. Optical, LDT and AFM studies were done on broad (0 1 2) plane for LAL single crystals and (2 0 3) plane for L-alanine single crystals [9].

2. Experimental

2.1. Material synthesis solubility and crystal growth

The starting material was synthesized by taking L-alanine (Sigma Aldrich) and lithium chloride (Acros organics) in 1:1 molar ratio. The calculated amount of L-alanine was first dissolved in Millipore water of resistivity 18.2 MΩ cm and then known amount of lithium chloride was then added to the L-alanine solution with continuous stirring. The prepared solution was allowed to dry at room temperature and the salts were obtained by slow evaporation technique. The purity of the synthesized salt was further improved by successive recrystallization process.

The recrystallized salt was used for the preparation of saturated solution at room temperature (32 °C). The solution was then filtered

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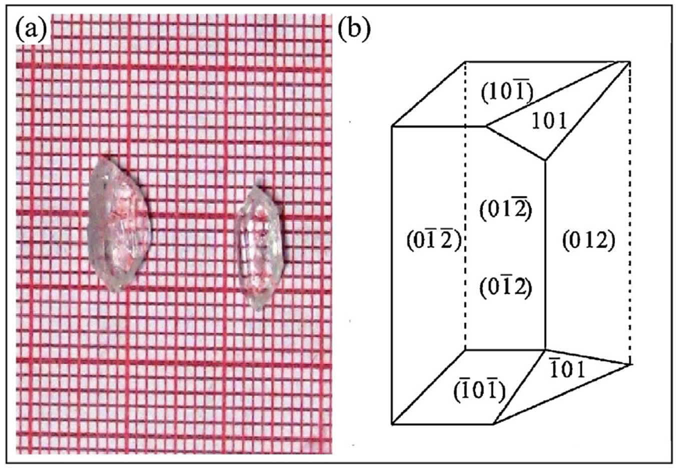

Fig. 1. Morphology and single crystals of L-alanine lithium chloride.

using Whatman filter paper of pore size 11 μm. Then the saturated solution of LAL was taken in a beaker with the perforated lid in order to control the evaporation rate, and kept at room temperature for crystallization. Single crystals of LAL were obtained after 18 days by slow evaporation method. Good quality single crystals were extracted for characterization studies. Morphology and single crystals of L-alanine lithium chloride were shown in Fig. 1a and b. Spectral studies for this crystal have been recently reported by us in Ref. [10].

The solubility of LAL was determined at four different temperatures viz., 30, 35, 40, and 45 °C. The solubility for 30 °C was determined by dissolving LAL salt in 100 ml of tripled distilled water taken in an air tight container maintained at the temperature with continuous stirring using ultra cryostat with magnetic stirrer at an accuracy of ±0.01 °C. The saturation point was confirmed by the formation of undissolved salt at the bottom of the beaker. Then 5 ml of the saturated solution was pippeted out and poured in a Petri dish. Then it was dried by keeping it in to the hot air oven. After evaporation of the solvent the Petri dish was weighed. Then the difference in the weight was taken in to account. The same procedure was repeated to estimate the solubility for different temperatures. The solubility graph was drawn and it is shown in Fig. 2.

3. Characterization studies

The title compound is subjected to single crystal XRD using computer controlled nonius MACH 3 automatic single crystal

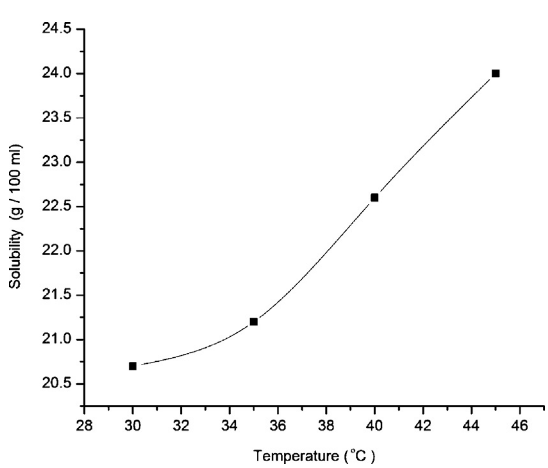

Fig. 2. Solubility of LAL.

X-ray diffractometer and its unit cell dimensions and morphology were determined. Fourier transform infrared (FTIR) spectrum was recorded by the KBr pellet technique using AVATAR 330 FTIR thermo Nicollet spectrometer for the range 400–4000 cm^{-1} to confirm the functional groups.

The surface morphologies of the grown crystal has been investigated using FEI Quanta FEG high resolution scanning electron microscope operated at 30 kV. To investigate the perfection of crystalline sample, etching studies has been done using proper etchants like water, methanol, and ethanol. Different etch pits were observed by different etchants at room temperature. Etchings of the surfaces were carried out by dipping the plates for 10 s at room temperature and then wiping with dry filter paper. Etch patterns was observed and photographed under a Carl Zeiss metallurgical microscope (Axios kop 40 MAT) provided by clemex vision PE software in reflected light. For etching purpose thin crystals of 5 mm thickness were cut from the grown crystal with the help of wet thread.

The surface characteristics were studied with the aid of an AFM (Nano surf easy scan 2, Switzerland) with a maximum XY-scan range of 70 μm. Optical studies has been carried out using ELICO SL 218 double beam UV–VIS spectrophotometer which records optical absorption spectrum in the range of 200–1100 nm. The photoluminescence measurements were carried out using the Jobin Yvon-spex make spectrofluorometer (Fluorolog version-3: Model FL3-11), 450 W high pressure Xenon lamp was used as an excitation source.

In order to determine the laser induced surface damage a Q-switched Nd:YAG laser (Litron model no: LPY704G-10) (1064 nm, 10 ns, 5 Hz) was used. The laser beam initially focused on the convex lens of focal length 30 cm and then focused in to the crystal. The crystal is mounted on a sample holder and slightly kept away from the focal spot of the beam to avoid any possible damage. The beam radius for the 1064 nm wavelength is ascertained to be 0.040 cm. Laser operation can be controlled by Gaussian remote control back panel where the energy/volts button controls the output energy of the laser by varying the charge voltage applied to the flash lamp.

The surface damage of the crystals in MW/cm^2 was calculated using the equation [11]

$$P = \frac{E}{\tau \pi r^2} \tag{1}$$

where "E" is the energy in mJ, "τ" is the pulse width in ns; "r" is radius of the spot in mm.

The damage occurring on the surface of the sample is observed with the help of scattered radiation of He-Ne laser from its surface.