Materials Chemistry and Physics 148 (2014) 457–462

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Studies on the optical, thermal and mechanical properties of nonlinear optical material – Di-L-eucine hydrochloride

Soma Adhikari, Tanusree Kar*

Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

HIGHLIGHTS

- Grown crystals are observed to be transparent and colorless with well defined appearance.
- TGA – DTA studies establish that the compound is stable up to its decomposition point at 208 °C.
- Grown crystal has a wide transparency window from 250 to 1650 nm.
- SHG efficiency of DLHC is found to be 1.3 times higher than that of KDP crystals.
- Fluorescence studies show DLHC exhibits blue fluorescence.

ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form
28 January 2014
Accepted 6 August 2014
Available online 27 August 2014

Keywords:
Optical materials
Crystal growth
Differential thermal analysis (DTA)
Photoluminescence spectroscopy
Mechanical properties

ABSTRACT

Single crystals of Di-L-eucine hydrochloride (DLHC) were grown by slow evaporation at constant temperature (40 °C). The compound crystallizes in the noncentrosymmetric space group $P2_1$. The physicochemical properties of the grown crystal were characterized by infrared spectroscopy, thermal and optical analysis, measurement of hardness. The second harmonic generation efficiency of the sample was investigated and it was found to be 1.3 times of KDP.

1. Introduction

Nonlinear optical (NLO) materials have attracted attention worldwide due to their potential applications in optical information processing, optical computing, optical communication, optical parametric oscillation, optical bi-stability, optical image processing, optical switching and frequency mixing [1–3]. They are also used in telecommunication, atmospheric sensing, lidar detectors, medical diagnostics, storage devices, computer display technology and underwater communication [4]. Crystalline salts of amino acids [5–12] have considerable interest for searching new NLO materials. This is due to the fact that all the amino acids except glycine contain chiral carbon atom and they crystallize in noncentrosymmetric space groups. Moreover aminoacids can exist as zwitterions in solids and in polar solutions such as water. Due to the overlap of π orbitals in such configuration, delocalization of electronic charge distribution leads to a high mobility of the electron density [13,14] and this facilitates enhanced nonlinearity.

Recently we have identified L-Leucine [15], an amino acid, as a potential NLO material. L-leucine is a branched chain amino acid possessing an aliphatic side-chain. It has the molecular formula $C_6H_{13}NO_2$ with a molecular weight of 131.17 g mol^{-1}. A number of complexes of L-leucine (L-leucine L-leucinium picrate [16], L-leucine nitrate [17] and L-leucine hydrobromide [18]) were reported in the literature. In this article, Di-leucine hydrochloride (DLHC) has been chosen for study as a probable nonlinear optical materials. The crystal structure of DLHC was first reported by Ljubo Golic and Walter C. Hamilton [19]. It belongs to the monoclinic crystallographic system, $P2_1$, with $a = 11.152$, $b = 5.116$ and $c = 15.405$ Å and $\beta = 108.94°$. In this instance, only very small crystals were grown, and they were unsuitable for optical investigations. Apart from the

* Corresponding author. Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; Fax: +91 33 2473 2805.
E-mail address: mstk@iacs.res.in (T. Kar).

http://dx.doi.org/10.1016/j.matchemphys.2014.08.015
0254-0584/

crystal structure no other studies on the growth of bulk single crystals and physicochemical characterization have been carried out till date. In the present paper, we report the bulk growth of DLHC crystals from its aqueous solution by slow evaporation of solvent. The grown crystals were characterized by X-ray powder diffraction, Fourier transform infrared (FT-IR) and CHN analysis. Solubility, growth morphology and the properties such as transmission spectrum, hardness, thermal analysis and photoluminescence were also investigated.

2. Experimental procedures

2.1. Synthesis, solubility and crystal growth

To synthesize DLHC a necessary quantity of L-leucine was dissolved in double distilled water with constant stirring at temperature 45–47 °C. Proportionate amount of hydrochloric acid was then added to the aqueous solution of L-leucine drop by drop through continuous stirring until a clear solution is obtained. The chemical reaction that occurs is as follows:

$$2C_6H_{13}NO_2 + HCl \rightarrow C_6H_{13}NO_2 \cdot C_6H_{14}NO_2^{+} \cdot Cl^{-}$$

The solution was finally filtered and allowed to evaporate slowly at ambient temperature. The pH of the solution at this stage was 2.3. Colorless small single crystals of DLHC were collected in 2 weeks time. The purity of the grown crystals was improved by repeated crystallization. Solubility of DLHC in water was measured as a function of temperature in the range of 30–60 °C (Fig. 1(a)). A thermostatically controlled vessel (100 ml) was filled with saturated aqueous solution of DLHC at 65 °C in the presence of precipitated solid to maintain equilibrium and then the composition of the solution was determined gravimetrically. The same procedure was repeated for other temperatures. The result indicates that though the solubility temperature coefficient of DLHC has a positive value but it is quite low, hence solvent evaporation technique is best suited for the growth of bulk crystals of DLHC. Accordingly bulk single crystals of DLHC of size 11 × 5 × 1 mm^3, were grown from its aqueous solution by solvent evaporation method at constant temperature, 40 °C, using a microprocessor controlled constant temperature bath stabilized within an accuracy of ±0.03 °C. The photograph of the as-grown single crystals of DLHC is shown in the Fig. 1(b).

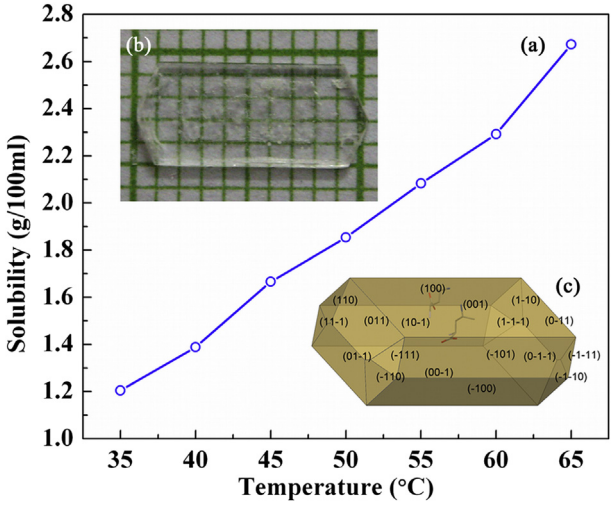

Fig. 1. (a) Solubility graph of DLHC in water. (b) Optical photograph of as grown DLHC crystal. (c) Morphology of DLHC crystal.

Morphology of the grown DLHC crystal {Fig. 1(c)} has been deduced by the Bravais-Friedel Donnay-Harker (BFDH) model [20,21] using the computer program Mercury [22] from the data of the crystallographic CIF file [19].

2.2. Characterization

Elemental analysis of C, H and N in DLHC was done using 2400 Series II (PERKIN ELMER) CHN analyzer. Identification of the grown crystals of DLHC were carried out by X-ray powder diffraction analysis using X-ray data recorded by a SEIFERT XRD 3000P X-ray diffractometer with nickel filtered CuK_α radiation (35 KV, 30 mA) having wavelength 1.5417 Å. The powder sample was scanned in steps of 0.02° for intervals of 2 s over a range of 4–50°.

The presence of functional groups and their vibrational modes were investigated by FTIR analysis [23] of DLHC. The FTIR spectrum was recorded between 400 and 4000 cm^{-1} using Perkin–Elmer 783 spectrophotometer with KBr pellet as reference.

In order to investigate the thermal behavior of DLHC, TGA and DTA thermograms were recorded simultaneously in a nitrogen atmosphere using the instrument SDTQ 600 V8.2. About 5 mg of the title compound in powder form was heated from 28 to 800 °C with a heating rate of 5 °C min^{-1} using alumina as reference. The UV–Vis absorption spectrum of the grown crystal of DLHC was recorded using VARIAN, CARY 5000 UV–Vis spectrophotometer in the range 200–2000 nm. Optically polished single crystal of thickness 0.95 mm was used for this study. Optical band gap of the material was calculated from the transmittance spectrum. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula,

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (1)$$

where, t is the thickness of the sample. The optical band gap (E_g) was evaluated from the transmission spectrum and the optical absorption coefficient (α) near the absorption edge using the Tauc's Equation (2) [24,25] given by

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \quad (2)$$

where, A is a constant, α is the optical absorption coefficient, h is Planck's constant, ν is the frequency of the incident photon, E_g is the optical band gap, and m is a constant which characterizes the nature of band transition. m can have values of 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption. $m = 1/2$ for allowed direct transition, $m = 3/2$ for forbidden direct transition and $m = 3$ for forbidden indirect transition, while $m = 2$ refer to indirect allowed transitions [26]. The extinction co-efficient (K) was obtained from the optical absorption coefficient, α, using the relation

$$K = \frac{\alpha\lambda}{4\pi} \quad (3)$$

where λ is the wavelength. 'K' defines how strongly a substance absorbs light at a given wavelength. The refractive index of DLHC crystal was measured with spectroscopic ellipsometer (Jobin Yvon).

Photoluminescence spectrum of the DLHC solution was recorded using Horiba Jobin Yvon, Fluoromax 4 spectroflurometer with a 450 W high pressure Xenon lamp as an excitation source at room temperature. The solution was excited at 230 nm and the emission spectrum was obtained.

Hardness of the material is a measure of resistance it offers to the local deformation [27]. The structure and composition of the