Optical Materials 62 (2016) 357–365

Contents lists available at ScienceDirect

Optical Materials

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

Growth and characterization of Bis(L-threonine) copper (II) monohydrate single crystals: A semiorganic second order nonlinear optical material

R. Subhashini [a], D. Sathya [b], V. Sivashankar [b], P.S. Latha Mageshwari [a], S. Arjunan [a,*]

[a] Department of Physics, R.M.K Engineering College, Kavaraipettai, Chennai, 601206, India
[b] Department of Physics, St.Xavier's College, Palayamkottai, 627002, India

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form
14 September 2016
Accepted 15 September 2016

Keywords:
Solubility
Single crystal growth
Optical properties
Dielectric
SHG
LDT

ABSTRACT

Highly transparent solitary nonlinear semiorganic optical material Bis(L-threonine) copper (II) monohydrate [BLTCM], was synthesized by a conventional slow evaporation solution growth technique. The grown crystals were subjected to structural, optical, electrical, thermal, mechanical, SHG and Laser damage threshold studies. Single crystal XRD shows that the material crystallizes in monoclinic system with noncentrosymmetric space group $P2_1$. FT-IR and FT-RAMAN analyses confirm the various functional groups present in the grown crystal. The transparency range of BLTCM was determined by UV–vis–NIR studies and various optical constants such as extinction coefficient (K), refractive index, optical conductivity and electric susceptibility with real and imaginary parts of dielectric constant were calculated using the transmittance data which have applications in optoelectronic devices. Dielectric studies of the crystal were carried out at different frequencies and temperatures to analyze the electrical properties. TGA and DSC analyses were performed to study the thermal behaviour of the sample. The hardness stability of the grown specimen was investigated by Vickers microhardness test. The output intensity of second harmonic generation was confirmed using the Kurtz and Perry powder method. The laser induced surface damage threshold of the crystal was measured using Nd:YAG laser.

1. Introduction

Nowadays, high power visible lasers have been widely used in various fields such as laser display, medicine, optical storage, biophotonics, undersea communication, marking and precision micro fabrications [1–3]. The frequency doubling of solid-state lasers operating in the near-infrared range by nonlinear optical (NLO) crystals is one of the most available methods to obtain visible laser sources with compactness, efficiency and reliability. Hence a second-order NLO material can be referred as the key for the future photonics technology. A novel nonlinear material with improved figures of merit has comported over the past few decades as a main vigour to coerce nonlinear optics from the laboratory to authentic applications [4,5]. Ideal NLO chromophores typically contain a good electron - donor and acceptor connected through a conjugated bridge. Efficient NLO chromophores are, therefore, electronically asymmetric and highly dipolar, and tend to adopt centrosymmetric arrangements as a result of the dominance of centrosymmetric dipole-dipole repulsions. Several approaches such as poled-polymers, Langmuir-Blodgett films, and self-assembled multilayers can be employed for the alignment of NLO chromophores into a noncentrosymmetric one [6–12]. Despite tremendous progress in these areas, fabrication of efficient NLO materials with high temporal and thermal stabilities remains a challenge. The qualities that evoke interest in the organic NLO crystals are their fast and large non-linear response over a broad range of frequency, structural diversity, and structural flexibility [13]. Moreover in organic nonlinear optical crystals, the external illumination by lasers of different wavelengths causes the changes in absorption spectra of material, which may occupy or depopulate the trapping molecular states. These photo induced changes are due to the formation of polarized electron–phonon states and may lead to an increase in the second-order non-linear optical susceptibility [14] but scarcely any practical usability because of their poor mechanical and thermal stability, and the infeasibility in growing large single crystals; per contra, typical inorganic NLO materials have

* Corresponding author. Tel.: +91 9444118583 (mobile).
E-mail address: arjunan_hce@yahoo.co.in (S. Arjunan).

http://dx.doi.org/10.1016/j.optmat.2016.09.041
0925-3467/

good mechanical and thermal properties, making the growth and process of large crystals easy but due to the lack of delocalisation in π-electrons they possess only passable non-linearity [15]. The advantages of inorganic and organic materials can be fraternized in semi-organic materials which have been designed and synthesized according to stoichiometric ratios [16,17]. Aminoacids, which plays a vital role in the field of nonlinear optical crystal growth, are attractive organic candidates, containing amine (-NH_2) and carboxylic acid (-COOH) functional groups along with a side chain (R group) specific to each amino acid [18]. There are numerous amino acid based NLO crystals have been reported and their properties were studied [19–21].

L-Threonine, belonging to a polar group having an uncharged R, is the isometric form of amino acids containing more than one asymmetric C atom. L-Threonine crystallizes with four zwitterionic molecules per unit cell linked by a three dimensional network of NH⋯O and O–H … bonds. L-Threonine can form variety of complexes viz., L-Threonine acetate L-Threonine picrate and L-Threonine formate, which shows very high second harmonic generation efficiency [22–24]. From the physical point of view, investigation of L-Threonine is relevant due to the technological importance of the material which shows a second harmonic conversion efficiency greater than one relative to Potassium di hydrogen phosphate and the other aminoacids [25,26]. Owing to this, L-threonine has been chosen as the organic counter part of our present investigation. The demand for single crystals has increased sharply in recent years and such demand requires the rapid growth of crystals in a shorter duration of time while maintaining the quality and size. However, the growth period of these single crystals is relatively long, normally lasting for one to two months. As complex of amino acids are believed to be more prone to induce a noncentrosymmetric space group in crystals, Bis(L-Threonine) copper (II) monohydrate (BLTCM) was chosen and was synthesized within a short span of ten days. The earlier reports [27,28] dealt with the synthesis and the crystal structure. As per the available literature there is no systematic report available on growth and characterization of BLTCM single crystal. In the present investigation we report here the structural, optical, electrical, thermal, mechanical, SHG and Laser damage threshold studies of BLTCM single crystal for the first time.

2. Experimental procedure

2.1. Crystal growth

BLTCM was synthesized [28] by taking L-Threonine (loba chemie) and basic copper carbonate in equimolar ratio (2:1) in deionized water. The prepared solution was stirred well for 3 h using a magnetic stirrer to get a homogeneous mixture. The solution was filtered and allowed for evaporation. After a growth period of 10 days, optically transparent and non-hygroscopic good quality blue single crystals were harvested. Repeated recrystallization results in highly pure good quality single crystals as shown in Fig. 1.

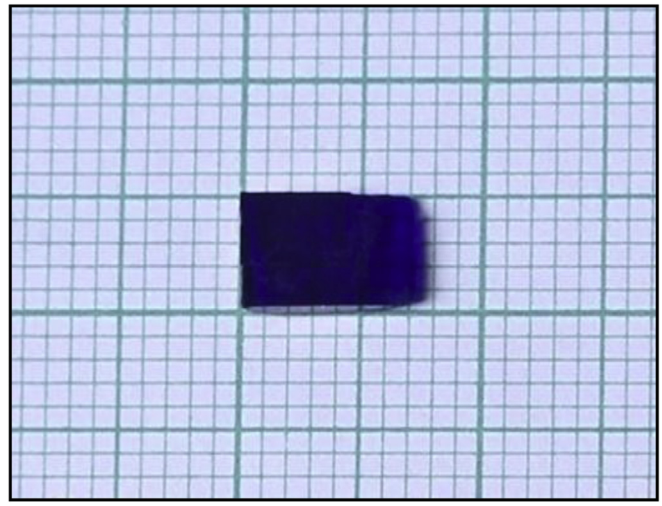

Fig. 1. As grown crystal of BLTCM.

2.2. Material characterization techniques

Single crystal diffraction studies of the grown BLTCM crystal were carried out using Bruker Kappa Apex II Single crystal X-ray diffractometer. The FT-IR spectrum was recorded using Perkin Elmer spectrophotometer by KBr pellet method, in the region 4000–400 cm^{-1}. FT-RAMAN spectrum was recorded for the crystal using Bruker: RFS 27 stand alone FT-RAMAN spectrometer in the range 4000–50 cm^{-1}. The percentage of Carbon, Nitrogen and Hydrogen present in the crystal has been recorded using Perkin-Elmer 2400 series CHNS Analyzer. The transmission spectra of the polished grown crystal were taken using Perkin Elmer LAMBDA35 spectrophotometer in the wide range 190 nm–1100 nm. Dielectric measurements of BLTCM were carried out by HIOKI HITESTER MODEL 3532-50 LCR meter for a frequency range of 50 Hz–50,000 Hz in various temperature ranges. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out using a SDT–Q600 TA thermal analyzer in the temperature range 25–1000 °C with a heating rate of 10 °C per minute in a nitrogen atmosphere. Vicker's microhardness test was performed using SHIMADZU HMV-2T MICROHARDNESS tester to determine the mechanical strength of crystal. The indentations on crystal were made for various loads for a dwell time of 10 s. Kurtz and Perry powder technique [29], was performed to confirm the existence of second harmonic generation in the crystal for which a Nd:YAG laser with fundamental radiation of 1064 nm was used as the optical source. The LDT measurement was carried out using Q-switched Nd:YAG laser for 10 ns laser pulses at a wavelength of 1064 nm operating in TEM00 mode.

3. Results and discussions

3.1. Solubility studies

The solubility study is one of the indispensable criterions to determine the growth rate of the crystals. Higher the solubility of a material, higher would be the growth rate of a crystal at an optimized condition. The knowledge of the solubility of solutes in different organic solvents is important in design applications inorder to make an appropriate solvent selection for liquid-liquid extractions or recrystallizations. The solubility test for the title compound was carried out using distilled water, ethanol and methanol. It is observed that the distilled water is the most suitable solvent to grow BLTCM single crystals. A constant volume of 100 ml of saturated solution was used in this experiment. The measurement was performed by dissolving the BLTCM salt in deionized water in an airtight container maintained at a constant temperature with continuous stirring. The solution was constantly stirred for 3 h using a magnetic stirrer for homogenization. The solubility of BLTCM was ascertained for five different temperatures namely 30, 35, 40, 45, 50 °C. The solubility curve of BLTCM crystal is depicted in Fig. 2. It is seen from the figure that the BLTCM has a positive gradient of solubility.