Optics and Laser Technology 101 (2018) 248–256

Contents lists available at ScienceDirect

Optics and Laser Technology

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

Full length article

Synthesis and physicochemical properties of bis(L-asparaginato) zinc(II): A promising new semiorganic crystal with high laser damage threshold for shorter wavelength generation

R. Subhashini, S. Arjunan *

Department of Physics, R.M.K Engineering College, Kavaraipettai, Chennai 601206, India

ARTICLE INFO

Article history:
Received 20 June 2017
Received in revised form 8 October 2017
Accepted 8 November 2017

Keywords:
Crystal growth
Optical properties
SHG
LDT
Thermal studies
Dielectric

ABSTRACT

An exceedingly apparent nonlinear semiorganic optical crystals of bis(L-asparaginato)zinc(II) [BLAZ], was synthesized by a traditional slow evaporation solution growth technique. The cell parameters were estimated from single crystal X-ray diffraction analysis. Spectroscopic study substantiates the presence of functional groups. The UV spectrum shows the sustenance of wide transparency window and several 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. The fluorescence emission spectrum of the crystal pronounces red emission. The laser induced surface damage threshold of the crystal was measured using Nd:YAG laser. The output intensity of second harmonic generation was estimated using the Kurtz and Perry powder method. The hardness stability was investigated by Vickers microhardness test. The decomposition and thermal stability of the compound were scrutinized by TGA-DSC studies. Dielectric studies were carried out to anatomize the electrical properties of the crystal. SEM analysis reveals the existence of minute crystallites on the growth surface.

1. Introduction

Nonlinear optical materials with large nonlinear susceptibilities has aroused much interest and are very much indispensable for the devices such as optical switching, optical modulation and computing devices, as the magnitude of this quantity dominates the device performance [1]. Organic compound provides a number of enticing opportunities in applications as nonlinear optical materials due to the presence of π-conjugated delocalized electronic structure. NLO responses in these broad class of materials (organic) is microscopic in origin, offering an opportunity to use theoretical modeling coupled with extremely synthetic flexibility to design and breed new materials but scarcely any practical usability because of their poor mechanical stability, thermal stability, and the infeasibility in growing large single crystals. Organic systems suffer in fact a loss of activity with time span due to the relaxation of chromophore alignment obtained through electrical poling. In contrast, typical inorganic NLO materials have good mechanical and thermal properties, making the growth and process of large crystals easy [2–5] but they possess only passable non-linearity and are more expensive to synthesis. The supremacy of organic and inorganic compounds can be amalgamated in a metal co-ordinated organic compound. In metal-organic compounds, metal centers can act as both donors and the bridging moiety in D–π–A system. Moreover, the metal–ligand bond is assumed to display large molecular hyperpolarizability due to the transfer of electron density between the metal atom and the conjugated ligand system [6]. Amino acids are potential candidates for growth of nonlinear optical (NLO) single crystal due to the presence of acidic carboxyl and basic amino group which paves the way for the formation of zwitter ion or dipolar ion as a result of internal neutralization reaction. This dipolar nature of amino acids helps to improve the crystal hardness [7] and the physical and chemical properties, making them as a peculiar candidate in the nonlinear optical field [8]. L-asparagine is a non-essential amino acid that helps in the metabolic control of cell functions of nerve and brain tissue. Besides its biological interest, there is a lot of curiosity in growing L-asparagine family of crystals due to its high second harmonic generation efficiency. L-asparagine can form variety of complexes like L-asparagine Monohydrate, L-asparaginium picrate, L-asparagine L-tartrate [9–11]. By selecting suitable constituent

* Corresponding author.
E-mail address: san.sh@rmkec.ac.in (S. Arjunan).

https://doi.org/10.1016/j.optlastec.2017.11.009
0030-3992/

ligands or encapsulating desirable guest molecules in L-asparagine, with a combination of crystal engineering and synthetic chemistry, advanced crystals with highly efficient optical nonlinearities can be achieved. In this view, single crystals of bis(L-asparaginato) zinc(II) [BLAZ] has been chosen for investigation. Literature survey shows the report of structure analysis of Bis (L-asparaginato)zinc(II) single crystals [12] but no detailed investigation has been made on this crystal. Hence the structural, optical, mechanical, thermal, electrical, SHG and Laser damage threshold studies of BLAZ crystal are reported here for the first time.

2. Experimental procedure

The premeditated analytical grade precursors of L-asparagine (37.0 mmol), zinc chloride ($ZnCl_2$, 18.5 mmol) and NaOH (37.0 mmol, to obtain solutions with neutral pH) were mixed in 100 ml of triple distilled water and stirred well for three hours at room temperature to yield a homogeneous solution [12]. The solution was filtered and allowed for evaporation. After the growth period of 15 days, non-hygroscopic, good quality, single crystals of BLAZ as shown in Fig. 1 were harvested.

3. Results and discussion

3.1. X-ray diffraction analysis

3.1.1. Single crystal X-ray diffraction

The Bruker Kappa Apex II Single crystal X-ray diffractometer is used to survey the cell parameters of the grown crystal at room temperature. The XRD analysis enlightens that the BLAZ crystallizes in monoclinic system with space group $P2_1$. The estimated lattice parameters values, tabulated in Table 1, are in good agreement with the reported values [12].

3.1.2. Penn gap analysis

The molecular weight of BLAZ, $C_8H_{14}N_4O_6Zn$, is 327.6 and its density is 1.82 g cm^{-3} [12]. Using these data, the valence electron plasma energy, $\hbar\omega_p$, is calculated from the equation,

$$\hbar\omega_p = 28.8(z.\rho/M)^{1/2} \quad (1)$$

where $Z = [(8 \times Z_C) + (14 \times Z_H) + (4 \times Z_N) + (6 \times Zo) + (1 \times Z_{Zn})] = 72$ is the total number of valence electrons, ρ is the density and M is the molecular weight of the grown crystal. The Penn gap and the Fermi energy is obtained from,

$$E_P = \hbar\omega_p/(\varepsilon_\infty - 1)^{1/2} \quad (2)$$

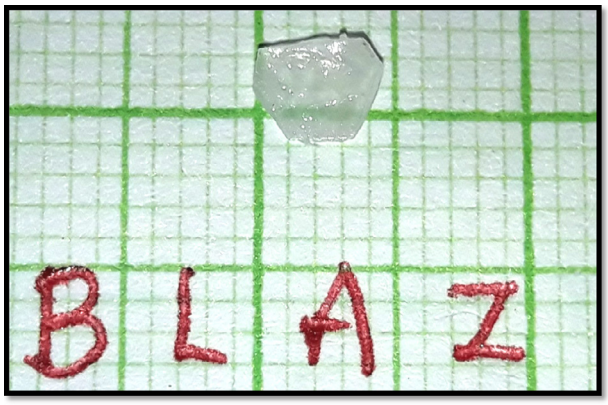

Fig. 1. As grown BLAZ crystal.

Table 1
Single crystal X-ray diffraction data.

Crystal data (parameter)	Present study
Crystal shape	Plate
Nature	Transparent and colourless
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimension	a = 12.263 Å, b = 5.062 Å, c = 9.717 Å α = 90.00°, β = 99.18°, γ = 90.00°
Cell volume	V = 584 $Å^3$

and

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (3)$$

Polarizability α is given by,

$$\alpha = \left(\frac{(\hbar\omega_p)^2 s_o}{(\hbar\omega_p)^2 s_o + 3E_p^2}\right) \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \quad (4)$$

where S_0 is a constant for a particular material. It is given by,

$$s_o = 1 - \left(\frac{E_P}{4E_F}\right) + \frac{1}{3}\left(\frac{E_P}{4E_F}\right)^2 \quad (5)$$

Polarizability α is also determined by the Classius–Mossotti equation,

$$\alpha = \left(\frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \quad (6)$$

where all the symbols have their own significance. The values are given in Table 2.

3.2. Spectroscopic studies

3.2.1. FT-IR analysis

The FTIR spectrum of BLAZ documented in the region of 4000–400 cm^{-1} using Perkin Elmer spectrophotometer by KBr pellet method is shown in Fig. 2. In the higher energy region FTIR spectrum, there is a broad intense band due to the N—H stretch of NH_3. The N—H symmetric stretching vibration occurs in the region 3551.28 cm^{-1}. The asymmetric NH_2 stretching vibration is observed to give a less intense peak at 3475.24 cm^{-1}. The symmetric NH_2 stretching appears as well-resolved sharp peak at 3417 cm^{-1}. N—H band of amino ligand produces peak at 3240 cm^{-1}. NH_2 scissoring mode lies at 1637.97 cm^{-1} [13,14]. The bands due to CH stretching mode appear just below 3000 cm^{-1}. 1618.74 cm^{-1} is assigned for C=O stretching vibration mode. The bending mode involving hydrogen atom attached to the central carbon falls at 1410.03 cm^{-1}. The absorbance peaks at 1079 cm^{-1} is due to stretching of the C—O bond. The vibrational peak lying at 616.74 cm^{-1} is due to torsional oscillation of NH_3. The two L-asparagine ligands each coordinate to the Zn atom through a carboxylic O and the amino N atom forming a trans square-planar configuration. Generally all the metals and

Table 2
Theoretical parameters of BLAZ crystal.

Parameters	Values	Parameters	Values
Plasma energy (eV)	18.214	Polarizability (cm^3)	
Penn gap (eV)	1.549	1. Penn analysis	6.9854×10^{-23}
Fermi energy (eV)	14.126	2. Clausius–Mossotti equation	6.9809×10^{-23}