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Growth Aspects of Semi-Organic Nonlinear Optical L-Theronine Lithium Bromide Single Crystals

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ABSTRACT

Single crystals of L-theronine lithium bromide (LTLB), a semi-organic NLO material have been grown from aqueous solution by the slow evaporation method. The grown crystals were transparent and was subjected to the following characterization studies. The lattice parameters of the grown crystals were determined by the single-crystal X-ray diffraction technique. The grown crystals were also characterized by recording the powder X-ray diffraction pattern and by identifying the diffraction planes. FTIR studies are performed to identify the presence of various functional groups in the grown crystal. Ultraviolet-visible spectral analyses showed that the crystal has UV cut-off at 263 nm combined with good transparency in the entire visible region and the optical band gap was estimated to be 4.1 eV. The second harmonic generation relative efficiency of the grown crystals were observed to be 1.13 times that of potassium dihydrogen orthophosphate (KDP).

Keywords: semi-organic NLO material, X-ray diffraction, FTIR, second harmonic generation

INTRODUCTION

Inorganic and semiorganic nonlinear optical (NLO) materials have higher optical quality, larger nonlinearity, good mechanical hardness and low angular sensitivity when compared to organic NLO materials [1]. Nonlinear optical materials have a great number of applications to perform functions like frequency conversion, high modulation, optical switching, optical memory storage and optical second harmonic generation (SHG). Moreover, optical non-linearity is highly dependent on the geometrical arrangement of the molecules, and it favours organic crystals more to exhibit large non-resonant optical non-linearities [2]. In the last decade the numerous applications of the nonlinear optical (NLO) crystals have been discussed in the field of science and technology [3-5]. Recently, the amino acid crystals have been subjected to extensive investigations by several researchers owing to their high NLO properties. In the solid state, amino acids contain a protonated amino group (NH_3^+) and deprotonated carboxylic group as well as amino group (NH_2). This dipolar nature exhibits peculiar physical and chemical properties in amino acid which makes them an ideal candidate for NLO applications.

In the recent decades, amino-acid family single crystals are gaining more importance with interesting organic and inorganic matrices to produce outstanding materials to challenge the established materials like niobates, borates and the formates. Thus, materials like L-hystidine tetrafluoroborate (L-HFB) [6,7], L-arginine tetrafluoroborate (L-ATFB) [8], L-Lysine-L-Aspartate (LLA) [9], L-theronine formate (LTF) [10] etc., have been projected because of their low UV cutoff and high NLO coefficients. Nonlinear α-amino acids show special features of interest such as molecular chirality and wide transparency in the visible and UV region. In this view the reported single crystals of L-theronine lithium bromide (LTLB) is a potential semi-organic NLO material. The optical quality LTLB crystals have been grown by the slow evaporation method. The crystal system was identified by X-ray diffraction technique. The functional groups were identified by FT-IR analysis. The transparency of LTLB was depicted by UV-Vis spectrum. SHG efficiency of the grown crystal was measured by powder Kurtz method using Nd:YAG laser.

MATERIALS & METHODS

The calculated amount of L-theronine (Sigma-Aldrich) and lithium bromide were mixed in equimolar ratio for the synthesis of LTLB salt. Deionised water was used as a solvent to dissolve the salt and the solution was stirred for 7 hours using magnetic stirrer till to get a saturated solution. To steer clear of impurities, the saturated solution was filtered and allowed to evaporate at room temperature. Optical quality crystals of dimension 10 X 2 X 2 mm^3 were obtained over a typical growth period of 22 days and the harvested crystals were shown in Fig. 1.

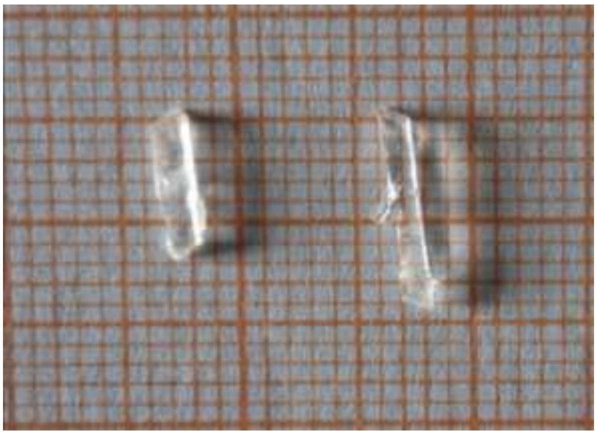

Fig. 1 As-grown crystal of LTLB

Single crystal X-ray diffraction analysis was carried out using a BRUKER APEX2 single-crystal X-ray diffractometer for unit cell dimensions and space group determination. The powder X-ray diffraction patterns were obtained using a powder X-ray diffractometer (BRUKER-binary V4 with Nickel filtered CUKα radiations (1.54060 Å), 40 KV, 30 mA).

Vibrational spectroscopy is an important tool in understanding chemical bonding and may provide useful information in studying the microscopic mechanism of the nonlinear optical properties of the materials. The infrared spectroscopy is effectively used to identify the functional groups of the grown crystals. The FT-IR spectra of the samples were recorded using Perkin Elmer spectrometer by the KBr pellet technique in the range 400-4000 cm^{-1}. Linear optical properties of the crystal have been studied using a UV-Visible spectrophotometer. To confirm the nonlinear optical property, the grown crystals have been subjected to Kurtz powder SHG test.

RESULT & DISCUSSION

a. X-ray diffraction analysis

Single crystals of LTLB were subjected to single-crystal X-ray diffractometer with MoKα radiation (λ = 0.71073 Å) to determine unit cell parameters and space group. LTLB belongs to orthorhombic system and crystallizes in space group $P2_12_12_1$ with unit cell parameters a = 5.17 Å, b = 7.76 Å, c = 13.68 Å, α = β = γ = 90° and cell volume is 549 $Å^3$. The measured cell parameters are in good conformity with the published values [11]. Fig.2 represents the X-ray pattern of LTLB and well-defined Bragg peaks are obtained at specific 2θ angles indicating that crystals are ordered.

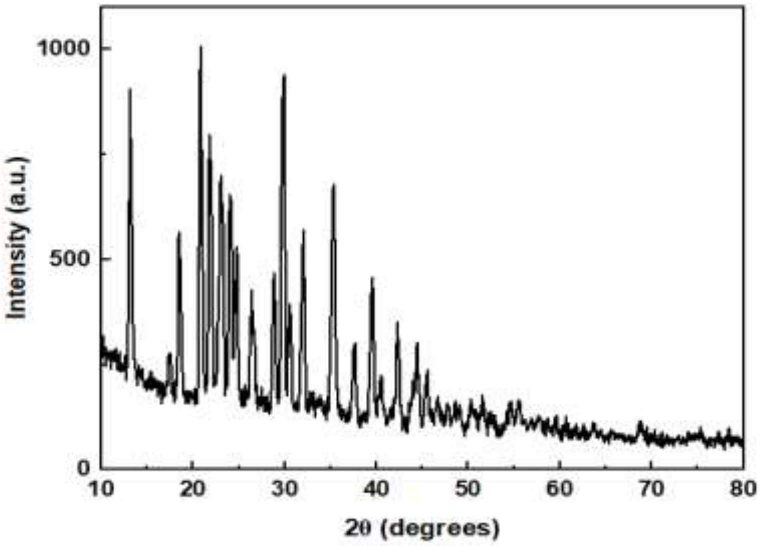

Fig. 2 Powder XRD pattern of LTLB

b. FT-IR spectral analysis

In the FTIR spectra of LTLB crystals a broad envelope is seen between 2500 and 3100 cm^{-1} this is because of hydrogen interaction with the other atoms such as N-H stretching of NH_2 and C-H stretching of CH_2. The band at 1628.55 cm^{-1} is due to C=O stretching vibrations and the symmetric stretching of CO_2 is observed at 1417.85 cm^{-1}. The bending vibrations of CH group are found corresponding to the peaks at 1248.25 and 1346.08 cm^{-1}. The rocking of NH_3 group is observed at 1113 and 1184 cm^{-1}. The peak at 932.74 cm^{-1} is associated with C-C stretching vibration. The bending and wagging vibration of CO_2 is observed at 769.36 and 701.53 cm^{-1} respectively. The band at 490.02 cm^{-1} is assigned to the torsional mode of NH_3. The transmission spectrum of LTLB crystal is depicted in Fig. 3.

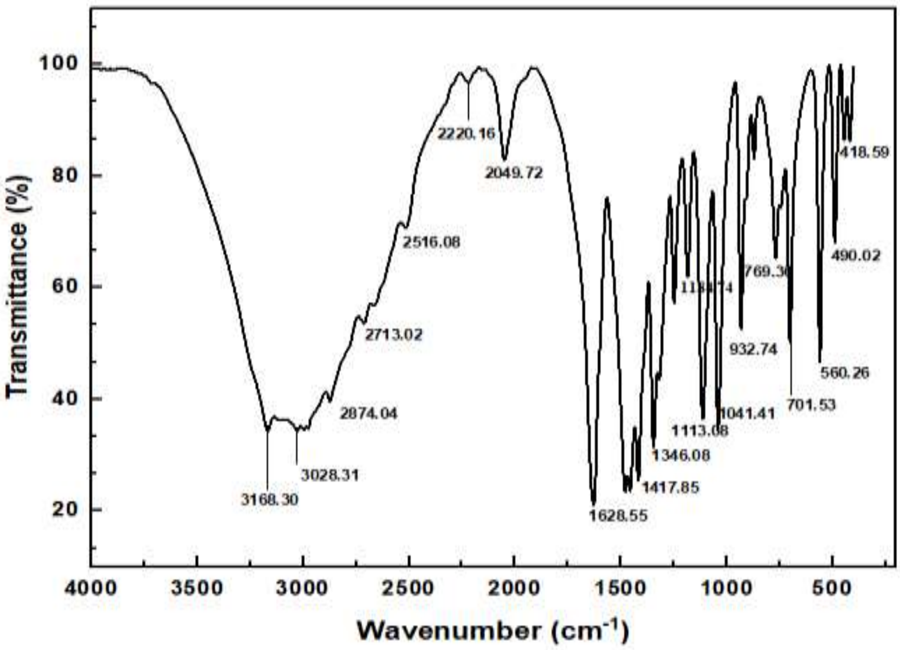

Fig. 3 FTIR spectrum of LTLB

c. Optical studies

The UV–Vis spectrum provides limited information about the structure of the molecule because the absorption of UV and visible light involves electronic transition in the σ and π orbital from the ground sate to higher energy states. The optical transmittance plays a key role in identifying the potential of the NLO material because a given material can be of practical use only if it possesses wide transparency window without absorption around the fundamental and second harmonic wavelength. The lower cut-off of transparency less than 400 nm is very important for the realization of SHG output in this range using diode and solid-state lasers.

The absorption spectra of LTLB crystal is measured in the range 200-800 nm using UV-visible Perkin Elmer lambda 950 UV-Vis-NIR spectrometer. The recorded transmission spectrum is shown in Fig. 4. It is observed that the crystal has good transparency window in the entire visible and IR region. The lower cut off wavelength is 263.87 nm. A graph between hυ and $(\alpha h\upsilon)^2$ was drawn where hυ is the energy of the incident photon and α is the optical absorption coefficient and is depicted in Fig. 5. From the Tauc's plot [12], the direct band gap energy of LTLB has been calculated by extrapolating the linear portion of the curve to zero absorption which is found to be 4.1 eV.

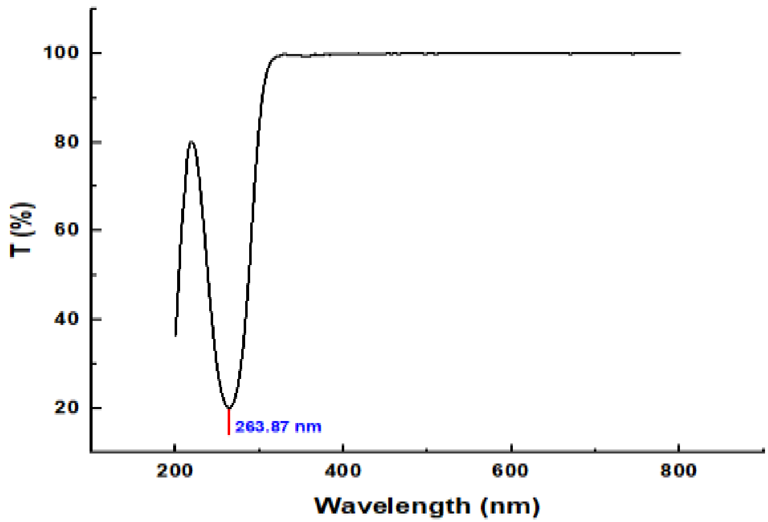

Fig. 4 Optical transmission spectrum of LTLB

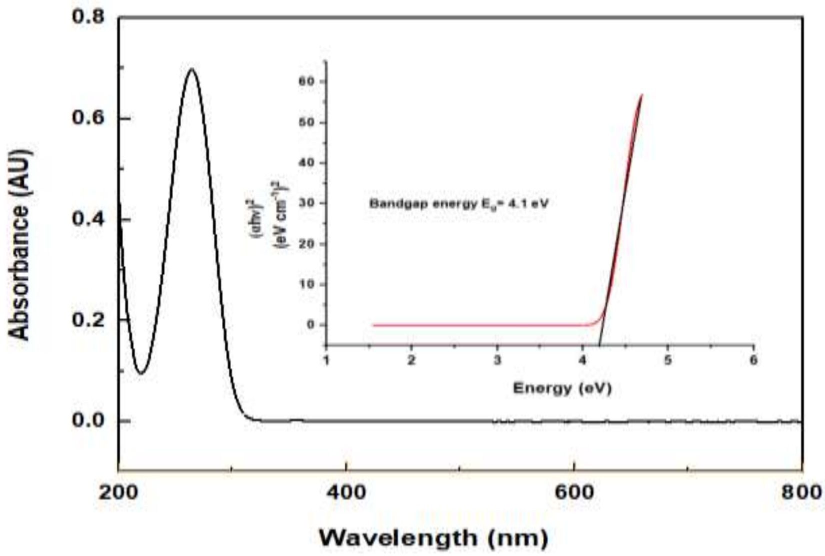

Fig. 5 Optical absorption spectrum of LTLB with Tauc's plot

d. Second harmonic generation efficiency

The second harmonic generation (SHG) efficiency of LTLB crystal was examined using the Kurtz and Perry [13] powder technique. A fundamental Nd:YAG laser beam of wavelength 1064 nm was allowed to strike the sample cell normally and a sample of potassium dihydrogen phosphate (KDP) was used as a reference material. The input pulse energy was 0.7 J/pulse and the pulse width of 6ns with a repetition rate of 10Hz were used. The second harmonic signal generated was confirmed from the emission of green light of wavelength 532 nm from the powdered sample. The emitted light passed through an IR filter was measured by means of a detector oscilloscope assembly. The outcome of SHG signal with the energy 7.9 mJ confirms the nonlinear behaviour of the grown LTLB crystal and its SHG efficiency is 1.13 times that of KDP crystal. A comparison of NLO property of LTLB crystal with a few well-known NLO crystals is presented in Table 1.

Compound	NLO efficiency
LTLB (Present Work)	1.13
L-theronine [14]	1.04
L-threonium acetate [15]	1.14
L-arginine phosphate [16]	0.30
L-threonine formate [10]	1.21
L-theronine zinc acetate [17]	3.3
L-theronine cadmium chloride [18]	0.7

Table 1 Comparison of NLO property of various NLO crystals

CONCLUSION

A semiorganic nonlinear optical crystal of LTLB have been grown from aqueous solution by solvent evaporation technique at room temperature. Single crystal X-ray diffraction studies reveal that the crystal LTLB belongs to orthorhombic system with space group $P2_12_12_1$. Powder X-ray diffraction pattern confirmed the formation of LTLB and its crystalline nature. The FT-IR spectra of LTLB crystal confirms the presence of various functional groups. The wide transparency window in the entire visible region indicates that the LTLB is suitable candidate for NLO applications. The optical band gap of the material was calculated as 4.1 eV. Kurtz powder SHG test confirmed the frequency doubling of the grown crystal and SHG efficiency is 1.13 times that of KDP. Hence, the grown material can also be considered as a potential NLO candidate for the fabrication of nonlinear optical devices involving frequency-doubling process.

Declaration by Author

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Conflict of Interest: No conflicts of interest declared.

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