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Growth, thermal, dielectric and mechanical properties of L-phenylalanine–benzoic acid: A nonlinear optical single crystal

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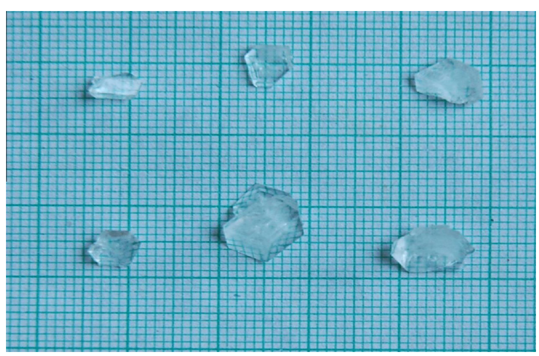
HIGHLIGHTS

- Systematic studies have resulted in the growth of high quality nonlinear optical material.
- The grown crystal has high laser damage threshold and the NLO efficiency is 1.6 times greater than that of KDP.
- The grown crystals were characterized and reported for the first time.
- The results suggest that LPB could be expected to be a suitable material for the NLO device fabrication.

GRAPHICAL ABSTRACT

Growth, thermal, dielectric and mechanical properties of L-phenylalanine–benzoic acid: A novel nonlinear optical single crystal.



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ABSTRACT

An efficient amino acid family nonlinear optical single crystal L-phenylalanine–benzoic acid (LPB) was conveniently grown by slow evaporation technique at room temperature. The crystal system and the lattice parameters were analyzed by single crystal X-ray diffraction studies. The grown crystal has excellent transmission in the entire visible region and its lower cut-off wavelength was found to be 248 nm. The SHG efficiency of the grown crystal was found to be 1.6 times higher than that of KDP crystal. The Laser damage threshold value of LPB has been found to be 6.5 GW/cm^2. The sample was thermally stable up to 134 °C. Microhardness, dielectric and AC/DC conductivity measurements were made along (001) plane and reported for the first time. Microhardness studies revealed that the sample belongs to hard nature. Frequency dependent dielectric constant was measured for different temperatures and found maximum dielectric constant of 14 for 363 K. Photoconductivity studies of LPB divulged its negative photoconducting nature.

Introduction

Versatile and efficient sources of blue light are important requirements for various applications including optical data storage, ophthalmologic or other medical techniques and laser dis-

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plays. In spite of the rapid development of blue laser diodes and concurrent physical principles like optical upconversion, optical second-harmonic generation (SHG) is still one of the important methods to achieve intense coherent blue and green light with good optical beam quality [1]. It has been generally understood that the second-order molecular nonlinearity can be enhanced by large delocalized π-electron systems with strong donor and acceptor groups [2,3]. From symmetry aspects, SHG is only possible in crystals belonging to the point group that lack a center of symmetry. Furthermore, efforts have been made to develop new inorganic, organic and semi-organic nonlinear optical (NLO) crystals [4–6]. Organic compounds are formed by weak Van der Waal's and hydrogen bonds and possess high degree of delocalization [4]. Hence they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance, etc. [5]. Many of natural amino acids are individually exhibiting the nonlinear optical properties because they are characterized by chiral carbons, a proton-donating carboxyl group and the proton-accepting amino group [6]. Among them, L-phenylalanine is an essential protein amino acid, which is used by the body to build neurotransmitters [7,8]. The crystal of the L-phenylalanine–benzoic acid (LPB) compound, $C_9H_{11}NO_2{\cdot}C_7H_6O_2$, the amino acid molecule exists as a zwitterion and the carboxylic acid molecule is in a unionized state. There is a strong O—H···O intermolecular hydrogen bond between the phenylalanine and benzoic acid molecules, and these molecular pairs form hydrogen-bonded double layers. Recently, the crystal structures of complexes of phenylalanine with maleic acid [9,10] and fumaric acid [11], trichloroacetic acid [12] and malonic acid [13] were elucidated. The structure of L-phenylalanine–benzoic acid was first reported by Suresh et al. [14]. The present investigation deals with the growth of LPB single crystal by slow solvent evaporation technique at room temperature. The grown crystals were characterized by studying their structural, optical, thermal, mechanical, and electrical and laser damage threshold properties and reported for the first time. The mechanical and electrical properties were performed along (0 0 1) plane of the grown crystal.

Experimental details

Synthesis of LPB

Stoichiometric amounts of L-phenylalanine and benzoic acid taken in 1:1 ratio were dissolved in double distilled water to prepare the aqueous solution of LPB. In deionized water, L-phenylalanine and benzoic acid undergo the following chemical reaction to produce LPB.

$$C_9H_{11}NO_2 + C_7H_6O_2 \longrightarrow C_9H_{11}NO_2 \cdot C_7H_6O_2$$

Synthesized salt of LPB was obtained from the solution by evaporating the solvent and collecting the precipitate formed at the bottom of the container having the solution.

Growth of LPB single crystals

Based on the solubility data, the supersaturated solution was prepared at room temperature for growth experiments. The solvent of the supersaturated solution was allowed to evaporate through the perforated lid of the container. Due to spontaneous nucleation, optically clear tiny crystals were formed in a period of 5–7 days. The defect free and well shaped ones were chosen and used as seed crystals for further growth experiments. Good optical grade and colorless crystals of dimension up to $10 \times 9 \times 4\ mm^3$ were grown over a period of 35–40 days by using slow evaporation technique. The photograph of as grown LPB single crystals is shown in Fig. 1.

Results and discussion

Single crystal XRD study

An automatic X-ray diffractometer (MESSRS ENRAF NONIUS CAD4-F, The Netherlands) was employed to collect the single crystal X-ray data of LPB single crystal. The unit cell parameters of LPB were determined using 25 reflections collected through random search routine with graphite monochromated Mo Kα (λ = 0.71073) radiation and indexed by the method of short vectors followed by the least squares refinement. The study revealed that LPB crystal belongs to monoclinic crystal system with a non-centrosymmetric space group $P2_1$ and the lattice parameters were found to be a = 5.421 Å, b = 7.435 Å, c = 17.816 Å, β = 93°, and the cell volume V = 718 Å^3. The experimental data has good agreement with the reported data [14].

FT-IR analysis

The FT-IR spectrum of LPB was recorded using BRUKER IFS-66V spectrometer in the range between 4000 and 400 cm^{-1}. The middle IR spectrum of LPB is shown in Fig. 2. The broad envelope between 3400 and 2500 cm^{-1} includes absorption of stretching bands due to NH_3^+ ion of the amino acid. The O—H stretch of COOH produces the characteristic peak at 3452 cm^{-1}. The NH_3^+ asymmetric and symmetric stretching vibrations are positioned at 3290 and 2598 cm^{-1} respectively. These two bands clearly indicate unprotonation of carboxylate ions. In other words, L-phenylalanine salt is zwitterionic with respect to its amino acid grouping. Strong carbonyl absorption at 1725 cm^{-1} identifies the COOH and COO^- groups of the compound. Multiple fine structures at the lower energy mode of the envelope indicates the strong hydrogen bonding interaction of NH_3^+ group with weak absorptions of COO^- group at 1598 and 1417 cm^{-1}. Further strong band observed at about 1217 cm^{-1} is due to C—COO^- stretching. The presence of L-phenylalanine ions in the crystal structure is reflected in the bands of the NH_2 rocking (780 cm^{-1}), COO^- wagging (555 cm^{-1}), NH_2 out-of-plane bending (703 cm^{-1}) and OH out-of-plane deformation (620 cm^{-1}). Moreover, rocking mode, symmetric deformation and wagging are found from the spectrum and are presented in Table 1.

Optical studies

Fig. 3 shows the optical absorption spectrum of LPB along with Tauc's plot. The good absorption property of the crystal in the entire visible region suggests its suitability for second harmonic

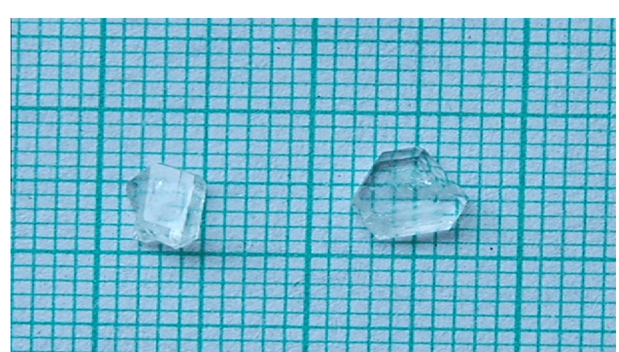

Fig. 1. Photograph of as grown LPB single crystals.