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Growth and dielectric, mechanical, thermal and etching studies of an organic nonlinear optical L-arginine trifluoroacetate (LATF) single crystal

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Abstract

L-arginine trifluoroacetate, an organic nonlinear optical material, has been synthesized from aqueous solution. Bulk single crystal of dimension 57 mm × 5 mm × 3 mm has been grown by temperature lowering technique. Powder X-ray diffraction studies confirmed the monoclinic structure of the grown L-arginine trifluoroacetate crystal. Linear optical property of the grown crystal has been studied by UV–vis spectrum. Dielectric response of the L-arginine trifluoroacetate crystal was analysed for different frequencies and temperatures in detail. Microhardness study on the sample reveals that the crystal possesses relatively higher hardness compared to many organic crystals. Thermal analyses confirmed that the L-arginine trifluoroacetate material is thermally stable upto 212 °C. The etching studies have been performed to assess the perfection of the L-arginine trifluoroacetate crystal. Kurtz powder second harmonic generation test confirms the nonlinear optical properties of the as-grown L-arginine trifluoroacetate crystal.

Keywords: A. Organic compounds; B. Crystal growth; C. Differential scanning colorimetry (DSC); D. Dielectric properties; D. Mechanical properties

1. Introduction

Organic nonlinear optical (NLO) crystals are more attractive owing to their potentially high nonlinearities and rapid response in the electro-optic effect compared to inorganic NLO crystals. The microscopic origin of nonlinearity in the organic molecular NLO materials is due to the presence of delocalized π-electron systems connecting donor and acceptor groups, which enhance the necessary asymmetric polarizability [1]. Among the several organic crystals, L-arginine derivative organic crystals have been reported to have improved properties such as high NLO coefficient, laser damage threshold and thermal stability comparable to that of inorganic materials. L-arginine phosphate monohydrate (LAP) has high angular sensitivity than KDP crystal. LAP has three times more nonlinear than that of KDP [2,3]. The refractive index and SHG measurements looked promising for L-arginine with acids like fluoride, chloride and acetate [4–6]. All the compounds in this class contain an optically active carbon atom and therefore all of them form acentric

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crystals. L-arginine trifluoroacetate (LATF), one of the important analogs of L-arginine, has better thermal stability and transparency than LAP [7]. The dielectric behavior of a material is an important factor as it has direct influence on the growth dynamics and NLO efficiency of the crystals. When the crystals are brought to the device applications, they are also required to have good mechanical strength and thermal stability without defects. Hence, we present in this paper, the investigations on the dielectric, mechanical, thermal and etching characteristics in addition to structural and optical properties of the LATF crystal.

2. Material synthesis and crystal growth

L-arginine trifluoroacetate was synthesized by dissolving equimolar ratio of L-arginine and trifluoroacetic acid in deionized water based on the following reaction.

$$\begin{aligned}&(NH_2)NHCNH(CH_2)_3CH(NH_3)COOH + CF_3COOH\\&\quad\rightarrow (H_2N)_2{}^{+}CNH(CH_2)_3CH(NH_2)COOHCF_3COO^{-}\ (\text{L-arginine trifluoroacetate})\end{aligned}$$

The synthesized salt was subjected to repeated recrystallization process in order to increase the purity. A saturated growth solution was prepared using recrystallized LATF salt in deionized water at room temperature. The prepared solution was slightly warmed, filtered and then allowed to evaporate very slowly. After a few days, colorless optical quality seed crystals were obtained. Bulk crystals of LATF were grown by slow cooling technique in a constant temperature bath with a temperature accuracy of ±0.01 °C, which is achieved by an optical heating arrangement. The LATF growth solution was maintained at the saturation temperature (42 °C) for 2 days followed by a temperature reduction. The solution was initially cooled at a rate of 0.05 °C/day and subsequently 0.1 °C/day as the growth progressed. LATF crystal of maximum size 57 mm × 5 mm × 3 mm grown over a growth period of 20 days is shown in the Fig. 1.

3. Characterisation

A RICH-SIEFERT X-ray diffractometer with a scan speed of 2°/min employing Cu Kα radiation (λ = 1.5418 Å) was used for powder diffraction studies. The optical transmittance spectrum of LATF crystal was recorded using CARY 5E UV-VIS-NIR spectrophotometer in the range 185–1000 nm. Kurtz powder SHG technique was used to confirm the nonlinear optical property of the crystal. The dielectric behavior of the LATF crystal was analysed using HIOKI 3532 50 LCR HITESTER instrument for different frequencies and temperatures. The Vicker's hardness number of as-grown LATF crystal was evaluated at room temperature using REICHERT MD 4000E ULTRA microhardness tester fitted with a diamond pyramidal indenter. The TGA and DSC studies of LATF crystal were carried out using PERKIN ELMER thermal analyzer (STA 409 C) in nitrogen atmosphere at a heating rate of 10 °C/

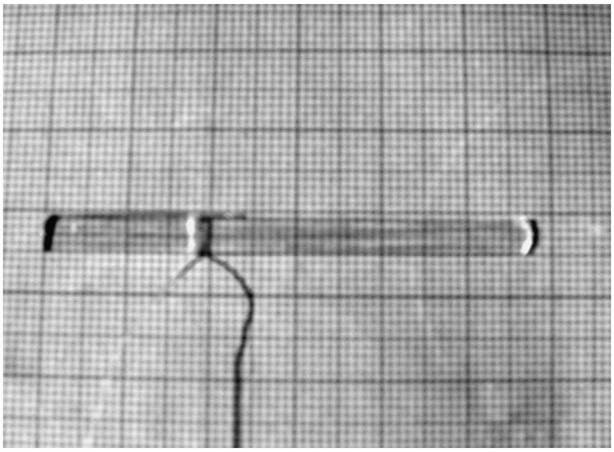

Fig. 1. LATF single crystal grown from aqueous solution by temperature lowering method.