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Structural, thermal, mechanical and optical properties of L-arginine diiodate crystal: A new nonlinear optical material

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Abstract

L-Arginine diiodate (L-Arg·2HIO_3) a new semi-organic nonlinear optical (NLO) material was synthesized by the standard method. The synthesized material was purified by repeated recrystallization process. Single crystals were grown by the slow evaporation and slow cooling methods. Crystal with excellent transparency were grown with maximum size of 20 mm × 10 mm × 10 mm and the grown crystals were characterized by single crystal XRD, FT-IR, FT-Raman, TGA-DTA, hardness study, and UV–vis-NIR studies. The second harmonic generation (SHG) of the material was confirmed using Nd:YAG. The L-Arg·2HIO_3 has NLO efficiency 1.3 times higher than the KDP crystal. Laser damage threshold studies revealed that the grown crystals possess high damage threshold values.

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Keywords: Solutiongrowth; Semiorganic; NLO; Laser damage threshold

1. Introduction

Nonlinear optical (NLO) materials find extensive optoelectronic applications such as optical frequency conversion, optical data storage and optical switches in the inertially confined laser fusion systems. Of late, second-order nonlinear optical (SONLO) materials capable of efficient frequency conversion of infrared or visible laser radiation to visible or ultraviolet (UV) wavelengths are of considerable interest in the field of telecommunications, high density optical recording, color display, medical diagnostics, etc. Therefore, presently there is a need to produce high efficiency NLO materials capable of generating blue light by second harmonic generation [1–4]. Materials with second-order optical nonlinearities, short transparency cut-off wavelength, high thermal and mechanical properties are needed to realize many of these applications. Inorganic materials are widely used in these applications due to their high melting point, high mechanical strength and high degree of chemical inertness. But the optical nonlinearity of these materials is poor. Organic compounds are often formed by weak van der Waal and hydrogen bonds and possess high degree of delocalization. Hence they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials are flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance, etc. A major drawback of crystalline organic NLO materials is difficulty in growing large, optical quality single crystals and also, the fragile nature of these crystals makes them difficult for the process in device applications. The inherent limitations on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device grade organic single crystals have made scientists to adopt alternate strategies. The obvious one was to develop hybrid organic–inorganic materials with some tradeoff in their respective advantages. This new class of materials has come to be known as semi-organics. One approach to have high efficiency optical quality organic based NLO materials in this class is to form compounds in which a polarizable organic molecule is stochiometrically bonded to inorganic host. Amino acids and their complexes belong to a family of organic materials that have NLO applications [5–7]. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (COO^-) group and the proton acceptor amino (NH_2) group in them. Discovery of nonlinear optical (NLO) property of L-Arg·H_3PO_4·H_2O (LAP) (where L-Arg is L-arginine) [8] has played an important role both in attracting attention to crys-

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talline salts of amino acids (in particular to L-arginine [9,10]) and also working out the conception of semi-organic crystals [11]. L-arginine also forms salts with arsenic acids (L-Arg·$2H_3AsO_4$) [9] and phosphoric acid (L-Arg·$2H_3PO_4$ [10], etc.) in the ratio 1:2. L-Arginine and L-arginine phosphate, for example, have shown promising results as efficient second harmonic generators and are being applied in devices such as optical parametric amplifiers [12].

2. Experimental

2.1. Material synthesis

The molecule (L-Arg) $(NH_2)NHCNH(CH_2)_3CH(NH_3)$ COO^- has two groups (a guanadyl and amino) which can be protonated. The starting material was synthesized by taking L-arginine and iodic acid in the stoichiometric ratio of 1:2. The required amount of these two starting materials for the synthesis of L-Arg·$2HIO_3$ salt were calculated from the following reaction,

$$(NH2)NHCNH(CH_2)_3CH(NH_2)COOH + 2HIO_3 \rightarrow (H_2N)_2{}^+CNH(CH_2)_3CH(NH_3)^+COOH(IO_3)_2{}^-$$

The calculated amount of iodic acid was first dissolved in deionized water of resistivity 18.2 MΩ cm^{-1}. Then L-arginine was added to the solution slowly by stirring. The prepared solution was allowed to dry at room temperature. The purity of the synthesized salt was further improved by successive recrystallization process. Bulk growth of L-Arg·$2HIO_3$ single crystal was carried out from aqueous solution by slow cooling technique, in a constant temperature bath controlled with an accuracy of ±0.01 °C. Three hundred milliliters of the growth solution was saturated at 45 °C and then filtered to remove any insoluble impurities. The seed obtained from slow evaporation method was used for the bulk growth. The solution was maintained at 45 °C for 2 days before seeding. The temperature was reduced at a rate of 0.1–0.2 °C per day as the growth progressed. The period of growth ranged from 30 to 35 days. Fig. 1(a and b) shows the as-grown crystal of L-Arg·$2HIO_3$ grown by slow evaporation and slow cooling methods with optimized solution pH value of 6. It is observed that unlike LAP solutions, no microbes were formed during the growth of L-Arg·$2HIO_3$ probably due to destructive nature of iodine on the growth of microbes.

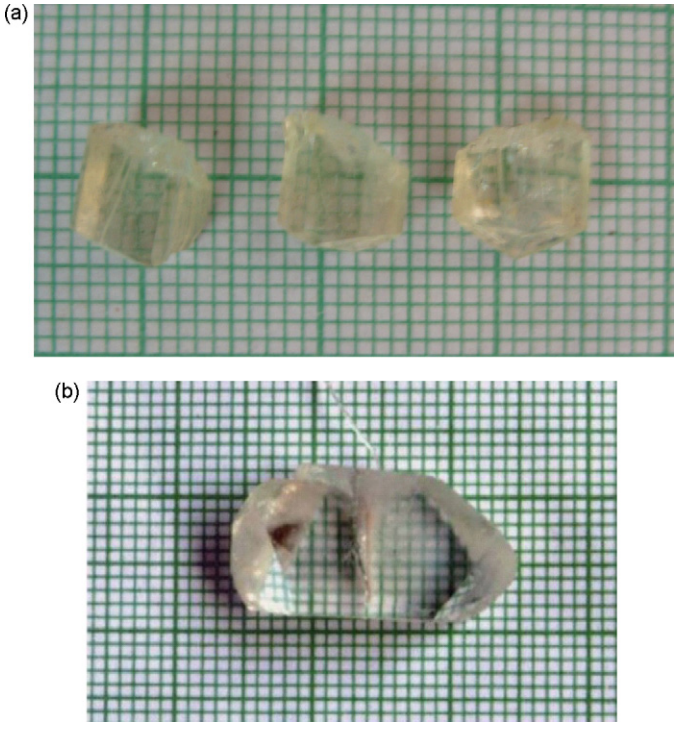

Fig. 1. (a) As-grown crystal of L-Arg·$2HIO_3$ by slow evaporation method. (b) Bulk single crystal of L-Arg·$2HIO_3$ by slow cooling technique.

3. Characterization studies

Powder X-ray diffraction analysis was also carried out using a Rich Seifert diffractometer with Cu Kα (λ = 1.5418 Å) radiation to verify the correctness of lattice parameter values. The FTIR spectrum of as-grown L-Arg·$2HIO_3$ crystal was recorded in the range 400–4000 cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method in order to study the functional groups. Linear optical property of the grown crystal was studied using a Simadzu UV–vis spectrophotometer. To confirm the nonlinear optical property, Kurtz powder SHG test was made on the grown crystals. An actively Q-switched diode array side pumped Nd:YAG laser is used to measure the laser-induced damage threshold for the grown crystal. The Vickers's hardness measurement was carried out on the grown crystals to assess the mechanical behaviour of the material. Thermo gravimetric (TG) and differential thermal analysis (DTA) for grown crystal were carried out using ZETZSCH-Geratebau GmbH thermal analyzer. Thermal stability and melting point of the material have been analysed with TG-DTA spectra.

4. Results and discussion

4.1. Powder X-ray diffraction studies

Finely crushed powder L-Arg·$2HIO_3$ crystal was subjected to powder X-ray diffraction analysis. The sample was scanned over the range 10–60° at a scan rate of 2° min^{-1}. The recorded X-ray pattern of L-Arg·$2HIO_3$ is shown in Fig. 2. The L-Arg·$2HIO_3$ crystal has retained its orthorhombic structure with lattice parameters $a = 6.9456$ Å, $b = 7.9501$ Å, $c = 25.046$ Å, $V = 1383.04$ $Å^3$, $\alpha = \beta = \gamma = 90°$, and space group $P2_12_12_1$.

4.2. Fourier transform infrared analysis

The FTIR spectral analysis of L-Arg·$2HIO_3$ was carried out between 4000 and 450 cm^{-1} in order to confirm the function groups present in the grown crystals. The resulting spectrum is

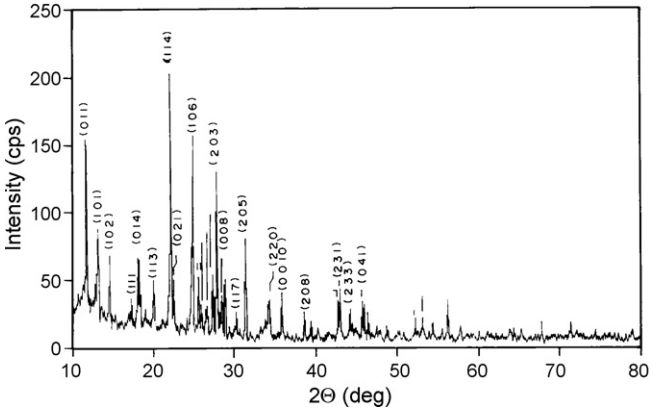

Fig. 2. Powder X-ray diffraction pattern of L-Arg·$2HIO_3$ crystal.