Optik 127 (2016) 4007–4010

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Investigation on crystallinity, stability and piezoelectricity of L-arginine 4-nitrophenolate 4-nitrophenol dihydrate single crystal

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ARTICLE INFO

Article history:
Received 29 October 2015
Accepted 12 January 2016

Keywords:
X-ray diffraction
Growth from solutions
Organic compounds
Nonlinear optical
Piezoelectric materials

ABSTRACT

L-Arginine 4-nitrophenolate 4-nitrophenol dihydrate single crystals have been grown from slow evaporation solution growth technique. Crystalline perfection of the crystal has been evaluated by high resolution X-ray diffraction technique and it reveals that the crystal quality is good and free from structural grain boundaries. Mechanical stability of the crystal has been analyzed by Vickers microhardness measurement and it exhibits reverse indentation size effect. The surface laser damage threshold for the crystal has been analyzed and its value is 0.504 GW/cm^2. Piezoelectric d_{33} co-efficient for the crystal has been examined and its value is 18 pC/N.

1. Introduction

Polar crystals are found to possess technologically useful properties such as NLO function (especially second harmonic generation, SHG), piezoelectricity, ferroelectricity, pyroelectricity and triboluminescence, where SHG, piezoelectric, and ferroelectric properties are of particular importance for their practical importance in areas such as telecommunications, optical storage, and information processing as well as mechanical energy transfer [1]. Recently, the research on organic NLO crystals is strongly motivated by the researchers because of their advantages over the inorganic NLO crystals such as large optical nonlinearities, flexibility for structural modifications, low dielectric dispersion, ultrafast response to external electric fields and low cost [2,3]. A number of polar organic NLO crystals have been reported, including 3-methyl-4-methoxy-4′-nitrostilbene (MMONS) [4], meta-nitroaniline (mNA) [5], (−)2-(α-methylbenzylamino)-5-nitropyridine (MBA-NP) [6], 4-nitro-4′-methyl benzylidene aniline (NMBA) [7], 3-methoxy-4-hydroxybenzaldehyde (MHBA) [8], 2-cyclooctylamino-5-nitropyridine (COANP) [9] and N-4-nitrophenyl-(L)-prolinol (NPP) [10].

L-Arginine 4-nitrophenolate 4-nitrophenol dihydrate (LAPP) is one of the polar organic NLO single crystals. Wang et al. [11] reported the crystal structure of LAPP. It belongs to the monoclinic crystallographic system with space group $P2_1$. It possesses transmission range from 500 to 2500 nm. LAPP crystal was phase-matchable with SHG efficiency as high as that of urea [11]. Mahadevan et al. reported [12] some characterization of LAPP single crystals.

In this article, we present the growth of LAPP single crystals by slow evaporation solution growth technique with controlled evaporation. The grown crystals were characterized by single crystal X-ray diffraction (XRD), high resolution X-ray diffraction (HRXRD), Vickers micro hardness, laser damage threshold (LDT) and piezoelectric measurement for investigating the structural, crystalline perfection, stability and piezoelectricity of the crystal.

2. Experimental

2.1. Crystal growth

LAPP was synthesized by reacting L-arginine (Merck-GR grade) and 4-nitrophenol (Alfa Aesar) in the molar ratio of 1:2, respectively in Millipore water (resistivity of 18.2 MΩ cm) at room temperature. Fig. 1 represents the reaction scheme for LAPP compound. In order to improve the quality of single crystals, the synthesized material was purified by recrystallization process (3 times). The saturated solution was prepared at 32 °C using constant temperature water bath (with ±0.1 °C accuracy). The solution temperature was raised to 37 °C to avoid the nucleation during the filtration and maintained at 32 °C for slow evaporation crystal growth processes. After growth period of 30 days, single crystals of LAPP (Fig. 2) of size 15 × 11 × 3 mm^3 were obtained.

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http://dx.doi.org/10.1016/j.ijleo.2016.01.088
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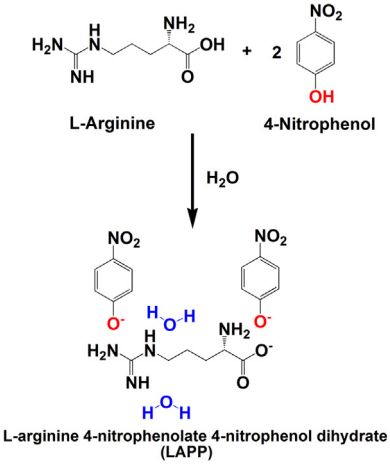

Fig. 1. Reaction scheme for LAPP.

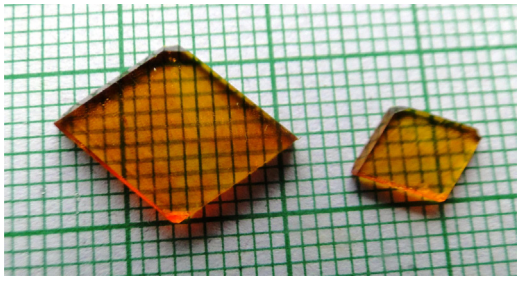

Fig. 2. As grown crystal.

2.2. Single crystal XRD study

The single-crystal XRD measurement for LAPP crystal was carried out using an Enraf Nonius CAD 4/MACH with MoK_α radiation (λ = 0.71073 Å) at 293 K.

2.3. HRXRD study

The crystalline perfection of LAPP crystal was analyzed by PANalytical X'Pert PRO MRD HRXRD system, with Cu $K\alpha_1$ radiation. The rocking curve of the crystal for the (2 0 −2) diffraction planes was recorded in symmetrical Bragg geometry using the (0 0 1) natural facets by performing an ω scan with triple-axis geometry. The monochromated X-ray beam incident on the specimen was obtained using a hybrid four-bounce Ge (2 2 0) monochromator with a parabolic multilayer mirror assembly. The diffracted beam from the specimen was detected using a Xenon detector with a triple-axis analyzer.

2.4. Microhardness study

As grown surface of (0 0 1) of LAPP crystal (2 mm thickness) was subjected to Vickers microhardness study by MAT SUZAWA – MMTX 7 series load – B type hardness tester fitted with Vickers pyramidal indenter. The measurements were made at room temperature and the indentation time was kept as 5 s for all loads. For each load several trials of indentations were carried out and the successive indentations were made at different sites of the plane.

2.5. Laser damage threshold study

The multiple shots of LDT study of the LAPP single crystal was analyzed by a Q-switched Nd: YAG laser operating at 1064 nm radiation and repetition rate is 10 Hz with the pulse width of 10 ns. For surface damage, as grown (0 0 1) surface of the sample is placed at the focus of a lens of focal length 30 cm. The diameter of the focused laser spot was 1 mm. The laser exposure time on the sample was kept as 30 s for all energies and energy of the laser beam was measured by Model No. EPM 200 coherent energy/power meter.

Table 1
Lattice parameters of LAPP single crystal.

Lattice parameters	Present study	Previous study [11]
a	7.853(3)(Å)	7.866(5)(Å)
b	10.354(9)(Å)	10.376(2)(Å)
c	13.754(4)(Å)	13.830(2)(Å)
β	98.09(3)°	98.21(9)°

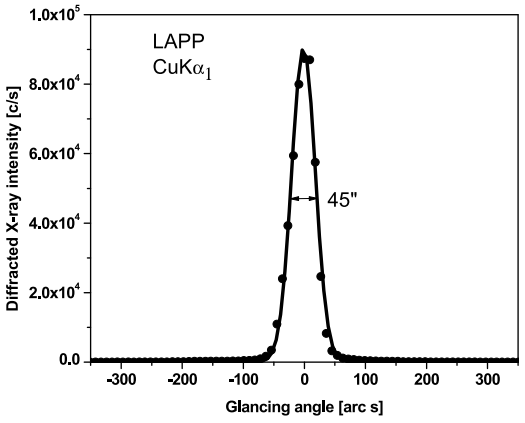

Fig. 3. Rocking curve.

2.6. Piezoelectric study

The piezoelectric study for (0 0 1) facet of LAPP crystal (2 mm thickness) was carried out using precision piezo meter system PM 300. In order to obtain good electrical contact, both faces of the crystal were coated with silver paste. For piezoelectric measurements, poling conditions were optimized by observing the response of the crystals under different applied electric fields, durations of poling and temperatures. LAPP single crystals were poled by applying a field of 10 kV/cm for 30 min at ambient temperature. A precision force generator applied a calibrated dynamic force of 0.25 N (frequency of 110 Hz) on the poled crystals which generated a charge and the output was measured from oscilloscope, which gives the d_{33} coefficient in units of pC/N.

3. Results and discussion

Single crystal XRD analysis indicates that the obtained lattice parameters of LAPP are consistent with the reported values [11] as presented in Table 1. The compound belongs to monoclinic crystal system with space group $P2_1$ and point group C_2.

Fig. 3 shows the high-resolution X-ray diffraction curve (DC) recorded for a typical LAPP specimen. As seen in the figure the DC is quite sharp without any satellite peaks which may otherwise be observed either due to internal structural grain boundaries [13] or due to epitaxial layer which may sometimes form on crystals grown from solution [14]. The full width at half maximum (FWHM) of the DC is 45 arcs, which is very close to that expected from the plane wave theory of dynamical X-ray diffraction [15]. The single sharp DC with very low FWHM indicates that the crystalline perfection is quite good without having any internal structural grain boundaries.