Hindawi Publishing Corporation
Journal of Chemistry
Volume 2013, Article ID 305932, 4 pages
http://dx.doi.org/10.1155/2013/305932

Research Article

Chemical Etching, AFM, Laser Damage Threshold, and Nonlinear Optical Studies of Potential Nonlinear Optical Crystal: Bis (L-Glutamine) Potassium Nitrate

Redrothu Hanumantharao and S. Kalainathan

Crystal Research Center, VIT University, Tamilnadu, Vellore 632 014, India

Correspondence should be addressed to S. Kalainathan; kalainathan@yahoo.com

Received 27 February 2012; Revised 26 June 2012; Accepted 27 June 2012

Academic Editor: Mohammad A. Al-Ghouti

A novel semiorganic nonlinear optical crystal bis (L-glutamine) potassium nitrate (BGPN) grown by slow evaporation technique at ambient temperature. The grown crystal surface has been analyzed by chemical etching and atomic force microscopy (AFM) studies. Amplitude parameters like area roughness, roughness average, valley height, valley depth, peak height, and peak valley height were measured successfully from AFM studies. Etching studies were carried out by various solvents like water, methanol and ethanol. The etching study indicates the occurrence of different types of etch pit patterns like striations and steplike pattern. The laser damage threshold energy has been measured by irradiating laser beam using a Q-switched Nd: YAG laser (1064 nm). Second harmonic generation (SHG) studies have been performed by famous Kurtz powder technique with reference to standard potassium dihydrogen phosphate single crystals (KDP). It is found from this technique that SHG efficiency of BGPN is in comparison to that of standard KDP crystals.

1. Introduction

Nonlinear optical applications find a variety of applications to perform functions like frequency conversion, light modulation, optical switching, optical memory storage, and optical second harmonic generation (SHG) [1, 2]. Amino acids are interesting organic materials for NLO applications as they contain donor carboxylic (COOH) group and the proton acceptor amino (NH_2) group in them, known as zwitter-ions. Recently, a large number of amino-acid-based crystals have been reported for successful nonlinear optical applications such as L-alanine acetate, L-alanine cadmium chloride, L-glutamic acid hydrobromide, and L-valine hydrobromide) [3–6] in the literature. A new semiorganic non linear optical crystal from amino acid family Bis (L-Glutamine) potassium nitrate has been investigated under study. From single-crystal XRD data, it is observed that crystal belongs to orthorhombic system, space group $P2_12_12_1$ with $a = 6.28 \pm 0.01$ Å, $b = 4.98 \pm 0.01$ Å, $c = 14.49 \pm 0.01$ Å. The present study deals with surface analysis of BGPN crystal which is very important as far as the fabrication of devices is concerned.

2. Materials Synthesis and Growth

Good-quality single crystals of BGPN were grown by using solution growth technique. High-purity (Sigma Aldrich) starting materials of L-Glutamine and potassium nitrate were purchased. Calculated amounts of L-Glutamine and potassium nitrate were dissolved in the solvent of triple distilled Millipore water as a solvent. Good quality single crystals of BGPN have been harvested in a period of 14 days shown in Figure 1.

3. Characterization Techniques

To investigate the perfection of crystalline sample, etching studies have been done using proper etchants like water, methanol, and ethanol. Different etch pits were observed by different etchants at room temperature. Etchings of the surfaces were carried out by dipping the plates for 10 sec at room temperature and then wiping with dry filter paper. Etch patterns were observed and photographed under a Carl

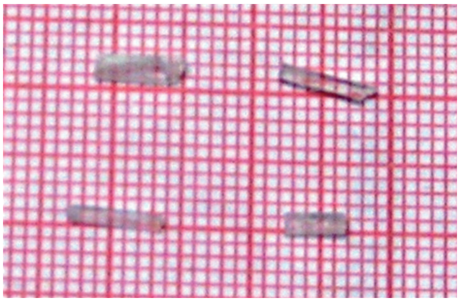

Figure 1: As-grown single crystals of BGPN.

Zeiss metallurgical microscope (Axioskop 40 MAT) provided by clemex vision PE software in reflected light. For etching purpose, thin crystals of 5 mm thickness were cut from the grown crystal with the help of wet thread.

The surface characteristics were studied with the aid of an AFM (Nanosurf easyscan 2, Switzerland) with a maximum XY scan range of 70 μm. SHG studies were carried out using Q-switched Nd: YAG laser (1064 nm Quanta-ray Series, USA) emitting a fundamental wavelength of 1064 nm.

4. Results and Discussion

4.1. Chemical Etching. The crystallization perfection and growth features can be analyzed by etching studies. Fast etchants like water, ethanol, and methanol could produce well-defined etch pits on the surface. Etching of crystal for each etchant can be done for an etching time of 10 s. The corresponding dislocation etch pits can be shown on the surface of the polished sample as shown in Figures 2(a)–2(c).

Striation-like pattern ise observed from Figure 2(a) when water was used as an etchant. Figure 2(b) shows steplike pattern when ethanol was used as an etchant. This is because at high growth rates, the two-dimensional nucleation at corners predominates, so that step generation occurs primarily wherever the supersaturation is the greatest. Figure 2(c) shows striations when methanol was used as an etchant. The patterns obtained are quite stable and did not degrade for a longer time [7].

4.2. AFM Studies. A 14.9 μm × 15 μm images are recorded using microfabricated cantilever, whose dimensions are of length (l) = 450 μm, width (w) = 45 μm, thickness (t) = 1.5 μm, provided tip height 12 μm. Spring constant of the cantilever is estimated to be 0.15 N/m.

AFM images recorded on the crystal surface, shown in Figure 3.

In view of three-dimensional image, hillocks and valleys are observed. Using the software (Nanosurf scan version 1-4-0-3) the parameters like roughness average, the mean value, root-mean-square value, the valley depth, the peak height, and peak-valley height have been estimated. Measuring area roughness determines the mean height difference between two plateaus.

The parameters measured from AFM studies are listed in Table 1.

In general the Amplitude parameter Arithmetic average of roughness (S_a) is estimated to be

$$S_a = \frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{N} l\eta\left(x_i y_j\right) l, \qquad (1)$$

where “M” is number of points per profile and “N” is number of profiles. $\eta(x, y)$ is the data set of rough surface of the wavy surface or the primary surface texture, depending on a requirement of the surface analysis. In general, “η” is obtained by using filtration techniques.

Arithmetic average of roughness (S_a) is a dispersion parameter defined as the arithmetic mean of the absolute values of the surface departures above and below the mean plane within the sampling area.

Other parameter root-mean-square deviation of the surface (S_q) is a dispersion parameter defined as the root mean square value of the surface departures within the sample area is found to be

$$S_q = \sqrt{\frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M}\eta^3\left(x_i y_j\right)}. \qquad (2)$$

Peak-valley height (S_y) can be estimated by

$$S_y = S_p - S_v, \qquad (3)$$

where “S_p” is the peak height (highest value) and “S_v” is the valley depth (lowest value).

4.3. Laser Damage Threshold Studies. In case of non linear optical crystals, the harmonic conversion efficiency is proportional to the power per unit area of the fundamental beam. Hence, a convenient way to increase the efficiency is to focus the beam on the crystal. But this often leads to the breakdown of the materials catastrophically damaging the maximum permissible power for a particular crystal defined as damage threshold. The laser damage threshold of an optical crystal is an important factor affecting its applications. If the material has a low laser damage threshold, it severely limits its applications, even though it has many excellent properties like high optical transmittance and high SHG efficiency [8, 9].

The energy density of the material was calculated using the formula, energy density = E/A, where E is the input energy measured in mJ and A is the area of the circular spot. Good quality crystals were mounted on the crystal holder in the path of Nd: YAG laser which generates pulses at 1064 nm fundamental radiation at a frequency of 10 Hz and pulse duration of 10 ns, and the energy of the beam was increased from 5 mJ in steps of 5. The crystal was exposed to the laser for a time period of 30 s for all measurements. The damage was observed, and the energy of the laser beam was measured by Coherent energy/power meter (model no.EPM 200). The laser damage threshold of BGPN was measured 75 mJ/cm^2, respectively, which is higher than that of urea (1.5) crystals [10].

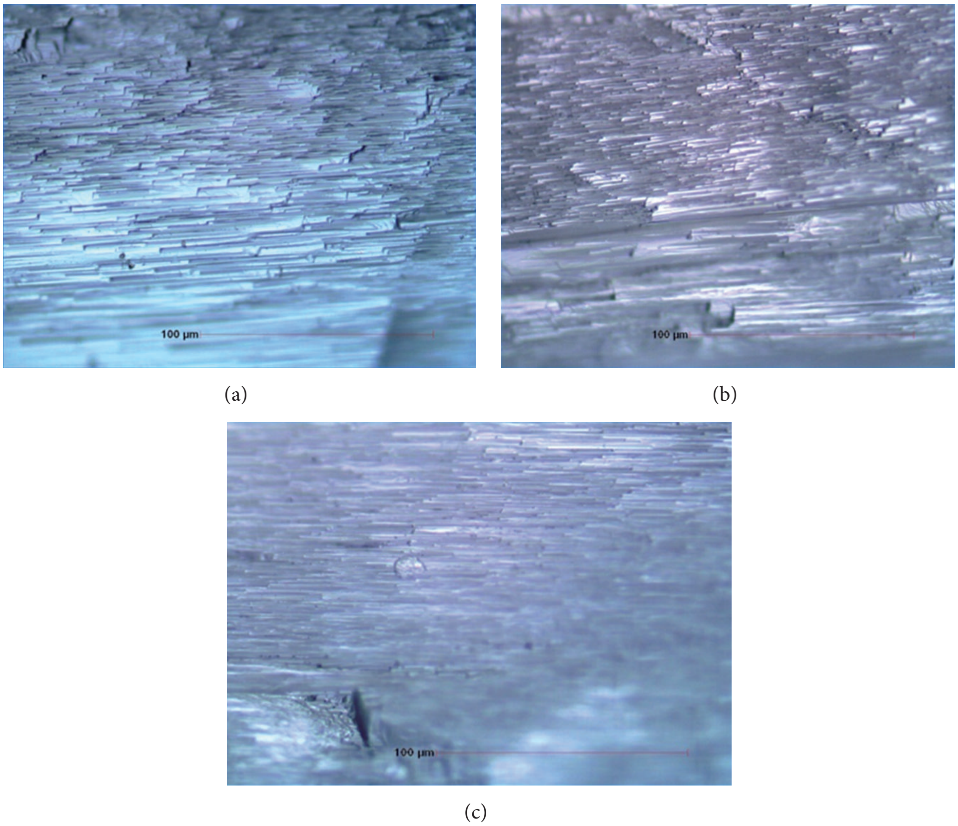

Figure 2: (a) Etch patterns with water. (b) Etch patterns with ethanol. (c) Etch patterns with methanol.

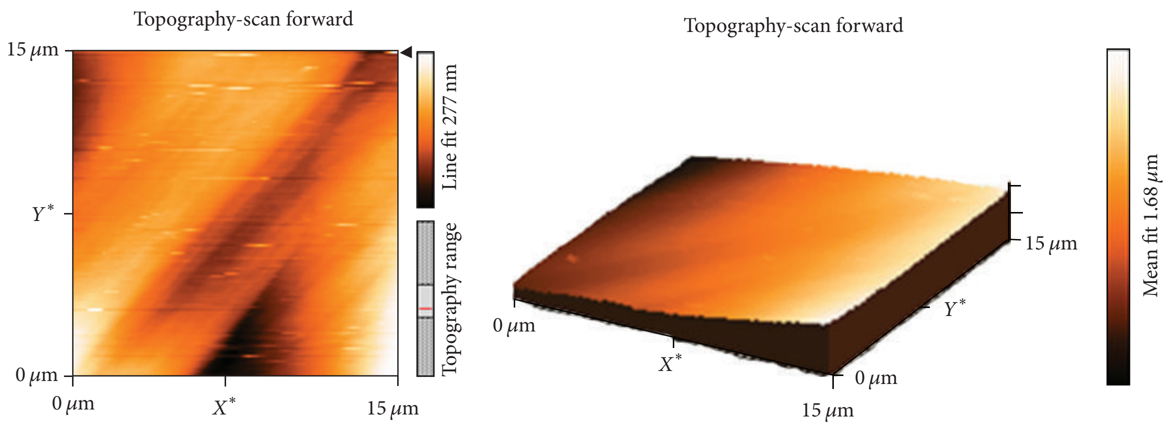

Figure 3: AFM image of BGPN single crystal.

Table 1: Amplitude parameters of BGPN measured by AFM.

S. no	Amplitude parameter	Value
1	Roughness average (S_a) (nm)	39
2	Root mean square (S_q) (nm)	47
3	Peak-valley height (S_y) (μm)	0.38
4	Peak height (S_p) (μm)	0.22
5	Valley depth (S_v) (μm)	−0.15
6	The mean value (S_m) (nm)	0.12

4.4. Nonlinear Optical (SHG) Studies. The second-order nonlinearity (SHG efficiency) of materials crystallized in noncentrosymmetric crystal structures has been confirmed by the most widely used Kurtz powder technique [11]. For SHG measurement, the grown BGPN crystals are powdered well with an average particle size range 125–150 μm filled in a microcapillary tube about 1.5 mm diameter. The crystalline powder illuminated using Q-switched Nd: YAG laser (1064 nm, Quanta ray series, USA) emitting a fundamental wavelength of 1064 nm was used. The input laser energy incident on the capillary tube was chosen to be 0.68 J, an energy level optimized not to cause any chemical decomposition of the sample. The SHG was confirmed by the emission of bright green radiation (532 nm). The SHG efficiency of BGPN is observed to be 1.12 times to that of standard KDP crystal.

5. Conclusion

Single crystal of Bis(L-Glutamine potassium nitrate) has been grown by slow evaporation method. The surface properties of the grown crystals were investigated by Etching and AFM, and the results are discussed in detail. Etch pits on the grown surfaces has been studied by different etchants. From AFM studies, the surface topography can be properly analyzed by amplitude parameters. The LDT value for BGPN crystal was found to be 75 mJ/cm^2. Kurtz powder technique shows that the SHG sufficiency of BGPN is nearly 1.12 times to that of standard KDP crystal.

Acknowledgments

The authors acknowledge sophisticated analytical instrumentation facility, IIT madras for providing single-crystal XRD data and VIT University for providing the facility for AFM studies.

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