Optics and Laser Technology 106 (2018) 321–326

Contents lists available at ScienceDirect

Optics and Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Growth and characterization of nonlinear optical crystal Gamma glycine by the additive of lithium bromide

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ARTICLE INFO

Article history:
Received 10 December 2017
Received in revised form 3 April 2018
Accepted 25 April 2018

Keywords:
Crystal growth
Crystal structure
X-ray diffraction
Nonlinearoptical crystals
Organic compounds
Harmonic generation

ABSTRACT

Single crystal of γ-glycine, a polymorphic form of glycine, was grown by slow solvent evaporation technique by the additive of lithium bromide. It was grown from the aqueous solution of glycine and lithium bromide in 2:1 M ratio respectively at room temperature. Good quality of γ-glycine single crystals was harvested up to the dimension of $25 \times 22 \times 20\ mm^3$. In order to reveal its properties, the grown single crystals were subjected to various characterizations. Powder X-ray diffraction of the grown crystal was recorded and indexed. The unit cell parameters of the crystals were estimated by single crystal x-ray diffraction and they were compared with the literature values. The identification of the functional groups and hence the compound present in the crystalline sample by FTIR analysis confirms the polymorphic form of glycine. Optical transmittance studies were carried out by UV–Vis-NIR transmission spectrum in the range of 200–1100 nm wavelength. The powdered sample of the crystal was subjected to Kurtz Perry powder technique to find the coefficient of Second harmonic generation. The second harmonic generation (SHG) conversion efficiency of γ-glycine crystal is more than twice when compared with KDP crystal. The grown γ-glycine crystal was further characterized by Thermo gravimetric analysis (TGA) and Differential thermal analysis, to find its thermal stability and decomposition temperature. Dielectric constant and Dielectric loss were determined at different frequencies with respect to various temperatures. The mechanical properties such as microhardness and yield strength were evaluated by Vicker's microhardness tester.

1. Introduction

The theory of nonlinear optics (NLO) builds on the well understood theory of linear optics, particularly that part known as the interaction of light and matter. Ordinary matter consists of a collection of positively charged cores and surrounding negatively charged electrons. Light interacts primarily with matter via the valence electrons in the outer shells of electron orbital [1]. Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material in nonlinear manner by the presence of highly coherent and intense light. There are many technologically important crystals such as potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate, barium titanate and lithium iodate etc., which are currently used as a frequency converter in laser. The importance of second harmonic generation lies in the fact that it is one of the principal methods of effective conversion of infrared radiation into visible and visible into ultraviolet [2]. In the recent years deep ultraviolet (DUV) NLO crystalline materials have attracted attention due to the importance of these materials lie in the urgent demand of coherent DUV light. The material $KBe_2BO_3F_2$ (KBBF) is a good candidate for efficient generation of DUV light by direct second harmonic generation (SHG) and its lower cut off wavelength lies at 155 nm [3]. Generally the hyperpolarisability depends on the frequency of the applied field, which occur only in noncentrosymmetric molecules.

In general amino acid organic compounds show a good efficiency of second harmonic generation. Among all amino acid compounds, glycine is a simplest form and acts as an amphoteric in nature. Hence the molecule can combine with anionic, cationic and overall neutral constituents, and produce large number of possible glycine compounds [4]. It is usually used as a model compound for the polymorphic kind of research [5]. Gamma glycine is one of the polymorph of glycine exhibiting noncentrosymmetric in nature, which would not be obtained from the commercially available glycine compound itself. But when the nucleation forms from the aqueous solution of glycine with some nonreactive

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https://doi.org/10.1016/j.optlastec.2018.04.036
0030-3992/© 2018 Published by Elsevier Ltd.

additives, it transform from symmetric to noncentrosymmetric molecule. The additives maintain the optimum value of pH in the solution rather than reacting with the glycine compound. The growth of gamma glycine with the effect of ammonium nitrate, sodium chloride, potassium chloride, sodium hydroxide, sodium fluoride, sodium nitrate, sodium acetate, potassium nitrate and lithium nitrate was already reported [6–9]. In this scientific paper, we are presenting a report for the growth of γ-glycine nonlinear optical single crystal by slow solvent evaporation technique with the effect of lithium bromide. Due to the presence of lithium bromide as an additive in the glycine aqueous solution and making the pH of the solution favour to grow Gamma phase, glycine crystallizes in noncentrosymmetric structure with the space group $P3_1$ instead of centrosymmetric structure.

2. Materials and methods

Commercially available glycine (Merck) and lithium bromide (Merck) was taken in two different beakers separately by 2:1 M ratio. Using Millipore water as a solvent, a saturated solution of lithium bromide was prepared at room temperature. Then the measured quantity of glycine was added little by little into the solution. A slightly under saturated homogeneous solution was prepared after 3 h continuous stirring. Then the prepared solution was filtered and made to evaporate at room temperature slowly by covering the beaker using a perforated polythene cover. A good quality of γ-glycine single crystal was harvested after 20 days with the dimension of $25 \times 22 \times 20$ mm^3. The photograph of the crystal is shown in the Fig. 1. The additive compound lithium bromide is white solid and extreme hygroscopic in nature. Its existence in the glycine solution makes the pH value 6.1, which facilitates to form γ-glycine crystal. The prolonged maintenance of this pH value by the lithium bromide in the solution helps to grow bulk Gamma glycine crystal.

3. Experimental

The Gamma glycine crystals grown in the aqueous solution containing lithium bromide were subjected to various studies to reveal its properties. In order to confirm the grown crystalline material, it was subjected to single crystal X-ray diffraction, which was carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation. Powder X-ray diffraction pattern of the grown γ-glycine crystal was recorded using Seifert Dyz 2002 model powder X-ray diffractometer with CuKα (λ = 1.540598 Å) radiation for structural analysis and crystalline nature of that material. The grown sample was crushed into very fine powder and was used to scan over the range of 10–70° at a scanning rate of 1°/min. The intensity of the diffracted beam was recorded as a function of 2θ and the corresponding peaks were indexed. This diffracted pattern agrees well when it was compared with the literature report. The presence of functional groups plays an important role in nonlinear optical performances [10]. This would be obtained by the identification of asymmetrical protonated functional group. The functional groups present in the grown crystalline sample were analyzed by Perkin Elmer spectrum one FT-IR spectrometer. Fourier transform infrared spectrum was recorded between 4000 and 450 cm^{-1}. Material which is to be used for photonic device such as laser and optical fiber should possess high optical transmittance in the visible region. So optical transmittance studies is a prominent one for any kind of photonic devices. To determine the optical transmission in the visible and ultraviolet region and find the suitability of the γ-glycine crystal for optical device, UV–Vis-NIR transmission spectrum was recorded in the range 200–1100 nm using Perkin-Elmer Lamda 35 UV–VIS spectrometer. A polished crystal of 3 mm thickness was used for recording the spectrum.

The Second Harmonic generation (SHG) may be used as a tool to evaluate at least qualitatively the bulk homogeneity of the samples under investigation [11]. It is a relevant technique for frequency conversion effect in a laser device. The SHG behavior of powdered sample of particle size 120 μm, which was prepared by a sieve with the same size of mesh, of the grown Gamma glycine crystal, was analyzed using Kurtz-Perry powder technique. Thereafter it was compared with the standard KDP crystal in powder form with same range of size. For this a high intense Nd: YAG laser source was used whose beam wavelength and energy is 1064 nm and1.95 mJ respectively. The radiation was allowed to pass through the sample taken in the form of powder in a microcapillary tube. In order to find the phase change, decomposition and melting

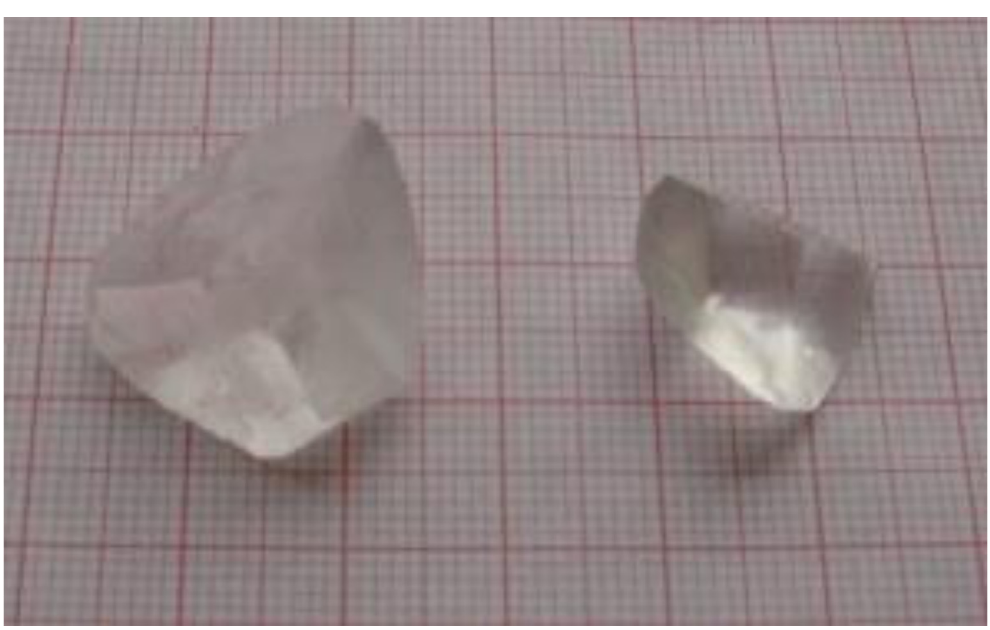

Fig. 1. Photograph of γ-glycine crystal.