Optik 125 (2014) 934–938

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis, optical, dielectric, thermal and mechanical properties of a nonlinear optical amino acid crystal: Bis-glycine hydrobromide

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ARTICLE INFO

Article history:
Received 7 March 2013
Accepted 6 July 2013

Keywords:
Slow evaporation
Dielectric measurement
Second harmonic generation
Tauc plot
SEM

ABSTRACT

A semi organic material Bis-glycine hydrobromide ($C_4H_{11}N_2O_4^+Br^-$) has been synthesized by slow solvent evaporation technique. The grown crystal was subjected to single crystal X-ray diffraction studies and its crystal parameters were confirmed. The FTIR analysis confirms the presence of various functional groups present in the title compound. The Kurtz powder second harmonic generation test shows that the crystal is a potential candidate for optical second harmonic generation. The UV–vis spectrum reveals the transparency of the crystal and enumerates the direct band gap energy of the material. The dielectric constant and the dielectric loss were studied as a function of frequency. The thermal studies indicate that the material is thermally stable up to 290 °C. The hardness number was calculated to be 110 kg/mm^2 from the Vicker's microhardness test.

1. Introduction

Glycine is a sweet tasting, non-essential amino acid that was first isolated in 1820 from gelatin and is also found in good quantity in silk fibroin. Also glycine is 'crystal friendly' since it easily crystallizes along with the added inorganic constituents like acids or salts [1–6]. Though such extensive researches have been established with glycine, still its adaptive crystallization, moderate requirements of its growth optimization, simplest morphological properties, its polymorphism that unambiguously predicts the variation in physical parameters, enables the researchers to grow glycine crystal with different combination of inorganic salts and characterize the same for its properties. In the past nine years, numerous research papers have been contributed in glycine and its substituent additives in the field of crystal growth.

The title compound Bis-glycine hydrobromide (BGHBR) have already been reported by Narayana Moolya et al. [7], Sampath Krishnan et al. [6]. In both the papers, the basic properties of the grown crystals were intricately analyzed. This paper deals with the detailed growth process along with electron microscopy images to envisage the purity of the sample unlike the other two papers. And few characteristics seem to be enhanced due to its high degree of transparency and quality.

2. Synthesis and growth technique

Before starting the synthesis process, the commercially available raw materials were purified by repeated recrystallization process and the recrystallized salt was used for the present studies. Commercially available analar grade glycine and hydrobromide were mixed in the ratio of 2:1 in the mixed solvent of water:acetone (in the ratio 1:1). The solution was stirred for about 6 h and subsequently heated to obtain a homogenous solution. Then the saturated solution was filtered using Whatmann's filter paper and poured into a beaker with perforated lid. Now the beaker was suspended in a constant temperature bath which was maintained at a temperature of 40 °C. After a period of 50–55 days, flawless bulk transparent crystals were harvested having dimensions 12 mm × 3 mm × 4 mm. The non-hygroscopic crystals obtained were of good quality with negligible inclusions as evident from Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Single-crystal X-ray diffraction is a non-destructive analytical technique providing detailed information of the internal lattices confirming the structure of the crystal. This single crystal XRD analysis was carried out independently for the grown BGHBR crystals using Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer

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http://dx.doi.org/10.1016/j.ijleo.2013.07.109

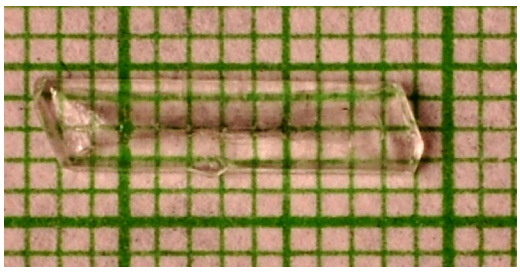

Fig. 1. Photograph of the BGHBR crystal as grown.

Table 1
Crystal lattice parameters of the BGHBR crystal.

Lattice Parameters	For the grown BGHBR crystal	As reported in the paper [7]	Literature [8]
a (Å)	8.0915	8.9015	8.21
b (Å)	18.1552	18.1662	18.42
c (Å)	5.2645	5.3745	5.40
V (Å)^3	805.11	790.007	807.68
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic

with MOK$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The experimental values are tabulated in Table 1 and compared with the literature [7,8]. It is evident that the unit cell volume is high and close to the available literature [8] which attributes to the packing density contributing to the mechanical strength of the crystal.

3.2. FTIR analysis

This analysis was accomplished by Alpha-T/Bruker Spectrometer in the frequency range 400–4000 cm^{-1}. The sample used was in pellet form in KBr phase. The FTIR spectrum is depicted in Fig. 2 is found to be matching with the literature [7].

The broad and strong bands lying in between 3115 cm^{-1} and 2300 cm^{-1} are due to the absorption of the superimposed O—H and NH_3^+ stretching. The bands observed at 1634 cm^{-1} and at 1495 cm^{-1} are assigned to asymmetrical and symmetrical NH_3^+ bending respectively. The strong band observed at 1742 cm^{-1} is assigned to the protonated carbonyl group of one of the glycine anions. The band observed at 1446 cm^{-1} is assigned to the carbonyl group of the other glycine anion. The band at 1957 cm^{-1} is assigned to a combination of the asymmetrical NH_3^+ observed at 1634 cm^{-1} and torsional oscillation band observed at 501 cm^{-1} [7].

3.3. Second harmonic generation

Second harmonic generation is a method for probing interfaces in atomic and molecular systems. In second harmonic generation (SHG), the light frequency is doubled, essentially converting two photons of the original beam of energy E into a single photon of energy $2E$ as it interacts with noncentrosymmetric media. Because of the non-zero second harmonic coefficient, the noncentrosymmetric structures are capable of emitting SHG light. The second harmonic generation studies were carried out by Kurtz and Perry powder technique and the efficiency of the sample was compared with microcrystalline powder of KDP. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1.064 μm was employed. In the present investigation, the laser pulse of 8 ns with spot radius of 1 mm was used. The input laser beam was passed through the IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube. When a laser beam of 0.68 mJ was passed through the sample, the output voltages of 55 mV and 50 mV were obtained for KDP and BGHBR respectively. KDP sample was used as the reference material and the powder SHG efficiency of the BGHBR single crystal was found to be 0.91 times that of KDP. This is even more than the value obtained by Narayana Moolya et al. in his paper [7].

3.4. Linear optical properties

The optical transmission range for the BGHBR crystal was recorded in the range 200–2000 nm using Shimadzu UV-1061 UV–vis spectrophotometer. Fig. 3 shows the spectra recorded. The lower cut-off wavelength of BGHBR was found to be 220 nm. This lower cut off wavelength is relatively low when compared with the other semi-organic NLO crystals and even lower than that reported by Narayana Moolya et al. in his paper [7]. The lower cut-off wavelength makes the crystal suitable for UV tunable laser and SHG applications. The less absorption and the wide range of transparency extending from 250 nm to 800 nm in the visible region of the spectrum is another added advantage in the field of optoelectronics [2].

From Fig. 3, the measured transmittance (T) is used to calculate the absorption coefficient (α) using the formula $\alpha = 2.303 \log(1/T)/t$

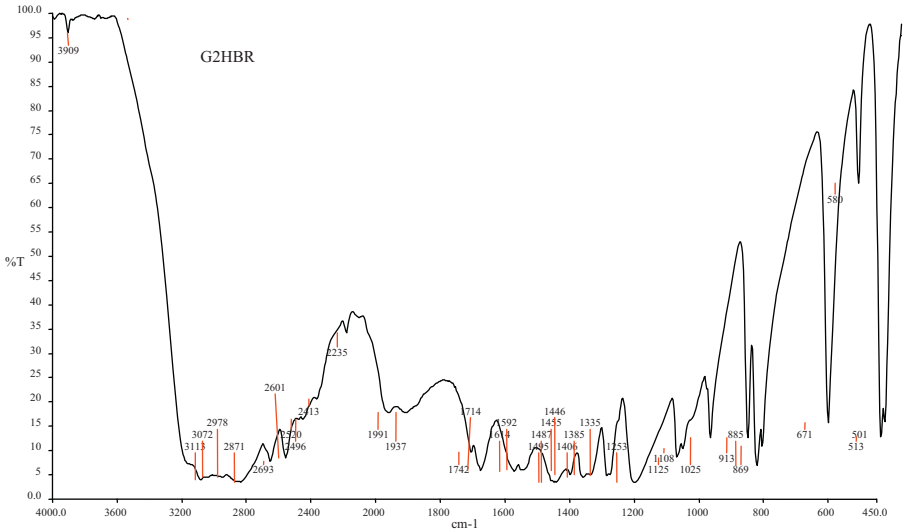

Fig. 2. FTIR spectrum for the BGHBR crystal.