Chapter 9

Growth and optical studies of bis glycine hydrogen bromide (BGHB) single crystal: New nonlinear optical material

9.1 Introduction

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics [1-5]. In recent past, there have been extensive efforts to develop nonlinear optical (NLO) crystals [6-13]. The key factor for material selection does not depend only on the laser conditions, but also on the physical properties such as transparency, damage threshold, conversion efficiency, phase matching and temperature stability [14, 15]. KDP group of materials remains the most widely used crystals for frequency conversion in spite of their modest nonlinearities [16-18]. The inorganic materials were exploited for various optoelectronic applications [16]. Various organic NLO materials with high nonlinear optical coefficients have been reported in the literature [19-22]. However, most of the organic NLO materials are susceptible to damage because of their poor mechanical and thermal properties [2-4, 16, 23]. Hence new types of hybrid NLO materials called semiorganic have been built from organic-inorganic complexes in which the high optical non-linearity of a purely organic compound
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is combined with the favorable mechanical and thermal properties of inorganic materials.

Amino acid group of materials is being used as a highly feasible second order NLO material for the growth of single crystals [4, 5, 7, 10, 14, 15]. Considerable efforts have been made to combine amino-acids with interesting organic and inorganic matrices to produce outstanding materials to challenge the established inorganic materials like niobates and the borates [3, 4, 7, 10]. Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acids/ salts. The materials like L-arginine phosphate (LAP) [24], L-arginine hydrochloride [25], L-histidine tetrafluoroborate (L-HFB) [26], L-Alanine tetrafluoroborate (L-AlFB) [27], L-histidine bromide (LHB) [28], etc., have been projected and are becoming prominent in view of their high laser damage threshold, wide transparency windows, low UV cutoff and high NLO coefficients.

Amino acids in solution at natural pH are predominantly zwitterions rather than unionized molecules. The amino group in protonated -NH₃⁺ and carboxyl group is dissociated -COO⁻. Glycine is the simplest amino acid. Unlike other amino acids, it has no asymmetric carbon atom and is optically inactive [29]. The complexes
of glycine with inorganic acids and salts like bis glycine hydrogen chloride, bis glycine sodium nitrate, glycine nitrate, γ glycine crystals are promising materials for second harmonic generation [15, 30-32].

To the best of our knowledge we are reporting first time the growth and characterization of bis glycine hydrogen bromide (BGHB) crystal in the present communication. It is a potential semi-organic NLO material crystal. The BGHB crystals were grown by the slow evaporation technique. The grown crystals were characterized by single crystal X-ray diffraction, FTIR, TGA and UV-vis spectroscopy. SHG efficiency of the grown crystal was measured by powder Kurtz method using Nd: YAG laser.

9.2 Experimental

9.2.1 Synthesis

The BGHB salt was synthesized by dissolving the high purity AR grade glycine and hydro bromic acid in molar ratio of 2:1 in deionised water at room temperature. The fully reacted solution was filtered and crystalline BGHB salt was obtained by slow evaporation. The insoluble impurities were removed by repeated recrystallization and filtration. The synthesized salt was used for the growth of seed crystals and bulk growth of the crystal.

9.2.2 Crystal Growth

The growth of the crystal was carried out in constant temperature bath controlled with an accuracy ±0.01°C by slow
evaporation technique. The saturated solution of BGHB was prepared at constant temperature 32°C and filtered to remove insoluble impurities. The seed crystals obtained from slow evaporation were employed for growth of bulk crystals. The good quality transparent crystals were harvested after 25 days. The grown crystals are shown in Fig. 9.1.

Fig. 9.1 Photograph of BGHB single crystal

9.3 Characterization

SHG property of synthesized salts was studied by Kurtz and Perry powder SHG test at Dept. of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore. The grown BGHB crystal was subjected to various characterization viz. single crystal X-ray
diffraction, FTIR analysis, UV-visible spectral study, Thermal study by TGA.

9.4 Results and Discussion

9.4.1 SHG Measurement

Current interest in quantum electronics is focused on finding materials which have suitable non-linear optical properties so that it can be used as a active media in efficient second harmonic generators, tunable parametric oscillators and broad-band electro-optic modulators. The SHG behavior of BGHB has been studied in accordance with the classical powder method developed by Kurtz and Perry [33]. It is an important and popular tool to evaluate the conversion efficiency of NLO materials. A Q-switched Nd: YAG laser beam of wavelength 1064 nm with an input power of 6.2 mJ/ pulse, and a pulse width of 8 ns with a repetition rate of 10 Hz were used. The powdered sample of BGHB with a uniform particle size was packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532nm component and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. The generation of the second harmonic was confirmed by a strong bright green emission emerging from the powdered sample.
9.4.2 Single Crystal X-ray Diffraction Analysis

Single crystal BGHB was subjected to single-crystal X-ray diffraction using a Brukers Axs (Kappa Apex2) diffractometer. The observed cell dimensions of the grown crystal are \( a = 5.12 \, \text{Å} \), \( b = 12.02 \, \text{Å} \) and \( c = 5.49 \, \text{Å} \) with unit cell volume \( V = 314 \, \text{Å}^3 \) and \( \alpha = \gamma = 90^\circ \) and \( \beta = 111.70^\circ \). The single crystal X-ray diffraction analysis reveals that the compound crystallizes in the monoclinic \( P \) system.

9.4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectrum was recorded in the range of 450-4000 cm\(^{-1}\) employing a Perkin Elmer Spectrum FTIR spectrometer by KBr pellet technique. The FTIR spectrum is shown in Fig. 9.2. The broad band between 2400 and 3100 cm\(^{-1}\) resulting from superimposed O–H and NH\(_3^+\) stretching bands. The peaks in this band at 3063 cm\(^{-1}\) may be assigned to N–H stretching vibrations. The peaks at 2737 cm\(^{-1}\) attributed to C–H stretching mode vibration. The symmetric and asymmetric stretching modes of COO\(^-\) are seen at 1594, 1445, 1418 and 1389 cm\(^{-1}\). This observation confirms that one glycine can exist in zwitterionic form. C–H and O–H bend of the COOH group are observed at 1238, 1308 and 1349 cm\(^{-1}\) respectively. In plane vibration give rise to band at 642 cm\(^{-1}\). The strong absorption due to asymmetric and symmetric deformation of NH\(_3^+\) occurred at 1576, 1515 and 1502 cm\(^{-1}\) respectively. The O–H out of plane deformation (980 and 926 cm\(^{-1}\)
C –C stretching (890 cm⁻¹), C –H deformation (1099 and 801 cm⁻¹), N –H deformation (763 cm⁻¹), C–C deformation (583 cm⁻¹), \( \text{NH}_3^+ \) rocking (1109 cm⁻¹), and –COO⁻ (499 cm⁻¹) vibrations were also observed. All these observations demonstrate the existence of glycine in its salt form with hydro bromic acid.

![FTIR spectra of BGHB single crystal](image)

**Fig. 9.2 FTIR spectra of BGHB single crystal**

### 9.4.4 UV-Visible Spectral Study

A good optical transmittance is desirable in an NLO crystal since the absorptions if any, in an NLO material near the fundamental or the second harmonic will lead to the loss of conversion efficiency in those wavelengths. To determine the transmission range and hence to know the suitability of BGHB single crystals for optical applications, the UV-vis spectrum was recorded in the range of 200-1100 nm using...
Shimadzu UV 1600 photo spectrometer. The UV-vis absorption spectrum is shown in Fig. 9.3. The lower cut off of the BGHB crystal is at 227 nm, the wide range of transparency in UV, entire visible and IR region makes it a very potential material for blue light emission. It can be seen from absorption spectra that there is no absorption in range 227 nm to 1100 nm enables the use of this material for second harmonic generation (SHG) applications.

![Bis-Glycine HBr](image)

**Fig. 9.3 UV-vis spectra of BGHB single crystal**

### 9.4.5 Thermo Gravimetric Analysis (TGA)

The thermo gravimetric analysis (TGA) was carried out by using TAQ-500 analyzer at a heating rate 25°C/ min. for temperature range 25 - 400°C. The TGA curve shows that material has very good thermal stability up to 206.60°C. The two major weight losses are seen. The first weight loss is at about 23.22% in temperature range 206.60 to 233.26°C.
and another is at about 26.77% in temperature range 261.97 to 291.63°C. There is no phase transition till the material melts, this increases the temperature range for the use of crystal for NLO application. The absence of water in molecular structure is confirmed by the absence of weight loss around 100°C. There is no decomposition up to melting point, this ensures thermal stability of material for possible application in lasers. Fig. 9.4 shows TGA thermo gram for bis glycine hydrogen bromide (BGHB).

![Fig. 9.4 TGA thermo gram of BGHB single crystal](image)

### 9.5 Conclusions

Optically good quality single crystals of BGHB were grown by slow evaporation technique. The SHG property was confirmed by Kurtz and Perry powder SHG test. The single crystal X-ray diffraction studies confirm the monoclinic structure of the grown crystal. FTIR
confirms the presence of all functional groups in the grown crystal. UV-vis absorption study confirms low cutoff at 227 nm wavelength. The grown crystal is transparent in UV, entire visible and IR region. This is an added advantage for NLO applications. Thermo gravimetric analysis (TGA) reveals that the grown crystal is thermally stable up to 206.60°C. Thus the optical, NLO and thermal properties of grown crystal indicate suitability of the crystal for optoelectronic and photonic applications.
References


