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Investigations on the physicochemical properties of the nonlinear optical crystal for blue green laser generation

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Abstract

Bisglycinehydrogenchloride (BGHC) an intriguing material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural, optical and physicochemical properties were characterized by X-ray powder diffraction, FTIR, Raman and UV–vis spectra. The title crystal has found to crystallize into noncentrosymmetric orthorhombic $P_{2_1}_{2_1}_{2_1}$ space group. The material has a wide transparency in the entire visible region. It is found that the cutoff wavelength lies in the UV region. The mechanical response of the crystal has been studied using Vickers microhardness technique. The Kurtz powder second harmonic generation test shows that the compound is a prospective crystalline material for second order nonlinear optical application. © 2007 Elsevier B.V. All rights reserved.

Keywords: Bisglycinehydrogenchloride; X-ray diffraction; FTIR; Optical transmission; Second harmonic generation

1. Introduction

Development of novel molecular and crystal design technique for assembling the materials is a nifty concern. In particular, semi-organic system provides many structure and bonding schemes for the molecular engineering of new materials. Semiorganic nonlinear optical (NLO) crystals in recent years are attracting a great deal of attention due to their high NLO coefficient, high damage threshold and high mechanical strength compared to organic NLO crystals. The crystal engineering of this nonlinear optical material is based on the anchorage of organic molecules exhibiting a large NLO efficiency on the amino acid group, which ensure convenient, thermal, mechanical and optical stabilities. Materials with large second order optical nonlinearities, transparency at all wavelengths involved and stable physicochemical performance are needed in order to realize many applications [1,2]. In recent years, amino acid family crystals are of interest due to their attracting nonlinear optical properties [3–5]. Amino acid family crystals are gaining importance as highly feasible second order NLO materials. Considerable efforts have been made to combine amino acids with interesting organic acid, inorganic materials to produce

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outstanding materials to challenge the existing prospective materials. These materials exhibit promising structural background in view of their zwitterionic and protonated forms and structural stabilization with hydrogen bonding. These factors accounting for the delocalization and corresponding enhancement in second order NLO activity. An amino acid exists as a dipolar ion in which carboxyl group is present as carboxylate ion and the amino group is present as ammonium ion. Thus, the presence of zwitterion influences the physical and chemical properties of amino acids [6]. Complexes of amino acid with inorganic salts are promising materials for optical second harmonic generation as they tend to combine the advantages of the organic amino acid with that of the inorganic acid/salt. Glycine and its methylated analogues form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or antiferroelectric behaviour often associated with transition to commensurate or incommensurate phases. According to the structural studies made on the structural aspects of glycine and its isomorphs [7-13], it has been found that there exist two kinds of glycine groups, glycinium ions and zwitterions. Such configuration of glycine ions is interconnected by short N-H...O hydrogen bonds, which is essentially responsible for the ferroelectric and nonlinear optical behaviour of the title crystal. In the present investigation, large and high optical quality BGHC single crystals have been grown by slow evaporation solution technique. Thus, the crystal growth

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and characterization of the title compound is outlined in this paper.

2. Experimental

2.1. Synthesis and crystal growth

BGHC was synthesized from glycine and hydrochloric acid taken in the molar ratio of 2:1. The calculated amount of the reactants were thoroughly dissolved in double distilled water and stirred well for 2 h to yield a homogeneous mixture. The mixture was evaporated to dryness by heating below an optimum temperature of 60 °C. To prevent possible decomposition, the colourless crystalline sample of the title compound was obtained and recrystallized several times before starting the growth process. The stoichiometric reaction is given as follows

$$2(\text{NH}_2\text{CH}_2\text{COOH}) + \text{HCl}$$

$$\rightarrow (\text{NH}_3^+\text{CH}_2\text{COO}^-)(\text{NH}_3^+\text{CH}_2\text{COOH})\text{Cl}^-$$
B

2.2. Solubility

In order to determine the crystalline habit and large size single crystal with good quality, the growth condition such as solvent, temperature and pH are to be optimized. The solubility of the material, which is available for growth and hence defines the size of the crystal that can be grown. The selection is very definitive for the growth of good quality crystal. The equilibrium solubility and its temperature dependent are essential for solution growth. The data from the solubility curve will suffice to start growing fair quality crystal [14]. The solubility of the title compound was assessed in different solvents apart from deionized water. The title material was crystallized in very small size and found to be defective in all the other solvents. Deionized water was suitable for crystallizing large and transparent colourless single crystal.

The solubility of BGHC was evaluated as a function of temperature in the temperature range 30 °C. A thermostatically controlled vessel was filled with the solution of the title compound and with some undissolved BGHC and stirred for a day. The next day a small amount of the supernatant solution was pipetted out and the concentration of the solute was determined gravimetrically. Fig. 1 shows the solubility curve of the title compound. We infer that the title compound exhibits good solubility and a positive solubility temperature gradient in water.

Single crystals of the title compound have been grown from saturated solution at a pH of 4.3 by slow evaporation solution growth technique at 35 °C using constant temperature bath having controlled accuracy of 0.01 °C. The crystals with perfect shape and transparency were formed by spontaneous nucleation in the supersaturated solution. The growth of the title compound needed a week, single crystals with good optical quality having rectangular shape having dimensions of 20 mm \times 0.7 mm \times 0.4 mm have been obtained.



Fig. 1. Solubility curve of BGHC.

3. Spectral measurements

3.1. X-ray diffraction studies

The structural properties of single crystals of BGHC have been studied by X-ray powder diffraction technique. The X-ray diffraction studies were carried out using SEIFERT diffractometer with Cu K α_1 ($\lambda = 1.5406$ Å) radiation. The powdered samples were scanned over the range $10-70^{\circ}$ at a rate of 1° per minute. From the powdered X-ray data, the various planes of reflections were indexed using XRDA 3.1 program and the lattice parameters were evaluated. The indexed X-ray diffraction pattern is shown in Fig. 2. The XRD data prove that the crystal is orthorhombic in structure with the space group $P2_12_12_1$, a well-known noncentrosymmetric space group thus satisfying the requirements for second order NLO activity. The unit cell is found to be tetra molecular. The lattice parameter values reveal a very close agreement with reported values [15] thereby confirming the identity of the grown crystal. The crystallographic data is given in Table 1. It has been observed that $P2_12_12_1$ is one among the popular space group and it allows maximal contribution of the molecular nonlinearity of the macroscopic crystal nonlinearity. It can be implied that A-phase occurs as a zwitterion of the type NH₃⁺CH₂COO⁻, while B-phase has the normal glycine configuration. This molecule receives an additional H⁺



Fig. 2. The indexed X-ray diffraction pattern of BGHC.

Table 1 Crystallographic data of BGHC

BGHC		
C4H11N2O4Cl		
186		
Orthorhombic		
$P2_{1}2_{1}2_{1}$		
5.2990		
8.1181		
18.0622		
90		
90		
90		
777.00923		
4		
D_2^4		
$20\mathrm{mm} \times 0.7\mathrm{mm} \times 0.4\mathrm{mm}$		



Fig. 4. FT Raman spectrum of BGHC.

ion from HCl and these H⁺ acts as ionic connection between molecules A and a pair of Cl⁻ ions. The carboxyl group is a proton donor and the amino group is a proton acceptor. In the glycine molecule carboxylic acid group donates its proton to the amino group to form molecule A i.e. $NH_3^+CH_2COO^-$. The Cl chains are bonded on both sides to two molecules by means of hydrogen and Vanderwaals bonds. Thus, the hydrogen bonding and Vanderwaals forces existing in the intermolecular and intramolecular structure of the molecule. The dipole moment of the title crystal is large, which influences the essential nonlinear optical properties such as second harmonic generation (SHG) efficiency etc.

3.2. FTIR measurements

The room temperature mid Fourier transform infrared spectrum of BGHC shown in Fig. 3 was recorded in the region $400-4000 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} using PerkinElmer Fourier transform Infrared Spectrophotomer, model SPEC-TRUM RX1, using KBr pellets containing a fine BGHC powder obtained from the grown single crystals, equipped with a LiTaO₃ detector, a KBr beam splitter, He–Ne Laser source and boxcar apodization used for 250 averaged interferogrammes collected for both the sample and the background.

3.3. FT Raman measurements

The FT Raman spectrum was recorded on a BRUKER IFS 66V model interferometer equipped with an FRA-106 FT Raman accessory. The observed spectrum given in Fig. 4 was recorded in the $3500-100 \text{ cm}^{-1}$ stokes region using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within 1 cm⁻¹.



Fig. 3. Experimental FTIR spectrum of BGHC.

4. Results and discussions

4.1. Vibrational spectral analysis

Vibrational spectroscopy is an important tool in understanding the chemical bonding and provides useful information in studying the microscopic mechanism of the NLO properties of new materials. From the spectral analysis it is confirmed that the amino groups are protonated and counter balance the negative charge of the chlorine ion functionality. Thus, the molecular structure of the synthesized compound was confirmed by the spectral analysis. The absence of C=O and NH₂ group frequencies and the presence of COO⁻ and NH₃⁺ frequencies indicate that the molecule exists in zwitterionic form and the molecules are held by their dimensional network of hydrogen bonds. The internal vibrations of glycinium cation may be classified into those arise from functional groups NH₃⁺, CH, COOH. However, their vibrations may be strongly coupled between themselves. The observed wavenumbers, relative intensities obtained from the recorded spectra and the assignments proposed for the title nonlinear optical crystal is given in Table 2.

4.2. Vibrations of NH_3^+ group

The broad band observed in high wavenumber region indicates the presence of hydrogen bonding in the title crystal. The hydrogen bonds connect a cation pair to the adjacent anion of another in pair. Thus, it is formed between carboxylate group

Table 2

Observed IR and Raman wavenumbers (in cm⁻¹) of BGHC and its vibrational assignments

Wavenumber Raman	Wavenumber FTIR	Assignments
3476w	3434m	$v_{as}(NH_3)^+$
-	3343m	$\nu_{as}(NH_3)^+$
3104w	3117ms	$v_{s}(NH_{3})^{+}, \varphi$ (C-H) stretching
2966ms	2611w	$v_{as}CH_2$
-	2168w	$\nu_{s}CH_{2}$
	1720ms	v(C=O)
1680m	_	$\delta_{as}(NH_3)^+$
-	1607ms	$\delta_{as}(NH_3)^+$
1440ms	1497m	$\nu(\text{COO}^-), \delta \text{CH}_2$
-	1407ms	$\rho CH_2, \omega CH_2, \nu C - O$
1338ms	1330m	ω CH ₂ , ν C–C ν (COO) ⁻ , $\delta_{in plane}$
		C–O(H), $\delta_{\text{in plane}}$ (C–H)
1266ms	_	τCH_2 , $\delta_{in plane}(C-H)$, $\rho(NH_3)^+$
1138w	1123m	$\delta_{\text{in plane}}(C-H), \rho NH_3^+, \nu (C-C)$
1050ms	1036m	$\nu(C-C)$
986w	_	$\delta_{\text{out of plane}}(\text{C-H}), \rho \text{NH}_3^+$
-	926w	C—(O)H out of plane
894s	890ms	v(C-C)
686ms	686ms	(COO) ⁻ scissoring
-	607ms	$\delta_{\text{in plane}}(C-C-C), \delta(C-N)$
502ms	503s	$\tau(NH_3)^+$
466ms	-	$\rho(\text{COO})^-$
356w	-	$\delta(C-N)$
332ms	-	Lattice modes

 ν : stretching; ρ : rocking; δ : deformation; ω : torsion; φ : ring: w: weak; m: medium; ms: medium strong; s: strong.

of amino acid cation and the amino group and also between the amino group and the chlorine atom. In several cases, specific intermolecular hydrogen bonding networks have been used as a steering force for structure accentricity in crystal engineering particularly of Etter's [16,17] and Gunter's group [18–20]. The hydrogen-bonding network seems to tailor the molecular dipoles of the ionic species in similar direction.

A broad strong absorption in the $3300-2300 \,\mathrm{cm}^{-1}$ correspond to the NH₃⁺ ion of the amino acid. Generally N–H and O-H bonds participate in hydrogen bonding. Hence this region results from superimposed OH of COOH, HCl and NH₃⁺ stretching bonds, hence their stretching vibrations should be shifted to low wavenumber side and also they are asymmetric. The ammonium group NH3⁺ exists with pyramidal symmetry in free state. Its normal mode of vibration are $v_1(A_1)$, $v_2(A_1)$, $v_3(E)$ and $v_4(E)$. All the modes of vibrations are both IR and Raman active [21,22]. The charged amino group has stretching wavenumber $3300-2500 \text{ cm}^{-1}$ [23]. The medium intensity band at 3434 and 3343 cm⁻¹ appearing in IR and a very weak intensity band at Raman at 3476 cm^{-1} are due to NH_3^+ asymmetric structural mode. The symmetric and asymmetric bending NH₃⁺ mode $v_4(E)$ are identified as medium intensity at $3117 \,\mathrm{cm}^{-1}$ and a strong mode at 1497 cm⁻¹ in the infrared and Raman spectra of the title crystal. The NH_3^+ deformation appears at 1607 cm^{-1} which is attributed to the extensive hydrogen bonding of the crystal.

4.3. CH₂ vibrations

The stretching vibrations of CH₂ group are best resolved in the Raman spectrum and the internal vibrations of CH₂ group are well separated from other parts of the glycine molecule. The carbon hydrogen stretching vibration give rise to hydrogen bonds in the region 3100–3000 cm⁻¹ in all the amino acid compounds. In IR spectrum the bands due to this group are observed in 3042 and 2611 cm⁻¹, which formally are assigned to ν_{as} CH₂ and ν_{s} CH₂, respectively. The wavenumbers of methylene group are well compared with those reported for amino acids [24].

4.4. Carboxyl vibrations

The deprotonated carboxylic group (COO⁻) has two important characteristic absorption bands around $1600-1420 \text{ cm}^{-1}$, which are asymmetric and symmetric stretching modes, respectively. In the title crystal, the bands around 1607, 1497, 1407 cm^{-1} in the infrared spectrum suggest the presence of COO⁻ group. They also attributed to the Fermi resonance with the CH₂ rocking mode. The in plane and out of plane C–OH occurs at 1330 cm⁻¹ as a strong band in the Raman.

The protonated carboxyl group R–COOH is characterized by three main IR bands O–H stretching, C=O stretching at $1700-1780 \text{ cm}^{-1}$ and O–H bending at $1200-1300 \text{ cm}^{-1}$. The presence of protonated free carboxylic acid group in the ionic part of the glycinium ion is observed at 1720 cm^{-1} .

The presence of glycinium ion is reflected in the highly mixed bands of the C–O stretch, C–O–H in plane and out of plane deformation. The wagging, twisting and rocking of CH_2 have also been observed. The other skeletal modes of vibrations such as C-N, C-C, O-C=O have been identified and assigned. The external modes that are due to the translatory and rotatory modes have been appeared in Raman below $200 \,\mathrm{cm}^{-1}$. The C–H in plane bending is expected in the region $1300-1000 \text{ cm}^{-1}$. The out of plane C-H bending are appeared as a strong band at 890 cm^{-1} . The medium band at 1330 cm^{-1} in IR and the Raman counterpart at 1338 cm⁻¹ is assigned to C–O stretching which may be coupled with C-H bending mode. So they cannot be separated and identified in an unambiguous manner. The conjugation and the influence of hydrogen bonding type network in the crystal results in the lowered C=O stretching wave number. The simultaneous IR and Raman activation of C=O stretching modes clearly point to the charge transfer into action between carboxyl through C=O group with lone pair of chlorine. The intramolecular charge transfer from the carboxyl groups to the chlorine group makes the molecule highly polarized and into a molecular charge transfer into action may be responsible for the NLO properties of the title compound.

5. Optical studies

5.1. Transparency range

The optical transmittance plays an important role in identifying the potential of the NLO material. Because the material can be of utility if it has wide transparency window with reduced absorption around the fundamental and second harmonic wavelength. The UV–vis transmittance has been performed using PerkinElmer Lambda 35 UV visible spectrophotometer in the region 200–1100 nm. The lower cutoff wavelength lies around 200 nm which is due to the π – π * transition in this compound. The reduction in absorption around Nd:YAG laser fundamental wavelength contributes the resistance of the material to laser damage threshold. The step decrease in transmittance around 200 nm may be assigned to electronic excitation in COO⁻ group. As there is no change in transmittance in the entire visible range up to 200 nm the materials can find application as window in spectral instruments in that region.

6. Nonlinear optical studies

Kurtz Perry technique remains an extremely valuable tool for initial screening of NLO materials [25]. A quantitative measurement of the conversion efficiency of BGHC was determined by the modified version of powder technique developed by Kurtz and Perry. The crystal was ground into powder and it was packed densely between two transparent glass slides. An Nd: YAG(DCR 11) laser was used as a light source. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter and it is 5.7 mJ/pulse. The transmitted fundamental wave was passed over a monochromator (Czerny turney monochromator), which separates 532 nm (SHG signal) from 1064 nm and absorbed by a CuSO₄ solution. Suitable filters were used to remove the residual light. The green light was detected by a photo multiplier tube (Hamamatsu RC 109, a visible PMT) and displayed on a storage oscilloscope (TDS 3052 B 500 MHz phosphor digital oscilloscope). KDP crystal was powdered to the identical size and was used as reference materials in the SHG measurement. The non-zero measured powder SHG signal is reliable with the SHG activity, which can be correlated with noncentrosymmetric crystal structure. The relative efficiency of BGHC with that of KDP has been measured. It is found that the efficiency of the title crystal (142 mV), which is 15 times greater than that of KDP (9 mV). The result of SHG is also supporting for further studies.

7. Microhardness measurements

Hardness of the material is a measure of resistance, it offers to deformation [26]. The transparent crystals free from cracks were selected for microhardness measurements. The indentations were made on the grown surface with the load ranging from 25 to 300 g using Vickers microhardness tester. Leitz–Wetzlar fitted with a Vickers diamond pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vickers hardness number H_v was calculated from the following equation

$$H_{\rm v} = 1.8544 \times \frac{P}{d^2} \,\mathrm{kg/mm^2}$$

where *P* is the applied load in kg and *d* is the diagonal length of the indentation impression in micrometer and 1.8554 is constant of a geometrical factor for the diamond pyramid. A plot obtained between $\ln(P)$ against $\ln(d)$ gives a straight line which is derived from the Meyers law, the relation connecting the applied load is given by $P = ad^n$. Here *n* is the Meyer's index or the hardening coefficient that has been calculated from the slope of the straight line. The value of *n* is 2.04. According to Onitsch, *n* is greater than 2 when hardness decreases with the intensity of load. It satisfies the prediction of Onitsch [27]. The plot of hardness (H_v) versus load for the title crystal is shown in Fig. 5.



Fig. 5. Plot of H_v vs. Load of BGHC.

8. Conclusions

Bisglycinehydrogenchloride was synthesized by the reaction of glycine with hydrochloric acid in water. The solubility curve shows that it has reasonable solubility in water. A single crystal of BGHC was grown from the aqueous solution by slow evaporation method. FTIR and Raman confirmed the various molecular group vibrations and protonation of amino acids in the grown crystals. As there is no change in transmittance in the entire visible range up to 200 nm, these materials can find application as window in spectral instruments in that region. The output SHG relative efficiency was found to be 15 times greater than that of KDP. The vibrational spectral analysis also justifies the presence of carboxylic group and the title molecule is a positive ion with the charge formally residing on the NH₃⁺. Hence the BGHC have nonlinear polarizability and exhibit SHG property. Vickers hardness was carried out and found that the present material obeys the Indentation Size Effect. Based on these facts it could be concluded that the present material has good propensity for nonlinear optical activity.

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References

- [1] V.A. Kuznetsov, T.M. Okhrimenko, M. Rak, Proc. SPIE 100 (1997) 3178.
- [2] V.A. Kuznetsov, T.M. Okhrimenko, M. Rak, J. Cryst. Growth 164 (1998) 193.
- [3] S. Aravazhi, R. Jayavel, C. Subramanian, Mater. Chem. Phys. 50 (1997) 233.

- [4] S. Aravazhi, R. Jayavel, C. Subramanian, Mater. Res. Bull. 32 (1997) 279.
- [5] K.L. Bye, P.W. Whipps, E.T. Keve, Ferroelectrics 4 (1972) 253.
- [6] V. Krishnakumar, R. Nagalakshmi, Spectrochim. Acta Part A 64 (2006) 736.
- [7] S. Hoshino, Y. Okaya, R. Pepinsky, Phys. Rev. 115 (1959) 323.
- [8] S. Sato, J. Phys. Soc. Jpn. 25 (1968) 185.
- [9] J. Baran, A.J. Barnes, H. Ratajczak, Spectrochim. Acta 51A (1995) 197.
- [10] S. Natarajan, C. Muthukrishnan, S.A. Bahadur, R.K. Rajaram, S.S. Rajan, Z. Kristallogr. 198 (1992) 265.
- [11] M.J. Buerger, R. Barney, T. Hahn, Z. Kristallogr. 108 (1956) 130.
- [12] P. Piret, J. Meunier-Piret, J. Verbist, M. Van Meerssche, Bull. Soc. Chim. Belg. 81 (1972) 539.
- [13] S.C. Bhattacharyya, N.N. Saha, J. Cryst. Mol. Struct. 8 (1978) 209.
- [14] S. Gunasekaran, M.N. Ponnusamy, Cryst. Res. Technol. 41 (2) (2006) 130.
- [15] B. NarayanaMoolya, S.M. Darmaprakash, J. Cryst. Growth 293 (1998) 86.
- [16] T.W. Panunto, Z. Urbanczyk-Lipkowska, R. Johnson, M.C. Etter, J. Am. Chem. Soc. 109 (1987) 7786.
- [17] M.C. Etter, P.W. Baures, J. Am. Chem. Soc. 110 (1988) 639.
- [18] F. Pan, M.S. Wong, C. Bosshard, P. Gunter, V. Gramlich, Adv. Mater. Opt. Electron. 6 (1996) 261.
- [19] M.S. Wong, F. Pan, V. Gramlich, C. Bosshard, P. Gunter, Adv. Mater. 9 (1997) 554.
- [20] M.S. Wong, F. Pan, M. Bosch, R. Spreiter, C. Bosshard, P. Gunter, V. Gramlich, J. Opt. Soc. Am. B 15 (1998) 426.
- [21] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1990.
- [22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.
- [23] D.N. Sathyanarayana, Vibrational Spectroscopy, Theory and Applications, New Age International (P) Limited Publishers, New Delhi, 1996.
- [24] M. Diem, P.L. Polavarupu, M. Obodi, L.A. Nafie, J. Am. Chem. Soc. 104 (1982) 3329.
- [25] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
- [26] B.W. Mott, Micro Indentation Hardness Testing, Butterworths, London, 1956.
- [27] E.M. Onitsch, Microskope 95 (1950) 12.