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Synthesis, Growth, and Characterization Studies of a Semiorganic Nonlinear Optical Single Crystal of Gamma Glycine

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ABSTRACT

Single crystals of semiorganic nonlinear gamma glycine have been successfully synthesized by taking glycine and calcium chloride grown by slow evaporation method using water as a solvent. The gamma phase was confirmed by single crystal X-ray diffraction and powder X-ray diffraction analysis. Presence of various functional groups of gamma glycine was identified by Fourier transform infra-red (FT-IR) spectrum. Its nonlinear optical property has been tested by Kurtz powder technique. Its optical behavior was examined by Ultraviolet-vis spectrum and found that the crystal is transparent in the region between 245–1100 nm. Hence it may be very much useful for the second harmonic generation (SHG) applications. Its mechanical behavior has been assessed by Vickers microhardness measurements. Thermal analysis was performed to study the thermal stability of the grown crystals.

Keywords: Nonlinear optical crystal, solution growth technique, and characterization Techniques, second harmonic generation, optical application

1. Introduction

Nonlinear optical materials play a major role in the emerging photonic and optoelectronic technologies. The most popular nonlinear optical materials used to generate the SHG signal so far have been inorganic bulk crystals with rather small second-order nonlinear optical susceptibilities, such as potassium dihydrogen phosphate (KDP), lithium triborate (LBO), β-barium borate (BBO), lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$) etc., [1]. But due its lower SHG efficiency and laser damage threshold, materials scientist focused their attention on organic materials because they possess large second-order nonlinear optical susceptibilities due to delocalized π-electrons.

Inorganic materials are much more mature in their application to NLO than the organic materials. The large nonlinearity in organic materials arises from the

strong charge transfer and high polarizability. One major difference between inorganic and organic crystals is that only relatively weak van der walls forces are hydrogen bonding, resulting in rather poor mechanical properties often couples the molecules in pure organic crystals. Hence the molecules being held together by comparatively weak dispersive forces, the molecular identity in organic crystal is preserved. Accordingly, the molecular absorption will control the absorption spectrum of the crystal. Hence, organic materials are perceived as being structurally more diverse and are believed to have more long-term promise than inorganic [2].

The organic materials have an enormous array of exciting properties that are almost continuously "tunable", telecommunications, frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability and other applications. The oriented nonlinear optical fields will be strengthened by the production of new nonlinear optical materials [3, 4]. The large second order optical nonlinearity originates from organic π conjugated molecules having an electron acceptor group at one end and donor group at the opposite end [5-7]. It is well established that donor-acceptor compounds with their large differences between ground state and excited state and dipole moments as well as large transition dipole moments can exhibit large molecular second order optical nonlinearities [8-11].

In 1987, a new type of semiorganic materials was discovered. It was a combination of materials of both organic and inorganic types [12, 13]. Many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties. The salt of amino acids like L-arginine [14], L-histidine [15], L-threonine [16], LAP [17], DLAP [18], LAHCl [19], LHB [20], LHFB [21], LTA [22] and BGHC [23] are reported to have high second harmonic conversion efficiency compared to KDP. Previous reports show that the amino acid group of glycine is mixed with H_2SO_4 [24], $CaNo_3$ [25], $SrCl_2$ [26], $CoBr_2$ [27] to form single crystals. But none of these are reported to have nonlinear optical (NLO) property.

Glycine family crystals have been subjected to extensive research by several researchers [28-33] for their efficient nonlinear optical properties. In the present article we have reported the material synthesis, growth and characterization of gamma glycine by solvent evaporation method using calcium chloride. The grown crystals have been subjected into thermal, optical, mechanical and spectral studies of GG.

2. Experimental

2.1. Synthesis and growth

Before starting the synthesis process, repeated recrystallization processes purified the commercially available raw materials and the recrystallized salt was used for the present studies. Glycine calcium chloride was synthesized by 4:1 ratio of high purity Glycine salt (Loba Chemie) and calcium chloride (AR grade). The synthesized salt of GG was grown by the slow evaporation low temperature solution growth technique.

The reaction undergoes in the following way:

$$C_2H_5NO_2 + CaCl_2 \longrightarrow C_2H_5NO_2.CaCl_2$$

The saturation of GG was obtained by dissolving the recrystallized material with continuous stirring of the solution using a magnetic stirrer. On reaching saturation, the equilibrium concentration of the solute was determined gravimetrically. The saturated solution was further purified by filtering through the glass filter paper provided with fine pores of 1-micrometer porosity. The filtered solution was tightly closed with thick filter paper so that the rate of evaporation could be minimized. The solution was kept in an undisturbed condition. Transparent optical quality single crystals of dimensions 15 x 9 x 5 mm^3 were obtained after 25 days. The grown crystal is shown in Figure 1.

Figure 1. As grown single crystal of GG

3. Characterization studies

The harvested single crystal has been analyzed by different instrumentation methods in order to check its suitability for device fabrication. Powder X-ray diffraction analysis has been carried out for the as grown specimen of GG. The presence of functional groups was identified from the Fourier transform infra-red (FT-IR) spectral analysis. Its optical behavior has been analyzed by UV-Vis. analysis and found that there is no absorption in the entire visible region. The relative second harmonic generation has been carried out by Kurtz powder technique in order to confirm its second harmonic generation efficiency. Thermal stability of the sample was tested using differential scanning calorimetry and thermo gravimetry analysis respectively.

3.1. Single crystal and Powder X-ray diffraction analysis

The single crystal X-ray diffraction has been carried out using ENRAF NONIUS CAD4 diffractometer. From this measurement we found that the lattice dimensions of a = b=7.025 Å, c = 5.476 Å, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ and volume V = 235 $Å^3$. The powder form of the specimen was subjected to powder X-ray diffraction analysis using a Rich Seifert diffractometer with CuKα (λ = 1.5417 Å) radiation. The sample was scanned over the range of 10-70 degrees at a scan rate of 1 degree per minute. The recorded spectrum is shown in Figure 2.

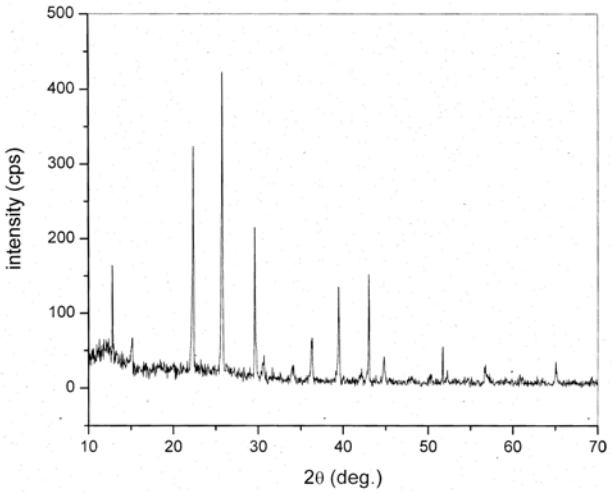

Figure 2. Powder X-ray diffraction pattern of GG

The powder X-ray diffraction experiment showed that the synthesized material and the grown crystals were the single phase of GG. The unit cell parameters were calculated using the TREOR programme. This experiment proved that the grown single crystal belongs to hexagonal crystal system. The lattice dimensions are listed in Table 1. The observed values were good in agreement with the single crystal X-ray diffraction values.

Table. 1 Single crystal XRD data of GG

Identification code	GG
Chemical formula	$C_2H_{11}NO_9CaCl_2$
Unit cell dimensions	$a = b = 7.025$ Å
	$c = 5.476$ Å
	$\alpha = \beta = 90^{\circ}$
	$\gamma = 120^{\circ}$
Volume	235 Å^3
System	Hexagonal
Space group	P_{31}

3.2. Fourier Transform Infrared analysis

The powdered specimen of GG has been subjected to FT-IR analysis by using PERKIN ELMER RX1 Fourier transform infra-red spectrophotometer. Using KBr pellet technique in the wavelength range between 400 and 4000 cm-1 carried out the FTIR analysis of GG. The recorded Fourier transform infra-red (FT-IR) spectrum of GG is shown in Figure 3.

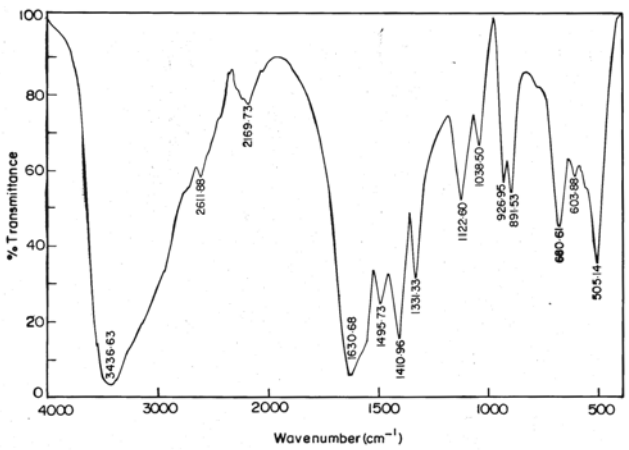

Figure 3. FTIR spectral pattern of GG

The transmission due to the carboxylate group of free glycine is normally observed in the region 607, 1413 cm^{-1}. Where as in the case of GG, these peaks were shifted to 603, 1410 cm^{-1} respectively. Similarly, the transmission peaks due the NH_3^+ group of free glycine were observed at 1133, 2614 cm^{-1}, but in the present case these are shifted to 1122, 2611 cm^{-1}. This observation confirms that glycine exists in the zwitterionic form and the involvement of NH_3^+ in hydrogen bonding is evident by the fine structure of the band in the lower energy region (assignment given in Table 2). The peaks at 891, 1410 cm^{-1} are attributed to CCN, COO^- stretching groups respectively. There is no incorporation of calcium chloride in the title compound as it is evident from the above said analysis.

Table 2. FTIR Spectral Data for GG Crystal

IR band (cm^{-1})		
Glycine	Gammaglycine (GG)	Assignment
504	505	COO^-
607	603	COO^-
694	680	COO^-
893	891	CCN
910	926	CH_2
1033	1038	CCN
1133	1122	NH_3^+
1333	1331	C – H
1413	1410	COO^-
1445	1495	CH_2
2614	2611	NH_3^+
-	3436	O– H (H_2O)

3.3. UV-Vis-NIR Spectral studies

The optical property of the GG was assessed by using LAMBDA-35 UV-Vis spectrometer. The crystal is well polished and the specimen 3 mm thick was subjected to transmission measurements in the spectral region of 200 – 1200 nm. It had good transparency 75 % and the lower cutoff wavelength of the crystal is found to be 245 nm, and thus to ascertain the fact that the crystal could be used for laser applications. The recorded spectrum is shown in the Figure 4. As there is no change in the transmission in the entire visible region, it is an advantage as it is the key requirement for materials having NLO properties [34].

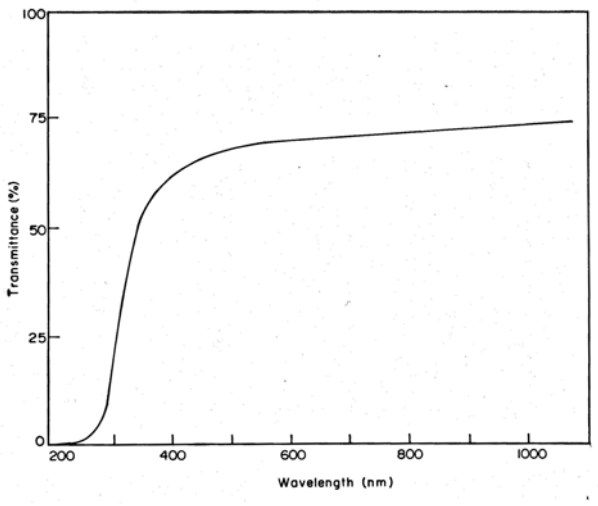

Figure 4. UV-vis – NIR spectrum of GG

3.4. Kurtz powder technique for second harmonic generation Test

The second harmonic generation (SHG) conversion efficiency of GG was measured by powder Kurtz and Perry powder technique [35]. The crystal was grounded into a fine powder and densely packed between two transparent glass slides. A Q switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to strike the sample cell. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube. The powdered material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. The output power intensity of GG was found to be 1.5 times that of KDP.

3.5. Mechanical properties

The definition of hardness depends entirely on the method of measurement, which will determine the scale of hardness obtained. The best general definition that can be given is that hardness is a measure of the resistance deformation [36]. An important use of microhardness study is the possibility of making an indirect estimate of other mechanical characteristics of materials having a specific correction with their hardness. It plays a key role in device fabrication. Transparent crystals

free from cracks were selected for microhardness measurements. There are different types of hardness tests available viz., static indentation test, dynamic indentation test scratch test, rebound test, pendulum recoil test, in which Vicker's Microhardness studies has been used for the present study.

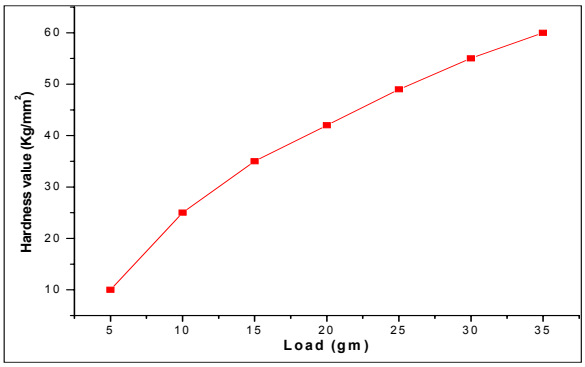

Figure 5. Hardness Vs. Load for GG

The mechanical property of the grown crystals has been studied using a LEITZ microhardness tester fitted with a Vickers diamond pyramidal indenter. A well-polished GG crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (8 s) for all the loads. The hardness number was calculated using the relation $H_v = \frac{(1.8544 * P)}{d^2}$ kg / mm^2. Where H_v is the Vickers microhardness number, P is the applied load in kg and d is the diagonal length of the indentation impression in the micrometer. A graph has been plotted between hardness number (H_v) and applied load (P) as shown in Figure 5. The hardness increased gradually with the increase of load and above 40 g cracks developed on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. Hence it may be suggested that the material may be used for the device fabrication below the applied load of 40g.

The relation between the load and size of the indentation is given by Meyer's law [37]. $P = ad^n$, where P is the load. *d* is the diagonal length of impression, *n* is the Meyer index or work hardening coefficient and *a* is the constant for a given material. From the slope of log P Vs. log d plot, the value of *n* was estimated, which gives the Meyer index number or work hardening index. The value of *n* is expected to be 2 but most of the experimental data show that it is always less than 2 [38-40]. From careful observations on various materials, Onitsch [41] pointed out that an *n* lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. The value of n observed in the present study is 2 suggesting that these crystals are soft substances. Hence gamma glycine crystal belongs to the soft material.

3.6. TG/DTA analyses

Thermo gravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. The thermo gravimetric analysis of GG crystal is carried out between 20 °C and 800 °C in the nitrogen atmosphere at a heating rate of 20 °C min^{-1} using Perkin-Elmer thermal analyzer (STA 409 PC). The obtained spectrum is shown in Figure 6. The first endothermic peak in DTA at 182 °C corresponds to the phase transition from gamma phase to alpha phase [42 – 44] reported that the transition point between gamma and alpha glycine exists at 165 °C. The present work gamma glycine crystal grown form a mixture of glycine and calcium chloride is stable upto 265 °C.

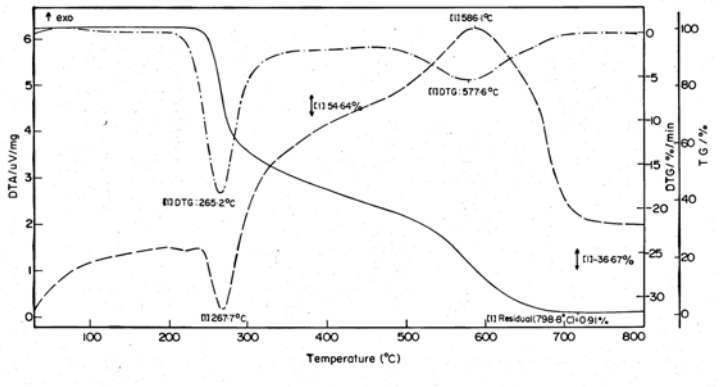

Figure 6. TG/DTA spectrum of GG

4. Conclusions

Single crystals of gamma glycine were successfully synthesized and the single crystals have been grown by solution growth technique. Its lattice dimensions have been determined from the powder X-ray diffraction analysis. The various functional groups in gamma glycine have been identified from the Fourier transform infra-red (FT-IR) analysis. The grown crystal has good transmission window in the visible region between 245 and 1100 nm suitable for NLO applications. Microhardness study estimates the mechanical strength of the crystal. The SHG test confirms the second harmonic conversion efficiency of the crystal and it is found to be 1.5 times better than that of potassium dihydrogen orthophosphate. From the thermal measurements we found that the compound is stable up to 265 °C and hence it may be useful for SHG applications below its melting point.

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