CHAPTER - 6
GROWTH AND CHARACTERIZATION OF A NOVEL SEMI-ORGANIC NONLINEAR OPTICAL SINGLE CRYSTAL : BIS GLYCINE SODIUM NITRATE

6.1 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 (LiNbO₃), potassium niobate (KNbO₃) 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 the molecules in pure organic crystals are often coupled by only relatively weak van der walls forces are hydrogen bonding, resulting in rather poor mechanical properties. 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 inorganics [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 shows that the amino acid group of glycine is mixed with H2SO4 [24], CaNo3 [25], SrCl2 [26], CoBr2 [27] to form single crystals. But none of these are reported to have nonlinear optical (NLO) property.
In the present chapter, glycine is combined with sodium nitrate to form a new semiorganic nonlinear optical material. BGSN (Na(NH₂CH₂COOH)₂NO₃). Semiorganic NLO material was synthesized and the solubility test was carried out. The single crystals were grown from an aqueous solution by the solvent evaporation technique. The material was characterized by single crystal XRD, FTIR spectral analysis, UV-Vis transmission studies, TG-DTA, microhardness and SHG properties.

6.2 SOLUBILITY

The solubility of BGSN was determined at five different temperatures viz., 30, 35, 40, 45 and 50 °C. The solubility was determined by 100 ml of solvent (water) was taken in an airtight container and recrystallization salt was added. The experiment was carried out in a constant temperature bath with the cryostat facility. The bath was set to 30 °C and the solution was stirred continuously for five hours using motorized stirrer by ensuring homogeneous temperature and concentration through out the volume of the solution. Once saturation was reached, the solution was further stirred for five hours and the equilibrium concentration of the solute was analyzed gravimetrically. Similarly several trials were made to get the concurrent values. The experiment was carried out at various temperatures, and the solubility curve is drawn. The solubility of BGSN in water is shown in Figure 6.1. The results indicated that there was a positive slope and the solubility of BGSN in pure double distilled water is quite high.
Figure 6.1 Solubility curve of BGSN
6.3 SYNTHESIS

Bis Glycine Sodium Nitrate (BGSN) was synthesized by taking high purity Glycine salt (SRL) and Sodium Nitrate (E-Merck) in the stoichiometric ratio of 2:1. The compound was formed according to the reaction mechanism

\[ 2\text{NH}_2\text{CH}_2\text{COOH} + \text{NaNO}_3 \rightarrow \text{Na(\text{NH}_2\text{CH}_2\text{COOH})}_2\text{NO}_3 \]

Glycine Sodium Nitrate Bis Glycine Sodium Nitrate

The calculated quantities of glycine and sodium nitrate were very well dissolved in double distilled water and stirred well for about 2 hours using a magnetic stirrer to obtain a homogeneous mixture. Then the mixture was allowed to ion evaporate by heating below an optimum temperature of 60 °C. The colourless crystalline samples of BGSN were harvested and they were used for bulk growth of BGSN single crystals.

6.4 CRYSTAL GROWTH

The synthesized salt was purified by successive recrystallization processes. The synthesized salt was used to prepare the concentrated solution of BGSN. Then the solution was filtered using whatman filter paper. The filtered solution was then taken in a beaker which was tightly closed with thick filter paper so evaporation could be minimized. After a time span of 30 days a good quality single crystal with dimension of 16 x 14 x 4 mm$^3$ was harvested from the mother solution. The grown crystal is shown in Figure 6.2.
Figure 6.2 As-grown crystal of BGSN
6.5 CHARACTERIZATION

In general, a wide range of techniques were established for the assessment of perfection and examination of defects in crystalline materials. The characterization techniques mainly used for the structural assessment of organic and semiorganic crystals are X-ray diffraction and optical studies. The grown crystals have been analyzed by different characterization techniques. The grown single crystal of BGSN was confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD-4 diffractometer. The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm\(^{-1}\). The optical properties of the crystals were examined between 200 and 1200 nm using LAMBDA-35 UV-Visible spectrometer. The NLO efficiency of the grown sample was confirmed Nd:YAG laser as the source. The mechanical properties of the grown crystals have been studied using a LEITZ WEITZLER hardness tester fitted with a diamond pyramidal indentor. The thermal behaviour of the grown single crystal was tested by PERKIN-ELMER thermal analyzer (STA 409 PC).

6.6 RESULTS AND DISCUSSIONS

6.6.1 Single crystal X-ray diffraction studies

The grown crystals of BGSN were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD-4 X-ray Diffractometer with MoK\(_\alpha\) radiation (\(\lambda = 0.7107\ \text{Å}\)) to obtain the unit cell dimensions. The cell dimensions were evaluated from them using standard software. From this measurement we found that the grown specimen belong to orthorhombic crystals system, having lattice dimensions \(a = 14.332\ \text{Å}, \ b = 5.267\ \text{Å}, \ c = 9.131\ \text{Å}\). The obtained values are given in the Table 6.1.
### Table 6.1 Single crystal XRD data of BGSN

<table>
<thead>
<tr>
<th>Identification code</th>
<th>BGSN</th>
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<tbody>
<tr>
<td>Cell parameters</td>
<td></td>
</tr>
<tr>
<td>a = 14.332 Å</td>
<td></td>
</tr>
<tr>
<td>b = 5.267 Å</td>
<td></td>
</tr>
<tr>
<td>c = 9.131 Å</td>
<td></td>
</tr>
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<tr>
<td>System</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>Na(NH₂CH₂COOH)₂NO₃</td>
</tr>
</tbody>
</table>
6.6.2 Fourier Transform Infrared analysis

The powdered specimen of BGSN has been subjected to FTIR analysis by using PERKIN ELMER RXI Fourier Transform Infrared spectrophotometer. The FTIR analysis of BGSN was carried out by using KBr pellet technique in the wavelength range between 400 and 4000 cm\(^{-1}\). The recorded FTIR spectrum of BGSN is shown in Figure 6.3. The transmission due to the carboxylate group of free glycine is observed at 504.2, 892.8 and 1614 cm\(^{-1}\) where as in BGSN, these peaks are shifted to 515.30, 930.34 and 1637.13 cm\(^{-1}\) respectively. The transmission peaks due NH\(_3^+\) group of free glycine generally appeared at 1110, 1131 and 1505 cm\(^{-1}\), but in the present case, these are shifted to 1116.13, 1344.38 and 1562.27 cm\(^{-1}\) respectively. Other peaks at 1023.52, 1415.62 and 2375.18 cm\(^{-1}\) were attributed to C-C-N, COO\(^-\) and CH\(_2\) respectively. From the spectrum the peak observed at 3431.96 cm\(^{-1}\) was assigned to the OH stretching vibration of H\(_2\)O (O – H) of BGSN molecule. Thus the FTIR spectrum confirmed the formation of BGSN and its characteristics frequencies were observed as mentioned above. From this spectroscopic investigation, the presence of all the fundamental functional groups of the grown crystal confirmed qualitatively.
Figure 6.3 FTIR spectrum of BGSN
6.6.3 UV-Vis-NIR Spectral studies

The optical property of the BGSN was assessed by using LAMBDA-35 UV-Vis spectrometer. It was observed from the spectrum that BGSN had a wide optical transmission window (200 – 1200 nm). It had good transparency 60 % and the lower cutoff wavelength of the crystal is found to be 240 nm, and thus to ascertain the fact that the crystal could be used for laser applications. The recorded spectrum is shown in the Figure 6.4. 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 [28].

6.6.4 Kurtz powder technique for Second harmonic generation Test

The second harmonic generation (SHG) conversion efficiency of BGSN was measured by powder Kurtz and Perry powder technique [29]. 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 BGSN was found to be twice that of KDP.
Figure 6.4 Optical transmission spectrum of BGSN crystal
6.6.5 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 [30]. 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.

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 BGSN 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

\[ H_v = \frac{(1.8544 \times P)}{d^2} \text{ kg/mm}^2 \]
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 6.5. 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 the of indentation is given by Meyer’s law [31]. $P = a d^n$, 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 [32-34]. From careful observations on various materials, Onitsch [35] 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.
Figure 6.5 Variation of Vicker's Microhardness number with applied load
6.6.6 Thermal analyses

The thermo gravimetric analysis of BGSN crystal was 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 spectrum obtained is shown in Figure 6.6. A careful examination of this weight loss showed two stages, one occurring below 262 °C due to weakly entrapped lattice water and the other occurring above 573 °C, due to the removal of strongly entrapped lattice water. The DTA analysis was also carried out in the same atmospheric condition. The endothermic peak at around 256 °C is assigned to melting point of the title compound. It is followed by decomposition and volatilization of the compound above 544 °C. Hence it may be useful for making the NLO devices below its melting point.

6.6.7 Differential scanning calorimetric analysis

Differential scanning calorimetric (DSC) study was performed using DSC 200 PC in the temperature range of 20-400 °C at a heating rate of 20 °C/min in the nitrogen atmosphere and the spectrum is shown in the Figure 6.7. From the figure, we understand that there is a sharp endothermic peak at around 256 °C. It belongs to the melting point of the specimen. The sharpness of the endothermic peak suggests that the good crystallinity of the specimen.
Figure 6.6 TG/DTA spectra of BGSN
Figure 6.7 DSC spectrum of BGSN
6.7 CONCLUSION

The title compound of BGSN was successfully synthesized and the single crystals were grown by slow evaporation solution growth technique at room temperature. The growth parameters of BGSN were optimized for the growth of good quality crystals. The grown single crystals were subjected for different instrumentation methods. Single crystal X-ray analysis revealed that the crystal belongs to orthorhombic system with space group Cc. The presence of various functional groups was identified from the FTIR spectral analysis. The UV-cutoff wavelength was found to be 240 nm and thus the material is a potential candidate for generating blue-violet light using a diode laser. The SHG efficiency was found to be nearly two times higher than KDP. The microhardness studies revealed that the BGSN crystal was a soft substance. The thermal analysis showed that the crystal was stable up to 256 °C. The compound was stable upto its melting point and that may be useful for making the NLO devices like second harmonic generators, optical data storage devices etc.
REFERENCES


