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Crystal growth, Thermal, Hardness, Etching Studies of a Semi-Organic Non-Linear Optical Single Crystal: $C_2H_5NO_2$. Na (NO_3)

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ABSTRACT

The title compound of $C_2H_5NO_2$.Na (NO_3) Glycine Sodium Nitrate (GSN), a semi-organic material has been grown from slow evaporation solution growth technique at room temperature. It is a potential material for nonlinear optical applications. The grown single crystals have been analyzed by single crystal X-ray diffraction. It belongs to monoclinic crystal system and its lattice dimensions were determined. The presence of functional groups was identified from FTIR spectral analysis. The title compound has good optical transmission in the entire visible region. The mechanical properties of grown crystals have been assessed by Vickers Microhardness tester. Its relative SHG efficiency has been tested by Kurtz powder method and it shows twice the output power intensity of that potassium dihydrogen phosphate (KDP). Thermal stability of the grown crystal was investigated by thermogravimetric and differential thermal analyses

Keywords: Crystal growth, characterization methods, optical material and properties

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 (βBO), lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$) etc., [1]. However, 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. Even though its SHG efficiency is higher, its mechanical property is not up to the mark. Hence, a new type of materials has been discovered i.e. semiorganic. It is a combination behavior of organic and inorganic type materials [2-3]. In the recent past, many organic amino acids are mixed with the inorganic salts in order to enhance its physical and chemical properties. Previous reports shows that the amino acid group of glycine is mixed with H_2SO_4 [4], $CaNo_3$ [5], $SrCl_2$ [6], $CoBr_2$ [7] to form a single crystals. But none of these are reported to have nonlinear optical (NLO) property. In the present study, glycine is combined with sodium nitrate to form a semiorganic nonlinear optical material. In this paper, we report the growth of Glycine Sodium Nitrate (GSN) $C_2H_5NO_2.Na(NO_3)$ single crystals by slow evaporation technique and its characterization.

2. Experimental details

2.1. Crystal growth

The title compound was synthesized by taking 1:1 mole ratio of high purity Glycine salt (E-Merck) and Sodium Nitrate (E-Merck) and dissolved in deionized water and heated below 60 °C for completion of the reaction. The synthesized salt was purified by successive recrystalization processes. The synthesized salt was used to prepare the concentrated solution of GSN. Then the solution was filtered using whattman filter paper. The filtered solution was taken in a beaker, which was tightly closed with thick filter paper so that the rate of evaporation could be minimized. After a time span of 25 days, a good quality single crystal was harvested from the mother solution (size $20 \times 14 \times 3$ mm^3).

2.2. Characterization

The as grown crystals were subjected to single crystal X-ray diffraction using ENRAF NONIUS CAD4 diffractometer in order to find out its lattice dimensions. Its functional groups were identified from FTIR analysis using PERKIN ELMER SPECTRUM RX1 Fourier Transform Infrared spectrometer. Its optical behavior was assessed by LAMBDA-35 UV-Vis spectrophotometer. The NLO efficiency of the grown sample was measured by Kurtz powder technique using Nd: YAG laser as a source. The mechanical properties of the grown crystals have been studied using a LEITZ microhardness tester fitted with a Vickers diamond pyramidal indenter. Thermal analysis was carried out using STA409 PC thermal

analyzer to study thermal behavior of the grown crystal. Etching study were carried out on the (100) plane of the GSN crystal using water as an etchant. The detailed discussions of the obtained results are presented in the following sections.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The grown crystals of GSN were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD-4 X-ray Diffractometer with MoKo radiation (λ = 0.7107 Å) to obtain the unit cell dimensions. The lattice dimension of the grown specimen was determined from the single crystal XRD analysis using SHELX programme. From the measurement we found that the grown specimen belong to monoclinic crystals system, having lattice dimensions a = 14.332Å, b = 5.267Å, c = 9.131Å. which are in good agreement with the reported values [8]. The obtained values are given in the Table 1.

Table. 1 Single crystal XRD data of GSN

Identification code	GSN
Cell parameters	a = 14.332 Å
	b = 5.267Å
	c = 9.131 Å
	α = 90°
	β = 119.01°
	γ = 90°
Volume	603 $Å^3$
System	Monoclinic
Space group	Cc

3.2. Fourier Transform Infrared analysis

The powdered specimen of GSN has been subjected to FTIR analysis by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer. The FTIR analysis of GSN was carried out by using KBr pellet technique in the wavelength range between 400-4000 cm^{-1}. The recorded spectrum is shown in Fig. 1. The transmission due to the carboxylate group of free glycine is observed at 504.2, 892.8 and 1614 cm^{-1}. Where as in GSN, these peaks are shifted to 515.30, 930.34, and 1637.13 cm^{-1} respectively. Similarly, the transmission peaks due NH_3^+ group of free glycine are 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} are attributed to C-C-N, COO^- and CH_2 respectively. From the spectrum the peak observed at 3431.96 cm^{-1} is assigned to the OH stretching vibration of H_2O (O – H) of GSN molecule. Thus, the

FTIR spectrum confirms the formation of GSN and its characteristics frequencies are observed as mentioned above.

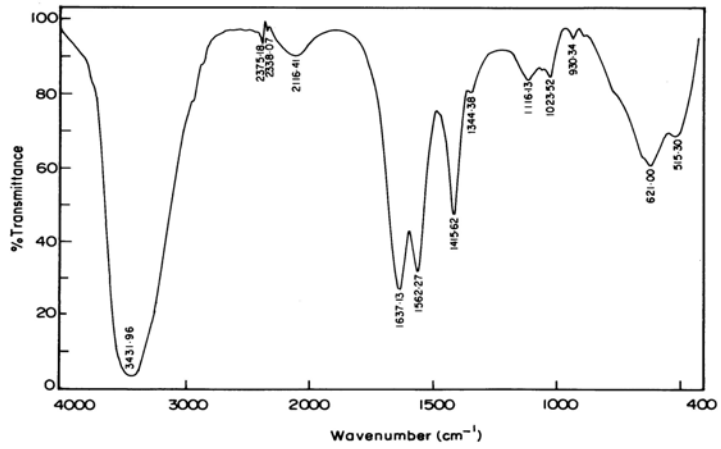

Fig.1. FTIR spectrum of GSN crystal

3.3. Linear and nonlinear optical studies

The optical property of the title compound has been assessed by using LAMBDA-35 UV-Vis spectrometer. It is observed from the spectrum that GSN has a wide optical transmission window (220–1100 nm). It has 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 can be used for laser applications. The recorded spectrum is shown in the Fig. 2. From the graph, it is evident that it has UV cut off wavelength is below 240 nm, which is sufficient for SHG laser radiation. The second harmonic generation (SHG) conversion efficiency of GSN was measured by powder Kurtz and Perry power technique [9]. 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 1064nm (pulse width 8ns) was allowed to strike the sample cell normally. The SHG output 532nm (green light) was finally detected by the photomultiplier tube. A sample of potassium dihydrogen phosphate (KDP), also powdered was used for the same experiment as a reference material in the SHG measurement. The output power intensity of GSN was found to be twice that of KDP.

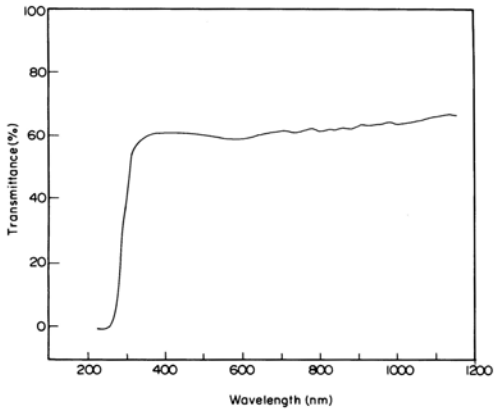

Fig.2. Optical transmission spectrum of GSN crystal

3.4. Mechanical properties

Hardness is one of the important mechanical properties of the materials. It can be used as suitable measure for the plastic properties and strength of a material. A well-polished GSN 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 sec) for all the loads. The hardness number was calculated using the relation $H_v = (1.8544\ P)/(d^2)$ 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 Fig. 3. 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.

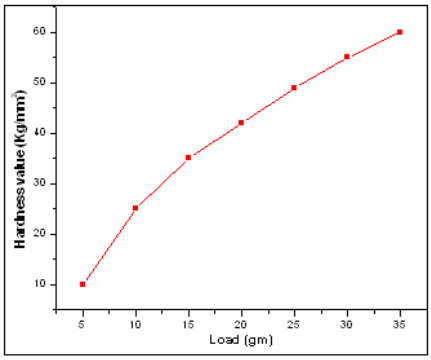

Fig.3. Variation of Vicker's Microhardness number with applied load

3.5. Thermal analyses

The thermo gravimetric analysis of GSN 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 Fig. 4. On a careful examination of this weight, loss shows 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.

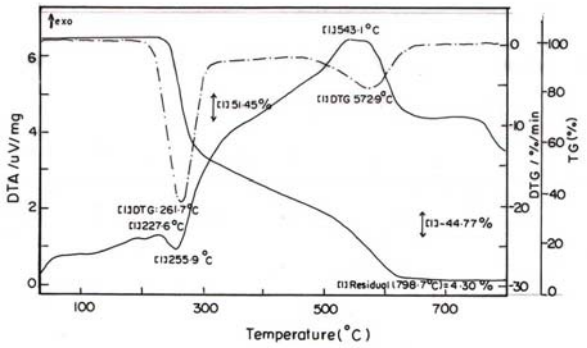

Fig.4. TG/DTA curves of GSN crystal

Differential scanning calorimetric (DSC) study was performed using DSC 200 PC in the temperature range 20-400 °C at a heating rate of 20 °C/min in the nitrogen atmosphere and the spectrum is shown in the Fig. 5. From the figure, we understood that there is a sharp endothermic peak at around 263 °C. It belongs to the melting point of the specimen. The sharpness of the endothermic peak suggests that the good crystallinity of the specimen. Hence, the compound the stable up to the melting point.

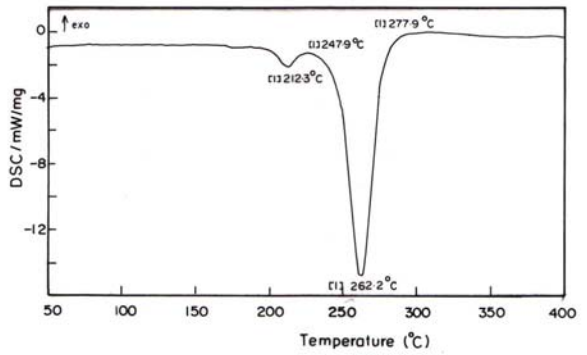

Fig.5. DSC curve of GSN crystal

3.6. Etching studies

The crystals with defects may destroy the mechanical and electrical properties, which affect the usefulness of the crystals. The nonlinear optical properties such as SHG efficiency, damage threshold etc, depend on the crystalline perfection. Etching is one of the selective tools to identify the defects in the as grown crystals. When the crystal is dissolved in a solvent, the reversal of the growth-taking place by giving the well defined etches pits. The etching time depends on the solubility of the crystalline material in different solvents. In the present work, water is used as an etchant and etching experiment has been carried out on (100) surface of GSN crystal. The material was dipped in the water for about 15 s and immediately taken it out and the surface etchant was removed gently by using cotton cloth. The recorded photographs are shown in Fig. 6. During etching, the weak surface layers have been removed. It may due to the vacancy of the atoms in some areas of the surface of the specimen.

Fig.6. Observed etch pits of as grown crystal of GSN

4. Conclusion

The title compound of GSN has been successfully synthesized and the single crystals have been grown by slow evaporation solution growth technique at room temperature. The growth parameters of GSN have been optimized for the growth of good quality crystals. The grown single crystals have been subjected for different instrumentation methods. Its lattice dimensions have been calculated from the single crystal XRD analysis. 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 mechanical and SHG behavior have also been analyzed. The thermal analysis has revealed the thermal stability of the crystal. From the etching studies well defined etch pits were observed on the surface of the specimen. It may due to vacancy of atoms on the surface of the specimen.

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