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GROWTH AND CHARACTERIZATION OF GLYCINE SODIUM NITRATE NON-LINEAR OPTICAL CRYSTAL

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ABSTRACT

Glycine and its related compounds takes place a major role in the field of non-linear optical studies and in fiber optical communication. Glycine sodium nitrate crystal is one such efficient Non Linear Ooptical material. Glycine Sodium Nitrate crystal has been grown by the conventional slow evaporation method. The crystalline nature of the grown Glycine Sodium Nitrate crystal has been confirmed with help of powder X-Ray Diffraction technique. Fourier Transform Infrared studies confirmed the functional groups present in the compound. Ultra Violet cut off wavelength has been found out as 280 nm. With the help of Differential Thermal Analysis curve the melting point of the title compound has been found out as 236.1 °C. It is noticed that the Non Linear Optical efficiency of the grown Glycine Sodium Nitrate crystal is about 0.43 times than that of the reference KDP crystal.

Keywords: Glycine Sodium Nitrate, X-Ray Diffraction, Fourier Transform Infrared Spectroscopy.

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INTRODUCTION

Non linear optics (NLO) is an innovative area of research and development which will play a key role in the field of optoelectronics and photonics. In recent years complexes of amino acids have been considered as attractive materials for NLO applications. Amino acids are interesting materials for NLO applications as they contain donor carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group in them, known as zwitterions which create hydrogen bonds, in the form of N-H+-O-C. They also have been used in the possible generation of non-centrosymmetric structures for effective NLO properties[1]. Recently, the amino acids are formed to have special feature such as molecular chairality, which secure acentric crystallography structures and the presence of weak Vander walls and hydrogen bond leads to wide transparency range in the visible and UV spectral regions and zwitter ionic nature of the molecule which favors the physico chemical stability[2]. Amino acid family crystals have been subjected to extensive investigation during the recent decades for their non linear properties. Glycine [NH_2CH_2COOH] is the simplest amino acid. Glycine remains as one of the most extensively studied amino acids, as it is known to form in numerable complexes with metals, inorganic salts and inorganic acids. Many researchers have investigated the properties of pure Glycine and its derivatives. So far, different polymorphic forms of Glycine ($C_2H_5NO_2$) have been already reported such as metastable α, unstable β and stable γ at ambient conditions[3]. Some complexes of Glycine with inorganic salts have already been reported such as Glycine zinc chloride[4], Glycine zinc sulfate[5], Glycine lithium chloride[6], Glycine calcium chloride[7], Glycine barium chloride[8], Glycine strontium chloride[9], Glycine potassium sulfate[10,11], Glycine magnesium chloride[12], Triglycine sulphate[13-15], Glycine silver nitrate[16], Glycine lithium sulphate[17], Glycine phosphate[18-20] and n-benzoyl Glycine crystal[21]. Glycine sodium Nitrate is one such efficient NLO crystal[22]. Recently various characterization studies on GSN crystals have been reported by many researchers[23-25]. In our present study, Glycine Sodium Nitrate (GSN) crystal has been grown by the conventional slow evaporation method, and GSN crystal has been characterized by powder X-Ray

Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Ultra Violet Visible near Infrared spectroscopy, Thermal, and Non Linear Optical studies.

EXPERIMENITAL

A stoichoimetric mixture of glycine and sodium nitrate in equimolar ratio was dissolved in deionized water and stirred, continuously for a period of 6 hours. The equation governing the reaction is-

$$C_2H_5NO_2 + NaNO_3 \rightarrow C_2H_5NO_2.NaNO_3 \quad (1)$$

The solution was filtered to remove the impurities and was left for slow evaporation. The grown GSN crystals have been harvested after a period of 21 days. The photograph of the grown crystal is shown in Fig.-1.

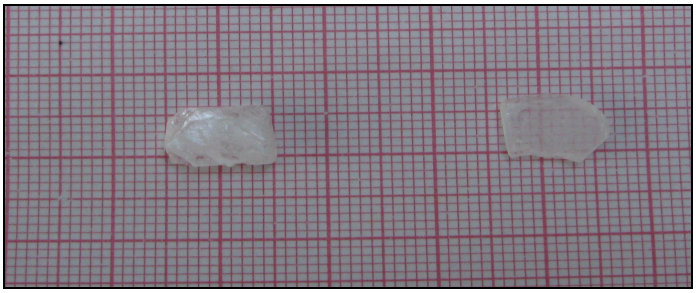

Fig.-1:Photograph of the grown GSN Crystal

RESULTS AND DISCUSSION

The powder XRD pattern was recorded at room temperature using Xpert pro Analytical X-ray diffractometer with cuKα radiation of wave length λ=1.5418Å. The samples were scanned over the range of 10^o – 70^o at a scan rate of 1^o per minute. The powder XRD pattern of the grown GSN crystal is shown in Fig.-2. The sharp peaks observed in the XRD pattern confirm the crystalline nature of the sample.

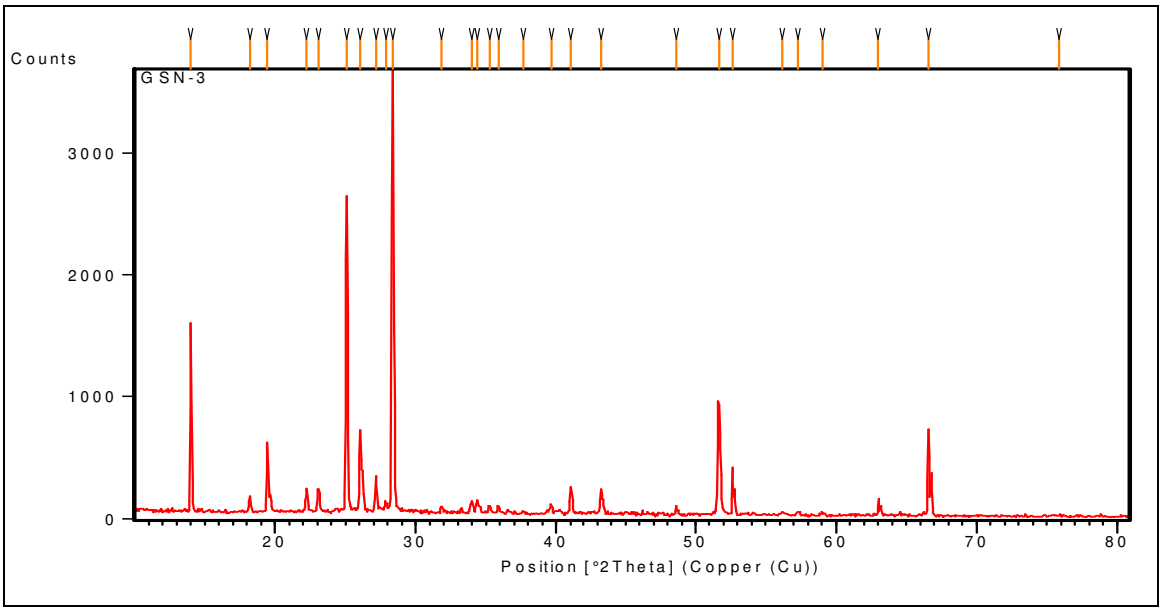

Fig.-2: Observed Powder XRD pattern of GSN Crystal

FTIR spectrum is important evidence that provides more information about the structure of a compound. The FTIR spectrum of the grown GSN crystal is recorded in the range of 400-4000 cm^{-1} using Perkin

Elmer Infrared spectrophotometer. The FTIR spectrum of the grown GSN crystal is shown in Fig. 3. The asymmetric stretching frequency of NH_3^+ functional group is found in 3417 and 3250 cm^{-1}. For amino acids, the asymmetric CH_2 stretching vibrations are generally observed in the region 3100-3000 cm^{-1}. In the present work, the narrow band at 3028 cm^{-1} is due to CH_2 asymmetric vibrations. The stretching vibration of CH_2 appears at 2625 cm^{-1}. The peaks occur at 2276, 2237 and 2013 cm^{-1} is due to the combination of asymmetrical NH_3 bending vibration and the torsional oscillation of the NH_3 group. The C=O stretching vibration of carboxyl group appears as a sharp band at 1623 cm^{-1}, which indicates the presence of a Glycine molecule. The absorption band at 1508 cm^{-1} is due to NH_3^+ bending. The very strong band appears at 1383 cm^{-1} corresponds to NO_3^- asymmetric stretching. NH_3^+ rocking is observed at 1117 cm^{-1}. The peaks occurring at 1036 and 934 cm^{-1} are associated with the CH_2 Rocking. The peaks at 888 and 831 cm^{-1} are assigned to the C-C stretching vibration. The strong band at 675 cm^{-1} is due to NO_3^- in plane deformation. The peak at 587 cm^{-1} corresponds to COO^- wagging. The strong peak at 507 cm^{-1} corresponds to the carboxylate group of free Glycine.

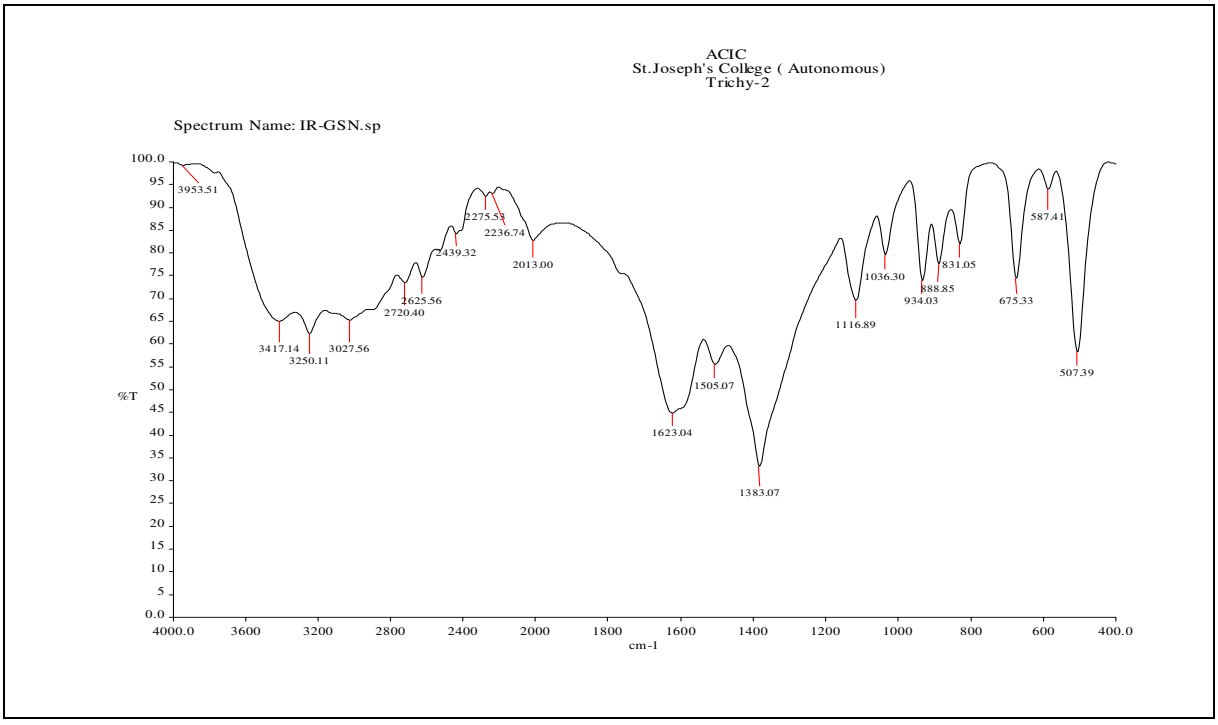

Fig.-3: FTIR spectrum of the grown GSN Crystal

Thus with the help of available data on the vibrational frequencies of amino acids, all the molecular groups present in GSN crystal could be identified. The detailed band assignments are given in Table-1.

Table-1

Wave number (cm^{-1})	Assignments
3417	$(NH_3)^+$ asymmetric
3250	Stretching
3028	CH_2 assymmetric stretching
2720	Overtones
2625	CH_2 stretching
2276	Combination of asy. NH_3
2237	Bending and torsional

2013	Oscillation of NH_3 group
1623	C=0 symmetric stretching
1508	NH_3^+ sym. Bending
1383	NO_3^- Assym. Stretch
1117	NH_3^+ Rocking
1036	CH_2 Rocking
934	
888	C-C stretching
831	
675	NO_3^- in plane bending
587	COO^- wagging
507	COO^- rocking

The UV study has been carried out by using a Lambda-35 Spectro photometer in the wavelength range of 100 – 1100 nm. The optical transmission spectrum of the grown GSN crystal is shown in Fig. 4. It is noticed that the grown GSN crystal has a wide transparency in the near UV region and entire visible region. The UV cut off wavelength has been found out as 290 nm. Good optical transparency in the entire visible region and lower UV cut off wavelength of GSN crystal suggests its suitability for NLO devices.

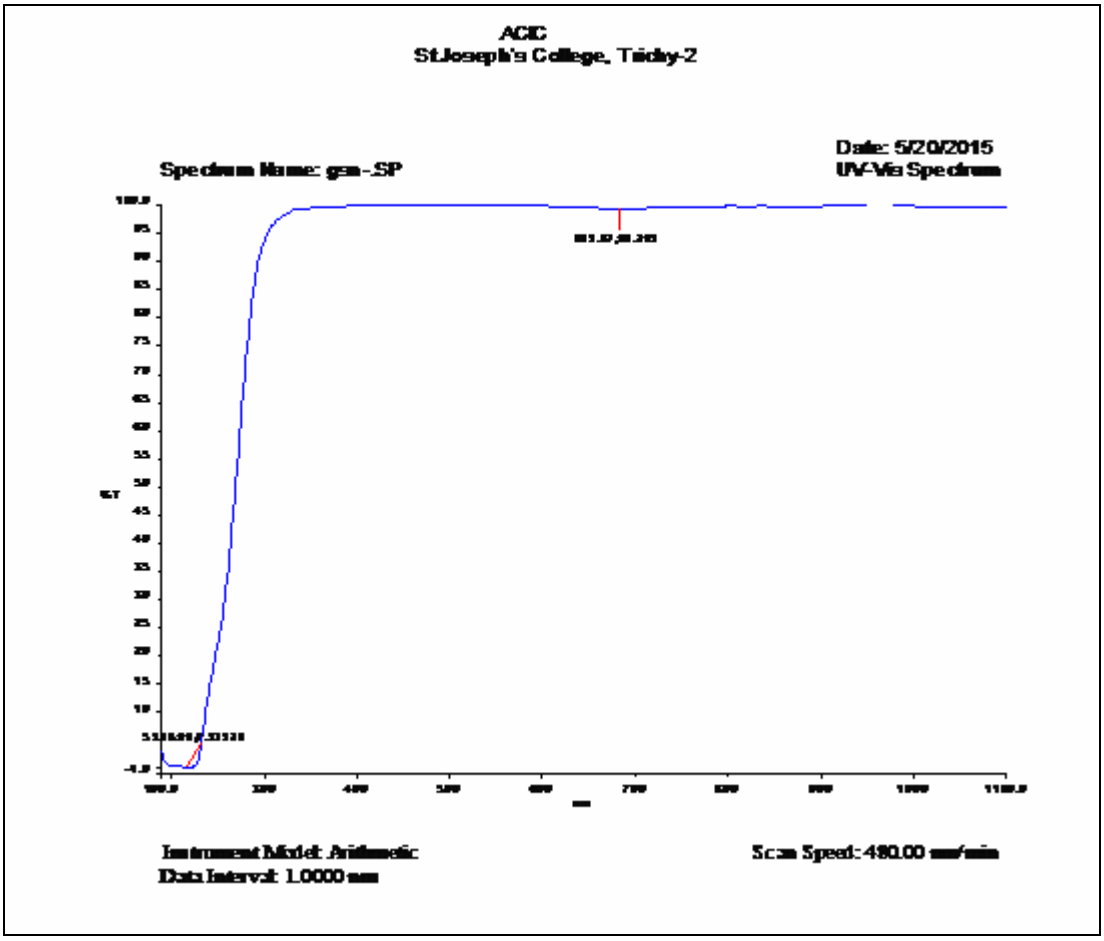

Fig.-4: Optical transmission spectrum of the grown GSN Crystal

In the present work, thermal analysis of GSN crystals were performed by using NETZSCH TGA/DSC instrument. The measurements have been carried out in nitrogen atmosphere at a heating rate of 20

°C/min in the temperature range of 30 °C to 400 °C. The recorded thermogram for GSN crystal is shown in Fig.5. The TGA trace of the GSN crystal shows that the there is no major weight loss upto 230 °C. There are two stages of decomposition. There is sharp weight loss (50%) in the first stage (230 °C – 280 °C) due to the evolution of carbon dioxide and hydrogen gases. In the second stage (280 °C-300 °C), the remaining 50% of the grown Glycine sodium nitrate crystal compound was lost at 300 °C due to the decomposition of sodium and Nitrogen molecules. DTA curve shows a sharp endothermic peak at 236.1 °C, indicates the melting point of the given GSN crystal.

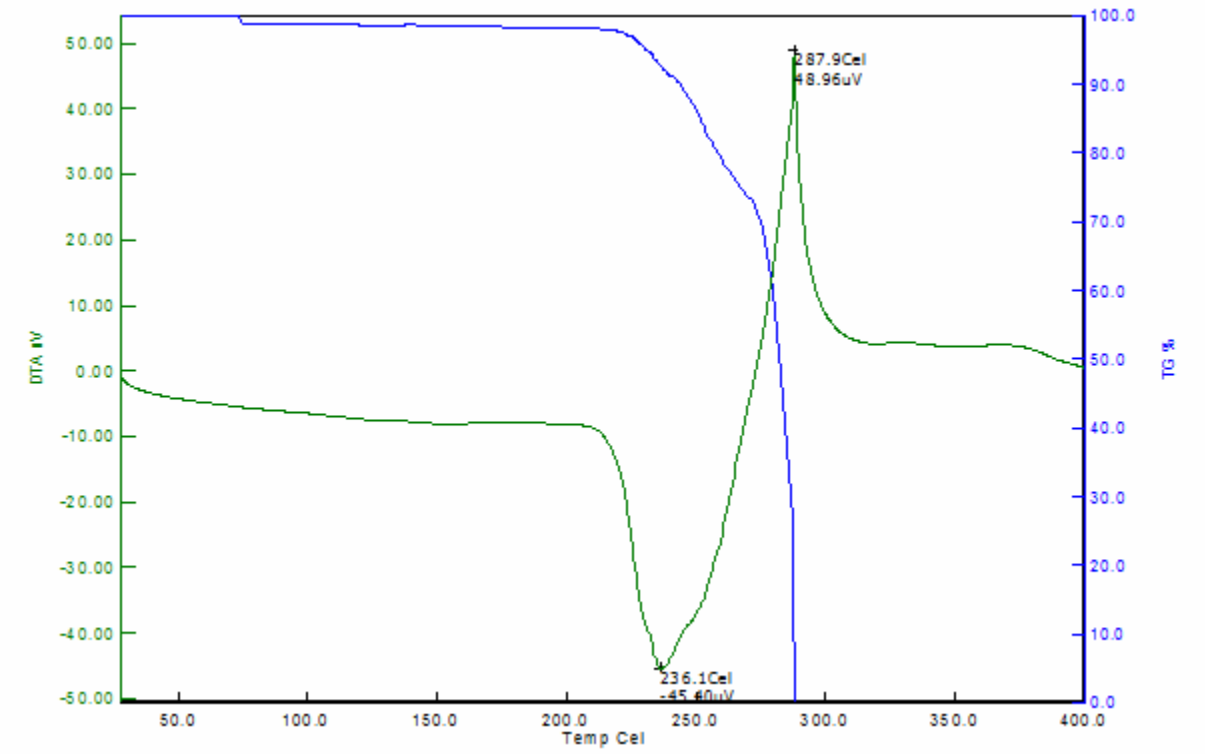

Fig.-5: TGA/DTA spectrum of the grown GSN Crystal

The NLO efficiency of GSN crystal was tested using Kurtz and Perry method. The sample was illuminated usinf Q-switched Nd: YAG laser with the first harmonic output of 1064 nm with a pulse width of 8 ns. The SHG was confirmed by the emission of green light (λ=532 nm). The second harmonic generation signal of 3.83 mJ for GSN crystal was obtained for an input energy of 0.68 J. But the standard KDP crystal gave an SHG signal of 8.8 mJ for the same input energy. Thus it is notices that the SHG efficiency of the grown GSN crystal is 0.43 times than that of KDP.

CONCLUSIONS

Glycine Sodium Nitrate crystal (GSN) has been grown by the conventional slow evaporation method. This slow evaporation technique is a very simple method to grow a good quality crystal. The XRD pattern of the grown crystal confirmed the good crystalline nature of the crystal. The measured relative value of the SHG efficiency of GSN crystal is about 0.43 times than that of KDP.

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