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Growth and Characterization of Pure and Lithium Nitrate Doped Gsn Single Crystals

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ABSTRACT

The work is a thorough study of pure and lithium nitrate doped GSN single crystals. These crystals were meticulously grown through the slow evaporation method, and a series of precise characterization techniques were meticulously applied to unravel their intrinsic qualities. To unveil the structural composition of the crystals, a Powder X-ray Diffraction analysis was meticulously conducted. Moreover, the identification of specific functional groups was facilitated through detailed Fourier Transform Infrared Spectral (FTIR) studies. Additionally, an exploration of the crystals' optical properties was carried out through comprehensive UV-Vis spectral studies, aided in revealing a lower cut off wavelength of 230 nm, shedding light on their NLO efficiency and behavior under various wavelengths of light.

Keywords: *GSN, semi organic crystals, Nonlinear optics, Slow evaporation*

1. Introduction

Crystals have piqued man's curiosity for centuries due to their beauty and scarcity. Crystals were employed for both development and ornamentation during the middle Ages. However, with the introduction of crystallography, all solids with distinct geometrical shapes were classified as crystalline solids. There are three major categories of solids: Crystalline, amorphous, and quasicrystalline [1]. A crystalline state is defined by the orderly arrangement of component molecules or ions into a definite pattern known as a lattice. The arrangement is irregular when the material is amorphous. When crystals form slowly, the atoms or component particles occupy certain locations during the process. These component particles settle down in places where their potential energy is lowest. As a result, an ordered arrangement of component particles emerges, repeating itself in all three directions. When there is long-range organisation in a solid, it is known as a crystalline solid. If the development process is rapid, these component particles do not reach the configuration of minimal energy. This produces long-range order, in which perfect periodicity is maintained at

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far greater distances than lattice periodicity. However, there is still a short-range order in which order exists in small locations.

Amorphous solids are defined by their short-range organisation. Quasicrystals, a third type of solids, are crystals that contain atoms in ordered arrays but whose patterns shift somewhat at regular intervals. Such patterns are referred to as quasi periodic. When heated, some organic crystals change into a state somewhere between solid and liquid [2]. This condition is known as the mesomorphic state or liquid crystal. Crystals can range in size from a fraction of a millimetre to tens of centimetres or even meters. There are three types of crystals: macro, micro, and nano. Macro crystals are visible (bulk single crystals) and range in size from a few millimetres to 10 -3 meters. Micro crystals are crystals that are extremely tiny. Nano crystals are crystals with size of 10-7 m or larger. The variation in crystal forms and sizes is controlled by two factors: the crystal's internal symmetry and the relative growth rate, which changes with the direction of crystal growth [3]. Single crystals have symmetrical periodicity throughout the material, and there are no inner borders. Twinned crystals are formed when two crystals are joined together, whereas multiplex crystals are formed when two or more crystals are attached together. They are often described as being polycrystalline in nature. Crystals have acute melting points, are stiff, and incompressible. Many of the key physical characteristics of crystals are due to their perfect ordering, including ferromagnetism, ferroelectricity, piezoelectricity, and birefringence [4].

Slow evaporation has emerged as a highly effective technique for crystal growth, having facilitated the successful growth of a wide array of compounds utilizing this method. By employing slow evaporation, a single solvent or a combination of two solvents is dissolved, and the resulting solution is left to evaporate gradually. This process can be carried out either under normal atmospheric conditions or within an inert atmosphere. The gradual evaporation method in crystal growth has proven to be particularly advantageous due to its ability to yield high-quality crystals with a high degree of purity. Not only does this technique promote crystal growth efficiency, but it also allows for a controlled and precise formation process, resulting in crystals exhibiting superior structural integrity. Additionally, the slow evaporation process offers researchers a versatile approach to growing crystals with varying properties and characteristics. This method has significantly broadened the scope of crystal growth possibilities, enabling the synthesis of crystals that may have been challenging to produce using other methods. Therefore, slow evaporation stands as a fundamental technique in the realm of crystal growth, offering researchers a reliable and versatile approach to achieving crystalline structures of varying complexities and compositions.

2. Materials and Methods

Growth of pure GSN

Single crystals of glycine sodium nitrate (GSN), a semi-organic nonlinear optical material, have been produced from solution via slow evaporation at room temperature. GSN's solubility has been determined in water. The amount of solute required to get supersaturated solution can be obtained using the formula [9],

$M = [M \times X \times V] \div 1000$

Where, M-Molecular weight of the solute, X-Supersaturated concentration in molar unit, V-Volume of the solution. The aqueous solution was evaporated under slow evaporation at room temperature.

Growth of 1 mole of Lithium Nitrate doped GSN

Single crystals of pure and lithium nitrate doped glycine sodium nitrate were grown from aqueous solution by slow evaporation technique. Glycine and sodium nitrate of high purity were dissolved in water in the ratio 1:1 to get a saturated solution. A Magnetic stirrer was used to obtain a homogeneous solution. The solution was then filtered and covered with a porous cover and kept undisturbed in a dust free environment. The amount of dopant required in grams is obtained using the formula,

$$M' = [M \times V \times P \times X] \div 100$$

where, M'-Molecular Weight of the dopant, V-Volume of the solution, X- Supersaturated concentration in molar unit. The solution is transferred to a beaker and kept in a dust free atmosphere to facilitate growth by slow evaporation at room temperature. A colorless crystal of GSN doped with 1 mole of lithium nitrate is produced using the slow evaporation approach.

Characterizations

X-Ray Diffraction studies

Power XRD patterns of the grown crystals were recorded using an automated X-ray power diffractometer (PANalytical XPERT-PRO MPD). This is a fully computerized X-ray diffractometer which was employed for X-ray diffraction studies. This is a versatile, sensitive and high-resolution X-ray diffractometer. The intensity of the diffracted beam was recorded against 2θin the range 1070° with CuKα radiation. Using the observed 2θ (Bragg angle) and d (interplanar spacing), all the reflection of the powder XRD pattern for pure and impurity added GSN crystal has been indexed.

UV-Vis spectral measurements

In the present study, the UV – Vis – NIR transmission spectra were recorded for the pure and impurity doped Lithium nitrate single crystals of 2 mm thickness. Perkin – Elmer Lambda 35 UV – Visible spectrometer in the range 190 – 1100.

Fourier Transform Infrared analysis

The FTIR spectra of pure and semi organic GSN crystals doped with impurity (0.2,0.4,0.6,0.8 and mole%), have been recorded in the in the range of 400-4000 cm -1 using Perkin Elmer Fourier transform infrared spectrometer (Model: Spectrum RXI) using KBr pellet method. The spectra were used to analyse the presence of different constituents and their bonding properties qualitatively.

3. Results and Discussion

XRD analysis

The diffraction pattern for the pure and doped GSN crystals was analysed using X' Pert Pro – P Analytic in the 2θ range from 10 o – 70 o with Copper (Kα) radiation (λ= 1.5406 Å) operating at a voltage of 40 kV and a current of 30 mA. The obtained XRD patterns are shown in the fig 1a,1b. The lattice parameters reveal the crystal belongs to the monoclinic system. The cell parameters a = 14.41904 Å, b = 5. 00504 Å, c = 9.27421 Å, β = 119.1078 and cell volumeV = 584.7714 Å 3, respectively were found using UNIT CELL software. The cell parameters for $LiNO_3$ doped GSN was found to be a = 14.72713 Å,b = 5.38668 Å, c = 9.08003 Å, β = 118.58167 and cell volume V = 632.5410 Å 3 respectively. The XRD pattern of the doped GSN crystal shows slight variations from the pure form of GSN crystals revealing the inclusion of the dopant into the lattice system [10], also the sharp peaks found in the diffraction pattern indicates the crystalline nature of the material [11].

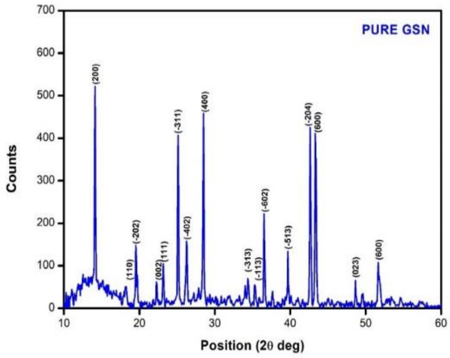

Fig. 2: XRD pattern of pure GSN

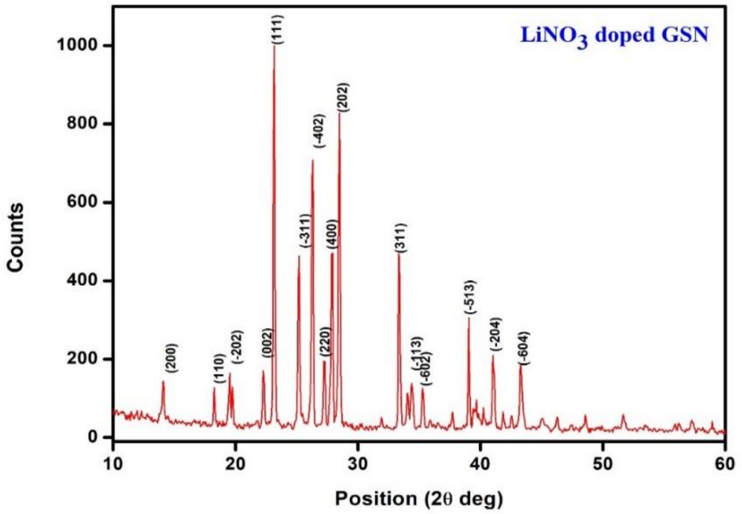

Fig. 3: XRD pattern of $LiNO_3$ doped GSN

UV- Vis Spectral Analysis

In the present work, UV-Vis-NIR spectra were recorded in the wavelength range of 190 nm – 1100 nm for the solutions of pure and Lithium nitrate doped GSN crystals using U-2900 spectrophotometer.

The ratio of absorbance and transmittance is particularly significant in the case of Nonlinear optical crystal applications as higher transmission efficiency of NLO crystals are a necessity [12]. The UV–Vis spectra for both the pure and doped crystals of GSN indicate greater transmittance percentage [13] and lower cut off wavelength of 230 nm, hence indicating greater NLO capability. The transmittance spectra for pure and doped GSN are shown in Figures 4 and 5. The absorbance spectra of pure GSN and lithium doped GSN are shown in figures 6 and 7, respectively.

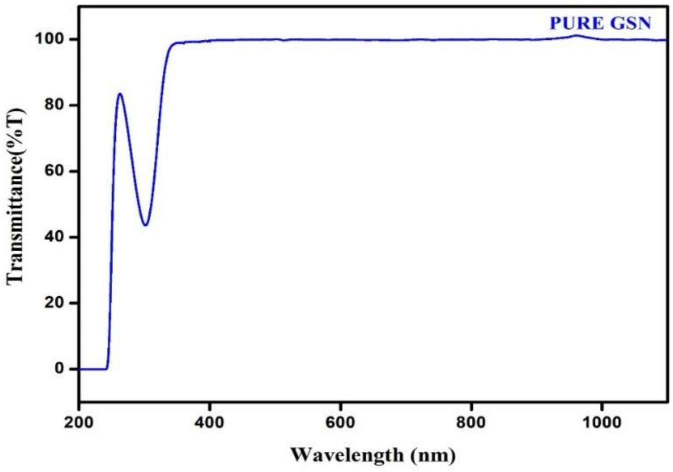

Fig. 4: UV – Vis transmittance spectrum of pure GSN

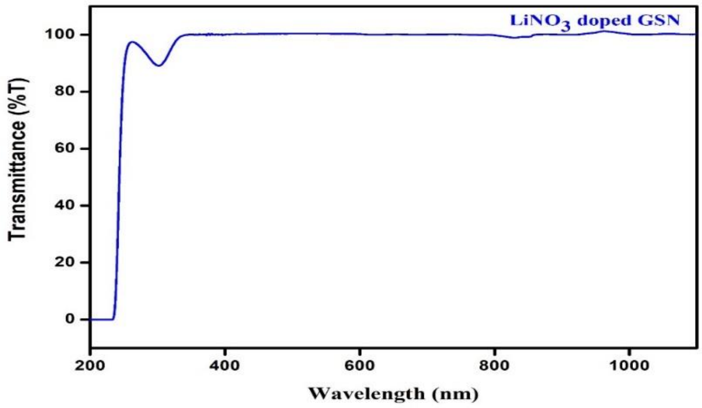

Fig. 5: UV – Vis transmittance spectrum of $LiNO_3$ doped GSN

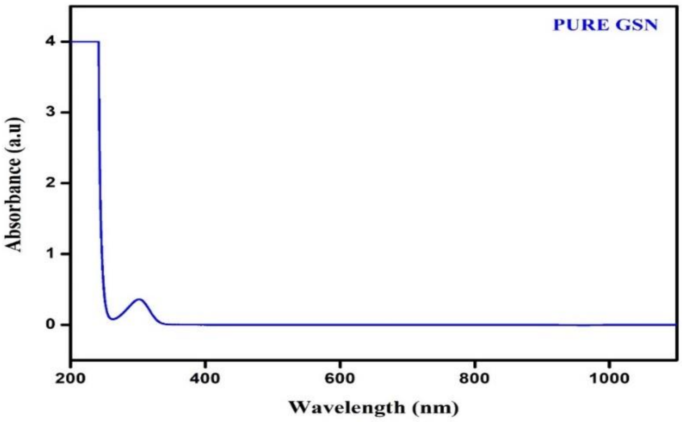

Fig. 6: Absorbance spectrum of pure GSN

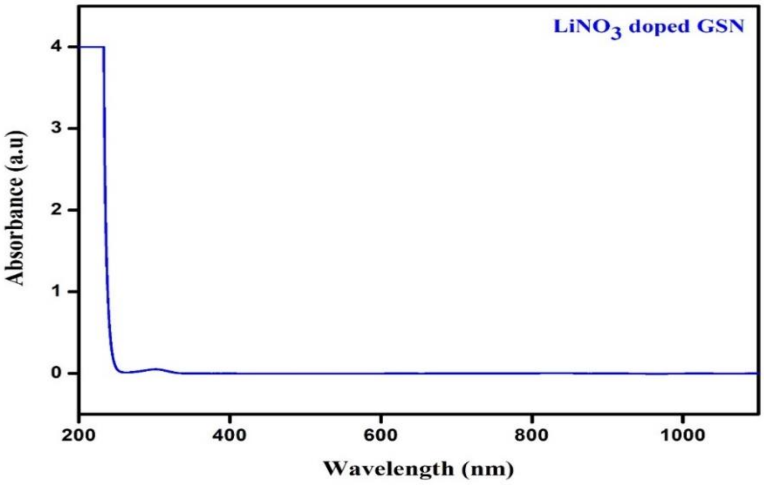

Fig. 7: Absorption spectrum of $LiNO_3$ doped GSN

FTIR Analysis

The peaks at 3257 cm^{-1} and 3260 cm^{-1} correspond to NH_3^+ Asymmetric stretching. CH_2 Asymmetric stretching is observed at the peaks at 2885 cm^{-1} and 2875 cm^{-1} respectively.

NH_3^+ symmetric stretching and NH_3^+ symmetric in plane bending is evident from the peaks at 2403 cm^{-1} and 1505 cm^{-1}. The presence of NO_3^- out of plane bending and NO_3^- in plane bending can be observed by peaks at 819 cm^{-1} and 673 cm^{-1}. Peaks at 1593 cm^{-1} and 505 cm^{-1} indicate the presence of COO^- asymmetric bending and COO^- rocking. The presence of C-N stretching is evident from peaks at 1023 cm^{-1} and 1028 cm^{-1}. Peaks at 2016 and 2019 represent a combination of torsional oscillation and asymmetric bending of NH_3^+. The presence of NH_3^+ Rocking and CH_2 Rocking is proven by the peaks at 1126 cm^{-1} and 913 cm^{-1}[14].

The slight variations in the FTIR peaks of $LiNO_3$ doped GSN, indicates the inclusion of the dopant into the Glycine lattice [15]. The peak allotment of pure and doped samples of Glycine is given in Table 1. The corresponding FTIR graphs are provided in fig 8 and 9 respectively.

Table 1: FTIR spectral analysis of pure and doped Glycine

Wavenumber (cm^{-1})		**Band assignment**
Pure GSN	**$LiNO_3$ doped GSN**	
3257	3260	NH_3^+ Asymmetric stretching
2885	2875	CH_2 Asymmetric stretching
2717	2711	Overtones/combinations
2629	2618	Overtones/combinations
2403	2411	NH_3^+ symmetric stretching
2016	2019	Combination of torsional oscillation and asymmetric bending of NH_3^+
1593	1598	COO^- asymmetric bending
1505	1505	NH_3^+ symmetric in plane bending
1381	1377	NO_3^- asymmetric stretching
1126	1120	NH_3^+ Rocking
1023	1028	C-N stretching
913	907	CH_2 Rocking
819	828	NO_3^- out of plane bending
673	678	NO_3^- in plane bending
505	507	COO^- rocking, ONa^+ stretching

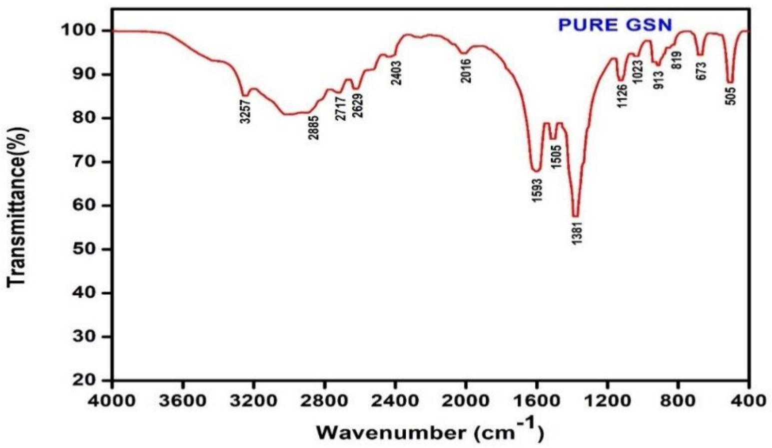

Fig. 8: FTIR spectra of pure GSN

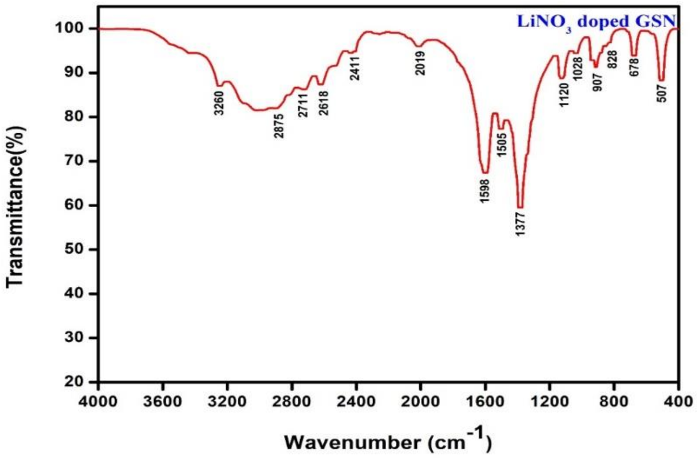

Fig. 9: FTIR spectra of $LiNO_3$ doped GSN

4. Conclusion

Single crystals of LiNO3 doped Glycine Sodium Nitrate crystals were grown employing slow evaporation technique. The XRD patterns of the doped GSN crystal differ somewhat from the pure form of GSN crystals, indicating the presence of the dopant into the lattice system.The sharp peaks found in the diffraction pattern indicates the crystalline nature of the material. The functional groups of grown crystals were confirmed by FTIRstudies. The UV-Vis spectra of GSN pure and doped crystals show a higher transmittance percentage and a lower cut off wavelength of 230 nm, this indicates greater NLO efficiency of these crystals.

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