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Research Article

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Solution growth and studies of undoped and lithium nitrate added glycine sodium nitrate single crystals

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ABSTRACT

Solution growth by slow evaporation method has been employed to grow semi-organic nonlinear optical crystals of pure and lithium nitrate doped glycine sodium nitrate (GSN). The grown crystals were subjected by single crystal and powder X- ray diffraction techniques to identify the crystal structure and diffraction planes. Fourier Transform Infrared (FTIR) spectra were recorded to identify the functional groups of the samples. Ultra Violet (UV)-visible spectral studies for the grown samples were carried out and analyzed. The investigations indicate the inclusion of the dopant into the lattice of GSN and enhancement of optical properties due to the incorporation of the dopant $LiNO_3$ into the lattice of GSN. Second harmonic generation (SHG) efficiency was measured by Kurtz-Perry technique. The obtained results from various studies were discussed.

Key words: semiorganic crystal; growth from solution; NLO; GSN; characterization; XRD; spectroscopy.

INTRODUCTION

Photonic and Optoelectronic technologies need nonlinear optical materials with high Second Harmonic Generation (SHG) efficiency and laser damage threshold [1]. Many nonlinear optical materials used to generate the SHG signal so far have been inorganic bulk crystals like potassium dihydrogen phosphate (KDP), lithium triborate (LBO), β-barium borate (βBO), lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$) etc and they have high SHG efficiency and laser damage threshold [2]. Organic nonlinear optical crystals are more resourceful materials for NLO applications compared to inorganic materials due to their large electro-optic coefficient with low frequency dispersion and high nonlinearity [3]. Due to chiral symmetric properties, complex of amino acid with organic acid is promising materials for NLO applications [4]. Amino acids with inorganic compounds are promising materials for nonlinear optical applications, as the high optical nonlinearity of the purely organic amino acids tend to combine with the favourable mechanical and thermal properties of the inorganic salt. It has been reported that some complexes of amino acids with simple inorganic salts may exhibit ferroelectric properties [5-7]. Some complexes of glycine with $CaCl_2$ [8], $BaCl_2$ [9], H_2SO_4 [10] and $CoBr_2$ [11] form single crystals but none of these are reported to have nonlinear optical property. Single crystals of glycine sodium nitrate(GSN) [12], glycine lithium sulphate [13] and benzoyl glycine [14] showed non-centrosymmetry and their quadratic nonlinear coefficients were examined. Single crystals of GSN were grown by Narayana Bhat [14], J. Thomas Joseph Prakash et.al. [15] and S.Palaniswamy and O.N.Balasundaram [16] and they have reported that SHG efficiency of GSN is almost double that of potassium dihydrogen phosphate (KDP). The present study of doping GSN with $LiNO_3$ has been undertaken to study if there is an improvement in the nonlinear optical and other characteristics.

EXPERIMENTAL SECTION

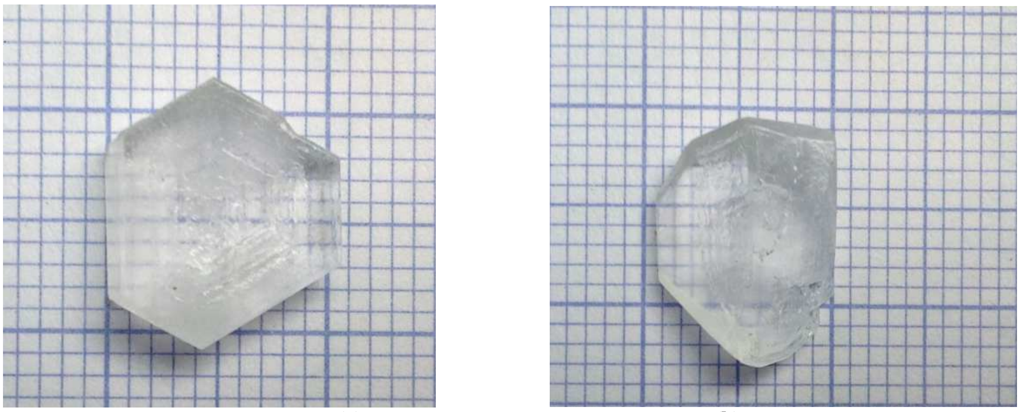
2.1. Crystal Growth

Single crystals of pure and lithium nitrate doped glycine soium nitrate were grown from aqueous solution by slow evaporation technique. Glycine and sodium nitrate of high purity were dissolved in deionised water in the ratio 1:1

to get a saturated solution. Magnetic stirring for an hour was performed to obtain a homogenous solution. The solution was filtered and covered with a porous cover and kept in a dust free environment. Good quality single crystals of glycine sodium nitrate were harvested after four weeks. The synthesis reaction for GSN salt is

$$NH_2CH_2COOH + NaNO_3 \longrightarrow Na\ (NH_2\ CH_2COOH)NO_3$$

The grown crystals were stable, colourless and transparent. Lithium doping was done by adding 1 mole % of lithium nitrate to the solution of GSN. Single crystals doped with lithium nitrate were harvested within four weeks. The photographs of the grown pure and 1 mol% of $LiNO_3$ doped GSN crystals are shown in figure 1(a) and 1(b) respectively.. The grown crystals are transparent and colorless. Morphology of $LiNO_3$ doped GSN crystals changes slightly from that of pure GSN crystal.



(a) (b)

Fig. 1: Photographs of pure and 1M % of $LiNO_3$ added GSN crystals

2.2. Characterization techniques

Powder X- ray diffraction (PXRD) spectrum for both the pure and doped GSN crystals were recorded using Panalytical X'Pert Powder X'Celerator Diffractometer in the 2θ range from 10 degree to 80 degree with CuKα radiation (λ=1.54060 Å). Fourier Transform Infrared (FTIR) spectra were recorded for the samples using Perkin Elmer Fourier Transform Infrared spectrometer by KBr pellet technique. The UV-Visible spectra were recorded in the wavelength range 200 nm to 1100 nm for pure and lithium doped GSN sample using U-2900 spectrophotometer.

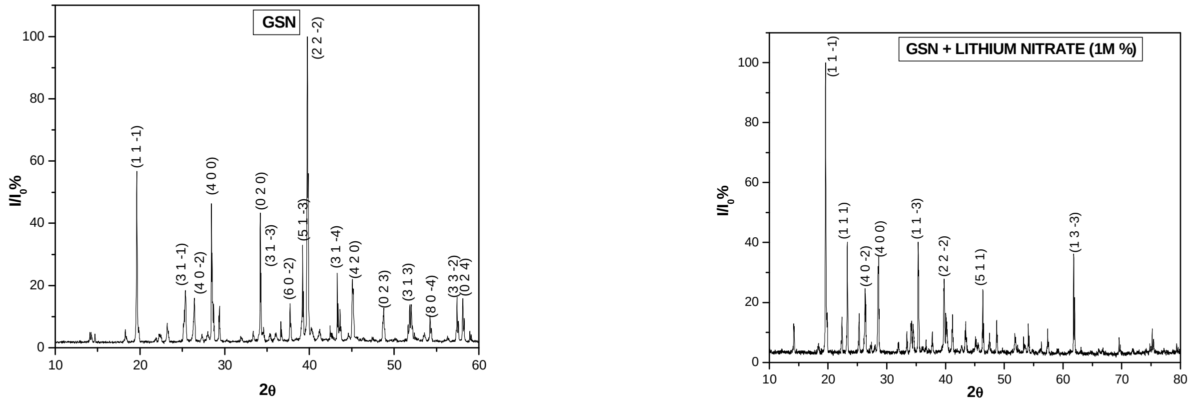
RESULTS AND DISCUSSION

3.1. Powder X-ray Diffraction (PXRD) analysis

The PXRD spectra for the grown crystals are shown in figure 2(a) and 2(b). The sharp and strong peaks confirm the crystalline nature of pure and doped GSN crystals. The diffraction peaks were indexed for the monoclinic system using INDEXING software [17]. The h k l values agree with the experimentally reported structure belonging to the monoclinic system space group Cc and the lattice parameters of pure and lithium nitrate doped GSN crystals were obtained using UNITCELL software and are given in table 1. Addition of dopant produces a small change in unit cell volume. This suggests that the dopant has entered the lattice without distorting it.

Table 1: Crystal data of pure and 1 M % $LiNO_3$ added GSN crystals

Lattice parameters	Pure GSN	$LiNO_3$ doped GSN
a(Å)	14.361	14.318
b(Å)	5.243	5.250
c(Å)	9.123	9.122
V(Å)^3	599.98	598.79
β	119.16°	119.17°



(a) **(b)**

Fig. 2 : Powder XRD pattern of pure and 1 M % $LiNO_3$ added GSN crystals

3.2. FTIR Spectral Analysis

To confirm the presence of glycine in zwitterionic form in GSN and to analyse qualitatively the presence of the functional groups in the grown crystals, the FTIR spectra of pure and 1M % $LiNO_3$ added GSN crystals were recorded between 4000 cm^{-1} and 400 cm^{-1}. Fig. 3(a) and 3(b) represent the FTIR spectra for pure GSN and 1 M % $LiNO_3$ doped GSN crystals. Free glycine, the simplest amino acid exists in neutral zwitterionic phase as NH_3^+ - CH_2 – COO^- in which the amino group exists as ammonium ion (NH_3^+) and the carboxyl group exists as carboxylate ion (COO^-). Amino acids in the form of zwitterions do not show N – H stretching at 3200 cm^{-1} but show a broad band with multiple peaks between 3600 cm^{-1} and 2600 cm^{-1} assigned to asymmetric stretching of NH_3^+ group [18]. In GSN crystal, same mode can be seen from 3237 cm^{-1} to 2277 cm^{-1}. The principal frequencies for the ionic groups in glycine are 1610 cm^{-1}, 694 cm^{-1}607 cm^{-1} and 504 cm^{-1} for the COO^- ion. In GSN crystal, these modes occur at 1621cm^{-1}, 676 cm^{-1}, 588 cm^{-1}, 507cm^{-1}. For the NH_3^+ group, the characteristic frequencies are observed at 1585 cm^{-1}, 1492 cm^{-1}, 1131 cm^{-1}. In GSN, these modes are found at 1500, 1499 cm^{-1}, 1120 cm^{-1}, confirming the existence of glycine zwitterions which facilitates the formation of complexes of glycine. The sharp peaks at 833 cm^{-1} and 1037cm^{-1} are assigned to the stetching vibrations of NO_3. The absorption peaks at 507cm^{-1} may also be attributed to modes implicating the alkaline cation namely $\gamma(ONa^+)$ carboxylate – sodium ion stretching mode [19]. For the doped crystal significant difference could not be observed except for the absence of an asymmetric stretch of NH_3^+ corresponding to the pure GSN frequency of 2883 cm^{-1}. This may be due to the inclusion of dopant in small quantity. The frequency assignment for the various absorption peaks observed in FTIR spectra for both pure GSN and 1 M % $LiNO_3$ doped GSN crystals are tabulated in table 2.

Table 2: Spectral Assignments for pure and 1 M % $LiNO_3$ added GSN crystals

GSN crystal (cm^{-1})	LGSN crystal (cm^{-1})	Assignments
3415	3418	O – H stretch of H_2O
3237	3248	NH_3^+ stretching and CH stretching
3009	3018	
2883		
2723	2723	
2623	2624	
2441	2439	
2277	2276	
2180	2183	N –H vibration
1621	1631	Asymmetric stretching (COO^-)
1500	1502	Symmetric in plane bending(NH_3^+)
1370	1380	Symmetric stretching of NO_3
1120	1118	twisting of NH_3^+
1037	1037	NO_3 stretching
933	934	CH_2 rocking
889	890	symmetric stretching of CCN
833	830	NO_3 asymmetric stretching
769	768	Scissoring (COO^-)
676	675	wagging (COO^-)
587	587	In plane bending (COO^-)
507	508	Rocking (COO^-), stretching(O-Na^+)

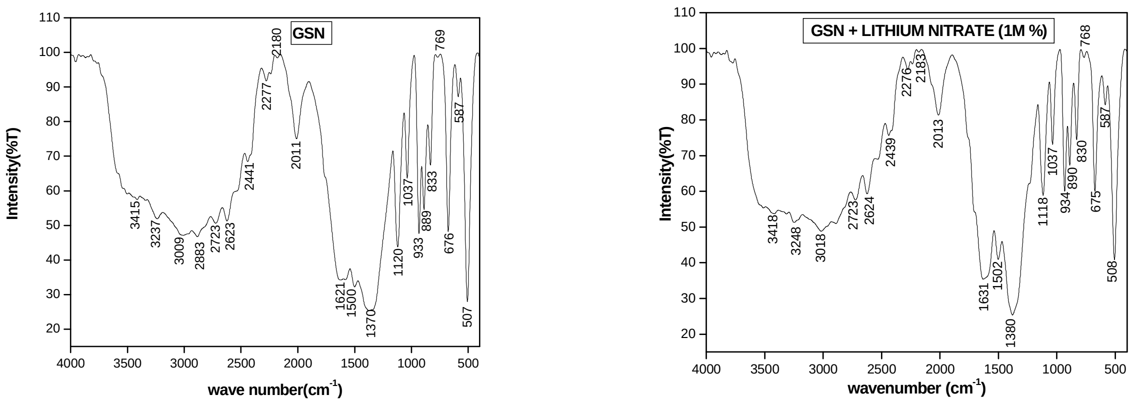


Fig. 3(a) **Fig. 3(b)**

Fig. 3 : FTIR spectra of pure and 1 M % $LiNO_3$ added GSN crystals

3.3. UV – Vis Spectral Studies

The UV – Vis spectra of pure and 1 M % $LiNO_3$ added GSN crystals are recorded in the wavelength range 200 nm to 1100 nm. NLO materials cannot be used for Second Harmonic Generation if they have absorption near the fundamental or second harmonic signal. From the spectrum of pure and 1 M % $LiNO_3$ added GSN crystals (Fig. 4(a) and 4(b)), it is inferred that both of them have the potential to be used for SHG in the case of Nd-YAG laser (1064 nm) to emit a second harmonic signal in the green region (532 nm). The pure and 1 M % $LiNO_3$ doped GSN crystals have good transmittance of 80 % and 84% respectievely, (i.e) there is a small increase of transmittance by 4% due to doping. The transparent window of pure GSN crystal is from 360 nm to 1100 nm. It can be concluded that lithium dopant improves the optical quality of GSN crystal. The lower cut-off frequency for pure and 1 M % $LiNO_3$ doped GSN crystal is found to be 321 nm and 324 nm respectievely.

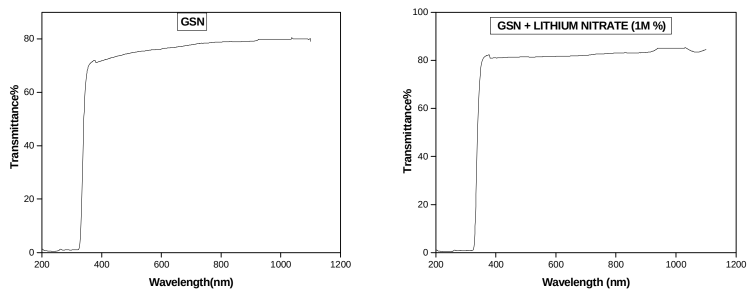


Fig. 4(a) **Fig. 4(b)**

Fig. 4 : UV-Vis spectra of pure and 1 M % $LiNO_3$ doped GSN crystals

CONCLUSION

Good quality single crystals of pure and 1 M % $LiNO_3$ GSN doped crystals were grown by slow evaporation technique. The powder XRD studies confirm the crystallinity of the grown crystals. The slightly different values obtained for the unit cell volume reveals that the dopant does not distort the basic crystal structure of GSN crystal. Doping has increased the transparency in the visible range. The crystals grown in the present study can be considered as promising NLO crystals as they have lower cut-off wavelengths between 200 nm and 400 nm i.e., 321 nm and 324 nm for pure and 1 M % $LiNO_3$ added GSN crystals respectively.

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