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Physical and chemical properties of glycine sodium nitrate Crystals doped with potassium nitrate

D.Dooslin Mary[1*], Gerardin Jayam[1] and M.Johnson[2], P.Selvarajan[3]

[1]*Department of Physics, Holy Cross College, Nagercoil-629004, Tamil Nadu, India.*
[2]*Department of Plant biology and Plant biotechnology, St.Xavier's College, Palayamkottai, Tamilnadu, India.*
[3]*Department of Physics, Adtianar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India.*
Corresponding author

ABSTRACT-- Solution growth by slow evaporation method has been employed to grow semi-organic nonlinear optical crystals of pure and potassium nitrate (KNO_3) doped glycine sodium nitrate (GSN). The phase of the grown crystals was identified using single crystal X-ray analysis. The grown crystals were subjected to powder X-ray diffraction technique to identify the crystal structure and diffraction planes. The incorporation of the dopant into the host crystal was confirmed using Energy Dispersive X-ray (EDX) analysis. Fourier Transform Infrared (FTIR) spectra were recorded to identify the functional groups of the samples. Microhardness study was done to estimate the mechanical strength of the grown crystals. Ultraviolet-visible spectra were recorded for the grown samples and analyzed. The investigations indicate the enhancement of optical properties due to the incorporation of the dopant (KNO_3) into the lattice of GSN crystals. Thermal stability of the grown crystals was studied using TG\DTA and it is observed that doping increases the thermal stability. Second harmonic generation (SHG) efficiency was measured by Kurtz-Perry technique. The obtained results from various studies are discussed.

Keywords: semiorganic crystal; growth from solution; NLO; characterization; XRD; EDX; FTIR; microhardness; TG/DTA; SHG

1. INTRODUCTION

Nowadays the quest for NLO materials is escalating due to their potential for application in opto-electronic and laser technologies, laser communication and data storage devices [1]. Some organic compounds surpass the inorganic compounds in their NLO response [2-4]. Most of the amino acids have good optical transparency and high SHG efficiency, a desirable property and many such crystals from the amino acid family have been reported [5-9]. Combining the amino acids with simple inorganic salts tend to enhance SHG efficiency. Large number of semiorganic crystals of alanine, arginine, histidine etc with inorganic compounds have been reported to have NLO responses with good thermal and mechanical stabilities [4, 6-7,10].

The recent focus is on the semiorganic compound, glycine sodium nitrate (GSN). It has been reported that GSN crystal has SHG efficiency greater than KDP, the popular inorganic NLO crystal in use [11]. Doping alters the mechanical, electrical and optical properties as well as the surface morphology depending upon the host material and dopants [12]. Hence the present study is devoted to the growth and characterization of both pure GSN and potassium nitrate doped GSN single crystals.

2. EXPERIMENTAL DETAIL

Single crystals of pure and doped glycine sodium nitrate were grown from aqueous solution by slow evaporation technique. Glycine (E-Merck) and sodium nitrate (E-Merck) were dissolved in de-ionized water in the ratio 1:1 to get a saturated solution. Magnetic stirring for an hour was used to obtain a homogeneous 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 is

$$NH_2CH_2COOH + NaNO_3 \longrightarrow Na\,(NH_2CH_2COOH)\,NO_3$$

The grown crystals were stable, colorless and transparent. Doping of GSN crystals was done by adding 1 mole % of potassium nitrate to the solution of GSN. Single crystals of GSN doped with potassium nitrate were harvested within three weeks. The photographs of the grown pure and 1 mol% KNO_3 doped GSN crystals are shown in figure 1(a) and 1(b) respectively. Morphology of KNO_3 doped GSN crystal does not change appreciably from that of pure GSN crystal.

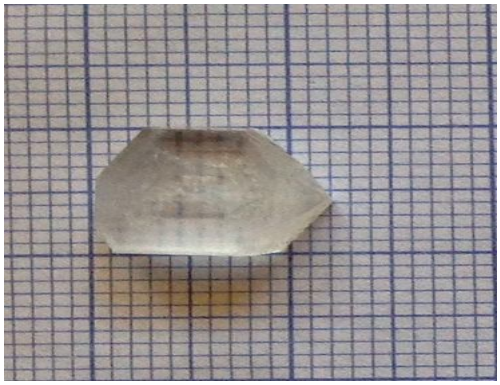

Fig. 1(a) Pure GSN crystal

Fig. 1(b) KNO_3 doped GSN crystal

3. Results and discussion

3.1 Single crystal X-ray analysis

Single crystal X-ray analysis was carried out using BRUKER 4-CIRCLE CCD with Mo K-alpha with graphite monochromater operated at 50 kV, 30 mA. Single crystal X-ray analysis reveals that pure and 1 M% of KNO_3 doped GSN crystals crystallize in the monoclinic system with space group Cc. The unit cell parameters were found to be a=14.39 Å, b=5.29 Å, c=9.11 Å, α= 90.0°, β= 118.99°, γ= 90.0° and cell volume V=607Å^3 for pure GSN and a=14.17 Å, b=5.30 Å, c=9.12 Å, α= 90.0°, β= 118.98°, γ= 90.0° and cell volume V=599 Å^3 for 1 M% KNO_3 doped GSN crystal. This is in close agreement with the data provided by Krishnakumar et al. [13].

3.2 Powder X- ray diffraction analysis

Powder X- ray diffraction (PXRD) spectrum for both the pure and doped GSN crystals were recorded using XPERT-PRO diffractometer in the 2θ range 10 degree to 70 degree with CuK_α radiations (λ=1.54060 Å). The PXRD spectra for the grown crystals are shown in figure 2(a) and 2(b). The sharp peaks indicate the crystallinity of the grown crystals. A slight change is observed between the 2θ values in the spectra of pure and doped GSN samples. The spectra were indexed for monoclinic system using INDEXING software package. The unit cell parameters of the pure and doped GSN were found from the indexed spectra using UNITCELL software. The (h k l) values agree with the reported values of cell parameters for pure GSN crystal [13]. The lattice parameters of pure and doped GSN crystals obtained using UNITCELL SOFTWARE package are given in table 1. The addition of dopants produces a small change in the lattice parameters. This suggests that the dopant has entered the GSN lattice without distorting it.

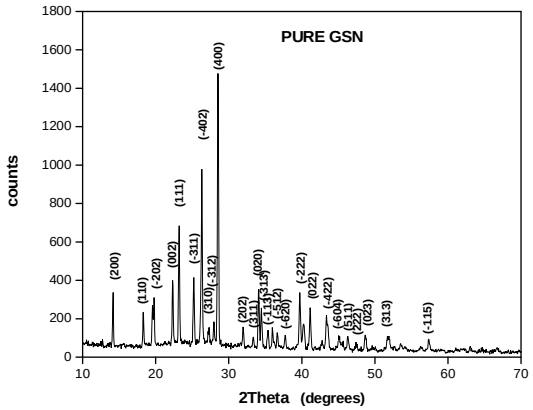

Fig.2 (a)

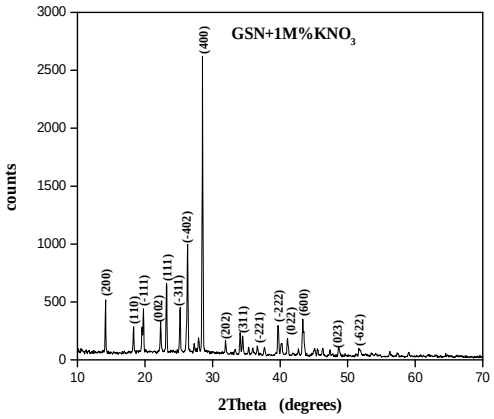

Fig.2 (b), Fig. 2: Powder XRD patterns of pure and 1 M% KNO_3 doped GSN crystals

TABLE 1: LATTICE PARAMETER VALUES OBTAINED FROM POWDER XRD STUDIES FOR PURE AND POTASSIUM NITRATE DOPED GLYCINE SODIUM NITRATE DOPED CRYSTALS

SAMPLE	LATTICE PARAMETERS
1)Pure glycine sodium nitrate crystal	a = 14.336 Å , b = 5.2279 Å , c = 9.1704 Å □= 90°, β = 119.0462°, □= 90° , V = 600.8517 Å^3
2) Potassium nitrate doped GSN crystal	a = 14.334 Å , b = 5.2613 Å , c = 9.1379 Å □= 90°, □= 90° β = 119.0743° , V = 602.3029 Å^3

3.3. Energy Dispersive X-ray (EDX) analysis

Energy dispersive X-ray (EDX) spectroscopy is used for finding elemental composition in the samples. When the sample is bombarded by the Scanning Electron Microscope's (SEM) electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state and an X-ray is emitted to balance the energy difference between the two electrons states. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample. The recorded EDX spectra for pure and potassium nitrate doped GSN crystals are shown in the figure 3. The EDX spectra clearly indicate the presence of the elements such as carbon, oxygen, nitrogen, potassium and sodium in the samples. The EDX spectrum of the doped crystal confirms the entry of K^+ ions into the GSN crystal.

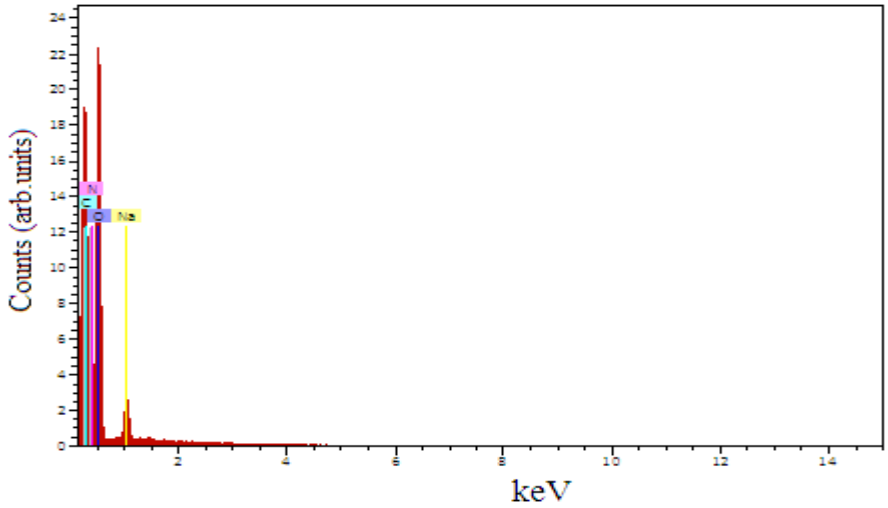

Fig. 3 (a)

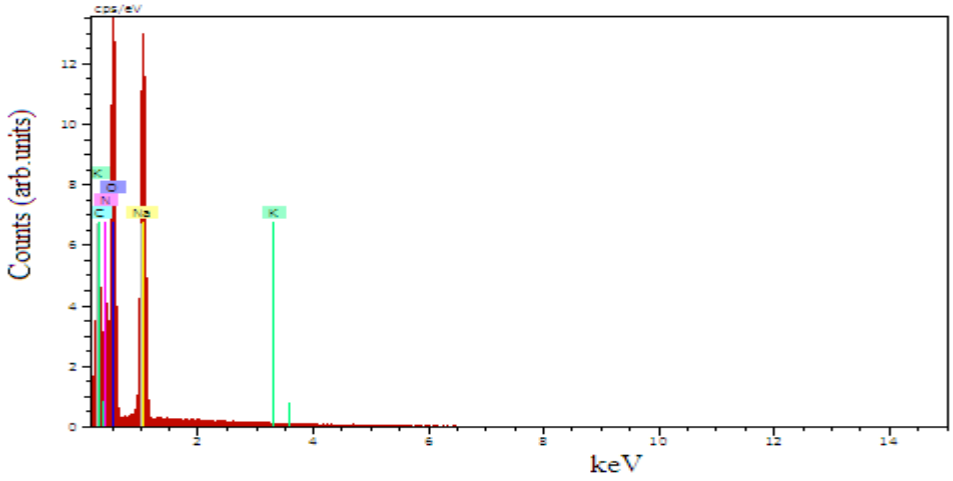

Fig. 3 (b), Fig. 3: EDX spectra of pure and 1 M% KNO3 doped GSN crystals

3.4 Fourier Transform Infrared (FTIR) analysis

In order to analyze the presence of functional groups, FTIR spectra were recorded in the range of 400cm^{-1} to 4000cm^{-1} using a Perkin Elmer FTIR spectrometer by KBr pellet technique. To confirm the presence of glycine in zwitterionic form in GSN and to analyze qualitatively the presence of the functional groups in the grown crystals, the FTIR spectra of pure and 1 M% KNO_3 doped glycine sodium nitrate crystals were recorded. The FTIR spectra of pure and 1 M% KNO_3 doped GSN are shown in figures 4(a) and 4(b). 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 [14]. In GSN, the same mode can be seen from 3237cm^{-1} to 2277cm^{-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 these modes occur at 1621 cm^{-1}, 676 cm^{-1}, 587 cm^{-1}, 507 cm^{-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 1580 cm^{-1}, 1500 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 1037 cm^{-1} are assigned to the stretching vibrations of NO_3. The absorption peaks at 507 cm^{-1} may also be attributed to modes implicating the alkaline cation namely (ONa^+) carboxylate-sodium ion stretching mode [15]. The frequency assignments for the various absorption peaks observed in FTIR is tabulated in table 2. For the doped crystal of GSN, some differences could be observed and this indicates the incorporation of dopant into the host GSN crystal.

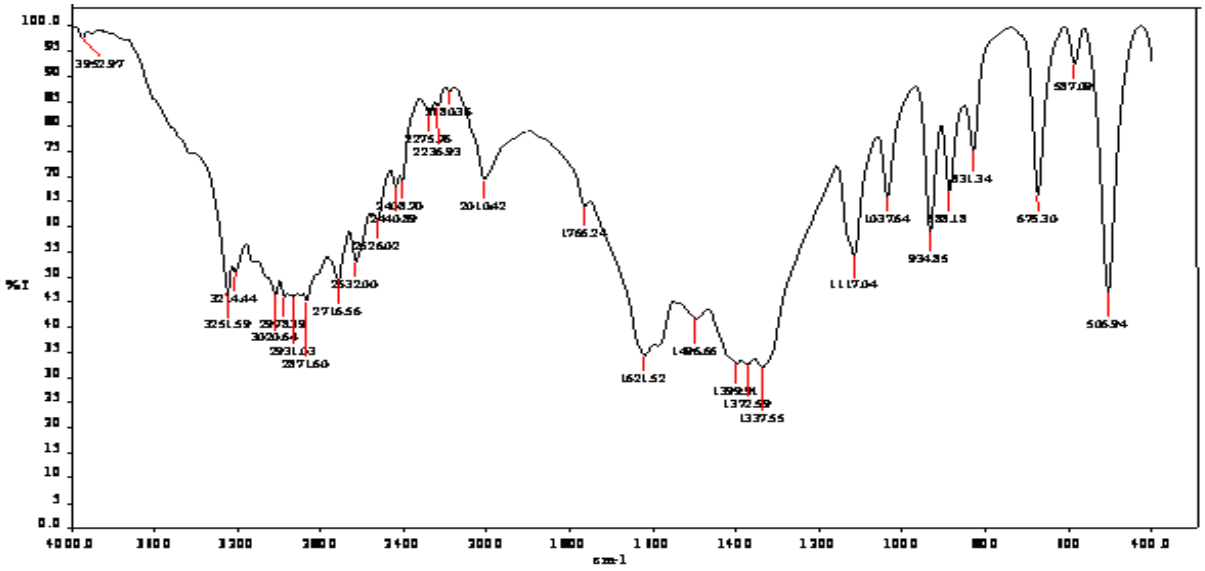

Fig.4 (a)

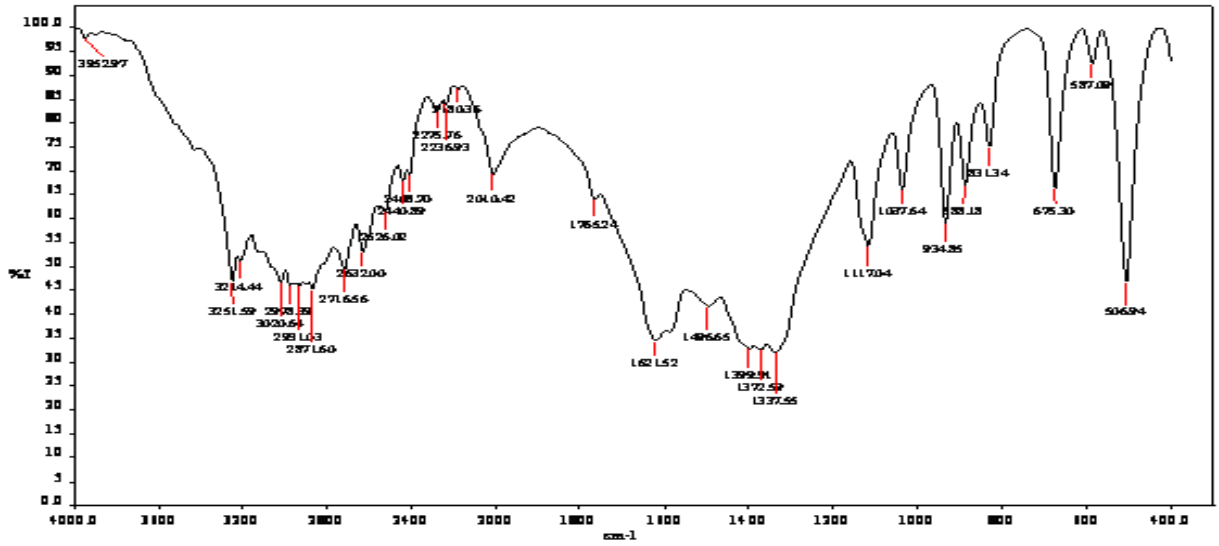

Fig.4 (b), Fig. 4: FTIR spectra of pure and 1 M% KNO3 doped GSN crystals

TABLE 2: FTIR BAND ASSIGNMENTS FOR THE GROWN CRYSTALS OF PURE AND POTASSIUM NITRATE DOPED GSN

WAVE NUMBER (CM^{-1})		BAND ASSIGNMENTS
PURE GSN	1 M% KNO_3 DOPED GSN	
3415	3422	N –H STRETCHING
3237	3246	NH_3^+ ASYMMETRIC STRETCHING
2883	-	NH_3^+ ASYMMETRIC STRETCHING
2723	2722	OVERTONES
2623	2627	OVERTONES
2441	2435	NH_3^+ SYMMETRIC STRETCHING
2277	2233	N –H STRETCHING
2011	2015	NH_3^+ ASYMMETRIC BENDING
1621	1620	COO^- ASYMMETRIC STRETCHING
1580	1597	NH_3^+ ASYMMETRIC BENDING
1500	1508	NH_3^+ SYMMETRIC IN PLANE BENDING
1370	1383	NO_3 SYMMETRIC STRETCHING
1120	1116	NH_3^+ ASYMMETRIC TWISTING
1037	1036	NO_3 STRETCHING
933	935	CH_2 ROCKING
889	891	C-C SYMMETRIC STRETCHING
833	831	NO_3 ASYMMETRIC STRETCHING
769	768	COO^- SCISSORING
676	676	COO^- WAGGING
587	587	COO^- IN PLANE BENDING
507	508	COO^- ROCKING, ONA^+ STRETCHING

3.5 Microhardness

The microhardness measurement was carried out on the pure and KNO_3 doped GSN crystals using Shimadzu HMV-2T Vickers microhardness tester. The load P was varied from 25 g to 100 g and the time of indentation was kept constant as 10 s for all trials. The diagonal lengths of indentation (d) were measured in mm for various applied load (P) in g. The Vickers hardness number H_v was calculated using the relation [16]

$$H_v\ (kg/mm^2) = 1.8544\ P/\ d^2$$

The variation of H_v with applied load P is shown in figure 5(a). H_v is found to increase with load revealing the presence of reverse indentation size effects. The Meyer's index n was calculated from the plot between log P versus log d as shown in figure 5(b). According to Onistch hard materials have n between 1 and 1.6, soft materials have n greater than 1.6. The value of n calculated using the least-square fitting method was found to be respectively 5.3034 and 3.5546 for pure and doped GSN crystals showing that both of them belong to the soft material category [17].

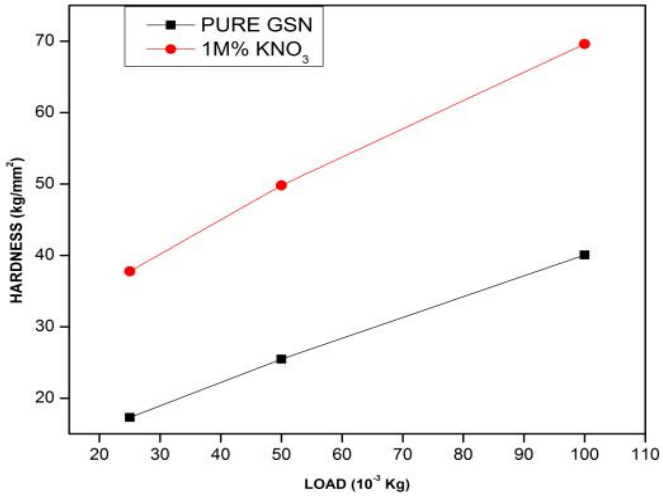

Fig.5 (a)

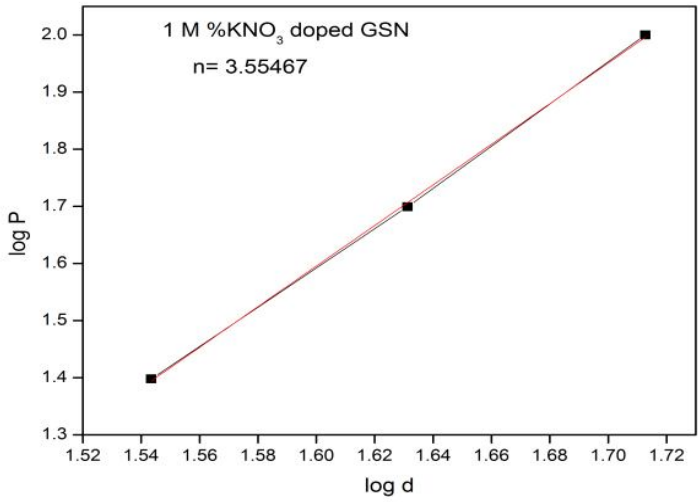

Fig.5 (b), Fig. 5: Plots of (a) hardness number versus load and (b) log P versus log d for the samples

3.6 SHG measurement

The Kurtz and Perry technique was used to investigate the efficiency of second harmonic generation (SHG) [18]. A high intensity Nd:YAG laser with fundamental radiation of 1064 nm beam energy 14.9 ms/pulse was used as the optical source. Powdered samples were packed into microcapillary tubes and placed in the path of the laser beam one by one. KDP was used as the reference with an output of 84 mV. Recorded values of output are 114 mV for pure GSN and 116 mV for doped GSN. Thus, the SHG efficiency of pure GSN is 1.36 times and doped GSN is 1.38 times that of KDP.

3.7 Thermal analysis

In order to study the thermal stability of pure and 1 M% KNO3 doped GSN crystals simultaneous TG\ DTA thermograms were recorded using Thermal analyzer SDTQ600 at a heating rate of 10 ^{o}C/min in nitrogen atmosphere for the temperature range of 25 ^{o}C to 1000 ^{o}C. The TG\DTA curves of pure and doped GSN are shown in figures 6(a) and 6(b). The TG curve of pure GSN has thermal stability upto 212 ^{o}C. The absence of weight loss around 100 ^{o}C indicates the absence of absorbed water or water of crystallization in the molecular structure of GSN. But as the crystal is heated from 25 ^{o}C to 1000 ^{o}C, it decomposes in four different stages accompanied by loss of weight. This is in close agreement with the already reported thermal behavior of GSN [19]. From 212 ^{o}C to 242 ^{o}C, there is a rapid and large weight loss (36%). Glycine can sublime without complete decomposition [20]. Therefore the 36% weight loss may be attributed to the sublimation and decomposition of glycine with the release of NH_3 and CO molecules. From 242 ^{o}C to 368 ^{o}C, there is a gradual weight loss of 21.5%.

The DTA shows an exothermic decomposition signal which marks the combustion of carbon from the organic part of the crystal. An additional weight loss (13%) occurs from 368 °C to 622 °C. The presence of an exotherm in the DTA curve for this temperature range corresponds to the decomposition of the inorganic part namely $NaNO_3$. At elevated temperatures the decomposition process continues until getting 19.36% residue which is due to the existence of the inorganic part as an oxide of sodium.

The DTA thermogram of 1 M% KNO_3 doped GSN has thermal stability upto 220 °C, which is nearly 8 °C higher than pure GSN. There is a rapid mass loss of 58% upto 337.9 °C as it decomposes with the liberation of NH_3, CH_4 and H_2O. Beyond 337.9 °C the loss of mass is gradual leaving 11.69% residue due to the inorganic part. The changes in the peak decomposition temperature and thermal stability may be attributed to the influence of different ionic radii of the dopants on the NO_3 ion of $NaNO_3$ [21].

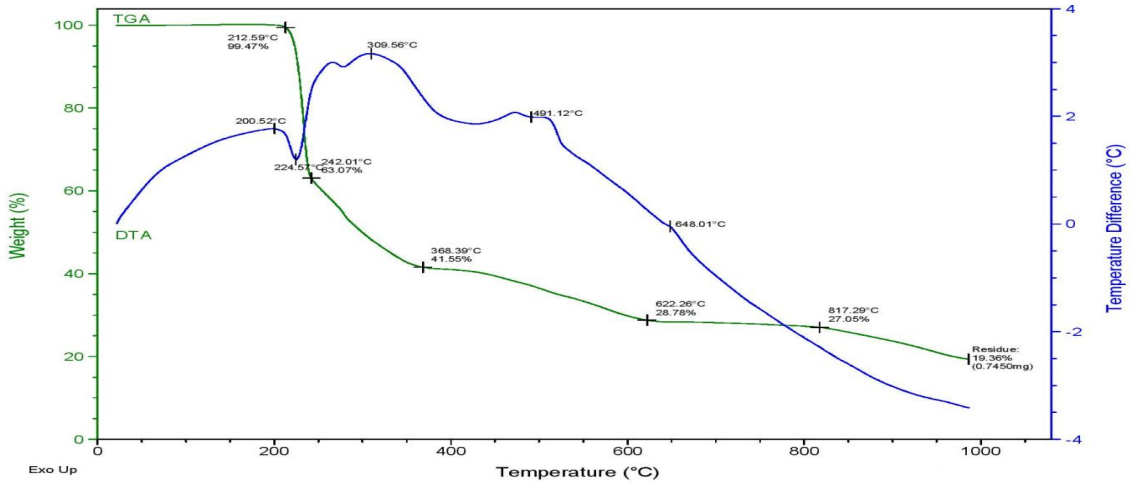

Fig.6 (a)

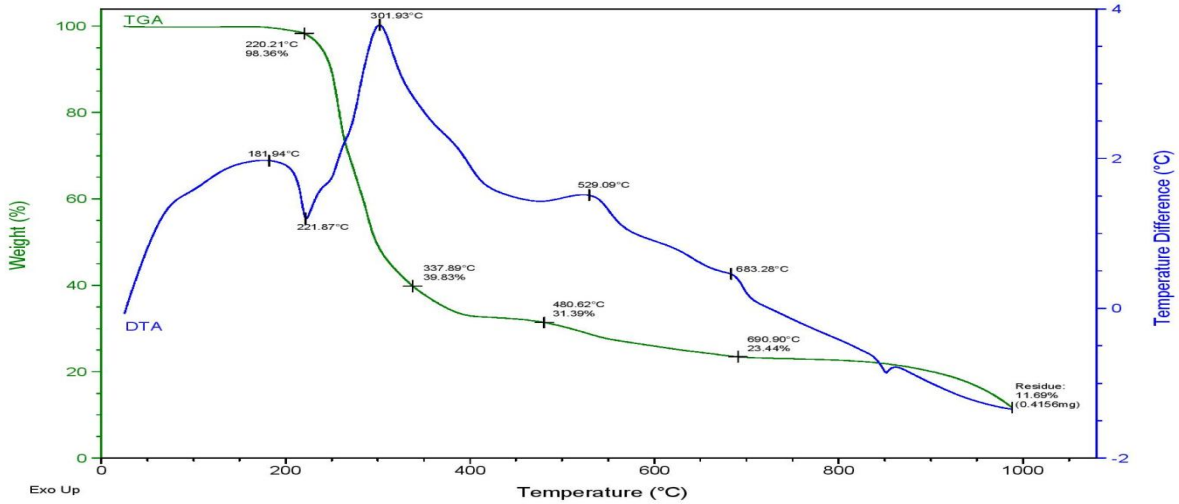

Fig.6 (a), Fig. 6: TG\DTA thermal curves of (a) pure and (b) potassium nitrate doped GSN crystals

3.8 U-visible spectral studies

The UV-vis-NIR absorption spectra were recorded in the wavelength range 200 nm to 1100 nm for pure and doped GSN using U- 2900 spectrophotometer. Figure 7(a) and 7(b) show the absorption spectra recorded for pure and doped GSN crystals. The low absorbance in the UV-vis-NIR regions predicts the probable use of these crystals in NLO applications. The UV cut-off wavelength of pure GSN is 329 nm. Doping with KNO_3 has changed this to 336 nm, thereby increasing the range of wavelength application by 7 nm.

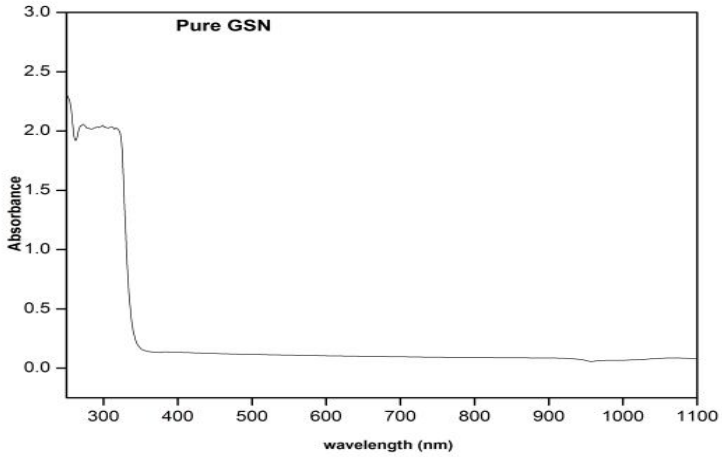

Fig.7(a)

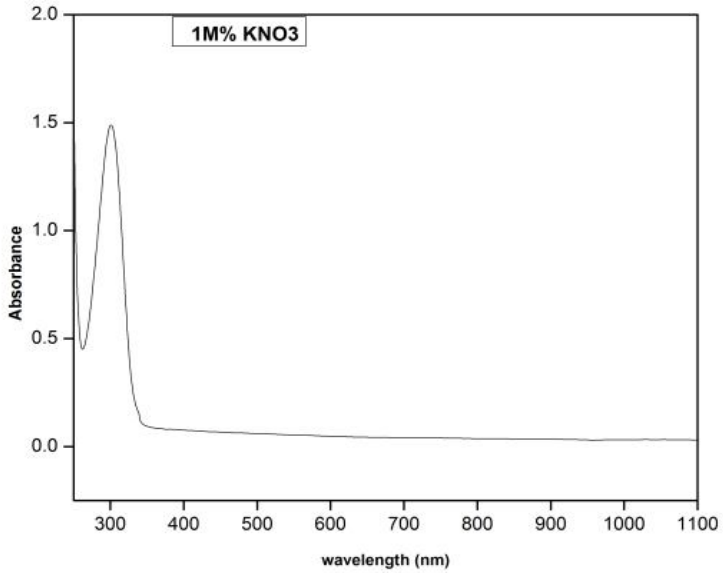

Fig.7 (b), Fig. 5: UV-visible-NIR spectra of pure and doped GSN crystals

4. CONCLUSION

Good quality single crystals of pure and potassium nitrate doped glycine sodium nitrate crystals were grown by slow evaporation technique. Single crystal data confirms that pure and doped GSN crystals crystallize in monoclinic system. The powder XRD studies confirm the crystallinity of the grown crystals. The EDX analysis confirms the formation of GSN and the entry of K^+ ions into the GSN crystal. The slightly different values obtained for the lattice parameters reveal that the dopant does not distort the basic crystal structure of GSN crystal. Doping has increased the transparency in the visible range. The FTIR spectra confirm the zwitterionic phase of glycine in both pure and doped crystals. The microhardness study reveals that both the crystals belong to soft category. The TG\DTA thermograms reveal a thermal stability upto 212 ^oC for pure GSN and 220 ^oC for doped GSN. The SHG measurements prove that the values of SHG efficiency of the pure and doped crystals are nearly 1.4 times that of KDP crystals. 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., 329 nm and 336 nm for pure and 1 M % KNO_3 added GSN crystals respectively.

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