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Growth and characterization of nonlinear optical semi organic crystal: glycine sodium nitrate (GSN)

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Abstract
A Semi organic non-linear optical single crystal of glycine sodium nitrate has been grown from aqueous solution by unidirectional crystal growth method. The phase of the grown crystal was identified using single crystal X-ray analysis. The functional groups present in the crystal were identified using FTIR analysis. Optical absorption studies have confirmed that the grown crystal possess less absorption in the entire visible region. A stable broad peak in the violet region was observed in the emission spectrum of the grown crystal was studied and the results are discussed in detail.

Keywords: Semi, spectrum, absorption, crystal, discussed

1. Introduction
Glycine is an organic compound is the simplest amino acids which exists in three phases α, β, γ [Jannatul Nayeemv *et al.* (2003)]. Glycine can be readily combined with variety of acids, organic and inorganic compo to produce a host of materials with interesting properties (Andriyevsky *et al.* (2007); Koralewiski *et al.* (2003)]. Glycine has been combined with sodium nitrate [Narayan Bhat *et al.* (2002)], silver nitrate (Rao *et al.* (1972)] to produce interesting nonlinear optical compounds. Also recent work in impact of additives with glycine such as sodium nitrate and barium nitrate [Mahendra *et al.* (2011)], barium nitrate and calcium nitrate [Mahendra *et al.* (2011)], sodium nitrate and potassium nitrate [Mahendra *et al.* (2012)] to produce interesting nonlinear optical compounds.
In these semi-organic hybrids the weak forces of organic solids are replaced by stronger ionic forces forming a complete new class of semi-organic materials suitable for electronic industries. The presence of donor NH_2 group, acceptor COOH group and due to intra molecular charge transfer, many naturally occurring amino acids themselves exhibit NLO behavior [Aggarwal *et al.* (2003); Razzetti *et al.* (2002)]. In the present investigation single crystal of glycinesodiumm nitrate (GSN) were grown by slow evaporation method. The grown crystals were characterized by, powder X-ray diffraction, FTIR, UV-vis NIR, SHG, Microhardness, dielectric, photoconductivity studies.

2 Experimental Methods
2.1 Synthesis of GSN
Commercially available AR grade (E-merk, purity > 98.0%) chemicals were used as the starting materials. The synthesis component of glycine sodium nitrate (GSN) was carried out by carefully using glycine and sodium nitrate in molar ratio 1:1 using double distilled water as a solvent. The solution was stirred well using magnetic stirrer to form a clear solution. GSN was synthesized according to the following chemical reaction.

NH_2CH_2COOH + Na (NO_3) → NH_2CH_2COOH [Na (NO_3)]
Glycine + Barium nitrate → Glycine sodium nitrate

3. Growth of GSN crystal
The saturated solution was taken in a beaker and the solvent evaporation technique was employed to grow single crystals of GSN. Since glycine has coordinating capacity to form different phases of metal glycine complexes. The mixtures of reactants had to be stirred to avoid co-precipitation of multiple phases. Hence, the solution was then filtered and allowed to evaporate at room temperature. Optical good quality triangle shaped crystals of GSN were harvested in a span of 10–20 days with dimension 8 x 7 x 3 mm^3. The photographs of the as grown crystals of GSN are shown in Figure1.1.

Fig 1: Photograph of as grown crystals of GSN

4 Results and Discussions
4.1 Powder X-ray diffraction analysis of GSN Crystal
Powder sample glycine barium nitrate was subjected to powder X-ray diffraction studies with CuKα (λ=1.5406 Å) radiation. The powdered sample of GSN was scanned in the range 10-80° at a scan rate of 1° per minute. In the powder XRD pattern well defined Bragg's peaks are observed which reveals that the grown crystal has highly crystalline nature. The recorded indexed powder XRD pattern of the grown glycine sodium nitrate is shown in Figure 1.2. The (hkl) values are indexed for corresponding intensity value using INDX software.

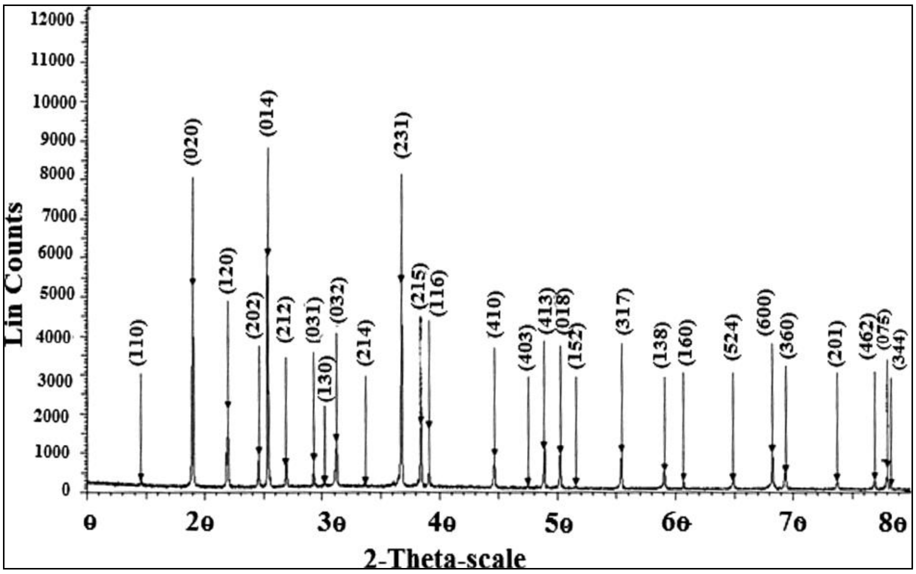

Fig 2: Powder XRD pattern of GSN

4.2 FTIR spectral studies of GSN crystal

In order to identify the presence of functional groups and chemical composition, the FTIR spectrum was taken using BRUKER IFS 66v spectrometer by KBr pellet techniques. Figure 1.3shows FTIR spectrum of the grown GSN crystal. The characteristic absorption peaks have been observed in the range 450–4000 cm^{-1}. Free glycine exists as a zwitter ion in which the carboxyl group is present as carboxylate ions and amino group exists as ammonium ions. The absorptions due to carboxylate group of free glycine are observed at 512.41 cm^{-1} and 726.91 cm^{-1} respectively. The wavenumber corresponding assignments are given in the Table 1.1

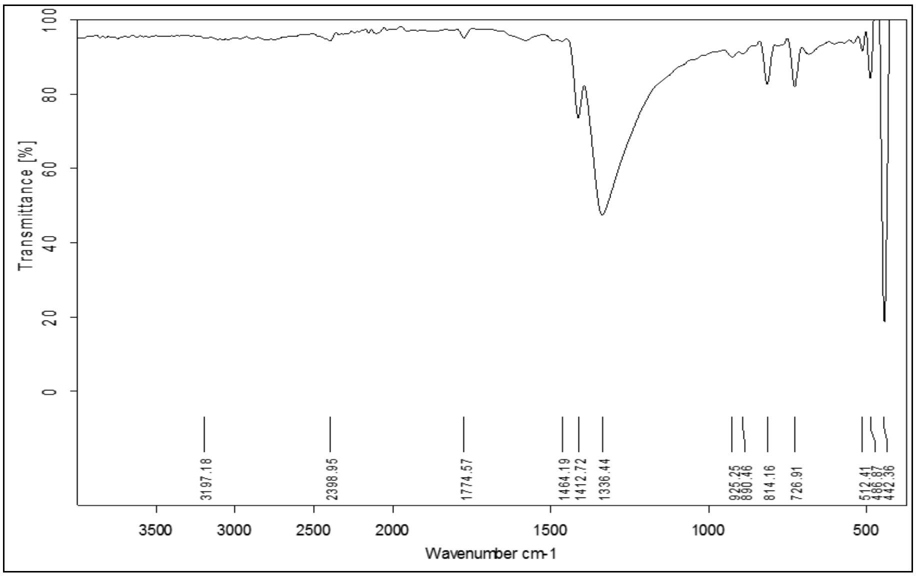

Fig 3: FTIR spectrum of the grown GSN Crystal

Table 1: Wavenumber assignment of GSN crystal

Wave number cm^{-1}	Assignment
512.41	COO^- rocking
726.91	COO deformation
925.25	CH_2 rocking
814.16	CCN symmetric stretching
1336.44	CH_2 wagging
1412.72	CH_2 scissor
1464.19	NH_2 deformation
1774.57	Amino acid bend
2398.95	Amino acid bend
3197.18	CH_2 asymmetric stretching

4.3 UV–visible spectrum analysis of GSN crystal

The selective electronic transmission spectrum of GSN crystal was recorded in the range 100–1000 nm. Optically polished single crystal of thickness 3 mm was used for this study. The recorded spectrum gives limited introduction about the structure of the molecule, because the absorption of UV and visible light involves promotion of the electron in the σ and π orbital from ground state to higher energy state. The transmission spectrum of as grown crystal of GSN is shown in the Figure 1.4. UV–visible spectral analyzing shows that crystal is transparent in the entire visible region. The UV cut off wavelength occur at 210 nm. It is well known that an efficient NLO crystal has an optical transparency lower cut off wavelength between 200 and 400 nm [Le Fur *et al.* (1993)]. The large transmittance window in the visible and NIR region enable very good optical transmission of the second harmonic frequencies of Nd: YAG laser.

4.4 Determination of optical bandgap of GSN crystal

Using the Tauc's relation, a graph has been plotted to estimate the optical band-gap. The optical band-gap of TGBC crystal has been calculated from $(\alpha h\nu)^2$ versus hν plot which is shown in Figure 1.5 and the value of optical band-gap is calculated as 5.4 eV.

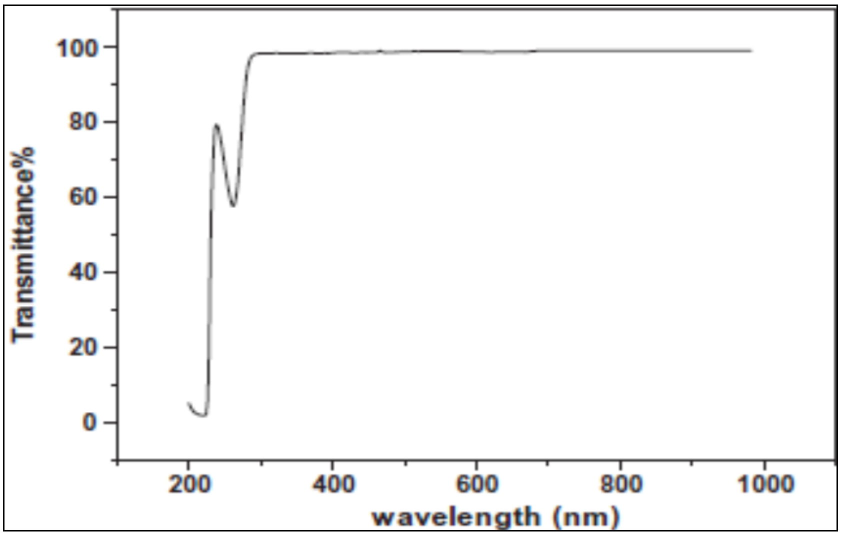

Fig 4: Optical transmission spectrum of GSN Crystal

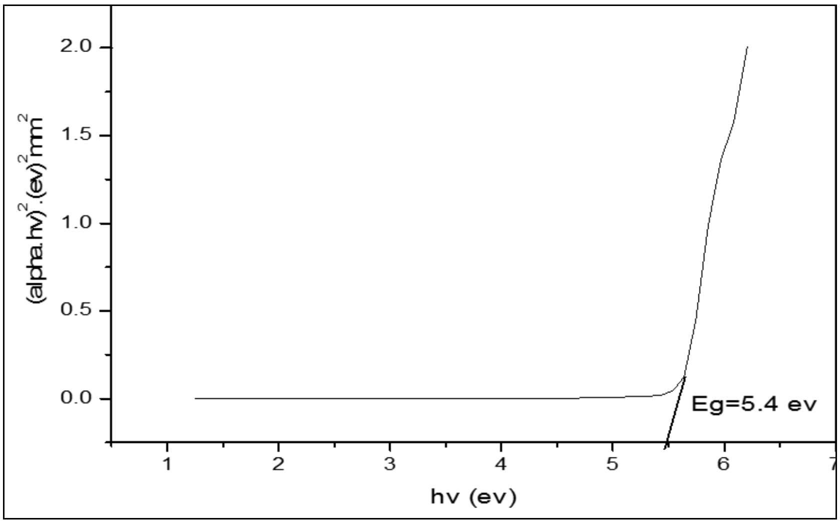

Fig 5: Tauc's plot of GSNcrystal

4.5 Kurtz powder SHG test of GSN crystal

In order to confirm the nonlinear optical property, powdered sample of GSN was subjected to KURTZ and PERRY technique, which remains powerful tool for initial screening of materials for SHG efficiency [Kurtz *et al.* (1968)]. A Q-switched Nd; YAG laser emitting 1.06 μm, with power density up to 1 GW/cm^2 was used as a source of illuminating the powder sample. The sample was prepared by sandwiching the graded crystalline powder with average particle size of about 90 μm between two glass slides using copper spices of 0.4 mm thickness. A laser produced a continuous laser pulses repetition rate of 10 Hz. The experimental setup used a mirror and 50/50 beam splitter. Here well-known material potassium dihydrogen phosphate (KDP) taken as a reference material. The input power was fixed at 0.68 J and the output power was measured as 6.9 mJ, which was compared to output 8.8 mJ of standard KDP. The diffusion of bright green radiation of wave length λ = 532 nm ($P_{2\omega}$) by the sample confirms second harmonic generation (SHG). The powder SHG efficiency of GSN crystal is about 0.8 times of KDP. The good second harmonic generation efficiency indicates that the GSN crystals can be used as suitable material for nonlinear optical devices.

5 Conclusion

Good optical quality semi-organic crystal of glycine barium nitrate (GBN) was grown successfully by slow evaporation technique with the dimension 8×7×3 mm^3. Powder XRD analysis reveal that GSN crystal is highly crystalline in nature. FTIR spectral studies confirm the presence of all the functional groups in grown crystal. UV–visible transmission study shows wide range of optical transmission bands and the lower cutoff wavelength at 210 nm. SHG studies on the grown GSN crystal shows that it is having NLO property and the SHG efficiency is 0.8 times that of KDP.

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