Growth, Structural and Optical Studies of Semi Organic Mixed Amino-Nitrate (GSA) Crystal

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ABSTRACT

The mixed amino-nitrate (GSA) crystals were grown from saturated solutions by slow evaporation technique with molar ratio (3:0.5:0.5), Transparent, elongated crystals of appreciable sizes (16 x 11 x 5 mm) were obtained in about 3-4 weeks time. The solubility of GSA has been determined in water. The grown crystal belongs to orthorhombic system with cell a= 18.478 a.u, b= 12.739 a.u and c= 5.015 a.u. with unit cell volume 1180.69 A.U^3. The presences of chemical components/ groups have been identified by CHN and EDAX analysis. Comparative IR and Raman studies indicate a molecule with a lack of centre of symmetry. A wide transparency window useful for optoelectronic applications is indicated by the UV Studies. Using Nd- YAG laser (1064nm), the optical second harmonic generation (SHG) conversion efficiency of GSA have been carried out. Also photoconductivity, I-V characteristics, dielectrics studies, and Vickers micro hardness measurement have been carried out.

Keywords: Crystal Growth, Structure, Optical Properties, SHG efficiency, Hardness

I. INTRODUCTION

The field of non-linear optics is based on the development of new materials which have strong interaction with the light beam. Semi-organic compounds have been recently recognized as potential candidates for such second harmonic generation (SHG). Amino acid complexes with variety of ionic salts are found to be suitable as non linear optical materials [1, 2]. The basic amino acid alpha glycine has been employed to synthesize many organic and semi organic materials exhibiting dielectric, ferroelectric, non linear optical and light sensing behavior [3, 4]. The molecular arrangement with large inter-atomic distances however leads to poor thermal and mechanical properties. The presence of inorganic element in the organic matrix is seen to enhance mechanical strength of the material making it suitable for applications.

These materials are promising element for feature photonic technologies, which involves application for information, image processing, frequency conversion and optical switching etc. The large NLO coefficients of organic molecules have been combined with mechanical strength imparted by the inorganic component. Varieties of amino acids like glycine, L-arginine, L-histidine etc. have been used [5, 6]. Glycine is found to exist in three polymeric crystalline forms namely α, β, γ, the simplest being the alpha form. α -glycine has been combined with $NaNO_3$ [7], $AgNO_3$ [8] and $CaNO_3$ [9] to produce interesting non linear optical compounds. In glycine sodium nitrate molecule the zwitterion of glycine is retained. The Na atom is seen to exhibit eight fold coordination and the polyhedron assumes the shape of a distorted hexagonal bipyramid. Moreover the glycine molecules are found to link through head-to-tail hydrogen bonds which are 'sandwitched' between the layers [10].

The organic matrix of glycine is found to be flexible to a variety of organic and inorganic components. In the present investigation single crystals of glycine barium- calcium nitrate (GSA) were grown and have been characterized by X-ray diffraction, FTIR, UV, SHG studies, I-V characteristics.

II. GROWTH AND SOLUBILITY

GSA crystals were grown by slow evaporation technique from saturated solution in doubled distilled water at 30°C with a pH of 4.6. The A.R grade α-glycine, sodium nitrate ($NaNO_3$), ammonium-nitrate (NH_4NO_3) supplied by Merck (India) with molar ratios 3:0.5:0.5. Transparent crystals of about 16 x 11 x 5 mm^3 were obtained in four weeks time (Figure 1). The size of a crystal is found to depend on the amount of the material available in the solution. The solubility was determined by dissolving the known amount of substance in distilled water at various temperatures (300-350K) using constant temperature bath.

$$[NH_2CH_2COOH]_3 + [NaNO_3]_{1/2} + [NH_4NO_3]_{1/2} \longrightarrow$$
$$[NaNO_3]_{1/2}.[NH_2CH_2COOH]_3.[NH_4NO_3]_{1/2}$$
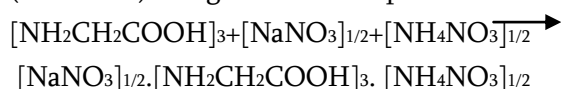
The size of a crystal was found to be depending on the amount of the material available in the solution which in turn is decided by the solubility of the material in solvent. The solubility of the synthesized material (GSA) was determined in distilled water at four different temperatures using constant temperature bath (Figure 2). The solubility is found to increased with temperature from 300-350K.
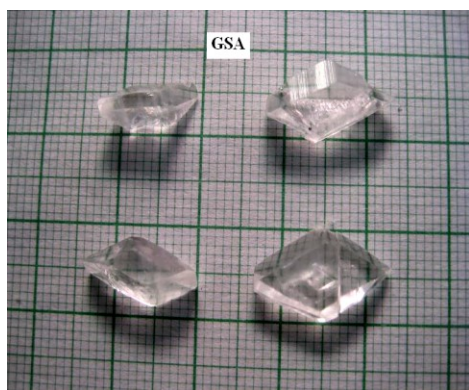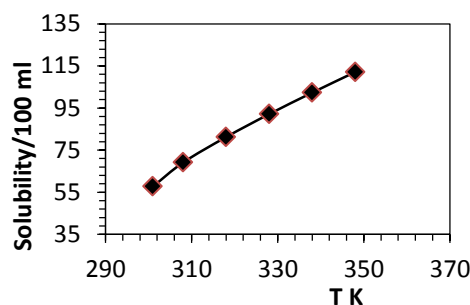

Maharashtra As grown GSA crystal

Figure 2. Solubility curve for GSA crystal

III. CHARACTERIZATION

The grown crystal were subjected to X-ray powder diffraction using JEOL JDX–8030 Series, a highly sophistsicated X-Ray diffractometer system with characteristic Cu-Kα radiation (λ =1.541 A.U). The sample was scanned in range from 10°-70° at rate of 5° per min [11, 12]. Density of GSA crystals was determined using the flotation method and a value of 1.251 g/cc was recorded. The melting point was found to lie at 145°C and the sample was found to finally decompose at 265°C. Heated sample showed effervescence near to decomposition temperature their by leading to bumping as also recorded in thermal (TGA/DTA) measurements. The FTIR spectra of sample were recorded in KBr phase in the frequency range from 400-4500cm^{-1} using Perkin Elmer 1600 series infrared spectrometer with resolution of 4cm^{-1} and scanning speed of 2 mm/s [13, 14]. Laser Raman Spectra was recorded in solid form using Ramanor HG-2S, Jobin Yvon spectrometer with Argon ion laser source (λ= 5145A.U) in range 200cm^{-1}-3500cm^{-1}. The absorption spectrum UV-Vis was recorded using U-2900, Hitachi system in range 100-1200 nm covering the entire ultraviolet and near visible region [15]. The nonlinear optical conversion efficiency was tested using a modified Kurtz and Perry setup [16-17]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used for SHG measurements with an input power 2.69 mJ/pulse. The pulse width was maintained at 8 ns at a repetition rate of 100Hz/pulse. The crystal of GSA were ground to a uniform particle size of about 125-

150 μm and then packed in a capillary of uniform bore and exposed to laser radiations. The second harmonic signal generated in crystalline sample was confirmed from the emission of green radiation (532nm) from the crystal. The intensity of green light was measured using photo multiplier tube and CRO. The I-V characteristic and photoconductivity was recorded using digital pico ammeter Model DPM 111. Polished crystals of thickness 4mm were silver plated on the opposite faces Silver coating was applied on the opposite sides of polished crystal and was placed between two copper electrodes forming a parallel plate capacitor. The dc input was increased from 0 to 30V in steps and the corresponding readings were recorded. A 100 Watt Tungsten filament lamp with iodine vapors' was used to expose the samples for photoconductivity measurements. The dark characteristics were recorded by covering the sample with a black cloth.

A. X-ray diffraction

The new GSA crystal was characterized by powered X-ray diffraction to confirm the phase. The analysis of the observed spectra was carried out using POWD- Interactive powder diffraction data interpretation and indexing software program, Version 2.2 (Australia). The XRD peaks were indexed and the grown crystal was found to have orthorhombic symmetry with lattice parameters a= 18.478 a.u, b= 12.739 a.u and c= 5.015 a.u. and the unit cell volume 1180.69 A.U^3. The intense peaks were recorded at 2θ = 20° to 40° with maximum intensity of around 7128 on plane (4 2 1) as shown in spectrum (Figure 3)
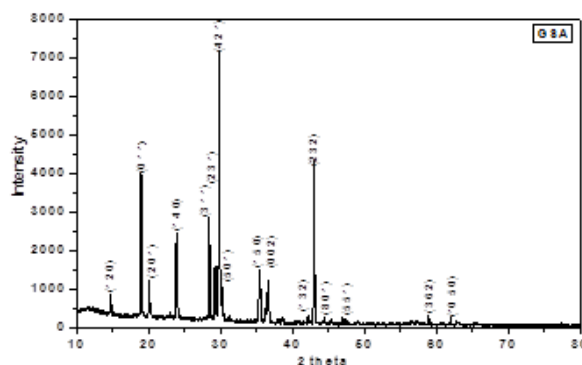

Figure 3. XRD Profile of GSA Crystal

B. FTIR and Raman Studies

Figure 4 shows FTIR spectrum of the grown GSA crystal. The characteristic absorption peaks have been observed in the range 400 cm^{-1} to 3200 cm^{-1} and active IR peaks were found to lie in region from 400 cm^{-1} to 1800 cm^{-1}.
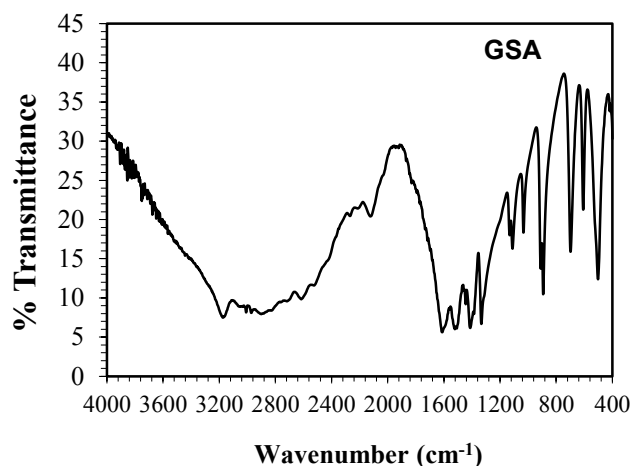

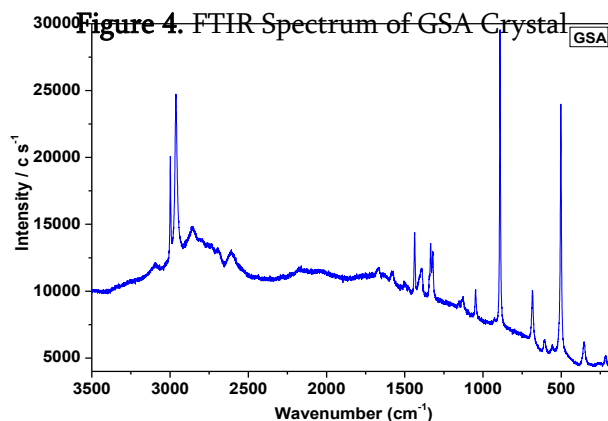**Figure 4.** FTIR Spectrum of GSA Crystal

Figure 5. Raman Spectrum of GSA Crystal

A broad characterization peak appears between 1700 cm^{-1}- 2800 cm^{-1}. Free glycine exists as a

zwitterion in which the carboxyl group is present as carboxylate ions and amino group exist as ammonium ion. The absorptions due to carboxylate group of free glycine are observed between 501 and 690 cm^{-1}. In the IR spectrum CH$_2$ stretching occurs at 2962.4 cm^{-1}. Amino acid combination band is found at 2166.9 cm^{-1}.The strong NH$_3^+$ deformation occurs between 1499 cm^{-1}- 1637.3 cm^{-1} and NH$_3^+$ stretching occurs between 2609 cm^{-1} & 2798.3 cm^{-1}. The CH$_2$ stretching is found to be weak in FTIR at 2966.3 cm^{-1}. The NO$_3^-$ symmetric stretch appears at 1048.2 cm^{-1} and NO$_3^-$ asymmetric stretching frequency lying at 1338 cm^{-1}. The Raman profile for the GSA crystals is shown in Figure 5. The both spectrum shows prominently COO$^-$ rocking/ wagging/bending, CCN symmetric stretching, CH$_2$ wagging/twisting, CH$_2$-Scissor, NH$_3^+$ deformatio,Amino acid combination bond,NH$_3^+$ deformation ,CH$_2$ stretching and the presence of NO$_3^-$ symmetric/asymmetric stretching etc.

C. UV Studies

The UV absorption spectrum for GSA crystal was recorded in the UV-vis region (Figure 6).The peak at 200-221 nm is due to n-π* transition [18-19]. The cut off wavelength λ$_{max}$ lies at 221.5 nm with corresponding energy gap of 5.61 eV. A wide transparent window is present between 265 nm- 1200 nm suggesting its use in optoelectronics devices.
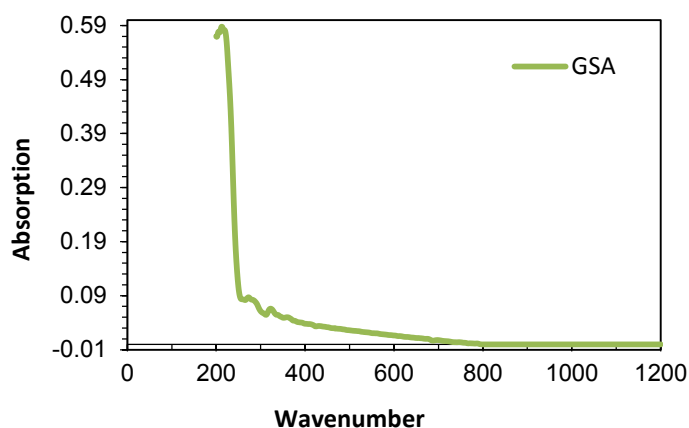
D. Powder SHG measurement

The grown GSA crystals were subjected to second harmonic generation test for NLO property. Using Nd:YAG Q-switched laser source, the crystal was ground into powder with particle size is about 125-150 μm and densely packed into two transparent slide was illuminated by pulse-laser beam with a wavelength of 1064nm . The SHG signal generated in the crystalline sample was collected and displayed as green light radiation (λ =532nm) on a cathode ray oscilloscope. A SHG signal of 5 mV was obtained compared to 185 mV of that of standard KDP crystal for the same input energy of 2.69 mJ/pulse. The SHG efficiency is found to depend upon the method and conditions during growth, composition and size of crystallites exposed during measurements.

E. I-V and Photoconductivity Studies

The I-V and photoconductivity characteristic (dark and bright current) of the GSA crystals with applied field is as shown in Figure 7. The voltage (V) was found to increase with current (I) linearly up to voltage of 100 V/cm. On exposure to light radiation bright current is found to be greater than dark current (positive photoconductivity). This enhancement of field dependent conductivity of the sample is due to the generations of mobile charge carrier caused due the absorption of photons [20].
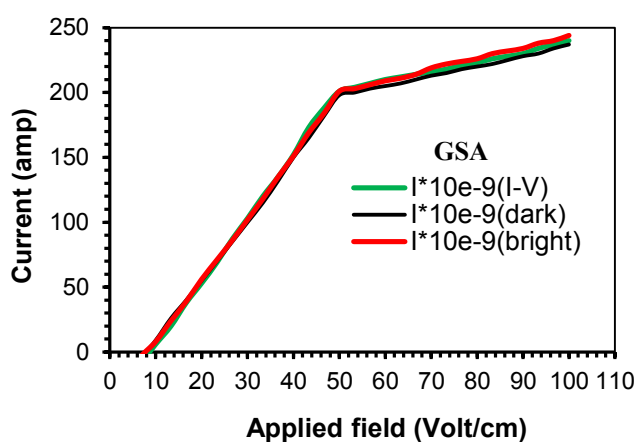

Figure 6. UV-Vis-NIR Spectrum of GSA Crystal

Figure 7. I-V and Photoconductivity plot

IV. CONCLUSION

Transparent crystals of acid mixed glycine -sodium-ammonium nitrate (GSA) crystal was successfully grown using slow evaporation method at room temperature from the aqueous solution and characterized by various techniques. The solubility was found to vary linearly in temperature range 300K-350K. The presence of fundamental groups has been verified by the comparative FTIR and Raman spectroscopic studies. The close match between the IR and Raman peaks indicate a molecule with lack of center of symmetry. The optical studies showed that the crystal have wide transparent window in the region 265 nm- 1200 nm useful for optoelectronic applications. The optical SHG efficiency of GSA crystal was carried out with respect to standard KDP. The I-V characteristics found to be linear upto100 V/cm and on exposures to light sample show positive photoconductivity which may be attributed to due to the enhancement of charge carrier through absorption of photons.

V. ACKNOWLEDGMENTS

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