

Second harmonic generation studies on Guanidine Nitrate added triglycine sulphate crystals

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Abstract:

The field of nonlinear optics became practically a reality after the invention of laser. High Performance electro-optic switching elements for telecommunications and optical information processing are based on materials with high nonlinear optical (NLO) properties. The development and encroachment of high technology, from transportation, computation to information is based on the availability of materials in the form of single crystals. AR grade chemicals such as glycine, sulphuric acid and Guanidine Nitrate were purchased commercially and were taken in 3:1:1 molar ratio. The reactants were dissolved using the double distilled water and a hot plate magnetic stirrer. The solution was heated for 3 hours at 60 oC for the reaction to take place. Then the solution was cooled to room temperature and filtered using a fine filter paper. The filtered solution was taken in a crystallizer for the growth of bulk crystals. The grown crystals TGSGN were harvested after a growth period of 30 days and the size of a typical grown crystal was 12 mm x 10 mm x 8 mm. The crystal structure was checked by XRD method and the grown crystal is observed to be crystallizing in monoclinic structure. The grown crystal was identified as the triglycine sulphate crystal doped with Guanidine Nitrate (TGSGN) by various studies. The SHG conversion efficiency of TGSGN crystal was found to be 0.96 times that of KDP. Thermo gravimetric analysis (TG) and differential thermal analysis (DTA) were used to study the thermal properties of the grown TGSGN crystal. The grown crystals were also subjected to FTIR, micro hardness and dielectric studies.

Key words: TGS crystal; doping; solution growth; NLO; XRD; FTIR; hardness; dielectric constant; TG/DTA; SHG.

1. Introduction

The nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics.

This can be essentially traced to the improvement of the performances of the NLO materials. There has been a growing interest in crystal growth process, particularly, in view of the increasing demand for materials for technological applications [1-3]. Crystals of amino acids and their complexes can be considered for a variety of applications. Among amino acids, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) is the simplest amino acid and it has three polymeric crystalline forms viz, α , β and γ forms. The β -form is the metastable form at ambient temperature, which spontaneously crystallizes from water, or may be obtained by evaporation of aqueous solutions [4-8]. Some of the glycine complexes in single crystalline forms have been grown and studied by many researchers [9-15]. When glycine combines

with sulphuric acid in the molar ratio 3:1, triglycine sulphate (TGS) crystal is formed and it is a suitable material for developing detectors of infrared radiation and target faces in vidicons based on the pyroelectric effect. Doping crystals with various kinds of dopants influences the solubility, growth rate, morphology, structural, electrical and other properties of the crystals [16-22]. In this work, TGS crystals are doped with Guanidine Nitrate and single crystals were grown by slow evaporation. The grown crystals were characterized by various studies such as FTIR, XRD, hardness studies, dielectric studies, SHG and thermal studies and the results are discussed.

2. Preparation and solubility

To prepare triglycine sulphate doped with Guanidine Nitrate (TGSGN), the estimated amounts of glycine, sulphuric acid and Guanidine Nitrate in the molar ratio of 3:1:1 were taken and dissolved in double distilled water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated until the synthesized salt of TGSGN (Triglycine sulphate doped Guanidine Nitrate) the sample was obtained. The pure TGS sample was also prepared for the comparison purpose. The solubility study was carried out using a hot- plate magnetic stirrer and a digital thermometer. A voltage regulator was attached with a hot plate magnetic stirrer in order to maintain the temperature constant. Initially the temperature was maintained at 30 °C. The synthesized salt TGSGN was added step by step to 50 ml of de-ionized water in an air-tight container kept on the hot plate magnetic stirrer and stirring was continued till a small precipitate was formed. Then 15 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 40 °C till the solvent was evaporated. By measuring the amount of salt present in the petri dish, the solubility (g/100 ml) of the sample was determined. The same procedure was followed to find solubility of the samples at other temperatures. The solubility curves for pure and Guanidine Nitrate added TGS samples are given in the figure 1. It is observed from the results that solubility increases with temperature for the samples and it is found to be more for Guanidine Nitrate added TGS sample. Since the solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility.

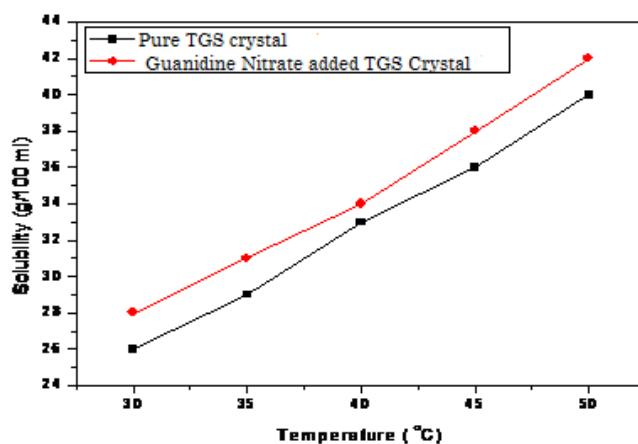


Fig.1: Solubility curves for pure and Guanidine Nitrate added TGS (TGSGN) crystals

3. Growth of crystals

The synthesized salt was used to grow single crystals of TGSGN by the solution method with slow solvent evaporations techniques at room temperature (30 °C). In accordance with the solubility data, saturated solution of the synthesized salt was prepared and it was constantly stirred for about 3 hours using a magnetic stirrer and was filtered using a 4-mico Whatmann filter paper. Then the filtered solution was taken in a borosil beaker covered with a porous paper and kept in a dust free atmosphere. The crystal was harvested after a period of about 20 days and it is shown in the figure 2.

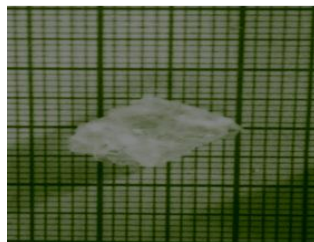


Fig.2: Photograph of the grown crystal of TGSGN

4. Analysing techniques

The grown single crystals of TGSGN were subjected to single crystal XRD studies using and ENRAE NONIUS CAD4 X-ray diffractometer. The Powder X-ray diffraction pattern of the samples was obtained using the powder X-ray diffractometer (Scientag powder X-ray diffractometer with the wavelength of 1.54056 Å at 35 kV; 10 mA). The samples were scanned over the required range for 2θ values (10–60°). Q-switched Nd: YAG laser (1064 nm, Quanta ray series) was used for the second harmonic generation (SHG) studies. Thermo gravimetric and differential thermal analysis were carried out simultaneously using thermal analyzer in nitrogen atmosphere at heating rate of 10 °C/min for temperature range 30-710 °C. The FTIR spectrum the sample crystal is recorded in the range of 500- 4000 cm⁻¹ using Perkin Elmer grating infrared spectrometer.

The micro hardness studies were carried out on the grown crystals using a LEITZ micro hardness tester, fitted with a Vickers diamond pyramidal indenter. A well polished crystal has been placed on the platform of the micro hardness tester and the loads of different magnitudes have been applied in a fixed interval of time. The indentation time has been kept 10 seconds for all the loads. Vickers micro hardness values have been calculated by using the formula $H_v = 1.8544 P/d^2$ kg/mm² where H_v is the Vickers micro hardness number, P is the applied load in kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramidal indenter. The dielectric constant and the dielectric loss of the samples were measured using LCR meter (Agilent 4284A) at the different frequency of for 30.01°C, 50.26°C, 70.02°C, 90.60°C, 110.41°C, 125.01°C various temperatures. Defect free and transparent crystals were selected and used for the dielectric measurement. For good conduction, opposite faces of the sample crystals were coated with good quality graphite. The dielectric constant and the dielectric loss were estimated under the different frequencies for different temperatures.

5. Results and discussion

5.1 XRD studies

Single crystal XRD data of TGS doped Guanidine Nitrate crystals was obtained using a single crystal X-ray diffract meter and the data are $a=8.403(3) \text{ \AA}$, $b=11.645(2) \text{ \AA}$, $c=5.685(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 110.46^\circ$,

$\gamma=90^\circ$. From the data, it is observed that the grown crystals crystallize in the monoclinic crystal system. The obtained crystallographic data for grown crystal of this work are found to be in good agreement with the reported values [23]. The unit cell parameters are slightly different when compared to the values of reported data and the changes of lattice parameters have been noticed and the changes in the lattice parameters are due to presence of Guanidine Nitrate dopants in TGS crystals. The presence of dopants in the host crystals may produce lattice strain, which leads to change of unit cell parameters of the host TGS crystals.

5.2 NLO studies

Nonlinear optical property of the grown Guanidine Nitrate added TGS crystals were studied by Kurtz and Perry SHG test [24]. A Q-switched Nd: YAG laser (1064 nm, Quanta ray series) was used as light source. A laser beam of fundamental wave length 1064 nm, was made fall normally on the sample cell. The sample was crushed into the fine powder and tightly packed in a micro capillary tube. The power of the incident beam was measured using a power meter. A KDP crystal powdered to the identical size of the sample of this work was used as a reference material in the SHG measurement. The input laser energy incident on the powdered sample was chosen to be 0.68 J. The Guanidine Nitrate doped TGS sample with a second harmonic signal energy of

7.9 mJ was obtained. The reference sample KDP gave SHG signal energy of 8.8 mJ for the same input beam energy. Thus the SHG efficiency of the Guanidine Nitrate doped TGS crystal has the relative SHG efficiency of 0.96 times that of KDP.

5.3 FTIR characterization

FTIR spectrum of Guanidine Nitrate added TGS crystals was recorded and presented in the figure 3. The broad band between 2800 and 3500 cm^{-1} in the spectrum indicates stretching frequencies superimposed OH and NH_3^+ modes. Multiple combination and overtone bands of CH_2 have been observed just below 3100 cm^{-1} . The absorption in the region 1600-1800 cm^{-1} is assigned to C=O stretching of COOH group. The peaks between 1715 and 1311 cm^{-1} in the FTIR spectra can be assigned to COO^- vibrational mode. The strong peak region 1112 and 1129 cm^{-1} in the samples is attributed to C – N stretching vibrations [25]. The strong absorption in the range 1022 and 1128 cm^{-1} is evidently due to sulphate part of the molecules. The peaks observed 902, 617, 565 and 501 cm^{-1} are due to NH^+ bending modes.

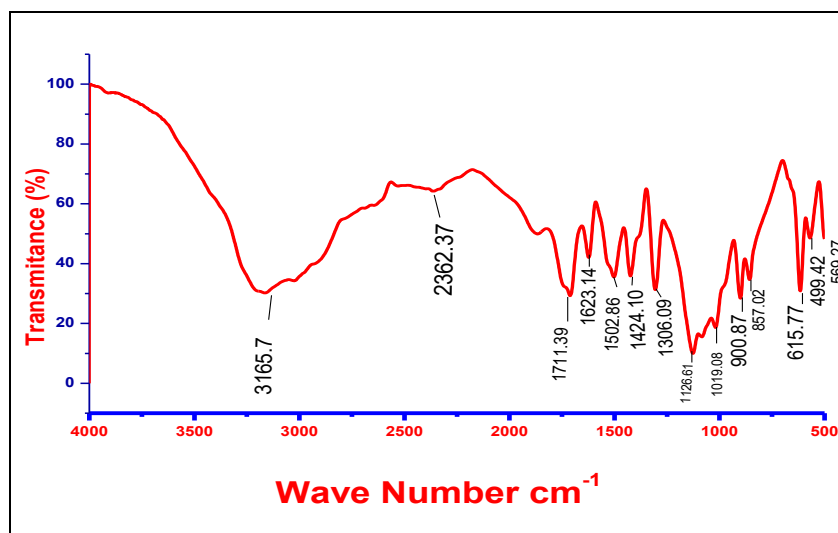


Fig.3: FTIR spectrum of Guanidine Nitrate doped TGS (TGSGN) crystal

5.4 Thermal characterization

The TG / DTA studies were carried out simultaneously on the sample in the temperature range 37 – 710 °C and the recorded thermal curves are displayed in figure 4. From the TG curves, it is noticed that there is a slight weight loss up to 220 °C for the sample and there is a maximum weight loss in the temperature range 230- 250 °C and hence the sample is found to be thermally stable and suitable for device applications. From DTA curves it is observed that the sample has an endothermic peak at 236 °C [26] which corresponds to the decomposition point of the sample.

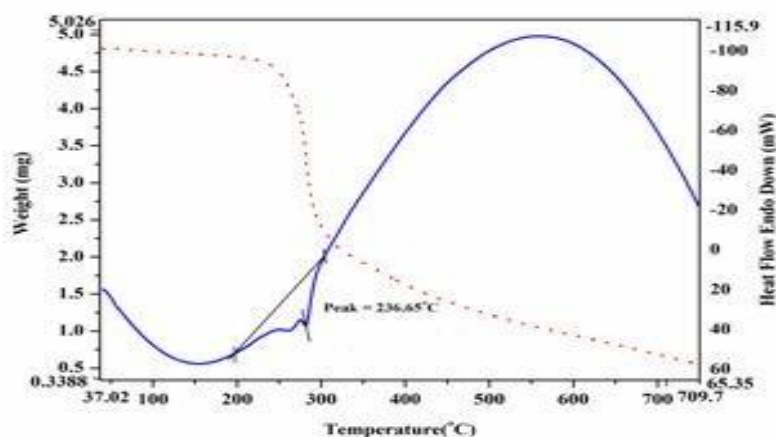


Fig.4: TG/DTA thermal curves for (TGSGN) crystal

5.5 Mechanical characterization

The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material. The average diagonal indentation (d) was measured for different loads and the micro hardness number was determined. A graph was plotted between hardness number (H_v) and applied load (P) and it is presented in the figure 5. At lower loads there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layers. At higher loads, the H_v shows the tendency to saturate. Beyond the load of 100 gm significant cracking occurs which may be due to the release of

internal stresses generated locally by indentation. For the comparison purpose, the hardness values are given in the figure 5 for pure and Guanidine Nitrate doped TGS crystals. It is observed that the Guanidine Nitrate doped TGS crystal is more harder than pure TGS crystal [27] and this is because the incorporation of Guanidine Nitrate in the interstitial positions of TGS crystal may strengthen the crystal bindings of doped TGS crystal.

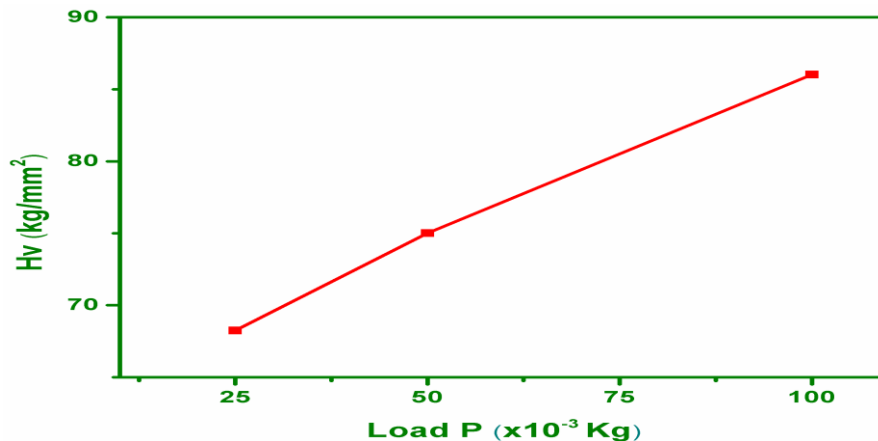


Fig.5: Plots of hardness number versus load for Guanidine Nitrate added TGS (TGSGN) crystals

5.6 Dielectric characterization

The temperature dependence of dielectric constant obtained for the grown crystals for different kHz frequency and 30.01°C, 50.26°C, 70.02°C, 90.60°C, 110.41°C, 125.01°C such temperatures is provided in figure 6 and that of dielectric loss ($\tan \delta$) obtained for the frequency different kHz and different temperatures is presented in figure 7. From the graphs, it is observed that as the temperature increases, the values of dielectric constant and dielectric loss increase for both pure and Guanidine Nitrate doped TGS crystals up to the Curie temperature (T_c) and then the values decrease. Above T_c , the dielectric constant decreases and obeys Curie- Weiss law. It is noticed that the Guanidine Nitrate added TGS crystal has higher dielectric constant and loss values compared to that of pure TGS crystal. Increase in dielectric constant for Guanidine Nitrate added TGS crystal at transition temperature is attributed to free charge carriers created by the dopants. The Curie point T_c for the samples was found to be the same.

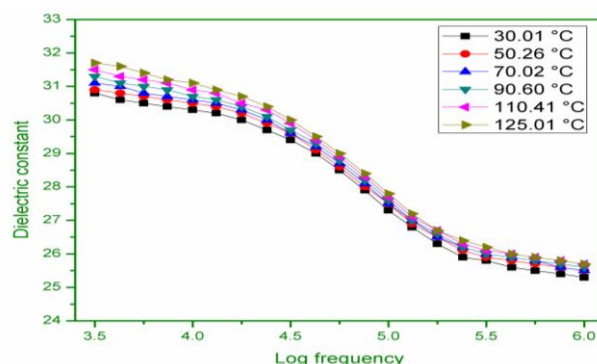


Fig.6: Variation of dielectric constant with different temperature at different frequency of Guanidine Nitrate added TGS (TGSGN) crystals.

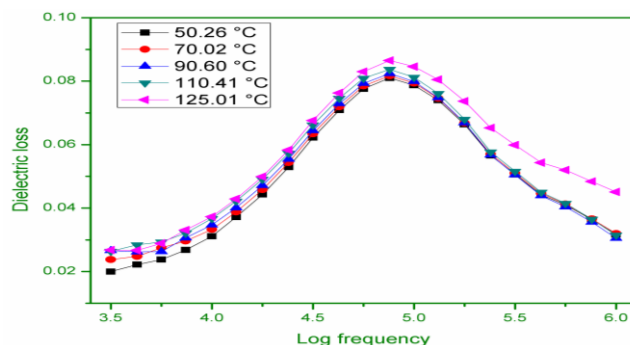


Fig.7: Variation of dielectric loss with different temperature at different frequency of Guanidine Nitrate added TGS (TGSGN) crystals.

6. Conclusions

Pure and Guanidine Nitrate doped TGS samples (TGSGN) were synthesized and solubility studies were carried out at different temperatures. In accordance with the solubility data saturated solutions were prepared and single crystals of pure and Guanidine Nitrate added TGS were grown by solution growth with slow solvent evaporation technique. The grown crystals are found to be transparent and colorless with well defined external appearance. The unit cell parameters have been evaluated by the single crystal XRD method. The powder SHG test confirms the NLO property of the sample crystals. From TG / DTA studies, the thermal stability of the grown crystals was confirmed. The functional groups of the sample were obtained by the FTIR spectrum analysis. The micro hardness studies were carried out to understand the mechanical strength of the samples. The dielectric constant and loss factor of the sample crystals were measured using an LCR meter and it is found that the values are found to be more for TGSGN crystal than that of pure TGS crystal.

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References

1. R.A.Laudise, R.Ueda and J.B.Millin, Crystal Growth and Characterization, North-Holland Publishing Co, (1975).
2. J.C. Brice, 'Crystal Growth Processes', Halsted Press, John Wiley and sons, New York, (1986).
3. H.S.Nalwa and S.Miyata S, 'Nonlinear Optics of Organic Molecules and Polymers', CRC Press Inc., New York, (1996).
4. H. Newman, H. Budzier, Ferroelectrics 133 (1992) 41.
5. L.Prokopova, J. Novotny, Z. Micka, V. Malina, Cryst. Res. Technol. 36 (11) (2001) 1189.
6. M. Banan, R.B. Lal, A.K. Batra, J. Mater. Sci. 27 (1992) 2291.
7. M.A. Gaffar, A.A. Al-Fadl, S.A. Mansour, J. Phys. D: Appl. Phys. 34 (1999) 915.
8. Jiann-Min Chang, A.K. Batra, R.B. Lal, Cryst. Growth Design 2 (2002) 431.
9. P. Selvarajan, B.N. Das, H.B. Gon, K.V. Rao, J. Mat. Sci. Lett. 11 (1992) 312.
10. S. Aravazhi, R. Jeyavel, C. Subramanian, Ferroelectrics 200 (1997) 390.
11. Hung-Wen Li, Gu-Shen Yu, Herbert I. Strauss, J. Phys. Chem. B, 102 (1998) 298.
12. R.Ezhil Vizhi, S.Kalainathan, G.Bhagavannarayana, Cryst. Res. Technol., 42 (2007) 1104.

13. S.Natarajan, K.Ravikumar, S.S.Rajan, Z.Kristallogr. , 168(1984) 75.
14. T.Balakrishnan, K.Ramamurthi, Materials Letters, 62(2008)65.
15. Genbo Su, You ping He, Hongshi Yao, Zikong Shi, Qingin Eu, J. Cryst. Growth 209 (2000) 20.
16. V. N. Shut, I. F. Kashevich, and S. R. Syrtsov, "Ferroelectric properties of triglycine sulfate Crystals with a nonuniform distribution of chromium impurities," Physics of the Solid State, vol. 50, no. 1, pp. 118–121, 2008.
17. K. Biedzycki, Solid State Commun. 118 (2001) 141.
18. H.V. Alexandru, C. Berbecaru, F. Stanculescu, L. Pintile, I. Matei, M. Lisca, Sensors and Actuators A 113 (2004) 387.
19. D. Sun, X. Yu, Q. GU, Cryst. Res. Technol. 34 (10) (1999) 1255.
20. B. Lal, A.K. Batra, Ferroelectrics 142 (1993) 51.
21. M.A. Gaffar, A.A. Al-Fadl, Cryst. Res. Technol. 34 (7) (1999) 915.
22. K.L. Bye, P.W. Whipps, E.T. Keve, Ferroelectrics 4 (1972) 253.
23. N. Theresita Shanthi, P. Selvarajan, C.K. Mahadevan, Current Applied Physics 9 (2009) 1155.
24. S.K.Kurtz, T.T.Perry, J.Appl. Phy. 39 (1968) 3798.
25. T.Balakrishnan and K.Ramamurthi, Cryst. Res. Technol, 41, no 12, 1184-1186(2006)
26. M.Lenin, M.Chandrasekar, G.Udayakumar, Growth and characterization of glycine Zinc Sulphate, int.jour.of chemtech, vol 6.no 4, pp 2683-2688.
27. E.M Onitsch, Mikroskopie 2,1941,135.
