

Growth and Characterization of Urea Nitrate Doped Triglycine Sulphate Single Crystals

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ABSTRACT

Pure and Urea nitrate ($\text{CH}_5\text{N}_3\text{O}_4$) doped triglycine sulphate single crystals have been grown from aqueous solution by solvent evaporation technique at room temperature. Highly transparent, well faceted, pure triglycine sulphate single crystal was harvested. Morphological change was observed in the urea nitrate doped triglycine sulphate single crystal. The unit cell parameters were determined from powder X-ray diffraction Patterns. FTIR analysis confirms the presence of functional groups. The chemical composition of the pure and doped crystal was analysed by EDAX. The emission of green light confirms the second harmonic generation of the pure and doped crystals.

Keywords : Ferroelectric, Pyroelectric, Sensors, Urea Nitrate, Piezoelectric, Sulphuric acid.

I. INTRODUCTION

The ferroelectric behaviour of Triglycine sulphate (TGS), $(\text{NH}_4\text{CH}_2\text{COOH})_2\text{H}_2\text{SO}_4$, was observed by Mathias and Remeika [1] in 1956. The crystal structure of TGS was reported by Hoshino et al [2]. The compound has most rectangular hysteresis loop and greatest dielectric non linearity of all known ferroelectrics. It has a high piezoelectric constant but a comparatively low dielectric constant. These properties take it a ferroelectric of great interest, which finds applications in thermal detectors, pyroelectric vidicon tube, transducer and sensors [3]. TGS exhibits a ferroelectric phase transition at Curie point 49°C .

TGS belongs to the polar point symmetry group $P2/m$ of the monoclinic system and above T_c [4]. TGS get spontaneously polarized along the b axis. Investigations show that TGS crystals have disadvantages such as easy depolarization by electrical, mechanical, thermal energy, microbial contamination

with time, high mobility of ferroelectric domains at room temperature and low curie point [5]. To overcome these defects, Scientist investigated that the substitution of selected amino acids found to enhanced the properties of the crystals [6,7,8,9,10,11]. Metal ion and Rare earth metal ions La, Ce and Nd doped TGS have been grown [12,13,14,15]. Hence the doped TGS was reported to be better than pure TGS crystal [16].

II. EXPERIMENTAL

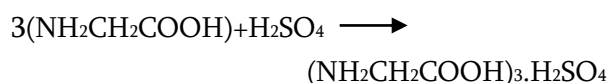
2.1. Materials

In the present investigation A R grade Glycine, Urea, Concentrated sulphuric acid, nitric acid and triple distilled water were used.

2.2. Synthesis of triglycine sulphate

Triglycine sulphate was chemically synthesized using glycine and concentrated sulphuric acid in the ratio 3:1. The volume of concentrated sulphuric acid required was diluted with triple distilled water. Calculated

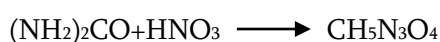
amount of glycine was dissolved in diluted sulphuric acid [17]. The temperature of the solution should be kept below 60°C to avoid oxidation of glycine. Glycine reacts with sulphuric acid as per the following reaction.



The synthesized material was collected, dried and recrystallized thrice to purify the material.

2.3. Synthesis of urea nitrate

Urea nitrate was chemically prepared from the neutralization of urea with concentrated nitric acid.



2.4. Preparation of pure and urea nitrate doped triglycine sulphate single crystals

In the present experimentation 400 ml of saturated solution of triglycine sulphate was prepared at average room temperature using the pre determined solubility data. The solution was stirred well using a magnetic stirrer for 5 hours. The solution was equally (200ml) distributed in two 250 ml beakers. One beaker was kept as standard, In the other beaker optimized value of (0.5mole %) as synthesized urea nitrate was added as the dopant. The temperature of the pure and doped solution was raised to 0.5° C and stirred well till the solute and the dopant dissolves. Both the solution was separately filtered using Whattmann filter paper. The pH of the solutions were measured as 3.5 and 3 for the pure and urea nitrate doped triglycine sulphate solutions respectively. The two crystallisers were covered with perforated polythene paper and kept in a vibration free platform for nucleation. The solvent evaporates very slowly in the isothermal condition. The slow evaporation of the solvent leads to super saturation of the solution. When the solution attains critical stage, self nucleation starts in both solutions and with in a period of seven days visible pure and urea nitrate doped triglycine sulphate seed crystals are formed. As the solvent evaporation is in progress , the seeds grows in size. After a period of 25 days fully grown,

well faceted, highly transparent pure and morphologically changed urea nitrate doped triglycine sulphate single crystals could be harvested. The grown crystal is depicted in figure 1a and 1b.

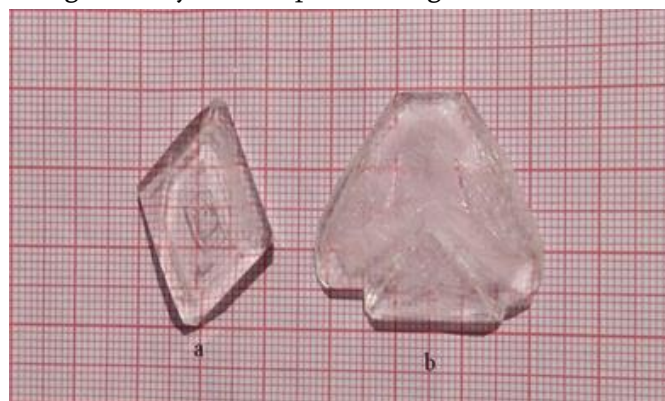


Figure 1a. pure TGS and Fig.1b. urea nitrate doped TGS.

III. RESULTS AND DISCUSSIONS

3.1. Morphological studies

Influence of foreign particles present in the growth media has long been recognized in changing growth habits of crystals. The effectiveness of different impurities in changing the surface morphology is different [18,19,20,21]. The morphology of pure triglycine sulphate and urea nitrate doped TGS was shown in figure 2a and 2b. When compared to the theoretical morphology, the as grown pure TGS crystals shows a resembling morphology with well defined faces. But in the urea nitrate doped single crystal, a change in morphology is observed. Different zones with triangular morphology is seen. The different zone and hence the change in morphology may be due to the effect of the dopant urea nitrate during the crystallization process. Urea nitrate is a bigger molecule compared to glycine molecule. Upon entering the TGS lattice this molecule creates strain in the crystal lattice.

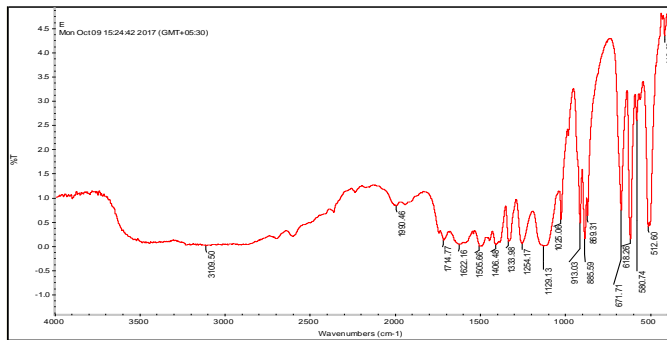


Figure 4b. FTIR spectrum for the urea nitrate doped TGS

All the functional groups were assigned for the pure and urea nitrate doped triglycine sulphate crystals with reference to the literature[23].

In the spectrum pure TGS a broad and very strong absorption band positioned in the range 2380-3800cm⁻¹ for O-H stretching of hydrogen bonded carboxyl groups and N-H stretching of NH₃⁺group. A peak observed at 1870 cm⁻¹ may be due to C=N. The C=O stretching vibration of carboxyl group appears as a sharp band at 1708 cm⁻¹. A peak observed at 1631 cm⁻¹ is due to the presence of amide group. The C-H bending vibration appears at 1503 cm⁻¹. The N-H bending vibration are presented 1425cm⁻¹. The peak observed at 1306,1130 and 1023cm⁻¹ was for the asymmetric S=O stretching frequency. A sharp peak observed at 903 and 868 cm⁻¹ is due to OH out of plane bending. The torsional oscillation of NH₃³⁺ group appears at 613,550 and 501 cm⁻¹.

The spectrum of urea nitrate doped triglycine sulphate crystal shows a broad and strong absorption band in the range 2200-3100 cm⁻¹ for the O-H stretching of hydrogen bonded carboxyl group and the N-H symmetric stretching mode of NH₃⁺ group. A peak observed at 1990 may be due to the presence of C≡N group. A peak obtained at 1714 cm⁻¹ shows the C=O stretching vibration of carboxyl group. A peak observed at 1622 cm⁻¹ shows the presence of amide group. A peak observed 1505 cm⁻¹ is due to antisymmetric mode of NH₃⁺. A peak observed 1406 and 869 cm⁻¹ may be due to N-O stretching and N-O out of plane bend respectively. The peaks observed at

1333 and 1025 cm⁻¹ is due to S=O asymmetric stretching mode. The peaks observed at 913 and 885 cm⁻¹ due is to O-H out of plane bend. The sharp peaks found at 671,618,580 and 512 cm⁻¹ may be due to the torsional oscillations of NH₃³⁺ groups.

3.4. Elemental Analysis

The energy dispersive analysis X-ray(EDAX) spectrum of pure and urea nitrate doped TGS has been taken to identify the elements present in the crystals and presented in Figure 5a and 5b.

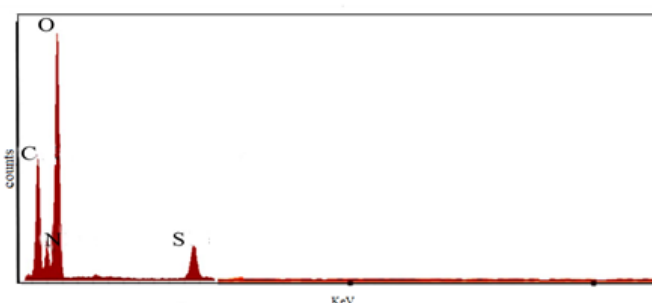


Figure 5a. EDAX spectrum of pure TGS

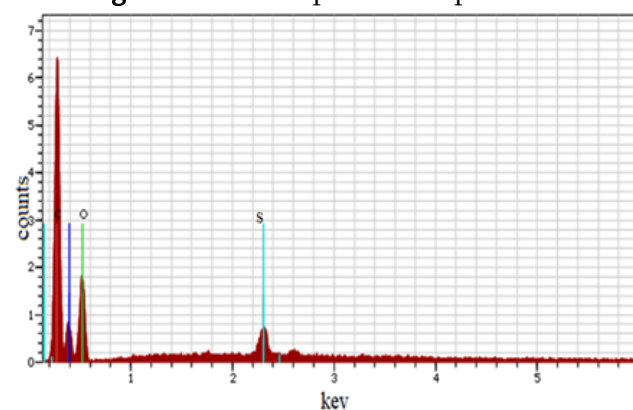


Figure 5b. EDAX spectrum of urea nitrate doped TGS

EDAX result of the pure triglycine sulphate and urea nitrate doped triglycine sulphate was presented in the table 2.

Table 2. EDAX data

Elem ents	*Pure Triglycine sulphate		Doped Triglycine sulphate		Differ in values	
	Atom ic Weig ht %	Weig ht %	Atom ic Weig ht %	Weig ht %	Atom ic Weig ht %	Weig ht %
C	25.51	20.43	49.18	43.44	23.67	23.01
O	55.23	58.90	26.68	31.39	-	-

					28.55	27.51
N	17.02	15.90	23.90	24.61	6.88	8.71
S	2.24	4.78	0.24	0.56	-2	-4.22

While comparing the various elements present in the doped triglycine sulphate with pure triglycine sulphate it was observed that in the urea nitrate doped triglycine sulphate the atomic weight percentage and the corresponding weight percentage of the element carbon was found to be increased. Similarly the atomic weight percentage and the corresponding weight percentage of nitrogen was also found to be increased. This increased in atomic weight percentage and weight percentage of both carbon and nitrogen atoms may be due to the presence of urea nitrate in the doped triglycine sulphate single crystals. But there is a reduction in the atomic weight percentage and weight percentage of the both the oxygen and sulphur atoms. This may be due to the partial removal of sulphate ions in the sulphuric acid of the triglycine sulphate single crystals.

3.5. SURFACE ANALYSIS

The Scanning Electron Microscope (SEM) of pure and urea nitrate doped triglycine sulphate single crystals were presented in figure 6a and 6b.

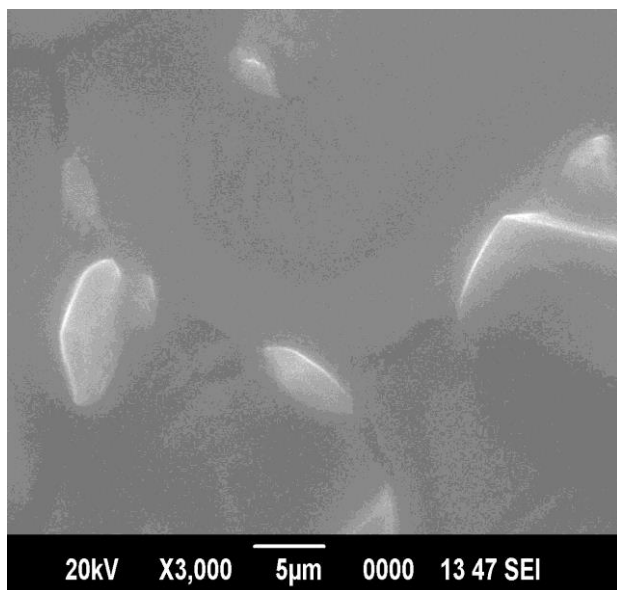


Figure 6a. Microphotograph of pure TGS

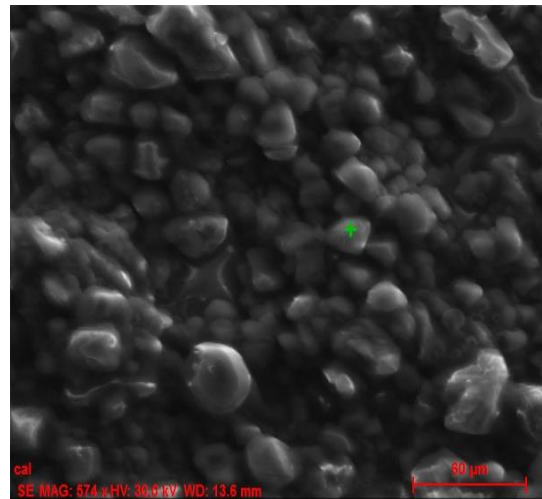


Figure 6b. Microphotograph of urea nitrate doped TGS

The microstructure of the grown pure and urea nitrate doped triglycine sulphate was analysed using scanning electron microscope. The SEM micrograph of the pure triglycine sulphate shows that the surface was smooth. But in the doped triglycine sulphate hillocks are seen. This may be due to the adsorption of the urea nitrate in the triglycine sulphate crystals.

3.6. Second Harmonic Generation Study

Q-switched High energy Nd:YAG Laser (QUANTA RAY MODEL LAB-170-10) was used in the present study. An incident wavelength of light 1064 nm was allowed to fall on the samples. The emission of green light with wavelength 532 nm confirms both the pure and urea nitrate doped crystal possess NON LINEAR OPTICAL property.

IV. CONCLUSION

TGS salt and the dopant urea nitrate was synthesized. Well faceted, highly transparent, good quality pure triglycine sulphate single crystal and urea nitrate doped TGS crystals could be grown. In the urea nitrate doped TGS single crystal, a change in morphology is observed and may be due to the effect of the dopant during the crystallization process. XRD studies reveal the monoclinic structure of the pure and doped crystals. FTIR spectra confirms the incorporation of the dopant qualitatively. EDAX study reveals that an increased in atomic weight

percentage and weight percentage of both carbon and nitrogen atoms and may be due to the presence of urea nitrate in the doped triglycine sulphate single crystals. Microphotograph of the pure TGS shows the smooth surface but hillocks are present in the urea nitrate doped single crystals. Investigation shows that the pure and urea doped TGS shows NON LINEAR OPTICAL property.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

- [1]. B. T. Mathias, G. E. Miller, and I. P. Remeika, *phys. Rev.* 104, 1849(1956).
- [2]. S. Hoshino, Yokaya and R. Pepinsky, *phys. Rev.*;115, 323(1959).
- [3]. K. B. Ashok, D. A. Mohan and B. L. Ravindra, "Growth and characterization of doped DTGS crystal for infrared sensing devices', "materials letters , vol. 57, No 24-25, pp 3943-3945 2003.
- [4]. Wood. E. A. , Holden, A. N. *Acta crystallogra.* 10, 145(1957).
- [5]. Gaffai. M. A. , Al-Fadl. A. A. , Mansour. S. A. , *J. Phys. D:Appl. phys.* 34(7), 915(1999).
- [6]. C. S. Fang. Yao Xi, A. S. Bhalla and L. E. Cross, *Ferroelectrics*, 51, 669(1983).
- [7]. H. Ishida and K. Imai, *Ferroelectrics*, 106, 315(1990).
- [8]. S. Aravazhi, R. Jayavel, C. Subramanian *material chemistry and physics* 50, 233-237 (1997).
- [9]. Novotn J, Brezina B &Zelinka J, *J crysl Res & technol*, 39, 1089(2004).
- [10]. Meera K, Muralidharan R, Tripathi A K & Ramasamy P, *J Mater Lett*, 55, 394 (2002), *J Crystal Growth*, 263, 524 (2004).
- [11]. Bharthasarathi T, Thakur O P & Murugakoothan P, *J physica B*, 405, 3945(2010).
- [12]. R. B. Lal and A. K. Bavtra, "Growth and properties of Triglycine sulphate (TGS)crystals:Review *Ferroelectrics*, Vol. 142 , PP. 51-82, 1993.
- [13]. Das H N & Podder J, *J. Therm Annal Calorim*, 110, 1107 (2012)
- [14]. Khanum F & Podder J *Inter J of optics Article ID 803797*, pages(2012)
- [15]. R. Muralidharan, R. Mohankumar, P. M. Ushasree, R. Jayavel and P. Ramasamy, "Growth and characterization of zinc thiourea", *Journal of crystal growth*, vol. 234, pp545-550, 2002.
- [16]. Sinha N, Goel N, Singh B K, Gupta M K, Kumar B, *J solid state chem.* , 190, 180(2012).
- [17]. Hottenhuis, M. H. J. and A. Oudenampsen 1988. *J. Crysl. Growth* , P 513, vol 92.
- [18]. Dunning, W. J. and N. Albon P 411 (1958) *In:Growth perfection of crystals* Wiley, NewYork. (R. H. Doremin, B. N. Roberts and D. Turnbull. eds).
- [19]. Dunning, W. J. , R. W. Jackson and D. G. Mead p. 303, (1965) *In Adsorption et crossance crystalline* R. Kern, ed, CNRS, Paris.
- [20]. Hottenhuis, M. H. J. and C. B. Lucasius (1986)*J. Crysl. Growth* vol 78, P379.
- [21]. A. A. chernov *modern crystallographyIII. crystal growth.* Springer ser. sol. st. vol. 36. Springer 1984.
- [22]. JCPDS DATA.
- [23]. "Infrared spectral interpretation a systematic Approach" Brain C Smith, CRC press LLC, Boca Raton, London, NewYork, Washington. D. C(1999).