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Growth and structural, spectral, optical characterization of pure, ammonium dihydrogen phosphate (ADP) and tartaric acid doped triglycine sulphate (TGS) single crystals

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Abstract: Ferroelectric crystals are interesting class of materials. They are similar to ferromagnetic materials in that, they exhibit hysteresis loops, spontaneous polarization and coercive field. Ferroelectric crystals have a number of practical applications and one of those is a pyroelectric infrared (PIR) detection. PIR devices can detect a person moving into or through a detection zone with high reliability. The slightest positive or negative thermal radiation change in contrast to a background, focused by the appropriate optics, triggers the sensor element. There is no interference between neighbouring units due to the passive nature of the detection principle. At the heart of every PIR detector is the pyroelectric crystal. The detectors use materials, such as triglycine sulfate (TGS) or lithium tantalite.In the present work, ADP and tartaric acid were employed as dopants. The grown crystals were subjected to different characterization studies inorder to study the properties of the TGS crystal. The results are discussed in this paper.
Keywords: Growth and structural, spectral, optical characterization, ammonium dihydrogen phosphate (ADP), tartaric acid doped triglycine sulphate (TGS) single crystals.

Introduction

Among ferroelectrics, triglycine sulfate (TGS) crystal is an interesting ferroelectric material which shows a ferroelectric transition at ambient temperatures (49°C). It is a useful pyroelectric material in the fabrication of infrared detectors and pyroelectric vidicon tubes operating at room temperature[1-3]. It also finds applications in the fabrication of capacitors, transducers and sensors. TGS crystal shows a typical second order ferroelectric phase transition at the Curie point. Below the T_c, TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization (*Ps*) arises along the b-axis and above T_c, it possesses the non-polar point group 2/*m* of the monoclinic system[4, 5]. It is observed by many researchers that undoped TGS crystals have some disadvantages over doped TGS crystals such as (i) the ferroelectric domains possess high mobility at room temperature, therefore it is necessary to stabilise domains, (ii) easy depolarization by electrical, mechanical and thermal means, (iii) microbial contamination with time during the growth and (iv) low Curie point etc[2,6-8].In order to overcome these disadvantages, variety of dopants such as amino acids, organic and inorganic compounds have been introduced in TGS crystals to achieve effective internal bias to stabilize the domains and to obtain the desired pyroelectric and ferroelectric properties.

The crystal structure of TGS crystal is presented in Figure 1. It consists of SO_4^{2-}, 2($N^+H_3CH_2$ COOH) (G1 and G2 in the crystal-structure diagram), and $N^+H_3CH_2COO^-$(G3) species held together by hydrogen bonds. These bonds are easily broken by the polar molecules of water that explains the hygroscopicity of TGS. Along the *b*-axis, the G1-SO_4 and G2-G3 layers are stacked alternately. The nearest two neighboring layers with identical chemical composition are rotated 180° around the *b*-axis against each other. The structure of the ferro electric phase of triglycine sulfate has been refined from neutron diffraction data by Kay et al [9]. The hydrogen bonding scheme proposed by Hoshino et al.,[10] has been confirmed.

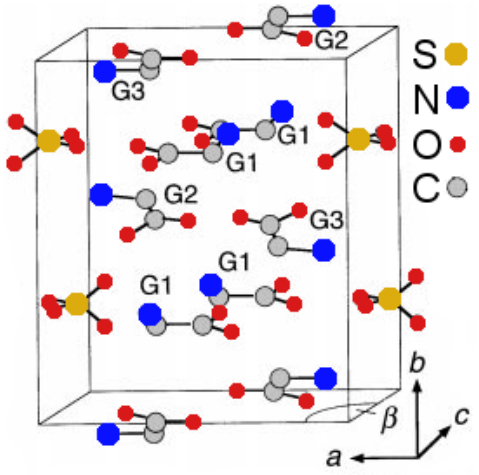


Figure 1 Structure of Triglycine sulphate crystal

The short hydrogen bond between glycine II and glycinium III that has been postulated to cause the transition has been found to have an O-O distance of 2.50 Å with the hydrogen atom 1.1 Å from the glycinium III ion. The glycinium I ion contains an ammonium group which moves about 1 Å in the transition. This group is 0.4 Å out of the plane of the carboxyl group.

Many researchers have introduced dopants to pure TGS and studied the properties of the crystal. Theresita Shanti et al.[11,12] have grown TGS crystals, with sodium bromide (NaBr) and sodium chloride (NaCl) as dopants. It was found that the addition of dopants increases the mechanical hardness of TGS crystals. Gaffar et al.[13] have studied the effect of divalent and trivalent ions on the dielectric constant and A.C. Conductivity of TGS crystals. A change in the dielectric constant and A.C. Conductivity were observed due to the presence of dopants.Ashish Nautiyal et al.[14] have used Green's function method and have made a theoretical study of the dielectric permittivity, acoustic attenuation, ratio of figure of merits and electric conductivity of TGS crystals without external D.C biasing. Balasubramnian et al.[15] have grown pure and copper sulphate doped TGS crystals. The mechanical properties of the crystals are increased due to the addition of dopants. It was also observed that there was no change in the dielectric parameters on doping. Stadnyk et al.[6] studied the effect of uniaxial pressure on the birefringence of TGS crystals with L-valine as admixture. It was established that the introduction of L-valine admixture results in the weakening of the temperature dependence of the birefringence of TGS crystals.

Doping with different amino acids such as L-alanine was carried out to improve the ferroelectric properties of TGS[17]. Ammonium dihydrogen phosphate (ADP) and L-tartaric acid are excellent nonlinear optical materials. ADP is a transparent crystal and is used widely in applications such as second harmonic generation, frequency mixing etc. It is an antiferroelectric crystal. L-tartaric acid crystals have large optical susceptibilities, inherent ultrafast response times and high optical thresholds for laser power[18, 19]. In the present work, ADP and tartaric acid were employed as dopants. The grown crystals were subjected to different characterization studies inorder to study the properties of the TGS crystal.

Experimental

Triglycine sulphate was synthesized from glycine and sulphuric acid in the molar ratio 3:1. The solvent used was water. 2.66 ml of sulphuric acid was diluted with 50 ml of double distilled water and 11.25 g of glycine was dissolved in the diluted solution. Glycine reacts with sulphuric acid according to the following reaction:

$3(NH_2CH_2\text{-}COOH) + H_2SO_4 \rightarrow [(NH_2CH_2\text{-}COOH)_3 .H_2SO_4]$

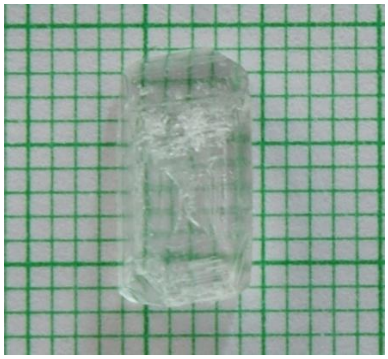
A saturated solution of TGS was prepared at 40°C. The solution was kept in a petri dish for a period of seven days. The TGS crystals were recrystallised many times to minimize the impurity content. Normally, recrystallization process tends to minimize the defects and impurities. A saturated solution was prepared from the recrystallised TGS salt. The solution was then filtered. The filtered solution was kept in a constant temperature bath of high accuracy. Fine seed crystals were obtained over an period of 10 days. These seed crystals were harvested into crystals by keeping in the mother solution over a period of 25 days. In the case of ADP doped TGS crystals, the saturated solution of TGS was first prepared. To this solution, 1% ADP was added as dopant. The seed crystals were obtained over a period of seven days and were kept in the parent solution to get good quality crystals. In the case of L-tartaric acid doped TGS crystals, the same procedure was followed. The prepared solutions were kept in a constant temperature bath set at 40 °C. Crystals of optimum size of pure, ADP and L-tartaric acid doped TGS crystals were obtained. The photographs of the as grown crystals of pure, ADP doped and L-tartaric acid doped TGS crystals are shown in Figure 2 (a) - 2 (c) respectively.

Results and Discussion

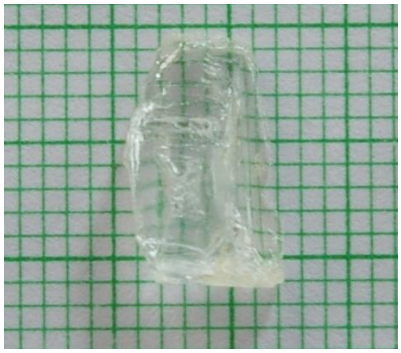
Single X-ray diffraction studies

The grown crystals of pure and doped TGS were subjected to single crystal XRD studies using single crystal X-ray diffractometer with MoK_α (λ = 0.7107 Å) radiation. The structure was solved by the direct method and refined by the full matrix least-squares technique using the SHELXL program.

The lattice parameters and the cell volume of the pure and doped TGS crystals are presented in Table 1. It is observed from the X-ray diffraction data that both pure and doped TGS crystals belong to monoclinic system. The lattice parameters of pure TGS are in agreement with the reported values by Theresita et al[11, 12]. In the case of doped TGS crystals, slight variations in the values of lattice parameters and cell volume are observed. It implies that the dopants, ADP and L-tartaric acid have been incorporated to the lattice of TGS crystals.



(a)



(b)

(c)

Figure 2 Photographs of as grown (a) pure (b) ADP doped and (c) L-tartaric acid doped TGS crystals

Table 1 Lattice parameters and cell volume of pure and doped TGS crystals

Crystal	*a* (Å)	*b* (Å)	*c* (Å)	Cell volume (Å^3)
TGS	9.15	12.64	5.72	638.26
ADP doped TGS	9.16	12.63	5.74	640.30
Tartaric acid doped TGS	9.15	12.58	5.74	638.10

FTIR Spectral Analyses

The FTIR spectra were recorded in the wave number region from 400 to 4000 cm^{-1} using KBr pellet technique. The spectra of pure and doped TGS crystals are presented in the Figure 3 (a)-3(c) respectively. The TGS crystals generally have a strong and broad absorption band in the range 2380 cm^{-1}-3800 cm^{-1} due to the OH stretching and NH_3^+symmetric stretching [20]. The very strong absorption band in the region 3161 cm^{-1} is assigned to NH stretching mode and OH stretching of COOH. The weak bands at 2532 cm^{-1} and 2393 cm^{-1} corresponds to CH_2 stretching vibrations. The strong bands at 1865 cm^{-1} and 1707 cm^{-1} are attributed to NH_3^+ asymmetric bending vibrations. There is a strong narrow band at 1618 cm^{-1}. This band is assigned to C=O stretching of COOH which indicates the presence of glycine molecule as glycinium ion[21]. The very strong peak at 1503 cm^{-1} corresponds to NH_3^+ symmetric bending. The peak at 1426 cm^{-1} is attributed to NH internal bending and NH_3^+ symmetric bending. The CH_2 bending vibrations is assigned to the peak at 1567 cm^{-1}. The very strong peaks at 1306 cm^{-1} and 1085 cm^{-1} correspond to asymmetric and symmetric S=O stretching respectively. The CN asymmetric vibrations are assigned to the peak at 1131 cm^{-1}.The characteristic SO_4 vibrations of TGS are attributed to the peaks at 1019 cm^{-1} and 1051 cm^{-1}.The peaks between at 665 cm^{-1} and 572 cm^{-1} corresponds to NH_3^+ torsional oscillations and are consistent with the literature[22].

Since the percentage of addition of dopants is very less, there is less variation in the FTIR spectra of pure, ADP and L-tartaric acid doped TGS crystals. However the characteristic bands of ADP and L-tartaric acid are found to overlap with the vibrational bands of TGS crystals. The combination of C=O stretching and OH bending bands generally occur in the wave number range 1425-1440 cm^{-1} for pure L-tartaric acid crystals[19]. In the present work, this is attributed to the peak at 1426 cm^{-1}. Similarly, a strong characteristic peak at 977 cm^{-1} is assigned to OH out of plane bending vibrations of L-tartaric acid. The characteristic bands of ADP such as P–OH and PO_4 vibrations are attributed to the peaks at 1085 cm^{-1}, 572 cm^{-1} and 460 cm^{-1}. Since the percentage of dopants is less, the spectra for pure and doped TGS crystals are similar in nature. The band assignments for pure TGS crystals are in good match with the already available literature values[8] and are presented in Table 2.

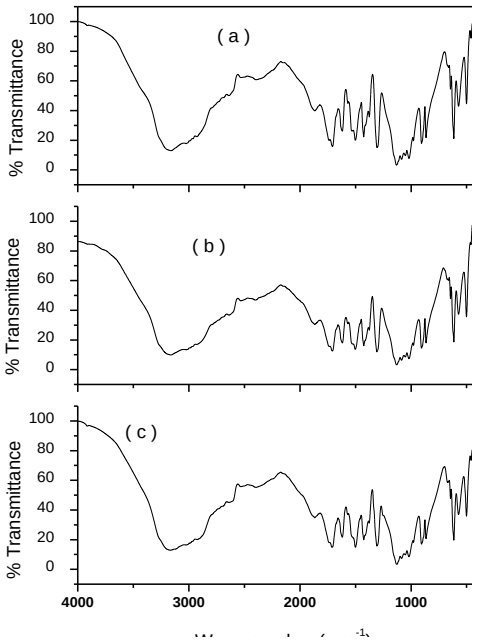


Figure 3 FTIR Spectra of (a) pure (b) ADP doped (c) L-tartaric acid doped TGS crystals

Table 2 Vibrational Band Assignments for pure and doped TGS crystals

Wave number (cm^{-1})			Vibrational Band Assignments
Pure TGS	**ADP doped TGS**	**Tartaric doped TGS**	
3161 (vs)	3166 (vs)	3163 (vs)	NH_3^+ symmetric stretching/OH stretching
2532 (w)	2533 (w)	2532 (w)	CH_2 stretching
2393 (w)	2394 (w)	2398 (w)	CH_2 stretching
1865 (s)	1867 (s)	1867 (s)	NH_3^+ asymmetric bending
1707 (vs)	1708 (vs)	1707 (vs)	NH_3^+ asymmetric bending
1618 (s)	1618 (s)	1618 (s)	C= O stretching of COOH
1567 (m)	1567 (m)	1568 (s)	CH_2 bending
1503 (vs)	1500 (vs)	1504 (vs)	NH_3^+ asymmetric bending
1426 (s)	1425 (s)	1425 (s)	Combination of NH internal bending and NH_3 symmetric bending/ Combination of C=O stretching and OH bending bands
1376 (s)	1376 (s)	1376 (s)	CO_2 symmetric Stretching
1306 (vs)	1307 (vs)	1307 (vs)	asymmetric S=O stretching
1131 (vs)	1128 (vs)	1130 (vs)	CN asymetric stretching
1085 (vs)	1085 (vs)	1085 (vs)	symmetric S=O stretching/ P – OH vibrations
1051 (vs)	1051 (vs)	1051 (vs)	SO_4 vibrations
1019 (vs)	1019 (vs)	1019 (vs)	SO_4 vibrations
977 (vs)	977 (vs)	977 (vs)	C – C stretching/OH out of plane bending vibrations
906 (vs)	906 (vs)	906 (vs)	C – C stretching
864 (vs)	864 (vs)	864 (vs)	C – C stretching
662 (w)	662 (w)	665 (w)	NH_3^+ torsional oscillations
645 (m)	645 (m)	645 (m)	NH_3^+ torsional oscillations
614 (vs)	614 (vs)	614 (vs)	NH_3^+ torsional oscillations
572 (m)	572 (m)	572 (m)	NH_3^+ torsional oscillations / PO_4 Vibrations
500 (m)	500 (m)	500 (m)	CO_2 bending
460 (vw)	459 (vw)	460 (vw)	PO_4 Vibrations

Optical studies

The UV-Vis spectra gives information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in sigma and pi orbital from the ground state to the higher energy states. An NLO material can be widely used if it has a wide transparency range. The optical absorption spectra were recorded from 200 nm to 800 nm for the pure and doped TGS crystals and are presented in Figure 3 (a)-(c) respectively.

From the spectra, it is found that the cut off wavelength for the pure and doped crystals are around 230 - 240 nm and the maximum transmission levels are in the wavelength range 250 - 800 nm which are most desirable characteristic of a NLO material for applications. As there is no absorption in the visible region, these crystals are suitable for NLO applications. The cut off wavelengths and the transmission levels are in good agreement with the reported values[11, 12].

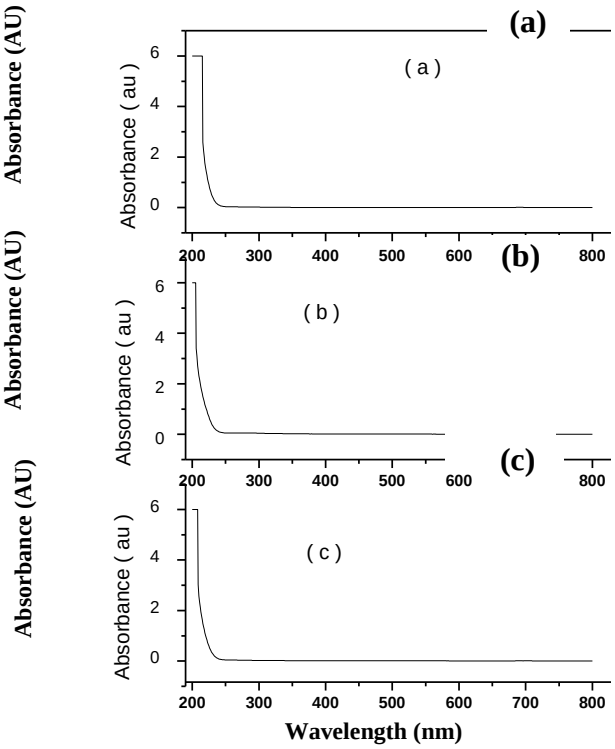


Figure 4 UV Spectra of (a) pure (b) ADP doped and (c) L-tartaric acid doped TGS crystals

Conclusion

Crystals of pure, ADP and tartaric acid doped TGS have been obtained by slow solvent evaporation technique. Its lattice parameters have been found from single crystal XRD analysis. The XRD studies indicate the incorporation of dopants in the lattice.The optical behaviour is assessed by UV-Visible studies and it indicates the crystals have transmission in the visible region. The FTIR studies indicates the presence of different functional groups in the crystals.

References

1. Itoh, K., and Mitsui, T., Studies of the Crystal structure of Triglycine Sulfate in connection with its Ferroelectric Phase Transition, Ferroelectrics, 1973, 5, 235-251.
2. Ashok K.B., Mohan D.A., and Ravindra B.L., Growth and characterization of Doped DTGS crystals for Infra-red sensing device, Materials Letters, 2003, 57, 24-25.
3. Berbacaru C., Alexandru H.V., Pintilie L., Dutu, A., Logofatu B., and Radulescu R.C., Doped versus Pure TGS Crystals, Materials Science and Engineering, 2005, 118, 141-146.
4. Wood E.A., and Holder A.N., Monoclinic Glycine Sulfate: Crystallographic Data, Acta Crystallographica, 1957, 10,145-146.
5. Hofmann G., Neumann N., and Budzier, H., Pyroelectric Single – element detectors and arrays based on modified TGS, Ferroelectrics, 1992,133, 41-45.
6. Fang C.S., Liu, H., Zhuo H.S., Wang M., and Xu D, A new modified TGS crystal, Cryst. Res. Tech., 1998, 30, 785-789.
7. Abu El-Fadl A., Effect of divalent ions doping on the absorption spectra parameters of triglycine sulphate crystals, Journal of Physics and Chemistry of Solids, 1999, 60, 1881-1893.
8. Raghavan C.M., Sankar R., Mohan Kumar R. and Jayavel R., Effect of amino acid doping on the growth and ferroelectric properties of triglycine sulphate single crystals, Materials Research Bulletin, 2008, 43, 305-311.
9. Kay M.I., and Klienberg R., The Crystal Structure of Triglycine Sulfate, Ferroelectrics, 1973, 5(1), 45-52.
10. Hoshino S., Okaya Y., and Pepinsky R., Crystal Structure of the Ferroelectric Phase of Triglycine Sulphate, Physical Review, 1959, 115, 323-330.

11. Theresita Shanthi N., Selvarajan P.,and Mahadevan C.K., Studies on Triglycine Sulphate crystals doped with sodium bromide grown by solution method, Indian Journal of Science and Technology, 2009, 2(3), 49-52.
12. Theresita Shanthi N., Selvarajan P., and Mahadevan C.K.,Growth, structural, mechanical, spectral and dielectric characterization of NaCl-added Triglycine sulfate single crystals, Current Applied Physics,2009, 9**,** 1155-1159.
13. Gaffar M.A., Al-Houty L.I., Al-Muraikhi M. and Mohamed, A.A., The effect of doping crystals of TGS with some Di- and Trivalent ions on its dielectric constant and A.C.Conductivity, Qatar Univ. Sci. Bull.,1987, **7**, 39-53.
14. Ashish Nautiyal and Upadhyay T.C., Dielectric, Acoustic, Thermal and electric behavior of Triglycine Sulphate Crystal by Mathematical Method, 2nd International Conference on Chemistry and Chemical Engineering,2003, 14, 165-173.
15. Balasubramaniam K., and Selvarajan P.,Studies on growth and various properties of Triglycine sulfate crystals doped with copper sulphate, Recent Research in Science and Technology,2010, 2**,** 6-13.
16. Yo V., Stadnyk, Yu.I.Kiryk, and Matviishyn, I.M.,Effect of Uniaxial pressure on birefringence of Triglycine Sulfate crystals with L- Valine admixture, Ukr. Journal of Physics, 2010, 55(4), 431-433.
17. Ravi G., Arunmozhi G., Aravazhi S., Anbukumar S., and Ramasamy P., Studies of some amino acids mixed Triglycine Sulphate crystals, Proceedings of the 4th International Conference on Properties and Applications of Dielectric Materials,1994,247-249.
18. Rode M.N., Muley G.G., Meshram D.V., Hussaini S.S., Dongre V.G., Pawar B.H., and Shirsat M.D,Growth and characterization of L-tartaric acid doped and mixed di-sodium hydrogen phosphate single crystal for laser applications, Optoelectronics and Advanced Materials - Rapid Communications, 2009, 3(9), 927-932.
19. Suresh S., and Arivuoli D., Growth, Theoretical, Optical and Dielectric Properties of L-Tartaric acid NLO single crystals, Journal of Optoelectronics and Biomedical Materials, 2011, 3(3), 63-68.
20. Farhana Khanum., and Jiban Podder., Synthesis, Growth and Electrical Transport Properties of Pure and $LiSO_4$ Doped Triglycine Sulphate Crystal, Journal of Crystallization process and Technology,2008, 1, 26-31.
21. Farhana Khanum., and Jiban Podder., Crystallization and Characterization of Triglycine Sulfate single crystals doped with Nickel Sulphate , Journal of Crystallization process an d Technology, 2011, 1, 49-54.
22. Krishna Kumar V., Rajaboopathi M., and Nagalakshmi R., Magnesium Chloride added triglycine sulphate crystals, Advanced Materials Letters, 2011, 2(2), 63-169.

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