Dielectric, Mechanical properties and Raman Analysis of TGS-ADP Mixed crystals

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Abstract : TGS was synthesized by taking the AR grade Glycine (CH_2NH_2COOH) and concentrated Sulphuric acid (H_2SO_4) in the molar ratio 3:1 respectively. The synthesized pure TGS is mixed with ADP in the molar ratio (9:1), (8:2), (7:3) and the crystals were grown from aqueous solution by slow evaporation method at room temperature. The grown crystals are subjected to Dielectric studies using a LCR meter. The Dielectric study confirms the contribution of space charge polarization. Vickers micro hardness measurement of the grown crystals reveals that hardness increases with load. The log p versus log d were plotted and work hardening co-efficient or Meyer indices (n) is determined. The functional groups are identified by Raman analysis.

Keywords : Crystal growth, Raman Analysis, Mechanical and Dielectric properties.

Introduction

Triglycine Sulphate crystals have technological importance for room-temperature infrared detectors, earth exploration, radiation monitoring and astronomical telescopes. TGS undergoes a second-order ferroelectric phase transition at Curie temperature $T_C = 49^0C$, ferroelectric and pyroelectric materials are polar and possess a spontaneous Polarization. However, this polarity can be reversed through the application of an electric field with ferroelectric materials [1-4]. They are similar to ferromagnetic materials in that they exhibit hysteresis loops. This material has found application in the fabrication and development of infrared detectors due to its high pyroelectric coefficient (p), reasonably low dielectric constant and best figure-of-merit. TGS crystals have been focused in various aspects such as growth rate, structural modification, pyroelectric, mechanical, optical and ferroelectric properties. Also the crystals are of particular interest for the photo induced nonlinear optical effects. TGS has a tendency to depole, which can be prevented by suitably mixing optically active molecules in the glycine site of TGS.

This paper describes the crystal growth, Dielectric studies, Mechanical properties and Raman analysis of Triglycinesulphate (TGS) mixed with Ammoniumdihydrogen Orthophosphate (ADP) in the molar ratio 9:1, 8:2 and 7:3 grown by slow evaporation method. The effects of mixing ADP crystals on the quality and performance of the crystals are analyzed. The results of the TGS mixed with ADP crystals are compared with the pure TGS crystals.

Experimental

Synthesis and Crystal Growth

Triglycine sulfate (TGS) was synthesized by taking glycine and sulfuric acid in the molar ratio 3:1.

$3(NH_2CH_2COOH)+H_2SO_4$ ➔

$(NH_2CH_2COOH)_3.H_2SO_4$
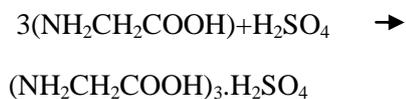
The required amount of sulfuric acid was diluted with triple distilled water. Then the calculated amount of glycine was added and dissolved in dilute H_2SO_4. The solution was heated until the salt crystallized. Extreme care was taken during crystallization to avoid the oxidation of glycine. The synthesized pure TGS is mixed with AR Grade Ammonium dihydrogen Orthophosphate (ADP) in the molar ratio (9:1), (8:2) and (7:3) separately in the triple distilled water with continuous stirring of 3-4 hours using magnetic stirrer.

Figure 1. Photograph of Pure TGS single crystals

Figure2.Photograph of TGS:ADP(9:1)single crystals

The completely dissolved solution was filtered using micro filter. The solution was allowed to evaporate at room temperature.

Optically good quality large-size single crystals were obtained in a period of 30 days. All the grown crystals were found to be very stable and transparent. The grown crystals are shown in the figure 1- 4.

Figure 3. Photograph of TGS:ADP(8:2)single crystals
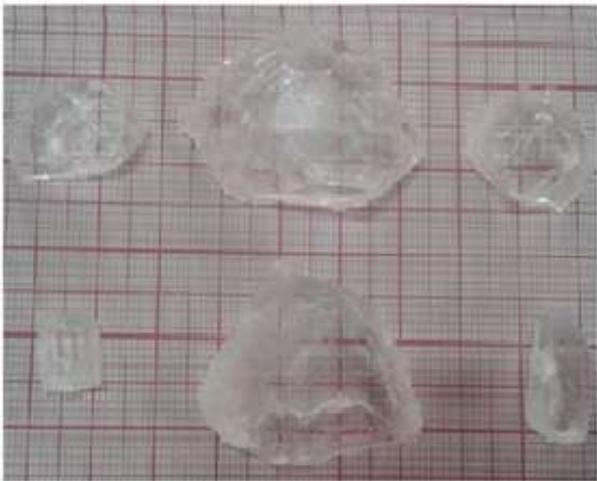
Figure 4. Photograph of TGS:ADP(7:3)single crystals

Results and discussion

Dielectric studies

Suitably cut and polished crystals section of pure and TGS mixed ADP in the molar ratio 9:1, 8:2 and 7:3 crystals was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε) and dielectric loss (tanδ) were calculated using the relations (1) & (2)

$$\varepsilon = \frac{Cd}{A\varepsilon_o} \text{----------- (1)}$$

$$\tan\delta = D\varepsilon \quad \text{------------ (2)}$$

where C is the capacitance of the sample, d the thickness of the sample, A the area of the face in contact with the electrode and ε_o the permittivity of free space.
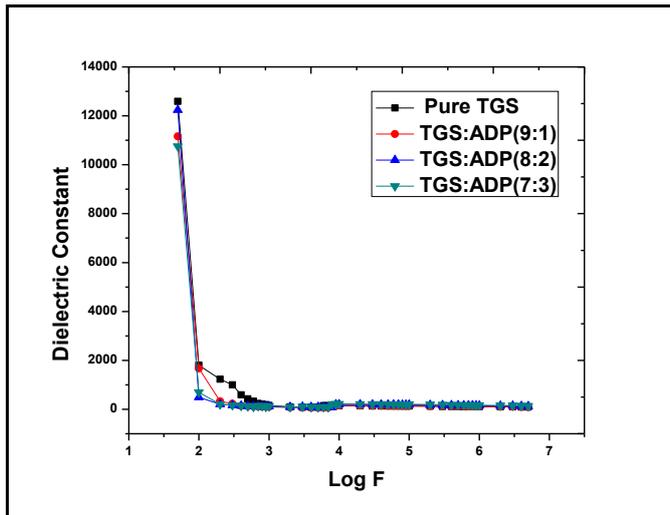
Figure 5. Variation of dielectric constant with log frequency for grown crystals

The variations of dielectric constant (ε) and dielectric loss (tanδ) at room temperature for pure TGS and TGS mixed ADP in the molar ratio 9:1, 8:2 and 7:3 crystals are shown in Figure 5 and 6. It is observed that the dielectric constant (ε) decreases with the increase in the frequency. The dielectric constant of a material is generally composed of four types of contributions, ionic, electronic, orientational and space charge polarizations. At low frequencies all polarizabilities are operative hence ε is high. As frequency increases one polarization mechanism after another is frozen out. The first to stop contribution to ε is orientational component, then the ionic and lastly the electronic.

It is seen that a.c. conductivity is governed by the presence of a small number of free charges which result in small leakage or conduction currents and by the displacement of bound charges that give rise to polarization or displacement currents in the solid state dielectrics whereas in the d.c. conductivity there is no contribution from localized charges.
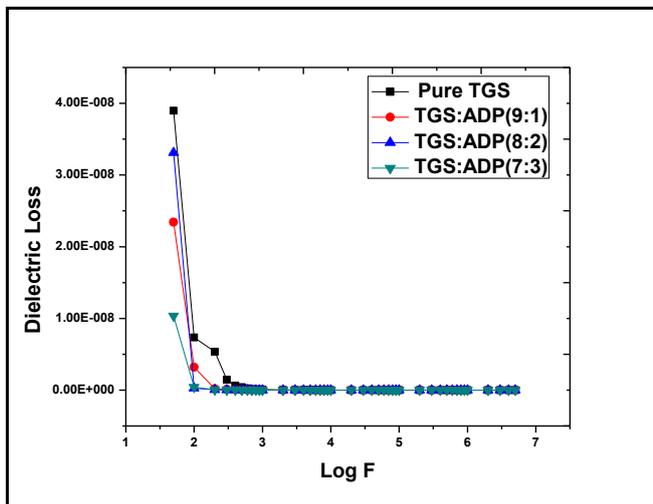
Figure 6. Variation of dielectric loss with log frequency for grown crystals

Further ionic conduction plays a major role at higher temperatures for both a.c and d.c conductivity because at higher temperatures some ions detach from the sites of crystal lattices [5]. At low frequency space charge polarization is dominant mechanism in the transport processes which is absent at high frequencies. The space charge polarization decreases with increase in frequency due to inertia of the ions to follow the variation infield. The variation in resistivity and conductivity with thefrequency for the grown crystals are shown in Figure 7 & 8. The a.c resistivity and a.c conductivity were calculated using the relation (3 & 4)

$$\rho = \frac{A}{2\pi fCd} \ \text{------------------ (3)}$$

$$\sigma\rho = \frac{1}{\rho} \qquad \text{---------- (4)}$$

Where C is the capacitance, d is the thickness, A is the area of the crystal and f is the frequency of the applied field. It is observed that a.c resistivity decreases rapidly as frequency increases. Obviously reverse trend was observed for a.c conductivity of the grown crystals which is considered to be a normal dielectric behavior [6].
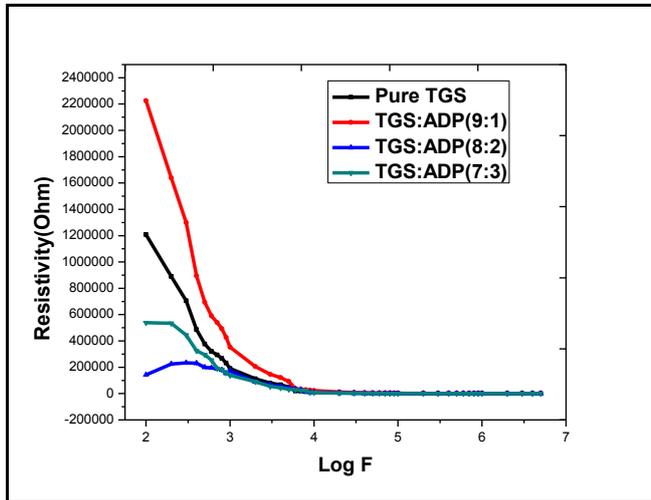
Figure 7. Variation of AC resistivity with log frequency for grown crystals
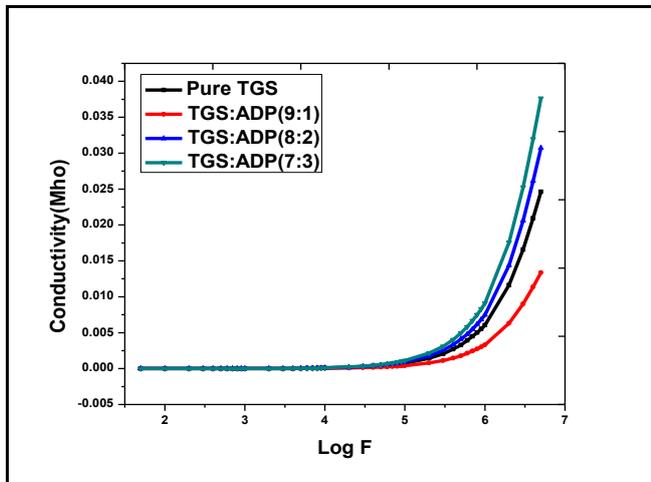
Figure 8. Variation of AC conductivity with log frequency for grown crystals

Ramananalysis

The Raman spectra of grown crystals were recorded for (101) planes at room temperature in the wave number range of 200 to 2000 cm-1. Raman spectra in the range of 200 to 2000 cm-1 is shown in Figure 9. The spectra of pure TGS, TGS:ADP (9:1), TGS:ADP (8:2) and TGS:ADP (7:3) crystals contain the internal modes of vibrations at 974 cm^{-1} (ν1), 575 cm^{-1} (ν2), 663 cm^{-1} (ν3), 868 cm^{-1} (ν4), 890cm^{-1} (ν5), 1309cm^{-1} (ν6), 1435cm^{-1} (ν7), and 1605 cm^{-1} (ν8). The peaks with very small intensity are corresponding to the lattice vibrations of crystals through the absorption or emission of optical phonons. The Phonon life time (τ) can be deduced from the Raman scattering by using energy time uncertainty relation (5)

$$\frac{1}{\tau} = \frac{\Delta E}{h/2\pi} = 2\pi\Gamma \qquad \text{---------- (5)}$$

where ΔE is the uncertainty in the energy of the phonon mode, h/2π is the Planck constant, and Γ is the FWHM of the Raman modes in cm^{-1}. The phonon life time is a combination of two characteristic decay time such as an harmonic decay of the phonon into two or more phonons so that energy and momentum are conserved (τ_A) and perturbation of translational symmetry of the crystals due to the presence of impurities, defects and isotropic fluctuations (τ_1). So the calculated phonon life time is an addition of two characteristic decay time

$$\left(\frac{1}{\tau} = \frac{1}{\tau a} + \frac{1}{\tau 1}\right).$$

The calculated phonon life time values and the vibrational frequencies corresponding to the band assignments of pure TGS and TGS: ADP mixed crystals are listed in Table 1.

Table 1. Phonon life time and symmetry of grown crystals

Reference (cm^{-1})	FWHM (Γ) cm^{-1}	Phonon life time (τ) μs	Symmetry
575	22.17	71.78	PO$_4$ Stretching
619	23.77	66.95	PO$_4$ Stretching
663	24.67	64.51	PO$_4$ Stretching
863	12.27	129.71	P-OH deformation/K-O Stretching
890	19.21	82.85	HO-P-OH bending
974	18.42	86.40	O=P-OH bending
1037	19.41	81.99	P-O-H symmetric stretching
1108	26.23	60.67	P-O-H symmetric stretching
1309	33.23	47.89	CH$_2$ bending, P=O symmetric stretching
1409	16.68	95.41	O-H Stretching
1435	13.60	117.03	O-H Stretching
1605	25.78	61.73	O-P-OH symmetric stretching
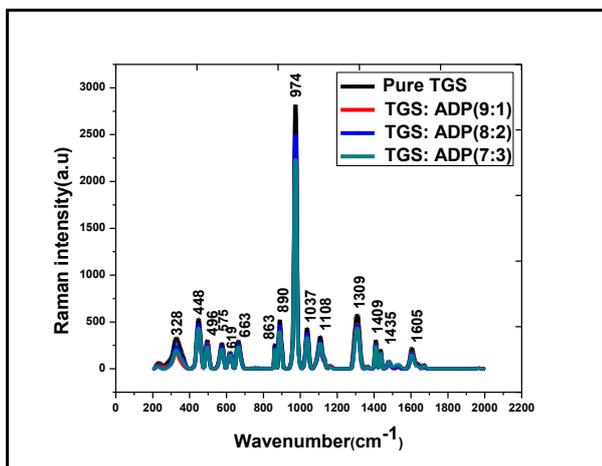
Figure 9.FT-RamanSpectrumof grown crystals

Micro hardness studies

Hardness of a crystal is due to the resistance offered by a solid to the movement of dislocation, practically which is caused by scratching or indentation [7,8]. Due to the application of mechanical stress by the indenter, dislocations are generally at the region of the indentation. Higher hardness value for the grown crystal indicates that more stress is required to form dislocation thus confirming the crystalline perfection. Vickers hardness studies have been carried out using Future Tech Micro hardness tester FM-800. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. The grown crystals of

pure and TGS:ADP mixed crystals of different molar ratio was selected for micro hardness studies. Indentations were carried out using Vickers indenter for varying loads. For each load (p), several indentations were made and the average value of the diagonal length (d) was used to calculate the micro hardness of the crystals. Vickers micro hardness number was determined using the relation (6).

$$Hv = \frac{1.8544p}{d^2} \qquad \text{---------- (6)}$$

The load Vs. hardness values of pure and TGS:ADP mixed crystals of different molar ratio are shown in Figure 10. It is observed that hardness increases up to a load of 100g, above which cracks start developing which may be due to the release of internal stress generation with indentation. The addition of ADP to TGS crystal has enhanced the hardness of the crystal.
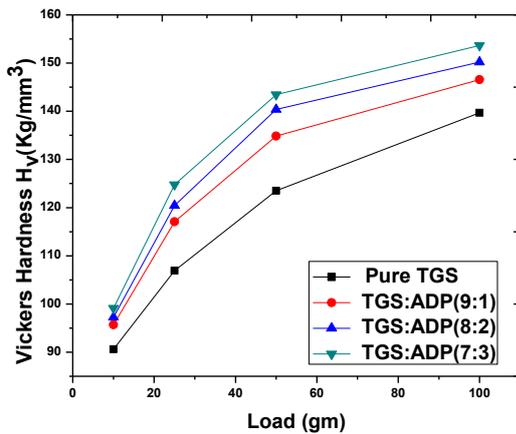
Figure 10. Plot of micro hardness study for grown crystals
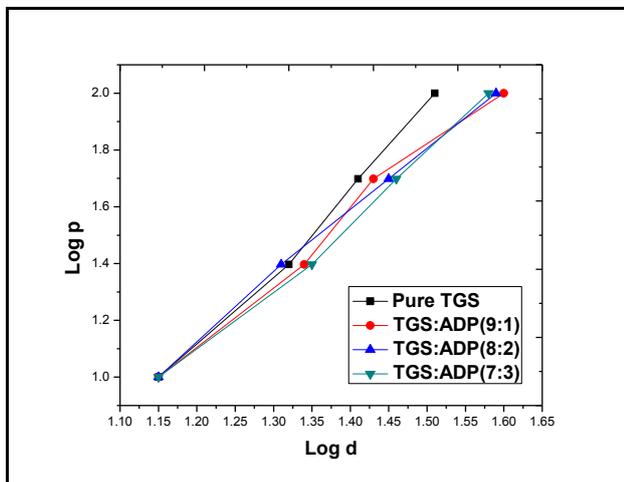
Figure 11. log p versus log d plot of grown crystals

The log P Vs. log d plots are also plotted and are shown in Figure 11. The plots are found to be nearly straight line. From the slope of the best fitted lines, the work hardening co-efficient or Meyer indices (n) were obtained and are given in Table 2. The Meyer's law [9] is expressed in relation (7).

$$P = K_1 d^n \qquad \text{--------- (7)}$$

Where K_1 is the material constant.

According to Onitsch and Hanneman 'n' should lie between 1.0 and 1.6 for hard material and above 1.6 for soft ones [9]. The 'n' values observed in the present study are more than 1.6. This indicates that all the grown crystals belong to soft material category.

Table 2. Work Hardening Co-efficient of grown crystals

Sample	Work Hardening Co-efficient (n)
Pure TGS	2.78
TGS:ADP (9:1)	2.26
TGS:ADP (8:2)	2.20
TGS:ADP (7:3)	2.33

Conclusion

Optically transparent good quality single crystals of pure TGS and TGS-ADP mixed in the molar ratio (9:1), (8:2) and (7:3) were grown by slow evaporation method from the mixtures of aqueous solution at room temperature. The presence of various functional groups was confirmed by Raman spectrum. The dielectric studies show that the grown crystal has low dielectric constant and low dielectric loss. From the micro hardness investigations made on the grown crystalline material, the crystal has maximum surface hardness and is soft material having low yield strength. As the crystal has low dielectric constant, dielectric loss, and maximum surface hardness implies that this crystal can be used as a potential material for optical applications.

Acknowledgements

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