© September 2023| IJIRT | Volume 10 Issue 4 | ISSN: 2349-6002

Triglycine Sulphate (TGS) Crystal mixed with Ammonium Dihydrogen Orthophosphate (ADP): Growth and its Characterization

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Abstract**— Triglycine sulphate (TGS) is a ferroelectric crystal. The ferroelectric crystals find important applications in optoelectronics, photonics and used in the fabrication of high sensitivity infrared detectors at room temperature. 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 Ammonium dihydrogen Orthophosphate (ADP) in the molar ratio (9:1), (8:2) and (7:3) and the crystals were grown from aqueous solution by slow evaporation method at room temperature. The chemical composition of the grown crystals is confirmed by Energy Dispersive X-ray Analysis (EDAX). The solubility of grown crystals is determined using water as a solvent. The solubility curve shows that the TGS-ADP mixed crystal has higher solubility than the pure TGS. The grown crystals were crushed to a uniform fine powder and subjected to XRD analysis. Appearance of sharp peaks confirms the good crystalline nature. Using Scherer's equation particle size has been calculated. The Second harmonic generation efficiency is determined by Kurtz powder technique. The KDP crystal is used as a reference material, it is found that the relative SHG conversion efficiency of the grown crystals is greater than KDP sample which indicates the suitability of crystals for various applications. Optical transmission spectra are recorded for the crystals in the wavelength region 200 to 1100 nm using Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The electronic band transitions is studied from the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) and the band gap energy has been calculated. The functional groups have been identified by Fourier Transform Infrared spectroscopy (FTIR). The experimental results evidence the suitability of the grown crystals for optoelectronic applications.**

Keywords**— Ferroelectric crystal, EDAX, Solubility, powder XRD, Second Harmonic Generation, UV-Vis, FTIR.**

I. 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 Solubility, crystal growth, structural, Optical, and SHG efficiency of Triglycine sulphate (TGS) - Ammonium dihydrogen Orthophosphate (ADP) mixed 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-ADP mixed crystals are compared with the pure TGS crystals.

II. EXPERIMENTAL

A. *Synthesis*

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.

B. *Crystal Growth*

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. The completely dissolved solution was filtered using micro filter. The solution was allowed to evaporate at room temperature. Triple distilled water was used as the solvent.

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.

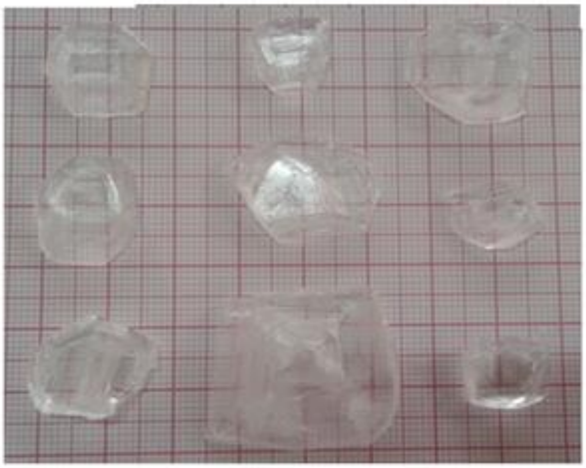

FIGURE 1. Photograph of as grown Pure TGS Single crystals

FIGURE 2. Photograph of as grown TGS mixed ADP (9:1) Single crystals

FIGURE 3. Photograph of as grown TGS mixed ADP (8:2) Single crystals

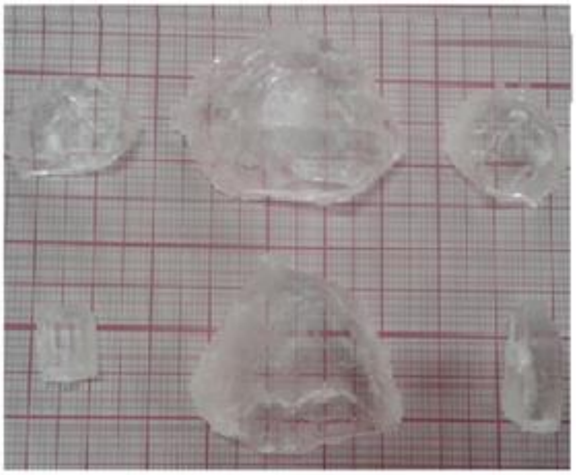

FIGURE 4. Photograph of as grown TGS mixed ADP (7:3) Single crystals

III. RESULTS AND DISCUSSION

A. *Energy Dispersive X-Ray Analysis (EDAX)*

In order to confirm the presence of ADP in pure TGS crystals, the sample of grown crystals were subjected to Energy Dispersive X-ray Analysis. Figures 5a-5c shows the EDAX data of TGS:ADP mixed crystals. From the EDAX and XRAD data, it is confirmed that the ADP has gone into the lattice of the TGS crystals.

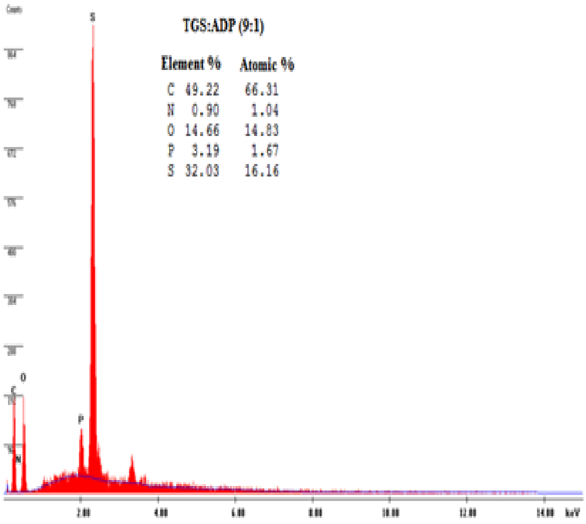

FIGURE 5a. EDAX Spectra of TGS:ADP (9:1) grown crystal

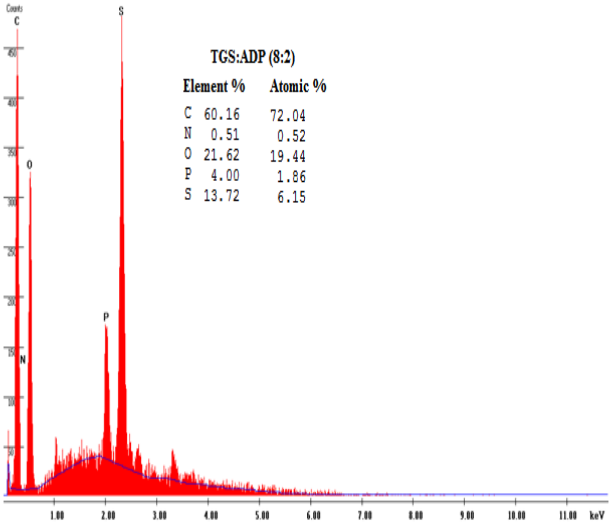

FIGURE 5b. EDAX Spectra of TGS:ADP (8:2) grown crystal

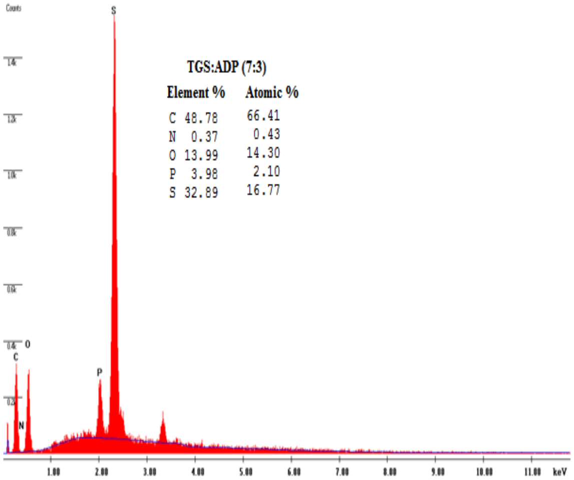

FIGURE 5c. EDAX Spectra of TGS:ADP (7:3) grown crystal

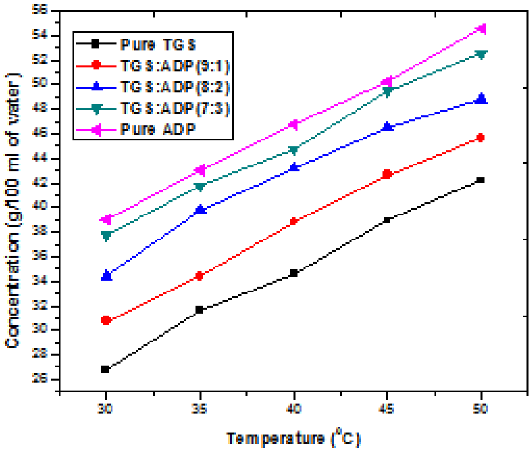

FIGURE 6. Solubility Curve of the grown crystals

B. Determination of Solubility

The Solubility studies were carried out in a constant temperature water bath (CTB). The solution was stirred continuously for 6 hours to achieve stabilization using an immersible magnetic stirrer. Solubility was determined by gravimetric analysis for different temperatures (30–50^0 C). The solubility curve of pure TGS, pure ADP, TGS mixed ADP is shown in Figure.6. It is observed from the solubility curve that the solubility of TGS mixed ADP increases with increase in the molar weight of ADP and with respect to pure TGS and pure ADP and has positive temperature co-efficient.

C. XRD Analysis

Good quality grown crystals were crushed to a uniform fine powder and subjected to XRD analysis using XrdwinPD 4-dectris computer based diffractometer with a characteristic Cu Kα (1.540598) radiations from 10^0 to 100^0 at a scan rate of 10^0/min. Appearance of sharp peaks confirms the good crystallinity of the grown samples. The observed values are in good agreement with the reported values [5-6]. The XRD spectra of pure TGS and ADP mixed TGS crystals are shown in Figure 7. Using Scherer's equation (D-S) particle size has been calculated and is given in the Table 1.

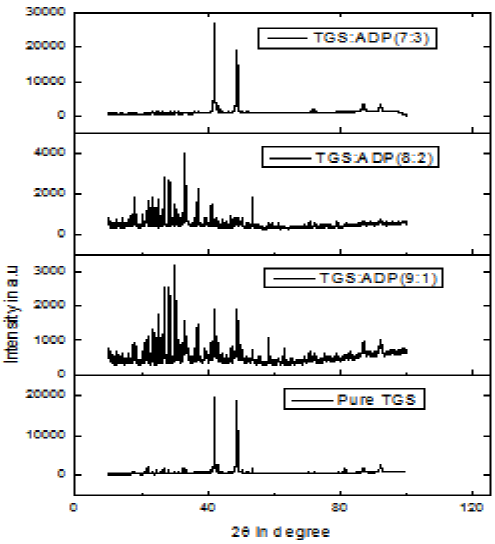

FIGURE 7. Powder X-ray diffraction patterns of grown crystals

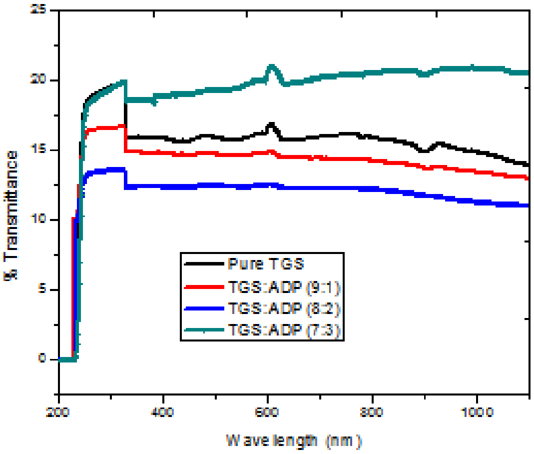

FIGURE 8. UV-Vis transmittance spectra of grown crystals

Good optical transmittance and lower cut off wavelength are very essential properties for nonlinear optical (NLO) crystals [7]. It is observed from the figure that the Pure TGS shows 19% of transmittance, TGS- ADP (9:1) shows 17% and TGS -ADP (7:3) shows 21% of transmittance. The large transmission in the entire visible region enables it to be a good material for electro-optic and NLO applications. The above results indicate that the addition of ADP to pure TGS increased the transmittance. The plot of $(\alpha h\nu)^2$ versus photon energy hν as shown in Figure 9. The wide optical band gap of TGS:ADP mixed crystals is found to be 5.4227eV, 5.3458eV and 5.1890eV for the molar ratio (9:1), (8:2) and (7:3) respectively suggests its suitability for optoelectronics applications.

TABLE 1. Particle Size Calculated by Scherer's equation.

Sample (Crystals)	**Average Particle Size (nm)**
Pure TGS	26.784
TGS:ADP (9:1)	32.052
TGS:ADP (8:2)	38.145
TGS:ADP (7:3)	15.091

D. Optical Transmission Studies

Crystal plates of pure TGS and ADP mixed TGS crystals were cut and polished without any coating for optical measurements. The dimensions of the crystals were 10x10x5mm^3. Optical transmission spectra were recorded for the crystals in the wavelength region 200 - 1100 nm using Perkin-Elmer Lambda 35 UV-Vis spectrometer. The recorded UV-Vis spectrum is shown in the Figure 8.

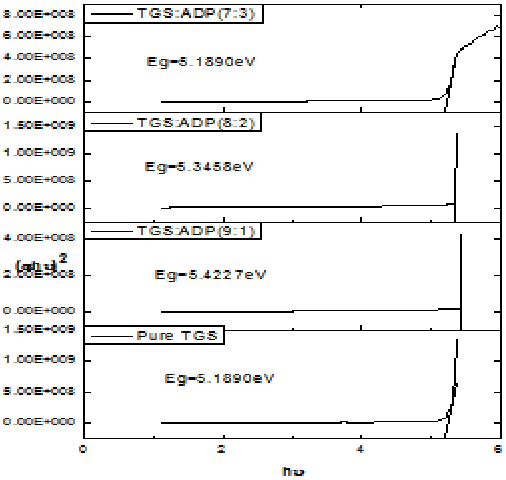

FIGURE 9. $(\alpha h\nu)^2$ **versus photon energy hν of the grown crystals**

E. FTIR SPECTROSCOPY

The Fourier transform infrared (FTIR) spectra for the powder samples of the grown crystals was recorded in the frequency region 400 - 4000 cm^{-1} using Perkin Elmer spectrometer. The FTIR spectra of pure TGS and TGS-ADP mixed crystals are shown in Figures 10-13.

The mid IR spectrum of TGS shows a broad envelope between 1800 and 2800cm^{-1}. It includes the OH stretch of hydrogen bonded carboxyl groups, the asymmetric stretching mode of NH_3^+ at 3135.386cm^{-1} and CH_2 stretching modes just below 3000 cm^{-1}. The broadening that extends between 2800 and 2200cm^{-1} includes overlapping of bands due to the stretching modes of hydrogen bonded NH^{3+} overtones and combination bands. The C=0 stretch of carbonyl groups display its characteristic peak at 1701.972 cm^{-1}. The CH_2 bending modes of glycine are located at 1374.381cm^{-1} and1423.164cm^{-1}. The NH_3^+ displays its characteristic bending modes at 1423.164, 1491.936 and 1529.171cm^{-1}. The intense and sharp peaks position between 900 and 1000cm^{-1} are assigned to stretching modes of carboxyl and sulphate ions. The peaks due to NH_3^+ oscillation are seen at 895.083, 862.292 and 674.687cm^{-1}. Table 2. shows the vibrational frequencies corresponding to the band assignments of pure TGS and TGS:ADP mixed crystals. The following vibrational assignments showed the hydrogen bonding extends throughout the TGS mixed ADP molecules. These hydrogen bonding results in the modification of stretching frequencies of O-H group of TGS and the carboxyl group of ADP molecules [8]. This confirms the presence of ADP in the pure TGS crystal.

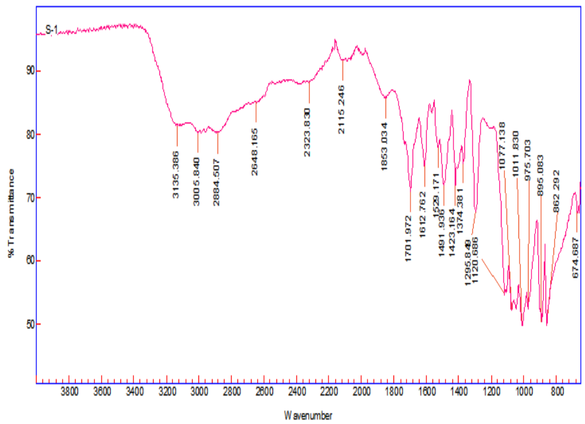

FIGURE 10. FTIR spectrum of pure TGS crystal

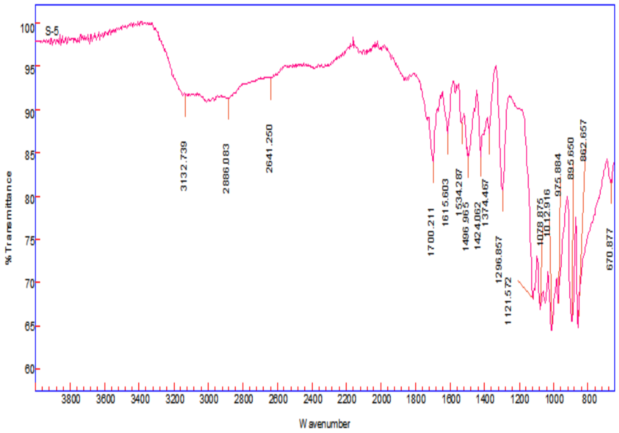

FIGURE 11. FTIR spectrum of the TGS:ADP (9:1) crystal

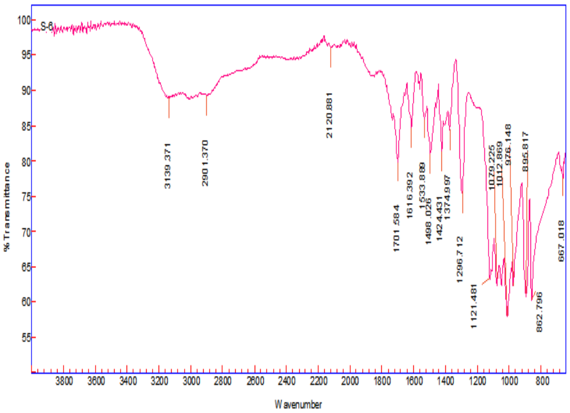

FIGURE 12. FTIR spectrum of the TGS:ADP (8:2) crystal

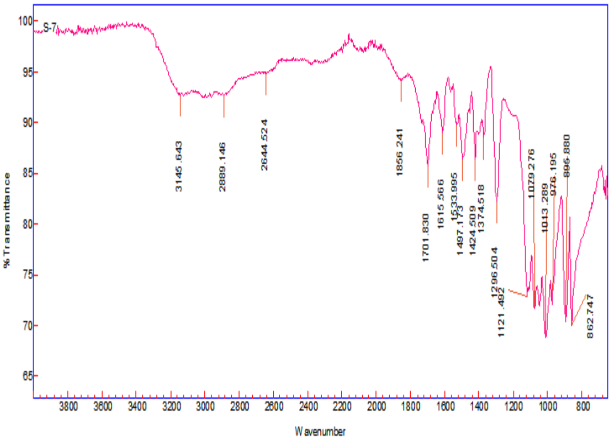

FIGURE 13. FTIR spectrum of TGS:ADP (7:3) crystal

Table 2. Vibrational frequencies for Pure TGS and TGS mixed ADP crystals

Pure TGS	TGS:ADP (9:1)	TGS:ADP (8:2)	TGS:ADP (7:3)	Assignments
3135.386	3132.739	3139.371	3145.643	O-H stretching, H-bonded
3005.840	--	--	--	O-H stretching
2884.507	2886.083	2901.370	2889.146	O-H stretching
2648.165	2641.250	--	2644.524	Intermolecular H-bonded-OH streching
2323.830	--		--	C-H stretching
2115.246	--	2120.881	--	O-H Stretching
1853.034	--	--	1856.241	P-O-H symmetric stretching
1701.972	1700.221	1701.584	1701.830	O-P-OH symmetric stretching
1423.164	1424.062	1424.431	1424.509	O-H stretching
1374.381	1374.457	1374.997	1374.518	CH_2 bending, P=O symmetric stretching
1011.830	1012.830	1012.869	1013.289	P-O-H symmetric stretching

975.703	975.884	976.148	976.195	O=P-OH bending
895.083	895.650	895.817	896.880	HO-P-OH bending
862.292	862.657	862.796	862.747	P-OH deformation/K-O stretching
674.687	670.877	667.018	--	PO_4 stretching

F. Second Harmonic Generation Studies (SHG)

The Second harmonic generation efficiency was determined by Kurtz powder technique [9]. Laser beam coming from the source has very high energy. Its intensity is reduced by using glass plates and Neutral density (ND) filter which reduces the intensity and it allows only 1064nm wavelength to incident on the sample taken in a microcapillary tube. Output from the sample is passed through the monochromator which is intensified by photomultiplier tube and finally the signal is observed and read on the Oscilloscope. A Q-switched Nd:YAG laser beam of wavelength 1064nm and 8ns pulse width with an input rate of 10Hz was used to test the NLO property of the sample. The second harmonic signal of 532nm green light was collected by a photomultiplier tube [10]. The optical signal incident on the PMT was converted into voltage output at the cathode ray oscilloscope as shown in Figure 14.

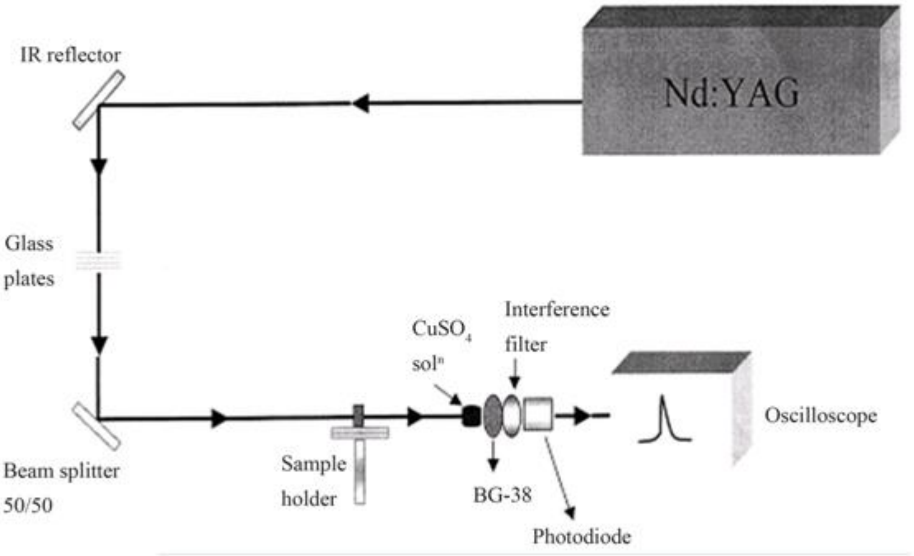

Figure 14. Schematic experimental setup for SHG efficiency measurement.

The grown crystals were crushed into fine powder and tightly packed in a microcapillary tube. It was mounted in the path of Nd-YAG laser beam of energy 5mJ/pulse. The KDP crystal was used as a reference material. The transmitted beam voltage for pure KDP was 80mV, for the pure TGS crystal 98mV, 99mV for TGS-ADP (9:1). 63mV for TGS-ADP (8:2) and 72mV for TGS-ADP (7:3) sample. It is found that the SHG efficiency of the TGS-ADP (9:1) mixed crystal is 1.237 times greater than KDP, TGS-ADP (8:2) is 0.787 times greater than KDP and TGS-ADP (7:3) is 0.9 times greater than KDP. The measured values are given in Table 3. The relative SHG efficiency of the grown crystals is higher than that of KDP sample which indicates the suitability of crystals for application in nonlinear optical devices and optoelectronic devices.

Table 3. SHG Signal and SHG efficiency of grown crystals

Details of the sample	SHG Signal	SHG Efficiency w.r.t KDP	SHG Efficiency w.r.t TGS
Pure TGS	98mV	1.225	1
TGS:ADP (9:1)	99mV	1.237	1.010
TGS:ADP (8:2)	63mV	0.787	0.642
TGS:ADP (7:3)	72mV	0.9	0.734

IV. 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. Powder XRD, FTIR and EDAX analysis confirm the fact that the ADP has gone into the lattice sites of the TGS crystals. The presence of various functional groups was confirmed by FTIR spectrum. The UV-Vis-NIR transmission spectra show a wide transparency window without any absorption. TGS-ADP mixed crystals generate optical second harmonic frequency of an Nd:YAG laser. It is found that the SHG efficiency of the TGS-ADP (9:1) mixed crystal is 1.237 times greater than KDP, TGS-ADP (8:2) is 0.787 times greater than KDP and TGS-ADP (7:3) is 0.9 times greater than KDP. The relative SHG efficiency of the grown crystals is higher than that of KDP sample which indicates the suitability of crystals for application in nonlinear optical devices and optoelectronic devices. This study will be helpful to grow high quality TGS crystals with good piezoelectric, laser damage threshold and SHG efficiency for various applications.

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