LASER RAMAN, FTIR SPECTROSCOPIC INVESTIGATION AND INFRARED LIGHT TESTING OF M_2SO_4 (M = K, NH_4, Li) DOPED TRIGLYCINE SULPHATE(TGS) CRYSTALS

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Abstract

In this paper, crystals of undoped Triglycine Sulphate, $(NH_2CH_2COOH)_3.H_2SO_4$, (abbreviated as TGS) and M_2SO_4 (where M = K, NH_4, Li) doped TGS have been grown by solution growth method. The grown crystals were characterized by laser Raman and FTIR spectroscopy to study the vibrational characteristics of the various functional groups present in the crystals. Laser Raman spectra were observed by Ocean Optics QE65000 Visolator Raman Spectrophotometer. FTIR spectra were observed by using Perkin-Elmer Spectrum-100 FTIR Spectrophotometer. Vibrational characteristics and mode assignments of constituent molecules of SO_4^{2-}, COO^-, C—C, CO_2—CH_2—CH_2, NH—NH_3, NH_3 and CO_2 were reported. Furthermore, infrared (IR) light transmission experiments were tested by using laboratory-prepared IR driving circuit to show the IR windows materials.

Keywords: Undoped and M_2SO_4 doped TGS crystals, laser Raman, FTIR, various functional groups, IR windows materials

Introduction

Triglycine Sulphate, $(NH_2CH_2COOH)_3.H_2SO_4$, crystal is considered as one of the potential materials for its wide range of applications, namely, UV tunable laser, second harmonic generation, and pyroelectric infrared sensors due to its high pyroelectric coefficient, optical transmission, and reasonably low dielectric constant (Choudhury, 2008; Krishnakumar, 2011). It is a hydrogen bonded ferroelectric crystal having a typical second-order phase transition at Curie temperature of 49°C (Andriyevsky, 2007). TGS has a major

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disadvantage that it depolarized by thermal, mechanical, and electrical means. In order to overcome this difficulty, several studies have been attempted with different organic and inorganic dopants to achieve effective internal bias to stabilize the domains and desired pyroelectric and ferroelectric properties of TGS crystals (Arunmozhi, 2002; Bajpai, 2008).

Alkali halides such as NaBr and KBr-doped TGS crystals were grown, and the effects of the dopant have been investigated. Metal ion dopants have been added to modify the properties of TGS crystal (Khanum, 2012; Renugadevi, 2013). Due to the vast applications of TGS crystal, in this work, single crystals of undoped TGS and M_2SO_4 (M = K, NH_4, Li) doped TGS have been grown by slow evaporation method and their molecular vibrational characteristics were studied by laser Raman and Fourier Transform Infrared (FTIR) spectroscopic method. Furthermore, IR radiation and the crystals interaction experiments were tested by using laboratory-prepared IR driving circuit.

Experimental Details

Growth of Crystals

The crystals of triglycine sulphate have been grown by slow evaporation method. Analar (AR) grade glycine and concentrated sulphuric acid were dissolved in deionized water with the molar ratio of 3:1. The solution was heated at 50°C to obtain synthesized TGS crystal. The synthesized salt was again dissolved in triple distilled water and then recrystallized by natural evaporation process. This process was repeated three times to improve the purity of the material. The seed crystals of pure TGS were prepared by natural evaporation method. The chemical reaction for obtaining TGS salt is as follows:

$$3(NH_2CH_2COOH)+H_2SO_4 \rightarrow (NH_3^+.CH_2.COO^-).(NH_3^+.CH_2.COOH)_2.(SO_4)^{2-}$$

To obtain M_2SO_4 (M = K, NH_4, Li) doped TGS crystals, each of the 1 mole% K_2SO_4, $(NH_4)_2SO_4$ and Li_2SO_4 was added to the saturated mother solution. Transparent and homogeneous crystals were obtained within four weeks. At room temperature, the undoped TGS and M_2SO_4 doped TGS

crystals are colourless. Photographs of the as-grown crystals are shown in Figures 1(a- d). Crystal growth process is shown in Figure 2.

(a) Undoped TGS (b) K_2SO_4 doped TGS (c) $(NH_4)_2SO_4$ doped TGS (d) Li_2SO_4 doped TGS

Figure 1. Photographs of (a) undoped TGS, (b) K_2SO_4 doped TGS, (c) $(NH_4)_2SO_4$ doped TGS and (d) Li_2SO_4 doped TGS crystals

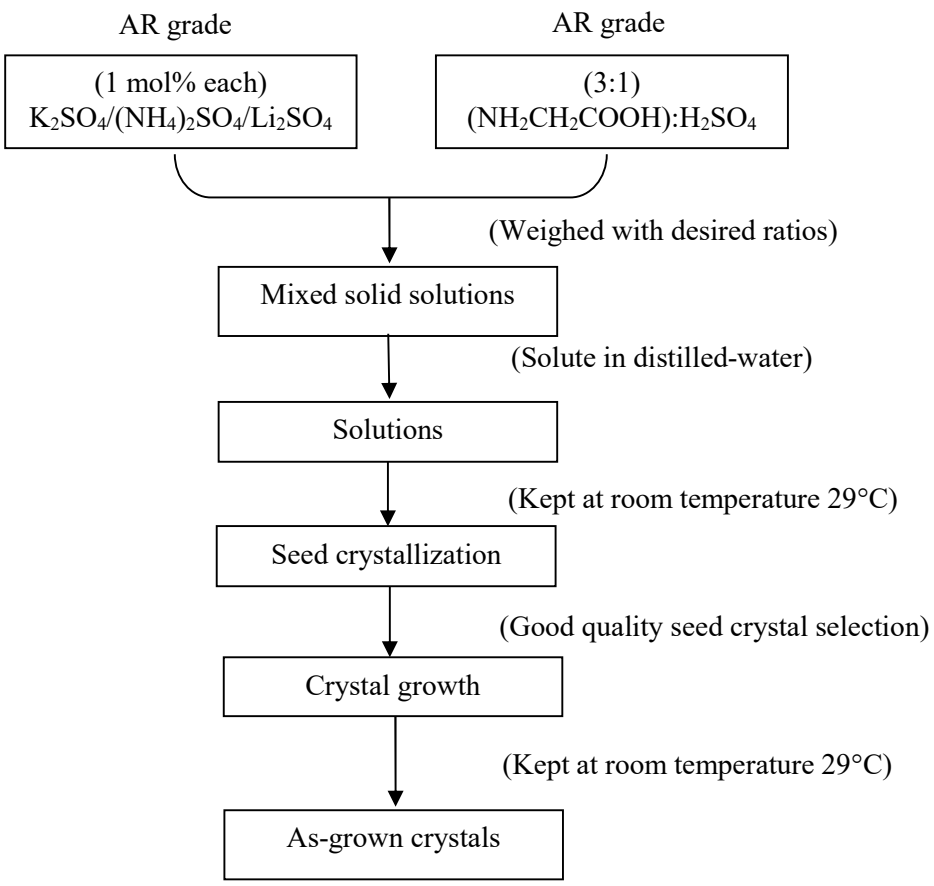


Figure 2. Flow diagram of the crystal growth process

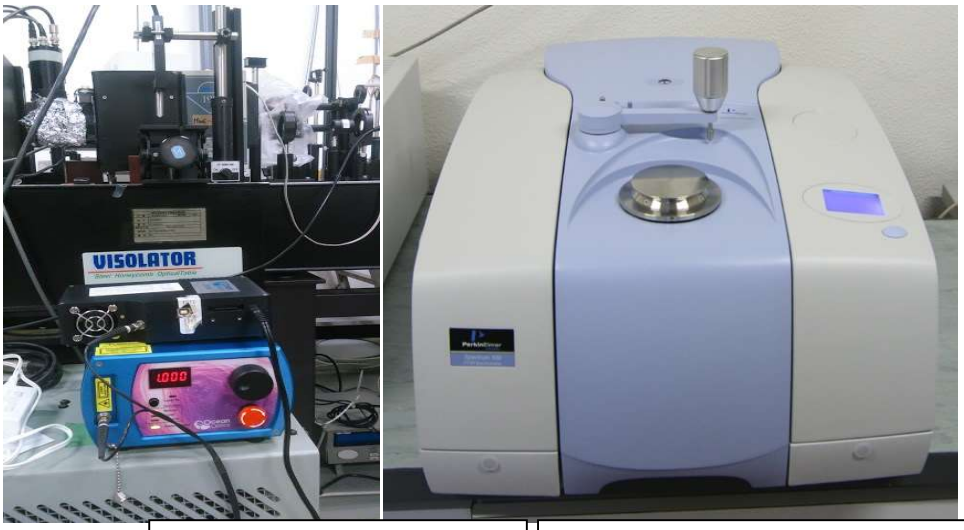
Raman and FTIR Measurements

The vibrational frequencies of a molecule can be probed by using infrared and Raman spectroscopy [Stuart, (1996)]. In all spectroscopic methods, there is a mechanism by which the incident radiation interacts with the molecular energy levels. Raman Spectroscopy can be used to study the vibrational properties of crystals, powders, polymers and even coloured samples (solutions). Raman Scattering is an inelastic scattering of light from molecules. Raman spectroscopy, the mechanism has its origins in the general phenomenon of light scattering, in which the electromagnetic radiation interacts with a pulsating, deformable (polarizable) electron cloud. In the

specific case of vibrational Raman scattering, this interaction is modulated by the molecular vibrations.

Raman spectra of the as-grown crystals were collected on PC controlled Ocean Optics QE65000 Visolator Laser Raman Spectrometer (Institute of Advanced Energy, Kyoto University, Kyoto, Japan) in the Raman shift range of 400 cm^{-1} – 2000 cm^{-1} region.

Infrared (IR) spectroscopy is an important relatively inexpensive and efficient analytical method for characterizing materials. IR spectroscopy is used for obtaining an abundance of information such as thermodynamic data, bond length and diffusion data. On the other hand IR spectroscopy is limited in the ability to obtain accurate quantitative measurements and the range of inorganic and organic materials that are IR visible. The spectrum that is obtained from IR spectroscopy is due to the vibrational modes of the molecules. FTIR transmission spectra of the crystals were observed by using Perkin-Elmer Spectrum-100 FTIR Spectrophotometer (MIR & IR Spectroscopy Laboratory, Kyoto University, Kyoto, Japan) in the wave number range of 500 cm^{-1} – 3500 cm^{-1} region. Photographs of the Ocean Optics QE 65000 Visolator laser Raman spectrometer and Perkin-Elmer Spectrum-100 FTIR Spectrophotometer are shown in Figures3(a) and (b).



(a) Raman spectrometer (b) FTIR Spectrophotometer

Figure 3. Photographs of (a) Ocean Optics QE65000 VisolatorLaser Raman Spectrometer and (b) Perkin-Elmer Spectrum-100 FTIR Spectrophotometer

Infrared (IR) Light Testing Experiments

For the applications of IR windows materials, IR light testing experiments were also performed in this work. Experimental conditions were as follows:

Experimental work is mainly two parts;

(i) IR testing experiments of IR driver circuit without sample (crystal) and

(ii) IR testing experiments of IR driver circuit with sample (crystal).

In IR testing experiments,

- IR driver circuit power "ON".
- The as-grown crystal was polished with the filtered-paper to get smoothing surface.
- The crystal was placed at the IR beam in the IR driver circuit (LED).

Photographs of IR testing experiments without samples and with samples are shown in Figures 4(a – s).

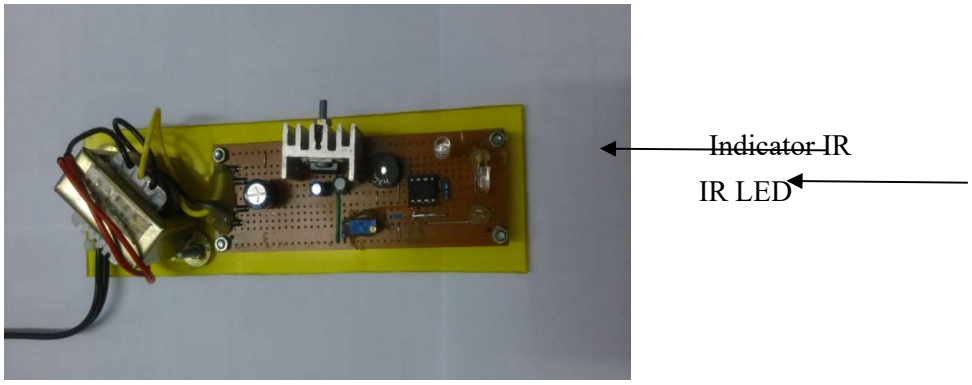


Figure 4.(a) IR driver circuit (Power OFF)

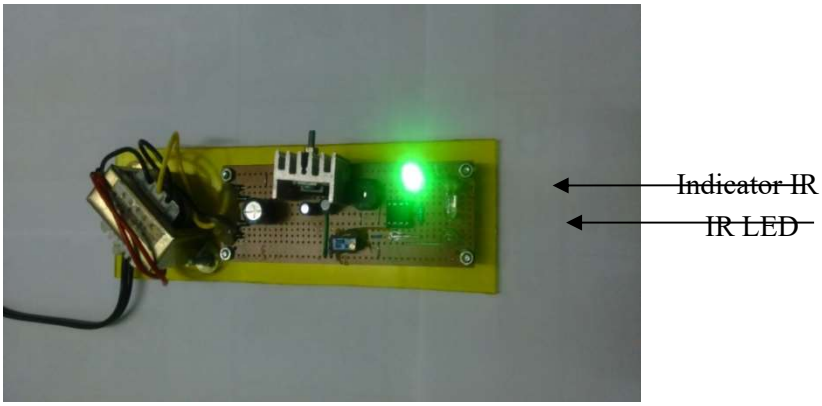


Figure 4.(b) IR driver circuit (Power ON) (Top-view)

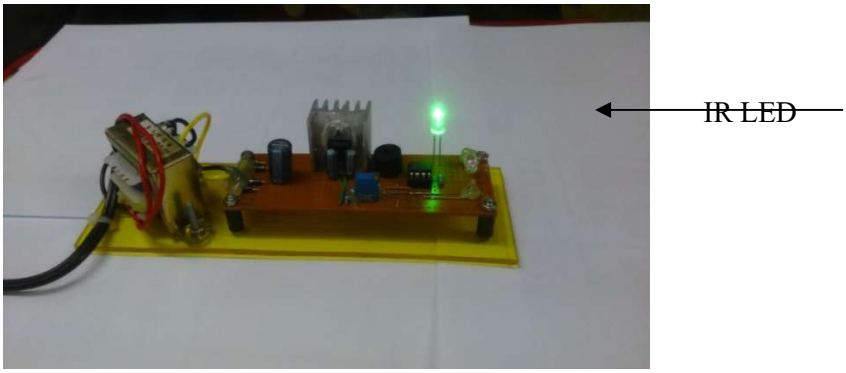


Figure 4.(c) IR driver circuit (Power ON) (Side-view / transmitted IR light source as an electrically ceramic light source)

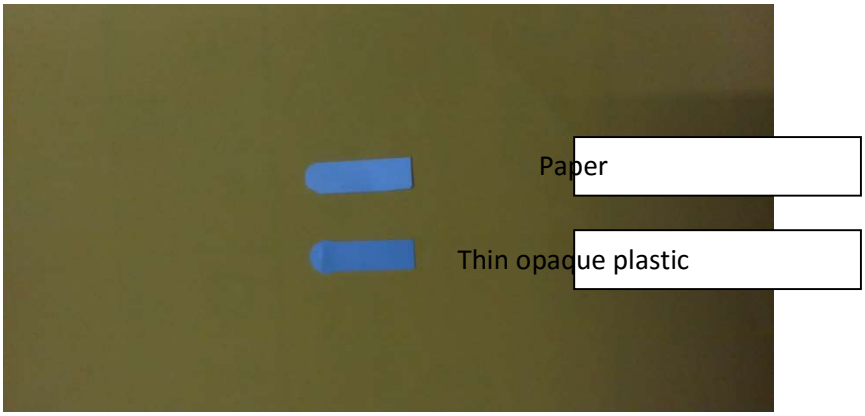


Figure 4.(d) Filters (upper - paper) and (lower – thin opaque plastic)

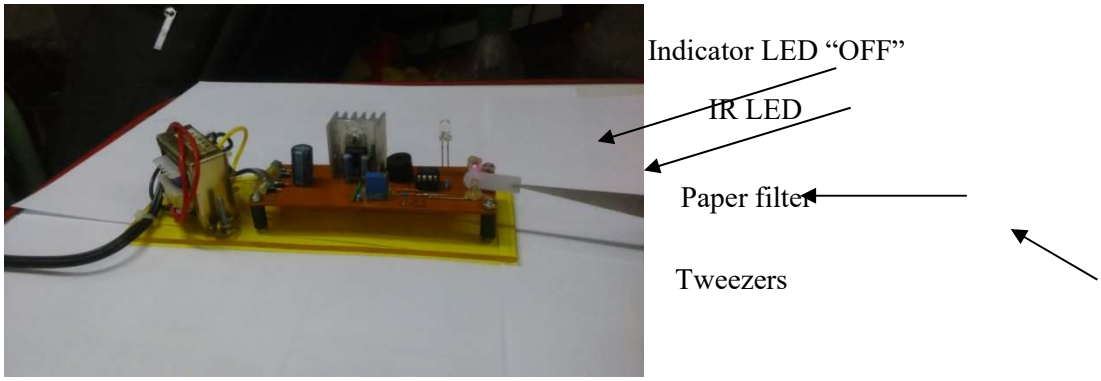


Figure 4(e). Testing of paper as an IR-filter

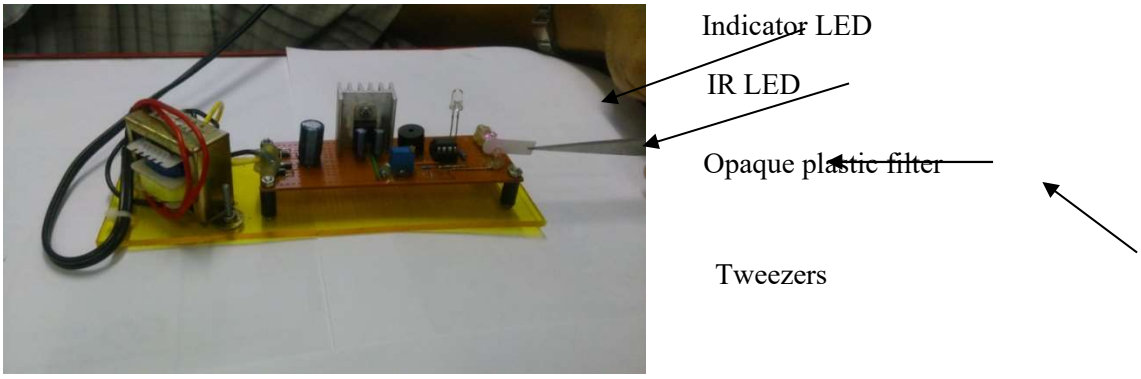


Figure 4.(f) Testing of thin opaque plastic as an IR-filter

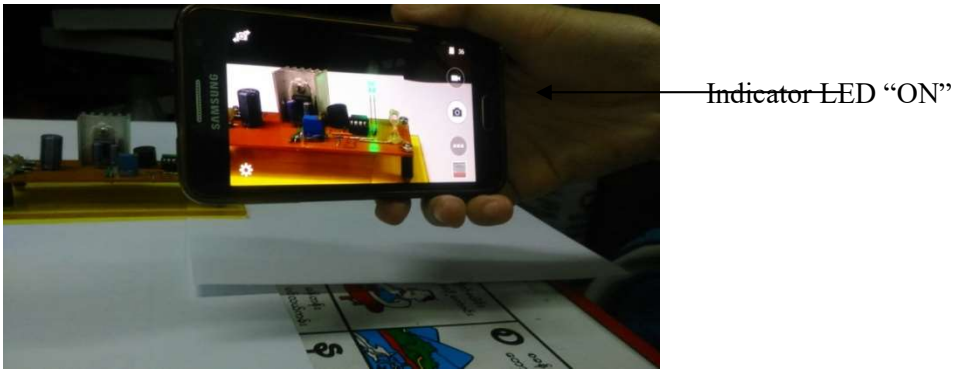


Figure 4(g). Testing of cell-phone camera with interaction of IR (indicator LED "ON")

(h) Length of undoped TGS

(i) Thickness of undoped TGS

Figure 4.(h) Length and (i) thickness of undoped TGS crystal

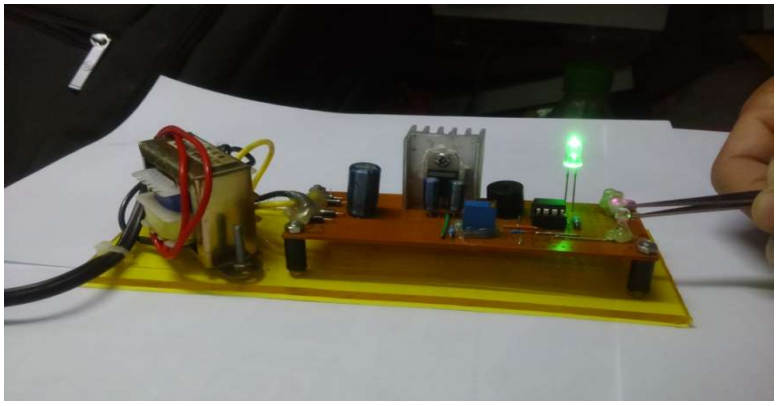


Figure 4.(j) Testing of IR windows material of undoped TGS crystal

(k) Length of K_2SO_4 doped TGS

(l) Thickness of K_2SO_4 doped TGS

Figure 4.(k) Length and (l) thickness of K_2SO_4 doped TGS crystal

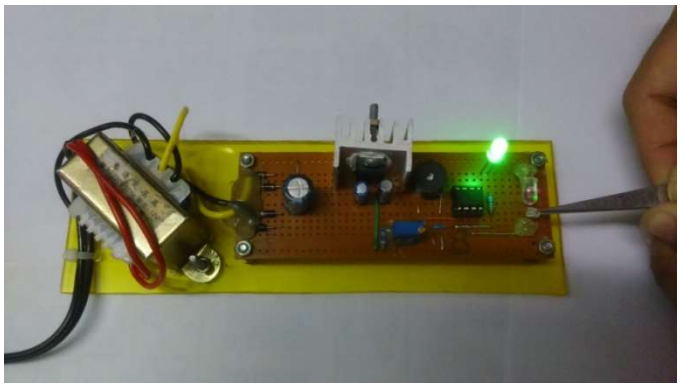


Figure 4.(m) Testing of IR windows material of K_2SO_4 doped TGS crystal

(n) Length of $(NH_4)_2SO_4$ doped TGS (o) Thickness of $(NH_4)_2SO_4$ doped TGS

Figure 4.(n) Length and (o) thickness of $(NH_4)_2SO_4$ doped TGS crystal

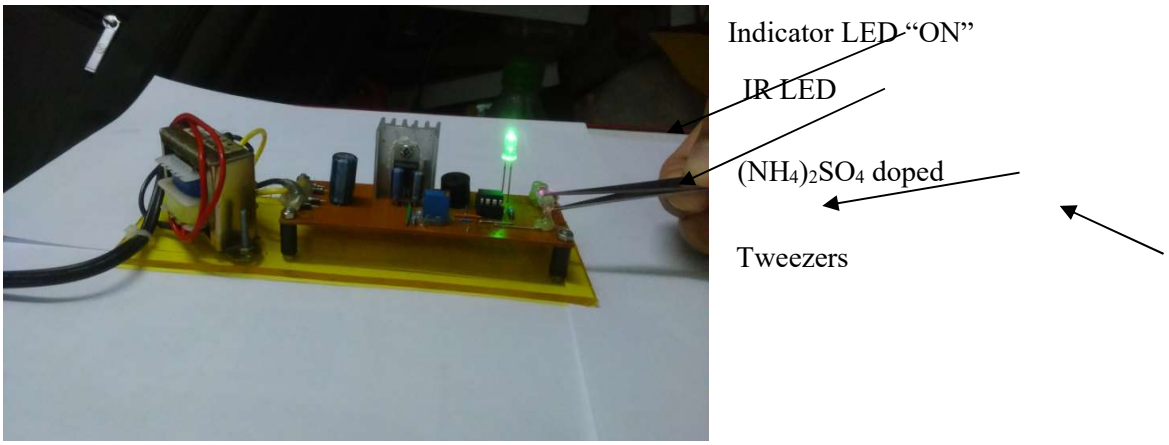
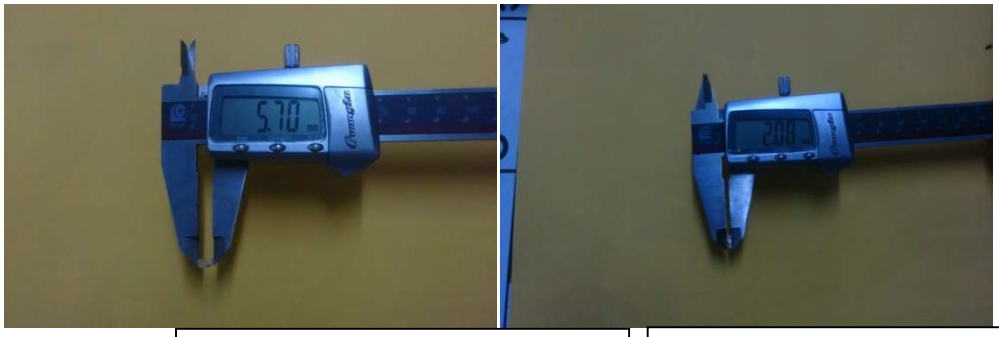


Figure 4.(p) Testing of IR windows material of $(NH_4)_2SO_4$ doped TGS crystal



(q) Length of Li_2SO_4 doped TGS (r) Thickness of Li_2SO_4 doped TGS

Figure 4.(q) Length and (r) thickness of Li_2SO_4 doped TGS crystal

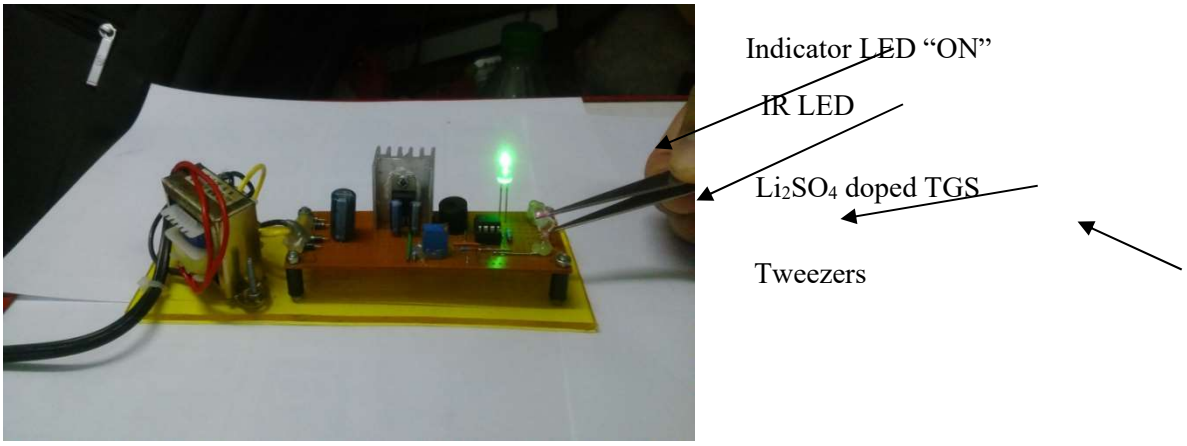


Figure 4.(s) Testing of IR windows material of Li_2SO_4 doped TGS crystal

Results and Discussion

Raman Study

According to FTIR theory, the mid-infrared spectrum can be divided into four regions and nature of a group frequency may be generally determined by the region in which it is located. These regions are normally as follows;

(i) The X—H stretching region (2500 cm^{-1} – 4000 cm^{-1})

(ii) Triple bond region (2000 cm^{-1} – 2500 cm^{-1})

(iii) Double bond region (1500 cm^{-1} – 2000 cm^{-1})

(iv) Fingerprint region (400 cm^{-1} – 1500 cm^{-1}). [Stuart, (1996)]

According to vibrational analysis using factor group theory, the sulphate, SO_4^{2-} molecule in free-state is tetrahedral-pyramidal type T_d-symmetry and it processes four normal modes of vibrations. These four normal modes are $n_{vib} = A_1 + E + 2F_2$ and namely; $\upsilon_1(A_1)$-symmetric stretching, $\upsilon_2(E)$-bending, $\upsilon_3(F_2)$-dipole and $\upsilon_4(F_2)$-polarization respectively [Ross, 1972). In general, most of the cases, SO_4^{2-} molecule may be distorted from the ideal T_d symmetry due to their crystalline environments or dopant effects.

Triglycine Sulphate, $(NH_2CH_2COOH)_3.H_2SO_4$, (TGS), of course, is an organic-inorganic molecules. Frequencies of organic compounds are generally appeared in the regions of over the frequency 1500 cm^{-1}. These frequencies are often shifted into the low and high frequency regions. In the present work, the absorption lines at over the frequency 1400 cm^{-1} were indicated that the organic molecules in TGS crystal.

Raman spectra of the crystals are shown in Figures5(a – d). As shown in figures, four normal vibrations were appeared in all Raman spectra. In all spectra, the Raman line at 978 cm^{-1} indicates the υ_1-mode (symmetric-stretching) is influence on others three types of vibrations because this it is a very strong Raman active mode. The υ_3-mode (dipole character) of SO_4^{2-} at room temperature phase is often splitting. In the present work, the Raman lines at about1045 cm^{-1} and 1113 cm^{-1} or 1043 cm^{-1} and 1115 cm^{-1} assigned as the υ_3-mode of SO_4^{2-}. The υ_2-mode and υ_4-mode are not clearly changed in the undoped and doped crystals. Raman spectra of the crystals are shown in Figure 6.The observed Raman shift and vibrational characteristics are tabulated in Table 1.

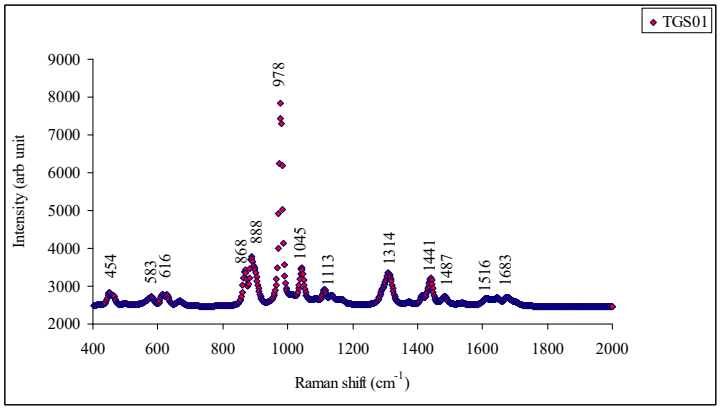


Figure 5.(a) Raman spectrum of undoped TGS crystal

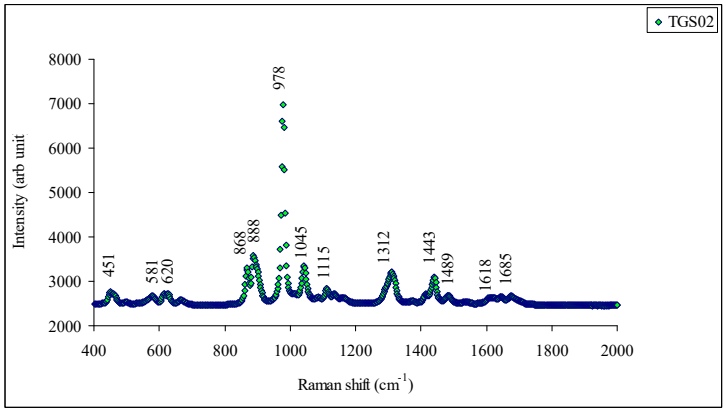


Figure 5.(b) Raman spectrum of K_2SO_4 doped TGS crystal

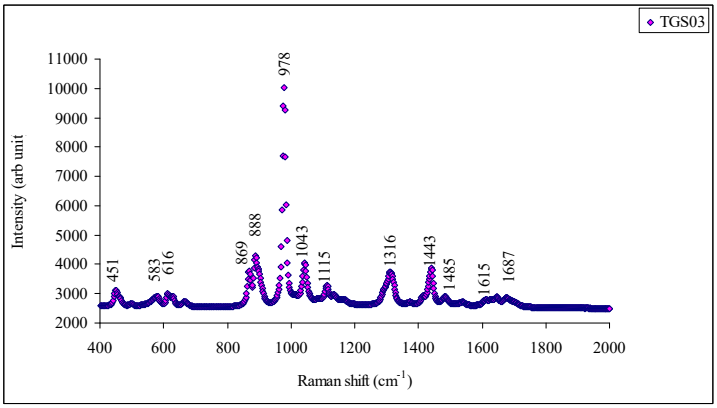


Figure 5.(c) Raman spectrum of $(NH_4)_2SO_4$ doped TGS crystal

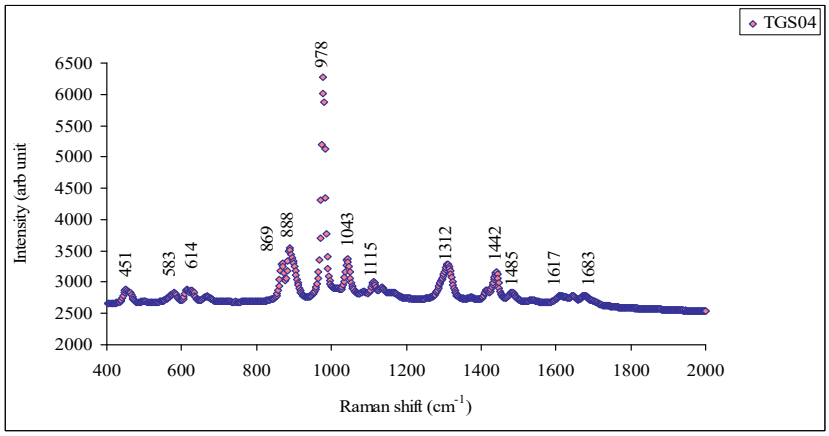


Figure 5.(d) Raman spectrum of Li_2SO_4 doped TGS crystal

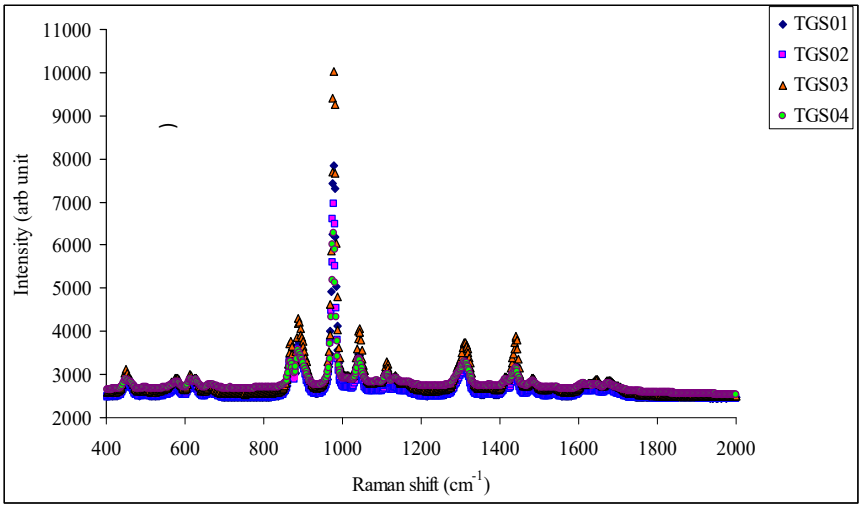


Figure 6. Raman spectra of undoped and M_2SO_4 (M = K, NH_4, Li) doped TGS crystals

Table 1. Raman shifts and corresponding vibrational mode assignments of undoped and M_2SO_4 (M = K, NH_4, Li) doped TGS crystals

Raman shift (cm^{-1})				Assignment
TGS	**K_2SO_4/ TGS**	**$(NH_4)_2SO_4$/ TGS**	**Li_2SO_4/TGS**	
1683	1685	1687	1683	CO_2-bending
1616	1618	1615	1617	NH_3-asymmetric bending
1487	1489	1485	1485	NH-in plane bending + (NH_3)-symmetric bending
1441, 1314	1443, 1312	1443, 1316	1442, 1312	CO_2-symmetric stretching+ CH_2-twisting+ CH_2-bending
1113, 1045	1115, 1045	1115, 1043	1115, 1043	υ_3-mode (SO_4-dipole)
978	978	978	978	υ_1-mode (SO_4-symmetric) stretching
888, 868	888, 868	888, 869	888, 869	C—C- stretching
672	672	672	672	COO-scissoring
616	620	616	614	υ_4-mode (SO_4-polarization)
583	581	583	583	COO-rocking
454	451	451	451	υ_2-mode (SO_4-bending)

FTIR Study

FTIR transmission spectra of the crystals are shown in Figures 7. (a – d). In this work, the observed wavenumbers can be assigned. In the FTIR spectra, only one normal mode of SO_4^{2-} was found. In Figure 7(a), the collected wavenumbers of undoped TGS crystal matches with the data reported by other authors [Krishnakumar, (2011)]. FTIR transmission spectra of undoped TGS and M_2SO_4 (where M = K, NH_4, Li) doped TGS crystals with stack are shown in Figure 8.The collected wavenumbers and their vibrational mode assignments are given in Table 2. The band observed in the wavenumber range of about 3000 cm^{-1} – 3500 cm^{-1} showed the stretching bands H_2O and the band appeared in each of the spectrum.

Discussion of Infrared (IR) Light Testing Experiments

From IR testing experiments without samples, it can be discussed as follows:

- In IR testing with cell-phone camera, the output green coloured indicator LED indicates "ON" and also IR light (from IR LED) is also emitted.
- In IR testing with paper, the output green coloured indicator LED indicates "OFF" and also IR light (from IR LED) is not emitted.
- In IR testing with thin opaque plastics, the output green coloured indicator LED indicates "OFF" and also IR light (from IR LED) is not emitted.

From IR testing experiments with samples, it can be discussed as follows:

- In this experiment, the output green coloured indicator LED is "ON" and also IR light transmits from the circuit (IR LED). It is found that the crystals are exhibited as IR transmitters or IR windows materials. The crystals can be applied as the IR windows materials of IR transmission measurements for the vibrational characteristics of liquid and gas molecules samples.

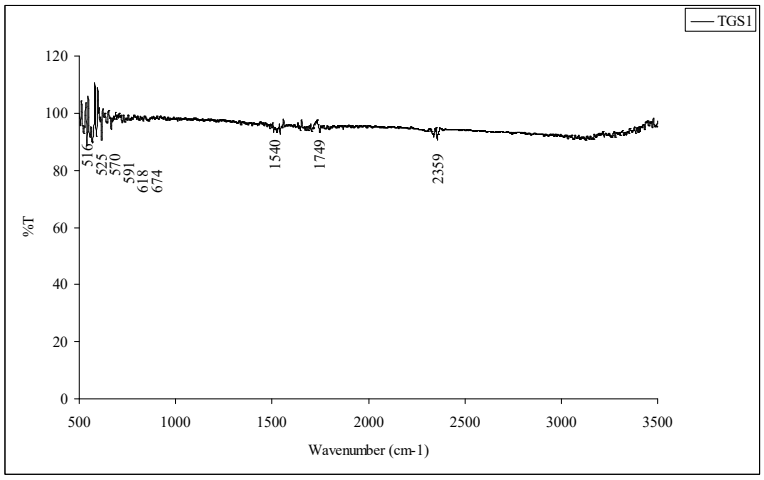


Figure 7.(a) FTIR transmission spectrum of undoped TGS crystal

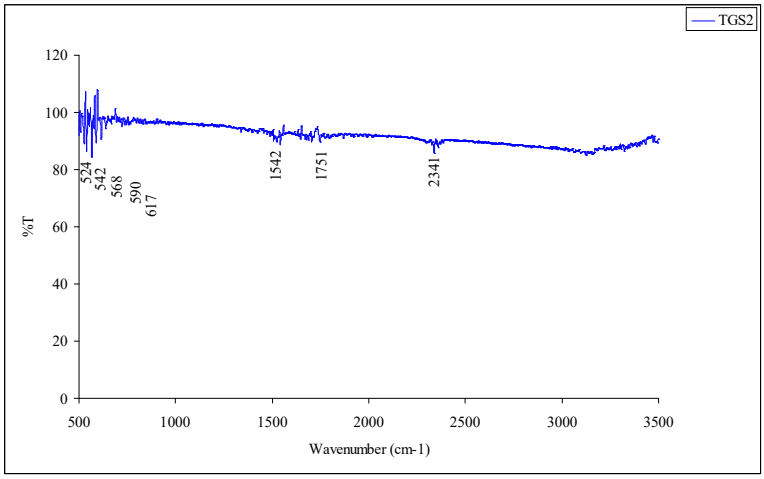


Figure 8.(b) FTIR transmission spectrum of K_2SO_4 doped TGS crystal

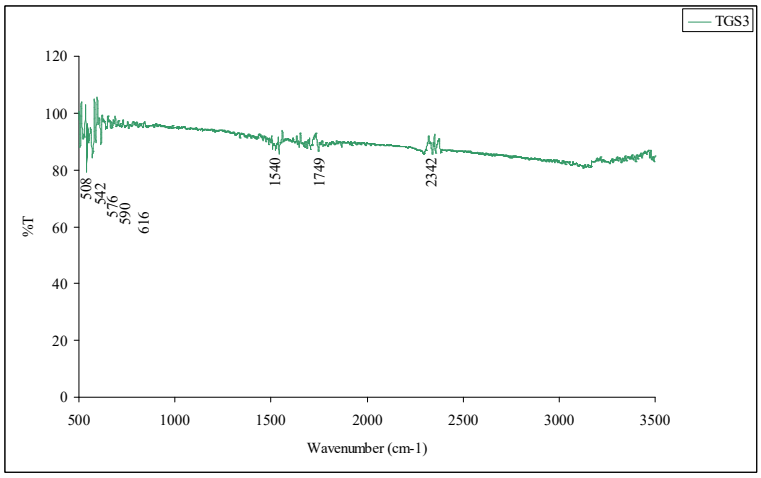


Figure 7.(c) FTIR transmission spectrum of $(NH_4)_2SO_4$ doped TGS crystal

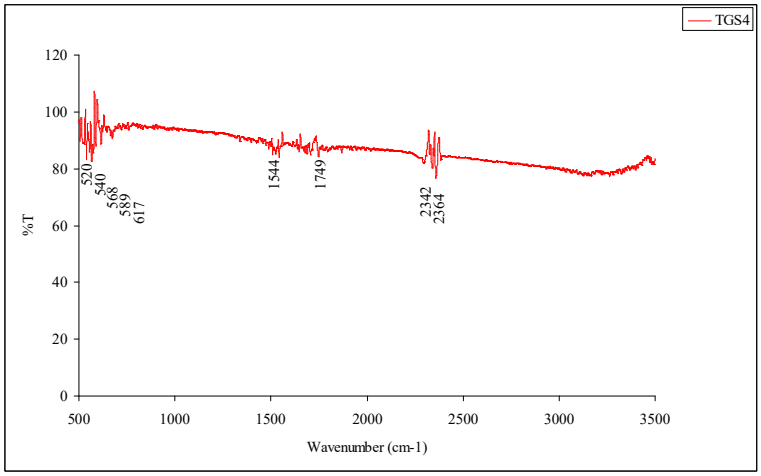


Figure 7.(d) FTIR transmission spectrum of Li_2SO_4 doped TGS crystal

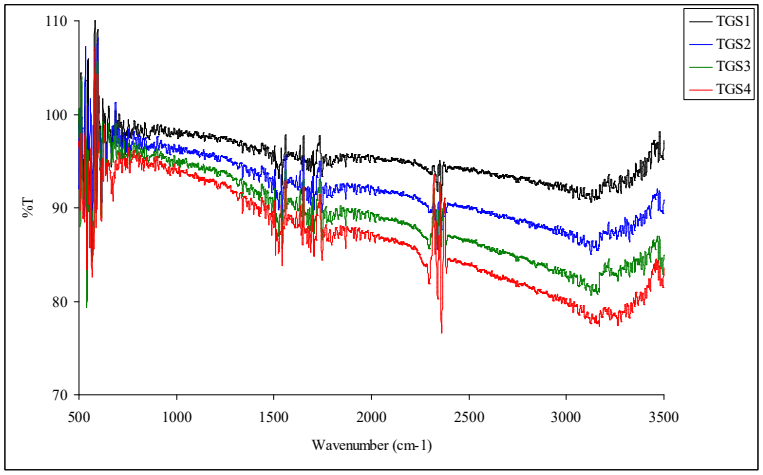


Figure 8. FTIR transmission spectra of undoped and M_2SO_4 (where M = K, NH_4, Li) doped TGS crystals

Table 2. The observed wavenumbers and corresponding vibrational mode assignments of undoped TGS and M_2SO_4 (M = K, NH_4, Li) doped TGS crystals

Wavenumber (cm^{-1})				Assignment
TGS	**K_2SO_4/TGS**	**$(NH_4)_2SO_4$/TGS**	**Li_2SO_4/TGS**	
2359	2341	2342	2342, 2364	CO_2- bending
1749	1751	1749	1749	Combination band
1540	1542	1540	1544	NH_3-asymmetric bending
674	-	-	-	COO-scissoring
618	617	616	617	SO_4-polarization
570, 591	568, 590	576, 590	568, 589	COO-rocking
516, 525	524, 542	508, 542	520, 540	COO-twisting

Conclusion

Crystals of undoped and M_2SO_4 (M = K, NH_4, Li) doped TGS have been grown by slow solution growth method. The as-grown crystals were characterized by Raman and FTIR spectroscopy. Furthermore, for the applications of IR windows materials, experiments were performed in which the crystals were used as IR transmitters. Experimental results were concluded as follows:

- Raman spectra showed that four normal modes of SO_4^{2-} and vibrational characteristics of organic molecules such as COO^-, C—C, CO_2-CH_2-CH_2, NH-NH_3, NH_3 and CO_2 were observed and assigned in this work.
- FTIR spectra were found to be the same in patterns and most of the wavenumbers of absorption lines were the same in values. Only one normal modes of T_d-symmetry type SO_4^{2-} were found and assigned in this work. Others vibrational modes of organic molecules were found and assigned by molecular vibrational theory.
- The observed Raman lines were agreement with the wavenumbers of FTIR spectra. From the experimental results, the samples responded to infrared (IR) radiation because the wavelength of laser in Raman spectrometer was

1064 nm (monochromatic and/or IR-laser) due to the appearance of Raman lines of the crystals and the wavelength range FTIR Spectrophotometer were 20000 nm – 2857 nm (or wavenumber range of ~ 500 cm^{-1} - 3500 cm^{-1}). It showed that the crystals exhibited as the IR response materials or IR sensing materials. From the IR light testing experiments, the crystals exhibited as the IR transmitters or IR windows materials. According to experimental results, the crystals of undoped TGS and M_2SO_4 (M = K, NH_4, Li) doped TGS can be applied as the IR sensing materials and IR windows materials.

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