Growth and characterization of dyes doped TGS Crystals for IR detector applications

D. NARAYANASAMY[a], P. KUMARESAN[b], P. M.ANBARASAN[c]
[a]*Department of Physics, SKP Institute of Technology, Tiruvannamamalai, Tamil Nadu, India*
[b]*Department of Physics, Thiru. A. Govindasamy Government Arts College, Tindivanam-604 002, Tamil Nadu, India*
[c]*Department of Physics, Periyar University, Salem-636 011, Tamil Nadu, India*

Magnetic stirrer was used to prepare saturated solution. All crystals were grown by slow evaporation process. The FTIR spectra of all grown crystals have been recorded in the range of 400 - 4000 cm^{-1} using Bruker FT-IR 8400 spectrophotometer by KBr pellet technique. To determine the lattice parameters, powder X-ray diffraction analysis was performed by Philips X'pert PRO X-ray diffractometer system with Cu-K_α (λ = 1.54178Å) radiation at room temperature (25˚C) with an operating voltage 40 kV and the tube current was 30 mA. In the present work, optical transmission and absorption spectra were recorded by Systronics UV-Double beam spectrometer in the wavelength range 190 to 1100 nm.

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1. Introduction

Crystals of triglycine sulfate $(NH_2CH_2COOH)_3H_2SO_4$ (TGS), are known as ferroelectric materials [1,2]. It is also known as pyroelectric material which finds application in the fabrication of infrared detectors, pyroelectric vidicon tube operating at room temperature, in the fabrication of capacitors, transducers and sensors [3]. In the ferroelectric phase, the Curie temperature, Tc, is 49°C and the crystal systems in monoclinic with space group P21. The lattice parameters of pure TGS are a = 9.41 Å, b= 12.53 Å, c = 5.9 Å and β = 111.13° [4].

The presence of dyes dopants like methyl orange, methyl red with low concentration raises the internal bias field and makes the crystal permanently poled [5-8]. Dyes such as methyl orange and methyl red doped TGS crystals were grown and the effect of the dopant on the growth, structural, mechanical and dielectric properties have been investigated [9-11]. However the investigations on TGS doped with dyes are analysed. In general transition metals possess a high density, a high melting point and boiling point. The objective of the present work is to see the effect of dyes as dopant on growth, structural, optical, mechanical and electrical properties of TGS crystals.

2. Experimental

2.1 Material synthesis

Commercially purchased Analar Reagent (AR) grade glycine and concentrated sulphuric acid (H_2SO_4) were used for synthesis and growth. Glycine and H_2SO_4 in the molar ratio of 3:1 were dissolved in de-ionized water. The solution is filtered and transferred to a Petri dish for crystallization. Fully transparent and good quality crystals were obtained in a period of 25 days. The purity of the synthesized salts of TGS was improved by successive re-crystallization.

2.2 Determination of solubility

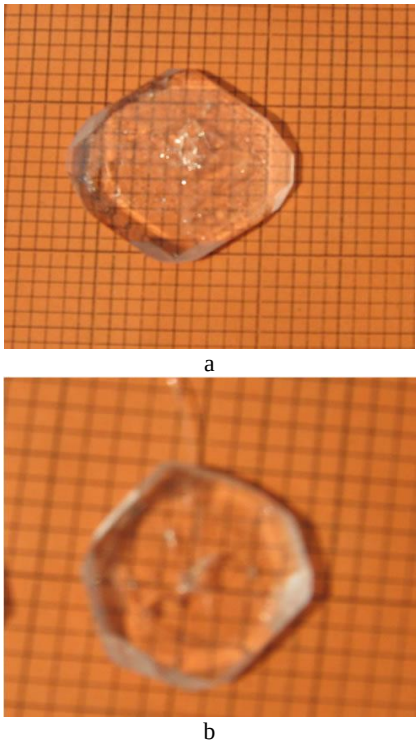
The re-crystallized salt of TGS was added to 100 ml of deionized water in an air tight container for the measurement of solubility in the temperature range 30-50^{o}C. Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer (accuracy is ±0.1^{o}C). The temperature was controlled using a voltage regulator attached to the magnetic stirrer. Initially, the solution was kept at 30^{o}C and stirred continuously for about 2 hours. After attaining the saturation, the solubility was determined gravimetrically [12]. The same procedure was followed for other temperatures of TGS salt.

2.3 Synthesis and growth

TGS single crystals were grown using slow solvent evaporation technique. Glycine and H_2SO_4 is in the molar ratio of 3: 1 was dissolved in de-ionized water. The supersaturated solution was prepared according to the solubility data. The solution is filtered and transferred to a Petri dish for crystallization. The solution was transferred to a big tray and allowed to rapid evaporation. Within 7 days 80% of the solvent was evaporated and the synthesized TGS crystals were collected. The crystallized salt was again dissolved in triple distilled water and re-crystallized. This was repeated three times to improve the purity of the material. The saturated solution of TGS was filtered and allowed to crystallize by slow evaporation process. Tiny seed crystals with good transparency were

obtained within 5 to 7 days. Among them, defect free seed crystals were collected. To obtain dyes doped TGS, 0.5 mole% and 0.5 mole% methyl orange and methyl red was added separately to the solution of TGS. Growth of undoped and methyl orange doped TGS crystals were carried out by natural evaporation technique at room temperature.

The re-crystallized salts of undoped and methyl red doped TGS were used to prepare the saturated solution separately. The solutions were constantly stirred for about 5 hours using a magnetic stirrer and were filtered using 4 micro Whatman filter papers. Then the filtered solutions were kept in glass beakers covered with porous paper and the seed crystals were suspended into the solution by nylon thread. Fully transparent and good quality crystals were obtained within 30 days. The purity of the synthesized salts of TGS was improved by successive re-crystallization.The grown crystals are shown in (Fig. 1). The doped crystals grow much faster in comparison to the pure crystals. It is also observed that the doped crystals are platy shaped which is suitable for using optical devices. This is due to adsorption of impurity onto the surface of the crystals during the growth [13].



a

b

Fig. 1. (a) methyl orange doped TGS crystal, 1(b)methyl red doped TGS crystal

3. Results and discussion

3.1. Powder X-Ray diffraction analysis

The grown crystals were subjected to powder X-ray diffraction analysis to find the crystal structure. Powder X-ray diffraction pattern of pure and doped TGS crystals are shown in Fig. 2. The lattice parameters were calculated and presented in Table 2. From the data, it is observed that undoped and methyl orange doped TGS crystals crystallize in monoclinic system.

It is observed that the lattice parameters are slightly increased when TGS is doped with methyl red and also increased with dopant concentrations. The rate of adsorption of methyl red impurities may be increased with the rate of deposition of growth entities that increases the lattice parameter values. For higher concentration, the higher amount of impurities may be adsorbed at the surface terrace.

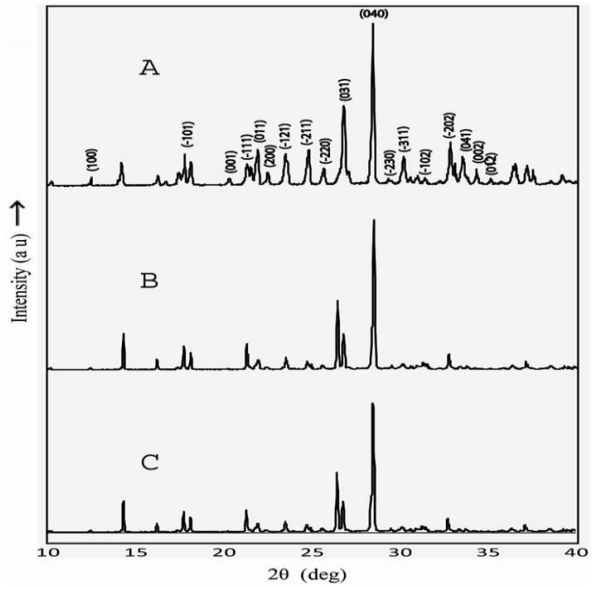


Fig. 2. X-ray powder diffraction pattern for (A) pure TGS (B) 0.5 mole% methyl orange doped TGS and (C) 0.5 mole% methyl red doped TGS crystal.

3.2. Transmission spectral analysis

The optical transmission spectral analysis of the grown crystals was carried out between 190 to 1100 nm. For optical fabrications, the crystal should be highly transparent in the considerable region of wavelength [14,15]. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices [16,17]. From the transmittance spectra (Fig. 3), it is noticed that undoped TGS crystal has a transmittance of more than 84.26% in the visible region. Methyl orange doped TGS crystal has lower transmission percentage compared to undoped TGS crystal and the transmittance decreased with the increase in molar concentration of methyl orange. A strong absorption is observed at 230 nm for pure TGS crystal and this corresponds to the fundamental absorption and UV cut off wavelength. It was observed that the transmittance for the methyl red doped crystal decreases and hence absorbance increases in the entire UV-visible region of the spectra in compared to spectrum of pure TGS crystal. From the

results it seems that the cut-off wavelength for undoped and methyl orange doped TGS crystals remain same.

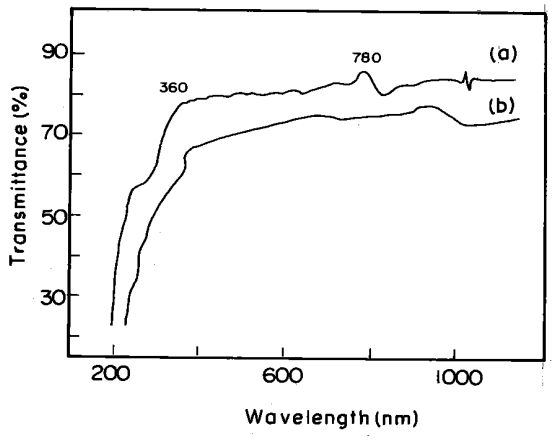


Fig. 3. UV-Visible transmittance spectra for (a) Pure TGS, (b) TGS + 0.5 mole% of methyl orange doped TGS crystals.

3.3 FTIR studies

Fourier Transform Infrared Spectroscopy Studies The spectrum of undoped TGS and KBr doped TGS are shown in Fig. 4. The pure TGS crystal shows a broad and strong absorption band in the range 2380 - 3800 cm^{-1} for the O-H stretching of hydrogen bounded carboxyl groups and the N-H stretching NH^{3+} group [18]. The C=O stretching vibration of carboxyl group appears as a sharp band at 1685 cm^{-1}. The C-H bending vibrations appear at 1493.93 cm^{-1}. The asymmetric S=O stretching frequencies can be assigned to frequency 1309 cm^{-1}. A strong band at 1118.76 cm^{-1} arises from C-O stretching. The transitional oscillation of NH^{+3} groups appears at 619, 572.8 and 501.5 cm^{-1}.

All the observations clearly confirm the presence of the functional groups in the grown crystals, which is in good agreement with the reported values. The FTIR spectra of 0.5 mole% and 0.5 mole% methyl orange doped TGS are shown in Fig. 4, although it provides similar feature as that of undoped TGS spectrum. The FTIR spectrum of pure TGS shows a broad envelope between 2380 - 3800 cm^{-1} which is shifted and peak becomes broader in methyl red doped TGS crystals. For 0.5 mole% methyl orange doped TGS each peak in the finger print region is characterized by the absorption of fine structure which is not observed either in pure or in 0.5 mole% methyl red doped TGS crystals. In addition the overtone bands are resolved for 0.5 mole% and 0.5 mole% methyl red doped TGS spectrum which is present in the pure TGS at 2350 cm^{-1}.

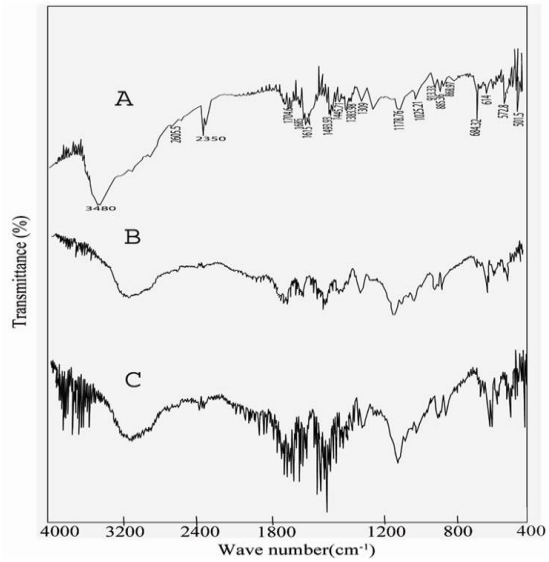


Fig. 4. FTIR Spectra (A) pure TGS (B) 0.5 mole% methyl orange doped TGS and (C) 0.5 mole% methyl red doped TGS Crystal

3.4 Vicker's microhardness study

Hardness of a material is a measurement of the resistance, it offers to local deformation. Vicker's microhardness (Hv) is a measure of hardness of a material calculated from the size of an impression produced under load by $H_v = 1.8544P/d^2$ kg/mm^2 where, P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of geometrical factor for diamond pyramid. It was observed that doped crystal is harder than the pure crystal. Microhardness increases with dopant concentrations and for loads above 50 g, cracks started to develop. Micro hardness increases for the presence of methyl orange into the lattice site of the crystals.This is may be result of loosely packed lattice with reduced bond energy due to the introduction of methyl red into the TGS crystals.

4. Conclusions

Good quality single crystals of pure and doped glycine phosphate ferroelectric single crystal were grown using low temperature solution growth method. TGS salts were synthesized and good quality, well faced and transparent pure TGS and methyl orange and methyl red doped TGS crystals have been successfully grown from aqueous solution by slow evaporation technique. The grown undoped and doped TGS crystals are observed were analyzed. FTIR spectra confirmed the presence of the dopant qualitatively. XRD studies reveal the monoclinic structure of the grown crystals.

Transmission study shows that the as grown crystal is highly transparent (84.26%) in the entire visible region which may be a suitable candidate for optical devices. The structural perfection study of the grown crystals ascertained the good crystal quality. Dyes effectively influence the phase transition temperature in comparison with the other dopants.

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*Corresponding author: logeshkumaresan@yahoo.com