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Doping Induced Optical Bandwidth Modification of Tri Glycine Sulphate Crystal

Vijeesh P.[1], Dr. Annieta Philip K.[2], and Dr. Supriya M.H.[3]

[1]Dept. of Electronics, Cochin University of Science and Technology, Kochi, Kerala, India, namastheviji@gmail.com
[2] Dept. of Physics, The Cochin College, Kochi, Kerala, India, annietaphilip@gmail.com
[3] Dept. of Electronics, Cochin University of Science and Technology, Kochi, Kerala, India, supriyadoe@gmail.com

Abstract: **Tri glycine sulphate is a ferroelectric and pyroelectric material and hence finds applications in infrared detectors at room temperature. Doping with various dopants alters the IR sensitivity of triglycine sulphate significantly. Doping changes the absorbance, Transmittance properties of the material. Doping also changes the bandgap of Triglycine sulphate. The optical bandwidth of Triglycine sulphate is modified by doping with Zinc Sulphate, Cadmium Chloride, and Barium Chloride.**

Index Terms: **Absorbance, Doping, Reflectance, Slow Cooling Solution Growth, Triglycine Sulphate, Optical Bandwidth.**

I. INTRODUCTION

The importance and applications of non-linear photonic crystals increased with the advancements in modern technologies. The progress in crystal growth techniques helped to employ them in several photonic applications. Modifying the properties of non-linear photonic crystals also emerge as a topic of research in recent years.

Many properties of triglycine sulphate crystals were studied by researchers all over the world.(Krishnakumar, 2008; Parimaladevi, 2009; Aravazhi, 1997) Tri glycine sulphate $(NH_2CH_2COOH)_3$. (H_2SO_4) (TGS) is one of the prominent material which is used for IR detector applications. It is a ferroelectric and pyroelectric material (Renugadevi, 2013). TGS has a spontaneous polarization along the b axis as it is the ferroelectric axis, and it shows the maximum pyroelectric coefficient of ~ 3×10^{-2} μC cm^{-2} K^{-1} at room temperature (Xu, 1991). Therefore the (010) face is of importance the morphology of TGS crystal. TGS has a second-order (order-disorder type) continuous phase transition at its Curie temperature (T_c), which is 49°C below it the crystal exhibits the ferroelectric phase, and above it, the crystal shows the paraelectric phase (Kayand, 1961). Above and below the Curie temperature, the crystal shows a monoclinic structure. It shows space group P_{21} in the ferroelectric phase and cento-symmetric space group $P_{21/m}$ in the paraelectric phase (Verma, 2010). The lattice parameters of TGS are a=9.41Å, b=12.64 Å, c=5.73 Å, and β=110°23' (Basu, 2018 & Sewell, 1955). In the present study, we try to improve the morphology and sensor parameters of TGS by doping with various dopants.

The optical properties of a material are of much importance in many applications. The interaction of the material with optical radiations mainly characterizes the optical properties of a material. It includes absorption, transmission, reflection, emission, refraction, scattering, or diffraction effects. The optical properties of a material are related to its atomic bonding and chemical structure (Pankove, 1971; Fox, 2008; Zanatta, 2019). In the case of indirect bandgap semiconductors, the optical transitions involve photons and phonons for conserving momentum. This leads to a lower rate of transition. The energy gap in these cases can be determined using the Tauc Plot(Tauc, Grigorovici & Vancu, 1966)

Various techniques are used to study the optical properties of a crystalline sample. Optical transmission, Optical reflection, and Optical absorption studies of samples are used for optical characterization of the material using UV-Vis-NIR spectroscopy. Transmittance is the ratio of the transmitted intensity to incident intensity. The optical absorption coefficient is the ratio of the absorbed portion(that remains after transmission and reflection) to incident intensity.

The present work is an attempt to study the optical band gap modifications in triglycine sulphate(TGS) by doping with Cadmium Chloride(CTGS), Zinc Sulphate(ZTGS)a and Barium Chloride (BTGS).

II. EXPERIMENTAL

A. *Materials used for the synthesis*

AR grade Glycine, Concentrated Sulphuric Acid, De-ionized water, Zinc Sulphate, Cadmium Chloride, Barium Chloride

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B. *Equipments*

We use an indigenously designed crystallizer (fig.1.) for the growth of the crystals. The crystallizer consists of a double-walled chamber with an RTD temperature sensor (PT-100) and a heater immersed in water between the walls. The temperature of crystallizer can be controlled with a PID based temperature controller and can set any desired cooling rate for facilitating slow cooling solution growth. A stepper motor assembly is provided for making regular rotatory movements in the test liquid for evenly distributing the temperature and maintaining the concentration of the solution. The crystallizer uses a seed hanger with stepper motor assembly for constant regular rotation of the inserted seed crystal. We used seed crystals inside the supersaturated test liquid for enhancing the growth of the crystal without multinucleation. We kept the supersaturated test solution in an open glass dish for two days for the formation of seed crystals.

Fig.1. Crystallizer with stepper motor and PID based temperature controller

We used a laser shadowgraph arrangement to monitor the growth of crystal inside the container. Two quartz windows are provided on vertically opposite sides of the crystallizer for facilitating laser to pass through it for shadowgraph. Shadowgraph technique visualizes the refractive index variations inside the test liquid. This technique is also used for determining the saturation temperature of the liquid, below which the seed crystal starts growing(Fig.2.).

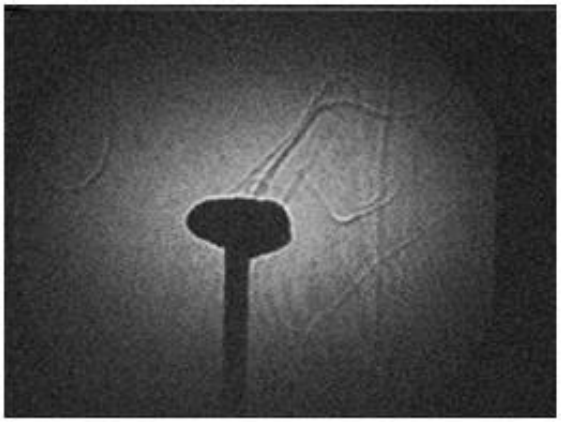


Fig.2. Shadowgraph showing growth plumes

C. *Material Synthesis*

TGS was synthesized from AR grade glycine (CH_2NH_2COOH) and concentrated sulfuric acid in the molar ratio of 3:1.

$3(NH_2CH_2COOH)+H_2SO_4 \rightarrow (NH_2CH_2COOH)_3H_2SO_4$

The required amount of Glycine is added to dilute sulphuric acid with continuous stirring of the solution, at a temperature of 60^0C. Synthesized TGS is then separated by evaporation, and it is again dissolved in double distilled water and filtered using vacuum filtration and allowed to evaporate again for eliminating impurities. The TGS obtained is dried, and a portion of the same is dissolved in double distilled water to make a supersaturated solution based on the solubility data reported [Berbacaru, 2005; Khanum, 2011; Sestak, 1966; Ashok, 2003).

The prepared solution is again filtered using vacuum filtration and 0.2μm filter paper for eliminating the dust particles and bacterial growth from the solution. The prepared solution is maintained at a temperature above saturation temperature for a day to eliminate the possibility of micro-clusters and to reduce the possibility of secondary nucleation during the growth process.

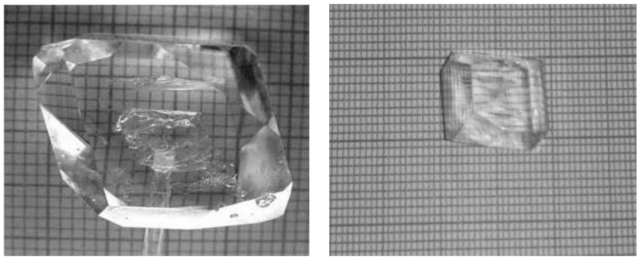
D. *Crystal Growth – pure TGS*

We used slow cooling solution growth for the growth of the crystal. The prepared supersaturated solution of triglycine sulphate is transferred to the crystallizer at 50^0C. A seed crystal fixed to seed hanger is then immersed in the test solution. The saturation temperature of the solution is determined as 47^0C by shadowgraph arrangement. The temperature of the solution is reduced from 47^0C to 32^0C in 3 days. A good quality crystal of dimensions 1.8cm X 1.4cm X 0.5cm is grown in three days of growth run(Fig. 4(a)).

E. *Crystal Growth – Doped TGS*

Many researchers reported that doping with appropriate dopants modifies the properties of TGS crystals (Kissinger, 1956). Variation. Here we tried to modify the optical bandwidth of Triglycine sulphate by doping with Zinc Sulphate, Cadmium Chloride, and Barium Chloride.

To synthesize doped TGS, we add 1 mole% of various dopants(in different experiments) (Zinc Sulphate, Cadmium Chloride, and Barium Chloride) into the solution while adding TGS. Slow cooling solution growth method adopted in this case also. Good quality crystals were obtained in all cases. (Fig. 3b, 3c, 3d)



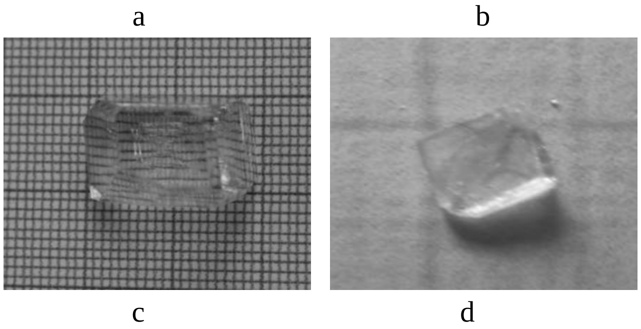


Fig. 3. a.Pure TGS b.ZTGS c.CTGS d.BTGS

F. Shadowgraph Imaging

Shadowgraph technique is employed to visually monitor the growth of crystals in all the above experiments. A collimated beam of LASER is allowed to pass through the quartz window provided on the wall of the crystallizer (Balasubramanian, 2014). When the laser ray passes through a region of varying refractive index, it deviates from the original path which can be seen on the screen kept on the other side. The change in intensity carries information about the convective field in the solution and the evolution of crystal morphology (Roopa, 2016). Figure 4 shows the recorded shadowgraph image, and the growth rate reduces with time. This reduction was due to reduced solute concentration. We employed a Mach-Zehnder interferometer also for visualization of the growth of crystal(Fig. 5.).

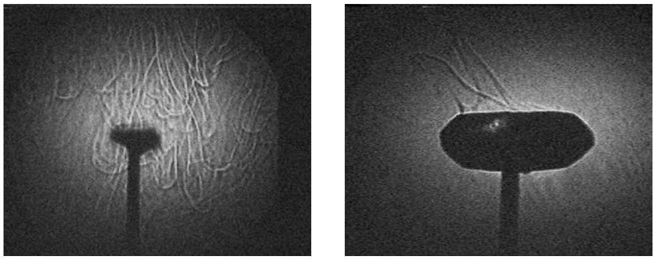


Fig. 4. Shadowgraph images of the growth process

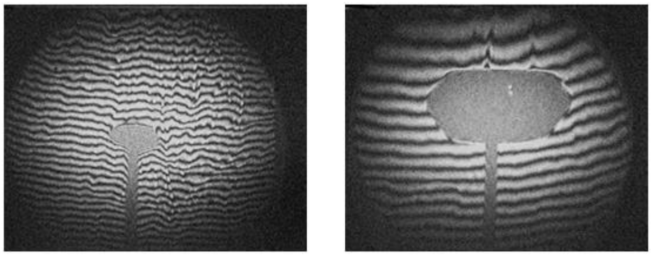


Fig. 5. Mach-Zehnder images of the growth process

III. CHARACTERIZATION

A. Fourier Transform Infrared Spectroscopy

The chemical bond structure of a sample can be determined using FTIR spectroscopy. The functional groups present in a sample can be determined using this (Vijeesh, 2018). It is normally done in the range of 450 cm^{-1} to 4000 cm^{-1} for pure and doped triglycine sulphate. The FTIR spectra of pure and doped TGS are shown (figure 6). The functional groups were identified from FTIR data, and it is the same as that reported in the literature. It also shows the increase in transmittance parameters with doping.

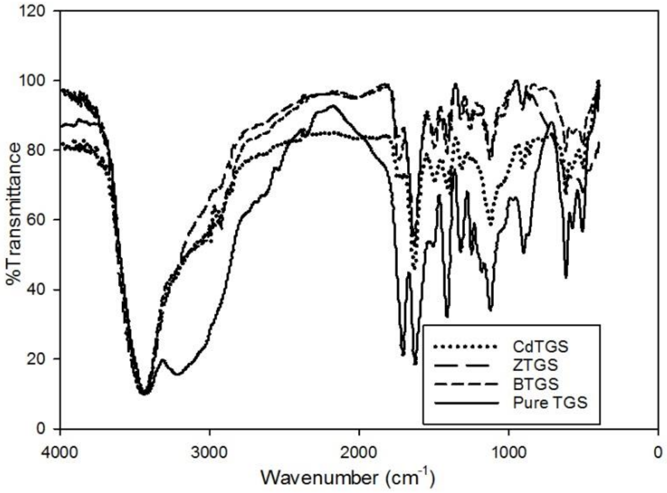


Fig. 6. FTIR Spectra of pure and doped TGS

B. UV-Vis-NIR Spectroscopy

The nature and quality of the crystal etc. can be obtained by studying the optical properties of the material. The transmittance and absorbance spectra obtained from UV-Vis analysis helps to study optical properties. The UV-Vis spectral analysis of the samples was done in the wavelength range of 200 to 1250 nm (Fig. 7.). The $CdCl_2$ doped sample shows a clear shift in transmittance and thereby change in the bandgap energy.

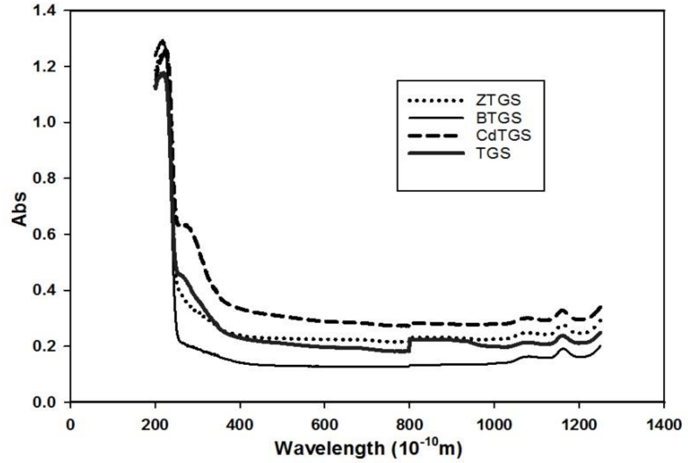


Fig. 7. Absorbance Spectra of Pure and Doped TGS

C. Optical bandgap.

The optical properties of a material are of much importance in non-linear photonic materials. The interaction of the material with optical radiations determines the optical properties. It includes absorption, transmission, reflection, emission, refraction, scattering, or diffraction effects. The optical properties of a material are related to its atomic bonding and chemical structure. So we tried to modify the optical bandwidth of TGS by doping with Zinc Sulphate, Cadmium Chloride and Barium Chloride. The optical bandgap of the materials was determined using the Tauc plot(figure 8) from the absorbance data of the materials.

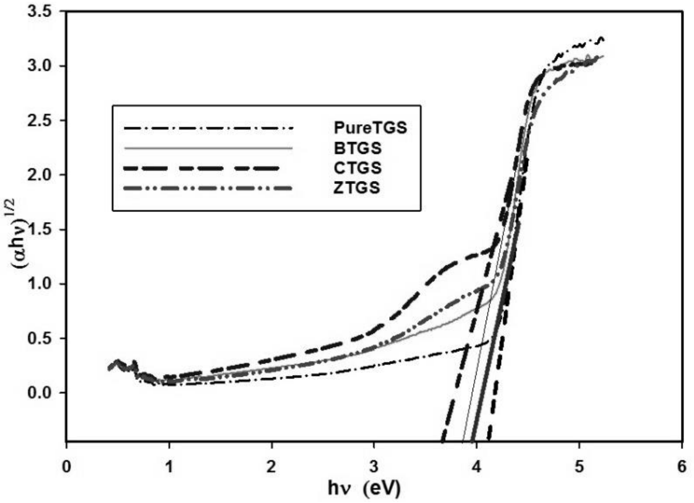


Figure 8: Tauc Plot for determination of optical band gap

The tabulated band gap of pure and doped TGS was shown in table 1. The analysis clearly shows the variation of optical bandwidth of TGS with doping. It is significantly modified in the case of CTGS, making it more suitable for IR detector applications.

Table I. Optical Bandgap of Pure and doped TGS

Sample	Pure TGS	ZTGS	BTGS	CTGS
Band Gap (eV)	4.12	3.86	3.95	3.65

IV. RESULT AND DISCUSSION

Good quality crystals of pure and doped TGS were grown using a slow cooling solution growth technique. The synthesized samples were characterized using FTIR, UV-Vis-NIR spectroscopy and the optical bandwidth is determined using Tauc plot from absorbance data. Doping with Zinc Sulphate, Cadmium Chloride, Barium Chloride enhanced the transmittance properties of TGS crystal. The optical bandwidth of TGS also modified with doping with these materials, and it is more relevant in doping with Cadmium Chloride and hence shows a much improved IR sensitivity than pure TGS.

CONCLUSION

Triglycine sulphate crystals of good face purity were grown with and without the addition of dopants, and they were characterized for their optical properties. The doped TGS shows much enhanced optical bandwidth for IR sensing applications. The result obtained is of much importance as researchers are trying to improve the IR sensing ability of triglycine sulphate.

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