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Title Page

Performance of crystal violet doped triglycine sulfate single crystals for optical and communication applications

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ABSTRACT

Single crystals of 0.01 and 0.02 mol% crystal-violet dye doped triglycine sulfate (NH₂CH₂COOH)₃H₂SO₄ (TGS) have been grown by slow evaporation technique. Enhanced dielectric, optical, thermal and mechanical behavior has been achieved by dye doping. Monoclinic structures showing particular coloring pattern and morphology change with dye concentration were obtained. Various functional groups and dye incorporation in grown crystals were confirmed qualitatively by FTIR and Raman analysis. A significant increase in Curie temperature from 50 to 55 °C with decrease in maximum permittivity has been observed. UV-Vis spectra showed an increased transmittance window and increased optical band gap from 5.61 to 6.11 eV as a result of doping. Increase in the sharpness and intensity of photoluminescence peak with a blue shift have been observed in doped crystals. The thermal stability and the decomposition temperature were found to increase by about 10 °C in 0.01mol% dye doped TGS. The mechanical strength of the grown crystals was estimated by Vickers microhardness test and was found high for dye doped TGS. High piezoelectric charge coefficient d₃₃ of 16 pC/N was observed for pure TGS which decreased as a result of dye-effect. The fabrication of patch antenna was carried out after simulating its resonant frequency that makes it suitable for telecommunication applications.

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Single crystals of 0.01 and 0.02 mol% crystal-violet dye doped triglycine sulfate (NH₂CH₂COOH)₃H₂SO₄ (TGS) have been grown by slow evaporation technique. Enhanced dielectric, optical, thermal and mechanical behavior has been achieved by dye doping. Monoclinic structures showing particular coloring pattern and morphology change with dye concentration were obtained. Various functional groups and dye incorporation in grown crystals were confirmed qualitatively by FTIR and Raman analysis. A significant increase in Curie temperature from 50 to 55 °C with decrease in maximum permittivity has been observed. UV-Vis spectra showed an increased transmittance window and increased optical band gap from 5.61 to 6.11 eV as a result of doping. Increase in the sharpness and intensity of photoluminescence peak with a blue shift have been observed in doped crystals. The thermal stability and the decomposition temperature were found to increase by about 10 °C in 0.01mol% dye doped TGS. The mechanical strength of the grown crystals was estimated by Vickers microhardness test and was found high for dye doped TGS. High piezoelectric charge coefficient d_{33} of 16 pC/N was observed for pure TGS which decreased as a result of dye-effect. The fabrication of patch antenna was carried out after simulating its resonant frequency that makes it suitable for telecommunication applications.

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1. Introduction

Triglycine sulfate (TGS) is an important material in the fabrication of IR-detectors as the crystal offers both pyroelectric and ferroelectric properties at room temperature.¹⁻³ The monoclinic structure for TGS single crystal was reported by Hoshino et al.⁴ who reported its Curie temperature to be 47 °C, where because of second order ferroelectric phase transition its space group changes from P2₁ to P2₁/m. Later, many studies performed on TGS crystals showed its Curie temperature to be around 49-50 °C. ^{5,6} The structure of TGS is complex in the form of a grid composed of glycine molecules (N⁺H₃CH₂COO⁻) and SO₄ tetrahedron linked together via hydrogen bonding.⁷ However, one of the major drawbacks in TGS crystals is the depolarization with time leading to a decrease in its device efficiency.⁸ The ferroelectric and pyroelectric properties of TGS with various dopants are extensively studied. H.V. Alexandru et al. studied temperature dependence of pyroelectric coefficients for L- and D-alanine doped TGS crystals.⁹ K. Meera et al. showed from P-E hysteresis studies an increase in coercive field values for L-cystine doped TGS.¹⁰

In addition, ferroelectric crystals are well known for their outstanding optical properties as the occurrence of ferroelectricity provides a major contribution to the local electric field that results in enhanced optical properties. Dye-host interaction is a subject of high interest because of its potential applications in display and electro-optic devices. A small amount of dye can alter optical nonlinearity of ferroelectric host material drastically.¹¹ When optical field excites the dye molecules, a change in dye-host interaction leads to molecular reorientation within the host lattice. This effective modification of molecular reorientation results in a corresponding change of material properties. The affinity of the dye molecule for different planes of the crystal is different because the values of electrostatic potential between dye molecules and the various crystal planes

are different. The value of electrostatic potential depends on the nature of the charge molecules appeared on the crystal plane and different planes have exposed the different topology of the molecules which leads to the variation in the potential on the surface of the crystal plane.¹²

However, only a few reports are available on the potential of dye sensitization of these ferroelectric crystals and making them useful for optical applications.¹³ Optical properties are influenced due to organic-inorganic hybrids and play a key role in material properties.^{14,15} A dye is classified as an organic aromatic chemical group that is water soluble and strongly emits or absorbs visible light effecting the optical, thermal, electrical and mechanical properties of a material that are important for device fabrication.¹⁶ There are many classes of dyes according to their chemical constitution and chromophore group, out of which azo dyes and aryl group dyes are extensively utilized for industrial applications.^{17,18} Crystal-violet (CV) belongs to the class of triarylmethane dyes containing three aryl groups attached to a central carbon atom. Crystal violet having molecular formula C₂₅H₃₀N₃Cl was a material of choice in the present work because of its numerous advantages in medical and scientific community. CV is used as a pH indicator.¹² In the medical community, it is employed as a bacteriostatic agent and an active ingredient in Gram's stain. The dye is used as an external skin disinfectant in humans and animals. It is widely used as a purple dye for textiles such as cotton and silk, and in paints and ink printing.^{16,19} With dye inclusions, crystals offer rich stereochemistry and thus are promising candidates for solid state lasers, spectroscopic and photonic applications.²⁰

Inclusion of dye in salt crystals is found to show a variety of photo-chemical/photophysical phenomena and affects various other properties of salt crystals.^{13,19} Further, the incorporation of the dye in the TGS host matrix is expected to give rise to a considerable local

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strains and the associated electric polarization in the crystal, thus making it possible to affect dielectric and optical properties. The objective of this study is to investigate the effect of CV dye doping on the growth, morphology and properties of TGS single crystal. This paper presents the optical, thermal, dielectric and mechanical properties of 0.01 and 0.02 mol% CV doped TGS (T1C and T2C, respectively) in comparison to pure TGS single crystals. Because of the very significant increase in the surface area of the grown crystals, with enhanced photoluminescence, dielectric, thermal and mechanical properties, these CV doped TGS crystals proved beneficial for use as laser gain media for solid state lasers, light emitting device applications, telecommunication applications and other optoelectronic systems.

2. Experimental procedure

2.1 Crystal growth

Single crystals of pure triglycine sulfate were grown by slow evaporation technique taking high purity glycine (Sigma Aldrich) and sulfuric acid in the molar ratio 1: 3 with distilled water as solvent. The summary reaction for the complex formation is as follows:

$$3 (NH_2CH_2COOH) + H_2SO_4 \longrightarrow (NH_2CH_2COOH)_3.H_2SO_4$$
(1)

The solution was maintained at a temperature of 45°C during stirring to vary the solubility conditions of the solute in distilled water. The prepared homogeneous solution was filtered and kept for evaporation in a petridish. Transparent colorless crystals were obtained in 20 days. Dye doped single crystals were obtained by adding 0.01, 0.02 and 0.03 mol% of CV dye to the above solution keeping all the growth parameters alike. The dye doped crystals were obtained in a lesser

time of about 15 days. Similar growth promoting effect was also observed in other dye doped single crystals.²¹ Shape and size of the grown crystals changed significantly with addition of dye and is shown in Figure 1a-c. A typical coloring pattern for 0.01 mol% dye doped crystal (T1C) was observed giving evidence of different affinities of various facets for CV dye which markedly differ for 0.02 mol% crystals (T2C) producing morphological alteration and making them appear translucent. This morphological change is a result of rate of adsorption onto the crystal surface that affects solution properties by modifying interfacial surface tension leading to changes in its anisotropic growth rate.²² Also, with high concentration of dye dopant (~ 0.03 mol %), the morphology varied to a great extent giving crystals of irregular shapes or in the form of clusters. Hence, these crystals with higher doping were not considered for characterization purpose.

2.2 Characterization techniques

The grown crystals were subjected to powder X-Ray diffraction analysis using Rigaku Ultima IV X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å) using a tube voltage and current of 40 kV and 40 mA, respectively. To analyze the dye incorporation in the crystals hence obtained energy dispersive X-ray analysis (EDAX) was performed using a JEOL JSM 6610LV scanning electron microscope.For functional group confirmation, Fourier transforms infrared spectra using Perkin Elmer FTIR spectrometer in the range 500 – 4000 cm⁻¹ and Raman spectra using Renishaw Laser Raman spectrometer with argon ion laser at 514.5 nm in the range 110-1700 cm⁻¹ were recorded. Using Agilent E4980A LCR meter with a programmable temperature controller, the dielectric constant and losses were measured at a heating rate of 0.25 °C min⁻¹. For optical studies, the absorption spectra were recorded in the range 190-900 nm using Perkin lambda 35 spectrophotometer. The photoluminescence spectrum of the crystals have been recorded using

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FluoroLog 3-22 Spectrofluorometer with ozone free 450 W Xenon lamp as excitation source at room temperature with excitation wavelength of 240 nm. Thermal analysis were carried out using Diamond Perkin Elmer system in the temperature range 30 - 700 °C in nitrogen atmosphere at a heating rate of 20 °C min⁻¹. The variation in the piezoelectric charge coefficient d₃₃ with field of 2 kV/mm was measured using a piezometer (PM 300, Piezotest, UK). The hardness measurements were made on the smooth surface of the crystals of 2 mm thickness using a Vickers hardness tester fitted with a Vickers diamond pyramidal indenter. Patch antenna characteristics were measured using Agilent 8722ES vector network analyzer.

3. Results and Discussion

3.1 Powder XRD and elemental analysis

The typical morphology of grown crystal with corresponding faces is shown in Figure 1d and was found to change as a result of increasing dye concentration. Pure and CV dye doped samples were subjected to powder X-Ray diffraction analysis to identify the unit cell parameters for the as grown crystals. The samples were scanned over the range $5 - 45^{\circ}$ at the rate of 2° min⁻¹ and the diffraction pattern obtained are shown in Figure 1e. The observed values are in good agreement with the JCPDS XRD data (00-015-0947) of TGS. Marked variation in peak intensity of doped samples in comparison to pure TGS was observed confirming CV incorporation into TGS lattice. Also the spectra showed slight changes in the peak position which can be attributed to strains in the lattice, resulted because of incorporation of heavy CV molecules causing anisotropic effects in the lattice changing the positions and the shapes of the X-ray diffraction peaks.²³ Particular coloring pattern were obtained for dye doping in these crystals. The lattice parameters

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were determined from checkcell refinement software and are listed in Table 1. In order to establish the incorporation of crystal violet dye in TGS lattice, which cannot be predicted by mere coloration of the crystals, EDAX analysis was performed. The EDAX spectra of TGS and T1C crystals are shown in Figure 2. Although the presence of dye doping in crystals was confirmed using EDAX analysis, but it is difficult to be quantified due to small amount of crystal violet dye and analysis limitation to measure hydrogen composition. But presence of chlorine in T1C confirms dye-doping in the TGS crystal lattice.



powder diffraction pattern for the as-grown single crystals.

Crystal	a (Å)	b (Å)	c (Å)	β	Volume (Å ³)
TGS	9.4350	12.6671	5.7457	110.33	643.916
T1C	9.4045	12.6358	5.7331	110.38	638.638
T2C	9.3774	12.6229	5.7173	110.15	635.335
Table 1: Lattice parameters for TGS single crystals doped with crystal-violet (CV) dye					



3.2 Functional group analysis

The presence of crystal violet dye in the doped samples was qualitatively estimated by FTIR and Raman analysis. The infrared spectra were taken using KBr pellet technique and are shown in Figure 3a. For better understanding of the low frequency spectrum, Raman analyses were performed complementary to FTIR studies and are shown in Figure 3b. The –COOH group of TGS

causes protonation of NH₂ group, giving rise to COO⁻ and NH₃⁺ group. The FTIR shows a broad spectrum between 3350 – 2800 cm⁻¹ which arises because of the asymmetric and symmetric N-H stretching of NH₃ group, C-H stretching of the CH₂ group and O-H stretching of the hydrogen bonded carboxyl group.²⁴ The absorption around 1706 cm⁻¹ is assigned to the stretching of C=O bond, while in case of CV dve doped crystals, it was found to be very slightly shifted at 1708 cm⁻¹ which still shows the stretching of C=O bond. Similarly, in Raman spectra the peak positions in pure TGS crystal at 1649 and 1675 cm⁻¹ are slightly shifted in case of dye doped crystals. The bands at 1623 and 1567 cm⁻¹ in FTIR and corresponding Raman bands around 1609 cm⁻¹ are assigned to antisymmetric and symmetric stretching modes of COO⁻ carboxylate ion group. Bending vibrations of NH₃⁺ at 1538 and 1501 cm⁻¹ appear to conflate as a result of CV doping in FTIR spectra and found shifted to around 1484 cm⁻¹ in Raman spectra. The strong absorption in the range 1127-977 cm⁻¹ is because of SO_4^{2-} ion of the sulfate group that become less sharp with the increasing content of dye dopant confirming CV incorporation in the lattice devoid of sulfate group. Similar changes were also observed in Raman spectra in the wavenumber range between 1115 and 903 cm⁻¹ respectively. The peaks due to NH_3^+ oscillations are evident in the range 615 to 501 cm⁻¹ showing variation in absorption intensity with doping concentration. A corresponding broadening of bands along with minor changes in peak positions confirms CV incorporation in to TGS lattice.



Figure 3: (a) FTIR spectra of pure and dye doped TGS single crystals (b) Raman spectra of pure and dye doped TGS single crystals.

3.3 Dielectric studies

Dielectric studies were carried out to find the transition temperature and corresponding lattice dynamics as a result of dye doping. The crystals were polished and their opposite faces were coated with high grade silver paste to obtain a good conductive surface layer. The magnitude of dielectric constant depends on the displacement of polarized charges and was found to be higher in case of pure TGS crystals. In all the samples, the dielectric constant decreases with increasing frequency and attains saturation at higher frequency. The variation of dielectric constant with temperature at 10 kHz is shown in Figure 4a depicting an increase in phase transition temperature with increasing dye concentration. The transition temperatures were found to be 50 °C for pure TGS, 53 °C for T1C and 55 °C for T2C, respectively. Also, the incorporation of dye in TGS lattice has resulted in a decrease of dielectric constant value thereby tuning the dielectric polarization mechanism in the grown crystals. However, the dielectric losses as a function of temperature were

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found to increase with increasing dye concentration and are shown in Figure 4b. But the values obtained are still lower in comparison to other TGS-doped crystals.^{22,25} In case of dye doped crystals, a partial substitution of glycine molecules with dye dopant occurs and is expected to prevent glycine group displacements, thereby decreasing the height of phase transition maxima. The low values of dielectric constant and losses reveal the good optical quality of the grown crystals making them desirable for use in various optical and communication devices.



Figure 4: (a) Temperature dependence of phase transition in pure and dye doped TGS at 10kHz.(b) Dielectric losses in pure and dye doped TGS at 10kHz.

3.4 UV-Vis analysis

The main optical properties of any material are its absorption coefficient (α), refractive index (n) and extinction coefficient (k). These optical properties are influenced as a result of dye doping in crystals because of modifications in their dependence on the electromagnetic radiation. Moreover, the evaluation of optical constants is an important factor for the design and analysis of optoelectronic devices and laser frequency conversion applications in industries. Knowledge of

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refractive indices and extinction coefficient at energies other than the fundamental absorption edge guides in understanding the electronic band-structures of the materials. Also, a preferred lower cutoff in the transmittance analysis in the range between 200 and 300 nm is considered effective for optical applications.

Figure 5a shows the UV-Vis transmittance spectra for pure and CV dye doped TGS recorded in the wavelength range 190-900 nm. Figure 5a inset shows transmittance data of CV dye depicting four characteristic absorption peaks with highest intensity peak at 590 nm. The cut-off wavelength for pure TGS was observed to be 246 nm but with dye inclusion it shifted to 240 nm in both the samples T1C and T2C. A broad but weak absorption peak at 594 nm was observed for T2C but is obscured in case of T1C. The induced lowering in cut-off as a result of dye doping suggests the usefulness of these crystals in several optoelectronic applications.

3.4.1 Optical absorption coefficient

The optical absorption coefficient (α) is a function of incident photon energy that increases exponentially and then saturates, a behavior typically governed by the density of states in the conduction band. It can be calculated using transmittance data from the following relation: ^{21, 26}

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{d} \tag{2}$$

Where d is crystal thickness and T is the transmittance. According to the Tauc relation, the absorption coefficient is related to photon energy (hv) in the grown crystals as:

$$(\alpha h\nu)^2 = A(h\nu - E_q) \tag{3}$$

where E_g is the optical band gap and A is a constant, indicating the allowed direct interband transition. Figure 5b shows the plot of $(\alpha hv)^2$ vs photon energy for pure and dye doped TGS where the energy band gap was evaluated by extrapolating the linear portion of the curve to $(\alpha hv)^2 = 0.0$ and was found to increase with dye doping in TGS crystals.

3.4.2 Optical properties and constants

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The reflectance (R) in terms of absorption coefficient can be written as:²⁷

$$R = 1 \mp \frac{\sqrt{(1 - \exp(-\alpha d) + \exp(\alpha d))}}{1 + \exp(-\alpha d)} \tag{4}$$

The reflectance for the dye doped crystals nearly reduced by half as compared to pure TGS in the high photon energy region (Figure 5c), suggesting high transmittance in case of dye doped crystals.

The optical constants, refractive index (n) and extinction coefficient (k) were determined from the reflectance data and in terms of absorption coefficient as:

$$n = \frac{\left[-\{(R+1) \neq \sqrt{3R^2 + 10R - 3}\}\right]}{2(R-1)}$$
(5a)

$$\mathbf{k} = \lambda \alpha / 4\pi \tag{5b}$$

where λ is the wavelength and are shown in Figure 5c and 5d. The high value of n along with lower k values for dye doped crystals in comparison to pure TGS makes them a promising candidate for use in photonic device application such as light emitting diode (LED) and image sensors.

The optical conductivity (σ) of the grown crystals was determined using the following equation:²⁸

$$\sigma = \frac{\alpha n c}{4\pi} \tag{6}$$

where c is the velocity of light and spectra shown in Figure 5d (inset). From the spectra it was observed that the optical conductivity remains a constant till 5 eV photon energy, beyond which it increases linearly. As a consequence of its increased band gap and optical constant studies, the dye doped crystals can be of potential interest in optical applications.



CV dye. (b) Estimation of optical band gap energy, Eg (c) Variation of reflectance (R) and refractive index (n) as a function of photon energy (hv) (d) Variation of extinction coefficient (k) and optical conductivity as a function of photon energy (hv).

3.5 Photoluminescence properties

Most arylmethane dyes give low emission in fluid solvents as fluorescing particles interact with solution molecules influencing their properties. Hence PL was performed for the solid samples. PL emission spectra for all the samples were recorded under an excitation wavelength of 270 nm and are shown in Figure 6a and 6b. Changes were observed in the PL spectra of pure and dye doped TGS samples. A single broad peak was obtained in pure TGS which splits into two with dye doping. For pure TGS, blue green emissions centered at 450 nm were observed. For CV doped samples, a shift in blue green emissions centered with two peaks at 416 and 435 - 438 nm was observed.

This shift arises because of lattice defects, created in the form interstitials because of CV dve which is devoid of sulfur.²⁹ Moreover, it is because with dve doping, the effective band gap increases which resulted in the emitted photon to have comparatively higher energy values. Hence these high energy photons give photoluminescence peaks at shorter wavelength as evident from PL spectra. A red emission peak centered at 644 - 655 nm observed in addition to the blue green emissions which are a characteristic of CV dye. The intensity of this red emission increases with the increased dye doping in TGS and showing a corresponding decrease in blue green emissions. The emission of red fluorescence confirms the incorporation of CV in the TGS lattice. The

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decreased luminescence broadness of dye doped crystals with increasing concentration indicates usefulness of these crystals for developing coherent sources in applications that require violet-blue light.



of red fluorescence confirming crystal violet incorporation in the TGS lattice.

3.6 Thermal Analysis

Figure 7a – 7c represents the thermo gravimetric and differential thermal analysis (TGA-DTA) curves of pure and dye doped TGS crystals in the temperature range between 40 and 700 °C at the heating rate of 10 °C min⁻¹ in nitrogen atmosphere. There is no weight loss in the pure and dye doped TGS samples in the temperature range between 40 and 200 °C, establishing their high temperature thermal stability. The first phase of weight loss begins at 212 °C in pure TGS and can be attributed to the decomposition of glycine.²² With dye doping of 0.01 mol%, this weight loss starts at 220 °C making them thermally more stable than pure TGS. The TGA curves show that

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maximum weight loss (~ 55 %) for the pure and dye doped TGS occur in the temperature range of 210 - 260 °C because of glycine getting decomposed into CO_2 and NH_3 . But the associated weight loss percentage in case of 0.02 mol % dye doped TGS decrease to 45 % in this temperature range, evidently establishing a reduction in the decomposition rate of glycine with dye doping.

The endothermic peak at 229 °C in the DTA curve represents the decomposition of pure TGS. With dye doping, an increase in this endothermic peak up to 238 °C and thermal stability up to 220 °C was achieved for T1C crystal. On further increasing temperature, the gases CO_2 and O_2 might have evolved leaving behind sulfur in residual form. The well defined endothermic peaks in pure and dye doped crystals establish their good crystalline quality.



Figure 7: TG-DTA curve of (a) Pure TGS single crystal (b) 0.01 mol% CV doped TGS (T1C) single crystal (c) 0.02 mol% CV doped TGS (T2C) single crystal.

3.7 Piezoelectric Response

The interaction between mechanics and electrical fields of a structure can be described in terms of piezo-response of the material. It can be determined using stress-charge form with the help of a piezometer measuring the piezoelectric charge coefficient (d_{33}). For this measurement, a poling process was performed at an applied field of 2kV mm⁻¹ for an easy alignment of domains.

In response to the applied electric field, the piezoelectric charge coefficient value d_{33} was found to decrease with increase in dye concentration. With electric field optimization at a tapping force and frequency of 0.25 N and 110 Hz, pure TGS showed a d_{33} value of 16 pC N⁻¹. The d_{33} response decreased to about 9 pC N⁻¹ for T1C crystals which further decreased to only 1 pC N⁻¹ in case of T2C single crystals. The reduction in piezoresponse of the grown crystals can be attributed to their modified domain structure showing lack of polarization orientation as also evident from dielectric study.

3.8 Hardness Testing

The mechanical properties of the grown crystals were evaluated by Vicker's microhardness tester and shown in Figure 8a. The Vicker's microhardness number (H_v) was calculated using the equation: ³⁰

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$$H_{v} = \frac{1.8544 \ P}{d^2} \tag{7a}$$

where P is the applied load (in g) and d is the diagonal length of the indentation (in μ m). Microhardness number (H_v) as evaluated is used to examine the ability of a material to resist indenter penetration. This is significantly affected by the presence of cracks, pores, and inclusions and hence gives important information regarding tensile strength and yield strength of the grown crystals. The indentation marks were made on the surface of grown crystals by applying loads of 5, 10, 20 and 30 g with a constant indentation time of 15 s. As microcracks appear at higher loads, the maximum load value was restricted to 30g only.

Meyer's index (n) was evaluated for crystals in order to analyze the nature of grown crystals. According to Meyer's power law:

$$P = Ad^n \tag{7b}$$

where A is a constant for a given material. The value of n is evaluated from the slope of log d vs. log P plot and is shown in Figure 8b. The values of Meyer's index for crystal TGS, T1C and T2C came out to be 2.57, 1.68 and 1.71, respectively. This value of n lies in the range $1.0 \le n \le 1.6$ for hard materials and n > 1.6 for soft materials.³¹ In present case, all the samples having n > 1.6 suggests soft nature of the grown crystal material. However, smaller n value in the case of doped crystal suggests increasing hardness as a result of dye doping.

In pure TGS the value of hardness number increases from 5 g to 10 g, after which it becomes constant. It is due to the softer nature of the crystal which helps adjusting energy easily by sliding the parallel planes of the crystal and hence no cracks appeared. As the contribution of the dye is

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increased in the pure TGS crystal, its voids are filled by the dye molecules which help to prevent the sliding of parallel planes. The value of Meyer's index is decreased by the incorporation of dye molecule in pure TGS which is also used as an experimental evidence for increase in the hardness of the doped crystal. Moreover, due to increase in hardness of doped crystal and problem in the sliding of planes, cracks are observed beyond 10 g load in doped crystal.



of log d vs. log P for Meyer's index evaluation.

3.9 Patch antenna simulation and fabrication

The application of piezoelectric materials reaches at the very far level in technological devices. It has contributed in many aspects from energy harvesting to sensors level.³² To fulfill the demand of the various technical aspects of communication, where various constraints (size, weight and performance) matters, patch antenna are required.³³ We have fabricated a microstrip patch antenna based on piezoelectric substrate, which behaves both in wireless transmission as well as energy harvesting device. We have chosen 0.01 % CV doped TGS single crystal as a substrate for

fabricating GHz patch antenna due to its low dielectric constant and defects free transparent geometry.

The design of patch antenna was formulated by transmission-line model and dimensions of TGS crystal ($\varepsilon_r = 16.1$ and h = 1.98 mm) based patch antenna was computed for an operating frequency $f_r = 6.5$ GHz as follows:³⁴

Geometrical width of the patch antenna has been calculated as,

$$W = \frac{c}{2f_r} \sqrt{\frac{2}{\epsilon_r + 1}} = 7.89 mm$$
 (8)

The effective dielectric constant of the patch was computed as,

$$\varepsilon_{\rm eff} = \frac{\varepsilon_{\rm r} + 1}{2} + \frac{\varepsilon_{\rm r} - 1}{2} \frac{1}{\sqrt{1 + \frac{12h}{W}}} = 12.32 \tag{9}$$

The actual geometrical length was found by using following realtions

$$\Delta L = 0.412 \times h \frac{(\varepsilon_{\text{eff}} + 0.3)(\frac{W}{h} + 0.264)}{(\varepsilon_{\text{eff}} - 0.258)(\frac{W}{h} + 0.8)} = 0.76 \text{ mm}$$
(10)

$$L = \frac{c}{2f_{\rm r}\sqrt{\varepsilon_{\rm eff}}} - 2 \times \Delta L = 5.15 \,\,\rm{mm} \tag{11}$$



Figure 9: (a) Simulated S₁₁ parameter versus frequency and 3D far-field radiation pattern (in inset) at the resonance frequency of 6.5 GHz. (b) Experimentally measured S₁₁ parameter versus frequency in which a resonance peak at 7.0 GHz has been obtained. Photograph of fabricated rectangular patch antenna (in inset) by using 0.01 % CV doped TGS (T1C) single crystal as a dielectric substrate (' ϵ_r ' = 5.1).

CST microwave studio was used for the simulation of patch antenna at 6.5 GHz resonant frequency. The inset feed was given to patch antenna by 50 Ω microstrip line. Optimization of impedence matching between patch and microstrip line was performed in the CST environment by cutting the two rectangulat slots in the patch. Copper plate of thickness of thickness 1.04 mm and standard SMA connector were used to fabricate the patch antenna. Figure 9a shows the simulated S₁₁ parameter of the patch antenna at 6.5 GHz resonance frequency with a return loss of -19.6 db. The inset of Figure 8a shows the 3D far-field radiation pattern of the patch antenna. Due to the radiation blockage from ground, intensity of the radiation is directive from the top of patch. The inset of Figure 9b shows the fabricated patch antenna on the piezoelectric crystal substrate. From experimental analysis, operating frequency of the patch antenna was found at 7.0 GHz (Figure 9b) with a return loss of -17 db. Thus our fabricated patch antenna exhibited very good resemblance to the simulated values of operating frequency and return loss. The minor change in operating frequency (0.5 GHz) and return loss (2.6 dB) was observed in theoretical and experimental values. This may be due to an error in the measurement of dielectric constant, dimensions of used crystal substrate and copper strip.

CONCLUSION

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Pure and CV dye doped TGS single crystals have been grown by solution method. Grown crystals were observed to be transparent up to 0.01 mol% CV with characteristic dye coloring pattern. Dye inclusion showed anisotropic growth promoting effect altering their morphology. CV dye incorporation confirmed from XRD, FTIR and Raman analysis. Dielectric studies reveal an increase in phase transition temperature from 50 to 55 °C with corresponding decrease in dielectric constant value making them useful for optoelectronic applications. The crystals were found to show good transparency in the UV-Visible region with increased band gap and enhanced optical constants making them useful for photonic device applications. The decreased luminescence broadness and increased coherence makes them a promising photoluminescent material for use in light emitting applications that require violet-blue light. Thermal studies demonstrate a reduction in the decomposition rate of glycine along with an increase in thermal stability and decomposition temperature with dye doping. The crystals showed a decrease in piezoelectric charge coefficient value with increase in dye concentration. CV doped crystals were found to be mechanically more stable than pure TGS. A patch antenna on the 0.01 mol% CV doped TGS substrate was simulated and fabricated for telecommunication applications. A good resemblance in the experimentally observed values of resonance frequency and return loss vis-à-vis their simulated values were

achieved. Combined with piezoelectric and dielectric properties, this set up can also be used for pressure sensor and energy harvesting applications.

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References

- 1. T. Hang, W. Zhang, H.-Y. Ye and R.-G. Xiong, Chem. Soc. Rev., 2011, 40, 3577–3598.
- 2. M. Trybus, W. Proszak and B. Woś, *Infrared Phys. Technol.*, 2011, 54, 326–330.
- 3. J. Novotný, Z. Podvalová and J. Zelinka, Cryst. Growth Des., 2003, 3, 1–3.
- 4. S Hoshino, Y Okaya and R. Pepinsky, Phys. Rev., 1959, 115, 323-330.
- 5. S. Horiuchi and Y. Tokura, Nat. Mater., 2008, 7, 357–366.
- C. Rai, K. Byrappa and S. M. Dharmaprakash, *Phys. B Condens. Matter*, 2011, **406**, 3308– 3312.
- 7. S. Balakumar and H. C. Zeng, J. Mat. Chem, 2000, 10, 651-656.

- K. Ćwikiel, W. Medycki and J. Stankowski, *Solid State Nucl. Magn. Reson.*, 2004, 25, 125–128.
- H. V. Alexandru, C. Berbecaru, F. Stanculescu, L. Pintile, I. Matei and M. Lisca, Sensors Actuators, A Phys., 2004, 113, 387–392.
- K. Meera, A. Claude, R. Muralidharan, C. K. Choi and P. Ramasamy, *J. Cryst. Growth*, 2005, 285, 358–364.
- 11. R. Muenster, M. Jarasch, X. Zhuang, and Y. R. Shen, Phys. Rev. Lett. 1997,78, 42-45.
- Y. Asakuma, M. Nishimura, Q. Li, H. M. Ang, M. Tade, K. Maeda, K. Fukui, J. Molecular Str. THEOCHEM, 2007, 810, 7-13.
- N. Sinha, N. Goel, B. K. Singh, M. K. Gupta and B. Kumar, J. Solid State Chem., 2012, 190, 180–185.
- 14. X. Fan, S. Pan, J. Guo, X. Hou, J. Han, F. Zhang, F. Li and K. R. Poeppelmeier, J. Mater. Chem. A, 2013, 1, 10389.
- F. Zhang, Q. Jing, F. Zhang, S. Pan, Z. Yang, J. Han, M. Zhang and S. Han, J. Mater. Chem. C, 2014, 2 (4), 667.
- 16. B. Kahr and R. W. Gurney, Chem. Rev., 2001, 101, 893–951.

- 17. A. K. Gupta, A. Pal and C. Sahoo, Dye. Pigment., 2006, 69, 224-232.
- F. Guzman-Duque, C. Pétrier, C. Pulgarin, G. Peñuela and R. A. Torres-Palma, *Ultrason. Sonochem.*, 2011, 18, 440–446.
- 19. G. B. Rao, P. Rajesh and P. Ramasamy, Mater. Res. Bull., 2014, 60, 709-713.
- B. Raju, A. Saritha, G. Bhagavannarayana and K. Hussain, J. Cryst. Growth, 2011, 324, 184– 189.
- 21. S. Bhandari, N. Sinha, G. Ray and B. Kumar, Chem. Phys. Lett., 2014, 591, 10–15.

- 22. R. Parimaladevi, C. Sekar and V. Krishnakumar, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2010, **75**, 617–623.
- 23. B. Fultz and J. M. Howe, *Transmission Electron Microscopy and Diffractometry of Materials* (*Third Edition*), 2007.
- 24. T. Bharthasarathi, V. Siva Shankar, R. Jayavel and P. Murugakoothan, J. Cryst. Growth, 2009, 311, 1147–1151.
- 25. P. K. Bajpai, D. Shah and R. Kumar, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 2012, 270, 93–105.
- 26. N. Goel, N. Sinha and B. Kumar, Opt. Mater. 2013, 35, 479-486.
- 27. J. Dalal, N. Sinha, B. Kumar, Opt. Mater. 2014, 37, 457-463.
- 28. S. Kasap, P. Capper, Handbook of electronic and photonic materials; Springer: 2006 pp 47-77.
- 29. R. Kripal, A. K. Gupta, S. K. Mishra, R. K. Srivastava, A. C. Pandey and S. G. Prakash, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2010, 76, 523–530.
- 30. H. Yadav, N. Sinha, B. Kumar, Mater. Res. Bull. 2015, 64, 194-199.
- 31. G. Ray, N. Sinha, B. Singh, I. Bdikin and B. Kumar, Cryst. Growth Des., 2015, 15, 1852-1860.
- 32. H. Yadav, N. Sinha and B. Kumar, CrystEngComm, 2014, 16, 10700-10710.
- J. C. Myers, B. S. Strachan; X. Yang; P. Chahal, *IEEE 63rd Electron. Components Technol.* Conf. 2013, 1662.
- 34. C. A. Balanis, Antenna theory, John Wiley & Sons, Inc., 2007, ch. 14, pp. 722–752.