Special Issue Published in International Journal of Trend in Research and Development (IJTRD), ISSN: 2394-9333, www.ijtrd.com

Studies on Optical and Mechanical Properties of Salicylic acid Admixtured TGS Single Crystals

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Abstract-- Ferro electric crystals of salicylic acid admixtured TGS crystals were grown by slow evaporation solution growth method. The grown crystals were characterized using X-ray diffraction studies. Optical parameters like transmittance, absorbance, reflectance, optical absorption co-efficient, refractive index, extinction co-efficient, and band gap energy of the crystal were estimated from UV-Vis-NIR spectrum. The SHG efficiency was checked using Kurtz-Perry powder technique. Mechanical parameters such as work hardening co-efficient, yield strength, elastic stiffness constant, fracture toughness and brittleness index were obtained using Vickers micro hardness studies.

Key Words-- Solution growth, UV-Vis-NIR spectrum, SHG, Vickers micro hardness

I. INTRODUCTION

Triglycine sulfate (TGS) crystal is an interesting ferroelectric and pyroelectric material, which exhibits strong absorbing ability in the most part of infrared region. Due to this property, it is used for the fabrication of infrared detectors and pyroelectric vidicon tubes operating at room temperature. It also finds applications in the fabrication of capacitors, transducers and sensors. TGS crystal shows a typical second-order ferroelectric phase transition at the Curie point Tc=49 ^{o}C. Below the Tc, TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization Ps arises along the b-axis and above Tc, it possesses the non-polar point group 2/m of the monoclinic system [1-3]. TGS crystal has some disadvantages over doped TGS crystals such as i) the ferroelectric domains possess high mobility at room temperature therefore it is necessary to stabilize domains, ii) easy depolarization by electrical, mechanical and thermal means and iii) microbial contamination with time during the growth. In order to overcome these disadvantages, variety of dopants such as amino acids, organic and inorganic compounds have been introduced in TGS crystals to achieve effective internal bias to stabilize the domains and to get desired pyroelectric and ferroelectric properties [4-7].In this work, glycine, sulfuric acid and salicylic acid were mixed to form Triglycine Sulpho- Salicylate (TGSS) sample. The aim of this paper to report and discuss the mechanical and optical properties of Triglycine sulfate crystals admixtured with salicylic acid (TGSS).

II. SYNTHESIS, SOLUBILITY AND GROWTH

Salicylic acid admixtured TGS (TGSS) salt was synthesized by dis-solving high purity glycine, sulfuric acid and salicylic acid in the molar ratio 3:0.7:0.3 in de-ionized water and the re-crystallization was carried out to improve the purity of the synthesized Triglycine sulpho-salicylate (TGSS) salt. Solubility study was performed by gravimetrical method [8] and Fig. 1 shows the solubility curve for TGSS salt. From the result, it is observed that the solubility of TGSS sample in water increases linearly with temperature, exhibit-ing a high solubility gradient and positive temperature coefficient of solubility. Growth of TGSS crystal Solution method with slow evaporation technique was adopted to grow crystals of the synthesized TGSS salt. In accordance with solubility data, the saturated solution of TGSS sample was pre-pared and constantly stirred for about 3 h using a magnetic stirrer and was filtered using 4 micro Whatmann filter paper. Then the filtered solution was taken in a beaker and covered by perforated cover for controlled evaporation. The seed crystals of TGSS were obtained by spontaneous nucleation. The supersaturated solution of TGSS was carefully transferred into another glass beaker and kept at 30°C in the constant temperature bath. Two or three good quality seed crystals of TGSS were placed in the supersaturated solution and the solution was allowed to evaporate the solvent slowly into atmosphere. A typical single crystal with size12 mm × 10 mm × 6 mm was obtained within a period of 45 days. A grown crystal is shown in Fig. 2 and the grown crystals are found to be stable, non-hygroscopic at ambient temperature, transparent and colorless.

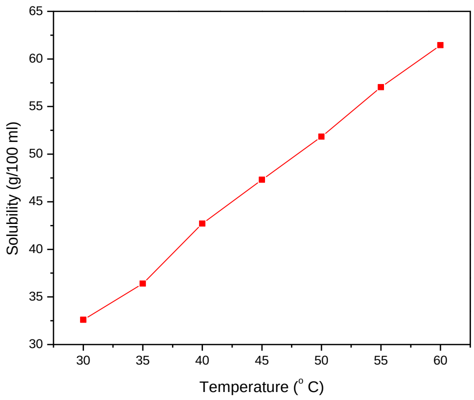

Figure 1: Solubility curve for TGS crystal admixtured with salicylic acid

Figure 2: The Photograph of TGS crystal admixtured with salicylic acid

III. SINGLE CRYSTAL XRD ANALYSIS

The structure of the grown TGSS crystal was analyzed by employing a Bruker-Nonious MACH3/CAD4single crystal X-ray diffractometer. From the single crystal X ray diffraction data, it is observed that the TGSS crystal belongs to monoclinic structure with the lattice parameters a = 5.828 (2) Å, b = 12.941 (4) Å, c= 9.728 (3) Å, α = γ =90°, β = 107.23° and V =700.7618 (2) Å3. The obtained structural data for the grown crystal of this work are almost coincided with those of pure TGS crystal and therefore the crystal structure of TGSS crystal is not changed [9].The slight changes in lattice parameters may be due to incorporation of admixtured material into the lattice of the crystal.

IV. OPTICAL PROPERTIES

To determine the transparency range of the grown TGSS crystal, UV-vis transmittance spectrum as recorded and is shown in Fig.3. Optically clear single crystal of thickness 2mm was used for this study. The cut- off wavelength of the crystal occurs at 225 nm. From the figure, it shows that the crystal was optically transparent in the wavelength range from 300 to 1100 nm and it is a feature that promotes possible optical applications in NLO devices. The crystal has sufficient transmission in the visible and IR region. The optical absorption coefficient (α) was determined using following formula α= ((2.303 log(1/T)t) where T is the transmittance and t is the thickness of the crystal. Optical transmittance range and transparency cut-off of single crystal are important factors for optical applications. The recorded transmittance spectra of TGSS crystals in the wavelength range of 200 – 1200 nm are shown Fig (3).Transmittance (T) = % T/100.The wave length is increased, transmittance is also increased. At about 225 nm a sharp fall to zero in the transmittance is observed for TGSS sample and the crystal has sufficient transmittance in the entire visible and near IR region. The sharp fall at 225 nm for the sample corresponds to the fundamental absorption edge, which is essential in connection with the theory of electronic structure .The band gap of TGSS is calculated using the formula Eg =1240/λ(nm), it is found to be (5.52) eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region.

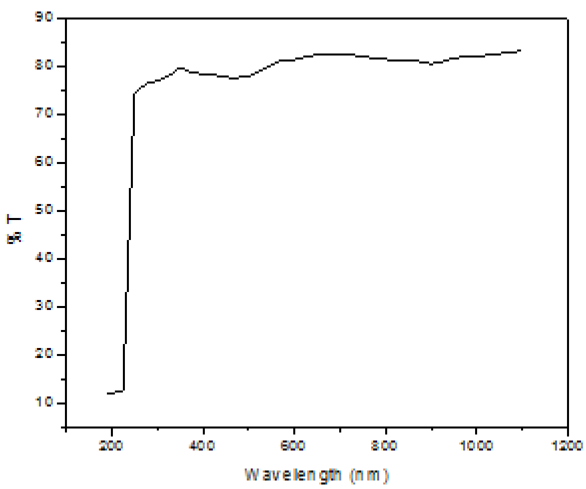

Figure 3: Wave length versus percentage of T.

From the above graph increasing the wavelength the percentage of T values also increased.

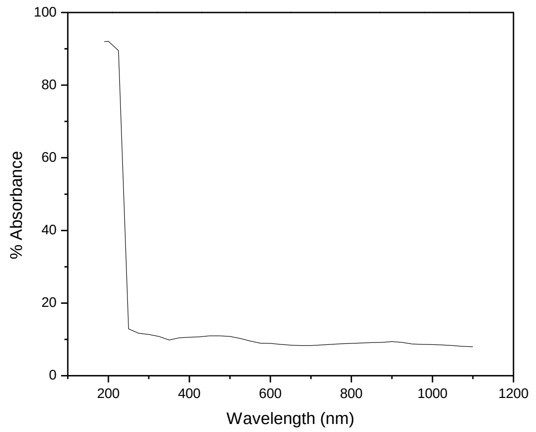

Figure 4: wave length versus absorbance.

From the above graph the absorbance wave length is 250nm.The absorbance is decreased; also the wave length is increased.

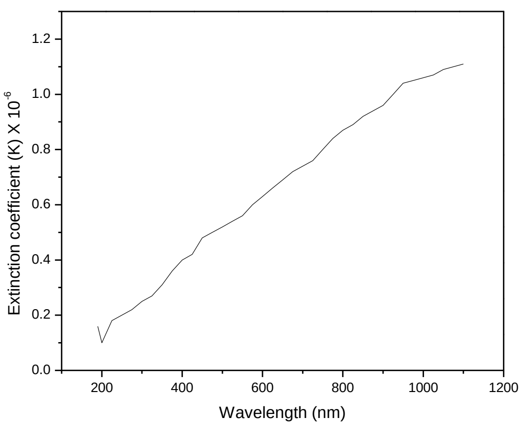

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Figure 5: Wavelength versus Extinction coefficient

The above graph was drawn between wavelengths versus extinction coefficient. Wave length increased the extinction coefficient also increased.

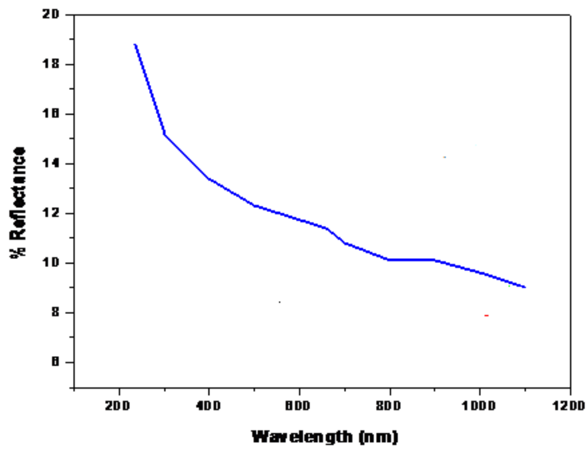

Figure 6: Wavelength versus Reflectance

The graph was plotted between Wave length (λ) and Reflection(R) as shown in Fig .6 .The relation is given by r(R)=1-(T+A). The Reflectance wavelength is 300 nm. The reflectance decreased also the wavelength is increased.

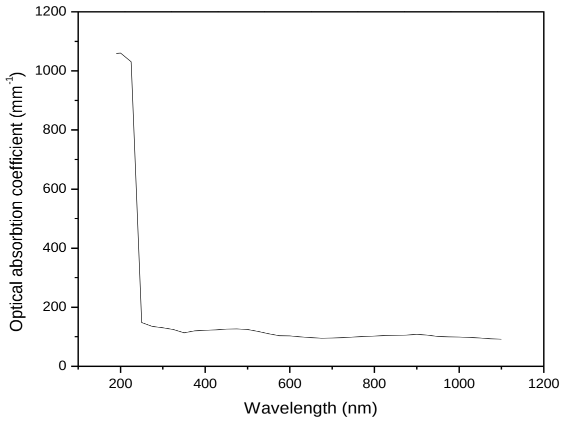

Figure 7: Wavelength versus Optical absorption co efficient

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons. The absorbance is decreased; also the wave length is increased.

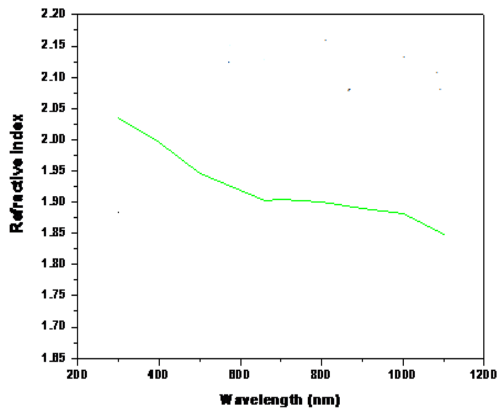

Figure 8: Wavelength versus Refractive index

The refractive index (n) can be determined from reflectance data using n= (1+√ R) / (1 − √ R).The plot between wavelength and refractive index (n) of TGSS crystal is shown in Fig. 8. From Fig. 8 it is observed that the refractive index decreases with increasing wavelength.

V. MECHANICAL PROPERTIES

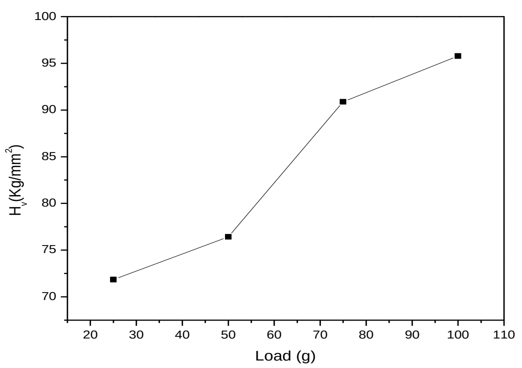

Figure 9: Dependence of hardness number (H_V) with load in grams for TGSS crystal.

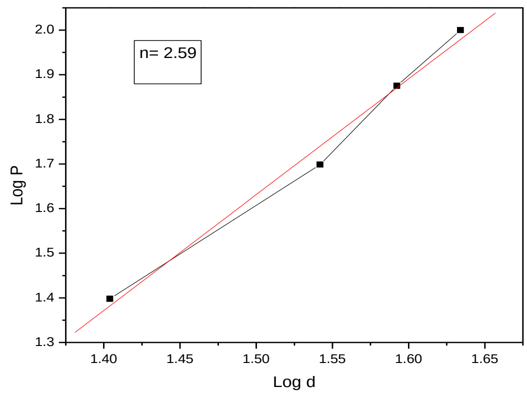

Figure 10: Plot of log P versus log d for TGSS crystal

Fig. 9 shows the variation of H_V as a function of applied loads, ranging from 25 to 100 g. It is clear from the Fig.9 shows that H_V increases with an increase in the load. It reveals that hardness number increases with increasing applied load. This phenomenon is known as reverse indentation size effect (RISE). When the material is deformed by the indenter, dislocations are generated near the indentation site. The major contribution to the increase in hardness is attributed to the high stress required for homogenous nucleation of dislocations in the small dislocation-free region indented [10]. The RISE can be caused by the relative predominance of nucleation and multiplication of dislocations. The other reason for RISE is that the relative predominance of the activity of either two sets of slips planes of a particular slip system or two slip systems below and above a particular load. The RISE phenomenon essentially takes place in crystals which readily undergo plastic deformation. The Mayer's index number was calculated from the Mayer's law, which relates the load and indentation diagonal length.

n P = kd , log P = log k + n log d where k is the material constant and n is the Mayer's index (or work-hardening coefficient). The above relation indicates that H_V should increase with the increase in P if n > 2 and decrease with P when n < 2. The 'n' value was determined from the plot of log P vs log d, as shown in Fig. 10. The slope of the plot of log P versus log d will give the work hardening index (n) which is found to be 2.59. The material TGSS is confirmed with large amount of mechanical strength which is better for device fabrications. According to Hanneman [11] the value of 'n' is less than 2 for hard materials and more than 2 for soft ones. Thus, TGSS crystals belong to the soft-material category. Since, TGSS is having moderately higher value of hardness number, the material is found to be suitable for device fabrications. The Yield strength (σy) and elastic stiffness constant (C11) was calculated by Wooster's empirical relation. The calculated stiffness constant for different loads was tabulated (Table 1). The crack length is measured from the centre of indentation mark to the crack end. Here, the crack length (l) is the average of two crack lengths for each indentation. Resistance to fracture indicates the toughness of material [12]. The fracture toughness of the indentation process gives an equilibrium relation for a well-developed crack extending under the centre loading condition;

$$K_c = \frac{P}{\beta_0 l^{3/2}}, l \geq \frac{d}{2}$$

Where β_0 is the indenter constant, equal to 7 for the Vickers's diamond pyramid indenter [13] and other symbols have their usual meanings. For the TGSS, the value of K_c is found to be 2.492×10^5 Kg $m^{-3/2}$, 3.108×10^5 Kg $m^{-3/2}$, 3.916×10^5 Kg $m^{-3/2}$ and 4.374×10^5 Kg $m^{-3/2}$ at 25, 50,75 and 100 g respectively.

Table 1: Yield strength and Stiffness constant for TGSS crystals

Sample	Load(g)	Yield strength (σ_y) x10 ^{6} Pa	Stiffness constant x 10 ^{15} Pa
TGSS	25	69.257	3.0428
	50	73.683	3.3912
	75	87.612	4.5915
	100	92.342	5.0341

Brittleness is another property, which affects the mechanical behaviour of a material, and is expressed in terms of the brittleness index (B_i) as.

$$B_i = \frac{H_V}{K_c}$$

The calculated values of B_i are found as 28.78 $m^{-1/2}$, 24.59 $m^{-1/2}$, 23.20 $m^{-1/2}$ and 21.89 $m^{-1/2}$ at 25 g, 50g , 75g and 100 g respectively.

VI. KURTZ-PERRY TECHNIQUE

Kurtz and Perry technique was used to check the NLO property of the samples. The grown crystals of salicylic acid added TGS were powdered and a high intensity Nd: YAG laser (λ=1064 nm) was used as source. The SHG was confirmed by the emission of green radiation (532 nm). The values of relative SHG efficiency of salicylic acid admixtured TGS crystals were found with reference to KDP. The obtained values of SHG efficiency is 0.86. Compared to that of pure TGS crystals salicylic acid added TGS crystals have more SHG efficiency and hence TGSS crystals are the potential candidates for NLO applications

CONCLUSION

Solubility studies of TGSS sample has been carried out at different temperatures and the single crystal of this sample has been grown from aqueous solution by slow evaporation method. XRD studies reveal that the structure of TGSS crystals is monoclinic. The XRD studies show that the crystalline perfection of the grown crystal is reasonably good. The NLO efficiency of TGSS sample is found to be 0.86 times that of KDP. The wider band gap of the material, significant transmittance and uniformity of refractive index in the entire visible region make the candidate ideal for device fabrication. The mechanical strength of the crystal is also sufficient to withstand the processes involved in device fabrication.

ACKNOWLEDGMENT

The authors like to thank the staff members of STIC, Crescent Engineering College (Chennai), St.Joseph's College (Trichy),) and M.K. University (Madurai) for having helped to carry out this research work.

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