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RESEARCH ARTICLE

INFLUENCE OF AMINO ACIDS ON THE GROWTH, STRUCTURAL, OPTICAL, MECHANICAL AND DIELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE (TGS) CRYSTALS

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ABSTRACT

Pure TriGlycine Sulphate (TGS) crystals were grown from aqueous solution by slow evaporation technique. The solubility of TGS increases with increasing temperature. The single - crystal XRD data of the grown TGS crystal were obtained using a single crystal X-ray diffractometer. The presence of various functional groups in the grown crystal is identified from FTIR analysis. The UV- visible spectrum analysis shows a strong absorption is observed at 228nm for all grown crystals. The forbidden energy gap is 5.438 eV. Micro hardness studies were carried out using vicker's microhardness tester. The dielectric constant of the grown TGS crystals was determined at various temperatures.

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INTRODUCTION

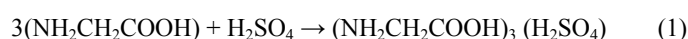
Triglycine Sulfate (TGS) crystal is a useful ferroelectric material founded in 1956 and has low dielectric constant and large pyroelectric coefficient. It finds applications in the fabrication of pyroelectric vidicon tubes, capacitors, transducers, sensors and also it is used in the infrared detection techniques as commercial products (Krajewski *et al.*, 1980; Sun *et al.*, 1999). TGS crystal shows a ferroelectric phase transition at the Curie point (49°C). Below the T_c , TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization arises along the b-axis and above T_c , it possesses the non-polar point group 2/m of the monoclinic system (Wood *et al.*, 1957; Newman *et al.*, 1992). It is observed that undoped TGS crystals have some disadvantages over doped TGS crystals such as high mobility of ferroelectric domains at room temperature, easy depolarization by electrical, mechanical and thermal means, microbial contamination with time during the growth and low Curie point etc., (Gaffar *et al.*, 1999; Prokopova *et al.*, 2001). Many organic and inorganic dopants have been used by researchers in order to overcome these disadvantages and to achieve effective internal bias to stabilize the domains and desired pyroelectric and ferroelectric properties (Lal *et al.*, 1993; Aravazhi *et al.*, 1997; Genbo Su *et al.*, 2000; Biedzycki *et al.*, 2001). Many metallic ion dopants such as Fe^{3+} , Cr^{3+} ,

Mn^{2+} , Ni^{2+} have been added to modify the properties of TGS crystals (Bye *et al.*, 1972; Eisner *et al.*, 1978; Gaffar *et al.*, 1999). Rare earth metal ions such as La, Ce and Nd modified the morphology and coercive field values (Muralidharan *et al.*, 2002). In this work, amino acids L-leucine and L-lysine has been introduced separately into the lattice of TGS crystal to alter various physical and chemical properties. The objectives of present work are to investigate the effect of the dopants (L-leucine and L-lysine) on the growth, structural, optical, mechanical and dielectric properties of TGS crystals.

MATERIALS AND METHODS

Sample preparation and Synthesis Studies

Analar Reagent (AR) grade of glycine and concentrated sulphuric acid (Merck India) in the molar ratio of 3:1 were used for synthesis of pure (undoped) Triglycine sulphate (TGS) salt. The required amount of sulphuric acid was diluted with de-ionized water. Then the calculated amount of glycine was added to the diluted acids to get the mother solution. The solution was heated until the synthesized salt of TGS was obtained. During the synthesis temperature of the solution was maintained at 50°C in order to avoid the oxidation of the sample. The chemical reaction for obtaining TGS salt is given below,



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1 mole % of L-leucine and L-lysine was added to the solution of TGS separately and it was heated at 45°C to obtain the L-leucine-doped and L-lysine -doped TGS salt. The purity of the synthesized salts of undoped, L-leucine-doped and L-lysine -doped TGS was improved by successive re-crystallization.

Solubility

The solubility of TGS in various solvents and found that water is the best solvent for crystallization of TGS. The re-crystallized salt of TGS was added to 50 ml of de-ionized water in an air tight container for the measurement of solubility in the temperature range 30-50 °C. Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer (accuracy is $\pm 0.1^\circ\text{C}$). Here the temperature was controlled using a voltage regulator attached to the magnetic stirrer. Initially, the solution was kept at 30 °C and stirred continuously using the magnetic stirrer for about 2 hours. After attaining the saturation, the solubility was determined gravimetrically (Srinivasan *et al.*, 2000). The same procedure was followed for other temperatures and for doped TGS salts. The solubility curves for pure and doped TGS salts are displayed in the Fig.1. From the results, it is observed that solubility increases with temperature for the samples and it is found to be more in doped TGS salts than that for the pure TGS sample. Solubility data is necessary to prepare the saturated solution of the sample at a particular temperature.

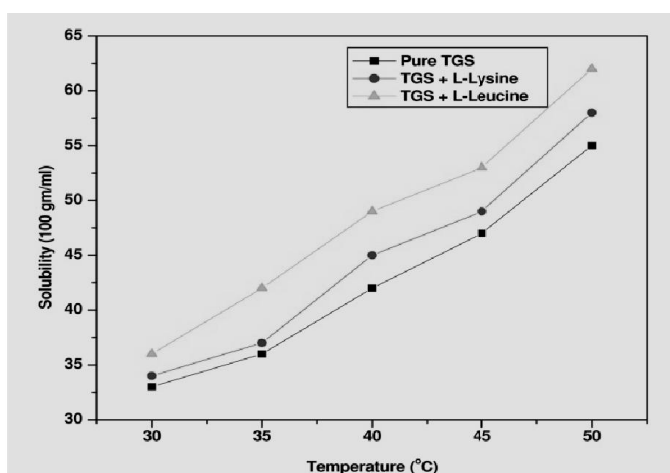


Fig. 1. Solubility curves for Pure TGS and doped TGS salts

Solution method with slow evaporation technique was adopted to grow the single crystals of the synthesized salts of undoped and doped TGS. In accordance with the solubility data, the saturated solutions were prepared and were constantly stirred for about 3 hours using a magnetic stirrer and were filtered using 4 micro Whatmann filter papers. Then the filtered solutions were kept in borosil beakers covered with porous papers and the beakers were kept in constant temperature water bath. The grown crystals were harvested after a period of 30 days and they are displayed in the photograph (Fig. 2). It is noticed that the pure (undoped) and doped TGS crystals are colourless and transparent. There are morphological alterations in the TGS crystals when it is doped with L-leucine and L-lysine. This is due to adsorption of impurity onto the surface of the crystals during the growth (Gaffar *et al.*, 1989 a).

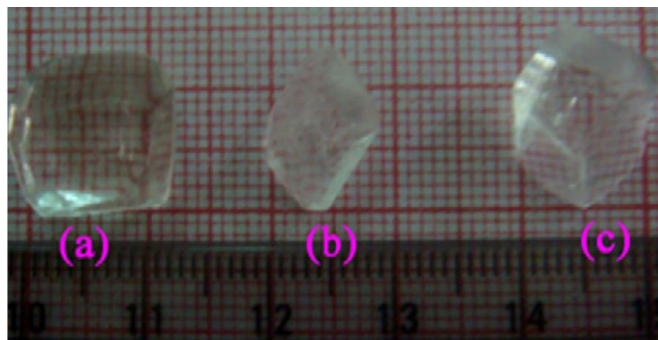


Fig. 2. Grown Crystals (a) Pure TGS (b) L-Lysine doped TGS and (c)L-Leucine doped TGS

RESULTS AND DISCUSSION

X-ray diffraction studies

Fig. 3 shows the XRD pattern of the pure and doped TGS crystals, obtained using the X-ray diffractometer (Model: ENRAF NONIUS CAD4), and the crystallographic data are given in Table (1). The space group and number of molecules per unit cell for the grown pure and doped TGS crystals were found to be P_{21} and 2 respectively.

Table 1. Crystallographic data of Pure and doped TGS

	a (Å)	b (Å)	c (Å)	β (Å)	Cell Volume(Å) ³
Pure TGS	9.5203	12.6983	5.7213	110.2020	649.1032
TGS + L-Leucine	11.1849	12.0256	5.4993	100.9852	726.1365
TGS + L-Lysine	10.2521	12.6269	5.7803	94.7180	745.7415

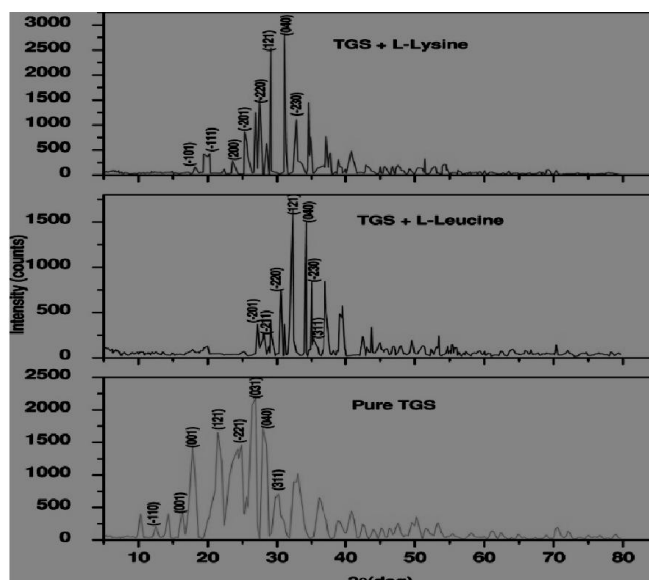


Fig. 3. XRD pattern for Pure and doped TGS crystals

The prominent peaks of pure TGS were (011), (-121), (-221), (031), (040) and (311), the prominent peaks of L - Leucine doped TGS were (111), (-220), (-221), (031), the prominent

peaks of L - Lysine doped TGS were (111), (-220), (031), (040), (-230). The spectra shows slight changes in peak intensities and peak positions, which may be attribute to strain in lattice. The slight increase in lattice parameter and volume of unit cell of the doped crystals is attributed due to the replacement of smaller lattice glycine molecules by larger L - Leucine and L - Lysine molecules, the lattice could be strained. In the case of doped crystals, the changes in the relative intensity and peak positions confirm the presence of substituted amino acids (Gaffar *et al.*, 1989 b; Lock *et al.*, 1971).

FTIR analysis

The presence of functional groups in the pure TGS and amino acid doped TGS can be confirmed by FTIR analysis.

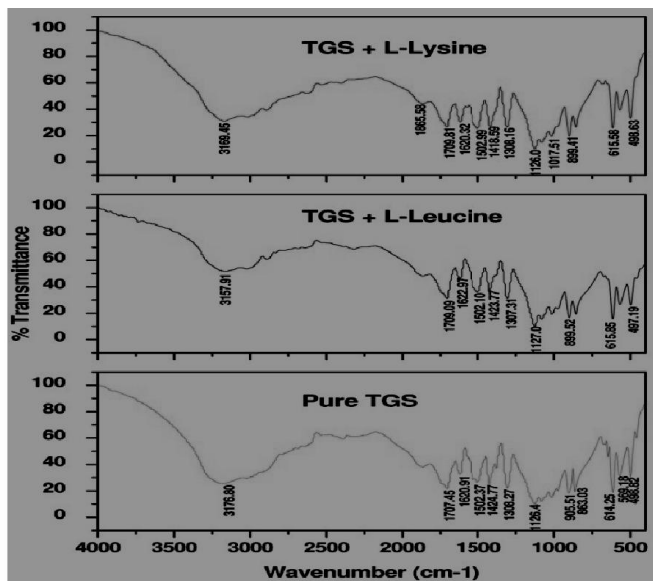


Fig. 4. FTIR analysis for grown crystals

FTIR spectra (Fig. 4) of pure and doped TGS recorded for a powder samples using KBr pellet technique in the frequency range of 400 – 4000 cm^{-1} . In the TGS, the NH stretch, OH stretch and aliphatic CH stretch overlaps to each other at a frequency of 3201 cm^{-1} . The absorption in the range of 1700 -1870 cm^{-1} is mainly due to the C=O stretching of the carboxylic acid (COOH) group. The Bending mode due to NH_3^+ is clearly seen at 1425, 1503 and 1537 cm^{-1} . The strong absorption in the range 1018 – 1126 cm^{-1} is mainly due to the SO_4^{2-} ion. The peak due to NH_3^+ oscillation occurs at 614, 572 and 499 cm^{-1} . The peak at 1376 cm^{-1} is due to the presence of CH_2 bending. The presence of L-leucine in TGS is confirmed by resolving of NH, OH and CH peaks. Hence it is presumed that the L-leucine molecules would be brought near the NH_3^+ and COOH groups of TGS through its alcoholic OH group. L-lysine doped TGS shows the same effect as L-leucine doped TGS. The assignments for the absorption bands/peaks of the FTIR spectra are given in accordance with the data reported in the literature (Raghavan *et al.*, 2008). It is noticed that some of bands of spectra of the doped TGS samples are either broadened or narrowed and this indicates the presence of dopants in the doped TGS crystal. There is no major difference in the FTIR spectra of L-leucine doped TGS

and L-lysine doped TGS because both are isomers and the presence of dopants (L-leucine and L-lysine) in the growth solution with low concentration (1mol%) does not affect much in the FTIR spectrum. If the concentration is high, then the solution becomes unstable. But the presence of low concentration of the dopants influences the ferroelectric properties of TGS crystals.

UV- visible-NIR spectroscopy

The UV-visible - NIR spectroscopy was performed on the samples by using UV - 700 SHIMADZU SPECTROPHOTOMETER. The recorded transmittance spectra of pure and doped crystals in the wavelength range 200-1100nm are shown in Fig.5.

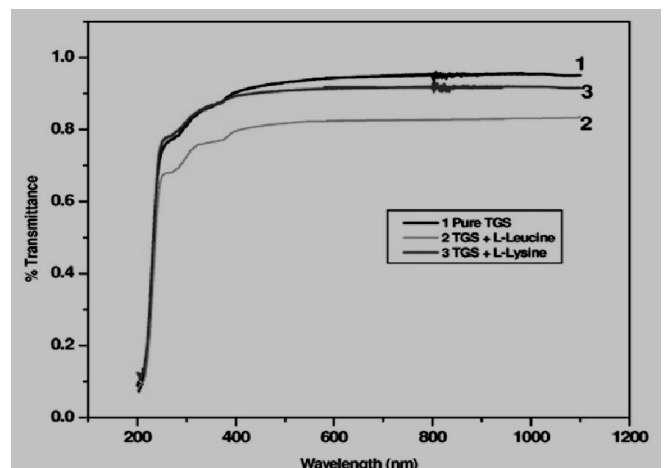


Fig. 5. UV Transmittance spectra of Pure and doped TGS crystals

A strong absorption is observed at 228 nm for all the grown crystals of this work and this corresponds to the fundamental absorption of UV cutoff wavelength. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Using the formula $E_g = 1240 / \lambda$ eV (λ is in nm), the band gap is calculated to be 5.438 eV. The observed behaviour of the spectra and band gap value found in this work are in good agreement with UV-Visible spectral data of TGS crystal reported in the literature (Senthil Pandian *et al.*, 2008).

Microhardness Test

In order to study the mechanical properties, micro hardness measurements were carried out on the grown pure and doped TGS crystals. At lower loads, hardness is relatively low and it increases for higher loads and remains constant up to a load of 25gm. Above 25gm load significant cracking occurred due to release of internal stress generated locally by indentation. Doped crystals have relatively higher hardness values than pure crystals. Increase in the bond energy with doping is believed to cause the higher hardness values. Selected smooth surface of the cleaved plates of the b - plane was subjected to vicker's micro hardness measurements. The hardness number was calculated using the relation,

$$H_v = 1.8544 P/d^2 \text{ kg/mm}^2 \quad (2)$$

where, H_v is the vicker's microhardness number, P is the applied load and d is the diagonal length of the indentation impression. The load dependence of the microhardness number for pure and doped TGS crystals were measured and is shown in Fig. 6.

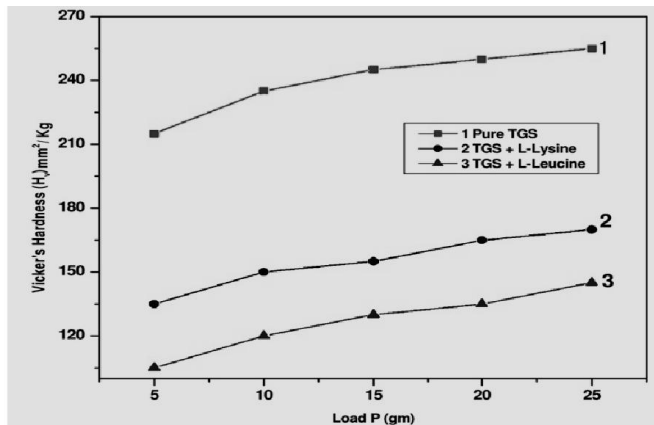


Fig.6. Microhardness studies for Pure and doped TGS Crystals

The phenomenon of dependence of microhardness of a solid on the applied load is known as the reverse indentation size effect (Sangwal, 2000). Meyer's law relates that load and size indentation as $P=k_1d^n$, where k_1 is the material constant and n is the Meyer's index. Hence $\log P = \log k_1 + n \log d$. The slope of the graph of $\log P$ against $\log d$ gives the values of n and it is determined to be $n=3.75$. It is in good agreement with theoretical prediction ($n > 1.6$ – Soft material, n lie between 1 & 1.6 – hard material) and hence the grown pure and doped TGS crystals belong to the group of soft materials (Hanneman M., 1941; Onitsch E.M., 1947). The hardness of the L-lysine doped TGS crystal was found to be less than that of pure TGS crystal and the hardness of L-leucine doped TGS crystal was much less than L-lysine doped and pure TGS crystal. This is attributed due to the incorporation of the doped ions into TGS lattice, which makes the doped crystals loosely bound.

Dielectric studies

L-lysine doped TGS crystals showed changes in the dielectric properties due to local strain created by the higher dipole moment of lysine molecules. Dielectric permittivity measurement was carried out on the polarizing plane in the temperature range 30 °C - 70 °C at a frequency 1KHz. The temperature dependence of dielectric constant for pure, doped L-lysine and L-leucine TGS crystals were illustrated in fig.7, which shows that the dielectric constant for doped crystals decreases when compared to pure TGS. In the case of pure TGS, Curie temperature (T_c) is 51°C. The T_c for doped L-lysine and L-leucine are 55°C. Dielectric constant is reduced for doped crystals. The lowering of ϵ_{max} and shifting of T_c to higher temperatures in the case of doped TGS crystals may be understood in the following way.

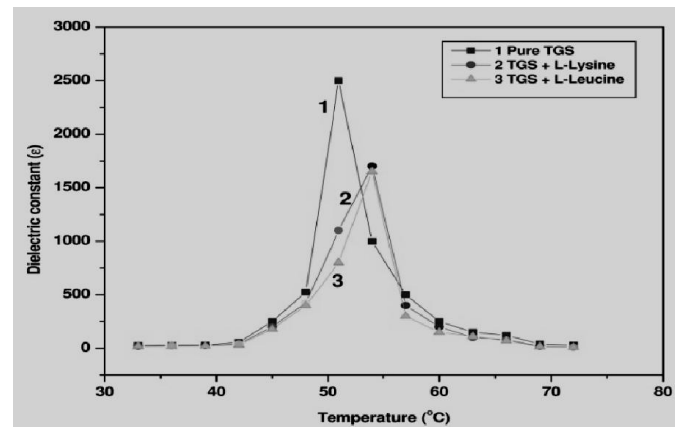


Fig. 7. Variation of dielectric constant with temperature for pure and doped crystals at 1000 Hz

When a large size molecule goes substantially in TGS lattice replacing some of the glycine molecules, it produces local strains. The decrease of dielectric constant is also attributed to the increasing of dipole moments of the molecules.

Conclusion

XRD studies for the grown crystals have been carried out and it is found that the structures of the grown TGS crystals are monoclinic. The unit cell parameters of the grown crystals were obtained from the XRD studies. The various functional groups of the grown TGS crystals have been identified from FTIR Spectra. From the UV-visible spectral analysis, a strong absorption is observed at 228 nm for all grown crystals and the forbidden energy gap is 5.438 eV. The density of the grown crystals was measured by the floatation method. Microhardness studies reveals that the hardness of the L-lysine doped TGS crystal was found to be less than that of pure TGS crystal and the hardness of L-leucine doped TGS crystal was much less than L-lysine doped and pure TGS crystal. From the dielectric studies, it is observed that the dielectric constant of the doped TGS crystals is reduced when compared to pure TGS.

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