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GROWTH AND CHARACTERIZATION OF CALCIUM CHLORIDE DOPED TRIGLYCINE SULPHATE SINGLE CRYSTALS

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***Abstract*: Single crystals of Triglycine sulphate doped with Calcium Chloride (TGSCACL) were grown from aqueous solution by low temperature solution growth technique. Density of the sample was measured by floatation method. From EDX analysis, the presence of calcium chloride in grown crystals was identified. Crystalline quality and cell parameter values were found using powder XRD analysis. The various functional groups of the grown crystal have been identified by FTIR spectra. Mechanical strength of TGSCACL crystal was investigated by Vicker's Microhardness test. The optical nature of the grown crystals was studied by UV - VIS - NIR spectra. The dielectric studies have been performed by measuring dielectric parameters.**

***Keywords*: Slow evaporation, XRD, EDX, Microhardness studies.**

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1. INTRODUCTION

Triglycine Sulphate(TGS) is well known ferroelectric and pyroelectric material below its critical temperature (49°C). This material has found application in the fabrication and development of infrared detectors due to its high pyroelectric coefficient(p), reasonably low dielectric constant(ε_r) and best figure of merit($p/\ \varepsilon_r$) [3]. It belongs to monoclinic system both in ferroelectric and paraelectric phases [5]. The space group transforms from P_{21} in ferroelectric phase to centro symmetrical P_{21}/m in paraelectric phase [13]. The main disadvantages of the TGS crystals are a) depolarization with time and b) Low Curie temperature[17]. In order to overcome these unfavorable features, variety of dopants such as aminoacids, metallic, rare earth, organic and inorganic compounds have been introduced [6]. Various metallic ion dopants such as Mn^{2+}, Ni^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+} etc. were added to modify the optical properties of TGS crystals. Rare earth metal ions such as La, Ce and Nd were used to modify the morphology and coercive field values of TGS crystals [44]. Incorporation of inorganic additives into an organic material can alter various physical properties in order to achieve better performance in opto – electronic devices. The presence of metallic species in organic compounds raises the hardness of the compounds considerably [3]. The objective of the present work is to investigate the effect of addition of Calcium chloride as dopant on growth, structural, optical, mechanical and electrical properties of TGS crystal.

2. MATERIALS AND METHODS

2.1 Materials

AR/BDH grade chemicals, *viz.*, glycine, Con. H_2SO_4, Calcium chloride were purchased and used as such. Deionized water was used as solvent.

2.2 Crystal growth

The required amount of Con.Sulphuric acid (0.9 mol) was diluted with distilled water. Then calculated amount of glycine (3 mol) was added. The solution was kept in magnetic stirrer for 1 hr and stirred well. Then calculated amount of Calcium chloride (0.1 mol) was added and stirred for 2 hrs and kept for growth. After 5 days crystal started growing. Growth period is 30 days. Fig. 1, shows the photograph of obtained TGSCACL crystal.

Fig.1. Photograph of grown TGSCACL crystal

3. RESULTS AND DISCUSSION

3.1 Energy dispersive X – Ray (EDX) analysis

EDX has been performed to identify the elements present in grown crystals. The EDX spectrum of TGSCACL crystal is shown in Fig. 2.

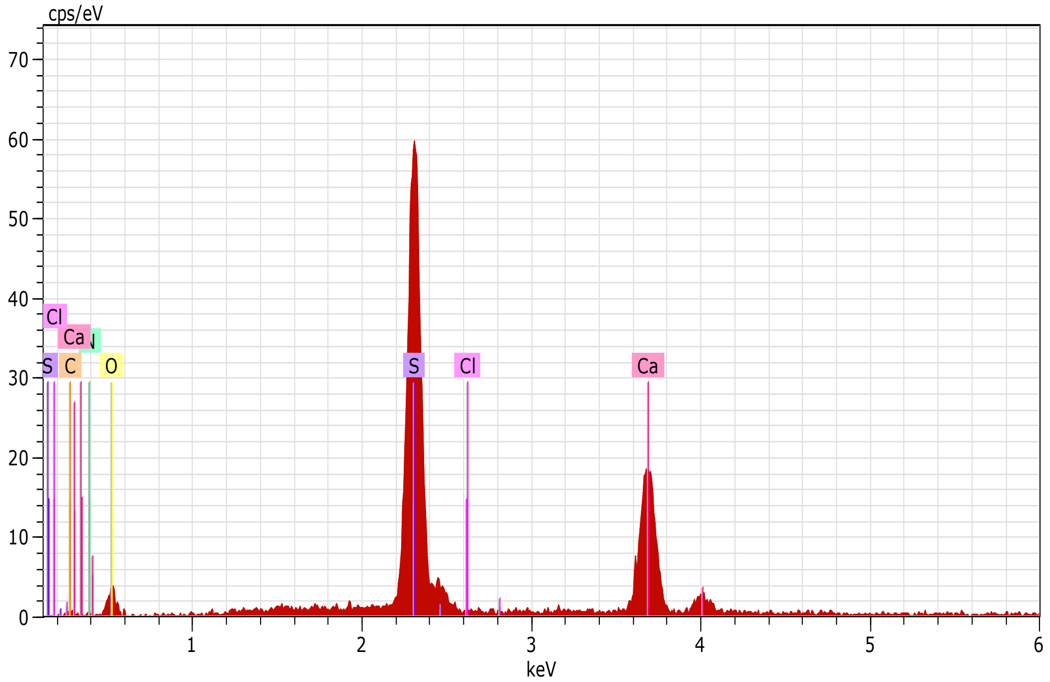

Fig.2. EDX spectrum of TGSCACL crystal

The atomic and weight percentage of elements present in TGSCACL crystal is shown in Table I.

Table I: Atomic and weight percentage of TGSCACL crystal

Element	**Atomic %**	**Weight %**
C	8.15	14.41
N	7.08	10.73
O	32.13	42.65
S	32.41	21.47
Ca	20.07	10.64
Cl	0.17	0.10
Total	**100.00**	**100.00**

3.2 Powder X – Ray diffraction

The indexed X – ray diffraction pattern of TGSCACL crystal is depicted in Fig. 3. Sharp peaks show good crystalline quality of grown crystal. All the observed peaks were indexed for (h k l) values using JCPDS files.

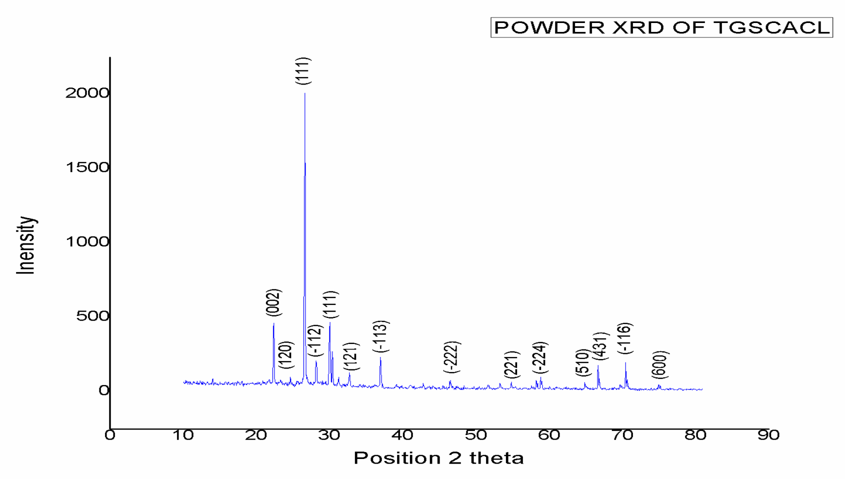

Fig. 3. Powder XRD pattern of TGSCACL crystal

Predominant peak 2θ = 26.6° corresponds to (1 1 1)

3.3 FTIR analysis

TGSCACL crystal was powdered and mixed with KBr to form pellets for obtaining optical transmission spectra in mid IR region using SHIMADZU FTIT – 8400 spectrophotometer. The spectrum is presented in Fig. 4.

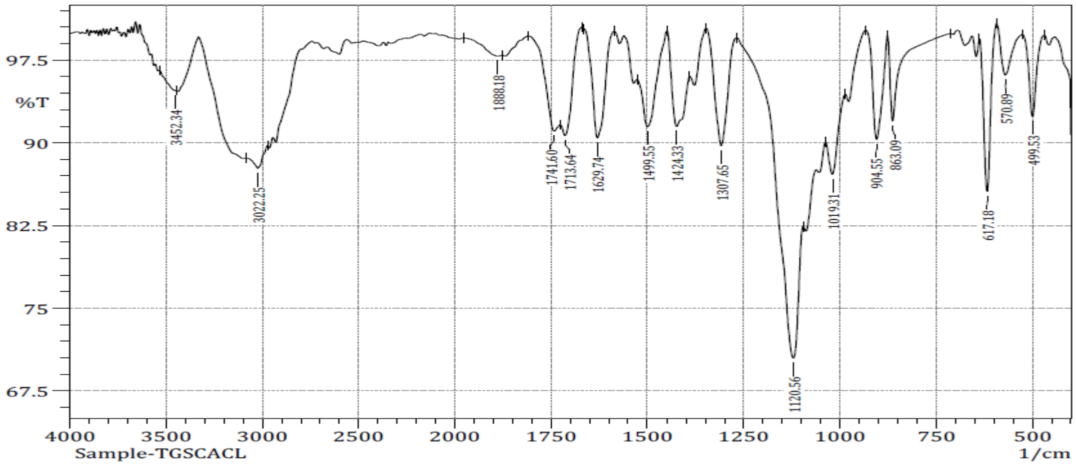

Fig. 4. FTIR spectrum of TGSCACL Crystal

The functional groups which play the predominant roles in the observed spectrum are discussed below.

NH_3 vibrations:

NH_3 vibrations show zwitterionic configuration of amino acids. The position of NH_3 stretching bands are observed at high frequency regions, which indicates the formation of strong hydrogen bonding [6]. The broad absorptions near 3452 cm^{-1} is due to NH_3 stretching. The bending vibration of NH_3 appeared at 1499cm^{-1}. The rocking vibration of NH_3 appears at 904.55cm^{-1}. The torsional oscillations of NH_3 are appearing at 617.18cm^{-1}, 570.89cm^{-1} and 499.52cm^{-1} .

COO^- vibrations:

Amino acids usually exist as zwitterions in crystals. They have an ionized carboxyl group (COO^-) and the amine salt NH_3^+ [15]. The peaks occurred at 1629.74$cm^{-1}$and 1424.33cm^{-1} for TGSCACL crystal referred the asymmetric and symmetric stretching of COO^- respectively. This indicates the presence of zwitterions.

Carboxyl vibrations:

Amino acids in cationic form depending on the strength of interaction are expected to give a band around 1700cm^{-1}due to stretching motion of C=O atoms [6]. The medium band near 1713$cm^{-1}$for TGSCACL crystal is due to stretching of C = O bond [15]. It appears at 1733.89cm^{-1}. This indicates the presence of glycine molecule as $NH_3^+CH_2COOH$ (glycinium ion).

***SO_4 vibrations*:**

In pure TGS, SO_4^{2-} ion has four fundamental vibrations at 1128cm^{-1}, 977cm^{-1}, 570$cm^{-1}$and 499cm^{-1}. The peak at 977cm^{-1} is non degenerate mode, 499cm^{-1}doubly degenerate mode and 1128cm^{-1}, 570$cm^{-1}$are due to triply degenerate vibrations [15]. In the case of TGSCACL crystal 499.53cm^{-1}, 570.89cm^{-1} and 1120.56cm^{-1} are due to sulphate vibrations.

The frequency of the observed bands and their assignments are listed in Table II for TGSCACL crystal.

Table II: FTIR analysis of TGSCACL Crystal

Wave number (cm^{-1})	**Tentative assignment**
499.53	Torsional oscillation of NH_3 / Sulphate vibration
570.89	Torsional oscillation of NH_3 / Sulphate vibration
617.18	Torsional oscillation of NH_3^+ / Stretching of Sulphate ion
863.09	Stretching of C- C
904.55	NH_3 rocking / C – C stretching
1019.31	Stretching of C – N, wagging of CH_2, bending of C – C
1120.56	Rocking of CH_2, Stretching of C – C, Stretching of SO_4^{2-}
1307.65	Bending of CH_2, Stretching of C – C
1424.33	Symmetric stretching of COO^-
1499.55	NH_3 bending
1629.74	Asymmetric stretching of COO^-
1713.64	Stretching of C = O
1888.18	Vibration of C –C
3022.25	Stretching vibration of CH_2
3452.34	Asymmetric stretching of NH_3^+

3.4 Vicker's Microhardness test

Hardness is the measurement of mechanical strength and resistance at which local deformation takes place of the Crystal.

For different applied loads, the hardness values (H_v) are calculated using the relation

$$H_v = 1.8544 \frac{P}{d^2} \rightarrow (1)$$

Where,

P → load applied

d → diagonal length

1.8544 → constant of geometrical fraction for diamond pyramid

The variation of applied load (P) with the Hardness number for TGSCACL crystal is given in Fig. 5.

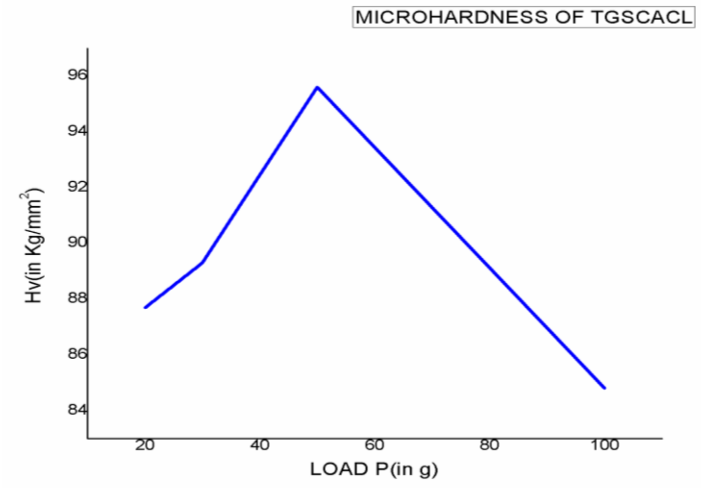

Fig. 5. Microhardness of TGSCACL Crystal

The hardness value of TGSCACL crystal increases with increase in applied load up to 50g which depicts mechanical strength is good for grown Crystal. Maximum hardness was observed at 50g above that cracks started developing around the indentation mark. It is due to release of internal stress generated locally by indentation [33].

In the present study the increase in hardness value of TGSCACL crystal, while comparing with pure TGS from reported literature [26], is attributed to the fact that the metal chloride incorporation into the TGS lattice probably enhanced the strength of the bonding with host molecules. An increase in hardness value will have significant effect in the infrared detector's element in fabrication and processing such as ease in polishing, and less wastage due to cracking/ breaking while polishing [3].

The Meyer's equation $\mathbf{P = k\ d^n}$ relates the load and indentation diagonal length. The Meyer's index number was calculated via,

$$\log P = \log k + n \log d \rightarrow (2)$$

Where,

k → material constant

P → load applied

n → Meyer's index (or) work hardening coefficient

d → diagonal length

The value of n is calculated by plotting log P Vs log d as shown in Fig. 6.

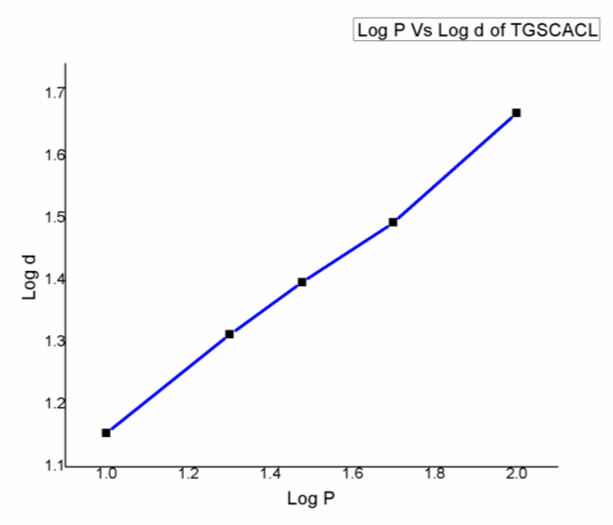

Fig.6. log P Vs log d of TGSCACL crystal

From graph the value of n was calculated as 2 for TGSCACL crystal. The value of n should be between 1 to 1.6 for harder materials and above 1.6 for softer materials. Thus TGSCACL belongs to soft material category, which matches with TGS crystal which also belongs to soft materials as per reported literature [3].

3.5 UV- Visible – NIR spectra

Optical properties of the grown Crystals were investigated by UV – Vis- NIR Spectra.

UV – Vis - NIR spectra gives information about structure of the molecule because the absorption of UV and Visible light involves promotion of electron in Sigma (σ) and Pi (π) orbital from ground state to higher energy state [8]. Good optical transmittance and lower cut off wavelength are very important properties to behave as an NLO material [44].

To find the transmission range of TGSCACL crystal, absorption spectra was taken using UV– 2400 PC Series from the wavelength range 200 nm to 900 nm. The recorded absorbance and transmittance spectra of TGSCACL crystal are shown in Fig. 7.

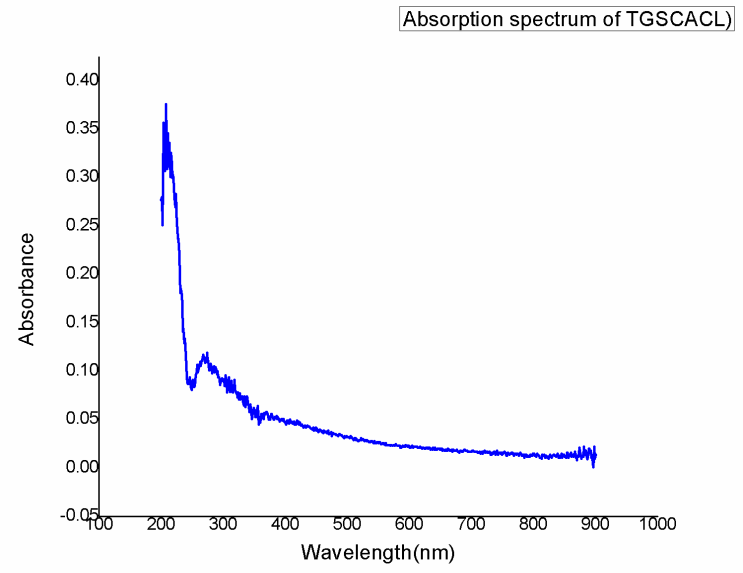

Fig.7. Absorption spectrum of TGSCACL Crystal

There is no absorption of light to appreciable extent in visible range, which is the intrinsic property of all amino acids [46]. The absorption at lower wavelength reveals that there must be higher energy transition corresponding to C = C – NO_2 group [7].

The lower cut-off wavelength of TGSCACL crystal is 241.16 nm.

The band gap energy can be calculated using the formula,

$$\mathbf{Eg} = \frac{hc}{e\lambda} \qquad \rightarrow (3)$$

The band gap energy of TGSCACL crystal is 5.151 eV.

The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\boldsymbol{\alpha} = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad \rightarrow (4)$$

Where T is the transmittance and t is the thickness of the crystal. Energy band gap values are also obtained from Urbach plots as shown in Fig. 8, as 5.19 eV.

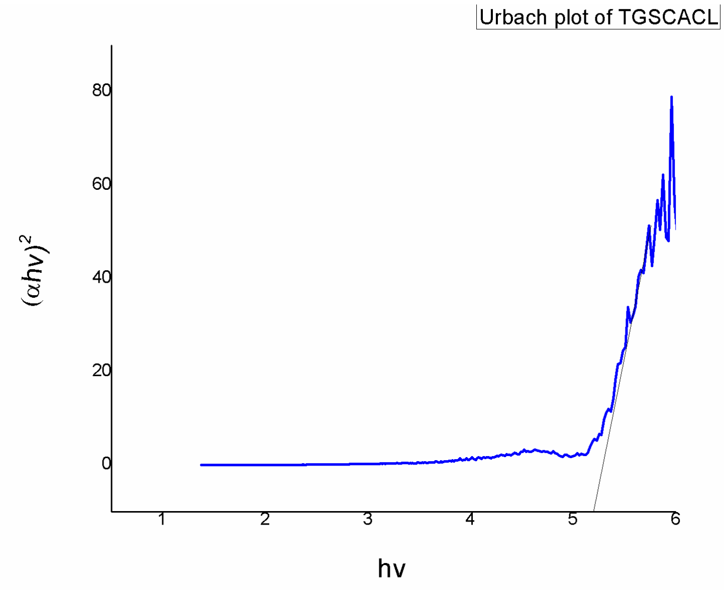

Fig. 8. Plot of $(\alpha h\nu)^2$ Vs Photon energy hν for TGSCACL Crystal

3.6 Dielectric studies

TGSCACL crystal is subjected to dielectric studies with conventional two terminal sample holders using LCR meter.

The dielectric constant (ε_r) and dielectric loss (tan δ) were calculated using equations [5] and [6].

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \qquad \rightarrow (5)$$

$$\tan\delta = D/\varepsilon_r \qquad \rightarrow (6)$$

Where,

A → Area of the sample

d → Distance between the plates

C → Capacitance

D → Dissipation factor

ε_0 → Permittivity of free space, $8.854 \times 10^{-12}\ \mathrm{Nm^2C^{-2}}$

The variation of dielectric constant (ε_r) with frequency at 30°C for TGSCACL crystal is shown in Fig. 9.

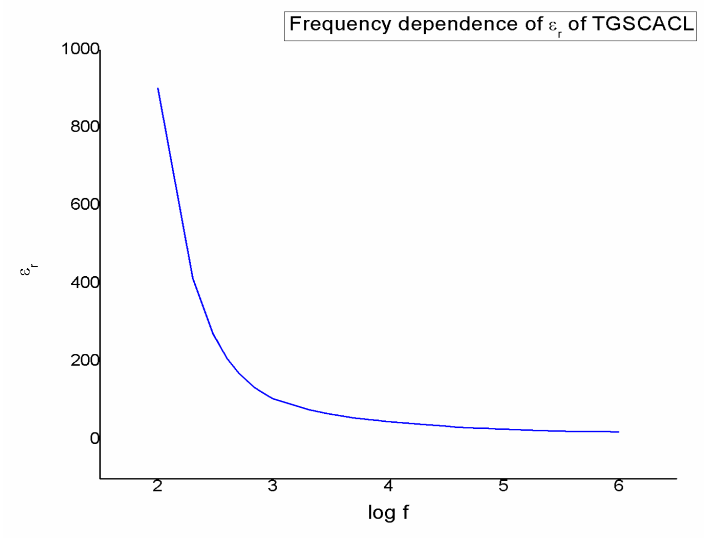

Fig. 9. Variation of dielectric constant with frequency for TGSCACL Crystal

The high value of dielectric constant (ε_r) at low frequency is contributed by space charge polarization. It is generally active at low frequency which indicates the perfection of grown crystals [3].

Variation of dielectric loss (tan δ) with frequency is shown in Fig. 10.

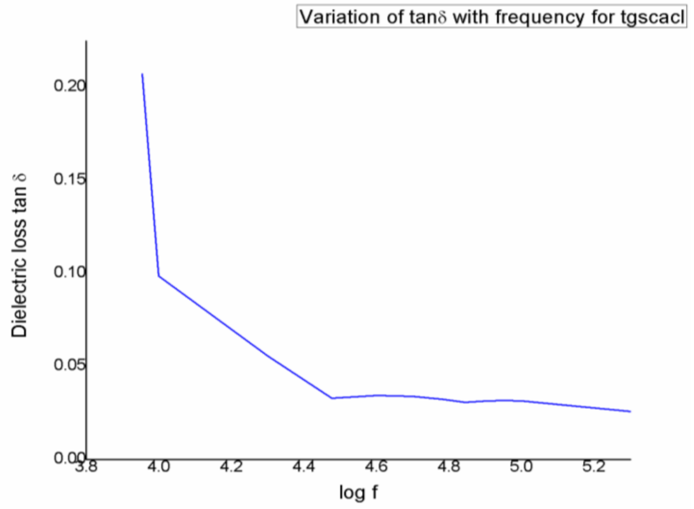

Fig.10. Frequency response of dielectric loss for TGSCACL Crystal

Low value of dielectric loss of TGSCACL indicates that there is low inertia counteracting to polarize [3].

AC conductivity can be calculated using the formula [21]

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta \quad \rightarrow (7)$$

Where,

f → frequency

ε_0 → permittivity of free space

ε_r → dielectric constant

tan δ → dielectric loss

AC conductivity (σ_{ac}) of the grown crystals for different frequency of TGSCACL crystal is shown in Fig.11.

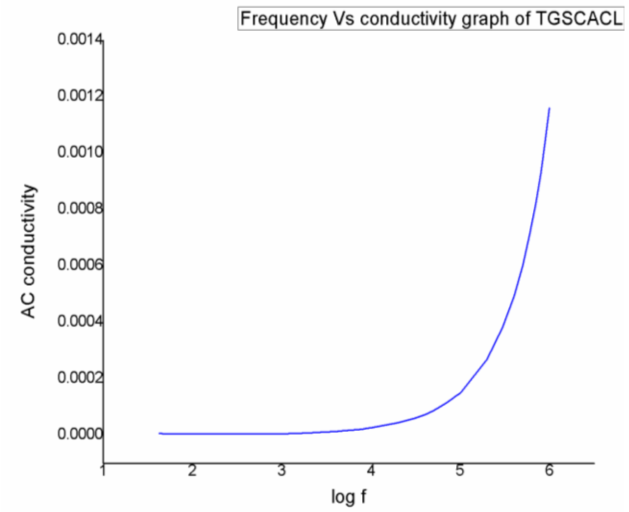

Fig. 11. Frequency Vs Conductivity graph of TGSCACL Crystal

4. CONCLUSION

In this dissertation work, Triglycine sulphate doped with Calcium chloride crystals were grown using slow evaporation method at room temperature. From EDX analysis it is found that Calcium chloride is well absorbed and incorporated into the interstitial sites of the TGS crystal. Powder XRD revealed good crystalline nature of grown crystal. From FTIR analysis, the presence of various functional groups was confirmed for grown crystal. Mechanical strength of TGSCACL crystal was investigated by Vicker's Microhardness test. Meyer's index was calculated to be 2, which depicts it belongs to soft material category. From UV –Vis – NIR results cut off wavelength and band gap energy of TGSCACL crystal was found to be 241.16 nm and 5.15 eV respectively. Variation of dielectric constant with frequency was studied for TGSCACL crystal. Frequency response of dielectric loss shows low value of dielectric loss for TGSCACL crystal. This indicates that there is low inertia counteracting to polarize.

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