

# MgCl<sub>2</sub> added triglycine sulphate crystals

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## ABSTRACT

Single crystals of pure and MgCl<sub>2</sub>-added triglycine sulphate crystals were grown from aqueous solutions by low temperature solution growth technique. From the powder XRD technique crystal system remains same (Monoclinic) and the unit cell parameters are slightly different from the pure TGS. FTIR and FT-Raman spectra were recorded to identify the vibrational activity of the various functional groups present in the title crystals. To determine the concentration Mg<sup>2+</sup> ion in the MgCl<sub>2</sub>-added triglycine sulphate crystals inductively coupled plasma optical emission spectrometer (ICP-OES) study was carried out. The amount of MgCl<sub>2</sub> (mol %) incorporated into the crystal is very low, a factor of 10<sup>-2</sup> in comparison to the actual amount taken in the solution. UV-VIS-NIR study shows that there is wide transparency in the visible region and the band gap energies were calculated. The mechanical strength of the grown crystals were known by hardness numbers and work hardening coefficient values. Dielectric constant and dielectric loss of the crystals were studied as function of frequency. Copyright © 2011 VBRI press.

**Keywords:** Crystal growth; powder diffraction; dielectric properties; hardness.



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include single crystal growth and characterization of Nonlinear optical materials and Rare earth intermetallics - Flux technique, Magnetism and Superconductivity.

## Introduction

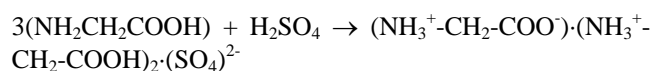
Among the amino acids, triglycine sulphate (TGS) is a well known ferroelectric and pyroelectric material below its critical temperature (49 °C). This material has found application in the fabrication and development of infrared detectors due to its high pyroelectric coefficient ( $p$ ), reasonably low dielectric constant ( $\epsilon_r$ ) and best figure-of-merit ( $p/\epsilon_r$ ) [1]. TGS crystals have been focused in various aspects such as growth rate, structural modification, pyroelectric, mechanical, optical, ferroelectric properties and to overcome the depolarization effect in this material by a number of authors [2-3]. Also the crystals are of particular interest for the photoinduced nonlinear optical effects [4]. The analysis of the crystal structure of TGS shows that the two hydrogen atoms of sulphuric acid are protonated to the carboxylic group of two zwitterionic molecules and thereby the name di-glycinium sulphate and the carboxylic hydrogen atom combined with the amino group of the third glycine molecule and forms a zwitterion and so it may be called as glycine di-glycine sulphate [5]. In this structure the phase transition in which above the Curie temperature it belongs to monoclinic system in the centrosymmetrical class  $P2_1/m$  space group and below the transition temperature, the mirror plane disappears and the crystal belongs to the noncentrosymmetrical class  $P2_1$  space group. Pure TGS crystals possess many disadvantages such as (i) high ferroelectric domain mobility at room temperature, (ii) polarization reversal by electrical mechanical and thermal means, (iii) microbial contamination during the growth and (iv) low Curie

temperature. In order to overcome this unfavorable for practical application features variety of dopants such as amino acids, organic and inorganic compounds have been introduced [6-9]. Due to the competent nonlinear optical efficiency of amino acids and its complexes many researchers have reported with inorganic salts and that has proved as a good candidate for nonlinear optical applications [10-12]. Various metallic ion dopants such as  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Cu^{2+}$  etc., added to modify the optical properties of TGS crystals [13-16]. Rare earth metal ions like La, Ce and Nd were used to modify the morphology and the coercive field values of TGS crystals. Incorporation of inorganic additives into an organic material can alter the various physical properties in order to achieve better performance in opto-electronic devices. The presence of metallic species in the organic compounds generally raises the hardness of the compounds considerably [17]. Recently alkali metal chloride doped TGS have been reported as high dielectric constant and low hardness values [18]. Hitherto no attempts were made to modify the physical and optical properties of pure TGS by adding magnesium chloride. Hence the main objective of the present work is to investigate the effect of the dopant on the structural, spectral, mechanical, optical and dielectric properties of TGS crystals.

## Experimental

### Single-crystal growth

Triglycine sulphate was synthesized by using AR (analytical reagent) grade glycine and sulphuric acid in the molar ratio of 3:1. Calculated amount of glycine was slowly added and dissolved in diluted  $H_2SO_4$ . The solution was subjected to slow evaporation and extreme care was taken while crystallizing the salt to avoid oxidation of the glycine. Hence the solution temperature was maintained at  $55^\circ C$  and recrystallization was done to reduce the impurity content in the crystallized salt. The way of reaction performs as follows



A salt of 0.5M of  $MgCl_2$  was added to the saturated solution of TGS to obtain  $MgCl_2$  added TGS (McTGS) crystals. This solution was stirred well and filtered out to remove the unsaturated particles. The filtered out solution was hermetically sealed and put into a constant temperature bath at  $40^\circ C$ . Well transparent  $MgCl_2$  added TGS single crystals were obtained in 25 days. Fig. 1 shows the photograph of pure and doped crystals.

### Methods of characterization

The grown McTGS crystals were crushed into fine powder for X-ray diffraction studies. This powder sample was subjected to diffraction using SEIFERT diffractometer at room temperature with  $Cu\ \alpha$  radiation of wavelength ( $\lambda = 1.5406\text{\AA}$ ) to identify the lattice parameter. The FTIR spectrum of McTGS crystal was recorded in the region  $400-4000\text{ cm}^{-1}$  at a resolution of  $\pm 2\text{ cm}^{-1}$  using

PerkinElmer spectrophotometer. The FT-Raman spectrum was recorded on a BRUKER IFS 66v model interferometer equipped with FRA-106 FT-Raman accessories at a resolution of  $\pm 6\text{ cm}^{-1}$ . The amount of  $Mg^{2+}$  ion in McTGS crystals was determined by PerkinElmer Optima 5300 DV ICP-OES with wavelength range of 163-782 nm. Lambda 35 UV-VIS-NIR spectrophotometer was used to record transmittance spectra of TGS and McTGS crystals in the region of 200-1000 nm. Hardness of the grown crystal was measured using a Leitz-Wetzler hardness tester fitted with a Vickers diamond pyramidal indenter and attached to a Leitz incident light microscope. In hardness measurement, load variations in measurement were applied over a fixed interval of time 15sec. Suitably cut and polished sample of TGS and McTGS were subjected to dielectric studies using computer controlled impedance analyzer N4L PSM1735 with conventional two terminal sample holders. The dielectric constant and dielectric loss were calculated using the equation  $\epsilon_r = Cd/\epsilon_0 A$  and  $\tan\delta = D/\epsilon_r$ , where A is the area of the sample, d is the distance between the two plates, C is the capacitance, D is the dissipation factor or energy loss per cycle and  $\epsilon_r$  is the dielectric constant.



Fig. 1. Photograph of TGS and McTGS single crystals.

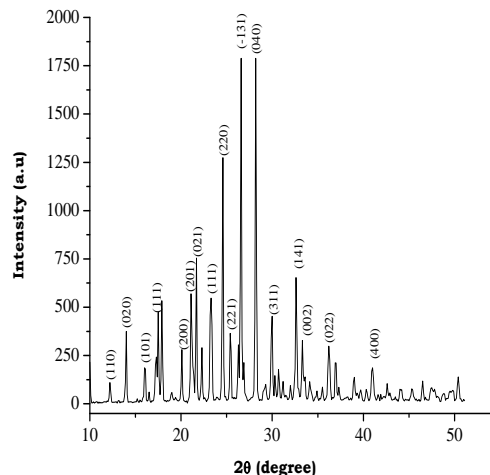


Fig. 2. Powder XRD pattern of McTGS.

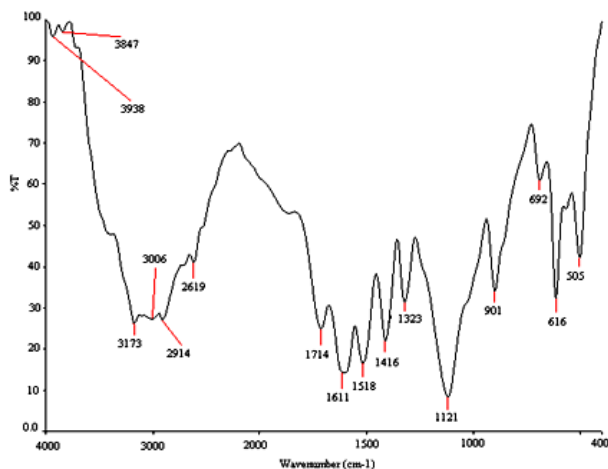
## Results and discussion

### Powder X-ray diffraction technique

The indexed X-ray diffraction pattern is depicted in **Fig. 2**. X-ray powder diffraction patterns of McTGS showed that the system of McTGS crystal is similar to that of TGS, but the lattice parameters of McTGS had slightly different values from those of the TGS [5]. The unit cell parameters were calculated by monoclinic crystallographic equation using peak position. The McTGS unit cell parameter values are  $a = 9.405(5) \text{ \AA}$ ,  $b = 12.623(7) \text{ \AA}$  and  $c = 5.721(4) \text{ \AA}$   $\beta = 110.34(2)$  with  $V = 637.001 \text{ \AA}^3$ .

### ICP-OES elemental analysis

ICP-OES is based on the principle that a sample solution is introduced into the core of ICP and all elements in the solution become thermally excited and emits light at their characteristic wavelength. The emitted wavelength is amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards. This technique is used to find qualitative and quantitative determination of magnesium present in the McTGS crystals. To determine the exact weight percentage of  $\text{Mg}^{2+}$  present in McTGS crystals, 20 mg of fine powder of the crystal was dissolved in 25 ml of triple distilled water. This prepared solution was subjected to ICP optical emission spectrometer. The amount of magnesium present in the sample was determined as 7.561 ppm (0.9%) for magnesium wavelength 285.21 nm. From the above analysis, it is found that the concentration of magnesium is low as to form a complex and hence it can be concluded that the magnesium can be incorporated in void or interstitial space within the crystal lattice of McTGS crystals.

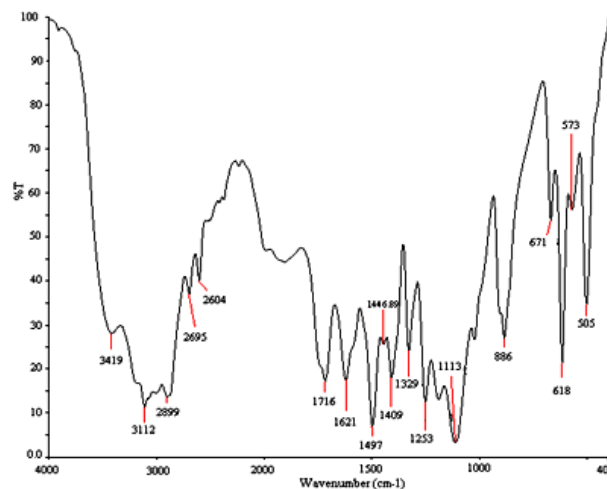


**Fig. 3.** FTIR spectrum of TGS.

### FTIR and FT-Raman analysis

The recorded FTIR spectrum of pure and doped TGS crystal is given in **Figs. 3 & 4** respectively and the Raman in **Fig. 5**. In FTIR and the Raman spectra the intensity and frequencies of our pure TGS crystal matches with the data

reported by other authors [19]. The observed peak wave numbers, relative intensities and their assignments are given in **Table 1**. The absorption band at  $3405 \text{ cm}^{-1}$  in the IR spectrum of pure TGS is assigned to antisymmetric  $\text{NH}_3^+$  stretching. For the doped crystal this mode generates peaks at  $3442 \text{ cm}^{-1}$  in the Raman and at  $3419 \text{ cm}^{-1}$  in IR spectrum.



**Fig. 4.** FTIR spectrum of McTGS.

Wavenumber ( $\text{cm}^{-1}$ )			Wavenumber ( $\text{cm}^{-1}$ ) assignments
Pure	Doped (FTIR)	Doped (Raman)	
3405ms	3419ms	3442m	$(\text{NH}_3)^+$ antisym str
3173s	3112s	3021ms	$(\text{NH}_3)^+$ sym str
2914s	2899s	2980s	$\text{CH}_2$ str
2619ms	2695ms	2653m	$\text{CH}^2$ str
1714s	1716s	-	Overtone and combination
1611s	1621s	-	amide
1518s	1497s	-	$\text{NH}_3^+$ antisym b
1416s	1409s	1361ms	$\text{NHib} + \text{NH}_3$ sym b
1323ms	1329s	1321ms	$\text{CO}_2$ sym str + $\text{CH}_2$ tw + $\text{CH}_2$ b
1121s	1113s	-	$\text{NC}_2^\alpha$ str + $\text{NC}_3^\alpha$ str
901ms	886ms	866	C-C str
692m	671m	669ms	$\text{COO}^-$ Scissoring, $\delta$ Out of plane (C-C)
616ms	618s	628m	$\text{C}_2$ ob + $\text{C}_2$ Nt + $\text{C}_1$ O ob
505ms	505ms	442m	$\rho(\text{COO})^-$ , $\tau(\text{NH}_3)^+$

Str = stretching, b = bending, ob = out-of-plane bending, ib = in-plane bending t = torsion, tw = twisting w = weak, m = medium, ms = medium strong, s = strong.

The peak appeared at  $3173 \text{ cm}^{-1}$  in the FTIR spectrum of pure crystal is assigned to the symmetric stretching of  $\text{NH}_3^+$  and in the doped TGS it is shifted to  $3112 \text{ cm}^{-1}$ . This mode generates peak at  $3021 \text{ cm}^{-1}$  in the Raman spectrum of McTGS crystal. In the pure TGS, C-H stretching vibration is observed at  $2914 \text{ cm}^{-1}$  in the FTIR. This peak is observed at  $2980 \text{ cm}^{-1}$  in the Raman and  $2899 \text{ cm}^{-1}$  in the FTIR for the doped TGS. The peaks occurring at 1323 and

1518  $\text{cm}^{-1}$  in the pure TGS sample are associated with the symmetric and the antisymmetric vibrations of  $\text{COO}^-$ , respectively, and indicates the presence of glycine as a zwitterion. The strong narrow band at 1611  $\text{cm}^{-1}$  due to the  $\text{C}=\text{O}$  stretching which indicates the presence of the glycine molecule as  $\text{NH}_3^+\text{CH}_2\text{COOH}$  (glycinium ion) [20].

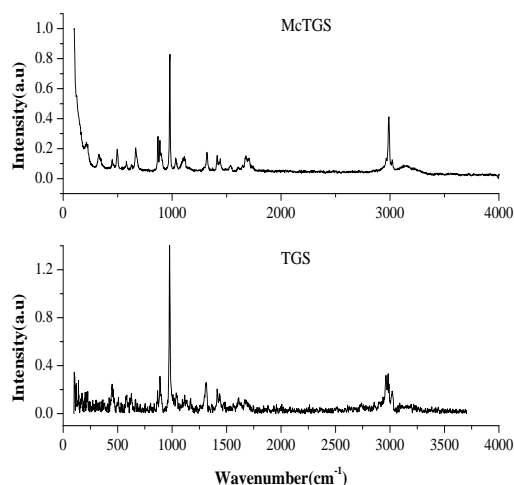


Fig. 5. Raman spectrum of TGS and McTGS.

Many bands are significantly red shifted from the corresponding bands for the doped TGS crystals, which shows a significant charge transfer between the metal ion and glycine [17, 21]. The vibration at 1497, 1329 and 1621  $\text{cm}^{-1}$  in the doped crystals strongly suggest the presence of both zwitter and glycinium ions. Weak intensity peaks at 573  $\text{cm}^{-1}$  show non hydrogen bonded hydroxyl groups [22]. Due to the doping,  $\text{COO}^-$  of the zwitterion would prefer to accept the magnesium to form a glycinium ion rather than to remain isolated in the crystal lattice. Hence, all glycine molecules would rather exist as glycinium ions. In contrast, the presence of both the zwitter and glycinium ions in doped samples can be understood only in terms of very low incorporation of  $\text{MgCl}_2$  into the crystal lattice as evidenced from the compositional analysis. Since major shifts corresponding to the internal modes in the IR region have not been observed, the formation of any other complex compound in the McTGS crystals is ruled out.

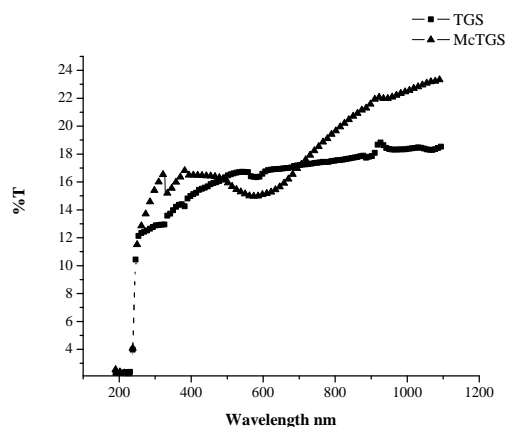


Fig. 6. Optical transmittance spectrum of TGS and McTGS.

### UV-VIS- NIR studies

The present experimental study investigates the optical band gap of McTGS crystals. The recorded transmittance spectra of pure and McTGS crystals are shown in Fig. 6. The measured transmittance ( $T$ ) was used to calculate the absorption coefficient ( $\alpha$ ) using the formula

$$\alpha = \frac{2.3026 \log(1/T)}{t}$$

where,  $t$  is the thickness of the sample. The  $(\alpha h\nu)^2$  value versus the photon energy is presented in Fig. 7. The energy gaps of the materials were determined by the absorption spectrum. The absorption coefficient  $\alpha$  of a crystalline solid obeys the following relation  $(\alpha h\nu) \propto (h\nu - E_g)^n$  where  $E_g$  is the energy gap,  $n$  is the index that characterizes the optical absorption process.  $n = 1/2, 3/2, 2,$  and  $3$  for direct allowed, forbidden and indirect allowed, forbidden transition respectively. As it is shown in Fig. 7 the band gap was obtained by plotting  $(\alpha h\nu)^2$  versus  $h\nu$  in the high absorption range followed by extrapolating the linear region near after the absorption edge to the energy axis. The band gap of pure and McTGS crystals were calculated and the values are 4.70, 4.45 eV respectively. For doped crystal  $E_g$  was shifted to low energy region which is expected and in accordance with the fact that energy gap decreased with increasing defect concentration in the crystal lattice.

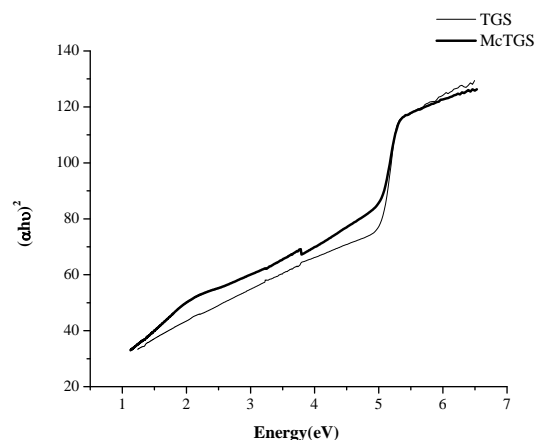
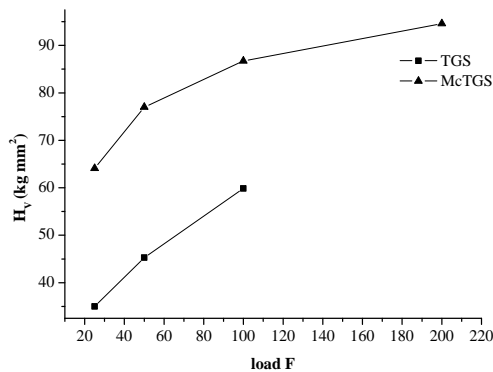


Fig. 7. Plot of  $(\alpha h\nu)^2$  vs. photon energy  $h\nu$ .

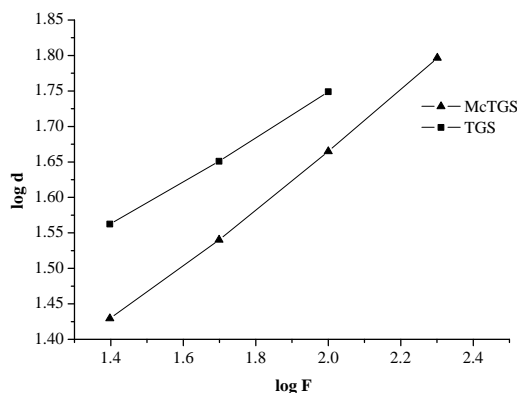
### Hardness measurement

Hardness of a material is a measurement of the resistance it offers to local deformation such as scratching and indentation. Fig. 8 shows the variation of Vickers microhardness number for TGS and McTGS crystals with different loads. When the crystal is an ideal, the measured hardness value is independent of applied load. But in practice, a load dependence of hardness value is observed. The variation of hardness value with load has been observed and can be interpreted in different ways. Mott has explained that this type of load variation by assuming that the index  $d$  is not 2 but less than 2 [23]. In present study the increase in hardness value of McTGS crystal is attributed to the fact that the metal chloride incorporation into the TGS

lattice probably enhances the strength of the bonding with the 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. The Meyer's equation  $F = kd^n$  relates the load and indentation diagonal length. The Meyer's index number was calculated via  $\log F = \log k + n \log d$ , where  $k$  is the material constant  $F$  is the load and  $n$  is the Meyer's index. The value of  $n$  is calculated by plotting  $\log F$  versus  $\log d$  and it is shown in **Fig. 9**. Reciprocal slope of the straight line gives the value of  $n$  as 2.4 for McTGS crystals. For pure TGS, the  $n$  value is 3.2. The value of  $n$  should lie between 1 to 1.6 for harder materials and above 1.6 for softer materials [24]. Thus both TGS and McTGS crystals belong to the soft material category.



**Fig. 8.** Vickers hardness profile of TGS and McTGS as function applied load.

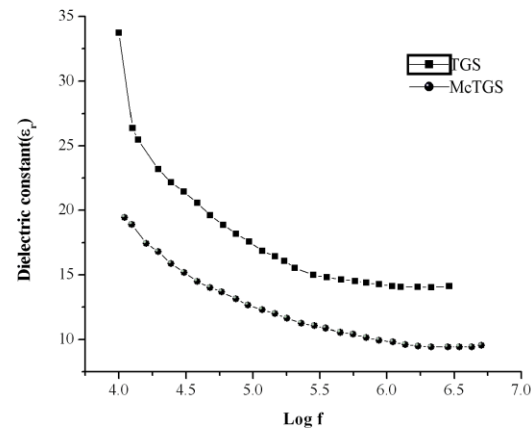


**Fig. 9.** Plot of  $\log F$  vs.  $\log d$ .

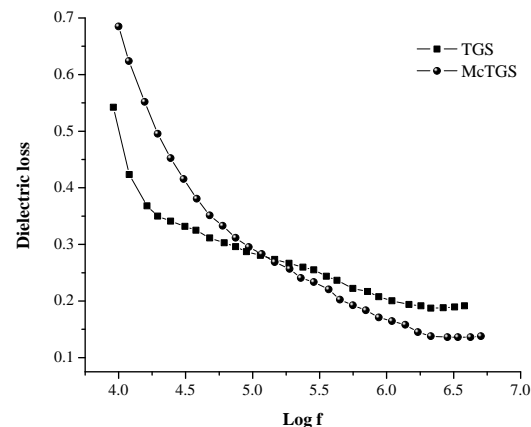
*Dielectric studies*

The relative permittivity is an important electrical property of the dielectric materials. For most materials the value of dielectric constant ( $\epsilon_r$ ) depends on the frequency of the alternating electric field, chemical structure and the imperfection of the material and also the temperature and pressure [25]. This part is devoted to the discussion of frequency dependence of dielectric constant and dielectric loss of the pure and McTGS crystals at room temperature

and the variation are displayed in the **Figs. 10 & 11** respectively. When increasing frequency, the value of dielectric constant is decreasing for both pure and McTGS crystals. This nature of variation governs the various polarization mechanisms. The high value dielectric constant at low frequency is contributed by space charge polarization. It is generally active at low frequency which indicates the perfection of the grown crystals [26]. Thus the sway of space charge polarization is predominant in low frequency region [27]. When compared with pure TGS, the low value of dielectric constant of McTGS crystal shows the quality of the crystal [28-29]. The dielectric loss of the materials strongly depends on the rate of change of time varying field. The low value of dielectric loss indicates that there is low inertia counteracting to polarize or orienting the molecules in a field. In **Fig. 10**, the McTGS crystal shows the low value of dielectric loss even at high frequency. Hence the low value of dielectric constant and dielectric loss of McTGS at higher frequency is important for the fabrication of materials towards photonic, electro optics devices and high frequency response devices.



**Fig. 10.** Frequency dependent dielectric constant of TGS and McTGS crystals.



**Fig. 11.** Dielectric loss vs. log frequency.

## Conclusion

Optically transparent good quality TGS and McTGS crystals were grown by slow evaporation solution growth technique. The lattice parameters values of McTGS were good agreement with pure TGS crystals. However, the slight changes in the lattice parameters are attributed to the inclusion of dopand in the pure TGS crystals. The vibrational assignments of the Raman and FTIR analysis confirm the incorporation of the  $MgCl_2$  in the grown crystals. From the results of optical study it was found that energy gap of the McTGS crystals is 4.45 eV which is less than that of pure TGS. Also the mechanical hardness is well enhanced due to metal chloride doping. The work hardening coefficient is found to be 2.4 which suggest that the McTGS crystal belongs to the family of soft materials. Compared with pure TGS crystals the low value of dielectric constant and dielectric loss of McTGS crystals shows the utility of the materials for fabrication of photonic and electro optics devices.

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