International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 3 Issue 1, January - 2014

Electrical Measurements on Zinc – Magnesium Tris(Thiourea) Sulphate (ZMTS) Single Crystals

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Abstract

Pure and magnesium sulphate mixed zinc tris(thiourea) sulphate single crystals were grown by the slow evaporation method from aqueous solutions. The grown crystals were characterized by X-ray powder diffraction. The cell parameters of the grown crystals were estimated by single crystal X-ray diffraction technique. The observed results show that the small amount of magnesium molecules were incorporated in the crystalline matrix of ZTS crystals. DC and AC (with five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz) electrical measurements were carried out at various temperatures. The present study shows that the DC conductivity and dielectric parameters (viz. dielectric constant, dielectric loss and AC conductivity) increase with the increase in temperature for all the grown crystals. Activation energies were also determined.

1. Introduction

Zinc tris(thiourea) sulphate (ZTS), $Zn[CS(NH_2)_2]_3SO_4$, is a relatively new and promising semiorganic nonlinear optical material for frequency conversion of high power lasers. ZTS crystal shares the favourable polarizable property of the organic material and the mechanical properties of the inorganic material. Special features of this material are that it has a high laser damage threshold, a low UV cut off and 1.2 times higher second harmonic generation (SHG) efficiency than potassium dihydrogen orthophosphate (KDP). Also, ZTS crystal has excellent mechanical properties when compared to other semiorganic nonlinear optical crystals. Moreover, it is less hygroscopic than KDP [1]. ZTS belongs to the orthorhombic crystal system with the point group of mm2 and the lattice parameters are a = 11.130, b = 7.773 and c = 15.490 Å [2].

In the present work, ZTS has been mixed with various molar percentages of magnesium sulphate to improve the SHG efficiency to find its suitability as better alternative to other NLO materials for optoelectronics applications [3]. Magnesium tris(thiourea) sulphate (MTS), $Mg[CS(NH_2)_2]_3SO_4$ **,** is a semiorganic nonlinear optical material. MTS belongs to the monoclinic crystal system and the lattice parameters are a = 7.67, b = 5.48 c = 8.56Å and β = 13.11°[4].

Anandakumari and Chandramani [5] have recently reported that KDP crystals containing alkali halide impurities have shown appreciable increase in second harmonic generation efficiency compared to pure KDP crystals. It can be expected that impurity addition to ZTS makes this material more useful. Moreover, forming solid solutions with similar materials may also bring fruitful results. Aiming at discovering new useful materials, in the present study, we have made an attempt to grow and characterize mixed crystals based on ZTS and MTS. Eventhough the lattices of ZTS and MTS mismatch, the precursors molecules are isomorphous. As the mixed crystals are proposed to be grown from the precursors mixed in the required proportion, it is expected to be possible for the formation of ZTS – MTS mixed crystals. We report, herein, the results of our study.

2. Experimental

The ZMTS salt was synthesized by the stoichiometric incorporation of AnalaR grade (AR) zinc sulphate heptahydrate + magnesium sulphate heptahydrate and thiourea in the molar ratio 1:3. The component salts were very well dissolved in deionized water, which was thoroughly mixed using a magnetic stirrer and the mixture was heated at 50°C till a white crystalline salt of ZMTS was obtained. Temperature was maintained at 50°C to avoid decomposition as followed by the previous workers [6]. ZMTS salt was synthesized according to the reaction.

$Zn_xMg_{1-x}SO_4 .7H_2O + 3CS(NH_2)_2 \rightarrow Zn_xMg_{1-x}[(CS(NH_2)_2)_3]SO_4$

where x=0.0 to 1.0 in steps of 0.1

Single crystals of ZMTS were grown by the solution growth employing slow evaporation technique at room temperature (31°C). Transparent and colourless ZMTS crystals of size 7x7x4 mm^3 were harvested in 20-25 days except MTS crystal. The MTS crystal of size 9x8x5 mm3 was harvested in 30-35 days.

The grown ZMTS crystals were subjected to single crystal XRD analysis using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ = 0.71073 Å) to determine the unit cell dimensions.

DC electrical conductivity measurements were carried out in all the grown ZMTS crystals using the conventional two-probe technique at various temperatures ranging from 40 to 120 ^{0}C in a way similar to that followed by Perumal and Mahadevan [7]. The resistances of the crystals were measured using a million megohm meter. The observations were made while cooling the sample. The samples were cut into rectangular shape to the desired thickness of 1–2mm and polished. For good conduction opposite faces of the sample crystals were coated with good quality graphite. The samples were annealed in the holder assembly at ∼120 ^{0}C before making observations. The dimensions of the crystals were measured using a traveling microscope (L.C. = 0.001 cm). The DC conductivity (σ_{dc}) of the crystal was calculated using the relation $\sigma_{dc} = d/(RA)$, where R is the measured resistance, d is the thickness of the sample, and A is the area of the crystal in contact with the electrode.

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The capacitance (C_{crys}) and dielectric loss factor (tan δ) measurements were carried out on all the grown crystals using an LCR meter (Agilent 4284A) with five different frequencies such as 10^2, 10^3, 10^4, 10^5 and 10^6 Hz at various temperatures ranging from 40-120 °C in a way similar to that followed by Mahadevan and his co-workers [7-9]. The samples were annealed up to 120 °C to remove water molecules, if present. The observations were made while cooling the sample. Air capacitance (C_{air}) was also measured. The sample crystal was prepared as in the case of DC conductivity measurements. The dielectric constant of the crystal was calculated using Mahadevan's relation [8,9](as the crystal area was smaller than the plate area of the cell).

$$\varepsilon_r = \left(\frac{A_{air}}{A_{crys}}\right)\left(\frac{C_{crys} - C_{air}\left(1 - A_{crys}/A_{air}\right)}{C_{air}}\right),$$

where Acrys is the area of the crystal touching the electrode and Aair is the area of the electrode.

The AC conductivity (σ_{ac}) was calculated using the relation

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

where $\boldsymbol{\varepsilon_0}$ is the permittivity of free space (8.85 x 10^{-12} $C^2 N^{-1} m^{-2}$) and ω is the angular frequency.

The activation energy values were estimated using the relations

$$\sigma_{dc} = \sigma \exp[-E_{dc}/(kT)]$$

$$\sigma_{ac} = \sigma \exp[-E_{ac}/(kT)]$$

Here, k is the Boltzmann's constant, T is the absolute temperature, and σ is a constant depending on the material

3. Results and Discussion

3.1 Crystals grown and lattice parameters

A photograph of the grown ZMTS, $Zn_xMg_{1-x}[(CS(NH_2)_2)_3]SO_4$ (where x=0.0 to 1.0 in steps of 0.1) crystals is shown in Figure 1. The external appearance of the grown crystals is found to be different when magnesium content increases. The Lattice parameters observed for the grown ZMTS crystals are given in Table 1. Except MTS all the other crystals belong to orthorhombic system and the lattice parameters are found to be in line with those of ZTS crystals. The lattice parameters of ZTS and MTS crystals compare well with those reported in the literature [10, 4]. The grown crystals are represented as:

ZTS ➜ Pure ZTS
ZTS9 ➜ $Zn_{0.9}Mg_{0.1}[(CS(NH_2)_2)_3]SO_4$
ZTS8 ➜ $Zn_{0.8}Mg_{0.2}[(CS(NH_2)_2)_3]SO_4$
ZTS7 ➜ $Zn_{0.7}Mg_{0.3}[(CS(NH_2)_2)_3]SO_4$
ZTS6 ➜ $Zn_{0.6}Mg_{0.4}[(CS(NH_2)_2)_3]SO_4$
ZTS5 ➜ $Zn_{0.5}Mg_{0.5}[(CS(NH_2)_2)_3]SO_4$
ZTS4 ➜ $Zn_{0.4}Mg_{0.6}[(CS(NH_2)_2)_3]SO_4$
ZTS3 ➜ $Zn_{0.3}Mg_{0.7}[(CS(NH_2)_2)_3]SO_4$
ZTS2 ➜ $Zn_{0.2}Mg_{0.8}[(CS(NH_2)_2)_3]SO_4$
ZTS1 ➜ $Zn_{0.1}Mg_{0.9}[(CS(NH_2)_2)_3]SO_4$
MTS ➜ Pure MTS

Figure1. Photograph showing sample crystals grown. [**Top row**: from left are ZTS1,ZTS2,ZTS3,ZTS4, ZTS5, **Middle row**: from left are ZTS6, ZTS7, ZTS8, ZTS9, **Bottom row**: from left are ZTS and MTS]

Table 1. Lattice parameters and volumes of the grown ZMTS crystals

crystal	a (Å)	b (Å)	c (Å)	V ($Å^3$)	Angle	Crystal system
ZTS	7.77 [7.72]	11.11 [11.11]	15.48 [15.47]	1340 [1340]	α=β =γ =90°	Orthorhombic
ZTS9	7.78	11.12	15.47	1341	α=β =γ =90°	“
ZTS8	7.77	11.13	15.46	1339	α=β =γ =90°	“
ZTS7	7.76	11.14	15.45	1338	α=β =γ =90°	“
ZTS6	7.75	11.15	15.48	1337	α=β =γ =90°	“
ZTS5	7.77	11.14	15.47	1340	α=β =γ =90°	“
ZTS4	7.78	11.13	15.46	1338	α=β =γ =90°	“
ZTS3	7.77	11.12	15.45	1337	α=β =γ =90°	”
ZTS2	7.76	11.11	15.44	1339	α=β =γ =90°	“
ZTS1	7.74	11.08	15.42	1337	α=β =γ =90°	“
MTS	7.66 [7.67]	5.49 [5.48]	8.55 [8.56]	359 [360]	α =γ =90°, β=138.11	Monoclinic

Reported [10, 4] values are given in parenthesis.

3.2 Electrical properties

The DC electrical conductivities (σ_{dc}) observed in the present study are shown in Figure 2. The dielectric parameters, viz. dielectric constant (ε_r), dielectric loss factors (tan δ), and AC electrical conductivities (σ_{ac}) observed are shown in Figures 3-5. All the electrical parameters, viz. σ_{dc}, ε_r, tan δ and σ_{ac} are found to increase with the increase in temperature in the temperature range considered in the present study. Further, ε_r and tan δ values decrease whereas the σ_{ac} value increases with the increase in frequency. Moreover, as expected, the σ_{ac} values are found to be more than the σ_{dc} values. So, it can be understood that all the eleven crystals grown in the present study exhibit normal dielectric behaviour.

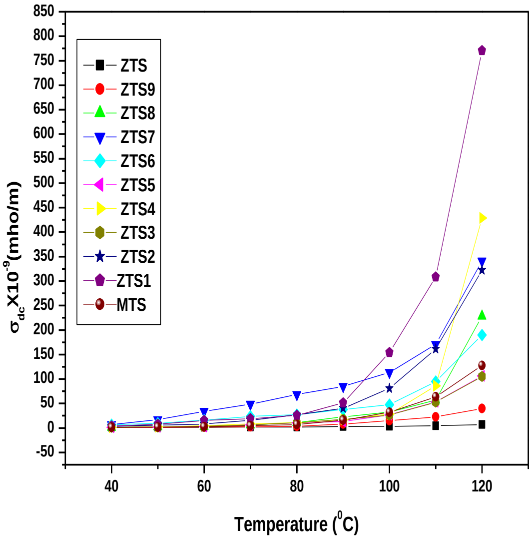
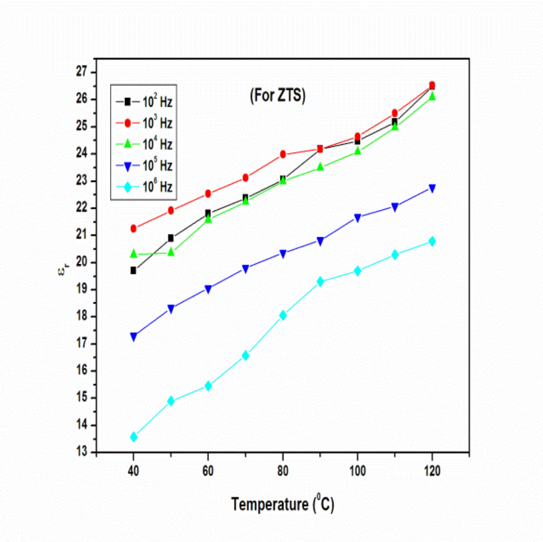
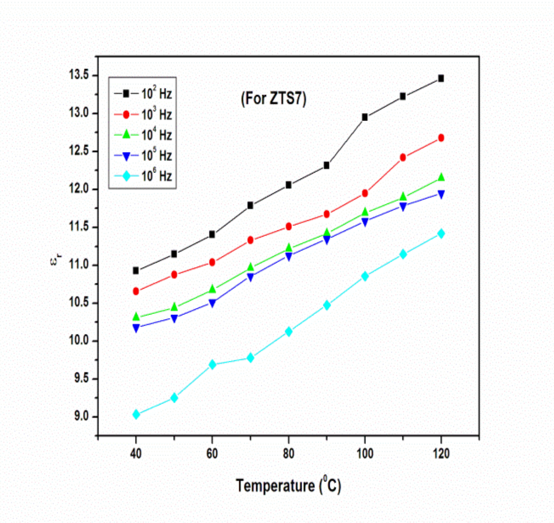


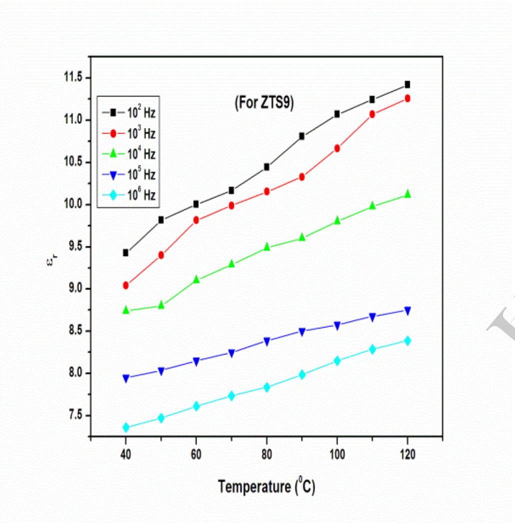
Figure 2. DC electrical conductivities observed for the ZMTS crystals


(For ZTS)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
40
60
80
100
120
Temperature (°C)

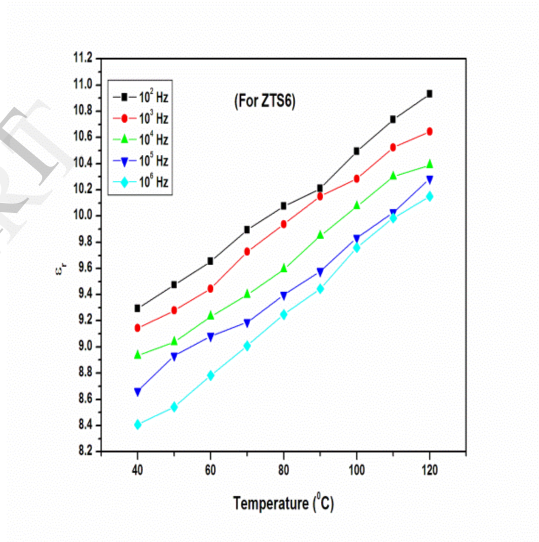
a)


(For ZTS7)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
40
60
80
100
120
Temperature (°C)

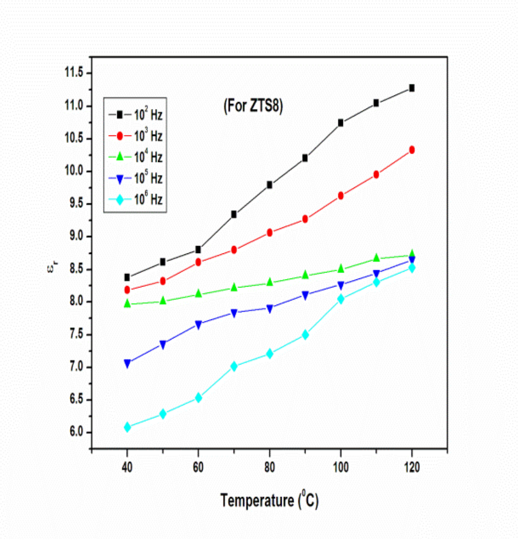
d)


(For ZTS9)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
40
60
80
100
120
Temperature (°C)

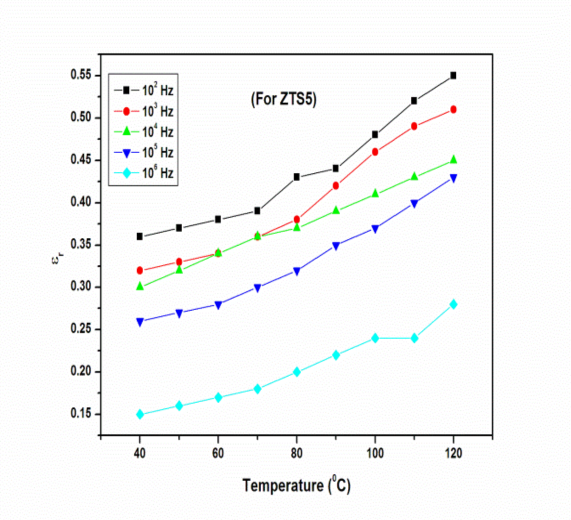
b)


(For ZTS6)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8
10.0
10.2
10.4
10.6
10.8
11.0
11.2
40
60
80
100
120
Temperature (°C)

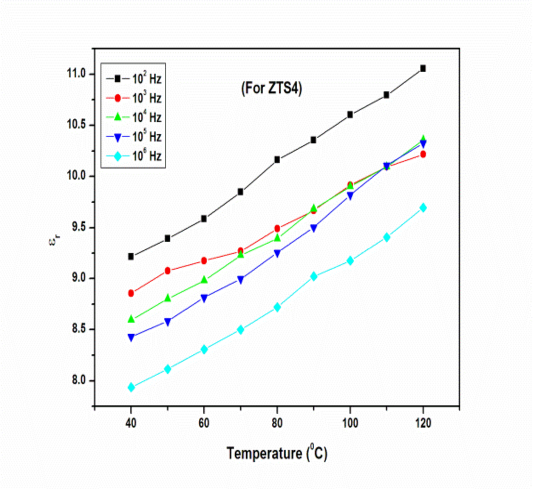
e)


(For ZTS8)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
40
60
80
100
120
Temperature (°C)

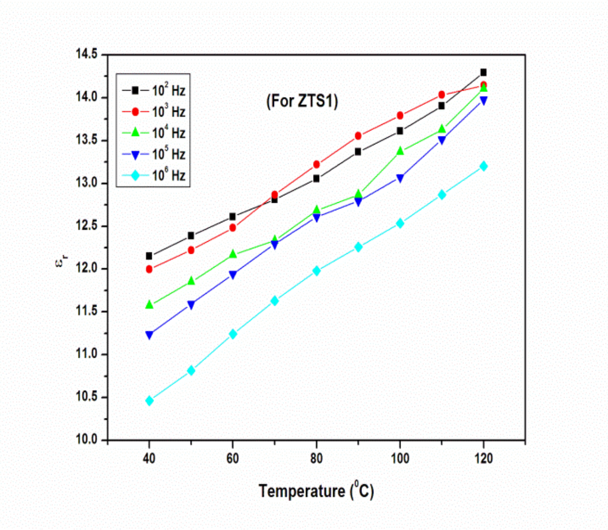
c)


(For ZTS5)
10² Hz
10³ Hz
10⁴ Hz
10⁵ Hz
10⁶ Hz
εr
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

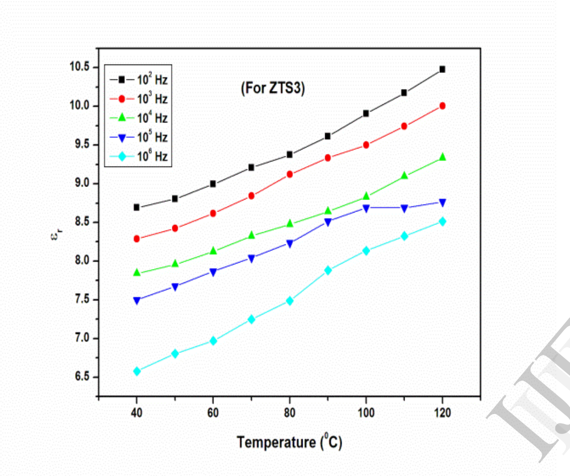
f)



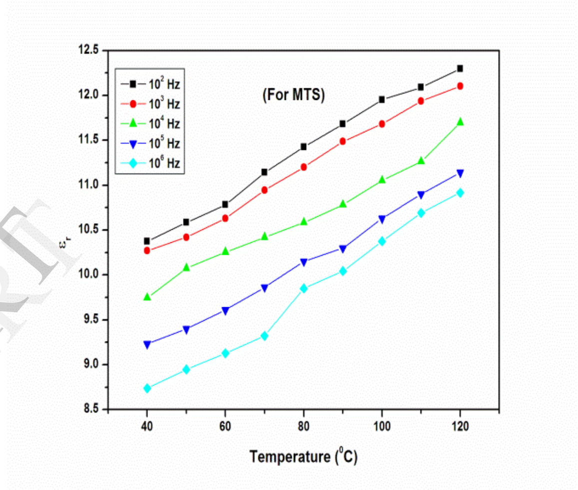
g)



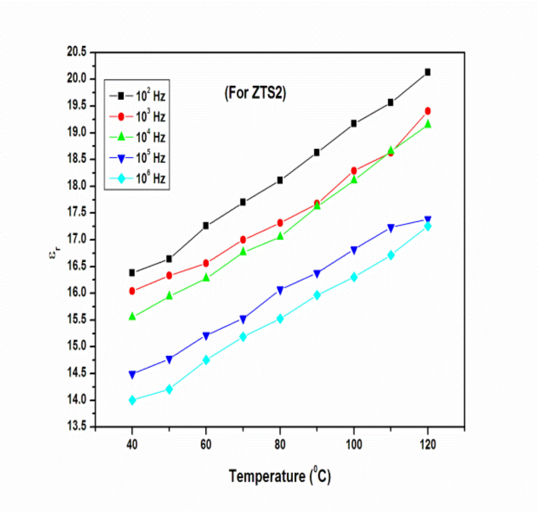
J)



h)

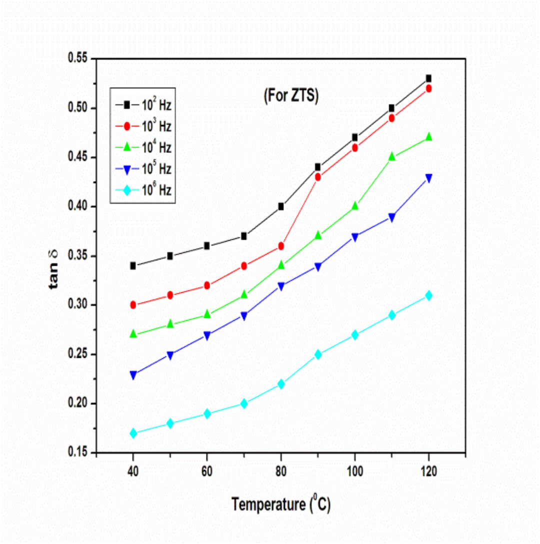


k)

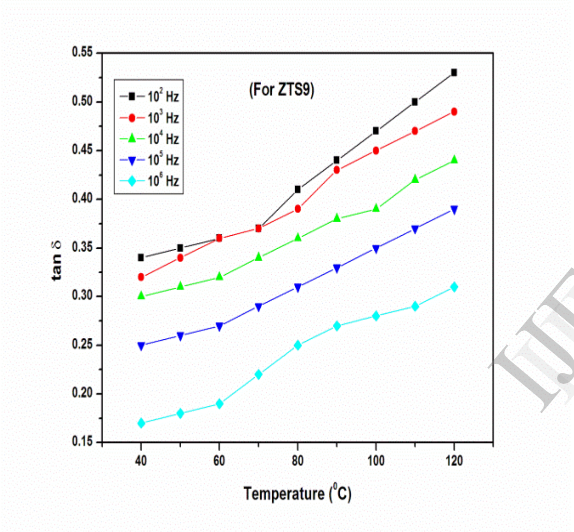


i)

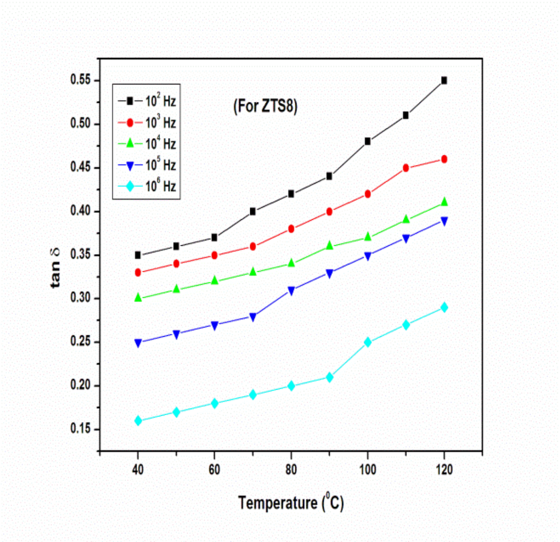
Figure 3: Dielectric constants observed for the ZMTS crystals


(For ZTS)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

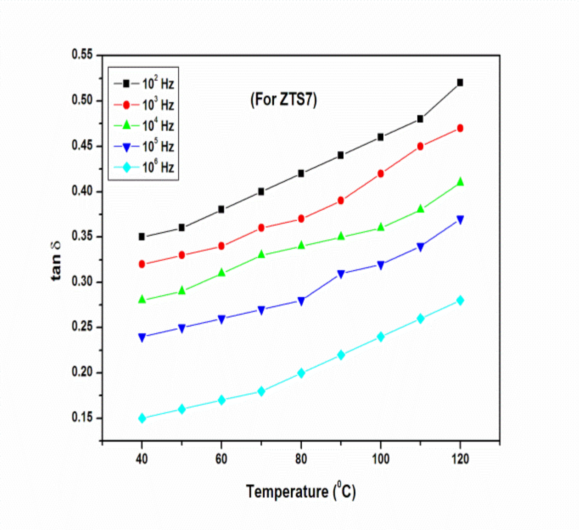
a)


(For ZTS9)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

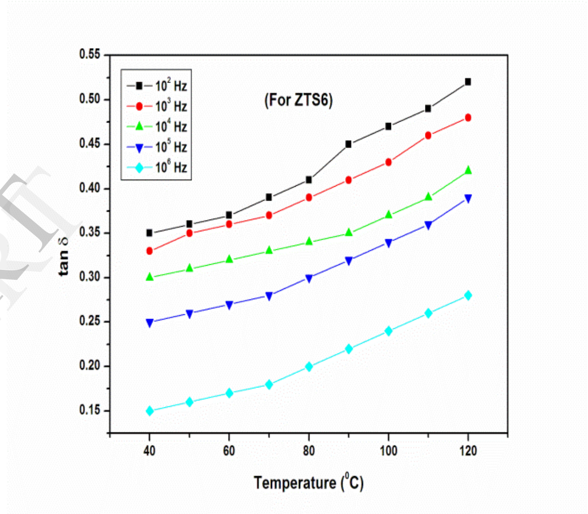
b)


(For ZTS8)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

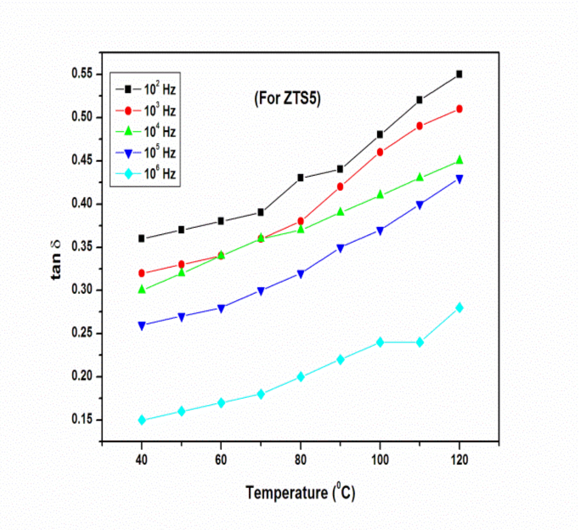
c)


(For ZTS7)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

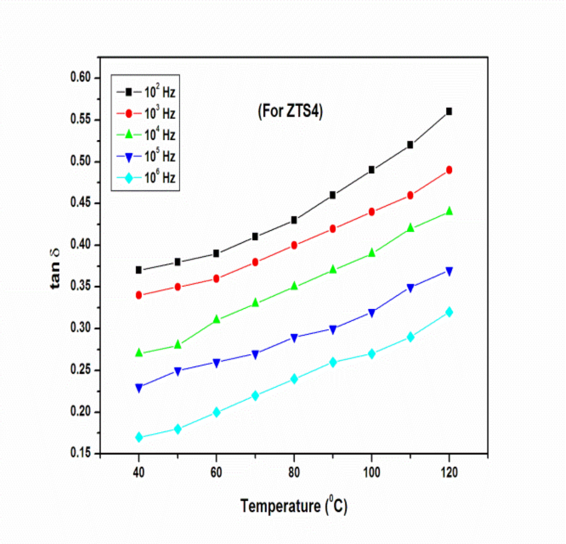
d)


(For ZTS6)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

e)


(For ZTS5)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
tan δ
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
40
60
80
100
120
Temperature (°C)

f)



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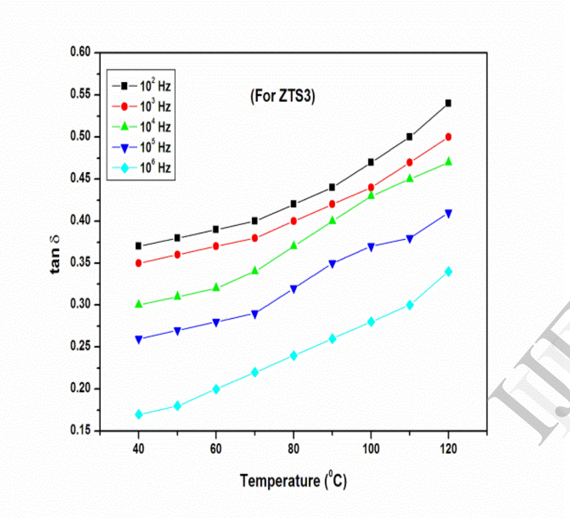

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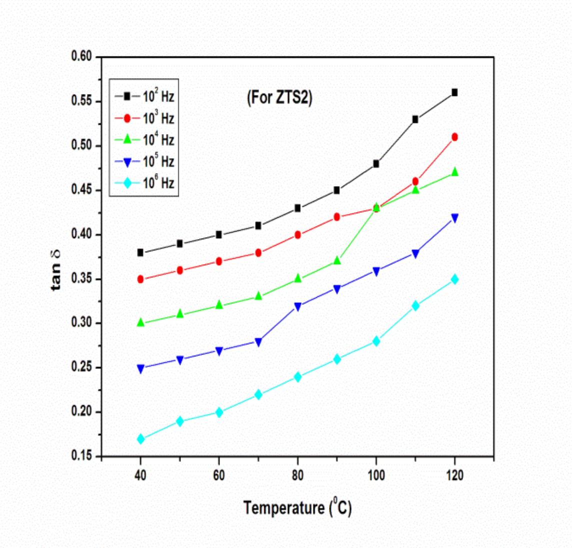
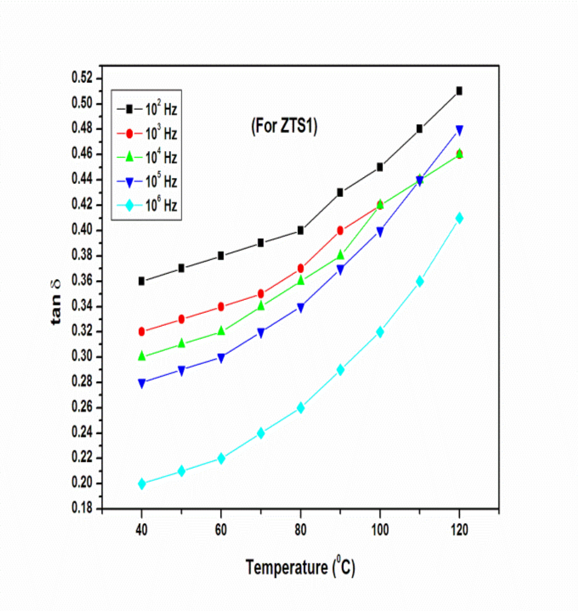
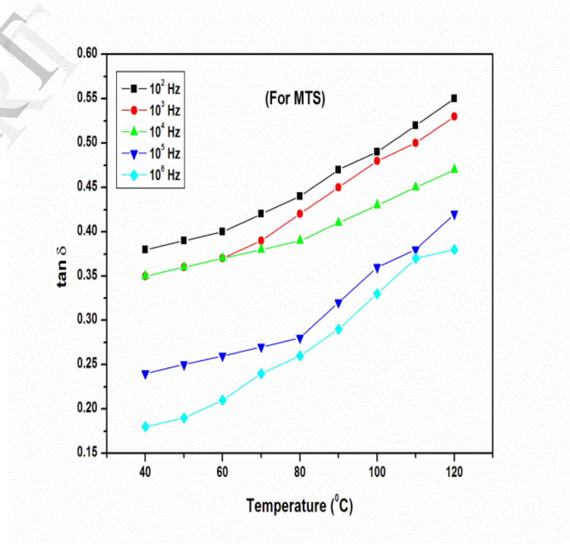


i)

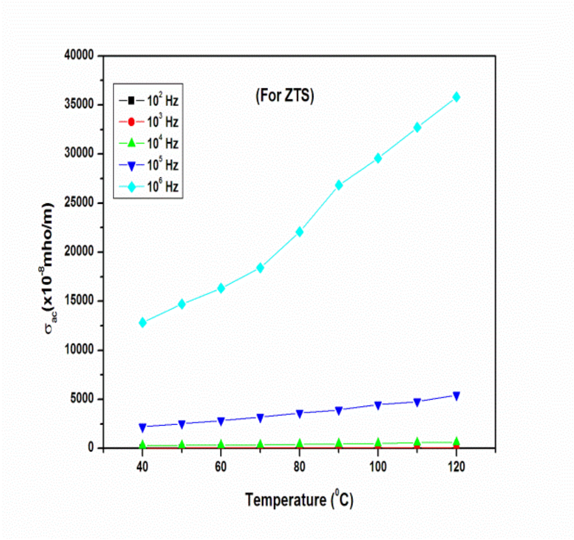


J)

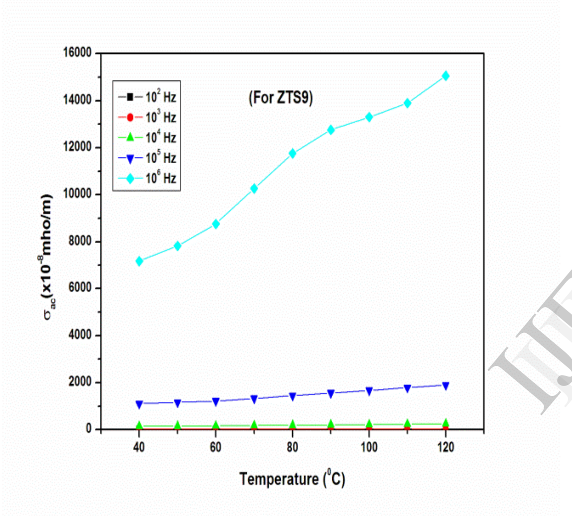


k)

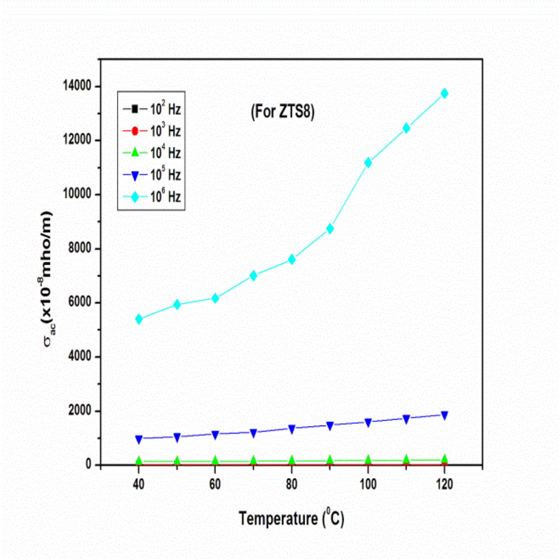
Figure 4: Dielectric loss factors observed for the ZMTS crystals


(For ZTS)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
5000
10000
15000
20000
25000
30000
35000
40000
40
60
80
100
120

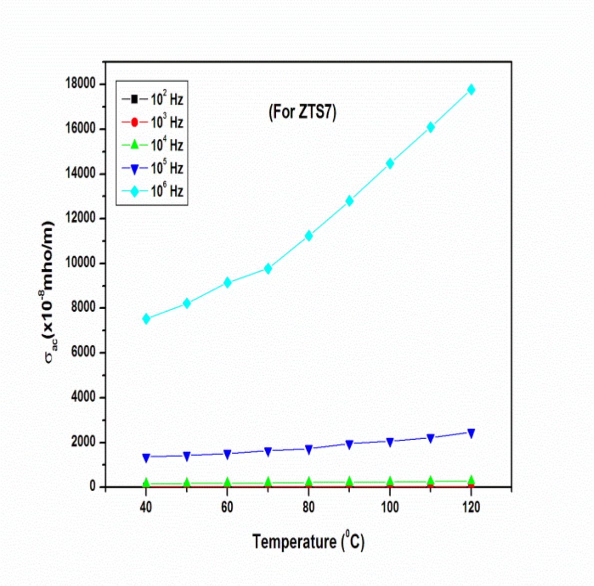
a)


(For ZTS9)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
2000
4000
6000
8000
10000
12000
14000
16000
40
60
80
100
120

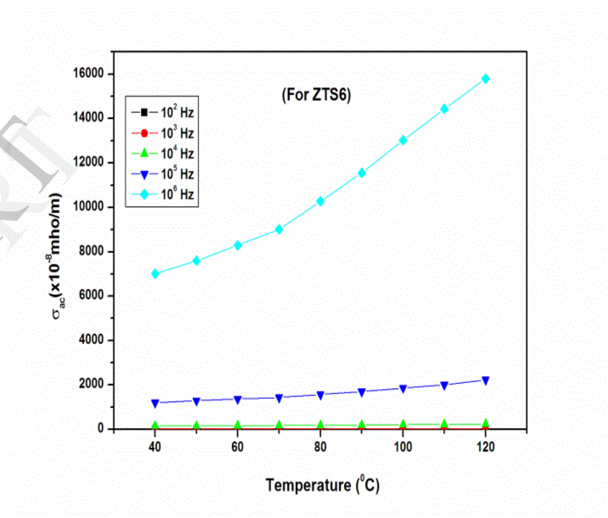
b)


(For ZTS8)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
2000
4000
6000
8000
10000
12000
14000
40
60
80
100
120

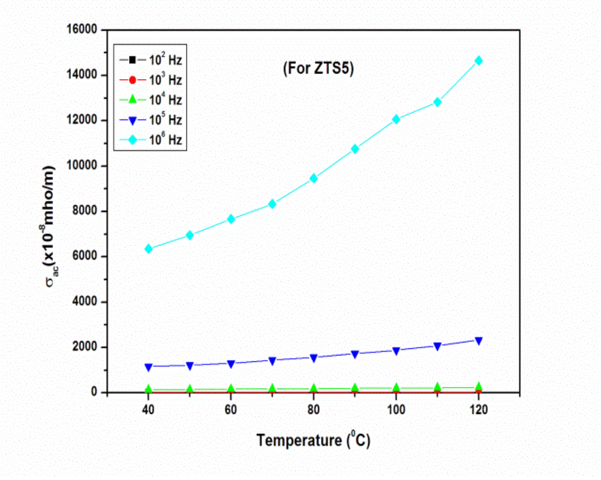
c)


(For ZTS7)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
40
60
80
100
120

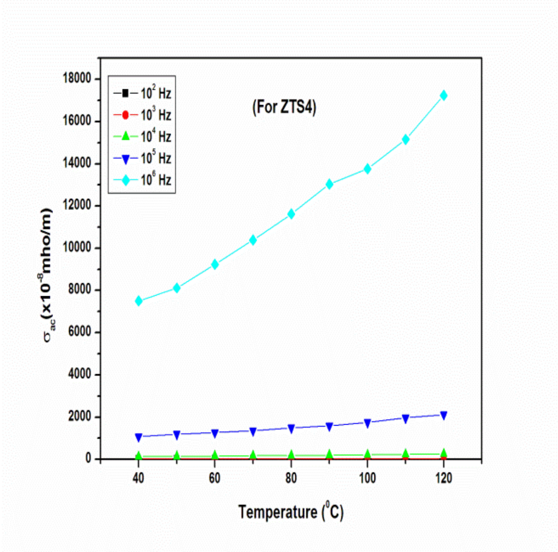
d)


(For ZTS6)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
2000
4000
6000
8000
10000
12000
14000
16000
40
60
80
100
120

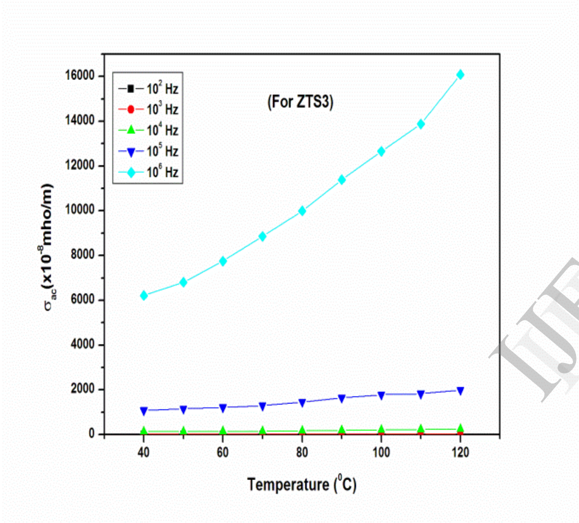
e)


(For ZTS5)
σ_{ac}(x10^{-8}mho/m)
Temperature (^{0}C)
10^2 Hz
10^3 Hz
10^4 Hz
10^5 Hz
10^6 Hz
0
2000
4000
6000
8000
10000
12000
14000
16000
40
60
80
100
120

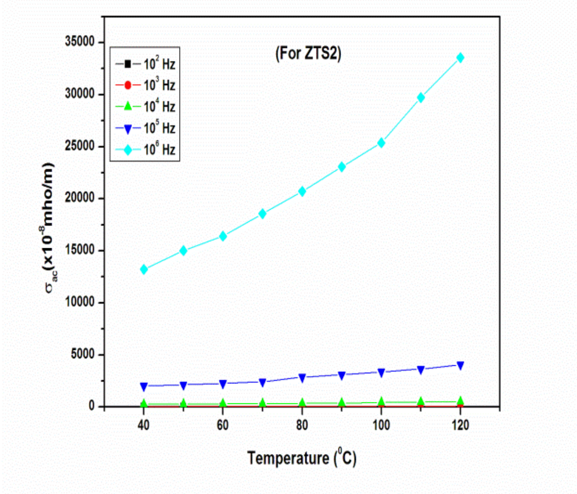
f)



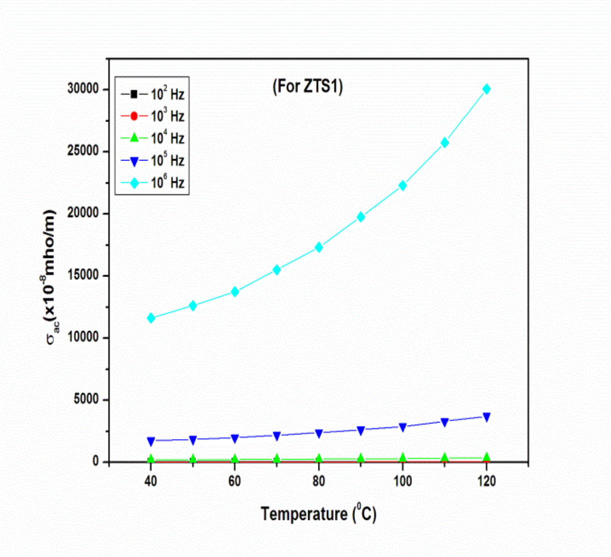
g)



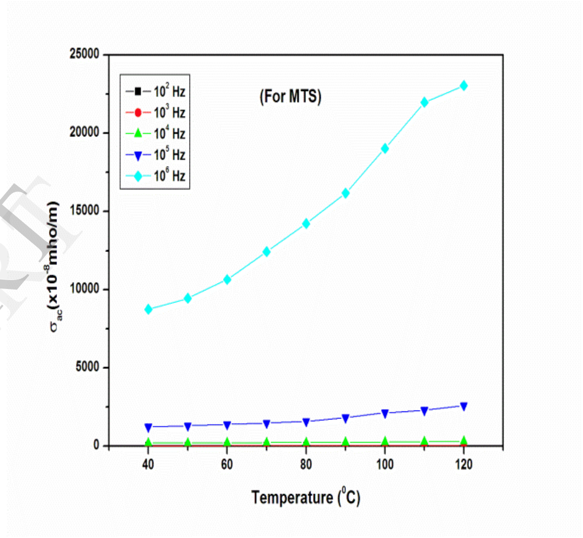
h)



i)



J)



k)

Figure 5: AC electrical conductivities observed for the ZMTS crystals

The electrical parameters of pure ZTS crystal observed in the present study are found to be in good agreement with the reported values [11]. Electrical conductivity of ZMTS crystals can be understood as due to the proton transport within the framework of hydrogen bonds. Also, the conductivity can be associated with the incorporation into the crystal lattice of impurities and the formation of corresponding defects in ionic crystals. The proton conduction may be accounted for by motion of protons accompanied by a D defect (excess of positive charge). Migration of these defects may only modify electric polarization and may not change the charge at an electrode. The motion of defects occurs by some kind of rotation in the bond with defects. The speed of displacement $v = \nu a$, where ν and a are the frequency and distance respectively of the jump (hopping of charge) from one bond to the other [12]. So, the increase of conductivity (both DC and AC) with the increase in temperature observed for the ZMTS crystals in the present study can be understood as due to the temperature dependence of the proton transport. Moreover, the conductivity increases smoothly through the temperature range considered in the present study.

The AC and DC activation energies (E_{ac} and E_{dc} respectively) observed in the present study are given in Table 2. E_{dc} value is found to be more than the E_{ac} value, as expected. Both the E_{dc} and E_{ac} values do not vary in a systematic way with the composition. The nonlinear composition dependence is felt for all the electrical parameters considered in the present study. This is similar to that reported in the literature for alkali halide mixed crystals [7, 13-15]. As done in the case of alkali halide mixed crystals, the nonlinear variation with composition of the electrical parameters observed in the present study for the ZMTS crystals can be attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries.

Table 2. DC and AC activation energies observed for the ZMTS crystals

Crystal	E_{dc} (ev)	E_{ac} (ev)
ZTS	0.209	0.094
ZTS9	0.472	0.087
ZTS8	0.625	0.093
ZTS7	0.457	0.081
ZTS6	0.411	0.077
ZTS5	0.571	0.086
ZTS4	0.675	0.081
ZTS3	0.572	0.074
ZTS2	0.605	0.079
ZTS1	0.666	0.066
MTS	0.598	0.073

The dielectric constant of a material is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is well established that the space charge polarization is very predominant at lower frequencies. This polarization is known to arise from charged defects or impurities present and also due to the creation and distribution of dipoles either within the bulk or at the surface of the crystal. The dipole orientational effect can sometimes be seen in some materials up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz. The large value of ε_r at low frequency is due to the presence of space polarization, which depends on the purity and perfection of the sample. Results obtained in the present study show that ionic polarization is dominating in ZMTS crystals. Moreover, Varotsos [16] has shown that the electronic polarizability practically remains constant in the case of ionic crystals. The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability.

4. Conclusions

Single crystals of ZMTS were grown by the slow evaporation method and characterized by single crystal X-ray diffraction and electrical (both AC and DC) measurements. The grown crystals were transparent and with well defined external appearance. The obtained unit cell parameters of pure ZTS and MTS crystals are in agreement with the literature values. The unit cell parameters values show that both pure and $MgSO_4$ mixed ZTS crystals are in an orthorhombic structure. The MTS crystal belongs to monoclinic structure. The electrical measurements of ZMTS crystals were carried out at different temperatures with various frequencies and it is observed that DC conductivity (σ_{dc}), dielectric constant (ε_r), dielectric loss (tan δ) and AC conductivity (σ_{ac}) values increase with the increase in temperature and also these values increase in the case of the $MgSO_4$ added ZTS crystals. All the electrical parameters considered in the present study (σ_{dc}, ε_r, tan δ, σ_{ac}, E_{dc} and E_{ac}) are found to vary nonlinearly with the composition (x values).

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