Cole-Cole Plot for TGS Single Crystals Doped with Calcium and Lanthanum Metal Ions

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Abstract: - **Cole-Cole plot is the graphical representation of dielectric data and is useful tool for characterizing electrical properties. TGS is an excellent ferroelectric and pyroelectric material of order-disorder type. In the present study, calcium and lanthanum doped TGS crystals were grown by slow evaporation technique. Static and electronic dielectric constant were determined by conventional two probe setup at frequencies 50Hz and 200KHz respectively. Cole-Cole plot were drawn using complex dielectric constants.**

Keywords:-TGS, rare earth, dielectric constant, cole-cole plot, ferroelectric material

I. INTRODUCTION

A widely used graphical representation of frequency – dependent complex dielectric functions $\varepsilon(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ for various materials is the well – known Cole – Cole plot[1,2] in which ε'' is plotted on the vertical axis against ε'. The Cole-Cole plot is particularly useful for materials which possess one or more well separated relaxation processes with comparable magnitudes and obeying the Debye or Cole-Cole plot reduces to a semicircle. However, when the material also possesses, a conductivity, the Cole-Cole representation becomes less useful, because the presence of a DC conductivity leads to a divergence of ε'' at low frequencies.

Stankowska et al [3] have studied the dielectric properties of TGS crystals admixture with D and DL-phenylalanine. Michenvick and kashevick [4] have studied the effect of impurity concentration gradients on the dielectric properties of triglycine sulphate crystals with the non- isomorphic impurity ions of chromium and mixed isomorphic crystals of TGS and TG selenite. R.Muralidharan et al [5] have studied the temperature dependence or dielectric constant for pure and rare earth doped TGS crystals and they have found that, the ferroelectric phase transition occurs at 49°C and there was no change in the transition temperature due to dopant addition. K.Balasubramanian at al [6] have also found that the ferroelectric phase transition occurs at 49°C for pure and copper sulphate doped TGS at 1KHz frequency.

In the present study, Cole-Cole plot were drawn from the complex dielectric constant values determined by parallel plate capacitor method.

II. EXPERIMENTAL DETAILS

Growth procedure: TGS salts were synthesized from AR grade Glycine and sulphuric acid. After successive recrystallization processes the purified salt were used for the preparation of the super saturated solution. Calcium and lanthanum were added in the ratio viz. 1:0.000, 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010 to the TGS solution and saturated at 45°C. Growth was initiated by a temperature reduction of the solution and slow cooling was employed. After a few days of growth, the crystals were harvested after a typical growth period of 10 days.

The capacitance and dielectric loss factor (tan δ) measurements were carried out by “Agilant LCR meter” for the frequencies viz. 50Hz, 100Hz, 1KHz, 10KHz, 50KHz, 100KHz, and 200KHz at various temperatures ranging from 30°C to 120°C while cooling the sample. Temperature was controlled to an accuracy available. Air capacitance (C_{air}) also measured for the thickness equal to that of the sample crystals. The sample cleaved perpendicular to the polar axis (b axis) with dimension (6 x 6 x 2 mm^3) were used. The sample crystals were polished and opposite faces were coated with good quality graphite to obtain a good conductive surface layer. They were annealed for two hours at approximately equal to 120°C to remove moisture content if present.

The dimension of the sample crystal were measured using a travelling microscope (LC = 0.001 cm), the dielectric constant of the crystal was calculated using the relation [7] (as the crystal area was smaller than the plate area of the cell)

$$\varepsilon_r=\left[\frac{C_{crys}-C_{air}\left[1-\frac{A_{crys}}{A_{air}}\right]}{C_{air}}\right]\left[\frac{A_{air}}{A_{crys}}\right]$$

Where, C_{crys} is the capacitance of the crystal (including air), C_{air} is the capacitance of the air, A_{crys} is the area of the crystal touching the electrode and A_{air} is area of the electrode.

The complex dielectric constant values ε' and ε'' were determined from the static (ε_s) and electronic (ε_∞) dielectric constant values

$$\varepsilon'(\omega) = \varepsilon_\infty+\varepsilon_s-\varepsilon_\infty/1+\omega^2\tau^2$$
$$\varepsilon''(\omega) = (\varepsilon_s-\varepsilon_\infty)\ \omega\tau/1+ \omega^2\tau^2$$

Were, ω is the angular frequency and τ relaxation frequency which was determined from debye frequency value determined from X-Ray diffraction data . ε' and ε'' were determined for the frequency range from 1 Hz to 1GHz.

Cole-Cole plot were drawn between ε´ and ε´´ at various temperature viz 30°C, 50°C (curie point temperature) and 70°C.

III. RESULTS AND DISCUSSION

The static and electric dielectric constant values along with relation time for all the grown crystals are provided in table 1. Cole-Cole plot drawn for the sample CaTGS (1:0.004) and LaTGS (1:0.004) are shown in figures 1 and 2 for illustration.

Table 1. Static and Electronic dielectric constant ,relaxation frequency of pure,Ca and La doped TGS crystals

System	Static dielectric constant (ε_s)			Electronic dielectric constant (ε_∞)			Relaxation time (τ) (x10^{-13}second)
	30°C	50°C	70°C	30°C	50°C	70°C	
Pure TGS	357.56	498.56	454.30	0.53	0.61	0.56	3.3
1:0.002 CaTGS	357.48	654.98	453.98	0.62	0.79	0.64	2.6
1:0.004 CaTGS	330.00	658.00	405.00	1.55	2.18	1.59	3.01
1:0.006 CaTGS	343.07	660.07	454.07	2.45	2.56	2.13	3.25
1:0.008 CaTGS	325.70	700.01	414.70	2.34	2.53	2.41	2.89
1:0.010 CaTGS	358.00	702.00	430.00	2.07	2.65	2.16	3.07
1:0.002 LaTGS	430.00	549.00	462.00	4.15	4.21	4.25	3.34
1:0.004 LaTGS	304.00	594.00	419.00	4.30	5.90	4.30	3.09
1:0.006 LaTGS	330.00	606.00	405.00	4.22	6.10	3.38	3.78
1:0.008 LaTGS	384.20	650.00	445.00	4.10	6.50	4.53	3.14
1:0.010 LaTGS	502.00	812.00	406.00	4.59	6.50	4.96	2.98

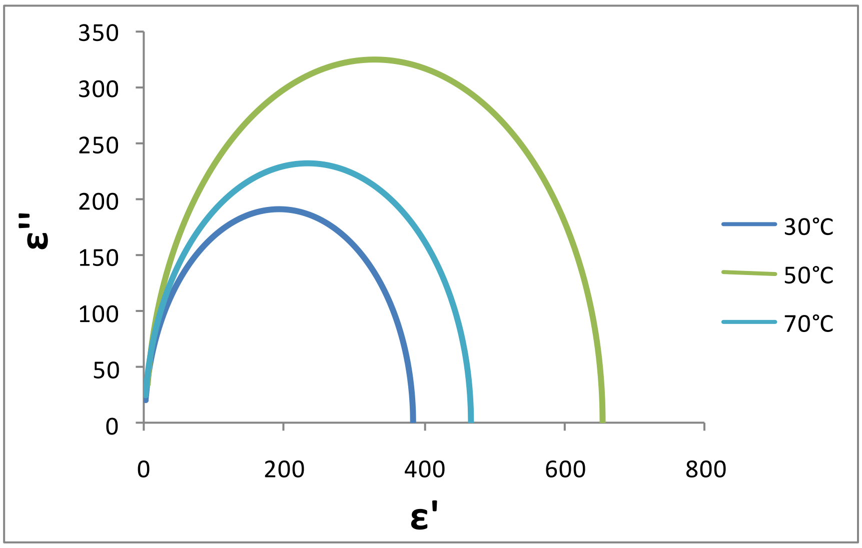

Figure 1. Cole-Cole Plot for 1:0.004 CaTGS crystal

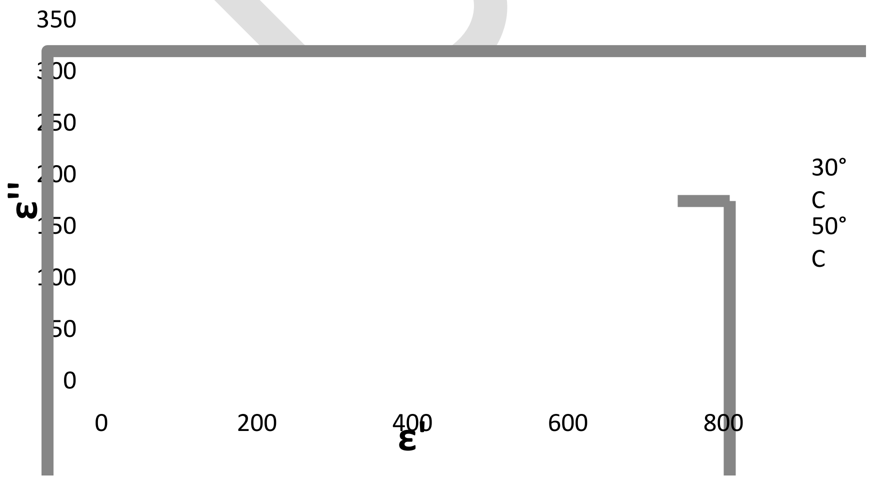

Figure 2. Cole-Cole Plot for 1:0.004 LaTGS crystal

The plots exactly fit into semicircle with different radius, radius of the circle at 50°C (curie point temperature) is maximum compared to the other , for all the eleven crystals. The radius of the semicircle at 70°C is greater than that for 30°C. As the dopant concentration increases (for both calcium and lanthanum dopant) the radius of the semicircle is also increased.

CONCLUSION

The Cole-Cole plots drawn in the present study exactly fit into semicircle for all the sample with different radius. The dopant addition increases the radius.

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