

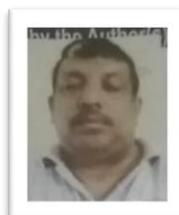
Conductivity and Dielectric Properties of CCTO: Silica 0:3 Connectivity Ceramic Glass Composites

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Abstract

Ceramic Glass 0-3 composites of CCTO ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) and Silica (SiO_2) were prepared by conventional oxide route and sintering method. Different weight ratios of active ceramic material viz. CCTO were dispersed throughout Silica matrix in its glassy state. The dielectric constant and its conductivity were studied. It was found that a ratio of 90:10 CCTO: SiO_2 gave the best dielectric values as well as conductivity. Biologically silica plays an important role in plants metabolism and cell wall structure.

Keywords: CCTO, Silica, Dielectric, Sintering Ceramic, Composite, Loss, Conductivity.

Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is a Wonder Material in the realm of electric charge storage and storage densities, because of its extremely large dielectric constant spread over a wide range of frequency and temperature^[1]. Futuristic electric vehicles needs tremendous amount of electrical power during its initial pick up. This initial surge of power cannot be supplied by rechargeable batteries alone, also a large stack of batteries will add to the weight of the vehicle, which any way is undesirable. One way to circumvent the problem is the use of capacitors with large capacitances and light weight. CCTO with its large dielectric constant turns out to be the ideal candidate to construct those kinds of capacitors. Apart from these uses there are a whole lot of areas like power electronics, power factor correction etc.

However CCTO also has its inherent drawbacks, it suffers from a high dielectric loss factor which renders it unsuitable for considerable period of charge storage. Implying substantial charge leakage happens when kept idle for a period of time^[2]. To arrest the leakage of charge many research groups all over the world have devised various methods. One way is to modify the perovskite lattice of CCTO by suitable ions. Another method is to construct a composite of CCTO with polymers or some stable non reacting substances^[3].

In this work we had devised our material along the composite path. A 0-3 composite with CCTO and Silica was prepared by dispersing CCTO ceramic in glassy Silica (SiO_2). Silica is mechanically stable and chemically inert, therefore the silica matrix lends robustness to the composite as well as sustains large electric fields without breakdown. 0-3 composite is a model of biphasic materials and this nomenclature was coined by Newnham^[4]. A glassy matrix was chosen because it is considered that glassy state is isotropic and it is easier to manufacture, implying the electrical and mechanical properties are uniform along all directions and very few parameters need to be considered while mass producing. Silica is main source of plants' cell wall and helps to resistance the plants from biotic as well abiotic factors. Rice bran is very useful to utilize industrial purposes. Diatomic cell wall has good quality silica which is used in Laboratories and biomedical equipment.

Experimental Method

Preparation of CCTO ceramics

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) polycrystalline ceramics were prepared by solid-state reaction. The materials used for preparing CCTO ceramic powder were as follows:

1. CuO (Copper Oxide, $\geq 99.90\%$)
2. CaO (Calcium Oxide, $\geq 99.95\%$)

3. TiO₂ (Titanium Oxide, ≥99.7%)

All the above materials mentioned in the list were procured from Sigma Aldrich.

These materials were ball milled in a mill lined with rubber and containing zirconia balls. The ball milling has been carried out for at least 24 hours with acetone as the dispersant. The ball milled powder was then sieved using a 5 µm mesh. The sieved powder was compacted lightly in a crucible made of high grade alumina. The mixed powders were then poured in a crucible and calcined in an electrical temperature-controlled furnace, strictly following the steps mentioned below:

Step 1

Starting from room temperature, the temperature of the furnace is raised to 500 °C in 3 hours at an even rate; it is then kept constant at 500 °C for 2 hours;

Step 2

The furnace temperature is then raised to 850 °C in 2 hours at an even rate. It is then maintained at a constant temperature of 850 °C for an hour;

Step 3

At last the furnace temperature is raised to 1250 °C from 850 °C in 2 hours at an even pace. It is then kept constant at 1250°C for 12 hours.

The reason for keeping temperatures constant for a few hours at 500 °C, 850 °C is because, water, alcohol or any organics that may still exist in the bulk of the material will vaporize at these soaking temperatures, while at 1250°C the solid state reaction gets initiated. The high temperature calcined powders were again milled in a ball mill and then sieved. They were then pressed into pellets of cylindrical shape of appropriate thickness. The pellets were then put in a high-temperature furnace to be sintered, like mentioned in step 3; but now starting from room temperature and holding at 1250°C for 12 hrs. The sintered pellet samples were first polished into a smooth cylinder. Thickness and diameter were then measured using a vernier calipers of accuracy 0.05mm. Density of the pellet were calculated and compared with the theoretical density^[5].

Preparation of the CCTO-Silica Glass Composites

The materials used for preparing the composites were as follows:

1. CCTO powders prepared in the lab as mentioned above
2. Silica Powder.
3. Acetone and PVA

CCTO: Silica Glass composites of 0-3 connectivity was prepared by mixing sintered powder of CCTO ceramic which was prepared according to the method mentioned in previous section. Silica procured from Sigma Aldrich was weighed according to its required ratio. From the density mentioned by the supplier (2.65 gm/cc) on the product sheet the weight corresponding to the volume was calculated. The density of CCTO powder (4.93 gm/cc) was elucidated using standard techniques. The first set of samples were prepared in such a way that the material contains ninety percent (90%) by volume of CCTO ceramic and ten percent (10%) by volume of

Silica. The calculated amount of the constituents of the composite (CCTO ceramic powder and Silica) were weighed and mixed thoroughly in a mortar and pestle made of Agate, acetone was added to this mixture to facilitate intimate blending. A slurry of the ceramic and silica was formed, now one assumes that CCTO powder has been evenly distributed into a matrix of silica. 0.5 % by weight of the prepared paste, Poly vinyl alcohol (PVA) was added, and the paste was again mixed so that the polymer distributes evenly throughout the volume of the mixture. The resulting slurry was poured into a rubber lined zirconia ball mill and was milled for 10 hours at a stretch. The consistency of the slurry was assessed by the amount of time required for the slurry to settle. The more time it takes to settle the better the mixing and hence finer the particles. Had the required consistency not reached. It was again ball milled for at least 5 hours. Again the consistency was checked as mentioned. The slurry was then dried by just leaving it in a vacuum oven with moderate vacuum and 70°C temperature. Lumps were formed due to drying of the slurry, these lumps were crushed in an agate mortar into granules and loaded into steel dies (moulds) which are designed to withstand high pressures and temperatures, the dies were also air tight so that application of pressure spreads uniformly into the bulk of the material poured into it without any material leaking out of the cavity. The mould loaded with the granules was then heated to 140°C accompanied with a pressure of 25 tonnes over the cross sectional area of the cavity. The temperature was held for 30 minutes after which the heater was put off and the mould was allowed to cool to room temperature while keeping the applied pressure on. After the mould reaches room temperature, the pressure was released, the mould was then opened and the material inside the cavity was removed. The Polymer acts as the gluing agent between the particles, thereby forming a bulk of desired shape. We thus obtained a green sample of the CCTO : Silica glass ceramic composite with a connectivity of 0-3. The cavity of the die was circular with a diameter of 2 inches (50 mm), therefore the shape of the sample was disc like, with an appropriate thickness. The thickness of the composite samples could be varied by adjusting the amount of granules being poured into the die. Since the diameter of the composite sample made with the above mentioned die / mould is a constant and therefore it cannot exceed 50 mm, more amount of granules will only result in a thicker composite sample. Calculated amount of granules was loaded into the mould so that the resulting sample yields a thickness not more than 1.5 mm. One can in principle mould the material into any desired shape and size using this procedure. All it needs is a mould with the design features as mentioned and a cavity of the desired shape.

In the present work the samples were chosen in the shape of thin discs with thickness not more than 1.5 mm. The green samples were then placed in the oven to be vitrified. The temperature of the oven loaded with the green sample was gradually increased to 1000°C so that the green samples do not

develop any cracks due to rapid heat shocks. When it reaches 1000°C it is kept soaked in the heat for an hour before it is rapidly cooled to room temperature. Vitrification results and ceramic glass composite is formed^[6]. The composite samples were lapped and polished so that discs of about 1.3 mm thickness with flat surfaces perfectly parallel to each other were formed. Some of the samples were coated with silver on its plane sides (faces) using a vacuum coating unit. Care was taken to mask away the silver electrodes from the edges of the samples. That is the silver electrode coated onto the samples had a diameter 2mm less than the diameter of the sample. For conductivity and dielectric studies electroded samples were used. The procedure mentioned above was repeated for samples of composition 80% by volume CCTO, 70%, 60%, 50%, 40% and 30%.

Experimental results of conductivity Studies

The conductivity of the sample was studied at different temperature. For the study a high voltage power supply (Aplab 5kV max) was used in series with the sample and electrometer. The current so obtained (I) was converted to current density (j) and the voltage applied (V) into the Field (E), by knowing the electrode area and thickness of the sample. To find the activation energies and the mechanism of conductivity in the sample, the conductivities were plotted against the reciprocal of the logarithm of the temperature in absolute scale^[7]. Here the activation energies (E_a) can be calculated. Since the conductivity follow the relation mentioned below.

$$\sigma = \sigma_0 \exp(-E_a/kT) \text{ ----- (1)}$$

which implies

$$\ln \sigma = \ln \sigma_0 - E_a/kT \text{ ----- (2)}$$

Therefore a linear relation exists between $\ln \sigma$ and $1/T$ whose slope is $-E_a$.

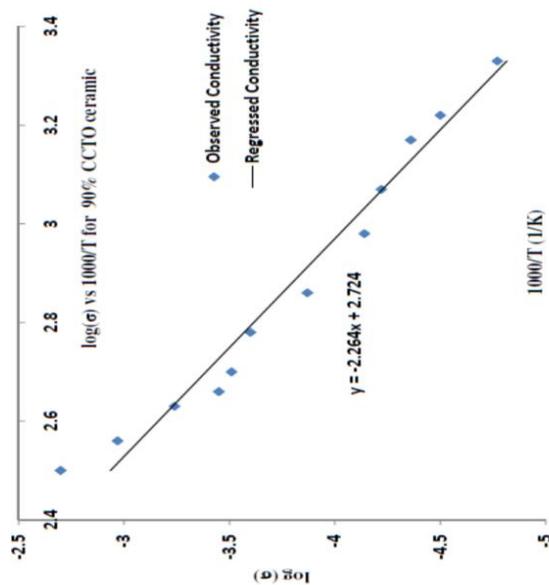


Fig.1: Plot of $\log \sigma$ vs $1/T$ for CCTO ceramic.

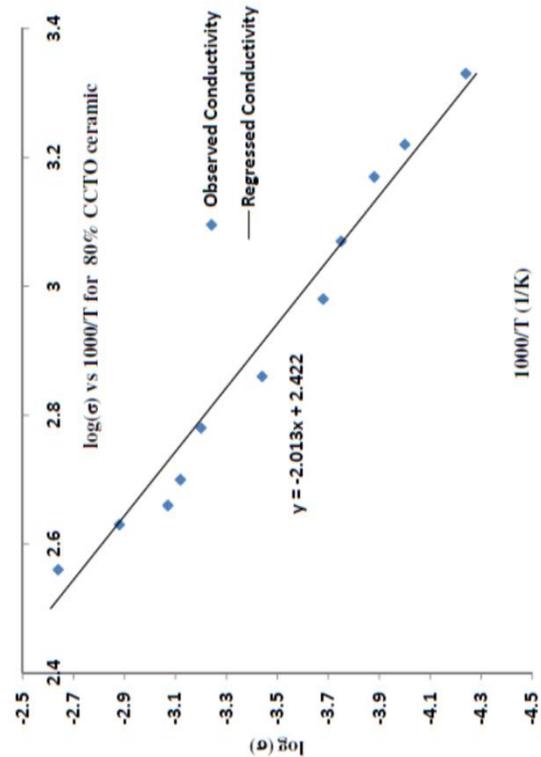


Fig.2: Plot of $\log \sigma$ vs $1/T$ for 90% CCTO composite

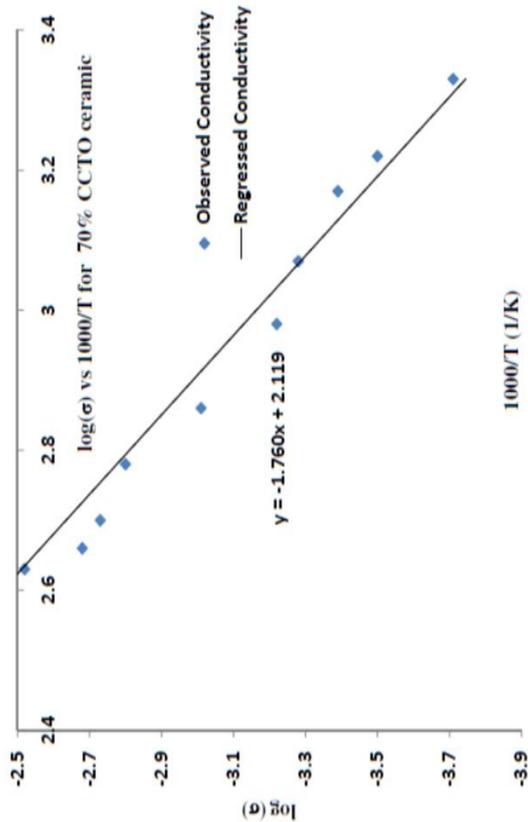


Fig.3: Plot of $\log \sigma$ vs $1/T$ for 80% CCTO composite.

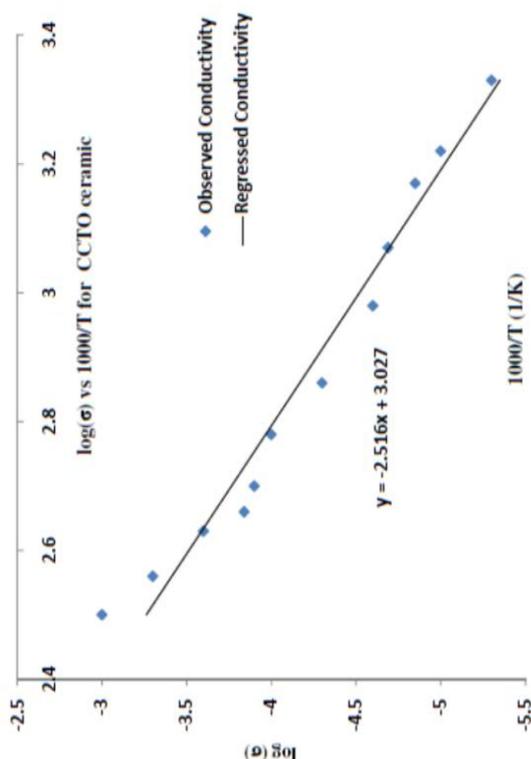


Fig.4: Plot of $\log \sigma$ vs $1/T$ for 70% CCTO composite.

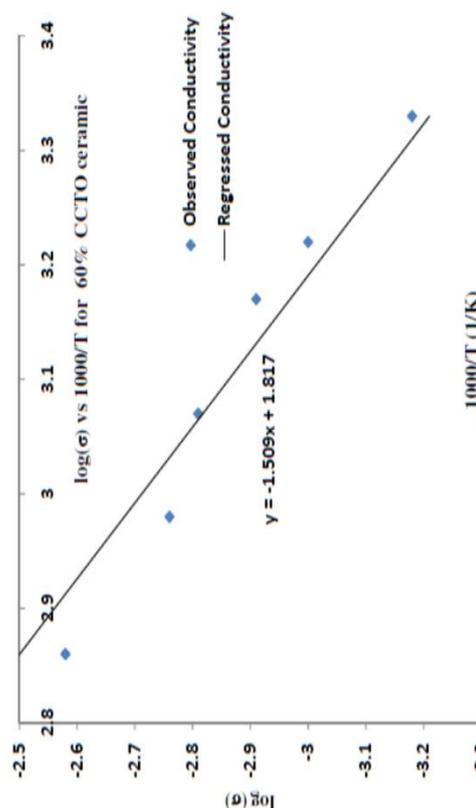


Fig.6: Plot of $\log \sigma$ vs $1/T$ for 60% CCTO composite

Figures 1-6 above shows the Arrhenius plot i.e. plot between $\log \sigma(T)$ and $1/T$ [log of conductivity at temperature T against the inverse of the absolute temperature]. The lower compositions are not shown to avoid monotony. The activation energies calculated from the plots are given in Table 1 below.

Table1. Activation Energies of the Various Composites

Samples	Activation Energy E_a (eV)
Pure CCTO	0.217
90 % CCTO	0.195
80 % CCTO	0.174
70 % CCTO	0.152
60 % CCTO	0.130
50 % CCTO	0.108
40 % CCTO	0.087
30 % CCTO	0.065

Experimental Results of Dielectric Studies

In the current study the dielectric constant and loss tangent was calculated directly from the values of the capacitance measured using HP 4192A impedance bridge. The capacitance was measured at different temperatures and frequencies. Since the allowed frequency of the bridge was only 10 MHz which is in fact a useful range for the material to be used in devices. Also temperature range was kept between the room temperature and T_C (ferroelectric transition temperature). The sample was enclosed in a container with control mechanism and the leads etc. were compensated within the impedance bridge. The

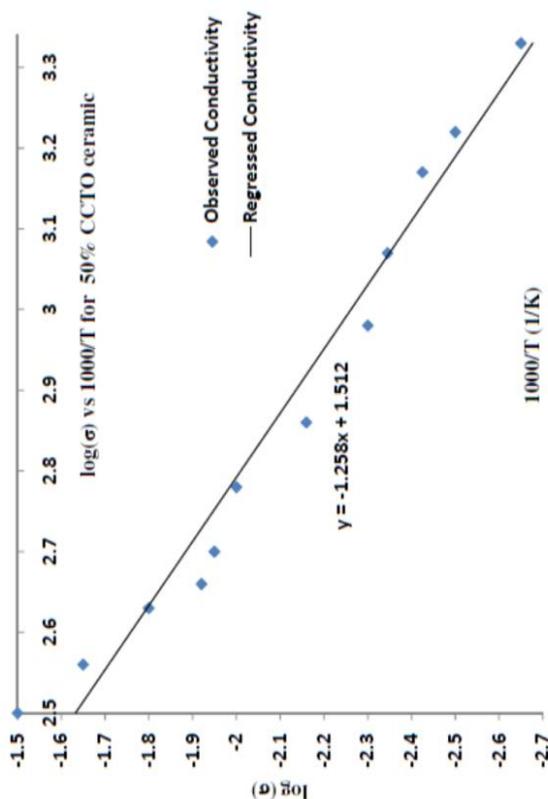


Fig.5: Plot of $\log \sigma$ vs $1/T$ for 50% CCTO composite.

plots of dielectric constant as a function of frequencies held at fixed temperatures ranging from room temperature to 300°C is shown below.

Fig.7. Dielectric constant of CCTO ceramic as a function of frequency measured at different temperatures. The temperature was varied from room temperature (30°C) to 300°C in steps of 50°C.

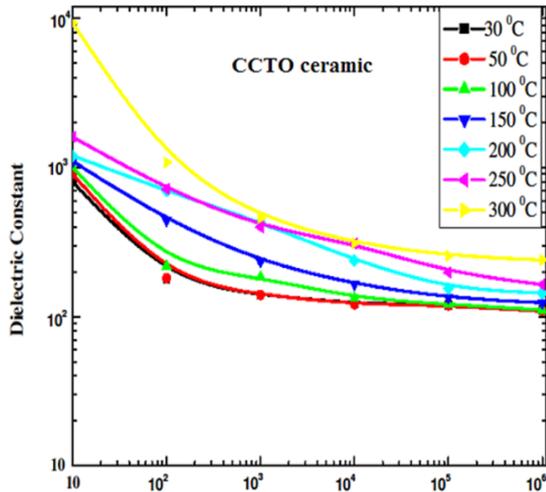


Fig.8. Dielectric constant vs frequency of 90% CCTO composite

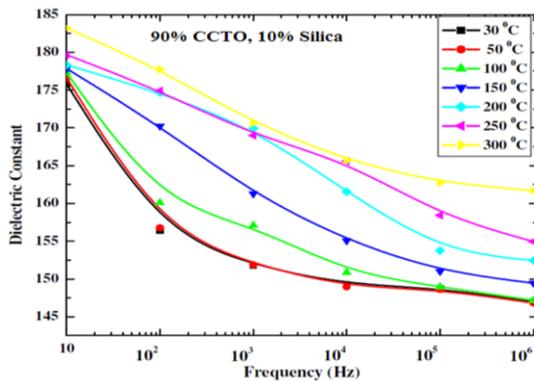


Fig.9. Dielectric constant vs Frequency of 80% CCTO composite

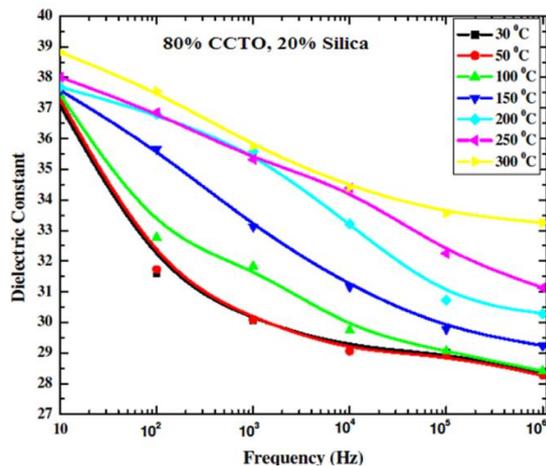


Fig.10. Dielectric constant vs frequency of 70% CCTO composite

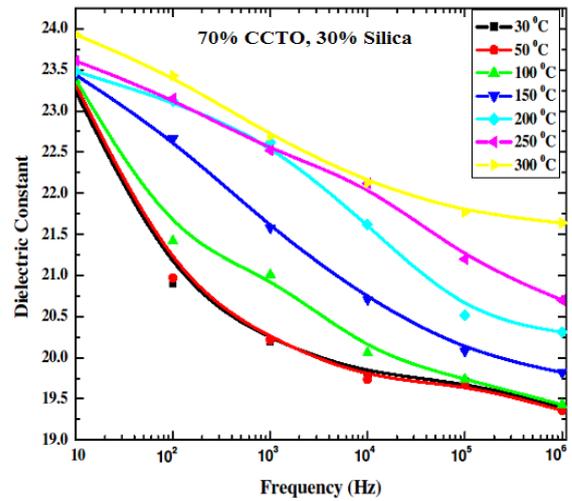
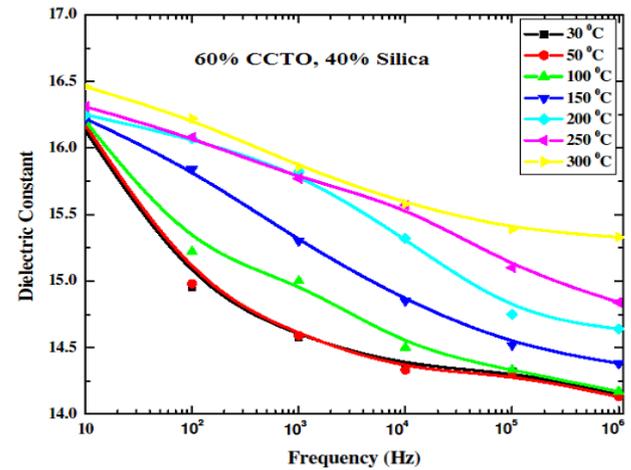


Fig.11. Dielectric constant vs Frequency of 60% CCTO composite



In the case of Dielectric loss we have a dramatic fall very similar to that of Dielectric constant. Figures 7 to 11 shows the values of Dielectric constants of the composites vis a vis the pure ceramic CCTO. Plots of Dielectric constants of less than 60% are not shown because the trend is similar. Figures 12 to 15 shows the imaginary part of Dielectric permittivity, which is a measure of loss. It is desirable for a Dielectric material to possess minimum loss.

Figure 12. Imaginary Part Of Dielectric Permittivity as a function of Frequency, for CCTO Ceramic

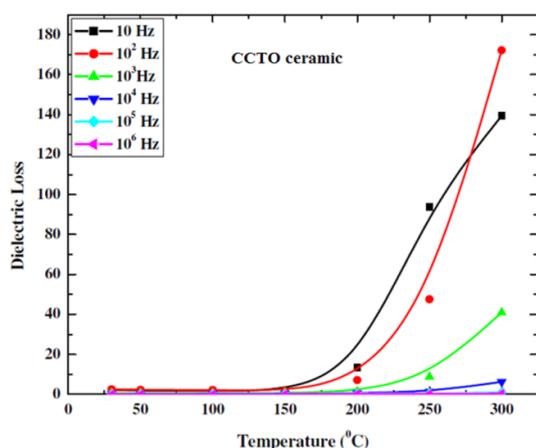


Figure 13. Imaginary part of Dielectric Permittivity as a function of Frequency, for 90% CCTO Composite

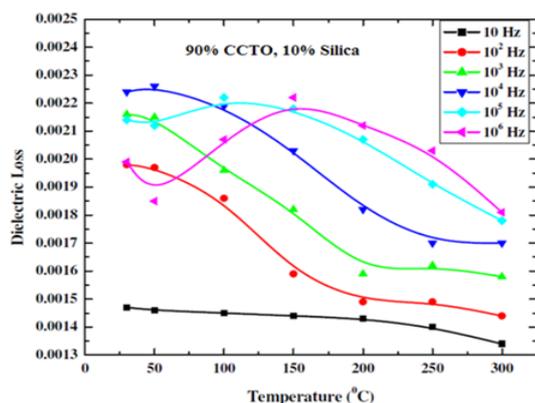


Figure 14. Imaginary part of dielectric Permittivity as a function of Frequency, for 80% CCTO composite.

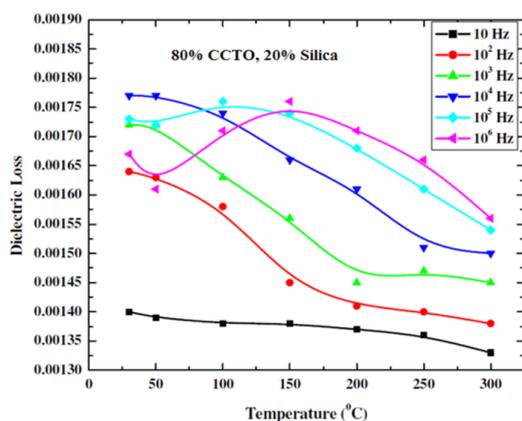
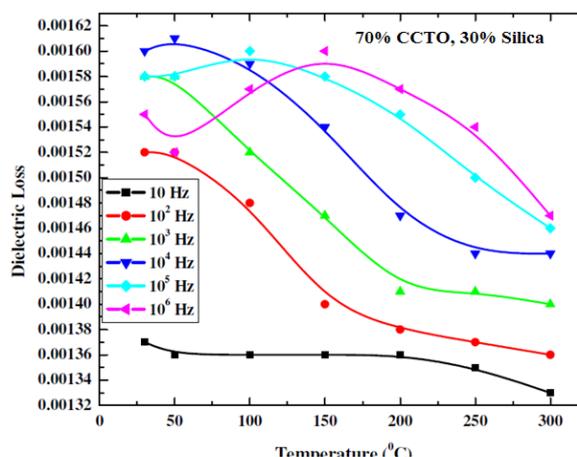


Figure 15. Imaginary part of dielectric Permittivity as a function of Frequency, for 70% CCTO composite.



The figures mentioned above demonstrates a key feature of the composites, i.e. on mixing CCTO ceramic in Silica the loss drastically falls off but stabilizes with temperature, the pure ceramic although having a high dielectric constant the loss factor shows an exponential trend with increasing temperature.

Results and Discussions

The conductivity of the samples is typical of a material whose electrical behaviour is like a semiconductor possessing charge carriers with low mobilities. The activation energies are typical of ions and oxygen vacancies within the bulk of the material^[8]. The activation energies calculated from the Arrhenius plots ($\log \sigma$ vs T^{-1}) which are illustrated in figures 1 to 6 and compiled in table 1, where E_a the activation energies ranging from 0.065eV to 0.217eV, are characteristic of ionic conductivity or shifting of oxygen vacancies in the bulk. The conductivity studies not only gives an idea of the properties of charge carriers, but it also supports the dielectric behavior of the complex permittivity of the material. The imaginary part of the complex permittivity of CCTO and its composites, ideally, is linked to the conductance of a material.

The dielectric constant and loss measurements on the composites are very interesting and it reveals a lot of insight into the material. The pure sample of CCTO exhibits giant dielectric constant at low frequency within the studied temperature range. As frequency increases, permittivity drastically decreases and approaching a constant value at 1 MHz. It has been reported that CCTO ceramics consist of insulating grain boundaries and semiconducting grains. The charge carriers accumulated at the interface between semiconducting grains and insulating grain boundaries resulted in an increase in the dielectric constant. The effect is termed interlayer boundary capacitance (ILBC)^[9]. The dielectric constant of CCTO ceramics and its composites measured at different temperatures are depicted in figures 7 to 11. One can see that there is a reduction of dielectric permittivity by two orders of

magnitude just by addition of 10% silica into the ceramic. This implies that in pure CCTO ceramic an interaction between grains or the role of grain boundaries is quite significant. This argument is all the more confirmed because further addition of silica does not bring down the permittivity as drastically. This in a way indirectly confirms the Inter layer barrier capacitance (ILBC) model for high dielectric constant in CCTO ceramics. This effect and similar explanation is also found in works by Arbatti et.al. [10], but in a different yet equivalent system. Dielectric loss factor of the sample exhibits dc conduction losses. It shows the dielectric loss of pure CCTO drastically decreases with increasing frequency. The dielectric loss increases with temperature from 30°C to 300°C as shown in figure 12. While figures 13 to 15 show that the loss remains a constant for the composites, rather it shows marginal decrease. The frequency and temperature effect on the dielectric loss illustrates the interfacial polarization of the grain boundaries within the sample^[11].

References

1. Subramanian M.A., Li D, Duan N, Reisner B.A., and Sleight A.W., "High dielectric constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ phases", *J. Solid State Chem.*, 151, 323-325, 2000.
2. R. S. Ernest Ravindran, P. Thomas and S. Renganathan., "Effect on dielectric, structural and thermal behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ in a Nylon 11 matrix", *Bull. Mater. Sci.* 42,28, 2019.
3. Vishnu Razdan, Abhishek Singh, Brad Arnold, Fow-Sen Choa, Lisa Kelly, N. B. Singh, "Effect of organic flux on the colossal dielectric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)", *Proc. SPIE 9493, Energy Harvesting and Storage: Materials, Devices, and Applications VI*, 949308 18 May 2015.
4. R. E. Newnham, D. P. Skinner, and L. E. Cross, "Connectivity and Piezoelectric-Pyroelectric Composites", *Mat. Res. Bull.* 13: 525 1978.
5. Mohsen Ahmadipour, Mohd Fadzil Ain, Zainal Arifin Ahmad, "A Short Review on Copper Calcium Titanate (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition, and Sensing Application", *Nano-Micro Letters*, 8, 4, 291–311, 2016.
6. M. Masturah, I. Norezan, A. K. Yahya, A. Zakaria, M. S. Mohd Deni & M. K. Talari, "Effect of V_2O_5 - TeO_2 Glass Addition on Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics Prepared by Solid State Method", *Transactions of the Indian Institute of Metals volume 66*, 325–328, 2013.
7. Zhuang Tang, Kangning Wu, Yuwei Huang, and Jianying Li, "High Breakdown Field $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics: Roles High Breakdown Field $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics: Roles of the Secondary Phase and of Sr Doping.", *Energies*, 10, 1031, 2017.
8. Suman Punia Neetu Ahlawat, Rajesh Punia, Kanta Maan Sangwan, & Sunita Rani., "Dielectric relaxation and conduction mechanism of complex perovskite $\text{Ca}_{0.90}\text{Sr}_{0.10}\text{Cu}_3\text{Ti}_{3.95}\text{Zn}_{0.05}\text{O}_{12}$ ceramic. *Ceramics International.* 44. 5996-6001, 2017.
9. Rainer Schmidt and Derek C. Sinclair, "Capacitors: Theory of Operation, Behavior and Safety Regulations", ISBN: 978-1-62417-586-2, Nova Science Publishers, Inc. 2013.
10. M. Arbatti, X. Shan, Z.-Y. Cheng, "Ceramic-Polymer Composites with High Dielectric Constant, *Advanced Materials*, Volume 19, 10, 1369–1372, 2007.
11. Wenhui Yang, Shuhui Yu, Rong Sun and Ruxu Du "Nano- and microsize effect of CCTO fillers on the dielectric behavior of CCTO/PVDF composites"., *Acta Materialia*, 59, 14, Pages 5593-5602. 2011.