International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 3 Issue 12, December-2014

# Studies on the Dielectric Constant and Conductivity of $CaCu_3Ti_4O_{12}$ : PET and $CaCu_3Ti_4O_{12}$ : PVC ceramic Polymer Composites

Ajay Pratap Singh[1]
Research Scholar, [1]Department of Chemistry,
Mangalayatan University, Aligarh , (U.P), India

Shilpi Saxena[2]
Lecturer, [2]Department of Chemistry,Amarnath Girl's
Degree College, Mathura, (U.P), India

Anil Govindan[3]
Associate Professor[3]Department of physics,M.M.H. (P.G.)
College, Ghaziabad (U.P.) India

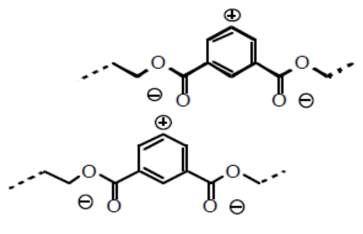
***Abstract*—Studies on the dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO) : PET and $CaCu_3Ti_4O_{12:}$ PVC ceramic polymer composites at varying percentages of the polymers was conducted. $CaCu_3Ti_4O_{12}$ was prepared by the modified solid state reaction method. The dielectric constant (ε') was measured in the frequency range from 10 Hz to $10^6$ Hz and the temperature ranging from 30°C to 300°C with the help of HP 4192A LF Impedance Analyzer. The results showed that the dielectric constants of the sample are frequency and temperature dependent. Dielectric constant decreases with increasing frequency and decreasing temperature due to interfacial polarization**

***Keywords*— $CaCu_3Ti_4O_{12,}$ dielectric constant, CCTO : PET and CCTO:PVC**

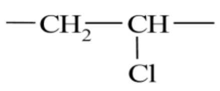


## I. Introduction

Polymers and ceramics have contrasting physical and chemical properties. Polymers have low densities; do not reflect or absorb light (they are white or colorless); do not conduct electricity; and are flammable. The chemical bonds in polymers are also different than those found in metals and ceramics. In the present study we have considered two polymers which are freely available and well studied, viz. Polyethylene Terephthalate (PET) and Poly Vinyl Chloride (PVC). The structures are mentioned below.



Polyethylene Terephthalate (PET) and



Poly Vinyl Chloride

Polymers possess very good dielectric strength which is why they are used as dielectrics in capacitors[1]. In the present study, the polymers are used not only to improve the dielectric strength but also as a matrix to hold $CaCu_3Ti_4O_{12}$ (CCTO)[2] ceramic particles in place, without the individual particles touching each other. The polymer matrix provides mechanical flexibility to the composite and acts as electrically inert phase within the composite. 0-3 composites are easy to prepare in the laboratory as well as to manufacture in large scale production units[3].

## II. EXPERIMENTAL PROCEDURE

$CaCu_3Ti_4O_{12}$ ceramics were prepared by solid-state reaction (calcinations and sintering). CaO, CuO, and $TiO_2$ were used as starting materials [4]. Stoichiometric amounts were weighed and mixed by ball milling for more than 24 hours. The ball milled powder was then sieved using a 5 μm mesh. The mixed powders were poured in a crucible and then calcined in air at 1100°C for 10 hours. The calcined powders were again ball milled and then sieved, for uniform particle size. The powder was then pressed into cylindrical pellets of appropriate thickness. The pellets were sintered at 1250°C for 11 hours and then cooled to room temperature in a programmable furnace. CCTO: Polyethelene Terephthalate (PET) composites
of 0-3 connectivity as well as CCTO: Poly Vinyl Chloride (PVC) composites were prepared by mixing pre sintered powder of CCTO ceramic, with PET and PVC powders, weighed according to the required ratio. Acetone was added as dispersant; it can wet the CCTO powder and dissolve PET and PVC so that the polymer gets evenly coated on each particle of the ceramic, yielding well defined 0-3 connectivity composites. 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 polymers. A paste of the ceramic and polymer is formed, now one assumes that CCTO powder has been evenly distributed into a matrix of the polymers. The paste is now injected into steel dies (moulds) and the mould loaded with the paste is then heated to 80°C (close to glass transition temperature of the polymers). The temperature was held for 30 minutes after which the heater was put off and the mould was allowed to cool to room temperature and the mould is opened and the material inside the cavity is removed. We get

an even sample which is tough and flexible, since the polymer now acts like an elastic solid, with CCTO ceramic powder distributed within the matrix like filler. This is now a 0:3 ceramic polymer composite samples. The resulting sample can be given a thickness of not more than 1.5 mm depending on the moulds used. The thickness can be further reduced by pressing the sample between two steel plates at elevated temperature under pressure. The procedure mentioned above was repeated for samples of composition 80% by volume CCTO, 70% and 60% etc. The dielectric properties[5] of the sample were determined using the HP 4192A LF Impedance Analyzer. The conductivity of the samples was measured using a Keithley Electrometer (610 C) and a temperature controlled sample holder. The current across the sample corresponding to different applied voltages were measured using the electrometer. A standard voltage source was used to apply electric field across the sample. Current variation with respect to temperature for a fixed voltage was plotted in real time on a plotter attached to the electrometer. By measuring the thickness and area of the sample the conductivity was measured.

## III. RESULTS AND DISCUSSION

Figure (1) represents the dielectric constant of CCTO ceramics measured at different temperatures. The pure sample of CCTO exhibits high dielectric constant at low frequency within the studied temperature range. As frequency increases, permittivity drastically decreases and approaching a constant value at 1 MHz. The increment of dielectric constant as frequency decreases could possibly be due to interfacial polarization[6]. The charge carriers may be blocked at the electrode interface under the influence of an electric field. It has been reported that CCTO ceramics consist of insulating grain boundaries and semiconducting grains[7]. The charge carriers accumulated at the interface between semiconducting grains and insulating grain boundaries resulted in an increase in the dielectric constant. One can see that there is a reduction of dielectric permittivity by two orders of magnitude just by addition of 10% PET or PVC into the ceramic (Figures 2 to 7). This implies that in pure CCTO ceramic an interaction between grains or the role of grain boundaries [8] is quite significant.

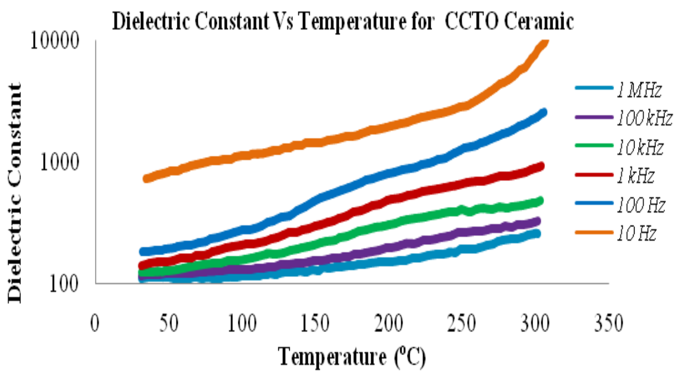



Figure 1. Dielectric Constant as a function of Temperature measured at different frequencies for pristine CCTO ceramic.

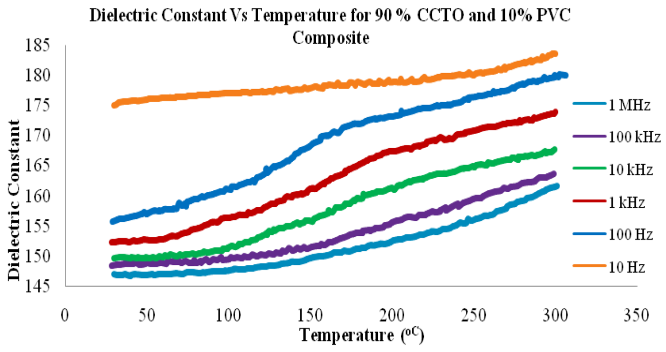



Figure 2. Dielectric Constant as a function of Temperature measured at different frequencies for 90% CCTO : 10% PVC ceramic polymer composites.

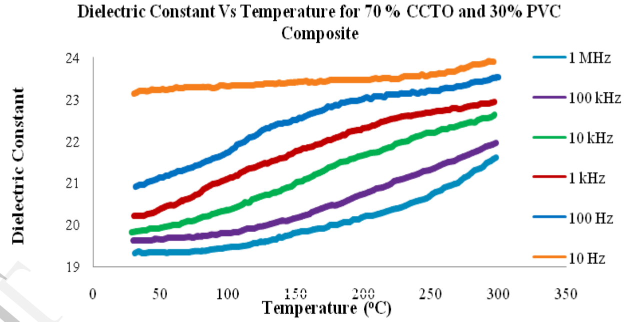





Figure 3. Dielectric Constant as a function of Temperature measured at different frequencies for 70% CCTO : 30% PVC ceramic polymer composites.

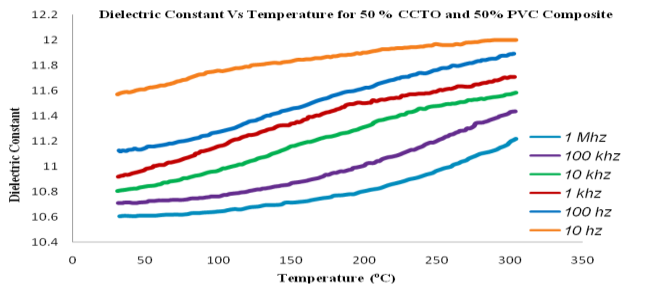



Figure 4. Dielectric Constant as a function of Temperature measured at different frequencies for 50% CCTO : 50% PVC ceramic polymer composites.

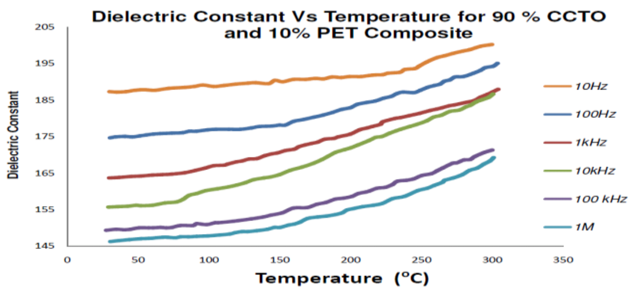



Figure 5. Dielectric Constant as a function of Temperature measured at different frequencies for 90% CCTO : 10% PET ceramic polymer composites.

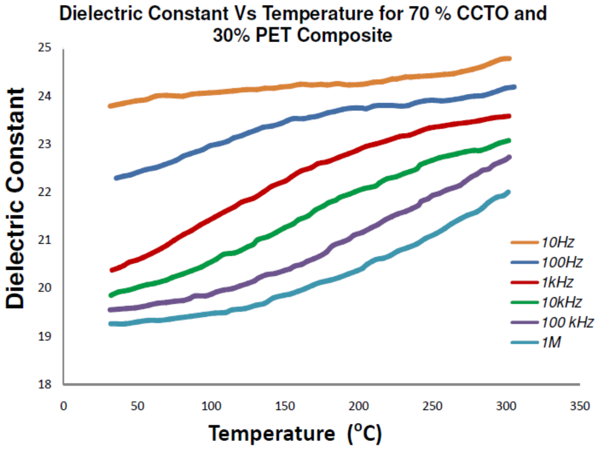



Figure 6. Dielectric Constant as a function of Temperature measured at different frequencies for 70% CCTO : 30% PET ceramic polymer composites

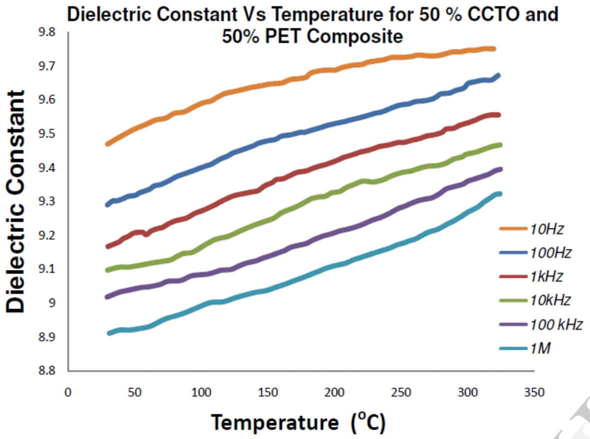



Figure 7. Dielectric Constant as a function of Temperature measured at different frequencies for 50% CCTO : 50% PET ceramic polymer composites.

The logarithm of conductivity of the ceramics as well as the composites against inverse of the temperature is graphically represented in Figures 8 to 14.

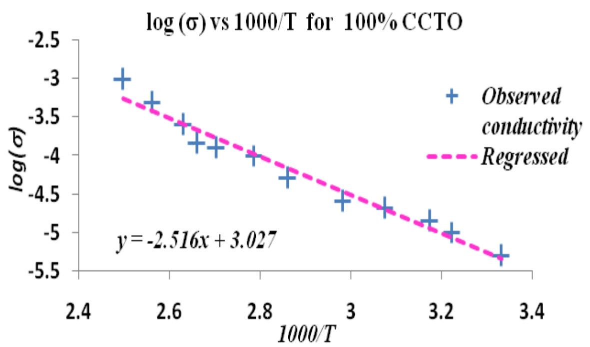



Figure 8. log (σ) vs 1000/T for 100% CCTO ceramic the straight line is the least square fit of the plot with respect to a line, and the slope ismentioned in the graph

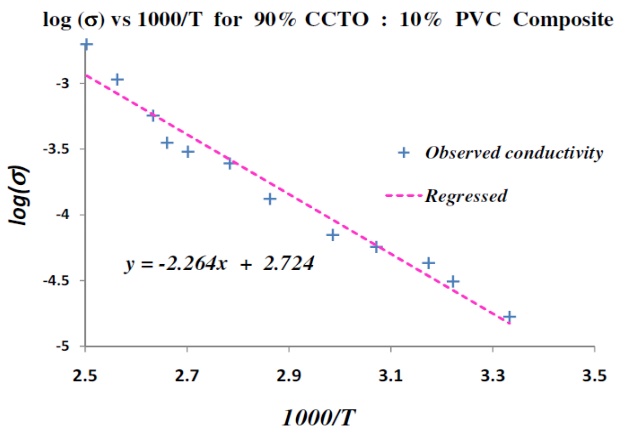



Figure 9. log (σ) vs 1000/T for 90% CCTO : 10% PVC ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph

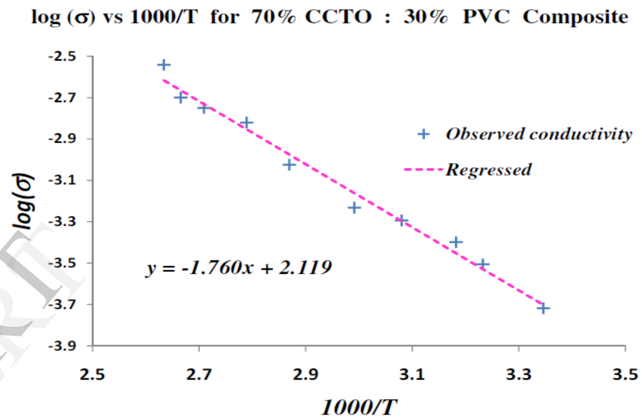



Figure 10. log (σ) vs 1000/T for 70% CCTO : 30% PVC ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph.

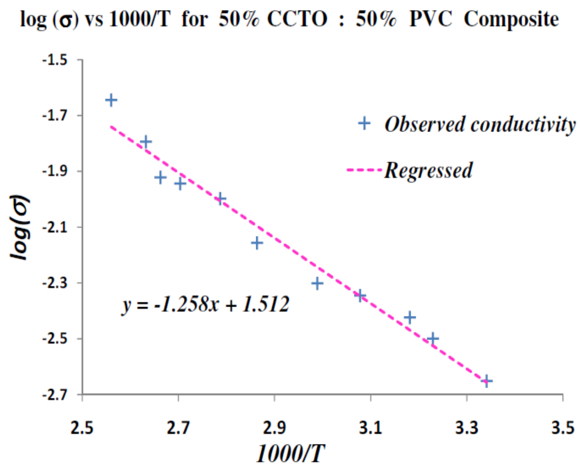



Figure 11. log (σ) vs 1000/T for 50% CCTO : 50% PVC ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph.

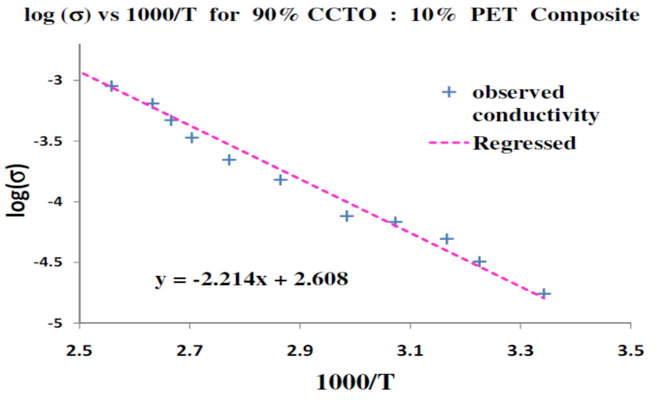



Figure 12. log (σ) vs 1000/T for 90% CCTO : 10% PET ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph.

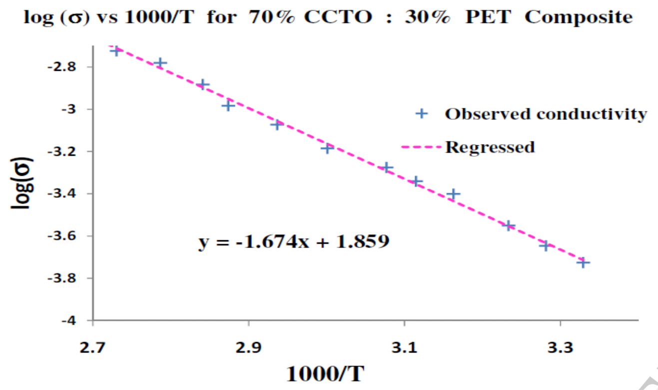



Figure 13. log (σ) vs 1000/T for 70% CCTO : 30% PET ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph.

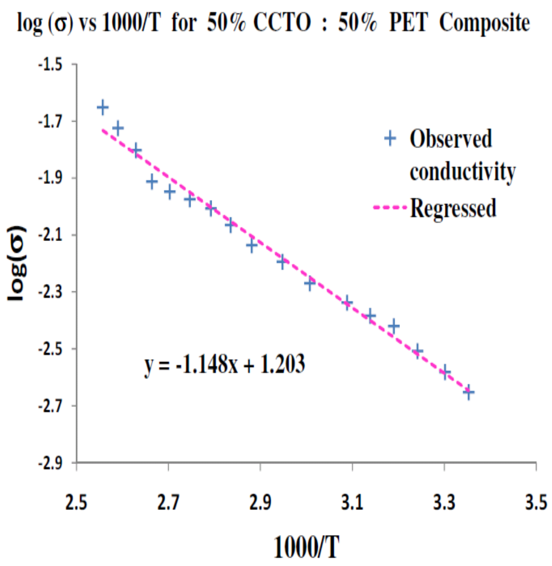



Figure 14. log (σ) vs 1000/T for 50% CCTO : 50% PET ceramic polymer composite, the straight line is the least square fit of the plot with respect to a line, and the slope is mentioned in the graph.

The activation energies of the composites were calculated from the plots first by finding a linear fit and then by extracting the values of activation energies from the respective slopes.

## V. CONCLUSIONS

One can observe from the experimental results that, CCTO with high dielectric constant was successfully prepared via conventional solid state reaction method. The dielectric constant increases with decrease in frequency. There is a reduction of dielectric constant by two orders of magnitude just by addition of 10% PET or PVC into the ceramic. Therefore it indicates 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 PET or PVC does not bring down the permittivity as drastically. This phenomenon in a way indirectly confirms the well accepted Inter layer barrier capacitance (ILBC) model for high dielectric constant in CCTO ceramics. The conductivity curves indicate that the charge carriers are predominantly oxygen vacancies since their activation energies lie in that range.

## ACKNOWLEDGMENTS

The authors are very much thankful to the authorities of National Physical Laboratory and Inter University Accelerator Centre, New Delhi (India) for providing necessary facilities



## REFERENCES

1. Xiong-Yan Zhao and Hong-Jie Liu, *Review of polymer materials with low dielectric constant,* Polymer International, Volume 59, Issue 5, pages 597–606, 2010
2. L. A. Ramajo, M.A. Ramírez, P.R. Bueno, M. M. Reboredo, M. S. Castro, *"Dielectric Behaviour of $CaCu_3Ti_4O_{12}$-Epoxy Composites"*, Materials Research, Vol 11, No. 1, 85-88, 2008.
3. Dias CJ, Das-Gupta DK, *"Inorganic ceramic/polymer ferroelectric composite electrets"*, IEEE Trans. Dielectr. Electr. Insul., 5(3): 706-734, 1996.
4. Bai Y, Cheng Z-Y, Bharti V, Xu HS, Zhang QM, *"High-dielectric constant ceramic-powder polymer composites*", Applied Physics Letter., 25 (76): 3804-3806, 2000.
5. J. Robertson, The European Physical Journal Applied Physics , 28 , (03) , , pp 265-291, 2004.
6. Kuo D-H, Chang C-C, Su T-Y, Wang W-K, Lin B-Y, *"Dielectric behaviour of multi-doped $BaTiO_3$ epoxy composites*", Journal European of Ceramic Society., 21(9): 1171-1177, 2001.
7. Bueno PR, Ramírez MA, Varela JA, Longo E, "*Dielectric spectroscopy analysis of $CaCu_3Ti_4O_{12}$ polycrystalline systems"*, Applied Physics Letter., 89(19):191117-3, 2006.
8. Lin Zhang and Z.-Y. Cheng, *Development of Polymer-Based 0–3 Composites with high dielectric constant.* J. Adv. Dielect. 01, 389 doi: 10.1142/s2010135x11000574, 2011.