Dielectric and Structural Properties of CCTO: PET Ceramic Polymer Composites with 0:3 Connectivity

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Abstract— A 0:3 composite of CCTO Ceramic and polyethylene terephthalate (PET) was prepared using conventional method. The samples of the composites were subjected to studies on dielectric constant, dielectric loss and X-ray diffraction. On addition of 10 percent of PET reduced the loss of CCTO from 10 to0 .0015 for the resulting composite. Mechanically the composite is soft and hence foldable, thereby a promising material for a variety of device application

Keywords— $CaCu_3Ti_4O_{12}$ dielectric constant,CCTO:PET,SEM,X-ray diffractogram

I. INTRODUCTION

$CaCu_3Ti_4O_{12}$ (CCTO) both in its crystalline and ceramic form has proved itself to be wonder material, due to its huge dielectric constant[1]. The source of its extra ordinary values of dielectric constant had remained debatable for long. However the accepted theory that exists as of now is the interlayer barrier capacitance (ILBC), where the domain boundaries and grain boundaries play a crucial role[2]. Even with a high dielectric constant CCTO could not replace conventional capacitor grade Barium Titanate ($BaTiO_3$) or Lead ZirconateTitanate (PZT), in device applications, because of its high loss compared to the latter materials. The work mentioned in this paper is mainly an attempt to make a device worthy composite material using CCTO ceramic and PET as the active and passive components respectively

II. EXPERIMENTAL

CCTO ceramic was prepared using conventional solid state reaction, the details of which has been mentioned earlier[3,4,5]. Unlike oxides of Lead, making of CCTO ceramic does not require an excess of volatile oxides to compensate for evaporation at high temperatures. A simple stoichiometric proportion of CaO, CuO and TiO_2 is all that is needed. The oxides and the polymer were procured from standard suppliers of research grade chemicals (Sigma Aldrich, USA). PET (ρ=2.45 g/cc) was weighed such that 10 % by volume of the composite contains the polymer, while 90% of the composite contains the ceramic. This was achieved by first dissolving PET in dichloromethane, and then adding CCTO powder to the solution mixing it thoroughly in an agate mortar and pestle till uniformly distributed. The paste thus formed (90% CCTO : 10% PET) was pressed between two parallel steel plates to form a sheet of the composite.It is worth noting that the consistency of the paste can be changed according to the amount of solvent added. This is an advantage during the process of device manufacturing, since complex forms can be injection molded using appropriate cavities.

The process of making the composite is repeated for higher percentages of PET viz. 20%,30%, up to 70% and corresponding CCTO percentages ie., 80%,70%,upto 30%. Beyond 70% PET in the composite does not yield any benefit in terms of dielectric constant or loss, therefore the properties of the higher percentages are not mentioned in the paper.

The density of the composite samples were elucidated using the Archimedes principle, i.e. by weighing the sample in air and water, this is done using a setup which is mainly a microbalance attached with a mechanism to hold the sample dipped in water while being weighed[6]. The X-ray diffractogram (XRD) of the sample was recorded using a diffractometer.The dielectric constants and loss were measured simultaneously at various temperatures and frequencies, on HP 4192A impedance analyser. Scanning electron micrographs (SEM) of the samples were also recorded.

Measuring dielectric constant of samples required metallic electrodes deposited on both the flat surfaces of the sample, this was carried out by vacuum deposition of silver using appropriate masks. In a similar way, to record SEM of the samples, it is required that the samples be coated with a thin film of gold or silver on the side of the sample exposed to electron beam. The coatings were performed using a sputtering set up, with Argon gas as the plasma source. A Denton sputtering system was used for this purpose. The thickness of the samples were maintained at 0.5mm and the electroded area had a diameter of 1cm.

III. RESULTS AND DISCUSSIONS.

The densities of the composite as well as CCTO ceramic was measured as mentioned above, and the values are tabulated in Table 1, and plotted in Figure 1. It can be seen that the curve shows a linear dependence,which can be interpreted as an absence of any interdiffusion of materials into each other viz. the ceramic and the polymer. It means that no compound formation take place and therefore it is ideally a 0:3 composite[7].

CCTO %	Density(PET Composite)g/cc
100	4.93
90	4.575
80	4.22
70	3.865
60	3.51
50	3.155
40	2.8
30	2.445

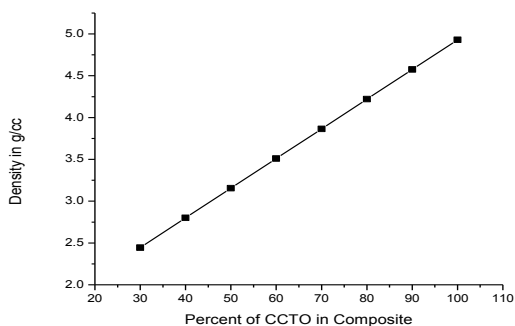Table1.Densities of the composite with CCTO percent.

Figure 1. Density of the composite as a function of percent of CCTO

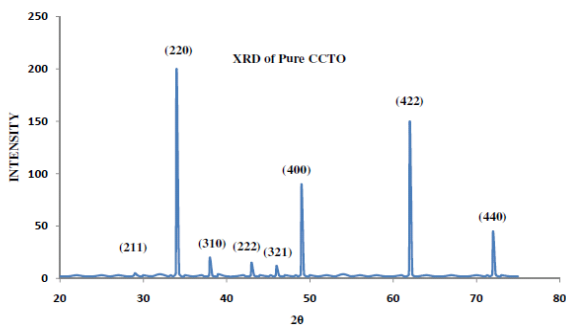The x-ray diffractogram of the samples are as shown in figures 2(a) to 2(h),

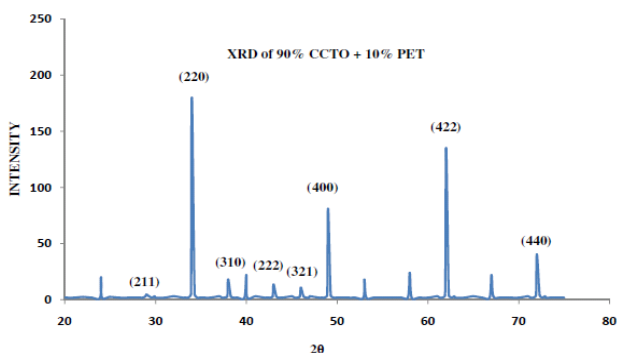Figure2(a):X-ray diffractogram of CCTO ceramic

Figure2(b) : X-ray diffractogram of 90% CCTO : 10% PET ceramic polymer composite
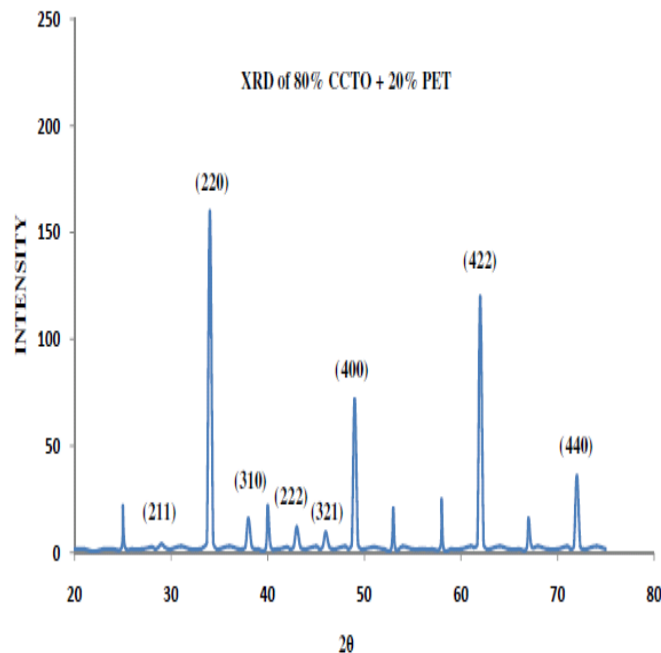
Figure 2(c) :X-ray diffractogram of 80% CCTO : 20% PET ceramic polymer composite
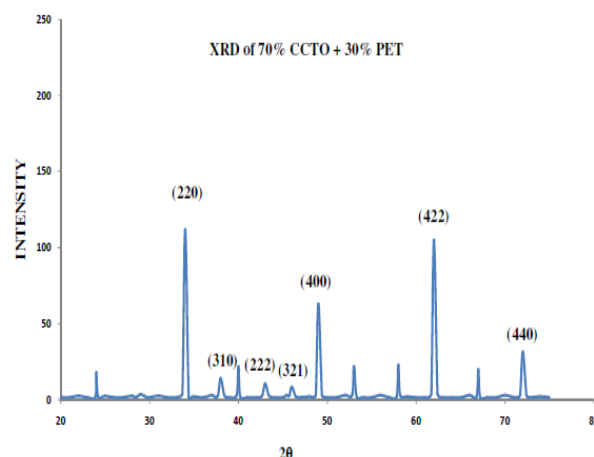
Figure 2(d) : X-ray diffractogram of 70% CCTO : 30% PET ceramic polymer composite
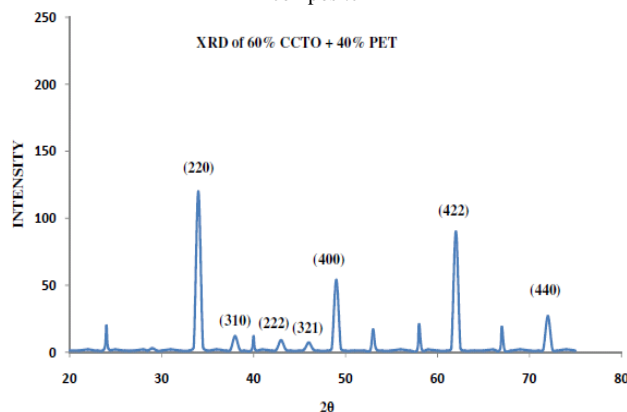
Figure 2(e) :X-ray diffractogram of 60% CCTO : 40% PET ceramic polymer composite
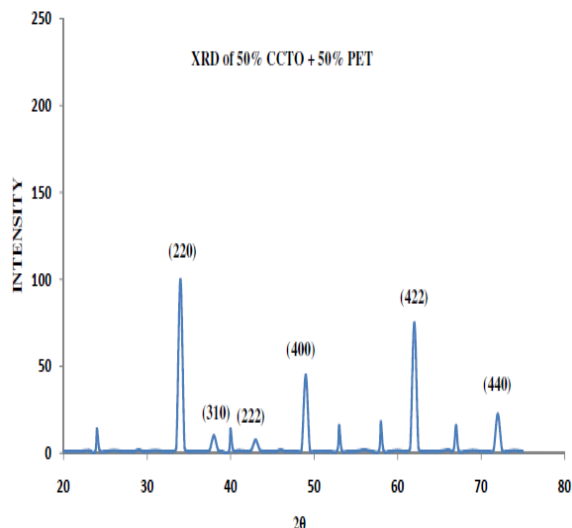
Figure 2(f) : X-ray diffractogram of 50% CCTO : 50% PET ceramic polymer composite
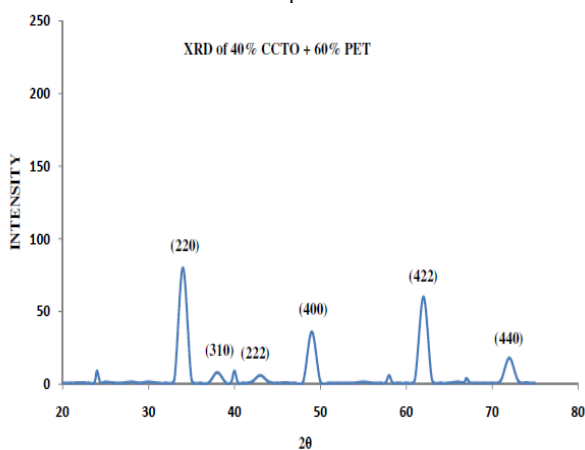

Figure 2(g) : X-ray diffractogram of 40% CCTO : 60% PET ceramic polymer composite
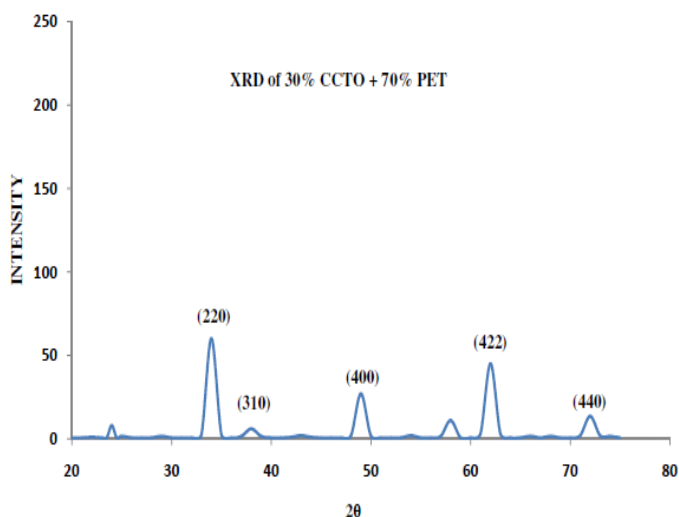

Figure 2(h) : X-ray diffractogram of 30% CCTO : 70% PET ceramic polymer composite

The x-ray diffractogram of the samples are as shown in figure 2(a) to 2(h),the peaks of CCTO are indexed by comparing it with *JCPDS File* No. 21-0140[8]. Since thepolymer does not exhibit any peaks due to lack of crystallinity, one can only get a rough estimate of the relative abundance of the polymer in

the composite by observing the diffractograms. One can easily notice the effect of added polymer in the ceramic composite. The more the polymer in the ceramic composite, less the sharpness of the CCTO peaks. This may be attributed to the strain induced by the polymer surrounding the ceramic particles leading to strain induced widening of the peaks of CCTO.The relative intensities of the peaks are also affected because of the background haze produced by the polymer as the x-ray beam passes through the bulk of the polymer.The diffractogram indicates that the material is indeed a 0:3 composite that is the active medium (CCTO) is suspended as particles in a sea of passive medium (PET), the particle of CCTO are not connected to each other, but separated from each other by the polymer. This kind of structure can drastically alter the mechanical properties of the active material. From a point of view of its mechanical properties, one can look upon the material as a polymer reinforced with ceramic. The synergy leads to properties not attainable by pristine ceramic or polymer taken alone. However the mechanical properties are not mentioned in the present work.

The dielectric constant of the ceramic and the polymer composites are plotted as a function of temperature at various applied frequencies in the figures 3(a) to 3(h) below. It is observable that an addition of polymer as low as 10% can bring down the dielectric constant by two orders of magnitude as compared to the pristine ceramic. This in a way indirectly supports the Inter layer barrier capacitance (ILBC) theory, which accounts for the high value of dielectric constant in CCTO[9,10,11]. This is because according to the theory the barrier layers are very thin but insulating, addition of the polymer widens the insulating barrier leading to an abrupt drop in dielectric constant. The dielectric loss curves (figure 4(a)-4(h)) confirms this argument because as the insulating barrier widens as a result of polymer addition.
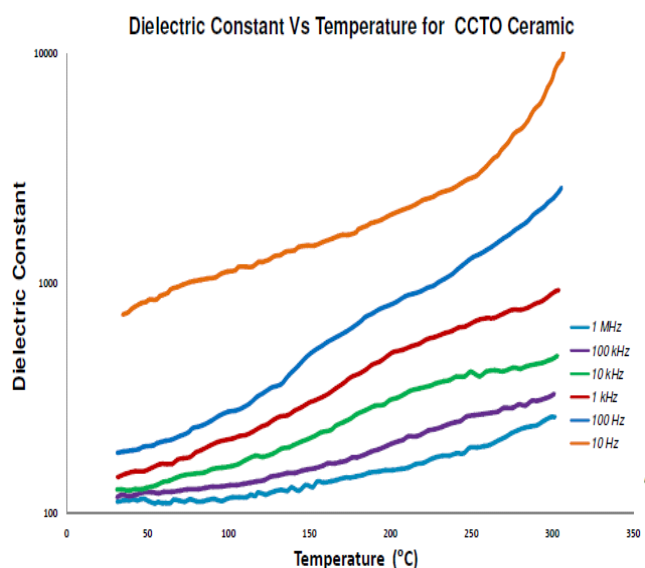

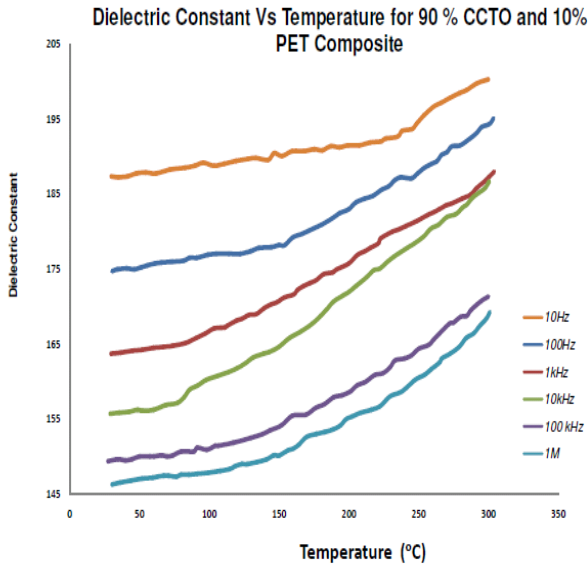Figure 3(a): Dielectric constant of CCTO Ceramic

Figure3(b): Dielectric constant of 90% CCTO : 10% PET Ceramic Polymer composite
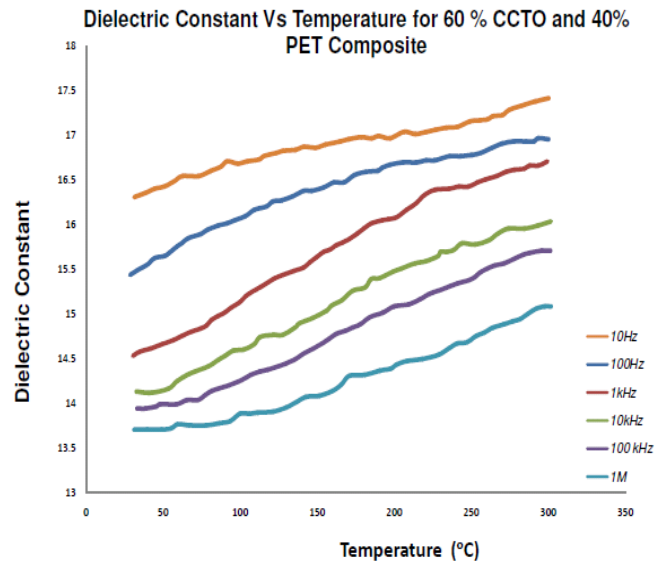

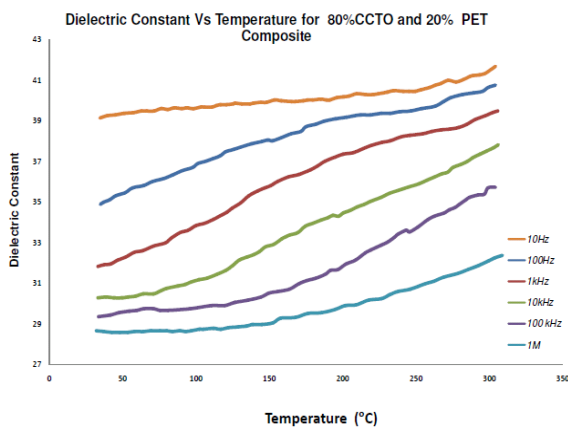Figure3(e): Dielectric constant of 60% CCTO : 40% PET Ceramic Polymer composite

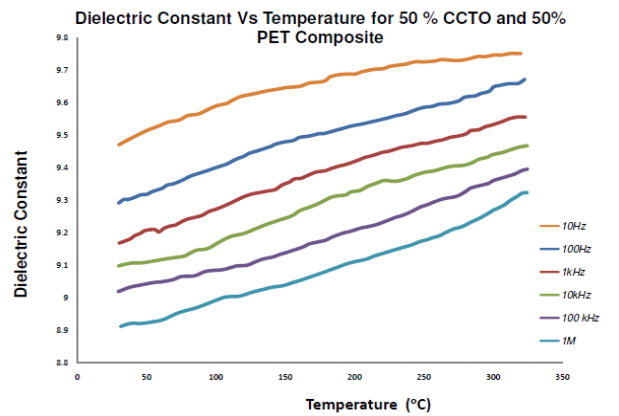Figure3(c): Dielectric constant of 80% CCTO : 20%PETCeramicPolymercomposite

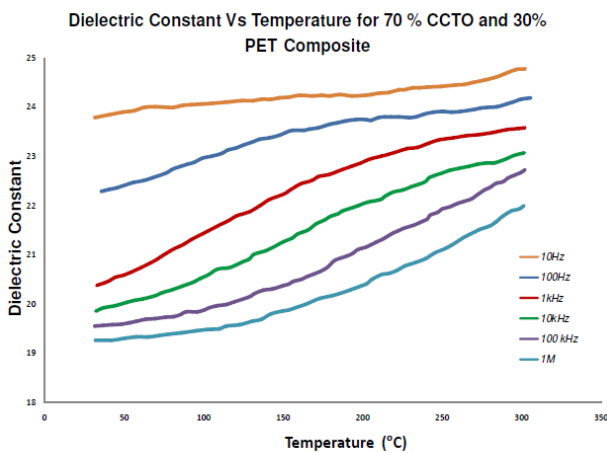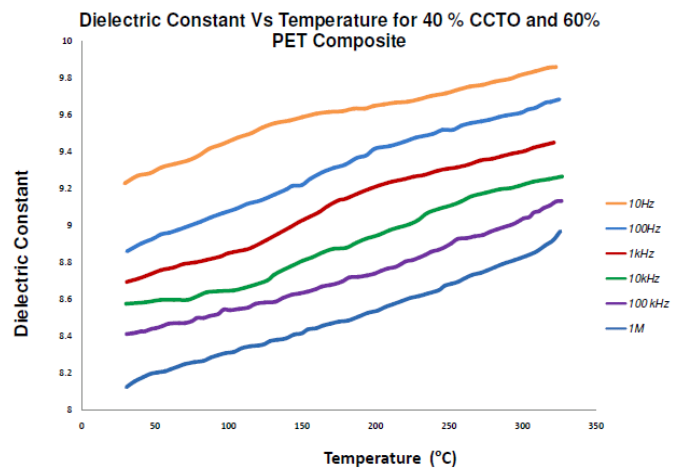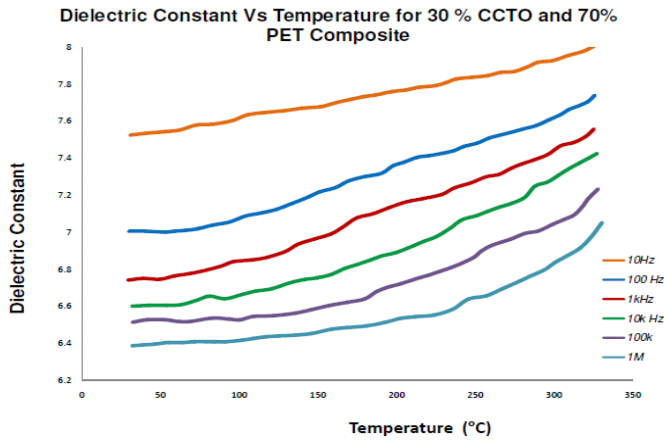Figure 3(f): Dielectric constant of 50% CCTO : 50% PET Ceramic Polymer composite

Figure 3(d): Dielectric constant of 70% CCTO : 30% PET Ceramic Polymer composite

Figure 3(g): Dielectric constant of 40% CCTO : 60% PET Ceramic Polymer composite

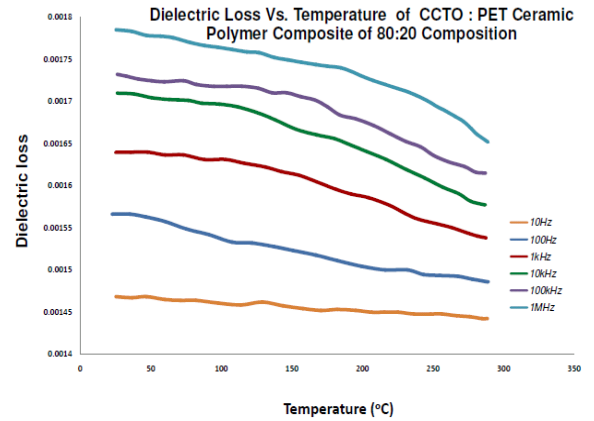Figure 3(h): Dielectric constant of 30% CCTO : 70% PETCeramic Polymer composite

Figure4(c): Dielectric loss of 80% CCTO : 20% PET Ceramic Polymer composite
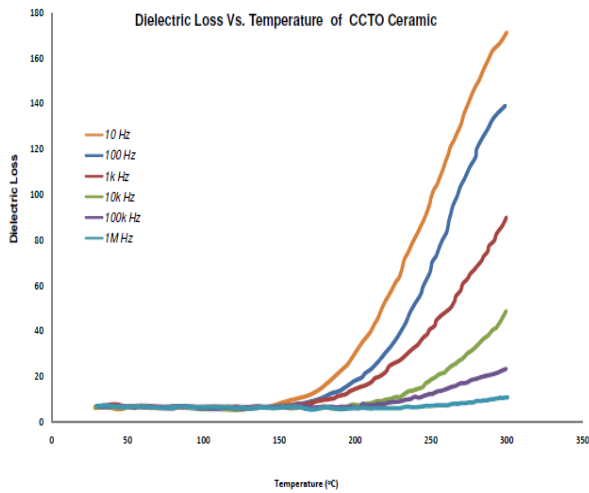

Figure 4(a): Dielectric loss of CCTO Ceramic

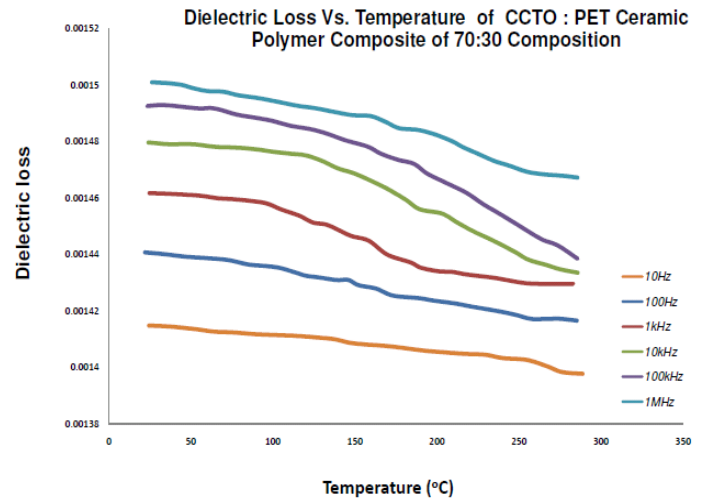With temperature at various frequencies

Figure 4(d): Dielectric loss of 70% CCTO : 30% PET Ceramic Polymer composite
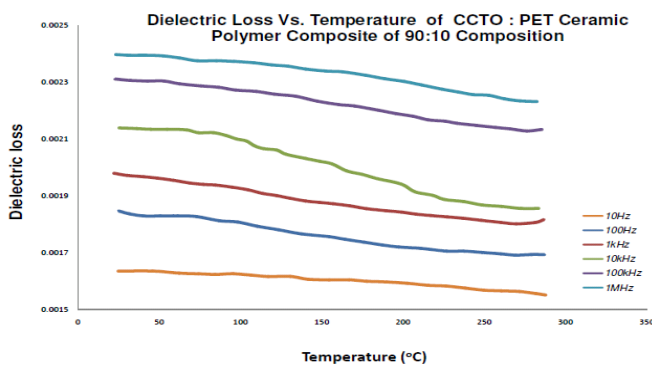

Figure 4(b): Dielectric loss of 90% CCTO : 10% PET Ceramic Polymer composite
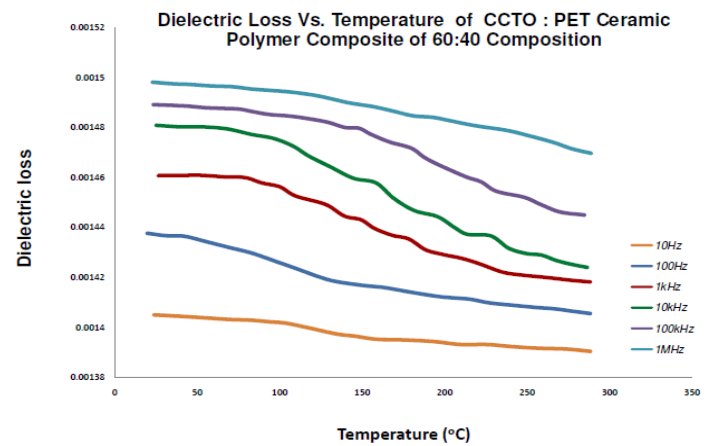

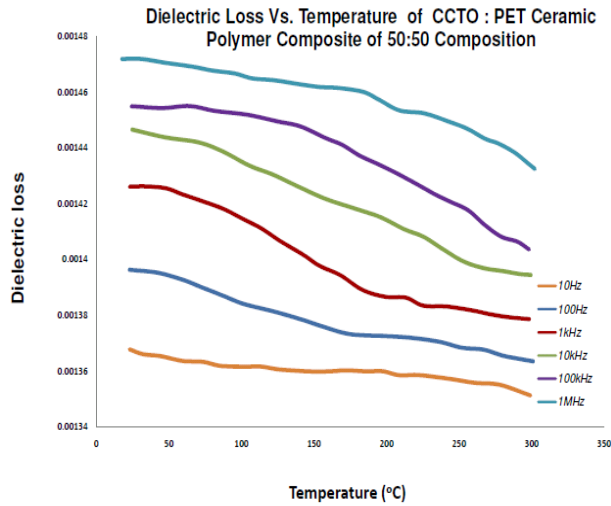Figure 4(e): Dielectric loss of 60% CCTO : 40% PET Ceramic Polymer composite

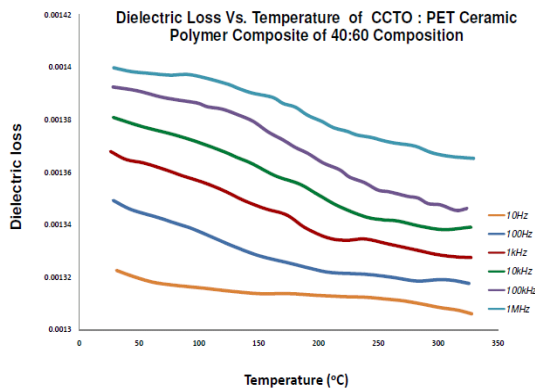Figure 4(f): Dielectric loss of 50% CCTO : 50% PET Ceramic Polymer composite
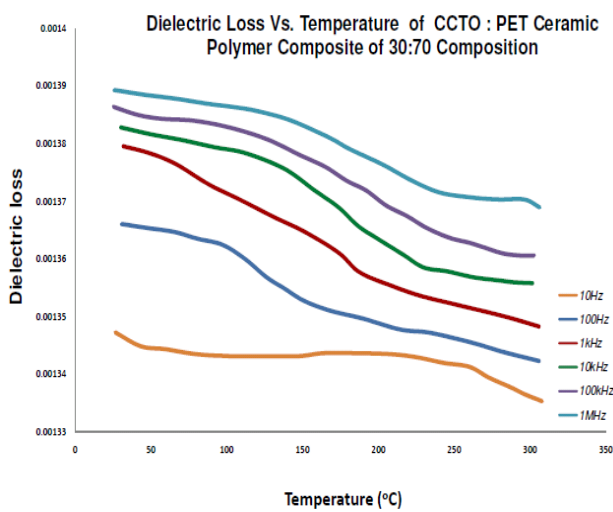

Figure 5(a): SEM photograph of pure PET sample

Figure 4(g): Dielectric loss of 40% CCTO : 60% PET Ceramic Polymer composite

Figure 5(b): SEM Photograph of 30% CCTO and 70%PET

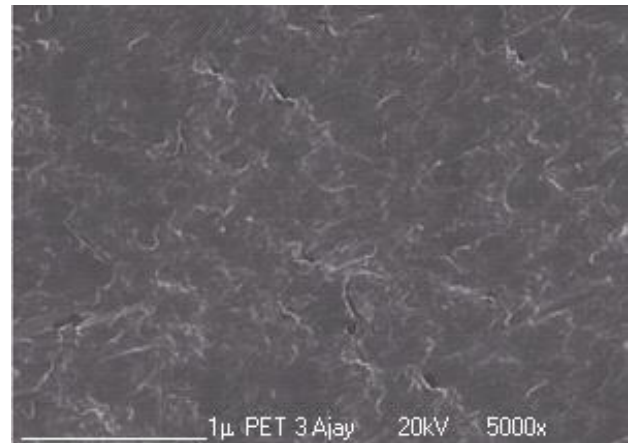Figure4(h): Dielectric loss of 30% CCTO : 70% PET Ceramic Polymer composite

Figure 5(c): SEM Photograph of 50% CCTO and 50% PET
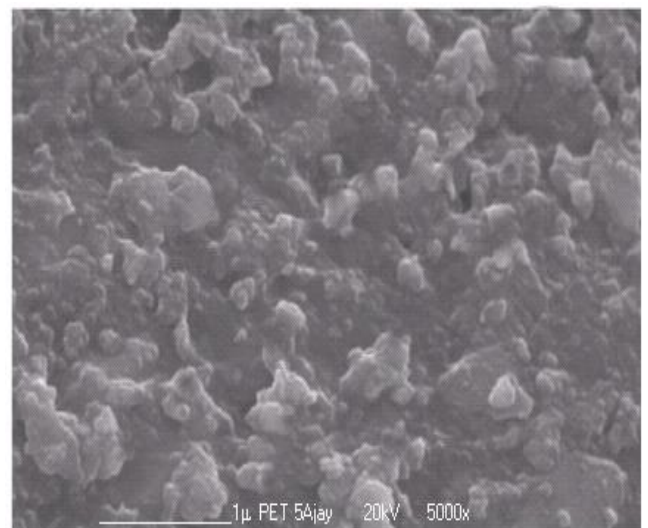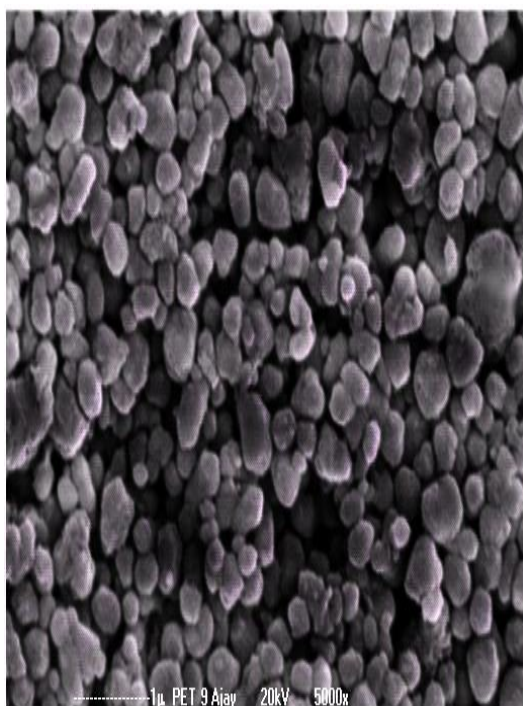
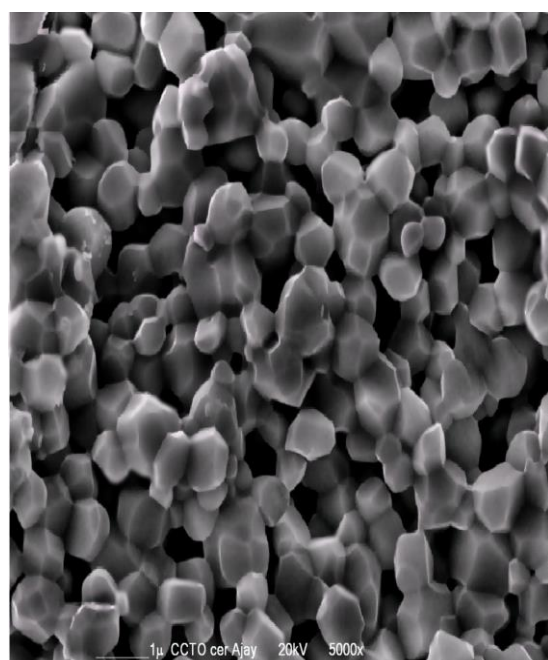Figure 5(d): SEM Photograph of 90% CCTO and 10%PET

Figure 5(e): SEM Photograph of CCTO ceramic

Figure 5(a) to 5(e) shows the SEM micrographs of the various samples. One can see that this resembles other polymer composites of 0:3 connectivity especially with PVDF (poly vinylidine fluoride) and PMMA[12]. One can very well observe the relative abundance and the distribution of the polymer in the composite bulk.

IV. CONCLUSION

The above work gives a peek into the behavior of the polymer PET as a passive matrix in the composites as well as confirms the ILBC theory suggesting the reason for huge dielectric constant of CCTO ceramic. It can be seen that further work in this area can be carried out, e.g. the effect of coupling agents (inter phase) between the ceramic and polymer components.

ACKNOWLEDGMENT

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