Dielectric behavior of CaCu$_3$Ti$_4$O$_{12}$: Poly Vinyl Chloride ceramic polymer composites at different temperature and frequencies

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**Abstract**

In this study, the efforts have been made to obtain relatively high dielectric constant polymer-ceramic composite by incorporating the giant dielectric constant material, calcium copper titanate (CCTO) in a PVC polymer matrix. We have prepared composites of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramic and Poly Vinyl Chloride (PVC) polymer in various ratios (by volume) in addition to pure CCTO. For this, CCTO was prepared by the conventional oxide route (solid-state reaction method). The structural, the microstructural and the dielectric properties of the composites were studied using X-ray diffraction, Scanning Electron Microscope, and impedance analyzer respectively. The study of dielectric constant and dielectric loss of the pure CCTO and the composites reveal that there is good range of dielectric constants and dielectric losses for the studied composites. The pure sample of CCTO exhibits giant dielectric constant at low frequency within the studied temperature range. As frequency increases, dielectric constant drastically decreases and approaching a constant value at 1 MHz. Above the intermediate temperature, the dielectric constant and dielectric loss for pure CCTO is more frequency dependent than its composites.

**Introduction**

Material/composite with high dielectric constants has interest for their technological aspects. The physical aspects of 0–3 dielectric composites have been recently studied by Zhang et al. [1] and references therein. Calcium copper titanate an inorganic compound of chemical formula CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramics, is high dielectric constant material extensively studied by various researchers and developers [2, 3] and the dielectric properties of CCTO-silicone resin composites in [4]. The mechanical properties of nano-crystalline CCTO power has been studied in [5] and reference therein, however some flair properties was discussed long back by Gleiter [6]. Recently, the dielectric characteristics of iron oxide-deposited nanosized calcium copper titanate hybrid films in an external magnetic field is discussed by Chi et al. [7] and dielectric performance of amorphous calcium copper titanate was well discussed in [8] and [9]. Although the studies gained momentum in the initial phases of its discovery, it could not bring in appreciable gains in the figures of merit, viz. dielectric constant and dielectric loss, at a later stage. There was a deluge of research papers indicating the source of its high dielectric permittivity. Till date the scientific community could not come to terms and decide whether the source of this high permittivity is due to extrinsic or intrinsic factors [10]. The work describes in this paper does not touch the subject regarding the source of the massive permittivity but the authors have tried to exploit its figures of merit so that a high dielectric material can be customized. When Poly Vinyl Chloride (PVC) is mixed with ceramic CCTO, a composite with high dielectric constant and good mechanical flexibility is formed. Similar work has been done by numerous researchers with similar aims in mind, but no one has tried with PVC as a matrix. In this article we had aimed at reducing dielectric loss at the cost of reduced permittivity, so that the composite, as a whole, turns out to be device worthy. PVC is cheaper compared to other polymers; it is easily available, ubiquitous, and compatible with most electronic materials.

**Experimental**

The ceramic powder of CCTO required to make the composite was prepared by a solid state reaction, wherein, stoichiometric proportions of CuO, CaO and TiO$_2$ were mixed thoroughly in a ball mill with ZrO$_2$ balls and rubber lined jar, acetone was used as dispersant. The ball milled powder was calcined at 1100 °C for about 10 hours so that CCTO ceramic is formed from the reactant oxide mixture. The so formed CCTO lumps are again ball milled for 10 hours. The powder
thus obtained was sieved in 5 μm mesh.

Composites of CCTO and PVC were prepared by mixing pre-weighed powders of PVC (average molecular weight ~22,000 g/mol) and CCTO ceramic. The mixing was carried out in a ball mill for almost 24 hours. The weighing was done taking the density of the materials into account so that, a 90:10 composite would mean it contains 90% of ceramic by volume and the rest of the composite contains the polymer. The ball milling process yields a powder of desired composition, it is then wetted with Tetrahydrofuran, so that PVC which dissolves in this liquid, turns the powder to a paste which can be pressed between metallic plates to form sheets or blow molded to form complex shapes. The composite so formed is said to be 0–3 connected, that is the ceramic (active phase of the composite) is connected in 0 dimensions while PVC (passive phase) is connected in all three dimensions. In other words one may say that the composite looks like ceramic particle dispersed in a matrix of PVC like plum in pudding. The metal oxides and PVC were purchased from Sigma – Aldrich, USA, to ensure purity and reproducibility. The process mentioned

![XRD patterns](attachment:image.png)

Fig. 1. XRD patterns pure CCTO (upper left panel), 90% CCTO (upper right panel), 70% CCTO (lower left panel) and 50% CCTO (lower right panel) with composites.
above for making the composite was repeated for various percentages of PVC viz. 50% and 30%, and corresponding CCTO ceramic percentages as well, i.e., 50% and 70%.

The X-ray measurements were carried out using a powder diffractometer (Rigaku, Cu Kα line). The diffractogram is actually a diffraction pattern as a result of the atomic planes in a crystal. The atomic planes act like a diffraction grating to the incident x-ray beam on the crystal. The peaks that are recorded in the diffractogram are due to Bragg’s reflection at various angles. The crystal structure of a ceramic (polycrystalline material) is elucidated from the positions of the peak by a numerical simulation, or by comparison with ASTM data of similar well studied material.

Dielectric constant and dielectric loss is measured using an impedance analyser (HP4192A). The impedance analyser is essentially a bridge (Anderson) circuit. The sample is effectively a parallel plate capacitor, whose capacitance and loss is measured using the impedance analyser. The dielectric constant and loss is calculated out from the capacitance by using the appropriate relation along with its geometry. Dielectric loss is a measure of loss of energy that goes into heating a dielectric in varying the electric field. For a good capacitor material, the dielectric loss should approach zero, for whatever the electric field applied.

**Results and discussion**

Fig. 1 shows the X-ray diffraction (XRD) effect of the CCTO-PVC composites with pure CCTO (upper left panel), 90% CCTO (upper right panel), 70% CCTO (lower left panel) and 50% CCTO (lower right panel) fractions. The X-ray diffraction result shows that the intensities of the diffraction peaks reduce up to 50% for the 50% CCTO composite. This figure suggests that the mixing of composite reduces the intensity of the X-rays counted detected at the counter. It can be seen from the diffractograms that as the percentage of PVC progressively increases the sharpness of the peaks and its relative intensity keeps on decreasing. This is in accordance to the general principle that a long range order in the material gives rise to sharp peaks. As the crystallite size of the material decreases it gives rise to broader peaks. This principle is used in calculating the average size of the particles in a given sample. From the figure, we can also see that when PVC ratio increases in the composite a background haze is also recorded along with the peaks, implying that the polymer is amorphous and therefore no characteristic lines are observed. The morphology of the CCTO and its composites measured by scanning electron microscopy (SEM) is shown in Fig. 2.

For the pure CCTO and composites, the variations of dielectric constant with the temperature for frequency ranges (10 Hz, 100 Hz, 1 KHz, 10 KHz, 100 KHz and 1 MHz) are shown in Fig. 3. At room temperature and at low frequency, the dielectric constant is high ~700 for pure CCTO (upper left panel), also the dielectric constant is more temperature dependent at low frequencies. At 10 Hz, the value of dielectric constant increases sharply (up to 10,000) as we move towards the higher temperature region, while for higher frequencies the value of dielectric constant increases only up to 1000. For homogeneous material the dielectric constant is related to the permittivity and permittivity is directly related to the electric susceptibility, which measure of how easily a dielectric polarizes in response to the electric field. Thus at low frequencies, pure CCTO resist more an electric field, while at higher frequencies it polarizes easily. The right upper panel of the figure depicts the variation of dielectric constant with temperature for different frequencies for the 90:10 CCTO and PVC. From this panel we can see that the value of dielectric constant
changes drastically from the pure CCTO as we add small amount of polymer in pure CCTO. It is also clear from this panel that dielectric constant is independent for a temperature range and then a small enhancement and again independent over a range of temperature. Such behavior is observed at higher and lower frequencies, while at intermediate frequencies such effect is week. The variation of dielectric constant with temperature for the composites in the ratio of 70:30 is given in the lower left panel of the figure. The value of dielectric constant is quite low and remains constant for the lower and higher frequencies but it increases linearly for the intermediate frequencies. For the composite 50% CCTO (right lower panel), the variation is dielectric constant with temperature shows nearly same behavior for all
the frequencies. It is constant and independent over a temperature range and then sudden enhancement and then constant again.

Fig. 4 depicts the dielectric loss with temperature at various frequencies for pure CCTO (upper left panel), 90% CCTO (upper right panel), 70% CCTO (lower left panel) and 50% CCTO (lower right panel) with composites. In the upper left panel of the figure, loss behavior of the ceramic is along expected lines, i.e. the loss keeps on increasing with temperature which is attributed to the increase in conductivity due to release of free charge carriers in the bulk of the material with the rising temperature. But in the other cases we can find that the behavior reverses, this can be seen as a phenomenon dictated by the polymer matrix. It is worth noting that the difference is negligible, yet from a device point of view one needs to take this into account. The behavior can be explained only by a model which describes the conductivity of PVC with temperature [11]. One may also attribute this behavior to some phase transition lurking within the studied temperature range, but unfortunately a calorimetric study is not available. A DSC (differential scanning thermo gram) of PVC encompassing the temperature range is desirable for a complete and comprehensive explanation [12].
It is evident from the above plots that PVC, the matrix has a substantial effect on the value of dielectric constant as well as the loss. The decrease in dielectric constant of the composite can be justified by the fact that PVC with negligible permittivity masks the dielectric permittivity exhibited by the ceramic CCTO [13]. Here the law of mixtures cannot be used because addition of PVC not only reduces the permittivity of the composite as a whole due to reduced volume ratio of the ceramic in the composite, but it also modifies the extrinsic factors which many researchers attribute towards the high permittivity of CCTO [14]. First and foremost the range of continuity of the ceramic which many researchers attribute towards the high permittivity of the composite can give rise to a slew of new devices which are diverse applications and finer material with unforeseen tolerances.

Therefore dependent at higher temperature in addition to very high values. For the composites the values of both the constant are appreciably low (dielectric constant ~10 and dielectric loss ~0.00136 for 50:50:CCTO:PVC) compared to the pure CCTO (dielectric constant ~few hundreds and dielectric loss ~few tens). Thus material mentioned above and studies undergone herein are found to be device worthy because of its low dielectric loss and relatively high dielectric constant compared to material used for devices in the present day scenario. PVC is a well-studied polymer and easily available the developed polymer composite can give rise to a slew of new devices which are flexible and machanable. These composites may be useful in capacitors and microelectronic devices. More studies in this line can bring about diverse applications and finer material with unforeseen tolerances.

Conclusion

For the pure CCTO, the dielectric constant and loss are more frequency dependent at higher temperature in addition to very high values. For the composites the values of both the constant are appreciably low (dielectric constant ~10 and dielectric loss ~0.00136 for 50:50:CCTO:PVC) compared to the pure CCTO (dielectric constant ~few hundreds and dielectric loss ~few tens). Thus material mentioned above and studies undergone herein are found to be device worthy because of its low dielectric loss and relatively high dielectric constant compared to material used for devices in the present day scenario. PVC is a well-studied polymer and easily available the developed polymer composite can give rise to a slew of new devices which are flexible and machanable. These composites may be useful in capacitors and microelectronic devices. More studies in this line can bring about diverse applications and finer material with unforeseen tolerances.

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