

Chapter-2

Review of Literature

Around the globe material scientists are involved in research and development of new multifunctional ceramic materials for device applications such as multilayer capacitors, optical shutters, modulators, computer memory, display, microwave communication devices, piezoelectric detectors, ferroelectric random access memory (FRAM) etc. In the field of the device applications, ferroelectric materials have occupied a significant position in material research because of their huge applications in various electronic, optoelectronic, computer memory and communication devices. Ferroelectric materials have been studied in the form of single crystal and polycrystalline ceramic oxides. For the study of ferroelectric properties, homogeneous single crystal is usually preferred due to minimum effect of surfaces and imperfections. But single crystals require particular care in their preparation, cutting and polishing to make them suitable for device applications. So ceramics can be considered as substitutes for single crystals because of the following reasons; (i) It is easier to fabricate/synthesize ceramics in to different shapes and sizes than their single crystal counterparts. (ii) There are additional structural/microstructural feature (i.e. grain shape, size and porosity, etc). These microstructural features can be exploited in the design of the electro-ceramic materials for particular device requirements. The presence of grain boundaries gives rise to additional effect and plays an important role for various physical properties, which is not present in single crystals. (iii) Ceramic oxides also possess good thermal, chemical and mechanical stability⁴¹⁻⁴³.

Barium titanate (BaTiO_3) is the first ferroelectric ceramic belonging to perovskite structure, discovered in 1945 and is used in capacitor application and piezoelectric transducer devices applications. After the discovery of ferroelectricity in BaTiO_3 , a large number of ferroelectric oxides of different structural family have been discovered and studied to find out their suitability for various device applications. After the widespread use of BaTiO_3 many other ferroelectric ceramics including lead titanate (PbTiO_3), lead zirconate titanate (PZT), lead lanthanum zirconate titanate

(PLZT), and relaxor ferroelectrics like lead magnesium niobate (PMN) have been developed and utilized for a variety of applications.

2.1 Ferroelectrics and Related Materials:

There are large numbers of crystals existing in nature. Based on the crystal symmetry they all can be grouped together into 230 space groups. Again these 230 space groups can be further divided into 32 point groups. Out of these 32 point groups, 11 are centrosymmetric (i.e., the centre of the positive charge coincides with the centre of the negative charge) and 21 are noncentrosymmetric (i.e. the centre of the positive charge and the center of the negative charge does not coincide). Out of 21 non centrosymmetric point group, except one point group all are piezoelectric. 10 out of the 20 point groups are called pyroelectric. They are also called polar crystals as they show the property of spontaneous polarization i.e. they exhibit electric dipole moment even in the absence of external electric field. Ferroelectric is a sub group of pyroelectric which is also a subgroup of piezoelectric.

Crystals are said to be ferroelectric if the magnitude and direction of spontaneous polarization can be reversed by application of an external electric field. The reversal of spontaneous polarization was first observed in Rochelle salt by Valasek in 1920⁴⁴. The value of the spontaneous polarization depends upon the temperature. The variation of the spontaneous polarization with temperature for a ferroelectric crystal is shown in figure 2.1.

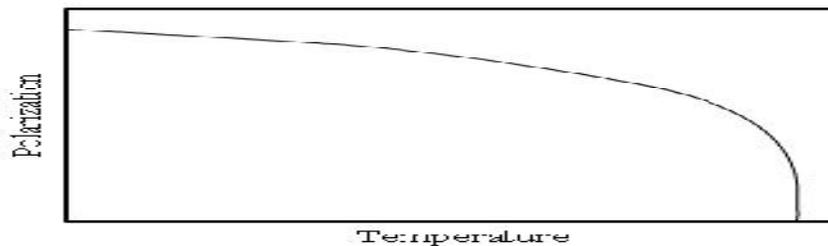


Fig- 2.1: Temperature dependence of the spontaneous polarization

From the figure, it is observed that the spontaneous polarization decreases with increase in temperature. At certain temperature the polarization disappears discontinuously or sometimes continuously, this is known as Curie point (T_c). The

crystal does not exhibit ferroelectricity above the Curie temperature and temperature below Curie point it is ferroelectric. At T_c there is a transition from ferroelectric state to paraelectric state. The room temperature dielectric constant of most of the ferroelectric materials are high and is maximum at T_c . Above T_c , the temperature dependent of the dielectric constant obeys Curie Weiss law $\epsilon = \epsilon_0 + C / (T - T_c)$, where ϵ is the permittivity of the material, ϵ_0 is the permittivity in vacuum, C is the Curie constant, T is the working temperature, T_c is the paraelectric Curie point or temperature at which the spontaneous polarization is zero.

In ferroelectric crystals there are regions with uniform polarization called ferroelectric domains where all the electric dipoles are aligned in the same direction. The most important characteristics of ferroelectric materials are the non linear relationship between the polarization and the field giving rise to a hysteresis as shown in the figure 2.2. An increase in the electric field strength gives rise to a rapid increase in the polarization and above certain applied field, the polarization saturate known as saturate polarization (P_s). When the external field is removed some of the domains remain aligned in the positive direction and the polarization doesn't fall to zero even if the applied field is zero. This is known as Remnant Polarization (P_r). The external field needed to reduce the polarization to zero is called coercive field strength (E_c).

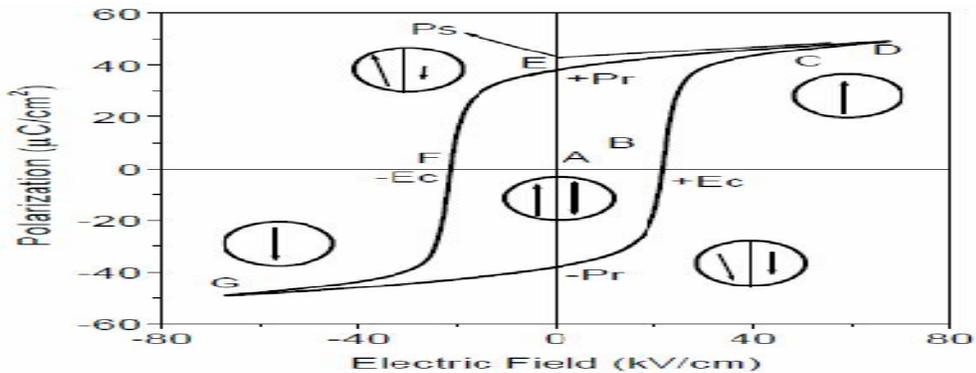


Figure-2.2: The Hysteresis Loop.

In polycrystalline materials (ceramics), true spontaneous polarization equal to that of a single crystal can never be reached and here it is more correct to speak of saturated rather than of spontaneous polarization. Generally, an ideal hysteresis loop is symmetrical. In some materials the coercive field, spontaneous and remnant polarizations and the shape of the loop may be affected by a number of factors including the thickness, the presence of charged defects, mechanical stresses, preparation conditions and pinning centres. Polarization-electric field (P-E) hysteresis loop is also a function of temperature and usually the area of the loop shrinks with the increase in temperature until a phase transition takes place. At this point no P-E loop is observed and this temperature is called Curie temperature T_c .

2.2 Phase Transition:

When the crystal structure changes with temperature in dielectric materials, then the materials undergo a phase transition. All the phase transitions in the crystals are due to change in the forces of interaction between the atoms in the crystals. The phase change results in various new properties of the crystals. The phase transition that changes the spontaneous polarization is called ferroelectric phase transitions. Phase transition can be classified into (i) First order phase transition (ii) Second order phase transition. In case of first order phase transition, the order parameter (in case of ferroelectric the order parameter is polarization) change discontinuously at transition point. If these parameters change continuously then the transition is called second order⁶.

The most important group of ferroelectric ceramic is the family of oxygen octahedral which can be further classified into four types. They are

- (1) Perovskite type
- (2) Tungsten-Bronze type
- (3) Spinel structure (Layered structure)
- (4) Pyrochlore type

Among them perovskite ferroelectric ceramics oxides is the most studied one because of their wide variety of technological applications. The perovskite structure

needs some explanation as the material under investigation belongs to this group. The simple perovskite structure has a general formula ABO_3 , where A is a large mono or divalent cation, B is a small tetra to pentavalent cation. It is cubic with A atoms at the cubic corner, B atoms at the body center and oxygen atoms at the face center (fig.2.3).

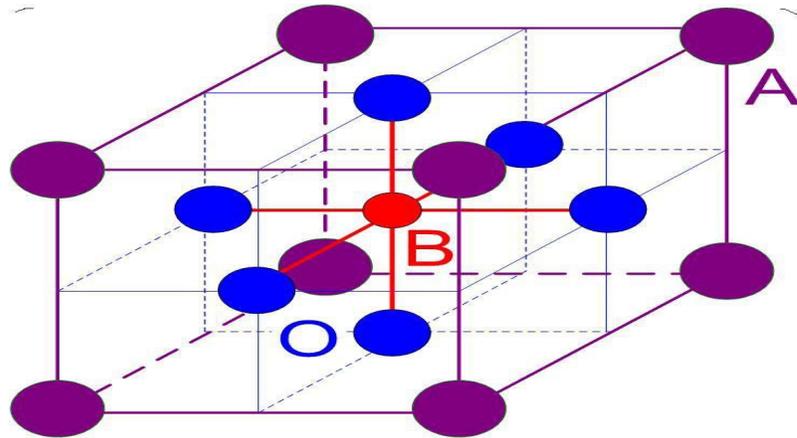


Fig-2.3: ABO_3 Perovskite Structure

2.3 CCTO and Related Material:

A great challenge in microelectronics is to decrease the size of passive components in general and capacitors in particular. For these reasons, there has been a considerable interest in the study of the giant dielectric permittivity of the cubic ABO_3 perovskite type $CaCu_3Ti_4O_{12}$ (CCTO) in the last decade. This material exhibits an extraordinarily high dielectric constant at room temperature of about 10^4 to 10^5 and good temperature stability in a wide temperature range from 100 to 600K^{15,17}. Due to high dielectric constant, it is widely utilized to manufacture electronic components such as multilayer capacitor, electronic devices in automobiles and aircrafts. They can also be applied to important devices such as DRAM (Dynamic Random Access Memory), microwave devices⁴⁵⁻⁴⁷. Many other materials also have a large dielectric

constant, e.g., $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (BCTO), $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (YCTO) and $\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (LCTO). All these large dielectric constant materials have similar dielectric behavior, i.e., they all exhibit a Debye-like relaxation and their dielectric constants are nearly independent of frequency and temperature well below the relaxation frequency. Among these, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has high dielectric constant, probably, due to internal barrier layer capacitance effect. Usually large dielectric constants are also found in ferroelectric materials e.g. BaTiO_3 and are related to atomic displacements within a noncentrosymmetrical structure. However, these perovskite materials exhibit high dependence on the temperature and the existence of the transition temperature is generally a problem for applications. The dielectric property of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ can be tailored by modifying its structure using suitable dopants.

2.4 Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO):

There are many methods such as conventional solid state reaction method, wet chemistry method, polymerized complex method, microwave heating method, sol-gel method, precursor solution method, co-precipitation method and molten salt synthesis method etc. for synthesizing $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Each method has own advantages and disadvantages. Polymerized Complex (PC) method is a chemical solution process, which has received considerable attention due to its relatively simplicity and usefulness for obtaining a homogeneous and fine powder precursor. Molten Salt Synthesis (MSS) method is a low temperature synthesis technique (750°C). It has been used to synthesize ceramic powders, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, LaAlO_3 and MgAl_2O_4 . Co-precipitation processes involve repeated washing in order to eliminate the anions coming from the precursor salts used, making the process complicated and very time consuming. Solution combustion technique is a very useful technique widely used for the synthesis of phase pure single as well as complex oxide material. It is based on the redox reaction between the oxidant and fuel present in the precursor solution. Sol-gel process use metal alkoxides as the starting materials, which are very expensive and extremely sensitive to the environmental conditions such as moisture, light and heat. Moisture sensitivity makes it necessary to conduct the experiment in dry boxes or clean rooms and also this method needs long heat-treatment times.

Solid state reaction method or mixed oxide process is a mechanical method, which is successful for a large scale production of bulk ceramic powders at its low cost and easy adaptability. Researcher and Scientists around the globe are working for the development of high purity phase pure $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with improved powder morphology, which will provide enhanced dielectric constant with low loss. Several powder processing technique have been tried among them conventional solid state reaction method seems to be promising one.

Liu, J. et al.⁴⁸ have synthesized fine crystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder using wet-chemistry method at relatively low temperatures and a shorter reaction time. The pure-phase sample was obtained at 800 °C for 0.5 h and the grain size of a pellet sample sintered at 1030 °C for 4 hr has a homogeneous distribution in the range of 0.4–1.5 μm . This method start with a homogeneous liquid solution of cation ingredients mixed in stoichiometric ratio at the atomic scale. Therefore, pure samples at the nanometer scale could theoretically be obtained at lower temperature and a shorter reaction time than that afforded by solid-state reactions. In this method, the metal oxides were formed in the first heat-treatment step and CCTO was produced by a subsequent solid-state reaction.

Mohamed, J. J. et al.⁴⁹ have synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by the solid state technique. The sample was calcined at 900 °C/12 hrs and sintered at 1050°C/24 hrs. Increasing sintering temperature was found to enhance the density and secondary phase formation of Cu_2O . A clear grain boundary and dense microstructure were observed in the sintered samples. The results showed that the sample sintered at 1040°C/10 hrs yielded a uniform grain size with the highest ϵ_r (33, 210).

Hutagalung, S. D. et al.⁵⁰ prepared CCTO by modified mechanical alloying technique, which is a combination of a ball milling and solid state reaction processes. The starting materials of $\text{Ca}(\text{OH})_2$, CuO and TiO_2 powder were weighed according to the stoichiometric ratio, mixed together and follow by fast ball milling in sealed alumina vial under ambient condition for 5 hours. The milled powders were subjected to calcination process at 600, 700, 800 and 900 °C in air for 12 hours, respectively. The yellow-brown calcined powders were then pressed into pellet disc shape using a stainless steel die set. Average size of the samples is 6 mm in diameter and 1 mm in

thickness. The prepared pellets were sintered in air at 1050 °C and soaking time of 24 hours. Phase analysis was conducted on the both calcined powders and sintered pellets by using XRD analysis. The XRD pattern results, showed, that a single phase CCTO was successfully formed in the samples that were calcined at 700-900 °C. The crystalline structure was improved after sintering at 1050 °C for 24 hours. Dielectric constant value of CCTO sintered pellets was obtained up to 11,903.

Thomas,P.et al.⁵¹ have synthesized and sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) by microwave processing at 2.45 GHz, 1.1 kW. The optimum calcination temperature using microwave heating was determined to be 950°C for 20 min to obtain cubic CCTO powders. The microwave processed powders were sintered to 94% density at 1000°C/60 min. The microstructural studies carried out on these ceramics revealed the grain size to be in the range 1–7 μm . The dielectric constants for the microwave sintered (1000°C/60 min) ceramics were found to vary from 11000–7700 in the 100 Hz–100 kHz frequency range. Interestingly the dielectric loss had lower values than those sintered by conventional sintering routes and decreases with increase in frequency.

Liu,L.et al.⁵² have synthesized the giant dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by sol-gel method by using nitrate and alkoxide precursor. The electrical properties of CCTO ceramics, showing an enormously large dielectric constant $\epsilon \sim 60,000$ (100Hz at room temperature), were investigated in the temperature range from 298 to 358K at 0, 5, 10, 20 and 40V dc. The phases, microstructures and impedance properties of final samples were characterized by X-ray diffraction, scanning electron microscopy and precision impedance analyzer. The dielectric permittivity of CCTO synthesized by sol-gel method was found three times larger than that synthesized by other low-temperature method as well as solid-state reaction method. The observed results were explained by internal barrier layer capacitor (IBLC) model of Schottky barriers at grain boundaries between semiconducting grains.

Thomas,P.et al.⁵³ have reported that the powders produced by the pyrolysis of the co-precipitated oxalates at 900 °C for 10 h yielded CCTO with $\text{CaTiO}_3 + \text{CuO}$ as the impurity phases. The phase-pure CCTO was obtained only after sintering the powders at 1050 °C. A complex oxalate precursor was developed in order to avoid

such difficulties in obtaining phase-pure CCTO powders at relatively lower temperatures. This method was found convenient for achieving chemical homogeneity, where the individual constituents intermix at the ionic level under controlled wet chemical conditions. The nano particles of CCTO with the crystallite size varying from 30 to 200 nm was reported to obtain at a temperature as low as 680 °C from the exothermic thermal decomposition of an oxalate precursor $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$. The powders derived from the oxalate precursor showed excellent sinterability, resulting in high-density ceramics which exhibited giant dielectric constants up to 40,000 (1 kHz) at 25 °C, accompanied by a low dielectric loss < 0.07 .

Yin, W.S. et al.⁵⁴ have prepared $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics by conventional solid state reaction method under various sintering temperatures from 900°C to 1075°C. The dielectric properties of the sample were measured using HP 4192A LF Impedance Analyzer. The complex permittivity was measured within the frequency range from 10Hz to 10^6 Hz and the temperature ranging from 30°C to 400°C. The results showed that the dielectric constant and dielectric loss factor of the sample was frequency dependent and temperature dependent. CCTO sample exhibits a high dielectric constant which is around 10^5 . Dielectric constant increases with decreasing frequency due to interfacial polarization.

Yu, H. et al.⁵⁵ have synthesized single-phase cubic perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders by microwave heating method with a relatively low energy consumption and short time, compared with conventional synthesis. The reaction evolution of forming CCTO has been suggested according to the XRD data. The ceramics from microwave-synthesized powder was found to have higher dielectric constant than that from conventional synthesized powder under the same sintering conditions.

Masingboon, C. et al.⁵⁶ have synthesized nano-sized powders of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by a polymerized complex method and calcined at 600, 700 and 800 °C in air for 8 h. The diameter of the powders ranges from 30 to 100 nm. The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders were characterized by TG-DTA (Thermo gravimetric differential thermal analysis), XRD (X-Ray diffraction), FTIR (Fourier transform infrared spectroscopy), SEM (Scanning electron microscopy) and TEM (Transmission electron microscopy). Sintering of the

powders was conducted in air at 1100 °C for 16 h. The XRD results indicated that all sintered samples have a typical perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ structure with some amount of CaTiO_3 and CuO . SEM micrographs of the sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics showed the average grain size of 10–15 μm . The samples exhibit a giant dielectric constant, ϵ' of 10,000–20,000. It was found that the dielectric constant is independent on the frequency and weakly temperature dependent over the temperature range of -50 °C to 200 °C. The Maxwell–Wagner polarization mechanism was used to explain the high permittivity in these ceramics. It was also found that all three sintered samples have the same activation energy of grains, which is 0.116 eV. On the other hand, the activation energy of grain boundaries was found to be 0.219, 0.391 and 0.641 eV for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared using the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders calcined at 600, 700 and 800 °C, respectively.

Chen, K. and Li, C.⁵⁷ have synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) with perovskite-like structure ceramic powder by heating a stoichiometric composition of CaCO_3 , CuO and TiO_2 in molten NaCl-KCl and $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ respectively. Phase compositions and particle morphology of the resultant powders have been investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results indicate that synthesis temperature could be decreased from 1000 °C (required by conventional solid-state reactions) to 750 °C in NaCl-KCl or to 850 °C in $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, and the flux type plays more important role on the phase compositions and morphology of resultant powders than synthesized temperature.

Maurya, D. et al.⁵⁸ have reported the synthesis of sol–gel derived CCTO thin films with varying calcium content and their dielectric characterization. The room temperature XRD patterns revealed the formation of a single perovskite phase. The dielectric constant, loss tangent and ac conductivity of these films have been investigated as a function of frequency at room temperature. The results show that with increase in the calcium content up to a certain limit, the dielectric constant of these films increases.

Ramajo, L. A. et al.⁵⁹ have analysed the dielectric behavior of composite materials (epoxy resin – barium titanate and epoxy – CCTO) as a function of ceramic amount. Composites were prepared by mixing the components and pouring them into suitable moulds. In some compositions, the matrix was reduced by tetrahydrofuran (THF)

incorporation. Samples containing various amounts of ceramic filler were examined by TG/DTA and scanning electron microscopy analysis. Dielectric measurements were performed from 20 Hz to 1 MHz and 30 to 120 °C. It was demonstrated that the epoxy – CCTO composites possessed higher permittivity than classic epoxy – BaTiO₃ composites.

Barbier, B. et al.⁶⁰ have synthesized CaCu₃Ti₄O₁₂ (CCTO) ceramics by a soft chemistry method (co-precipitation). In this study, electrical properties of CCTO - based pellets and thick films obtained from the same raw powders prepared by the co-precipitation method have been explored. CCTO pellets exhibit high values of the dielectric permittivity ($\epsilon_r \sim 14 \times 10^4$) and relatively small values of the dielectric losses ($\tan \delta \sim 0.16$) at 1 kHz and room temperature. No influence of the nature of metal electrode on the dielectric permittivity and losses has been observed. Moreover, the dielectric permittivity decreases when the diameter of the sample increases. These results are in contradiction with a metal ceramic interface related origin of the high dielectric permittivity, and in agreement with an IBLC effect origin. CCTO thick films present very high values of their dielectric permittivity ($\epsilon_r \sim 5 \times 10^4$) even if they are lower than the one of CCTO pellets. Such high values have never been reported before for thick films. From a physical point of view the difference in copper content, the difference in grain size, and possibly various oxidation states may explain the changes in the dielectric permittivity between films and pellets. Finally, from a technological point of view, the presented results pave the way to the use of CCTO for multilayer capacitors manufacturing.

Yuan, W. X. et al.⁶¹ have synthesized a giant dielectric-constant material CaCu₃Ti₄O₁₂ (CCTO) by using a modified solid-state reaction method. In this work, procedure was much less energy and time consuming comparing with typical calcining conditions. When CCTO prepared, a momentarily high temperature heating was applied at the end of the calcination, then followed it by a typical sintering process. It was found that, this additional heating converts the otherwise mixed-phase products into a pure phase and the CCTO samples prepared this special way possess a large dielectric constant, up to 19,000.

Sen, S. et al.⁶² have reported that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics were fabricated by the precursor solution technique. Structural and micro-structural characterization was undertaken by X-ray diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy. XRD analysis confirmed the formation of cubic phase with a lattice parameter value of 7.3985\AA . Spherical particles of average 65 nm sizes were observed from TEM micrographs after calcinations at 700°C .

Zheng, J. C. et al.⁶³ have reported a combined experimental and theoretical study of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Based on experimental observations of nanoscale regions of Ca-Cu antisite defects in part of the structure, density functional theory (DFT) calculations suggests a possible electronic mechanism to explain the gigantic dielectric response in this material.

Banerjee, N. et al.⁶⁴ have reported sol-gel method to synthesize pure and wide ranged La-modified $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics using mixed acetate-nitrate-alcoxide individual metal-ion precursors. SEM pictures revealed that grain size monotonously decreases with the extent of La incorporation. All the prepared ceramics manifested dielectric constant in the range $\sim 10^3$ – 10^4 . Dielectric loss was found to decrease with La incorporation and got optimized for 20% La^{3+} while retaining its high dielectric constant which may be industrially important. Room temperature Impedance spectroscopy suggested that decrease in grain resistance is responsible for reduction in dielectric loss according to Internal Barrier Layer Capacitor (IBLC) model.

Yuan, J. et al.⁶⁵ have investigated the dielectric and varistor properties of MgTiO_3 – $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ composite in term of a new composite with high dielectric permittivity and breakdown voltage. The MgTiO_3 – $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ composite ceramics were prepared by a traditional solid-state method. Analysis of microstructure indicated that MgTiO_3 addition can refine the grain size. Impedance spectroscopy results showed that the dielectric constant and loss of the composites were stable with the frequency and temperature. The activation energy calculated by the variation of electrical modulus was almost same (0.12eV) as previously reported one. Especially, the breakdown voltage of the composite ceramics can be adjusted from 200 to 1200 V/mm by controlling the ratio of the amount of CCTO and MgTiO_3 composites.

Felix, A.A. et al.⁶⁶ have studied electrical barriers existing at $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics using dc electrical measurements. The samples were electrically characterized by dc and ac measurements as a function of temperature, and semiconductor theory was applied to analyze the barrier at grain boundaries. The ac results showed the sample's permittivity is almost constant (10^4) as a function of temperature at low frequencies and it changes from 10^2 to 10^4 as the temperature increases at high frequencies. Using dc measurements as a function of temperature, the behavior of barriers was studied in detail. Comparison between Schottky and Poole-Frenkel models was performed, and results prove that CCTO barriers are more influenced by temperature than by electric field (Schottky barriers).

Xu, D. et al.⁶⁷ have prepared $\text{CaCu}_{3-x}\text{Zn}_x\text{Ti}_4\text{O}_{12}$ (CCZTO) ($x=0, 0.06, 0.1, 0.2$) ceramics by Sol-Gel method. The XRD pattern shows that the crystal structure of the sample with no Zn is basically single-phase. The SEM results indicate that the samples have porous structures and the grain size decreases with the content of Zn increasing. The dielectric properties of CCZTO were analyzed by Agilent 4294A. The experimental results show that the dielectric constants are less than those reported in other papers obviously because of their mesoporous structures. With the little doping amount ($x=0.06, 0.1$), a sharp decrease happened in the dielectric constant (ϵ_r). The higher ϵ_r was found when $x=0.2$, but its dielectric loss (D) had greatly increased and frequency stability of dielectric property became worse. The uniformity of grains was put forward to explain the results which showed great impact on the dielectric constant.

Wu, L. et al.⁶⁸ have investigated the dielectric properties of 1050 °C/12h sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics by using terahertz time domain spectroscopy in the frequency range of 0.2-1.6 THz at room temperature. When applying an external optical field, an obvious variation of dielectric constant was observed and reached up to 7%. However, the dielectric loss does not change appreciably. From the results, it was found that the change of refractive index has a linear relationship on scale with the applied light intensity. These findings were attributed to the change of spontaneous polarization in the ceramic caused by the excited free carriers.

Puchmark, C. and Rujjanagul, G.⁶⁹ have prepared $\text{CaCu}_{3.1}\text{Ti}_4\text{O}_{12.1}$ ceramics by a simple solid state mixed oxide method. The optimum temperature for calcination the formation of phase pure perovskite and lattice parameters "a" of unit cell close to lattice parameter was found about 900°C for 8 h. Phase formation was examined by X-ray diffraction technique. The sintering process was carried out at 1000, 1025 and 1050°C for 8 h. The results show that the microstructure of fracture mode for variation sintered samples change from intergranular to intragranular mode with increasing sintering temperature. The density, average grain size, Vickers hardness and dielectric constant were increased with increasing the sintering temperature.

Kashyap, R. et al⁷⁰ have prepared samples of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics by solid state reaction method. X-ray diffraction analysis confirmed single phase formation for the powder calcined at 1173 K. Sintering was done at different temperatures viz. 1348 K, 1373 K and 1398 K with a fixed heating rate of 3 K/min. Detailed study of dielectric properties was carried out for the CCTO samples sintered at 1373 K for different duration of holding times (2 h and 10 h). It is found that dielectric properties are sensitive to both sintering time and temperature. With increasing sintering time from 2 h to 10 h dielectric constant increases from 2.1×10^4 to 2.5×10^4 measured at 1 kHz at room temperature. Impedance spectroscopy has been used for separating out of grain and grain boundary contributions to the overall electrical properties.

Liu, Q. X. et al⁷¹ have prepared two kinds ceramics of pure $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and Sr/Mg doped $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{0.5}\text{Sr}_{0.5}\text{TiO}_3 + x\text{MgO}$ ($x=0.01, 0.03, 0.05, 0.1$, denoted as CCST-M-1, CCST-M-3, CCST-M-5, CCST-M-10, respectively) using the traditional solid phase reaction method. The dielectric properties were measured by HP 4194A Impedance/Gain-Phase Analyzer with the frequency range from 100 Hz to 1 MHz. The temperature dependence of dielectric constant and loss tangent were measured for different frequencies. The variation relation of the critical temperature with the frequency was fitted theoretically which is in agreement with the Arrhenius law for pure CCTO. According to a variable power law to describe the paraelectric dielectric constant of ferroelectrics with diffuse phase transitions, the theoretical fitting was carried out for doped samples, and it was suggested that all doped samples exhibited the Debye-like relaxation. Among the doped and pure CCTO samples, CCST-M-1 was of the lowest dielectric loss at the whole measurement frequency, and whose I–

V response curve was nonlinear suggesting a non-ohmic contact. The complex-impedance analysis results showed that the reduction in dielectric loss of CCST-M-1 sample can be attributed to the increase of grain boundary resistance. It is expected that these results are helpful to promote the CCTO-related materials to practical applications.

2.5 Factors affecting the properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO):

Subramanian, M.A. et al.¹⁵ have found high dielectric constants in oxides of the type $\text{ACu}_3\text{Ti}_4\text{O}_{12}$. The most exceptional behavior was exhibited by $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, which shows a dielectric constant at 1 kHz of about 12,000 that is nearly constant from room temperature to 300°C. The cubic structure of these materials was related to that of perovskite (CaTiO_3), but the TiO_6 octahedra are tilted to produce a square planar environment for Cu^{2+} . Most compositions of the type $\text{A}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (A = trivalent rare earth or Bi) show dielectric constants above 1000.

Homes, C.C. et al.¹⁸ have reported the optical response of high dielectric constant perovskite related oxide. Optical conductivity measurements on the perovskite-related oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ provide a hint of the physics underlying the observed giant dielectric effect in this material. A low-frequency vibration displays anomalous behavior, implying that there is a redistribution of charge within the unit cell at low temperature. At infrared frequencies (terahertz), the value for the dielectric constant is ~ 80 at room temperature, which is far smaller than the value of ~ 10^5 obtained at lower radio frequencies (kilohertz). This discrepancy implies the presence of a strong absorption at very low frequencies due to dipole relaxation. At room temperature, the characteristic relaxation times are fast (≤ 500 nanoseconds) but increase dramatically at low temperature, suggesting that the large change in dielectric constant may be due to a relaxor-like dynamical slowing down of dipolar fluctuations in nanosize domains.

Adams, T.B. et al.²⁰ have reported the influence of grain size on the magnitude of the barrier layer capacitance effect and show that giant RT (room temperature) effective permittivity values ϵ'_{eff} of >250000 can be obtained from $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. This was the highest ϵ'_{eff} value reported for an IBLC ceramic and may have important

technological ramifications as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic can be fabricated in a single step process at moderate temperatures in air.

Cohen, M.H. et al.²³ provide extrinsic models for the dielectric response of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The large, temperature-independent, low-frequency dielectric constant recently observed in single-crystal $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is most plausibly interpreted as arising from spatial inhomogeneities of its local dielectric response. Probable sources of inhomogeneity are the various domain boundaries endemic in such materials: twin, Ca ordering, and antiphase boundaries. The material in, and neighboring, such boundaries can be insulating or conducting. In this work, a decision tree was constructed for the resulting six possible morphologies and derives expressions for the dielectric constant for models of morphology. It was concluded that all six morphologies can yield dielectric behavior consistent with observations.

Li, J. et al.³⁶ studied the dielectric properties of polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) pellets sintered in the temperature range 1000-1200°C with impedance spectroscopy at frequency range of 10^2 to 10^7 Hz from 90 K to 294 K. A correlation has been suggested between the pair values of low frequency limit dielectric constant and the total resistivity and the sintering temperature. For example, the sample sintered at 1100°C demonstrates higher value of low frequency limit dielectric constant and lower value of total resistivity, while the sample sintered at 1000°C demonstrates lower values of low frequency limit dielectric constant and higher value of total resistivity. This correlation had been successfully explained by relating with the difference in grain size and grain volume resistivities of these two polycrystalline CCTO samples.

Mazumder, R. et al.⁷² has been observed that the loss factor of CCTO can be reduced by B_2O_3 addition. The low frequency dispersion of CCTO ceramics, which indicates Maxwell-Wagner type relaxation, is reduced by boron addition. Also the temperature dependence of dielectric constant is minimized by boron addition. From the present work it can be surmised that B_2O_3 addition can favourably modify the dielectric properties of CCTO ceramic for its practical applications as a capacitor material.

Bender, B.A. et al.⁷³ have studied the effect of processing on the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). Powders mixed via mortar and pestle yielded CCTO with a

room temperature permittivity of 11,700 and a loss of 0.047. However, attrition-milled powders led to CCTO with permittivities close to 100,000 which were in the same range reported for single crystal CCTO. Increasing sintering temperature in the range from 990 to 1050°C led to an increase in both the dielectric constant (714 to 82,450) and dielectric loss (0.014 to 0.98). Increasing sintering times also led to substantial improvements in permittivity. Grain size and density differences were not large enough to account for the enhancement in dielectric constant. The colossal effective dielectric constant of close to one million at room temperature was measured after annealing in flowing argon at 1000°C. The study suggests that the primary factor affecting dielectric behavior is the development of internal defects. It suggested that higher defect concentration within the core of a grain resulted in a higher conductivity of the core and therefore, higher effective dielectric constant but also higher loss. The giant permittivity of CCTO has been described by a model of conducting grains and insulating grain boundaries and the associated Maxwell–Wagner relaxation. However, this model requires that the insulating grain boundaries be thin, uniform, and robust to prevent percolation of the conducting grains.

Yang, J. et al.⁷⁴ have studied the electrode/sample contact effects on the dielectric properties of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. It was suggested that the colossal dielectric constant in CCTO is related partly originated from the electrode/sample contact effects which depends on the surface resistivity of the sample. When the surface resistivity of the ceramic is as high as $1.2 \times 10^8 \Omega \text{ cm}$, no obvious mobile space charges can be observed, and the dielectric properties of the sample are inert to the different metal electrodes and various sample thicknesses. However, after the surface resistivity is lowered to $3.1 \times 10^7 \Omega \text{ cm}$ through post annealing the sample in N_2 atmosphere at 750°C, the dielectric properties of the sample become sensitive to the different types of contacts due to the mobile space charges. The dielectric constant of the sample with Pt electrode showed a significant enhancement (up to 5000 at 10 kHz) as compared to that of the sample with Ag electrode.

Lia, J. et al.⁷⁵ have suggested that the presence of internal resistive barriers in a crystal of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ material. The barrier was associated with the numerous twin boundaries. The presence of defects in the bulk phase was reported responsible for its conducting behavior. The presence of Ti on the Cu site was unexpected but

very small amounts of Ti may be on the Cu site in CCTO. Depending on the synthesis temperatures the charge compensation took place by some reduction of Cu^{2+} to Cu^{1+} . On cooling, the Cu^{1+} would oxidize to Cu^{2+} giving up an electron to the Ti 3d band. So the bulk phase in CCTO becomes conducting.

Liu, J. et al.³² have studied the frequency and temperature dependences of permittivity and impedance of the compounds $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ ($\text{A}=\text{Ca}, \text{Bi}_{2/3}, \text{Y}_{2/3}, \text{La}_{2/3}$) in the ranges of 10^{-1} – 10^6 Hz and 150–200 °C. All compounds investigated display similar dielectric properties. Specifically, they all have a Debye-like relaxation and their dielectric constants are independent of frequency and temperature over a wide range. They all have two electrical responses in impedance formalism, indicating that there are two distinct contributions. In this study, the dielectric behavior was explained by Maxwell-Wagner relaxation arising at the interfaces between grains and their boundaries.

Yoo, D.K. and Yoo, S.I.⁷⁶ have reported important factors affecting the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) polycrystalline ceramics prepared by the conventional solid-state ceramic process. The relative dielectric constants (ϵ_r) up to several thousands (~3,000 at 1 kHz) were gradually increased with increasing the sintered density of samples in the case that no exaggerated grain growth occurred. An abrupt increase in ϵ_r values were, however, accompanied by the formation of abnormally grown large grains, and thus with increasing the population of abnormally grown grains, which could be achieved by a prolonged sintering at 1060°C, ϵ_r values were remarkably increased from several thousands to $\sim 10^5$. Optimally processed CCTO sample exhibited a very high ϵ_r of $\sim 90,000$ at 1 kHz.

Krohns, S. et al.⁷⁷ have reported dielectric measurements of the colossal dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ extending up to 1.3 GHz also covering so far only rarely investigated single-crystalline samples. Special emphasis was put on the second relaxation reported in several works on polycrystals, which the authors detect also in single crystals. For polycrystalline samples, the authors provide a recipe to achieve values of the dielectric constant as high as in single crystals.

Lee, S.Y. et al.⁷⁸ have reported the important roles of Cu composition in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) polycrystalline ceramics. For this purpose, $\text{CaCu}_{2.8}\text{Ti}_4\text{O}_{12}$ (Cu2.8) and $\text{CaCu}_{2.9}\text{Ti}_4\text{O}_{12}$ (Cu2.9) powders with a Cu-deficient composition, $\text{CaCu}_{3.1}\text{Ti}_4\text{O}_{12}$

(Cu3.1) and $\text{CaCu}_{3.2}\text{Ti}_4\text{O}_{12}$ (Cu3.2) powders with a Cu-excess composition and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (Cu3.0) (CCTO) powder were prepared. All of these samples were calcined at 950°C for 24h and then sintered at 1060°C for 12h using a conventional solid-state ceramic process. As the Cu composition decreased, the Cu-deficient samples changed from a duplex microstructure including abnormally grown grains and fine grains to a microstructure almost fully covered with fine grains without any abnormally grown grains. However, the Cu-excess samples showed fine-grained microstructures in which no abnormally grown grains were observed with Cu-rich secondary phases segregated at the grain boundaries compared with CCTO. Relative dielectric constants of the, ϵ_r values of the samples were strongly affected by the size and population of abnormally grown grains which were varied with the amount of Cu-rich secondary phases.

Shao,S.F.et al.⁷⁹ have investigated the effect of Cu-stoichiometry on the dielectric and electric properties of $\text{CaCu}_{3+y}\text{Ti}_4\text{O}_{12}$ ($y = 0, \pm 0.025, \pm 0.05, \pm 0.1$ and -0.15) ceramics prepared under various compositions by the conventional solid-state reaction method. X-ray diffraction study showed that all of the compositions had the good polycrystalline structures. Microstructural study suggests that Cu-deficiency samples exhibits the microstructures of uniform grain size distribution, whereas ceramics with Cu-stoichiometry and Cu-excess show microstructures of bimodal grain size distribution. Ceramics with Cu-stoichiometry shows the highest low-frequency dielectric permittivity and the lowest domain resistance.

Wang,C.M.et al.⁸⁰ have studied the dielectric properties of polycrystalline CCTO samples sintered at 1100°C in the dwell time range from 3 to 48 hrs prepared by conventional solid-state reaction technique. X-ray diffraction (XRD) patterns study showed no obvious change in crystal phase with various sintering times. The microstructural study indicated that the grain size was significantly increased with an increase of sintering time. The dielectric properties of CCTO ceramics are found very sensitive to processing.

Kim,K.M.et al.⁸¹ have studied the microstructure and dielectric properties of $\text{CaCu}_{3-x}\text{Ti}_4\text{O}_{12-x}$ ($3 - x = 2.8-3.05$) ceramics. The X-ray diffraction study showed that the powders ($\text{Cu}/\text{Ca} = 2.8-3.05$) heat-treated at 1140°C for 12 h were indexed to the

single CCTO phase. For simplicity, Cu/Ca (molar ratio) is denoted as C. The lattice parameters of CCTO powders with Cu/Ca ≥ 2.95 were slightly larger than the values for the CCTO powders with Cu/Ca ≤ 2.90 . The microstructure of the CuO-deficient CCTO specimens (C2.80, C2.85, C2.90) sintered at 1140^oC for 12 h. showed uniform microstructures and no abnormally grown grains were found throughout the specimens and the average grain sizes were 4.7, 4.9, and 4.8 μm , respectively. However, CuO-enriched CCTO specimens sintered at 1140^oC for 12 h showed a coarse-grained microstructure. The microstructural evolution showed quite different behaviors according to the CuO content. Normal grain growth (NGG) behavior was observed at Cu/Ca ≤ 2.9 , while abnormal grain growth (AGG) behavior was found at Cu/ Ca ≥ 2.95 . AGG can be induced by two important parameters; interface structure and the presence of an intergranular liquid phase. TEM (Transmission electron microscopy) study in order to analyze the distribution and amount of the intergranular liquid showed that the location of the liquid phase always coincided with a grain boundary, and the liquid was identified as being a CuO rich phase by EDS (Energy dispersive spectroscopy) analysis. It was reported that the amount of liquid increased with increasing CuO content in the specimen which indicates that the excess CuO added in the range of Cu/Ca ≥ 2.95 does not incorporate into CCTO lattice but increases the intergranular liquid phase. The ϵ'_{app} value was found to decrease in the liquid abundant at a lower frequency ($f = 10^1\text{--}10^4$ Hz) while the samples with liquid-enriched specimen with little intergranular liquid shows a large ϵ'_{app} value even in the frequency range of $10^3\text{--}10^5$ Hz. Moreover, the minimum loss tangent values increased significantly with increasing CuO content. This has been explained either by the compositional change in CCTO grains or by the variation in the intergranular phase. It has been suggested that the abnormal grain growth was advantageous to increasing apparent dielectric permittivity via a barrier layer mechanism. However, in order to achieve high apparent dielectric permittivity and low dielectric loss, the CuO-rich intergranular liquid phase should be minimized.

Cordeiro, M.A.L. et al.⁸² have reported an investigation of dc current-voltage measured in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. The experimental results show unusual I-V behaviors associated with the electrically inhomogeneous nature of the grains (mixture of semiconducting and insulating regions) and dependence on delay time. The data

strongly suggest that both the localization of current in the conductive region and local Joule self-heating effects are essential elements to explain the abrupt drop in the electric field. In addition, the hysteresis behavior recorded during the I-V measurements shows strong dependence on delay time, i.e., the time needed for the polarization phenomena to occur.

Jacob, K.T. et al.⁸³ have measured the isobaric heat capacity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) from 300 to 1100K using differential scanning calorimetry (DSC). The results were verified using drop calorimetric measurement of enthalpy increment ($H_T - H_{298.15}$) at $T = 973$ and 1073 K. The samples were dropped from room temperature into a calorimeter maintained at high temperature. The enthalpy and entropy increments are computed as a function of temperature and compared with values available in the literature. The results obtained in this study are consistent with available information on enthalpy and Gibbs energy of formation of CCTO.

Fiorenza, P. et al.⁸⁴ have reported conductive atomic force microscopy (C-AFM) investigation to provide local electrical characterization in a single crystal of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). The microstructure and dielectric properties were studied and provide evidence for an insulating secondary phase embedded within the semiconducting CCTO matrix. Such insulating electrical heterogeneities cannot be observed with macroscopic measurements such as conventional impedance spectroscopy and this study revealed that C-AFM is a powerful tool to assess the electrical homogeneity of semiconducting single crystals such as CCTO.

2.6 Ceramic Polymer Composites:

Electrical energy storage plays a key role in mobile electronic devices, stationary power systems, hybrid electric vehicles, and pulse power applications⁸⁵⁻⁸⁶. In particular, there is a growing need for capacitors that can accumulate a large amount of energy and then deliver it nearly instantaneously. This kind of “pulse power” is needed for a variety of military and commercial applications. Over time, these applications demand ever higher energy and power densities as well as higher rate capability.

The need for pulse power energy storage systems with high energy density has led to the development of polymer composite systems that combine the process ability and breakdown field strength of the polymer with the high dielectric constant of ceramic fillers. Ideally, the fillers help to increase the effective dielectric constant of the composite system without compromising the high inherent breakdown strength of polymers. Moreover, increasing the effective dielectric constant must be achieved without an unacceptably large increase in dielectric loss (i.e., energy dissipation). In reality, the objectives of high dielectric constant, high breakdown field strength, and low dielectric loss are not likely to all be achieved; the best solution will be a compromise. Consequently, much research is being carried out to develop improved polymer composite materials through a better understanding of the physical phenomena governing composite dielectric permittivity and breakdown field strength. As both of these issues are likely to involve the polymer-filler interface, research seeking a better understanding the chemistry and structure of the filler-polymer interface is a priority.

Most of the current studies on dielectric polymer composites focus on the enhancement of the dielectric permittivity using ferroelectric metal oxides $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.77})\text{O}_3\text{-PbTiO}_3$ (PMNT), and BaTiO_3 (BT). From the point of view of increasing the composite's effective dielectric constant, the availability of inorganic fillers with dielectric constants on the order of hundreds and even thousands makes it very appealing to introduce them into polymers, which generally possess dielectric constants less than 10. However, the resulting composite's effective dielectric constants generally fall short of expectations. Specifically, since the filler has a much greater permittivity than that of the polymer matrix, most of the increase in the effective dielectric constant comes through an increase in the average field in the polymer matrix, with very little of the energy being stored in the high permittivity phase. Also, the large contrast in permittivity between two phases can give rise to highly inhomogeneous electric fields. Lastly, incompatibility between the organophilic polymer matrix and the hydrophilic metal oxide filler impedes the formation of a homogenous composite. Thus, a major research direction in this field remains focused on modifying the inorganic filler surface to compatibilize the inorganic filler with the polymer matrix. Highly inhomogeneous fields and structural inhomogeneity

generally lead to a significant reduction in the effective breakdown field strength of the composite, limiting the increase in the energy storage capacity and energy density. Clearly there are several persistent issues that need to be overcome to increase the energy density and capacity of dielectric polymer composite materials.

The physical properties of composites can be the sum, combination, and product of properties of its constituents based on the properties or connectivity. For example, the total mass is simply the sum of their individual ones. The connectivity was first classified by Newnham et al.⁸⁷. Based on their connectivity and morphology of each phase, the dimension is defined as 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 3-2, and 3-3 for a 2-phase composite as shown in Figure 2.4, where 0/1/2/3 represent the number of dimensions for each component in the composite. For example, for 0-3 composite it is defined as 0-dimension particle (usually the ceramic particle) and is embedded inside 3-dimensions polymer matrix as shown in Figure 2.4 (blue color: polymer matrix, white color: ceramic particle).

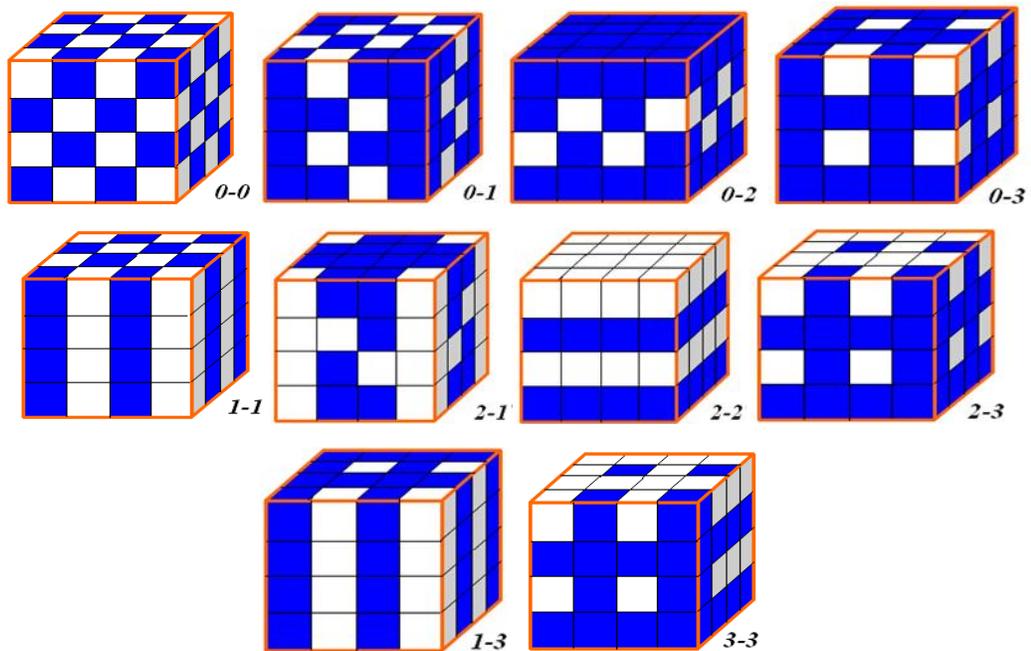


Figure-2.4: Ten Connectivity Patterns in Diphasic Composites

Ceramic-polymer 0-3 composites are widely used due to the fact that it is flexible and easy to fabricate. Different models have been introduced to simulate the effective dielectric constant of these composites. The volume-fraction average is a simple (but inaccurate) method to estimate the effective dielectric constant of a polymer composite material [60]:

$$\epsilon_{\text{eff}} = \Phi_1 \epsilon_1 + \Phi_2 \epsilon_2 \text{ -----(5)}$$

where the subscripts 1 and 2 represent the ceramic and the polymer phase, respectively, and Φ is the volume fraction of the constituents. According to the volume-fraction average model (equation-5), the effective dielectric constant of the composite, increases sharply at low volume fraction of the ceramic filler. Many studies involving both experiments and theory disprove the trend predicted⁸⁸⁻⁹¹ by equation (5).

For a random ceramic-polymer 0-3 composite, Lichtenecker's Logarithmic Law⁹² is shown by equation (6) to estimate the permittivity of 2- phase materials.

$$\log \epsilon' = \Phi_1 \log \epsilon_1 + \Phi_2 \log \epsilon_2 \text{ ----- (6)}$$

where ϵ_1 and ϵ_2 stand for the dielectric constant of ceramic and polymer and ϵ' stands for the dielectric constant of the mixture and Φ_1 and Φ_2 are the volume fraction of the ceramic particles and polymer matrix respectively. This theory applies with two requirements:

1. two components are independent of each other;
2. particles of both materials distribute uniformly in the entire structure.

Lichtenecker's equation is modified as

$$\log \epsilon' = \log \epsilon_2 + (1-k) \Phi_1 \log(\epsilon_1/\epsilon_2) \text{ ----- (7)}$$

where k is a fitting constant for composite material. The value for k is around 0.3 for most well dispersed ceramic-polymer composites.

Das-Gupta et al. also suggested⁹³:

$$\epsilon' = \epsilon_2 [2(1-\Phi_1)\epsilon_2 + (1+2\Phi_1)\epsilon_1] / [(2+\Phi_1)\epsilon_2 + (1-\Phi_1)\epsilon_1] \text{ ----- (8)}$$

If ceramic particles are sphere in shape, then the Maxwell-Wagner mixing Rule is used⁹⁴⁻⁹⁵:

$$\epsilon' = \epsilon_2 \{[\epsilon_1 + 2\epsilon_2 + 2\Phi_1(\epsilon_1 - \epsilon_2)] / [\epsilon_1 + 2\epsilon_2 - \Phi_1(\epsilon_1 - \epsilon_2)]\} \text{ ----- (9)}$$

Maxwell-Wagner mixing rule is effective for infinite dilution of the dispersed phase that the spherical ceramic particles are separated by distances greater than their characteristic size.

If ellipsoidal ceramic particles are randomly distributed into an a polymer matrix, the effective dielectric constant ϵ' is⁹⁶

$$\epsilon' = [\Phi_1 \epsilon_1 \beta + (1-\Phi_1)\epsilon_2] / [\Phi_1 \beta + 1-\Phi_1] \text{ ----- (10)}$$

where β is the field factor ($\beta = [1/\{1+L (\epsilon_1/\epsilon_2-1)\}]$) and L is defined as the “equivalent” depolarization coefficient of the particles in the direction of the applied field ($0 < L < 1$).

Regarding ellipsoid ceramic particles in polymer matrix, another estimation equation is given by Yamada et al.:

$$\epsilon' = \epsilon_2[1 + \{n\Phi_1(\epsilon_1 - \epsilon_2)/n\epsilon_2 + (\epsilon_1 - \epsilon_2)(1 - \Phi_1)\}] \text{ ----- (11)}$$

where n is a constant related to geometry of ceramic particles.

Based on the percolation theory, the Bruggeman model⁹⁷ was developed. This model treats the binary mixture as being composed of repeated units cells composed of the matrix phase with spherical inclusions in the center. The effective dielectric constant (ϵ') of the binary mixture is given by:

$$\Phi_1[(\epsilon_1 - \epsilon')/(\epsilon_1 + 2\epsilon')] + \Phi_2[(\epsilon_2 - \epsilon')/(\epsilon_2 + 2\epsilon')] = 0 \text{ ----- (12)}$$

From the literature review it is evident that not much work has been done on PVC and PET composites with CCTO as active material. Therefore there is a need to analyze and characterize composites based on these polymers⁹⁸. PVC and PET are structurally different yet mechanically similar⁹⁹.

2.7 Summary :

The relevant literature has been reviewed in this chapter. Also a review of CCTO and related material has been given. The study is continued in chapter- 3 where the Research Design and Methodology is given.