CHAPTER 2

LITERATURE REVIEW OF CCTO

2.1 INTRODUCTION

A major 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 high dielectric constant materials. The dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ material were first reported by Subramanian et al., in 2000 [91]. They first reported that large dielectric constants were found in ACu$_3$Ti$_4$O$_{12}$ (A = trivalent rare earth or Bi) type materials e.g., Bi$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (BCTO) [$\varepsilon_r = 1,871$], Y$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (YCTO) [$\varepsilon_r = 1,743$], La$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (LCTO) [$\varepsilon_r = 418$], Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (SCTO) [$\varepsilon_r = 1,665$] and Dy$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (DCTO) [$\varepsilon_r = 1,633$]. CaCu$_3$Ti$_4$O$_{12}$, displaying the most special behavior, show a dielectric constant about 12,000 at 1 kHz, remaining steady in a large temperature range, from 100 K to 400 K. As we know, some materials with dielectric constants higher than 1,000 are associated with ferroelectric properties and the dielectric constant changes greatly during the ferroelectric phase transition. This property limits their applications in industry because often it is required that the dielectric constant of the material is independent of the temperature. Therefore, CaCu$_3$Ti$_4$O$_{12}$ (CCTO), with its low dependence on temperature, is of great interest to us.

Ferroelectric materials, like BaTiO$_3$, always possess comparatively large dielectric constants due to ferroelectric phase transition and their perovskite structures. The dielectric response of BaTiO$_3$ mainly comes from the displacement of the Ti ions. With decreasing temperature, the Ti ion starts to displace from the
centre, and the perovskite structure of BaTiO$_3$ changes from cubic to tetragonal at \(-130\) °C, then to orthorhombic at 0 °C, and at last to rhombohedra at \(-90\) °C. However, in CCTO structure, the site symmetry of Ti is much less than that of BaTiO$_3$ structure, it is almost impossible for a ferroelectric phase transition to occur.

Shortly afterwards, other special features of CCTO were discovered by Ramirez et.al.,[92]. The crystal structure of CCTO is shown in Fig. 2.1. They reported that below 100 K the dielectric constant drops abruptly from around 12,000 to as low as 100, in addition to the fact that CCTO holds a large dielectric constant that barely varies in the temperature range from 100 K to 400 K. The reported dielectric loss, or tan\(\delta\), is less than 0.1 when the temperature is higher than 150 K, and a large peak occurs at around 100 K. Frequency dependence is also shown from 100 K to 300 K in a wide frequency range between 100 Hz to 1,000,000 Hz for both dielectric constant and loss. With the increasing frequency, the dielectric constant decreases in the entire temperature range and the dielectric loss peak shifts to higher temperature with small increase in the maximum value of the peak. This behavior satisfies the relaxational excitation well.

Kolve and Bontchev also proved that the giant dielectric constant of CCTO doesn’t come out of a classical ferroelectric phase transition by learning Raman spectroscopy of CCTO [93]. The large dielectric constants shown by many perovskite structure materials are caused by the atomic displacement within a non-centro symmetrical structure. However, after measuring the Raman spectra of CCTO microcrystal in various scattering configurations, all the main Raman lines were able to be assigned to definite phonon modes in close comparison with results of lattice dynamical calculations, and no evidence for structural phase transition was found in the temperature range of 20 K to 600 K. Same results were given by neutron powder diffraction that CCTO structure remains cubic down to 35 K. [94]
Therefore, the origin of this giant dielectric constant and its weak temperature dependence becomes an interesting topic. Several theories to explain this behavior have been proposed. One of the explanations proposed in 2002 by Adams et al., is widely accepted [94]. This theory states that the dielectric behavior of CCTO does not come from its intrinsic character but from some heterogeneity of its ceramic structure. There is no structural phase transition in the whole temperature range, which is to say the permittivity doesn’t come from the displacement of Ti ions, neither is it possible that the dramatic decrease originates from the relaxation out of the samples. However, during the sintering step of any ATiO$_3$- based samples (where A= Ca, Sr, and Ba), they lose small amount of oxygen and become conductive. Correspondingly, certain reoxidation creates insulating layers on the surface and along the internal boundaries of individual grains. This is called internal barrier layer capacitance (IBLC), which is considered the origin of the giant dielectric constant of CCTO.

Study of impedance spectroscopy proves that there exists no phase transition in CCTO material [95]. The origin of both the semi conductivity of the grains and the insulation is still to be discussed. The semi conductivity may possibly arise from the small loss of oxygen from the ceramics at high temperatures or from the intrinsic semi conductivity of the grains in case they are oxygen stoichiometric. The larger resistance of boundary layer, in the same way, is explained either by an intrinsic behavior of the boundary layers or by the oxygen-loss that induced insulating barriers in the ceramic. It is still unclear that which one of the two interpretations is correct so far.

The properties like high dielectric constant and loss of CaCu$_3$Ti$_4$O$_{12}$ depend upon the particle size and powder morphology [91]. The particle size and powder morphology of CaCu$_3$Ti$_4$O$_{12}$ depend on processing parameters namely temperature, heating rate, duration and atmosphere. Several Powder synthesis processes [96 - 101] have been tried for the synthesis of CaCu$_3$Ti$_4$O$_{12}$ among which
sol-gel process have enough emphasis now a days. CaCu₃Ti₄O₁₂ synthesized using sol-gel synthesis technique [19, 22] possesses high purity and close control of powder morphology, which will result in the desired microstructure and dielectric behavior.

Under this context, the present study was carried out to evaluate the effect of different processing parameters on the phase purity, particle size, and powder morphology of CaCu₃Ti₄O₁₂ and to study their effects on microstructure, sintering characteristics and the dielectric behavior of CaCu₃Ti₄O₁₂. The optimization of process parameters was based on the phase purity, crystallite size and density upon sintering time, grain size and density. Dielectric property increases with the increase in sintering time and density. Two main features are needed for any dielectric material in practical applications: high dielectric constant and low dielectric loss. An attempt has also been made to study the effect of cobalt, erbium, and zirconium addition on the properties of CCTO ceramics.

2.2 HISTORICAL DEVELOPMENT

The titanate compound CaCu₃Ti₄O₁₂ (CCTO) belongs to a family of the type, ACu₃Ti₄O₁₂ (where A = Ca or Cd) and has been reported in the year 1967 [102]. This composition has been extended [15] and the family of titanates with the body centered cubic (bcc) structure has been reported having the general formula, [AC₃] (B₄) O₁₂ (where A = Ca, Cd, Sr, Na or Th; B = Ti or (Ti+M5⁺), in which M = Ta, Sb or Nb; and C = Cu²⁺ or Mn³⁺). These solids have been synthesized by the ceramic methods and their accurate crystal structures (space group Im3, lattice parameter a=7.391 Å, and Z = 2) have been determined from the neutron diffraction data.

Several explanations have been provided for the origin of high dielectric constant for this solid. Accordingly, the giant dielectric constants may be attributed to: (i) the barrier layer capacitance arising at twin boundaries [91], (ii) disparity in
electrical properties between grain interiors and grain boundaries [95, 104, 105], (iii) space charge at the interfaces between the sample and the electrode contacts [106, 107], (iv) polarizability contributions from lattice distortions [108], (v) differences in electrical properties due to internal domains [109], (vi) dipolar contributions from oxygen vacancies [110, 111], (vii) the role of Cu off-stoichiometry in modifying the polarization mechanisms [112], (viii) cation disorder induced planar defects and associated inhomogeneity [113] or (ix) nanoscale disorder of Ca/Cu substitution giving rise to electronic contribution from the degenerate eg. States of Cu occupying the Ca site contributing to the high dielectric constant [114]. Although several explanations have been put forward, the actual mechanism of the origin of giant dielectric constants in CCTO is still debated as to whether it is intrinsic or extrinsic in nature.

CCTO has been prepared by the solid–solid reactions by stoichiometrically mixed starting materials of CaCO₃, TiO₂ and CuO. The mixtures are calcined at high temperature for long duration (typically 1000–1050 °C for 24-48hrs) with repeated intermediate grinding [95, 115-117]. This method of preparation is very cumbersome, often requiring temperatures approaching the melting point of CuO. Besides, this procedure suffers from the disadvantages of chemical inhomogeneity leading to coarse particle size for the product. In contrast, the wet chemical synthesis routes offer homogeneous products at lower temperatures in shorter duration. There exist a few research papers indicating that routes other than the solid-state reactions can prepare CCTO [19, 96, 118]. However, these methods [118, 119] are complex in nature by way of yielding multiphase products and required longer heat treatments to obtain the phase singularity. The powders prepared by the pyrolysis of the co-precipitated oxalates [120] at 900 °C for 10 h yielded CCTO with CaTiO₃+CuO as the impurity phases. The phase-pure CCTO was obtained only after sintering the powders at 1050 °C. To avoid such difficulties in obtaining phase-pure CCTO powders at relatively lower temperatures, presently developed a sol-gel route. This is a convenient method for achieving
chemical homogeneity, where the individual constituents intermix at the ionic level under controlled wet chemical conditions. The phase-pure CCTO nanoparticles have been realized from this sol-gel route.

2.3 STRUCTURE OF CaCu$_3$Ti$_4$O$_{12}$ (CCTO)

The structure of CaCu$_3$Ti$_4$O$_{12}$ is derived from the cubic perovskite (ABO$_3$) by an octahedral tilt distortion caused by size mismatch and the nature of the A cations. In CCTO, Ca$^{2+}$ is dodecahedrally coordinated by oxygen ions, while Cu$^{2+}$ is in square-planar coordination (oxygen as the nearest neighbor) and Ti$^{4+}$ coordinates six oxygen ions in a slightly distorted octahedron. The TiO$_6$ groups are tilted at about 20° with respect to the unit cell axis as shown in Fig.2.1 [112]. The crystal structure of CaCu$_3$Ti$_4$O$_{12}$ was further refined and found to remain centrosymmetric bcc over a wide range of temperatures.

![Structure of CaCu$_3$Ti$_4$O$_{12}$](image)

**Fig.2.1:** Structure of CaCu$_3$Ti$_4$O$_{12}$ shown as TiO$_6$ octahedral, Cu atoms bonded to four oxygen atoms, and large Ca atoms without bonds.

2.4 VARIOUS SYNTHESIS TECHNIQUES OF CaCu$_3$Ti$_4$O$_{12}$

Jianjun Liu et al., [98] had reported synthesis of fine crystalline CaCu$_3$Ti$_4$O$_{12}$ powder using wet chemistry method at relatively low temperatures
and a shorter reaction time. The phase pure sample was obtained when the precursor powder is calcined at 800 °C for 0.5 hrs. This method starts 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 obtained by solid-state reactions. In this method, the metal oxides are formed in the first heat-treatment step and CCTO is produced by a subsequent solid-state reaction. The samples sintered at 1030 °C for 4hrs have homogeneous grain size distribution in the range of 0.4–1.5 μm.

Chivalrat Masingboon et al., [99] have synthesized nano-sized powders of CaCu$_3$Ti$_4$O$_{12}$ by a polymerized complex method followed by calcination in the temperature range of 600-800 °C in air for 8hrs. The diameter of the synthesized powders ranges from 30 to 100 nm. Sintering of the powders was conducted in air at 1100 °C for 16 hrs. The XRD study revealed that all sintered samples have a typical perovskite CaCu$_3$Ti$_4$O$_{12}$ structure with some amount of CaTiO$_3$ and CuO. SEM micrographs of the sintered CaCu$_3$Ti$_4$O$_{12}$ ceramics have showed the average grain size of 10–15 μm. The samples exhibit a giant dielectric constant of 10,000–20,000. This method is found useful due to its relative simplicity CaCu$_3$Ti$_4$O$_{12}$ and usefulness for obtaining a homogeneous and fine powder precursor. But this method is still relatively complex, and needs long heat-treatment time.

Jianjun Liu et al., [98] have also synthesized the giant-dielectric-constant material CCTO by pyrolyzing an organic solution containing stoichiometric amounts of the metal cations, at a lower temperature and a shorter reaction time than that for conventional solid-state reaction. Synthesis from a solution affords intimate and homogeneous mixing of the metal ions at the atomic scale, thus reducing the diffusion path length required. A shorter diffusion length reduces reaction time and lower temperatures. The particle size of the powders ranges from 200 to 400 nm. The sintered samples at 1050 °C for 4 hrs of the cold-pressed pellets
show grain size in the range of 2-3 μm. The samples exhibit a giant dielectric constant of 11,500. However, this method still has the disadvantage that it involves handling chemicals in a glove box and refluxing of solutions. [121]

Hongtao Yu et al., [100] have synthesized single-phase cubic perovskite CaCu$_3$Ti$_4$O$_{12}$ powders successfully by microwave heating with a relatively low energy consumption and short time, compared with conventional synthesis. This method is very clean and nonpolluting and resulted in better reaction yields. XRD study suggests the formation of phase pure CCTO powder on calcinations at 800 °C for 2 hrs. The room temperature relative dielectric constant of 21400 at 1 kHz has been reported at on sintering at 1100 °C for 3hrs.

Laijun Liu et al., [22] have synthesized the giant dielectric constant material CaCu$_3$Ti$_4$O$_{12}$ by sol–gel method using nitrate and alkoxide precursor. The phases, microstructures and impedance properties of final samples were characterized by XRD, 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. A sol–gel process has shown considerable advantages, including excellent chemical stoichiometry, compositional homogeneity and lower crystallization temperature due to the mixing of liquid precursors on the molecular level [122, 123] as compared with other techniques. Ion diffusing displacement is shortened in sol–gel process. The phase pure powders were obtained on calcination at 900 °C for 1hr. The dielectric constant of CCTO ceramics was found to be 35000 at 1 kHz in the sintered samples at 1060 °C for 48 hrs.
Shao et al., [124] have prepared CaCu$_3$Ti$_4$O$_{12}$ ceramics by the conventional solid state reaction method under various sintering temperatures from 1000 to 1120 °C at an interval of 10 °C. Microstructures and crystalline structures were examined by scanning electron microscopy and XRD, respectively. It has been reported that the morphology changes significantly with the sintering temperature. Ceramic specimens prepared by this method have a good polycrystalline structure in spite of the different microstructures. The dielectric permittivity was found to increase with the sintering temperature and is closely related to the polycrystalline microstructure, particularly to the grain size. This suffers from the disadvantages of inhomogeneity and it also requires repetitive grinding and firing at high temperatures and long reaction time.

Thomas et al., [125] have reported that the powders produced by the pyrolysis of the co-precipitated oxalates at 900 °C for 10hrs yielded CCTO with CaTiO$_3$+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 nanoparticles 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 CaCu$_3$(TiO$_4$)(C$_2$O$_4$)$_3$.9H$_2$O. The powders derived from the oxalate precursor showed excellent sinter ability, resulting in high-density ceramics which exhibited giant dielectric constant up to 40,000 (1 kHz) at 25 °C, accompanied by a low dielectric loss <0.07.

Julie J. Mohamed et al., [126] synthesized CaCu$_3$Ti$_4$O$_{12}$ by the solid state technique. The sample was calcined at 900 °C/12 hrs and sintered at 1050 °C/24 hrs. An increasing the sintering temperature enhanced the density and secondary
phase formation of Cu$_2$O. 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 dielectric constant of 33,210.

Barbier et al., [101] synthesized CCTO powders by a soft chemistry method (Co-precipitation method). The sintered pellets showed a high room temperature dielectric Constant roughly 1.4 × 10$^5$ and relatively small dielectric losses ($\tan \delta \sim 0.16$) at 1 kHz. The study suggests that the high dielectric constant observed in this material is not related to an interface (electrode material) related mechanism but due to an internal barrier layer capacitor (IBLC) type. The samples prepared from the powder was found to exhibit a bimodal grain size distribution, with small grains of about 20 µm and large grains of size ranging from 50 to 200 µm. It was also been investigated that the nature of the electrode contact has no influence on the dielectric permittivity and the loss values of CCTO pellets. The dielectric permittivity strongly depends on the sample diameter while the dielectric loss remains constant whatever the diameter values.

Ke-pi Chen et al., [127] synthesized CCTO powders by molten salt method. CaCu$_3$Ti$_4$O$_{12}$ ceramic powder by heating a stoichiometric amount of CaCO$_3$, CuO and TiO$_2$ in molten NaCl–KCl and Na$_2$SO$_4$–K$_2$SO$_4$, respectively. The synthesis temperature was decreased from 1000 °C (required by conventional solid-state reactions) to 750 °C for NaCl–KCl or to 850 °C for Na$_2$SO$_4$–K$_2$SO$_4$. The flux type has a larger influence on the phase compositions and morphology of the resultant powders than the synthesis temperature does. The dielectric constant of the resulting ceramics is more than 10$^4$ over the wide frequency range from 100Hz to 100 kHz. The dielectric loss tangent of the resulting ceramics is lower than 0.2 in the frequency range from 100 Hz to 100 kHz. The dielectric behavior of both samples is similar to the results obtained for CaCu$_3$Ti$_4$O$_{12}$ ceramics that were synthesized by the sol–gel method.
Combustion synthesis using metal nitrates as oxidants and different organic compounds such as citric acid, α-alanine, glycine, urea and semioxamazide are used as fuel, is a useful technique for synthesis of high purity nano materials [128-133]. The solution combustion method is based on the advantage of the exothermic, fast and self-sustaining chemical reaction between the metal nitrates and a suitable organic fuel. Particle size and powder morphology of the product can be optimized by varying the different process parameters during the synthesis. [96]

Jha et al., [118] used, a polymeric precursor consisting of citric acid and ethylene glycol which on subsequent heat treatments led to pure CaCu$_3$Ti$_4$O$_{12}$ at 1000 °C. On sintering further at 1000 °C (20hrs), the samples showed high density (98%) and the dielectric constant was found to be of the order of 3000 at 1 kHz. The dielectric loss was varied between 0.3 and 0.35 (till 100 kHz) beyond that it was found to increase sharply from 0.35 to 0.7 in the frequency range of 100-500 kHz. The dielectric constant was found to decrease with frequency. Micro structural study revealed that the grain size of the samples prepared from the polymeric citrate precursor route was much smaller (0.5-1.0 μm).

2.5 FACTORS AFFECTING THE PROPERTIES OF CCTO

Chih-Ming Wang et al., [97] studied the dielectric properties of polycrystalline CCTO samples sintered at 1100 °C with soak time ranging from 3 to 48 hrs prepared by conventional solid-state reaction technique. XRD study showed no obvious change in crystal phase with various sintering time. The micro structural 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.

Li et al., [134] studied the dielectric properties of polycrystalline CaCu$_3$Ti$_4$O$_{12}$ (CCTO) samples sintered at the temperature ranging from 1000 to 1200 °C with impedance spectroscopy at the 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 resistivity of these two polycrystalline CCTO samples. Further, it has been suggested that donor doping of oxygen vacancies Vo' and Vo'' may be the reason to cause the difference in the grain volume resistivity of these two samples.

The effect of processing parameters on the dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) was studied by Bender et al., [116]. CaCu$_3$Ti$_4$O$_{12}$ was prepared using conventional ceramic solid state reaction processing technique. Powders mixed using 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 permittivity close to 10$^5$ which are in the [95] 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 loss (0.014 to 0.98). Increasing sintering time also led to substantial improvement 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, the higher the effective dielectric constant but also the higher is the 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 are to be thin, uniform, and robust to prevent percolation of the conducting grains [135-137].

Seunghwa Kwon et al., [138] had investigated the effects of cation stoichiometry on the dielectric properties of CaCu$_{3-x}$Ti$_{4+y}$O$_{12}$ ($x = +0.06, 0, -0.06; y = +0.08, 0, -0.08$) with varying cation stoichiometry prepared via the conventional solid state synthesis methods. The XRD study revealed that both Cu- and Ti-excessive CCTO compositions showed the evidence of a Cu$_2$O phase (with a low permittivity $10^8$ in the interior regions of nonstoichiometric CCTO ceramics. In addition, a CuO phase was also observed on the outer surface layer on all compositions. It was proposed that these phases were formed through limited reoxidation of Cu$_2$O during cooling.

Adams et al., [139] have also reported that a Cu$_2$O peak (~36.5 °) was found on the surface of undoped CCTO sample after sintering at a slightly higher sintering temperature of 1115 °C. The study suggests that there might be a transition temperature where either CuO or Cu$_2$O secondary phase is favorable depending on sintering temperatures and times. In contrast, both Cu and Ti-deficient CCTO compositions showed [94] no secondary phases. Both Cu- and Ti-deficient CCTO showed higher dielectric constants than stoichiometric CCTO and larger dielectric losses than undoped CCTO. The lower dielectric constant is attributed due to the presence of the Cu$_2$O phase in both Cu- and Ti excessive CCTO compositions.

Microstructure and dielectric properties of CaCu$_{3-x}$Ti$_4$O$_{12-x}$ ($3 - x = 2.8$–3.05) ceramics have been studied by Kang-Min Kim et al., [140]. The XRD study showed that the powders ($\text{Cu/Ca} = 2.8$–3.05) heat-treated at 1140 °C for 12hrs 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 $\geq 2.95$ were slightly larger than the values for the CCTO powders with Cu/Ca $\leq 2.90$. The microstructure of the CuO-deficient CCTO specimen ($C_{2.80}, C_{2.85}, C_{2.90}$) sintered at
1140 °C for 12hrs showed uniform microstructure and no abnormal grain growth was found throughout the specimen and the average grain sizes were 4.7, 4.9, and 4.8 μm, respectively. However, CuO-enriched CCTO specimens sintered at 1140 °C for 12 hrs showed a coarse-grained microstructure. The micro structural evolution showed quite different behavior 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 [141-143] and the presence of an intergranular liquid phase [144-149]. TEM 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 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 dielectric constant apparent value was found to decrease in the liquid abundant at a lower frequency (f = 10¹–10⁴ Hz) while the samples with liquid-enriched specimen with little intergranular liquid shows a large dielectric constant apparent value even in the frequency range of 10³–10⁵ 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. [150]

Jing Yang et al., [151] have studied the electrode/sample contact effects on the dielectric properties of the CaCu₅Ti₄O₁₂ ceramics. It was suggested that the colossal dielectric constant in CCTO is related to 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, Sleight et al., [152] had suggested that the presence of internal resistive barriers in a crystal of the CaCu$_3$Ti$_4$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$^+$. On cooling, the Cu$^+$ would oxidize to Cu$^{2+}$ giving up an electron to the Ti 3d band. So the bulk phase in CCTO becomes conducting.

Shao et al., [121] had investigated the effect of Cu-stoichiometry on the dielectric and electric properties of CaCu$_{2+y}$Ti$_4$O$_{12}$ ($y = 0, \pm 0.025, \pm 0.05, \pm 0.1$ and $\pm 0.15$) ceramics prepared under various compositions by the conventional solid-state reaction method. XRD study showed that all of the compositions had the good polycrystalline structures. Micro structural 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. Any off stoichiometry will result in the decrease of low-frequency dielectric permittivity and
the increase of domain resistance. All the samples showed a very similar dielectric dispersion.

2.6 ROLE OF DOPING

The role of dopant on the electric and dielectric properties of the perovskite-type CaCu$_5$Ti$_4$O$_{12}$ (CCTO) compound is evidenced [153]. Impedance spectroscopy study showed [107] that the relevant permittivity value is attributed to sintered CCTO due to grain boundary (g.b.) effects. The g.b. permittivity value of the pure CCTO was found to be increased by 1-2 orders of magnitude by cation substitution on Ti site and/or segregation of CuO phase, while the bulk permittivity keeps values 90<K<180. Electrons were responsible for the charge transport and mean bulk activation energy of 0.07 eV was obtained at room temperature for all the samples studied. The g.b. activation energy ranges between 0.54 and 0.76 eV. A Defect models related to the transport properties has been proposed, supported by electron paramagnetic resonance study. The grain boundary permittivity value k, experiment roughly 3400 of pure CaCu$_5$Ti$_4$O$_{12}$ found to be significantly increased up to $\sim$15x$10^4$, by cation substitutions on Ti site and/or segregation of CuO phase while the bulk permittivity keeps values 90<r<180, typical of many perovskitic compounds. It has been reported that a 2% substitution of Mn on Cu site results the decrease in permittivity value to about 100 in the temperature range 300 – 4.2 K [154]. It has been observed that cationic substitutions and CuO presence weakly influence the bulk specific capacitance, but Cgb increases with increasing CuO. It is also evident that the highest Capacitance grain boundary (Cgb) value does not occur in the samples containing highest CuO wt %.

The CuO residual phase increases the Cgb values possibly because of its segregation at the boundary, so contributing to an increase of disorder in that region. It has been suggested that only Cu deficiency causes a significant lowering of permittivity value with decreasing the Cu content in CCTO [112]. It has been observed that La 2%, V 2% and Cr 2% substitutions does not influence significantly
Cgb with respect to the pure CCTO. Other substitutions show significant changes, in particular the greatest effect was obtained by substituting Fe, Co and Ni although CuO impurity phase was detected in the samples. Indeed, some kind of cationic substitution in CCTO can deeply modify the grain surface so creating high efficiency (capacitive) dielectric layers. It is observed that the lattice parameters depend both on [16] doping ion and its amount, while the bond length shows only minor variation. This study suggests that grain boundary effects are responsible for the giant dielectric permittivity.