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Abstract

Novel energy materials possessing both high power density and high energy density have been constantly pursued with the development in sustainable energy industry. Dielectric capacitor is very efficient in offering high power density but its limited energy density from dielectric material impedes the further application for energy storage. CaCu$_3$Ti$_4$O$_{12}$ (CCTO) dielectric shows considerable potential for capacitive energy storage due to its giant dielectric constant and excellent temperature independence comparing with traditional ferroelectric ceramics. However, the dielectric property of CCTO is extrinsically originated and strongly related to preparation conditions. Furthermore, the breakdown voltage of CCTO is relatively low, which is undesirable for capacitive energy storage. Therefore, this thesis research is focuses on the synthesis and characterization of CCTO materials and CCTO-polymeric (polyvinylidene fluorides, PVDF) composites, in an effort to develop a new material system for high density energy storage.

A systematical in situ study of the high temperature phase evolution of CCTO solid state and sol-gel precursors was carried out via synchrotron X-ray powder diffraction. We found that the onset temperature for the CCTO phase formation is 800°C in the sol-gel precursor, lower than that in the solid state precursor (875°C). Intermediate phases were only observed in the sol-gel precursor. Both precursors are able to be treated to sub-micron sized powders by fast calcination. The phase formation sequence and mechanism during calcination are proposed. For the first time, the real time phase and lattice parameter evolution of CCTO upon sintering in ambient atmosphere is studied. It has been demonstrated that the Cu ions are not stable in CCTO structure during sintering, and lead to the formation of CuO secondary phase which precipitate at the grain boundaries. The Cu ions instability is the ultimate mechanism for the formation of the internal barrier layer capacitor structure in CCTO and therefore responsible for the giant dielectric constant.

In order to synthesize homogeneous CCTO fine powders, CCTO sol-gel precursors were selected and calcined by using microwave radiation for the first time. 89.1 wt.% CCTO was achieved from the sol-gel precursor by microwave heating, using only 17 min at 950°C. In
contrast, conventional calcination method required 3 h to generate 87.6 wt.% CCTO content at 1100°C. In addition, the CCTO powders prepared through 17 min microwave calcination exhibited a small particle size distribution. A lengthy hold time of 1 h by microwave sintering is required to obtain high dielectric constant (3.14×10³ at 1×10² Hz) and reasonably low dielectric loss (0.161) in the sintered CCTO. The dielectric response of the sintered CCTO samples is attributed to the space charge polarization and IBLC effect.

TiO₂ modified CCTO has been synthesized via a facile sol-gel precipitation process followed by solid state sintering. The morphology and chemistry of grain boundaries of CCTO were significantly tailored by TiO₂ modification, resulting in enhanced barrier layer capacitor effect. The formation mechanism of barrier layers based on the instability of Cu ions has been discussed. A new bimodal brick layer mechanism has been proposed. The optimized TiO₂ modified CCTO sample exhibits stable dielectric permittivity which is twice as high as the unmodified one, and shows relatively low dielectric loss from 10² Hz to 10⁵ Hz.

CCTO-PVDF composites were prepared by simple melt blending and hot molding techniques. The addition of CCTO remarkably enhanced the dielectric properties and thermal conductivity of PVDF composites, while the melting point of the PVDF composites (~170°C) was almost independent of the CCTO concentration. Based on the results of dielectric constant and dielectric breakdown voltage, the PVDF composite containing 40 vol.% CCTO fillers shows the optimized capacitive energy storage potential (7.81 J/cm³).

PVDF with β-SiC-CCTO hybrid fillers were also prepared. Results show that hybrid loading is preferred to achieve a reasonable combination of thermal conductivity (0.80 W·m⁻¹·K⁻¹), dielectric constant (~50) and dielectric loss (~0.07) at 10³ Hz in the composite containing 40 vol.% CCTO and 10 vol.% β-SiC. The strong dipolar and interfacial polarization are account for the enhancement of the dielectric constant, while the formation of thermally conductive networks/chains by β-SiC whiskers contribute to the improved thermal conductivity. However, the introduction of β-SiC whiskers into 40 vol.%-CCTO-PVDF binary composite could reduce the breakdown voltage. Composite with 40 vol.% singular CCTO addition still shows the optimal breakdown voltage of 22.58 kV/mm among composites while pure PVDF shows a value of 40.21 kV/mm.
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<tr>
<td>$\varepsilon$</td>
<td>Permittivity (F/m)</td>
<td>BT</td>
<td>BaTiO$_3$</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of vacuum (F/m)</td>
<td>PZT</td>
<td>Pb[Zr,Ti]O$_3$</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity (Dielectric constant)</td>
<td>LTNO</td>
<td>Li, Ti co-doped NiO</td>
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<tr>
<td>$\varepsilon_{eff}$</td>
<td>Effective dielectric constant of composite</td>
<td>PMN</td>
<td>Pb[Mg$<em>{1/3}$Nb$</em>{2/3}$]O$_3$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Energy density (J·cm$^{-3}$)</td>
<td>PMNT</td>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)O$_3$-PbTiO$_3$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity (W·m$^{-1}$·K$^{-1}$)</td>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance (Farad, F)</td>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>$E_b$</td>
<td>Breakdown voltage (kV/mm)</td>
<td>(E)SEM</td>
<td>(Environmental) Scanning electron microscope</td>
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<tr>
<td>CCTO</td>
<td>CaCu$_3$Ti$<em>4$O$</em>{12}$</td>
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<tr>
<td>PVDF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>IBLC</td>
<td>Internal Barrier Layer Capacitor</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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### CO-AUTHORS

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<td>He helped analyse the TEM results.</td>
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<tr>
<td>Zhaohui Huang</td>
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<tr>
<td>Weijun Zhang/Wei Gao</td>
<td>They conceived the experiments, and supervised the experiments, discussion and writing.</td>
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The content of Chapter 6 (Pages 91-98) is published as ‘CaCu3Ti4O12–PVDF polymeric composites with enhanced capacitive energy density’ at International Journal of Modern Physics B, 29 (2015) 1540003

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Chapter 1. Introduction

1.1 Motivation

Electrical energy is of great importance in modern era. Storage of electricity plays a critical role in the development of renewable energy industry including photovoltaic and wind energies. Batteries and capacitors are the two most important devices to store and supply electrical energy in various applications. A ‘Ragone plot’ (Figure 1.1) reveals the energy density and power density of different storage devices [1].

![Ragone plot](image.png)

Figure 1.1 Comparison of the power density and energy density for batteries, capacitors, and fuel cells [1].

Comparing with batteries which can store a large amount of chemical energy and offer electricity for a long period of time, dielectric capacitor shows huge power density which supports fast charging and discharging. Additionally, dielectric capacitor has high cycling efficiency and long calendar life without any chemical pollution, and it is usable in wide temperature range, especially at very low temperatures. Therefore, dielectric capacitor can be
used for power conversion purpose in many fields, for instance, computers, cell phones, hybrid electric vehicles and trains, medical devices, and even pulsed power weapons. However, the current generation of dielectric capacitors falls short of the requirement for energy density (> 30 J/cm³) and operational voltage (> 10 kV) [2]. Meanwhile, the appetite for storing electricity in the smallest possible volume never stops growing. Hence, it is critically important to improve the energy density of current dielectric materials and to develop new dielectric materials with high energy density.

1.2 Introductory perspective

1.2.1 Principles of capacitor and capacitive energy storage

A dielectric capacitor is a passive electrical component which can be used in an electric field to store and release electrical charge by the polarization and depolarization process of a dielectric material. Figure 1.2 shows the basic configuration of a dielectric capacitor consisting of two terminal conducting plates and a dielectric material.

![Figure 1.2 The basic configuration of a capacitor.](image)

For a parallel dielectric capacitor with surface area $A$ and thickness $d$, the ability to store electrical charge, capacitance ($C$), can be expressed as
\[ C = \frac{\varepsilon_r \varepsilon_0 A}{d} \] (Farads) \tag{Eq. 1.1} 

where \( \varepsilon_r \) is the relative permittivity (dielectric constant) of the dielectric material, and \( \varepsilon_0 \) is the real permittivity of vacuum (~8.855 \times 10^{-12} \text{ F/m})

According to Eq. 1.1, large surface area and thin dielectric material are favorable for high capacitance. In practice, capacitors are often made into multi-layered structure with very thin (~\( \mu \text{m} \)) dielectric material. Meanwhile, the larger the dielectric constant, the more electrical charge can be stored by the capacitor in a given field. Thus, dielectric material with high dielectric constant offers great electrical energy storage potential.

The overall energy \( (U) \) that a capacitor can store under a given voltage \( (V) \) can be calculated by Eq. 1.2 below [3].

\[ U = \frac{1}{2} CV^2 \tag{Eq. 1.2} \]

Thus, the energy density \( (\eta, \text{ J/cm}^3) \) can be deduced from Eq. 1.1 and Eq. 1.2, when given that the electrical field \( E = V/d \), and volume = \( A \cdot d \).

\[ \eta = \frac{u}{volume} = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 \tag{Eq. 1.3} \]

Eq. 1.3 shows that the energy density of a dielectric capacitor is limited by the dielectric constant of the dielectric material \( \varepsilon_r \) and the maximum applied electric field (i.e., dielectric breakdown voltage of the dielectric material, \( E_b \)). It can also be seen that compared to the dielectric constant \( (\varepsilon) \), breakdown voltage is more influential on the energy density as \( E_b \) shows square relation with \( \eta \), while \( \varepsilon_r \) only has linear relation with \( \eta \). But a high dielectric constant is still important to achieve useful capacitance values (e.g., tens of nF) in devices.

Although much efforts have been made to the electrochemical (super) capacitors, their power density and energy density are still limited due to the moderate mass transfer and faradaic reactions [4]. In addition, electrochemical processes usually have complex configuration and low operation voltage, high leakage current and limited cycling life. Therefore, to improve the energy density of dielectric capacitors becomes very appealing. To achieve the desirable energy density in a dielectric capacitor, challenges still remain for simultaneously obtaining high dielectric constant and high breakdown voltage, as well as maintaining the low dielectric loss.
1.2.2 Dielectrics for capacitive energy storage

Dielectrics are a critical part to capacitors as the dielectric materials define the energy density and electrical behaviors. There are many types of dielectric materials, e.g. solids, liquids, or even gases. Solid ceramics are the focus in the present study due to their high dielectric constant and excellent temperature stability.

Depending on different purposes, ceramic dielectrics can be divided into two groups in principle; one group offers high stability and low loss but often with relatively low dielectric constant, while the other is to offer high volumetric efficiency (high electrical energy storing potential) and often with very high dielectric constant. For example, dielectric materials with very low dielectric constant are typically used for integrated circuit (IC) devices particularly for ultra-large scale integration (ULSI) and high speed IC packaging. On the other hand, dielectric materials with very high dielectric constant are favorable for high speed dynamic random access memories (DRAMs).

Mica and titanium dioxide (TiO₂) are traditional dielectric ceramics but are limited due to their low dielectric constant. One important category with high dielectric constant is the ferroelectric ceramics, which are widely used in modern electronics. Ferroelectric ceramics are featured by a ferro-to-paraelectric transition at Curie temperature, at which their dielectric constant reaches maximum. Another important characteristic of ferroelectric ceramics is the polar axis along which there is spontaneous polarization, deriving from the displacement of positive and negative centers of charge of the ions in the structure.

Typical ferroelectric ceramics include barium titanate (BaTiO₃, BT), lead magnesium niobate (Pb(Mg₁/₃Nb₂/₃)O₃, PMN), lead zirconate titanate (Pb[Zr,Ti]O₃, PZT). Specifically, the discovery of BT during World War II is a breakthrough to replace mica materials in capacitors. The original study was dealing with the doping of TiO₂ by BaO, but it has been found that the dielectric constant of the doping resultant, BT, has a value of ~1000, ten times higher than any other ceramic known at that time. Even after seventy years, BT is still the most important multilayer ceramic dielectric material.

In the last decade, other ceramic materials such as Li, Ti co-doped NiO (LTNO) and CaCu₃Ti₄O₁₂ (CCTO) have also been reported to possess very high dielectric constants. Table
1.1 shows the dielectric constants of several ceramic candidates. The test condition is at about 1 kHz and room temperature. Several of them show very high dielectric constants \((>10^4)\) according to Table 1.1.

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<td>Al\textsubscript{2}O\textsubscript{3} [5]</td>
<td>~10</td>
<td>PZT [7]</td>
<td>~1\times10^3</td>
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<tr>
<td>TiO\textsubscript{2} [8]</td>
<td>~80</td>
<td>LTNO [9]</td>
<td>~2\times10^4</td>
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Much recently, extensive research interests have been put to CaCu\textsubscript{3}Ti\textsubscript{4}O\textsubscript{12} (CCTO) because its dielectric constant shows the unparalleled stability over wide range of frequency \((10^{2} - 10^{6} \text{ Hz})\) and temperature \((100 - 600 \text{ K})\) [12], while the ferroelectric ceramics often show strong nonlinear electrical behavior around Curie temperature with phase transition. Although the origin of CCTO’s giant dielectric constant is not fully comprehended, it has proved to be extrinsic, i.e. the high dielectric constant comes from the internal barrier layer capacitor (IBLC) effect [13]. Researchers are optimistic about that CCTO, the new material, will challenge the dominancy and take place of barium titanate based dielectrics over various microelectronic applications [14]. However, ceramic dielectrics have common drawbacks including brittleness, high density, high sintering temperature and difficult processing conditions. Most importantly, dielectric ceramics usually have low inherent dielectric breakdown voltages which would lead to sudden failure during operation when subject to high electric fields [15].

In response to the problems associated with ceramics, attention has been shifted to polymer materials which show the merit of high dielectric breakdown voltages, low leakage
currents, and excellent processing flexibility [16]. One straightforward strategy is to use polymer as matrix and ceramic as fillers, at a suitable ratio, to make composite with desirable dielectric properties, i.e. high dielectric constant and large breakdown voltage. Particularly, several studies show that a polymeric material, polyvinylidene fluoride (PVDF) has the promising potential for electrical energy storage [17, 18].

It has also been suggested that the addition of nanometer or sub-micrometer sized ceramic fillers with high dielectric constant into polymeric matrix could significantly enhance the effective dielectric constant while maintaining high breakdown electric field, thereby achieving high energy density in the composite materials [19, 20]. However, further studies on the compatibility and homogeneity is still necessary in order to better understand the factors that governing the dielectric constant and breakdown voltage, and to further optimize the dielectric properties of these composites.

1.3 Summary

Capacitors are important devices that can be used for electrical energy storage. Looking to the future, capacitors with excellent flexibility and adaptability will have broad applications, such as microsecond to fractional second electrical energy storage, pulsed power supply, filtering/smoothing devices, and power conditioning equipment [21]. To use capacitors in massive electrical energy storage, the major challenge ahead is to improve the energy storage density by developing new dielectric materials. Based on the idea of ‘1+1 > 2’, high dielectric constant and large breakdown strength are expected to come from in CCTO-PVDF dielectric composites to achieve high energy storage density.
2.1 Introduction to CaCu$_3$Ti$_4$O$_{12}$

2.1.1 Background

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has a perovskite-related ($ABO_3$) structure (Figure 2.1); the black Cu$^{2+}$ atoms are sitting at $A$ sites and sharing the corner ‘O’ with the tilted TiO$_6$ octahedrons to form the CuO$_4$ planes. The gray Ca atoms have no bond and locate at the cubic center. The structure belongs to the centro-symmetric space group $Im3$ down to 35 K.

Following the sensational discovery by Subramanian et al, CCTO starts to draw massive attention from scientific community due to its extremely high dielectric constant ($10^4$-$10^5$) with very small temperature (100 – 600 K) and frequency ($10^2$ – $10^6$ Hz) variation [11, 22]. Specifically, the dielectric constant of CCTO can reach up to $\sim$280,000 in polycrystalline ceramic and $\sim$100,000 in single crystals [13, 23].

In ceramic dielectrics with perovskite structure, a value of dielectric constant higher than 1,000 is usually attributed to the relaxor or ferroelectric behaviors which is susceptible to temperature, especially around Curie temperature ($T_c$). For example, the crystal structure of BaTiO$_3$ changes from cubic to tetragonal at $\sim$120°C ($T_c$), then to orthorhombic at 0°C, and lastly to rhombohedra at $\sim$90°C [24]. Those structural changes are always accompanied by the sudden change of dielectric properties, which is highly undesirable for device applications.

In comparison, the perovskite-derivative CCTO shows stable structure and dielectric constant over broad range of temperatures. Even when its dielectric constant exhibits a 1000-fold reduction below 100 K, there is still no detectable long-range structural change in CCTO by high resolution X-ray and neutron powder diffraction [11, 12]. Meanwhile, CCTO has no potential lead (Pb) pollution comparing with the traditional Pb-containing perovskite compounds. Based on the above advantages, CCTO is appealing for practical application and
has been considered the future dielectric material in microelectronics.

![A schematic diagram showing the crystal structure of CaCu₃Ti₄O₁₂](image)

Figure 2.1 A schematic diagram showing the crystal structure of CaCu₃Ti₄O₁₂ [25].

In addition to its giant dielectric response, CCTO shows remarkably strong nonlinear current-voltage behavior without the addition of any dopant. Chung et al reported that the nonlinear coefficient of CCTO can reach a value of 900 which is greater than the common varistor, ZnO [26, 27]. Several studies have also proved that CCTO nanostructures have good resistive-switching and gas sensing (H₂) properties [28, 29]. Thus, CCTO has also been considered a good candidate for switching and gas sensing applications.

### 2.1.2 Origin of the giant dielectric constant

It should be pointed out that the intrinsic dielectric constant of CCTO is only 40 – 50
calculated by the polarization capability of its constituent atoms [30, 31]. Based on this result, the huge value of dielectric constant (~10^5) in the non-ferroelectric and non-relaxor CCTO material is completely unusual. Extensive efforts have been made to fully understand the original polarization behind, because it is of great scientific importance as well as the usefulness for designing new materials in the future.

Many models have been proposed, for example, structurally frustrated ferroelectric relaxors (intrinsic mechanism), Schottky barriers (extrinsic mechanism), grain boundary barrier layer capacitor effect in polycrystalline CCTO, and nano domain structures or twin boundaries in single crystal. Nevertheless, so far the origin of this giant dielectric constant is still open to debate.

2.1.2.1 Intrinsic mechanism – frustrated ferroelectric relaxors model

In this model, CCTO is described as a structurally frustrated relaxor ferroelectric. Withers et al [32] have reported the observation of highly structured diffuse intensity distribution in CCTO along <001> columns direction (as shown in Figure 2.2), and claimed that such diffuse intensity must be associated with an one-dimensional displacement along the same direction, i.e. <001> columns of TiO_6 octahedra.

In traditional displacive ferroelectric like BaTiO₃, the high dielectric constant originates from the three-dimensional correlated shifts of Ti ions off the centers of the octahedral O₆ cages by ~0.1 Å along <001> direction. In CCTO, for comparison, the simulated result shows that the local displacement of Ti along <001> is 0.04 Å, and 0.07 Å along <111> direction, which supports the point that intrinsic incipient ferroelectric behavior does exist in CCTO. However, the Ti displacements in CCTO are not long-range ordered (i.e. connecting from column to column) due to the significant tilting of the TiO₆ octahedra.

The reason why CCTO does not show a typical ferroelectric phase transform at a certain temperature (even at a very low temperature of 100 K) is considered that the displacement of Ti ions is dynamic [22], and the whole <001> columns of Ti ions could not simultaneously change the polarization direction in a rigid octahedral frameworks. This is called structurally frustrated relaxor ferroelectric and hence prevents CCTO from showing ferroelectricity. The
authors have also pointed out that the extrinsic reasons cannot be ruled out, although they believe the displacement of Ti ions is the major reason.

2.1.2.2 Extrinsic mechanism – barrier layer capacitor model

It appears that the dielectric property of CCTO is intrinsic, because that the large dielectric constant could be obtained in CCTO single crystal, polycrystalline ceramic and thin film regardless of the synthesis and processing routes. However, after careful examinations by high resolution X-ray diffraction, neutron diffraction and impedance spectroscopy [11, 14, 22], it has been gradually realized that the mechanism behind is attributed to extrinsic factors, such as barrier layer capacitor effect [33].
Currently, the internal barrier layer capacitor (IBLC) model, consisting of insulating grain boundaries coupled with semiconducting grains, is the most accepted extrinsic mechanism to interpret the giant dielectric response in CCTO. Traditionally, IBLC is a sophisticated structure (grains-grain boundaries) that deliberately prepared in several ATiO\textsubscript{3} (A = Ca, Sr, and Ba) dielectrics in order to achieve high dielectric constant [35]. However, none of those titanates could show dielectric constant as high as CCTO. Taking this into consideration, it implies that the internal barrier in CCTO may not just in-between but inside the grains, which features the nano-domain structure [36, 37]. As such, IBLC could explain the giant dielectric constant both in polycrystalline and single crystal CCTO.

Figure 2.3 shows a schematic diagram of the internal barrier layer capacitor (IBLC) structure in CCTO. Those grey cubes stands for the semiconducting grains which surrounded by the insulating grain boundaries (colorless areas). Given an electric field, a substantial amount of electrical charge would accumulate at the interfaces of grain and grain boundaries due to the IBLC effect. Thus, the overall dielectric response would be significantly enhanced by such a unique structural configuration.

However, the emergence of sophisticated IBLC structure in CCTO is unexpected by a
simple step sintering in ambient atmosphere, which has drawn wide attention. A commonly accepted explanation is proposed based on the Cu ion instability within CCTO structure.

As stated previously, the body-centered cubic CCTO is structurally composed of TiO$_6$ octahedra framework, with CuO$_4$ square planes sharing corner oxygen and Ca atoms having no bonds. It is assumed that during sintering, Cu$^{2+}$ could be reduced to Cu$^+$ upon heating. Owing to the flexibility of perovskite structure, this valence reduction could be compensated by slight substitution of Ti$^{4+}$ onto Cu site. Upon cooling, the Cu$^+$ would reverse back to Cu$^{2+}$ and offer an electron to Ti 3d conduction band [38]. This supposition can be summarized into the following equations.

\[ \text{Eq. 2.1} \quad 3\text{Cu}^{2+} \xrightarrow{\text{heating}} 2\text{Cu}^+ + \text{Ti}^{4+} \]

\[ \text{Eq. 2.2} \quad \text{Cu}^+ + \text{Ti}^{4+} \xrightarrow{\text{cooling}} \text{Cu}^{2+} + \text{Ti}^{3+} \]

Hence, the resultant shows a general formula of \[ Ca(Cu_{2-x}^{2+}Ti_x^{4+})_5(Ti_{4-6x}^{4+}Ti_{6x}^{3+})_{O_{12}}, \]
where Ti$^{3+}$ stands for the electrons in Ti 3d band [39]. It is claimed that even an \( x \) value of less than 0.0001 can result in highly compositional and structural inhomogeneity in CCTO, and pose significant influence on the formation of IBLC. Several studies have attempted to provide supportive evidence for this supposition [34, 40]. Both simulated Cu$^+$ peaks and Cu rich secondary phase at grain boundaries could be identified in sintered CCTO.

Nevertheless, lack of \textit{in situ} information on high temperature structural evolution puts some doubt on the above supposition. CCTO usually needs multi-step calcination to achieve pure phase [41], so the minor phases (CuO$_x$) could be the undetectable remains from the incomplete solid state reaction during preparation, rather than Cu reduction and re-oxidation during sintering. The fundamental questions, how IBLC structure forms and why it is unique in CCTO, are remain to be answered. Further investigation is necessary to fully comprehend this mechanism.

2.1.2.3 Planar defects model

The planar defect model is used to explain the giant dielectric constant in single crystal CCTO, because according to IBLC mechanism, it requires that the barriers should exist in the
forms of planar defects or twin boundaries within a single crystal.

Whangbo and Subramanian have hypothesized that the structural defects in CCTO derive from the twinning are parallel to the (100), (010), and (001) planes [30]. Figure 2.4 shows the projection view of the perfect crystal arrangement of CCTO along (001) crystallographic direction. When divided by the horizontal blue line, (100) plane, a twinning with two surfaces is introduced. If one of the surfaces rotates by 90°, then the simplest plane defect appears.

![Figure 2.4 Projection view of the crystal structure of CCTO. The red, yellow, blue, and white circles represent the Cu, Ca, Ti, and O atoms, respectively [30].](image)

There are several basic units of the plane defects, e.g. CuO$_4$ square planes with Cu$^{2+}$ ions, CuO$_4$ pseudo-tetrahedra and bent CuO$_2$ units with Cu$^+$ ions, and TiO$_5$ square pyramids with Ti$^{4+}$ and Ti$^{3+}$ ions. These defects contain Cu$^+$, Ti$^{3+}$ ions and $V_O$ (oxygen vacancies), and can cause crystal structure disorders which are less conducting than the bulk, and thus create a new form of internal barrier layers. The high conductivity of the bulk CCTO, on the other hand, comes from the hopping of the localized electrons at the Cu$^{2+}$ sites. Therefore, the plane defect model provides an explanation for the giant dielectric constants in CCTO, not only for
single crystal, but also applicable to polycrystalline ceramic.

### 2.1.2.4 Nano domains

The model of nano domains has been proposed by Fang et al [36, 42] based on the speculations that a) both single crystal and the polycrystalline should have the same dielectric response mechanism, and b) sufficient evidences support that the internal barriers are responsible for the giant dielectric constant in CCTO. The nano domains model consisting of conductive domains and insulating domain boundaries is illustrated in Figure 2.5.

![Nano domains model showing the internal domains/domain boundaries in CCTO [36].](image)

It is suggested that those domain boundaries, including the lattice mismatch and chemical ordering, exist between strained and unstrained domains. The strained domains are constructed by various dimensional superlattices, shown in Figure 2.6.

A brick-layer model could be used to well depict the influence of nano domains on the final dielectric response of CCTO. The brick-layer model is described as [43]:

$$\varepsilon = \frac{\varepsilon_d t_d}{t_{db}}$$

Eq. 2.3

where $\varepsilon$ and $\varepsilon_d$ is the dielectric constant of the barrier layer structure and the domain boundary, while $t_d$ and $t_{db}$ is the thickness of domain and domain boundary. Based on the
observation that the domain size is about 0.2~0.5 μm, the domain boundary is about 0.2~1 nm, and the value of $\varepsilon_{d}$ is about 100, the calculated $\varepsilon$ would be about $10^4$~$10^5$ which is consistent with the experimental findings. Therefore, the nano domains model can explain the giant dielectric response both for single- and poly-crystalline CCTO.

![HRTEM images](image)

Figure 2.6 HRTEM images of (a) the grain interior with intertwined dark and bright domains, (b) dark domains possess a finer structure in CCTO sintered at 1065 °C for 20 h [36].

Other extrinsic factors such as the electrode/CCTO interface effect has also been studied in order to find explanation for the giant dielectric constant in epitaxial thin films where no internal boundaries present [44, 45]. This assumption is based on the evidence that the $I-V$ curve of CCTO film is nonlinear, asymmetric, and unsaturated on both reverse and forward directions. Since there is no grain boundary exists in thin film CCTO, the reason can only be attributed to the metal-semiconductor contact effect between the thin film and the electrodes.

In summary, the unique internal barrier layer capacitor (IBLC) structure is the primary cause for the giant dielectric constant in CCTO. However, the fundamental origin of the formation of this IBLC structure is still unclear. Further in situ investigation is necessary to clarify this question.
2.1.3 Influencing factors of dielectric properties in CaCu$_3$Ti$_4$O$_{12}$

As the dielectric properties of CCTO are closely related to IBLC structure which is extrinsic and sensitive to processing conditions [46], it is necessary to summarize the factors that would influence the final dielectric properties of CCTO.

2.1.3.1 Grain size

![SEM images of the surface of CCTO pellets sintered at 1000 °C for 20 h [47].](image)

Grain size is believed to be one of the critical factors that determine the dielectric response in CCTO. Several studies show that larger grains would lead to higher dielectric constant in CCTO [47, 48]. As shown in Figure 2.7, sample c has the mean grain size of 4.1±1.8 μm, while samples a and b show a similar grain size (1.2±0.4 μm). Comparing the dielectric constant, a and b have very similar value of dielectric constant although they show different density (71% for a, 81% for b). Sample c exhibits a dielectric constant of ~9000, 4 times higher than that of sample a, which is proportional to the ratio of grain size between c and a. Similar results and conclusion are obtained in other investigations [13].
In particular, an analytical model proposed by Pan et al [49] also suggests that the dielectric constant of CCTO would demonstrate a monotonically increase with increasing grain size, because large grains can have enhanced IBLC effect (especially well-developed domain structure). The influence of sintering time is considered as the same as grain size, because long sintering time would result in more ripened grain structure.

2.1.3.2 Grain boundary

![Figure 2.8 TEM image of a grain boundary in the 24 h-sintered CCTO [50].](image)

As the critical element of IBLC structure, grain boundaries play a very important role in the dielectric behavior of CCTO. Similarly, the brick-layer model could be applied to illustrate the influences of grain boundaries as well,

\[ \varepsilon = \frac{\varepsilon_{gb} t_g}{t_{gb}} \]  

Eq. 2.4

where \( \varepsilon \) and \( \varepsilon_{gb} \) are respectively the dielectric constant of the barrier layer structure and the grain boundary, and \( t_g \) is the average grain size, while \( t_{gb} \) is the average thickness of grain boundary. As such, large grains coupled with thin grain boundaries are most favorable to
achieve high dielectric constant. In CCTO ceramics, the grain boundary is typically few nanometers, as shown in Figure 2.8. The coarse-grained CCTO with thinner grain boundaries show higher dielectric constant than that with thicker grain boundaries [50].

2.1.3.3 Sintering atmosphere

Several studies have investigated the effect of the sintering atmosphere on dielectric properties of CCTO. Bueno et al reported a dielectric constant of 46000 in CCTO if sintered in O$_2$-rich atmosphere, 5 times higher than that sintered in ambient atmosphere. Meanwhile, CCTO shows a colossal value of 50000 if quenched from high temperature. It is considered that massive ‘active’ domains can be produced with high O$_2$ partial pressure and fast cooling.

However, another study shows quite opposite outcomes. CCTO sintered in pure O$_2$ atmosphere shows drastic decrease in dielectric constant than ambient-sintered one. Because the grain boundaries are very susceptible to the processing conditions, and under pure O$_2$ atmosphere, the grain boundary resistance and activation energy increase substantially, thereby resulting in depressed dielectric constant.

Other atmospheres like N$_2$ can also influence the grain boundary resistance ($R_{gb}$). Adams et al have found that the $R_{gb}$ of CCTO can decrease by several orders of magnitude after heat treated in N$_2$ at 800~1000°C. In addition, they suggest CCTO is thermally unstable at elevated temperature under N$_2$ atmosphere.

In short, giant dielectric constant can be obtained in CCTO under ambient atmosphere. Lengthy sintering time, ripened grains and thin grain boundaries are all favorable for realizing high dielectric constant. Grain boundary is more sensitive to atmosphere than CCTO grain.

2.2 Synthesis and modification of CaCu$_3$Ti$_4$O$_{12}$

CCTO can be fabricated into many shapes and forms, e.g. micrometer or nanometer powders, ceramic bulks, fibers, thin films and nanorods. It has been expected that the addition of nanometer/submicron dielectric fillers into a polymeric matrix could significantly enhance the effective dielectric constant of the composite while maintaining high breakdown
resistance. Hence, much attention has been paid to the fabrication of nano/submicron CCTO particles although it still remains challenging.

In order to improve the dielectric properties, especially lower the dielectric loss of CCTO, the doping modification is often applied. Other modification technique like core-shell structure has also been investigated. Here, we summarize a number of synthesis methods and modification techniques for fabricating CCTO.

2.2.1 Preparation of CaCu_3Ti_4O_{12}

2.2.1.1 Solid state method

As an oxide compound, CCTO can be synthesized via the standard solid state reaction by CuO, TiO_2 and CaO at high temperatures (typically ~1000°C) [51-53]. A typical procedure is described as follows.

The reagent grade of CuO, TiO_2 and CaCO_3 starting materials are weighed according to stoichiometric ratio of CaCu_3Ti_4O_{12}, and then well mixed in a ball mill with deionized water and milling medium for a certain period of time. The mixture is then dried in an oven at ~80°C and meshed prior to calcination at ~1000°C. During the calcination process, repeated intermittent grinding is conducted to help the formation of pure CCTO phase powders. Subsequently, CCTO powders are pressed into pellets and sintered under ~1100°C for 4~30 h to produce CCTO ceramic. The reaction involved is expressed as:

\[
\text{CaCO}_3 + 3\text{CuO} + 4\text{TiO}_2 \xrightarrow{\text{calcination}} \text{CaCu}_3\text{Ti}_4\text{O}_{12} + \text{CO}_2 \uparrow \quad \text{Eq. 2.5}
\]

Solid state method has the merits of simplicity and good controllability, which is valued and suitable in industry. However, high calcination temperature, lengthy sintering time and repeated grinding are required. Another concern is the compositional inhomogeneous due to the limited atomic diffusion among micron grains.

2.2.1.2 Sol-gel method
There are several types of sol-gel methods that use different starting materials to prepare CCTO precursors [54-57]. The key is to control the hydrolysis of titanium butoxide Ti(OC₄H₉)₄. This wet chemical synthesis route are pursued in order to lower the reaction temperature, shorten the reaction time and achieve high homogeneity in CCTO products.

A representative procedure could be simplified and summarized as follows. Reagent grade of Ca(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O and Ti(OC₄H₉)₄ are used as starting materials. Firstly, those three chemicals are weighed according to the stoichiometric ratio, and then dissolved into ethanol separately to form solutions. Secondly, these solutions are mixed in a beaker and kept stirring for 30 min to obtain a blue solution. Next, the ethanol is diluted by water with the volume ratio ethanol : water = 10:1, and added in dropwisely. After stirring of ~4 h, a blue gel is gradually emerged. The obtained gel is then aged for ~18 h at room temperature. The above procedures need to be performed in a fume hood. Finally, the gel is dried in an oven at 120°C.

The obtained brownish precursor is subsequently calcined at 800~900°C for ~2 h in a conventional muffle furnace in ambient atmosphere to get CCTO powders. The prepared powders can be shaped into tablets for further sintering at ~1050°C for 8 h and characterization.

Sol-gel method is the first choice to synthesize nanometer/submicron CCTO powder material, as it can reach homogeneity at the atomic level. At the same time, sol-gel procedures are complex and time consuming, and the required equipment such as glove box and a refluxing tube are needed in some cases [58].

One issue with sol-gel method is the mutually exclusion between the particle size and the phase purity. As shown in Figure 2.9 (a), the CCTO nano powders are not pure phase. Heat treatment at higher temperature (850°C) has been carried out to overcome this problem. However, the nano particles have fused to each other after and transformed into micron chain structures, as shown in Figure 2.9 (b). Therefore, the synthesis parameters have to be carefully controlled in order to obtained pure phase and well dispersed nano CCTO particles [56].

In addition, the sol-gel prepared precursors can be used to produce thin CCTO films by a facile spinning coating technique [59, 60].
2.2.1.3 Mechanical alloying

The mechanical alloying technique is initially used to prepare nano-structured alloy or ceramic powders. It has also been used to prepare nano-crystalline CCTO powder [43, 63]. High temperature calcination is not necessary via this route, and the resultant nano-crystalline powders are easy for shaping. However, the major drawbacks about mechanical alloying are the lengthy milling time (up to 100 h) with high rotating speed (>500 rpm) and the requirement of high energy ball miller. Contamination by ball material is another concern due to the long time milling.

During the mechanical alloying synthesis, CaCO$_3$ (or Ca(OH)$_2$), CuO, and TiO$_2$ are normally used as the starting materials. A high energy ball miller, such as Fritsch Pulverisette 6 planetary mill, can be used. Heavy and hard metal (stainless steel) container and balls (hard steel or WC) are also needed. The mass ratio of balls to sample is usually 8:1 or higher. In general, longer the milling time, better the formation of CCTO phase. According to the previous studies, at least 30 h milling is required to achieve reasonable phase purity [63]. The
calculated grain size of CCTO by mechanical alloying is ~25 nm.

The prepared nano powders can be used for further preparation of CCTO nano-ceramics via fast sintering such as spark plasma sintering (SPS). The final products have an average grain size of 150–200 nm [43].

2.2.1.4 RF Magnetron sputtering

Radio frequency (RF) magnetron sputtering has been used for growing CCTO nanorods and thin films on substrate (e.g., Pt/Ti/SiO₂/Si) [29, 64, 65]. The sputtering target, CCTO bulk, is made from standard solid state reaction using high purity CuO, TiO₂ and CaCO₃. The
The sputtering process is performed in a chamber which is firstly vacuumed and then back filled with the reaction gas (such as a mix of Ar and O$_2$ with the ratio of 2 : 3). The film thickness can be controlled by varying the deposition time and current. The substrate can be preheated up from room temperature to ~700°C. Normally, a conducting metal electrode (Pt) would be deposited onto the top of this film for further electrical properties evaluation. Finally, the sputtered sample will undergo a post deposition heat treatment to obtain the crystalized CCTO thin film.

The morphology (film or rods) of sputtered CCTO can be tuned by adjusting the substrate temperature, the target to substrate distance (usually between 5 to 15 cm), and the heat treatment atmosphere [66]. Figure 2.10 shows the FE-SEM images of CCTO nanorods with the cross sectional view. The aligned nanorods grow perpendicularly to the substrate (Figure 2.10 a), having a coverage density of ~50% (Figure 2.10 b) and exhibiting a mean diameter of 80 nm and a length of 900 nm (Figure 2.10 c). It can be seen that these nanorods are rich in grain boundaries which lead to a strong nonlinear current-voltage behavior. In addition, these arrays show two reversible resistance states, which can be used for resistive memory devices.

2.2.1.5 Electrospinning technique

Electrospinning technique has the reputation of facile fabrication of inorganic fibers. Liang et al [67] has successfully prepared pure phase CCTO fibers via electrospinning by playing with the precursor composition and calcination temperature.

In an optimized run, 1.2 mL tetrabutyl titanate, 0.208 g calcium nitrate and 0.528 g cupric acetate are firstly mixed with 20.0 mL ethanol and 0.4 mL acetic acid inside a glove box to form a solution. After 30 min, PVP is introduced, followed by a 2-h stirring to obtain a viscous green liquid which is the precursor for electrospinning. Subsequently, standard electrospinning equipment is used for the fabrication of CCTO fibers. The feeding rate is set to 6.8 mL/h through a needle with a diameter of ~1.23 mm. The accelerating voltage is 22.30 kV. The distance between the needle tip and collector (a piece of flat aluminium foil) is 16 cm. The as-spun CCTO fibers are dried at 60 °C for 12 h. The calcination is carried out at 600 – 1130 °C with a heating rate of 10 K/min followed by natural cooling. Figure 2.11 shows the
morphology of the prepared CCTO fibers after calcination. The fiber morphology is strongly
dependent on the calcination temperature due to the degradation of organic compounds. The
temperature of 950°C is optimum to obtain nano-crystalline CCTO.

![SEM images of CCTO fibers calcined at different temperatures](image)

Figure 2.11 SEM images of CCTO fibers calcined at different temperatures [67].

### 2.2.1.6 Microwave radiation

Microwave radiation is a relative novel technique that can be used for fast calcination and
sintering of CCTO. The conventional furnace can only heat samples via thermal convection
and conduction which is relatively slow and energy consuming. But microwave radiation can
heat the sample via molecular vibration in electromagnetic field, thus offer very fast and
homogeneous heating. By adjusting the temperature, holding time and output power,
microwave calcination can produce CCTO with small size at the nanometer of
sub-micrometer level.
Typically, CCTO solids state precursors (mixtures of CaCO$_3$, TiO$_2$ and CuO) are used for microwave calcination. In laboratory, the microwave furnace is usually a modified kitchen microwave oven (e.g., 2.45 GHz and 1.25 kW), which is capable of providing a temperature up to ~1400°C depending on the refractory materials.

The set-up inside the microwave oven chamber is shown in Figure 2.12. An alumina crucible contained CCTO precursors (10~30 g) is placed in a refractory container. In order to compensate the environmental temperature, several SiC microwave-susceptors are put around the alumina crucible. A Type B Pt-Rh thermocouple sheathed with platinum foil is placed proximally above the sample top to monitor and control the temperature. The control panel on the microwave oven provides a simple way to start the microwave calcination, and the microwave heating will be stop automatically. The prepared CCTO powders are then shaped into tablets for further microwave sintering and characterization. The sintering temperature is usually 1000°C for up to 1 h.
Based on the above description, the preparation methods can be divided into two main categories. One is based on the solid state reaction (e.g., conventional solid state method, mechanical alloying, microwave radiation, RF magnetron sputtering); while the other type is a number of wet chemical methods (e.g., sol-gel and electrospinning). The solid state category shows advantage of simple procedure, but wet chemical methods are good at morphology control, fine size and compositional homogeneity. Particularly, the magnetic sputtering, electrospinning and microwave calcination can be used to prepare CCTO with special morphology, such as film, nanorods, nano/submicron powders. In addition, care must be taken to the purity of the prepared CCTO.

2.2.2 Doping modification

CCTO possesses a flexible perovskite-like structure to allow various compositional doping modifications. There are three different cations sites, Ca, Cu and Ti in CCTO structure. Therefore, the doping modification could be categorized into Ca sites doping, Cu sites doping and Ti sites doping. Generally, the doping modification is carried out using individual metal oxides via solid state method. The microstructures and grain boundaries chemistry of CCTO ceramics can be significantly altered by different dopants.

2.2.2.1 Ca sites doping

La and Sr are popular candidates to substitute Ca ions in CCTO [69-72]. Sr-doped CCTO \((Ca_{1-x}Sr_xCu_3Ti_4O_{12}, 0 < x < 0.4)\) can result in an anomalous increase (3 times) in dielectric constant than the un-doped one when \(x\) reaching to 0.2. A locally stretched lattice structure with strong displacive ionic polarization is suggested to account for this increase [69].

On the other hand, La doping \((La_xCa_{(1-3x/2)}Cu_3Ti_4O_{12}, 0 < x < 0.05)\) can result in the suppression of the grain growth. The average grain size decreases with increasing La content. Besides, the breakdown voltage can be enhanced by La dopant. This enhancement is ascribed to that the addition of La can tune the IBLC effect and change the dielectric properties [71].
2.2.2.2 Cu sites doping

Cu sites can be substituted by Mn \((CaCu_{2.94}Mn_{0.06}Ti_4O_{12})\) and Zn \((Ca(Cu_{1-x}Zn_x)_3Ti_4O_{12})\) [73, 74]. However, the giant dielectric constant observed in CCTO cannot be observed in Mn-doped CCTO. Based on a impedance spectroscopic analysis, it is concluded that the substitution of 2% Mn onto Cu sites can reduce the bulk conductivity of CCTO [74]. In addition, Mn

\(^{4+}\) could reduce to Mn

\(^{3+}\) with John-Teller distortion upon cooling. This transform can compensate for the re-oxidation of Cu

\(^{+}\). Lastly, the grain boundaries and grains in CCTO may have the same phase (CCTO) but with slightly different composition, which is enough to offer significant electrical heterogeneity for giant dielectric response [74]. This implication, however, does not agree with the popular supposition that the grain boundaries are Cu

\(O_x\) phases.

As for Zn substitution, although it is an isovalent substitution to Cu sites, the introduction of Zn still causes a mixed valent structure among Cu and Ti ions [73]. Specifically, the ratio of Cu

\(^{1+}/Cu^{2+}\) and Ti

\(^{3+}/Ti^{4+}\) mixed valent state is enhanced by increasing Zn substitution \((0 < x < 0.1)\), which accounts for the giant dielectric response in Zn-doped CCTO.

2.2.2.3 Ti sites doping

Ti sites can be substituted by various transition metals such as V, Cr, Mn, Ni, Fe and Co, as they have similar ion radii \((50–60\ pm)\) at positive quadro-valence [72, 75]. Those dopants are all capable of increasing the effective dielectric constant in CCTO ceramics, because they can engineer the grain boundary chemistry and thus tune the permittivity, conductivity and activation energy of charge mobility around grain boundaries. Particularly, the grain boundary permittivity of pure CCTO can be increased by 1–2 orders of magnitude [72], which contributes to the enhanced IBLC effect and the giant dielectric constant.

Other dopants like Al or Hf can also be used for Ti substitution. The mechanism still lies in the tailoring of grain boundary structure and chemistry [76, 77]. However, the excessive addition of HfO

\(_2\) could lead to the appearance of HfTiO

\(_4\) secondary phase which would simultaneously lower the dielectric constant and dielectric loss.
Besides, the dopants such as GeO$_2$ and TeO$_2$ can facilitate the segregation of secondary phase around smaller grains, and cause the increase of grain and grain boundary resistance [78, 79]. As a result, the dielectric loss and dielectric constant would be both suppressed.

In summary, small changes in cation stoichiometry could produce significant changes in the level of conductivity and conduction mechanisms in CCTO. The grain boundary structure and chemistry are the key factor in CCTO’s dielectric behaviors.

### 2.2.3 Coating modification and multilayer arrangement

Recently, a novel modification technique, CCTO core-shell structure has gradually drawn attention. The shell is applied to CCTO particles prior to final sintering to promote the formation of secondary phases. Comparing with the metal oxides doping method, the core-shell structure can modify the microstructure and chemistry around CCTO’s grain boundaries by direct controlling of the composition and morphology of the surrounding shell. As shown in Figure 2.13, the BaTiO$_3$ partially coated CCTO is been achieved using sol-gel process [80].

Several materials have been used as the shell, which include Al$_2$O$_3$, BaTiO$_3$, SiO$_2$, TiO$_2$ and even carbon [80-84]. It is reported that the addition of insulating shells like Al$_2$O$_3$ and BaTiO$_3$ in CCTO can effectively improve the dielectric breakdown voltage and largely suppress the dielectric loss and leakage current. For example, by applying the Al$_2$O$_3$ partial coating, the dielectric breakdown voltage of sintered CCTO ceramic can increase by one order of magnitude, i.e. from 1.0 – 2.0 kV/cm to ~21 kV/cm [81]. It is believed that the Al$_2$O$_3$ enriched secondary phase, CuAl$_2$O$_4$, plays a very important role in improving the dielectric breakdown voltage.
Very similarly, the enhancement of dielectric properties in BaTiO$_3$ coated CCTO is also attributed to the uniform distribution of secondary phases, such as Ba$_4$Ti$_{12}$O$_{27}$ and CaTiO$_3$ [80]. Those secondary phases have the function of blocking the conduction hopping at grain boundaries, thus increasing the activation energy level and leading to a higher breakdown voltage. However, the dielectric constant would be reduced as well, which is claimed to be unavoidable.

Another technique to effectively lower the dielectric loss in CCTO is to deposit an insulation layer (e.g. SiO$_2$ or ZrO$_2$) between the CCTO multilayered films [65, 85, 86]. This layer can act as a barrier to prevent the conduction of free carriers or the oxygen diffusion, thereby effectively reducing the dielectric loss and the leakage current density.

In principle, both coating techniques and multilayer insulation could lower the dielectric loss and leakage current density due to the conduction blocking effect from secondary phases.
or the insulating barriers. Thus the coating can significantly improve the dielectric breakdown voltage, which is highly desirable for capacitive energy storage.

2.3 CaCu$_3$Ti$_4$O$_{12}$-polymeric composites

2.3.1 Background

The ceramic-polymer composites are gaining considerable attention for capacitive energy storage devices due to their advantages of light weight, mechanically flexible, and most importantly, the high volume efficiency (i.e. high energy storage density). It is expected that the ceramic and polymer composites would synergistically combine both large dielectric constant ($\epsilon$) and high dielectric voltage ($E_b$).

Many ceramic candidates have been studied, e.g., titanium dioxide (TiO$_2$) [87], barium titanate (BaTiO$_3$) [20], lead zirconate titanate (PZT) [88], lead magnesium niobate-lead titanate (PMNT) [89], Li-Ti co-doped NiO$_2$ (LTNO) [90], and CaCu$_3$Ti$_4$O$_{12}$ (CCTO) [91]. It was found that the addition of ceramic fillers could substantially increase the dielectric constant of the polymer composites. However, when introducing ceramic particles, especially nanoparticles into the polymer host, the breakdown voltage would also be affected because of the fillers agglomeration and phase separation.

Thus, speaking of achieving high energy density ($\frac{1}{2} \varepsilon_0 \varepsilon_r E^2$) by large $\epsilon$ and high $E_b$, it is not clear whether the reduction of $E_b$ caused by the inhomogeneity could be traded off by the enhancement of $\epsilon$. Moreover, apart from the homogeneity, other factors such as particles size and the volume fraction of the filler also play important roles in determining the final dielectric properties of the composites. In order to achieve high $E_b$, all these factors and parameters must be carefully controlled. Besides, surface modification of ceramic fillers is considered to be an effective method to improve the homogeneity and filler distribution.

In the present study, CCTO is chosen as the ceramic filler because of its high dielectric constant and excellent temperature stability, while the selection of polymeric matrix,
polyvinylidene fluoride (PVDF), is based on the facts that PVDF has 1) relatively high dielectric constant (~10) among polymers, 2) low processing temperature (~170°C), and 3) great energy storage potential [17, 18]. In this section, the basic physics, mixing rules and fabrication techniques of ceramic-polymeric composites are summarized. We have also reviewed the most recent development of CCTO-polymer dielectric composites.

2.3.2 Influencing factor of dielectric properties in composite

The concept of combining ceramic and polymer is straightforward and appealing at first glance, but the understanding about the mixing is rather limited. Many factors, e.g., filler concentration, filler particle size and shape, filler-matrix interface, filler distribution, and even processing condition can affect the performance of the composites. Several theoretical and statistical models have been summarized as follows.

2.3.2.1 Filler concentration

Lichtenecker logarithmic law of mixing is commonly used to estimate the effective dielectric constant ($\varepsilon_{\text{eff}}$) in a binary composite with variable filler concentration [92, 93]:

$$ log\varepsilon_{\text{eff}} = \varphi_1 log\varepsilon_1 + \varphi_2 log\varepsilon_2 $$  

where $\varphi_1$ and $\varphi_2$, $\varepsilon_1$ and $\varepsilon_2$ denotes the volume concentration and dielectric constant of the polymer matrix and the ceramic fillers, respectively. It shows that high filler concentration and large dielectric constant is favorable to achieve large $\varepsilon_{\text{eff}}$. However, in practice, the filler concentration has to be carefully controlled to avoid the loss of flexibility and reduction of breakdown voltage.

Another simple approach to predict $\varepsilon_{\text{eff}}$ is the Bruggeman model [94]:

$$ \varphi_1 \left( \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}} \right) + \varphi_2 \left( \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}} \right) = 0 $$  

Eq. 2.7

It is worth noting that the dielectric constant of the composite will increase rapidly while filler volume concentration is over 20%.

Other approaches including Kerner, Clausius-Mossotti, and Maxwell Garnet models have
also been employed to make reasonable prediction at relatively low filler concentration (\( \leq 20\% \)) [95-97]. When filler concentration is greater than 20\%, the Maxwell Garnett model would considerably underestimate the \( \varepsilon_{\text{eff}} \), while the Lichtenecker logarithmic law would substantially overestimate the \( \varepsilon_{\text{eff}} \) [98].

Based on a number of studies [99-101], it is gradually realized that there is a strong relationship between \( \varepsilon_{\text{eff}} \) and the filler-matrix interface, especially at high filling concentration (>20\%) when the filler size is small. Hence, those simplified models which do not take into account of the interface effects have limited applications.

### 2.3.2.2 Particle size and interface

![Diagram of a dielectric composite](Image)

Figure 2.14 Schematic diagram of a dielectric composite consisting of polymer matrix, ceramic particles, and interfacial phase.

The filler particle size coupled with interfacial effect shows nonmonotonic influence on the dielectric constant of ceramic-polymer composites [99, 102]. For instance, the dielectric constant of BaTiO\(_3\)-polymer composite increases with decreasing particle size of BaTiO\(_3\), and
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reaches the peak value when filler size is of 80 – 100 nm. But further decrease of particle size to smaller than 50 nm would result in a decrease of dielectric constant.

Composite with nano fillers has attracted much interest because nano size effect would pose significant influence on the dielectric property. By introducing nano particles into a polymer matrix, large interfacial areas are expected which result in enhanced interfacial polarization and $\varepsilon_{\text{eff}}$. Besides, nano particles can be used for the fabrication of micron/submicron thin films with increased breakdown voltage and high energy density.

A model that takes account of the particle size and the interaction between fillers and matrix has been proposed by Li et al [103]. This model consists of a polymer matrix (phase 1), spherical particle fillers (phase 2), and an interfacial phase with fixed thickness (phase 3), which is schematically shown in Figure 2.14. According to Figure 2.14, the volume concentration ($\phi$) of the interphase is given by:

$$\phi_3 = \frac{(r+l)^3-r^3}{r^3} \phi_2$$

Eq. 2.8

where $\phi_3$ and $\phi_2$ are the volume concentration of the interphase and filler respectively, and $r$ is the particle radius while $l$ is the thickness of the interphase. The $l$ is governed by the exchange constant and permittivity of polymer matrix, and it is independent to the particle size [104]. According to Eq. 2.8, it is evident that the interphase concentration $\phi_3$ would increase significantly as the particle size decreasing. Based on a self-consistent effective medium theory, the effective dielectric constant ($\varepsilon_{\text{eff}}$) can be expressed as:

$$\varepsilon = \varepsilon_1 + \phi_2 (\varepsilon_2 - \varepsilon_1) a_2 + \phi_3 (\varepsilon_3 - \varepsilon_1) a_3$$

Eq. 2.9

where $a_2$ and $a_3$ are the electric field concentration factor for corresponding phases. Particularly, $a$ can be calculated by

$$a_y = 1 - s [(\varepsilon_r - \varepsilon)^{-1} \varepsilon + s]^{-1}, y = 2,3$$

Eq. 2.10

where $s$ is the component of the dielectric Eshelby tensor and related to the depolarization factor. For spherical particles, $s = 1/3$.

Finally, a polynomial relation between $\varepsilon_{\text{eff}}$ and volume concentration ($\phi_y$, $y = 1,2$ and 3) and particle size ($r$) is obtained. Given the particle size, or volume concentration of the fillers, the optimized parameters can be established to achieve high $\varepsilon_{\text{eff}}$. 


Figure 2.15 Normalized energy density ($U^*/U_1$) of the composite as function of filler volume fraction ($f_3$) and size of fillers ($r/l$) [103].

According to Li’s model [103], the interfacial effect between the fillers and the host could shifts the transition threshold toward lower volume concentration, which means that a same value of dielectric constant can be achieved with lower filler concentration if the interfacial effect has played the role.

Li et al have also modeled the energy density of the composite but only took into account of the interfacial effect and ignored the introduction of any defects/voids. The modeling result is shown in Figure 2.15. For a typical interface thickness of a few nanometers (~10 nm), it implies that the particles size should be around 100 nm or smaller to take advantage of the interfacial effects.

However, over the percolation transition point (filler concentration reaching ~20%), this model is limited and less convincing; and the predictions made are inconclusive. While many other studies suggested that filler concentration higher that 20% is necessary to achieve large $\varepsilon_{eff}$ and great energy density [20, 105, 106], it is still open for debate whether micron or nano
sized fillers could offer higher energy density [107, 108]. Therefore, the microstructure of the composite must be carefully controlled. New model(s) to guide the fabrication of dielectric composites is highly desirable.

2.3.3 Fabrication techniques

Mixing technique of the ceramic-polymer composites is important to the final dielectric properties. Ceramic-polymer composites are usually synthesized by solid based blending (melt) [90, 109] and solution based mixing (dissolve) [110, 111].

The melt blending and hot pressing (both below 200°C) are the most popular solid based methods due to their good controllability, simple procedure and time saving. These methods are much suitable to fabricate sheets composite. The applied force during hot pressing process can help to obtain voids free samples, which is favorable for high breakdown voltage.

The solution based mixing, on the other hand, grants the composite with good homogeneity. It can be achieved by a typical dissolve-mix-vaporize pathway [110, 111]. At first, polymer is dissolved into an organic solvent. Subsequently, ceramic particles are introduced. Homogeneous suspension can be achieved by sonication treatment and continuous magnetic stirring. Finally, spin coating technique is used to prepare the thickness controllable thin film products. The organic solvent in the as prepared films can be removed by vaporization in oven.

Another technique that is worth mentioning is the in situ polymerization method which can achieve good distribution and stable interfacial effect by avoiding the agglomeration of the nano-sized fillers. In the resulting composites, the energy storing density is 9.4 J/cm³ which is determined from dielectric constant and dielectric breakdown measurements [2]. However, the dielectric constant of the in situ polymerized composite is unsatisfactory (~6.1), which limits the electrical energy storage.
2.3.4 Current research on CaCu$_3$Ti$_4$O$_{12}$-polymer composites

As stated previously, CCTO could be incorporated with polymeric matrix for the purpose of simultaneous large dielectric constant and high breakdown voltage, thereby realizing high energy density for capacitive energy storage. A few studies have been carried out on the CCTO-polymer composites. It is shown that the final dielectric response of CCTO-polymer material is strongly depends on several factors, including filler size, filler concentration, composite microstructure, and the nature of fillers and matrix. Recent researches dealing with CCTO-polymer composites are reviewed below.

2.3.4.1 Size effects – nano and micron CaCu$_3$Ti$_4$O$_{12}$

The filler size in the composites has an important effect on the dielectric properties of CCTO-polymer composites. Researchers from Oak Ridge National Laboratory (USA) have reported a binary composite of polyvinyl butyral (PVB) and nano CCTO [61, 62]. Films with thickness of ~50μm have been fabricated by the drop casting of a PVB-toluene solution with nano CCTO additive. The dielectric properties of this film have good temperature stability and can be adjusted by filler concentration. However, the highest concentration of CCTO (20 wt%) can only yield a small dielectric constant (~6) at 285 K, which is merely two times higher than that of the unfilled PVB (~3.2).

Later on, Tomas et al have reported another nano CCTO-PVDF thin film, which shows larger dielectric constant than previously reported CCTO-PVB [112]. When CCTO concentration is 30 vol.%, the PVDF composite demonstrates a peak value of dielectric constant of ~87 at 100 Hz (Figure 2.16). However, it is evident that high CCTO concentration would lead to large variation in dielectric properties over the frequency range of $10^2 - 10^6$ Hz.
Figure 2.16 Frequency dependent (a) dielectric permittivity and (b) dielectric loss (\(\tan\delta\)) of nano CCTO-PVDF composite as a function of volume percent of CCTO at 300 K [112].

Figure 2.17 Variation of AC (50 Hz) dielectric strength with respect to filler loading in PVDF-CCTO nanocrystal composites [112].

The AC (50 Hz) breakdown voltage results against different CCTO concentration have also been provided and shown in Figure 2.17. Apparently, the introduction of CCTO would substantially reduce the dielectric breakdown voltage of the prepared composites. The relatively dielectric breakdown voltage limits the use of CCTO-PVDF composite as
capacitive energy storage dielectric material. This is a real issue needs to be addressed.

Figure 2.18 Frequency variation of dielectric constant and dielectric loss of PVDF composite with nano and micron CCTO fillers and different volume fractions at room temperature [108].

Most recently, Yang et al have carried out a study to examine the influence of the CCTO particle size (micron and nano) on the dielectric properties in PVDF composite [108]. In this study, the PVDF composite containing 40 vol.% nano-CCTO fillers demonstrates a colossal dielectric constant over $10^6$, which is dramatically higher than that (~35) of the composite with the same content of micron CCTO (Figure 2.18). However, accompanying with the large dielectric constant, a high value of dielectric loss (~48) appears in nano CCTO-PVDF composites.

Meanwhile, the dielectric property of the nanocomposite exhibits strong dependence on the temperature and frequency. For example, the dielectric constant of nano CCTO-PVDF quickly decreases to $2.4 \times 10^3$ when the frequency is increased from $10^2$ to $10^4 \text{ Hz}$, and drops
further to 49 at 1 MHz. This drastic change in dielectric behavior over frequency in nanocomposite is attributed to the strong nano size effect induced interfacial polarization. Theoretically, there should be a moderate value of particle size that could simultaneously take the advantage of the nano size effect and minimize the fluctuation from strong interfacial polarization.

Overall, the problem with nano CCTO-PVDF composite is how to obtain homogeneous dispersed nanoparticles. Surface modification of fillers can play an important role and overcome this problem, which is reviewed in the following section. Efforts should also be made to adjust the filler concentration and minimize the detriment of nanoparticles to the breakdown voltage. Fundamental mechanism behind the enhancement by nano particles is still controversial and needs future investigation.

2.3.4.2 Surface modification-coupling agents

Surface modification of CCTO particles prior to melt mixing and hot pressing is used to improve the compatibility between CCTO fillers and the polymer host, thereby avoiding agglomeration, voids and phase separation, and finally realizing good dielectric properties.

Yang et al have studied a PVDF composite filled with surface modified micron CCTO by silane coupling agent (bis[3-(triethoxysilyl)propyl]tetrasulfide, also known as Si69). Figure 2.19 schematically shows the coupling process. It has been found that the distribution of CCTO is homogeneous as the Si69 has improved the interfacial bonding strength between CCTO and PVDF. Especially, when the ratio of Si69 to CCTO is around 0.1 mL to 1 g, the dielectric constant of CCTO@Si69-PVDF composites can reach the maximum value of 84 which is ~5 times higher than that of the non-treated CCTO-PVDF counterpart. In addition, the dielectric properties of modified CCTO@Si69-PVDF composites show good temperature stability from 20 to 160°C.

Therefore, it is useful to broaden the study to other coupling agents, such as titanate coupling agent, which has good chemical bridging effect to inorganic fillers.
2.3.4.3 Ternary composite with hybrid fillers

Ternary composite is considered to add more functions to binary composite. So far there are two basic purposes to add the third filler into a binary composite: one is to increase the dielectric constant by approaching the percolation threshold, the other is to increase the thermal conductivity.

Carbon fibers (CF) have been used to enhance the dielectric constant of BaTiO₃-PVDF composites. As shown in Figure 2.20, the addition of CF could considerable increase the effective dielectric constant especially when its concentration more than 10 vol.%. This enhancement is deemed to arise from the percolation effect when the filling concentration reaching to the critical percolation threshold. The conduction mechanism of the composite is controlled by the concentration of the conducting CF phase.

Other fillers such as β-SiC whiskers addition could significantly increase the thermal conductivity of BaTiO₃-PVDF composite according to the study of Li et al [114]. For instance, the ternary composite with 17.5 vol.% β-SiC whiskers has a dielectric constant of 325 at 10³
Hz, while the addition of 20 vol.% β-SiC whiskers increases the thermal conductivity of BaTiO$_3$-PVDF composite from 1.05 to 1.68 W·m$^{-1}$·K$^{-1}$ at room temperature.

Figure 2.20 (a) Variation of the dielectric constant and loss factor versus the volume fraction of CF fillers ($V_{BaTiO3}=20$ vol.%) at 100 Hz. (b) Microstructure of the composite in percolation threshold [115].

Therefore, the dielectric constant could be effectively increased by adding the third filler (normally in fiber-shaped material). Meanwhile, the improvement in thermal conductivity in ternary composite can increase the dielectric breakdown voltage somehow, and result in high
energy density. Further investigation is necessary to CCTO-containing ternary composites.

2.4 Summary and problem statement

CCTO material shows very promising dielectric properties, i.e. very high dielectric constant which is stable over wide range of temperature and frequency. Although it is widely accepted that the extrinsic factors especially the IBLC structure are the reason behind this unusual phenomenon, the formation mechanism of this unique structure is still not justified. To realize optimal IBLC effect, the synthesis parameters have to be carefully controlled.

The core-shell structure is considered to be an effective way to engineer the grain boundary morphology and chemistry, thereby tuning the dielectric properties of CCTO. Meanwhile, fast heating such as microwave radiation is favorable for preparing CCTO ceramic powders with much small particle size or grain size.

The straightforward strategy to combine CCTO and PVDF seems appealing. However, the dielectric property of CCTO-polymer varies over several orders of magnitude and affected by many factors, e.g., filler concentration, filler size, filler surface modification, filler distribution and polymer hosts. Particularly, the increase in the dielectric constant is often moderate but may be accompanied by strong frequency and temperature variation. Hence, nano CCTO particles might not be the best choice to achieve optimal energy storing performance, because the gain in dielectric constant may be traded off or even removed by the reduction in dielectric breakdown voltage. In addition, the agglomeration of CCTO particles would lead to an undesirable high dielectric loss. The energy density of the current generation of CCTO-PVDF composite is not high enough.

In order to improve the energy density, much effort needs to be made to the compositional and electrical homogeneity of CCTO-PVDF composites. Methods such as filler surface modification and the addition of hybrid fillers may be taken into consideration in order to make a difference in the current situation. However, the challenge still remains on simultaneously increasing permittivity while keeping high dielectric strength through technically feasible and economically competitive methods.
2.5 Research objectives and thesis outline

This thesis focuses on the synthesis, characterization and electrical properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) and CCTO-PVDF composites.

Firstly, efforts are devoted to the synthesis of high quality CCTO fine powders and dielectrically enhanced CCTO ceramics. As the dielectric property of CCTO is extrinsically originated (i.e. barrier layer structure) and related to the morphology and fabrication process, a systematic study on the phase and morphology evolution is performed to find out the optimal synthesis routes. In order to obtain real time phase transformation data, *in situ* high temperature X-ray diffraction is employed. Meanwhile, in-depth study on the subtle phase and microstructural changes in CCTO upon sintering is also conducted to provide information on the formation mechanism of the internal barrier layer capacitor (IBLC) which is responsible for the giant dielectric response.

In addition, to take the challenge of preparing homogeneous CCTO fine particles with minimized impurities, a fast and uniform microwave calcination technique is adapted. Moreover, as a direct and effective way to engineer the morphology and chemistry of grain boundary, core-shell modification onto CCTO particles with TiO$_2$ shell prior to final sintering is researched to tune the dielectric property especially to obtain lower dielectric loss.

Secondly, with the view of improving energy density upon PVDF based dielectrics, previously prepared micron sized CCTO and β-SiC-CCTO hybrid fillers are used to synthesize the homogeneous composites. Influence of filler concentration and morphology on the inherent properties including thermal conductivity, dielectric properties, breakdown voltage and energy storage density is comprehensively investigated.

This thesis is divided into 8 chapters. Chapter 1 briefly states the motivation of this study. Chapter 2 comprehensively reviews CCTO and its composite materials, and presents the current problems and the research objectives in this thesis study. Next, Chapters 3–7 are presented based on the individual published/submitted papers by the author of this thesis. To be specific, Chapter 3 concentrates on CCTO phase evolution in solid state and sol-gel
precursors using high temperature synchrotron radiation X-ray powder diffraction (SR-XRPD), and also presents the subtle phase and structural changes to explain the formation mechanism of IBLC. Chapter 4 compares the microwave radiation with conventional calcination in terms of synthesizing CCTO powders and ceramics from sol-gel precursor. The influence of different techniques on final dielectric properties is discussed. Chapter 5 deals with the core-shell modification of CCTO particles by TiO$_2$ shells prior to sintering, and systematically investigates the effect of TiO$_2$ shell on the morphology and dielectric properties of CCTO ceramics. Chapter 6 focuses on the preparation of CCTO-PVDF binary composite and its energy density. The optimal formula with the highest energy density is studied. Chapter 7 investigates the influence of $\beta$-SiC whiskers to CCTO-PVDF ternary composite. The effect of single and hybrid fillers with different composition on the dielectric response and thermal conductivity of the composites is examined. Particularly, the corresponding experimental procedures are included within each chapter. Finally, Chapter 8 presents the conclusions and future research work.
Chapter 3.  Investigation of phase evolution in CaCu$_3$Ti$_4$O$_{12}$ precursors and ceramic by \textit{in situ} synchrotron high-temperature powder diffraction


3.1 Chapter Abstract

\textit{In situ} synchrotron X-ray powder diffraction was used to study the high-temperature phase evolution of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) precursors prepared via solid state and sol-gel methods. After the precursors are heated to 1225°C, the CCTO phase is the main phase observed in the calcined powder, with the presence of some minor impurities. Comparing the two precursors, we found that the onset temperature for the CCTO phase formation is 800°C in the sol-gel precursor, lower than that in the solid state precursor (875°C). Intermediate phases were only observed in the sol-gel precursor. Both precursors are able to be calcined to sub-micrometric sized powders. Based on the synchrotron data along with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), the phase formation sequence and mechanism during calcination are proposed in this chapter. This chapter also provides real time qualitative phase information of CCTO upon sintering in ambient atmosphere. It has verified the appearance of CuO subtle phase in CCTO upon sintering. The \textit{in situ} observation of the lattice parameter evolution in CCTO well support the supposition that Cu ion instability is the formation origin of compositional inhomogeneity and IBLC structure and eventually responsible for the giant dielectric constant.

3.2 Introduction

Perovskite-type CaCu$_3$Ti$_4$O$_{12}$ (CCTO) materials have drawn considerable attention due to
its exceptional dielectric response [11, 12, 22]. It is reported that CCTO materials show a very high dielectric constant ($\sim 10^5$) with weak temperature dependence between 100 K and 600 K [11, 12], and its colossal dielectric response does not vary significantly in the frequency range from 20 Hz to 1 MHz at room temperature. These properties make CCTO materials appealing for applications in microelectronics and capacitive energy storage [116, 117]. Although the mechanism(s) of such a dielectric behavior is still open to debate, a commonly accepted theory is based on the internal barrier layer capacitor (IBLC) model [13, 36, 118], which suggests that semiconducting grains and insulating grain or domain boundaries form parallel capacitors, leading to an exceptionally high dielectric permittivity ($\varepsilon''$).

CCTO are generally synthesized via two major routes, i.e. conventional high-temperature solid state reaction method [119, 120] and sol-gel method [54, 56, 58]. In the solid state reaction method, stoichiometric mixtures of CaCO$_3$, TiO$_2$ and CuO are usually heated up to a high temperature ($1000 \text{–} 1150^\circ$C) and held for a long duration (4 – 50 h) [52, 119, 121]. The procedures of the solid state synthesis are straightforward; however, the reaction products are usually not structurally and compositionally homogeneous. The solid state reacted products often contain not only CCTO phase but also other impurities such as CaTiO$_3$ and CuO [122]. Besides, it is difficult to synthesize nano-sized CCTO due to the high temperature sintering. On the other hand, the sol-gel method can produce homogeneous CCTO with much smaller grain size than those produced by solid state reaction, but large-scale production of CCTO using this method is a challenge [56].

It has been well documented that the dielectric properties of CCTO depend strongly on its microstructure [13, 37, 46], composition [72, 118], and processing parameters [53, 123]. Chen et al [124] reported that the dielectric constant of CCTO at 10 kHz increases from $3.79 \times 10^3$ to $5.31 \times 10^4$ by increasing the calcination temperature from 1025 to 1125$^\circ$C. In order to further improve the properties of CCTO, a comprehensive understanding of the phase formation mechanism of CCTO precursors is critical. However, the investigations of the phase evolution during the synthesis of CCTO via both routes are limited [125, 126], in particular how and when the intermediate phases emerge. Synchrotron X-ray diffraction has ability of revealing phase evolution in situ and real time by monitoring spontaneous change in the XRD spectra. With the high resolution XRD data, we intend to investigate the phase evolution and reaction
mechanism of CCTO precursors involved both sol-gel and solid state reactions.

3.3 Experimental

3.3.1 Preparation of the sol-gel precursor complex

$\text{CaCu}_{3}\text{Ti}_4\text{O}_{12}$ precursor was prepared via a simple sol-gel process. A stoichiometric ratio (corresponding to $\text{Ca}:\text{Cu}:\text{Ti} = 1:3:4$) of ACS-reagent-grade calcium nitrate tetrahydrate $[\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}]$, cupric nitrate hemi-pentahydrate $[\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}]$ and titanium (IV) butoxide $[\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}]$ were used as starting materials. The $\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$ and $\text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O}$ were firstly dissolved into ethanol to form solution A ($[\text{Ca}^{2+}+\text{Cu}^{2+}] = 1 \text{ M}$). The $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ was dissolved into another baker with ethanol to form solution B ($[\text{Ti}^{4+}] = 1 \text{ M}$). Under magnetic stirring (300 rpm), solution A was slowly added into solution B, and a dark-blue sol resulted. Subsequently, certain amount of $\text{H}_2\text{O}$ diluted by ethanol (with a volume ratio of $\text{H}_2\text{O}$:ethanol = 1:1) was dripped into the sol and a sky-blue gel resulted. The gel was then aged for 12 hrs at room temperature, and then dried at 80°C to obtain the precursor complex. For \textit{in situ} synchrotron XRD experiments, thin tablets of 0.2 – 0.5 mm thick were prepared.

3.3.2 Preparation of the solid state mixture/precursor

$\text{CaCu}_{3}\text{Ti}_4\text{O}_{12}$ precursor was prepared by a typical solid state mixing method. Reagent-grade $\text{CaCO}_3$, $\text{CuO}$ and $\text{TiO}_2$ were weighed according to the stoichiometric ratio ($\text{Ca}:\text{Cu}:\text{Ti} = 1:3:4$) and charged in an agate pot with agate balls and ethanol. The mixing was conducted in a planetary ball-mill at 300 rpm for 180 min. After drying, the mixture was pressed into tablets with thickness of 0.2 mm for further characterization on synchrotron powder diffraction beamline.
3.3.3 High temperature synchrotron radiation X-ray diffraction

Firstly, in situ high-temperature X-ray diffraction (HT-XRD) of two different CCTO sources was conducted on the powder diffraction beamline equipped with an Anton Paar HTK-2000 strip furnace and a Mythen II microstrip detector at the Australian Synchrotron Centre. The energy of X-ray beam is 20 keV with a corresponding wavelength of 0.06188 nm. The thin tablet sample was placed on a platinum strip (used as both sample holder and heating element); and Pt/Pt-Rh thermocouples were used for temperature measurement and control. The diffraction data were collected in a continuous mode every 25 K from room temperature to 1225°C at a ramp rate of 200 K·min⁻¹. The data acquisition time was 4 min at each temperature.

Secondly, the in situ observation of subtle phase and structural changes of CCTO during sintering was conducted in dry air atmosphere. CCTO powders were prepared by conventional solid state calcination process. Solid state precursors from Section 3.3.2 were calcined at 950°C for 8 h using muffle furnace. To achieve pure CCTO phase, repeated calcination (3 times) and grinding were carried out and the result was confirmed by laboratory XRD. As-prepared CCTO powders were shaped into thin tablets with thickness around ~0.2 mm for further sintering and experiments on synchrotron powder diffraction. The set-up is the same as described above, except the energy used was 15 keV with a corresponding wavelength (λ) of 0.8262Å (because the experiments were conducted separately under different projects). The sample was firstly warmed up to 900°C at a fast rate (50 K/min), and then heated to the peak temperature of 1125°C at a slow rate of 3 K/min. Then, the sample was cooled back to 900°C at 3 K/min, and followed by a fast cooling to room temperature. After that, re-heating and re-cooling at fast rate of 100 K/min were also conducted. The data were collected in a continuous mode with each acquisition time of 30 s. The acquired data have been processed by Rietveld refinement.

3.3.4 Other Characterization techniques
Differential scanning calorimetry (DSC, NETZSCH, DSC-404-F3) and thermal gravimetric analysis (TGA, Shimadzu TGA-50 analyzer) measurements were carried out at a heating rate of 10 K-min$^{-1}$ under a flowing nitrogen atmosphere. An environmental scanning electron microscope (ESEM, FEI Quanta 200F) equipped with energy dispersive X-ray spectroscopy (EDX, EDAX Pegasus EDS detector) was employed to study the microstructure and elemental composition in different precursors after calcination at high temperatures.

3.4 Results

3.4.1 TGA-DSC analysis

The TGA and DSC results are presented in Figure 3.1. As shown in the TGA plot of the sol-gel precursor (Figure 3.1 (a)), the major weight loss of ~50% occurred between 100°C – 300°C and a further weight loss of ~10% continued until 570°C. The weight losses are also reflected by two DSC endothermic peaks at 240.7°C and 439.5°C, respectively. No obvious mass loss was observed above 570°C in the TGA plot. But the DSC trace shows an exothermic peak at 654.9°C and an endothermic peak at 827°C.

The TGA and DSC traces of the solid state precursor are shown in Figure 3.1 (b). On the TGA plot, a substantial weight loss (7%) was observed between 600 to 800°C, with a further 1% and 2% occurring at 900°C and 1100°C, respectively. The DSC trace reveals three endothermic peaks: one at 679°C, a weak one at 850°C and a very sharp one at ~1100°C. These results could be related to the decomposition of CCTO in N$_2$ atmosphere at high temperature:

$$CaCu_3Ti_4O_{12} \xrightarrow{N_2, \text{>1000°C}} CaTiO_3 + 1.5Cu_2O + 3TiO_2$$  \hspace{1cm} \text{Eq. 1}

which is proposed by Sinclair et al [127]. Overall, the TGA and DSC curves are consistent with each other, and are supported by the HT-XRD evidences provided later.
3.4.2 *In situ* Synchrotron HT-XRD

The HT-XRD results are presented in 2-dimensional mapping patterns (Figure 3.2 & Figure 3.3), which reveal the crystalline phase evolution as a function of temperature in the two CCTO precursors. The scale bar at the top-right stands for the diffraction intensity of each peak. The selected 2θ range (10° – 25°) covers the characteristic peaks of all phases.

As shown in Figure 3.2, for the sol-gel precursor, the nitrate-complex precursor remained in the sample below 300°C. With increasing temperature, several crystalline phases were
identified throughout the entire process. The dehydration of the precursor occurred from 100 to 300°C, consistent with the TGA results (Figure 3.1(a)). Within this temperature range, anhydrous Ca(NO$_3$)$_2$ emerged at 150°C by the dehydration of Ca(NO$_3$)$_2$·4H$_2$O. CuO formed at 300°C at the expense of the amorphous precursor, whereas the crystalline TiO$_2$-related phases were not detected in this temperature range and they could be in an amorphous state. CaTiO$_3$ and Rutile (TiO$_2$) then appeared at a temperature of 550°C and 825°C, respectively.

![Figure 3.2 The in situ synchrotron HT-XRD patterns of CCTO sol-gel precursor [A, precursor; B, Ca(NO$_3$)$_2$, 150–500°C; C, Corundum, >200°C; D, CuO, >300°C; E, intermediate(s), 475–700°C; F, CaTiO$_3$, >550°C; G, CCTO >800°C; H, Rutile, >825°C].](image)

The CCTO phase was identified in the temperature range of 800 to 1200°C. The quantity of the CCTO phase increased with temperature, as reflected by its diffraction intensity. However, it is noted that some minor phases such as CaTiO$_3$, CuO and TiO$_2$ still remained in the sample at 1225°C. A corundum phase and an unknown phase were also observed at 475–700°C (Figure 3.2). The detection of corundum was caused by exposure of alumina powder, which was put underneath the sol-gel precursor to avoid sticking of the precursor to the Pt
strip. The unidentifiable phase could be an intermediate phase occurring during the complex decomposition.

The Synchrotron HT-XRD patterns of the solid state CCTO precursor are shown in Figure 3.3. The crystalline phases involved in the phase transition process are displayed with letters a–f in the figure. It clearly shows that four phases existed in the starting powder mixture: calcium carbonate (CaCO$_3$), copper oxide (CuO), and two types of TiO$_2$ – anatase and rutile. CaCO$_3$ started to decompose at $\sim$650°C and decomposition finished at 700°C. The resultant CaO existed until 1125°C. Moreover, the minor phase anatase (TiO$_2$) in raw material completely changed into rutile (TiO$_2$) before temperature approached to 850°C [128]. After 875°C, CaO reacted with rutile to form CCTO, and this reaction completed at $\sim$1150°C.

Figure 3.3 The *in situ* synchrotron HT-XRD patterns of CCTO solid state precursor [a, CaCO$_3$, RT–700°C; b, CuO, RT–1150°C; c, Anatase, RT–850°C; d, Rutile, RT–1100°C; e, CaO, 650–1125°C; f, CCTO, 875–1225°C].

Unlike its sol-gel counterpart, the solid state precursor did not show any intermediate phase such as CaTiO$_3$. The main phase in the solid state process was CCTO accompanied with
trace amounts of minor phases, which were probably due to the incomplete reaction under the fast heating. The reaction time was not sufficient (60 min in total from 875 to 1225°C) for the mass transfer of the solid state reaction, which was limited by the internal diffusion. This statement is further confirmed by SEM (shown in Figure 3.4).

### 3.4.3 Microstructure and compositional analysis by ESEM/EDX

Figure 3.4 SEM of CCTO samples: (a) sol-gel precursor, (b) solid state precursor after fast heating at 1225°C, and the representative EDS analysis (insets).

The microstructure of the samples after HT-XRD synchrotron radiation was observed with an ESEM in a backscattering mode. Figure 3.4 shows the microstructure and
compositional analysis in the two types of CCTO after fast heating at 1225°C. It is evident that both samples demonstrated a fine grain size in the range of 200 nm to 2 μm. Unlike reported in the literature [51], no abnormal grain growth was observed in this study. Significant contrast difference in Figure 3.4 (a) suggests chemical inhomogeneity in the resultant samples after fast heating during HT-XRD detection. EDX result of a selected area EDS1 (square box in Figure 3.4 (a)) shows that the brighter grains are Cu rich (49.9 at.%, inset in Figure 3.4 (a)). SEM of the solid state specimen depicts a relatively uniform distribution of grain size; and no obvious compositional contrast could be observed. In accordance with the EDX result of the selected area EDS2 (square box in Figure 3.4 (b)), the oval-shaped grains are CCTO with an atomic ratio Ca:Cu:Ti close to 1:3:4, which is the stoichiometric ratio of CCTO (inset in Figure 3.4 (b)). These observations indicate that fast heating could be an effective way to suppress the abnormal grain growth and particle size less than 1 μm is expected. However, both precursors did not attain homogeneous phase composition due to the limited holding time for mass transfer.

3.4.4 *In situ* evolution of the phase and lattice parameter in CCTO upon sintering

*In situ* data on phase evolution of CCTO during sintering are provided in Figure 3.5. It is evident that CCTO is the major phase upon heating and cooling. It should be pointed out that very small amount of CuO is identified in CCTO starting powders which have already been calcined at 950°C for 24 h in ambient temperature beforehand. But previously we could not see these CuO peaks using ordinary lab XRD. This implies that a) CCTO is compositionally unstable under ambient calcination conditions; b) attention should be paid to the formation of this unique CuO phase in CCTO which might be the origin of CCTO’s unusual electrical properties. Moreover, according to Figure 3.5, the XRD peak intensity of CuO shows an increase as temperature increasing from ~900°C to 1125°C. Upon cooling to room temperature, peak intensity of CuO would fall back to its previous level. This peak intensity change indicates a reaction related to Cu may happen in CCTO during sintering.
Figure 3.5 The *in situ* synchrotron HT-XRD patterns of CCTO during sintering: two different arrows denote for CCTO and CuO respectively.

Figure 3.6 shows the evolution of lattice parameter ($a$) of CCTO during sintering. CCTO belongs to cubic symmetric system, so it has only one parameter, $a$. An obvious decrease in lattice parameter before and after sintering is shown in Figure 3.6. To be specific, firstly, lattice parameter increases as increasing the temperature. This should be ascribed to expanding of crystal structure at elevated temperature. At 887°C, however, lattice parameter starts to show a sudden downtrend even if the temperature is still increasing till 1125°C. After the maximum 1125°C, lattice parameter keeps decreasing upon cooling to room temperature.

In order to better understand the reason behind, a consecutively second-time sintering was conducted and the results are shown in Figure 3.6. This time, we can see the lattice parameter show monotonous change with heating and cooling, but does not change before and after sintering. Thus, we believe the decrease of lattice parameter in the first-time sintering must associate with significant structural change or reaction. Particularly, this reaction
becomes considerable at 887°C.

Figure 3.6 In situ observation of lattice parameter \((a)\) evolution in CCTO upon sintering.

3.5 Discussion

According to the thermal analyses (TGA & DSC) and in situ observation of the phase evolution above, the chemical reactions and crystallization sequence and mechanisms in these two CCTO precursors are proposed. In addition, based on the in situ observation of phase and lattice parameter evolution, the mechanism for the formation of IBLC structure in CCTO is discussed.

3.5.1 Reaction sequences in sol-gel precursor

In the sol-gel process, the gelation starts with hydrolysis of titanium butoxide, as shown
in Eq. 3.1,

\[ Ti(OC_4H_9)_4 + 4H_2O \xrightarrow{\text{diluted in ethanol solvent}} Ti(OH)_4 + 4C_4H_9OH \quad \text{Eq. 3.1} \]

Meanwhile, the complexation reaction develops among the freshly generated titanic hydroxide and metallic nitrates to yield a sky-blue gel. The gelation is expressed in Eq.3.2,

\[ Ti(OH)_4 + 3Cu(NO_3)_2 + Ca(NO_3)_2 + xH_2O \rightarrow CaCu_3(TiO_4) \cdot (NO_3)_4 \cdot xH_2O + 4HNO_3 \quad \text{Eq. 3.2} \]

After being dried at 80°C, the excess nitrite acid produced by the complexation reaction (Eq. 3.2) is evaporated completely. Following the gelation reaction, the gel is transformed into CCTO phase through the subsequent dehydration, decomposition and re-association reactions (Eq. 3.3 – Eq. 3.8).

\[ CaCu_3(TiO_4) \cdot (NO_3)_4 \cdot xH_2O \xrightarrow{\text{RT-200°C}} CaCu_3(TiO_4) \cdot (NO_3)_4 + xH_2O \quad \text{Eq. 3.3} \]
\[ CaCu_3(TiO_4) \cdot (NO_3)_4 \xrightarrow{\text{150°C}} Ca(NO_3)_2 + Cu_3(TiO_4) \cdot (NO_3)_2 \quad \text{Eq. 3.4} \]
\[ Ca(NO_3)_2 \xrightarrow{\text{150-500°C}} CaO + 2NO_2 \uparrow \quad \text{Eq. 3.5} \]
\[ CaO + Cu_3(TiO_4) \cdot (NO_3)_2 \xrightarrow{\text{300-500°C}} 3CuO + \text{intermediate(s)} + 2NO_2 \uparrow \quad \text{Eq. 3.6} \]
\[ \text{intermediate(s)} \xrightarrow{\text{550-700°C}} CaTiO_3 \quad \text{Eq. 3.7} \]
\[ 3CuO + 3TiO_2(\text{rutile}) + CaTiO_3 \xrightarrow{\text{>800°C}} CaCu_3Ti_4O_{12} \quad \text{Eq. 3.8} \]

The existence of the intermediate phase is a result of incomplete reaction Eq. 3.8 because the reaction time is insufficient (a total of 70 min from 800 to 1200°C). The intermediate phases could be also resulted from decomposition of CCTO at high temperatures [126].
3.5.2 Reaction sequences in solid state precursor

The reaction sequences involved in the solid state precursor can be summarized as follows (Eq. 3.9 – Eq. 3.11):

\[
\begin{align*}
\text{CaCO}_3 & \xrightarrow{650-700°C} \text{CaO} + \text{CO}_2 & \text{Eq. 3.9} \\
\text{TiO}_2 (\text{Anatase}) & \xrightarrow{\sim 850°C} \text{TiO}_2 (\text{Rutile}) & \text{Eq. 3.10} \\
\text{CaO} + 3\text{CuO} + 4\text{TiO}_2 & \xrightarrow{875-1225°C} \text{CaCu}_3\text{Ti}_4\text{O}_{12} & \text{Eq. 3.11}
\end{align*}
\]

It is noted that the decomposition process of CCTO sol-gel precursor is more complicated than its solid state counterpart during calcination. Specifically, there is an unidentified intermediate phase which is believed to convert into CaTiO$_3$ when further increasing the temperature. On the other hand, no intermediate phase such as CaTiO$_3$ appears in the solid state precursor prepared with a mixture of CaCO$_3$, CuO and TiO$_2$.

3.5.3 Instability of CaCu$_3$Ti$_4$O$_{12}$ during sintering

According to the facts in Figure 3.5 and Figure 3.6, CCTO is not stable at temperature above ~900°C. Meanwhile, an obvious decrease in CCTO’s lattice parameter at 887°C suggests that a significant structural change may happen at this point. Considering that CuO is the only subtle phase exists in CCTO and its peak intensity increases at ~900°C, therefore, we propose that the instability of Cu ions should be the reason behind. Cu ions would jump off the normal sites in CCTO crystal structure at elevated temperature to precipitate CuO secondary phase. No other impurity phase could be observed because CCTO can remain the crystal structure even if Cu ions are lost. Finally, the resultant is a Cu-deficient CCTO with a formula of CaCu$_{3-x}$Ti$_4$O$_{12}$. This result is different from the supposition by Subramanian et al [38].

In addition, based on the facts in many studies that Cu rich phase is located at the grain
boundaries in CCTO and form the IBLC structure [34, 40, 50], here we propose that the Cu ion instability is the ultimate origin for the compositional inhomogeneity and defect structure in CCTO, and leads to the formation of IBLC structures by precipitate CuO rich phase at the grain boundaries, which eventually responsible for the giant dielectric constant in CCTO.

3.6 Summary

(1) The phase evolution and reaction sequences in both sol-gel and solid state precursors have been established using in situ synchrotron high temperature X-ray diffraction (HT-XRD), along with thermal analysis techniques. The CCTO phase forms at a lower temperature (800°C) in the sol-gel precursor than in the solid state precursor (875°C). Intermediate phases such as CaTiO$_3$ appear in the sol-gel precursor but not in the solid state mixture. The crystallite size of the synthesized CCTO powder varies from 200 nm to 2 μm. The resultant sub-micrometric crystallite size is attributable to the fast heating rate of 200 K-min$^{-1}$ and the short holding time. This study contributes to the compositional optimization of nanoscaled CCTO as a high-performance electronic material.

(2) It has been found that CCTO is not 100% phase pure even if sintered via conventional calcination at 950°C for 24 h. CuO phase is well identified in CCTO during sintering. Based on in situ observation of the phase and lattice parameter evolution in CCTO during sintering, it implies that the Cu ions start to jump off its normal sites at 887°C, and this loss of Cu ion in crystalline structure results in an obvious decrease of lattice parameter in CCTO after sintering. It is supposed that the Cu ion instability is the fundamental reason for the compositional inhomogeneity and defect structure which leads to the formation of IBLC structures and finally accounts for the giant dielectric constant in CCTO.
Chapter 4. Microwave-assisted synthesis of high dielectric constant

CaCu$_3$Ti$_4$O$_{12}$ from sol-gel precursor

Contents published in *Journal of Electronic Materials* (Xin Ouyang et al. 2015).

4.1 Chapter Abstract

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) powders derived from sol-gel precursors were calcined and sintered via microwave radiation. The obtained CCTO powders were compared with that obtained via conventional heating method. For microwave heating, 89.1 wt% CCTO was achieved from the sol-gel precursor, after only 17 min at 950 °C. In contrast, conventional calcination method required 3 h to generate 87.6 wt% CCTO content at 1100°C. In addition, the CCTO powders prepared through 17 min microwave calcination exhibited a small particle size distribution of $D_{50}=3.826$ μm. It is found that a lengthy hold time of 1 h by microwave sintering is required to obtain high dielectric constant ($3.14\times10^3$ at $10^3$Hz) and reasonably low dielectric loss (0.161) in the sintered CCTO ceramic. Based upon the distinct microstructures, the dielectric responses of the CCTO samples sintered by different methods are attributed to space charge polarization and internal barrier layer capacitor (IBLC) mechanism.

4.2 Introduction

Ceramics with a high dielectric constant and reliable performance over a wide range of temperature and frequency have been constantly demanded in modern microelectronics and capacitive energy-storage applications [129, 130]. It has been reported that the addition of nanometer or submicrometer sized ceramic fillers of high dielectric constant into a polymeric matrix, to form a ceramic-polymer composite, could significantly enhance the effective
dielectric constant of the composite while maintain high breakdown resistance, thereby achieving high energy density in the composites [15, 20, 105, 108, 131, 132]. Many ferroelectric ceramics have been explored as the fillers, such as BaTiO₃ [20], PMNT [89], PZT [133]. Recently much attention has been paid to a cubic perovskite-like CaCu₃Ti₄O₁₂ (CCTO) titanate which has an exceptionally high permittivity ($\sim 10^5$) and extraordinary temperature and frequency stability [11-13, 22, 34, 46, 134]. Several models, among which the internal barrier layer capacitor (IBLC) mechanism is the most widely accepted to explain this unusual dielectric response [27, 135]. The CCTO microstructure has been suggested to have semiconductive grains surrounded by insulating grain boundaries [13]. However, recent work has pointed out that nanosized CCTO ceramics might have active and conductive grain boundaries [108].

To date, a number of methods are available to synthesize fine CCTO powders, e.g., solid state calcination [39, 119-121], sol-gel routes [54, 56, 58, 136-139], co-precipitation [140-142], and mechanical alloying method [63]. In terms of preparing homogeneous nano-sized CCTO powders, the wet chemical route such as sol-gel method is preferred because it is capable of molecular-level assembling, leading to compositional and structural homogeneity. However, sol-gel methods often involve complex procedures and require high temperature treatment of the amorphous precursor, and also result in multiphase products [56, 134, 138]. The dielectric response of CCTO strongly depends on the microstructure and phase composition in it and therefore much effort has been devoted to crystallization of CCTO sol-gel precursors. Several techniques have been developed, including traditional muffle furnace calcination [139, 143], organic solution pyrolysis [144] and fuel-assisted auto-combustion [145]. Our previous study [146] suggests that fast heating is preferable to fabricate sub-micrometer or nano-sized CCTO materials, as the amorphous precursors could rapidly crystallize while significant crystallite growth does not occur. Unfortunately traditional heating technique can hardly meet the requirement for a rapid heating rate over 100 K/min. Microwave heating, on the other hand, has proved to be a fast heating technique. This technique has been reported to be an effective alternative for synthesizing CCTO ceramics [41, 68, 147].

To the best of our knowledge, there is no report on microwave-assisted synthesis of nano-
and submicrometer sized CCTO ceramics from sol-gel precursor. It was our interest to use microwave radiation for the calcination and sintering of the CCTO precursors and compare the results with those synthesized with conventional calcination. Phase composition, microstructural evolution and dielectric properties were characterized. This work has shown that the microwave approach is superior to the conventional furnace sintering to obtain high performance CCTO ceramics.

4.3 Experimental

4.3.1 Preparation of CaCu$_3$Ti$_4$O$_{12}$ sol-gel precursor

CaCu$_3$Ti$_4$O$_{12}$ sol-gel precursor was prepared via a sol-gel process interpreted below. This experimental process was carried out in a fume hood with ambient atmosphere and temperature. In a typical run, firstly, 0.025 mol Ca(NO$_3$)$_2$·4H$_2$O and 0.075 mol Cu(NO$_3$)$_2$·2.5H$_2$O were dissolved into 100 mL ethanol to form a solution (Solution A), in which [Ca$^{2+}$] = 0.25 M and [Cu$^{2+}$] = 0.75 M. Secondly, 0.1 mol Tetrabutyl orthotitanate (C$_{16}$H$_{36}$O$_4$Ti) was dissolved into ethanol (100 mL) to form a solution of [Ti$^{4+}$] = 1 M (Solution B). Then, solution A was slowly added into solution B with magnetic stirring at 300 rpm at room temperature, and a dark-blue sol formed. Subsequently, 30 mL of H$_2$O diluted by ethanol (with a volume ratio of H$_2$O:ethanol = 1:10) was dripped into the dark-blue sol, and a blue gel formed gradually with 40 min stirring. Afterwards, the gel was aged for 12 h without further stirring at room temperature, followed by drying at 120°C for 24 h to yield a brownish precursor complex. All raw materials used are of ACS-reagent-grade.

4.3.2 Calcination of the precursor via conventional and microwave heating

The as-dried CCTO sol-gel precursor, prepared in Sec 4.3.1, was subsequently calcined by two different heating techniques. For conventional heating method, the precursor was heated in a muffle furnace (CTF, Carbolite) for 3 h at a temperature of 500°C to 1100°C. In
microwave heating, an adapted microwave furnace with a frequency and power capacity of 2.54 GHz and 1.25 kW (Thermwave, Research Microwave Systems) was used. The heating set-up is shown in Figure 4.1 (a).

![Figure 4.1](image)

Figure 4.1 (a) The heating set-up inside the chamber of microwave furnace and (b) a typical temperature–time profile of microwave heating.

An alumina crucible contained CCTO precursors (~30 g) was placed in a thermal insulating container and surrounded by SiC microwave-susceptors to compensate environmental temperature during microwave heating. A Type B thermocouple sheathed with platinum foil was placed proximally above the sample top surface to monitor and control the
temperature. The actual heating profile during microwave operation was recorded and presented in Figure 4.1 (b), showing an average heating rate of ~100 K/min before the prescribed temperature (950°C) was reached. The microwave furnace was switched off after the specified holding time, and the sample was taken out after it cooled down naturally. The microwave-calcined CCTO materials were selected for further sintering via both microwave heating and conventional furnace heating. Prior to sintering, the calcined CCTO was ball-milled (for 3 h with 300 rpm) and pressed into tablet samples. The pressed tablet samples were then sintered via both types of heating. In the conventional heating the samples were heated at 1100°C and the holding time was set for 0.5 h, 1 h, 4 h and 8 h, while in the microwave heating, the samples were sintered at 1050°C for 5, 10, 20, 30 and 60 min. The selection of different temperatures for conventional furnace (1100°C) and microwave furnace (1050°C) is based on the fact that samples heated by microwave generally possess higher inner temperature (by 20~50°C) than that detected by the thermocouple.

4.3.3 Characterization

The crystalline phase constituents were characterized by X-ray diffraction (XRD, Bruker D2 Phaser). Quantitative analysis of each phase in the as-calcined samples was carried out with the Rietveld method using software MAUD. The microstructure of the samples after calcination and sintering were examined with an environmental scanning electron microscope (ESEM, FEI Quanta 200F). The particle size of the ball-milled CCTO precursors after microwave calcination was tested by a particle size analyzer (Mastersizer 2000, Malvern). The sintered samples (~Ø13mm×3mm) were subjected to dielectric property testing after mechanical polishing. The dielectric constant (ε) and loss (tanδ) over a wide range of frequency (10^2 – 10^6 Hz) were determined using an impedance analyzer (Wayne Kerr 6500B) by a universal Agilent 16451B fixture.
4.4 Results

4.4.1 Phase analysis

The XRD patterns of samples calcined in the conventional and microwave furnaces are shown in Figure 4.2 (a). The quantitative analysis of each determined phase is presented in Figure 4.2 (b). In conventional heating, samples calcined at 500°C consisted of a major phase anatase (TiO$_2$), which disappeared completely if the sample was calcined at 700°C. Only at >800°C did CCTO become a predominant phase while the other minor phases such as rutile, CaTiO$_3$ and CuO gradually diminished.

The large-scale formation of CCTO within sol-gel precursor is expressed as Eq. 4.1:
This is consistent with our previous study [146]. When the precursor was calcined at the highest temperature of 1100°C for 3 h, 87.6 wt% of the precursor was transformed into crystalline CCTO. For comparison, microwave heating at 950°C was performed for different holding times. Within a short hold time of 15 to 20 min, CCTO emerged as a major phase, Figure 4.2 (c). Calcination for 17 min led to the highest CCTO yield of 89.1 wt% and a further increase in calcination time seems detrimental to CCTO yield. This might be caused by decomposition of CCTO if it is held for a lengthy time [39]. It is worth noting that usually multiple regrinding-and-reheating steps are needed to obtain a CCTO-dominated composition in the conventional heating [41]. When compared with the conventional muffle furnace heating, it is confirmed that the microwave calcination is advantageous to obtain a high CCTO yield at much lower temperatures. At present, 17 min by microwave calcination is optimized for achieving high CCTO phase content and is selected to produce CCTO powders for further microwave and conventional sintering.

4.4.2 Micromorphology of calcined $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ precursors

Figure 4.3 (a–c) shows the scanning electron microscopy (SEM) images of the CCTO powders calcined for 3 h by conventional muffle furnace at 700°C, 1000°C and 1100°C respectively. As the temperature increased, the precursor decomposition and solid state reaction took place, and the amorphous precursor gradually crystallized and became crystalline CCTO, which is manifested by the evolution of microstructure from fluffy clusters at 700°C (Figure 4.3 (a)) to ripened and well defined grains at 1100°C (Figure 4.3 (c)). Particularly, the larger crystallites grew at the expense of smaller ones as per the Ostwald ripening mechanism [148]. In the 1100°C-calcined sample, the crystallite size was in the range of 10 to 20 μm. In comparison, the CCTO powders calcined by microwave heating at 950°C are presented in Figure 4.4 (a–c). Samples via microwave heating show a strong tendency of grain coarsening with heating time, although these samples had a similar CCTO
content, as shown by the XRD analysis (80 wt% – 90 wt%). For instance, the mean crystallite size in the 15 min-calcined sample was 1 to 3 μm while in the 20 min-calcined sample it was 3 to 10 μm. It is noted that a few abnormally grown grains were observed (Figure 4.4 (c)), possibly because of the inhomogeneous temperature distribution during fast heating. This can be suppressed by doping which could lower the grain boundary mobility. Additionally, according to the particle size analysis of the ball-milled powders, the mean particle size (D_{50}) of CCTO after 15 min, 17 min and 20 min microwave calcination is 2.453 μm, 3.826 μm and 4.076 μm, respectively.

4.4.3 Dielectric properties

After calcined at 950°C for 17 min through microwave heating, CCTO powders were
further sintered by microwave and conventional furnace respectively before the impedance analyses were carried out. The dielectric constant (\(\varepsilon\)) and dielectric loss (\(\tan\delta\)) were determined from the capacitance measurements. Figure 4.5 (a) and (b) presents the frequency dependence of \(\varepsilon\) and \(\tan\delta\) of the samples sintered by microwave at 1050°C for different time. Samples sintered for a short time (5 and 10 min) displayed a high \(\varepsilon\) (~6×10³) and a high \(\tan\delta\) at <10³ Hz. An increased sintering time would lead to a significant decrease in \(\varepsilon\) and \(\tan\delta\). For instance, the value of \(\varepsilon\) dropped to 3.14×10³ for 60-min hold, from 6.58×10³ for 5-min hold, at 10² Hz. It is also noted that both \(\varepsilon\) and \(\tan\delta\) decreased sharply with frequency. In the higher frequency range, the effect of sintering time became insignificant; a similar value of \(\varepsilon\) was observed at 10⁶ Hz for all the samples regardless of sintering time.

Figure 4.5 Dielectric properties of the samples sintered by microwave at 1050°C (a, b) and conventional furnace at 1100°C (c, d) for different holding times.

The dielectric response of the samples sintered in the conventional muffle furnace is significantly different as shown in Figure 4.5 (c) and (d). First, an increased hold time led to a
significant increase in ε (Figure 4.5 (c)). The highest dielectric constant of \~2.5\times10^4 was observed at 10^2 Hz in the sample sintered for 8 h. Second, increasing hold time in muffle furnace also increased the dielectric loss tanδ (Figure 4.5(d)). It is noted that, for the same sintering time (1 hour for example), the sample sintered in the muffle furnace at 1100°C had a lower ε of 2.58\times10^3 (Figure 4.5 (c)), as compared to 3.14\times10^3 for the microwave sintered sample (Figure 4.5(a)).

The polarization mechanisms underlie in this high dielectric constant is related to the microstructures. Samples sintered for prolonged time by conventional heating attain more ripened grains and fine grain boundaries as compared to the short time microwave treated samples. Ripened CCTO grains with well-defined grain boundaries offer internal barrier layer capacitor (IBLC) structures which leads to intensive interfacial polarization over low frequency range (<10^3 Hz) and shows very high dielectric constant. However, samples after 5 and 10 min microwave sintering may have a different polarization mechanism which is responsible for the opposite effect of holding time on the dielectric constant, as the short-time microwave-sintered samples have inhomogeneous microstructure. Therefore, at low frequency the space charge polarization mechanisms become dominant, which is the major contributor to the dielectric response. Both interfacial and space charge polarization need relaxation and would decrease steeply under a high frequency, which is reflected by the rapid decreases of the dielectric constant in Figure 4.5 (a) and (c). Overall, the dielectric properties of CCTO materials largely depend on their microstructure and polarization mechanisms which are determined by the sintering process. Finally the product by microwave sintering for 1 h shows a good combination of high dielectric constant (2.5\times10^3) and low loss (0.161) at 10^3 Hz. The reason for choosing the frequency of 10^3 Hz instead of 10^2 Hz is to eliminate the influence of space charge polarization, although normally the optimized dielectric constant is achieved at 10^2 Hz.

4.5 Discussion

4.5.1 Phase and micromorphology
The distinct features of phase evolution (Figure 4.2) and micromorphology (Figure 4.3 and Figure 4.4) between microwave and conventionally calcined samples are mainly attributed to the different heating mechanisms. Conventional muffle furnace transfers heat via conduction and convection that usually creates temperature gradients, whereas microwave radiation straightforwardly delivers energy through the interaction at the molecular level with the electromagnetic field. The heating rate of microwave can be very fast depending on its frequency and power, and dielectric and magnetic properties of the materials. Fast heating via microwave offers fast reaction by 10 to 100 times so that the precursors can crystallize quickly without significant crystallite growth. One adverse effect of fast heating is the inhomogeneous temperature distribution, which may cause abnormal crystallite growth in the calcined sample (Figure 4.4 (c)). Based on the microstructural observations and XRD quantitative analysis, it is suggested that calcination at 950°C for 17 min by microwave would result in the best quality of CCTO powder.

4.5.2 Dielectric response

The dielectric response of a ceramic material strongly depends on the microstructures such as crystallinity, crystalline size, grain texture and grain boundaries [39, 46, 149]. The giant dielectric permittivity of CaCu$_3$Ti$_4$O$_{12}$ has been well explained by the internal barrier layer capacitance (IBLC) theory [13, 27]. In this theory, CCTO is a material of semiconductive grains surrounded by insulating grain boundaries. The microstructure-dependent effective dielectric constant ($\varepsilon_{\text{eff}}$) is given by Eq. 4.2 [43].

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{gb}} t_g}{t_{\text{gb}}}$$  \hspace{1cm} \text{Eq. 4.2}

where $\varepsilon_{\text{gb}}$ is the permittivity of grain boundary, $t_g$ is the average grain size and $t_{\text{gb}}$ is the average thickness of the grain boundary. Therefore, a thinner grain boundary and a larger grain would give rise to a higher dielectric constant. In a well sintered CCTO sample via conventional muffle furnace heating, large grains with clear grain boundaries are observed.
(Figure 4.6 (a)). Prolonging the sinter time would promote grain coarsening leading to an increased grain size and a decrease in grain boundary thickness. Hence, the enhanced IBLC structures will give rise to a high dielectric constant.

On the other hand, the CCTO samples sintered via microwave heating demonstrate different dielectric response (Figure 4.5 (a) vs. (c)). Fast microwave heating is able to rapidly crystallize the amorphous CCTO precursor, but seems unable to strongly speed the migration of grain boundaries and fully coarsen the CCTO grains, as shown in Figure 4.6 (b). When compared with long time conventionally sintered CCTO, the microwave-sintered samples with a much shorter holding time have relatively thicker grain boundaries and cannot form well-defined IBLC structures. As such, according to Eq. 4.2, a lower dielectric constant is expected in the microwave-sintered samples.

On the other hand, a short sintering time by microwave heating (5 and 10 min) is also capable of offering high dielectric constants in low frequency range. However, this unusually high dielectric constant (and loss) originates from another mechanism – intensive space charge polarization which shows a strong relaxation behavior even at low frequency range (< $10^3$ Hz) and is deeply suppressed when the frequency increases [150]. If the frequency is over
~10^3 Hz, the samples with longer sintering times by microwave exhibit a higher dielectric constant, as they have ripened grains and fine grain boundaries to form internal barrier layer capacitors (IBLC) structure that account for the giant dielectric constant. Besides, similar to some previous reports [34, 151], a large dielectric loss (derives from the IBLC leakage/conductivity) accompanied with a large permittivity was also observed in this study (Figure 4.5 (b) and (d)). In addition, the effect of both space charge polarization and IBLC/interfacial polarization diminishes with increasing frequency, which is again in agreement with the previous studies [78, 152]. Nevertheless, a good combination of high permittivity and low dielectric loss can be achieved by microwave heating.

4.6 Summary

The CaCu3Ti4O12 ceramic powders were successfully synthesized from sol-gel precursors, through microwave calcination and sintering. Microwave calcination outperforms conventional heating and needs only 17 min at 950°C to achieve 89.1 wt% CCTO with a small particle size (D_{50}=3.826 μm). The different dielectric responses of the CCTO sintered via these two different heating methods are attributed to the distinct microstructures. In the CCTO samples sintered in the muffle furnace for a much longer time, it is suggested that well-developed IBLC structures play a major role in determining dielectric permittivity and loss. In contrast, interfacial polarization combined with space charge polarization are the governing mechanisms for the CCTO samples sintered in the microwave furnace with a much quicker heating rate. A good combination of a high dielectric constant (2.5×10^3) and low dielectric loss (~0.161) at 10^3 Hz was obtained by microwave sintering at 1050°C for 1 h.
Chapter 5. Enhanced extrinsic dielectric response of TiO$_2$ modified CaCu$_3$Ti$_4$O$_{12}$ ceramics

Contents published in Ceramics International (Xin Ouyang et al. 2015).

5.1 Chapter Abstract

TiO$_2$ modified CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has been synthesized via a facile sol-gel precipitation process followed by solid state sintering. The influence of the precipitated TiO$_2$ crystallites on the microstructure, phase composition, and dielectric properties of CCTO has been investigated. The morphology and chemistry of grain boundaries in CCTO ceramics can be significantly tailored by the initial TiO$_2$ crystallites, which results in enhanced barrier layer capacitor structures. The formation mechanism of barrier layers based on the instability of Cu ions has been discussed. A new bimodal brick layer mechanism has been proposed to explain the effect of TiO$_2$ modification. The optimized TiO$_2$ modified CCTO sample exhibits stable dielectric permittivity which is twice as high as the unmodified one, and shows relatively low dielectric loss over the frequency range from $10^2$ to $10^5$ Hz. Such enhancement is deemed to arise from the modified and bimodal internal barrier layer capacitor effect.

5.2 Introduction

Over the last decade, extensive reports on the giant dielectric constant ($\varepsilon>10^4$) of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) have triggered much interest in microelectronics and pulse power applications where high-$\varepsilon$ dielectrics are in demand [11, 13, 19, 153]. Many mechanisms were proposed to explain the unusually high dielectric response in CCTO [36, 42, 44, 45, 118, 154], but it has been gradually realized that the polarization mechanism(s) behind is non-intrinsic
and attributed to the extrinsic reasons, e.g., internal barrier layer capacitor (IBLC) mechanism exists at grain boundaries or Schottky barrier between sample and contacts [155, 156]. Currently, IBLC mechanism is dominant because it can well explain the giant dielectric response not only in polycrystalline CCTO but also in single crystalline CCTO by incorporating domain structure within grains [36].

So far, the considerable dielectric loss of CCTO is a real road-block to its practical applications. Much effort has been made to reduce the dielectric loss of CCTO materials. One popular method is to use metal oxides doping. Dopants such as TeO₂ [78] and GeO₂ [157] can promote the segregation of the Cu rich phases along with the CCTO grain boundaries, by which the dielectric constant is improved (to ~10⁴). However this approach also causes an increased DC conductivity (leakage current) owing to the enhanced semiconducting nature.

Other dopants like La₂O₃ [70, 71], HfO₂ [76], ZnO [73] and MnO (MnCO₃) [74] are all capable of partially substituting Ca, Ti or Cu elements with a certain ratio. Through those small changes in cation stoichiometry, significant difference could be made to the conductivity and conduction mechanisms in CCTO ceramics. However, both dielectric loss and dielectric constant could be reduced by this type of heterovalent ion substitution. Another method is to fabricate complex CCTO/oxides multilayer films via sophisticated deposition methods [85, 86, 158]. By creating an effective barrier between CCTO thin films, the diffusion of free carriers can be substantially suppressed, thereby reducing the leakage current density.

Recently, a new approach has been put forward to surround mono-disperse CCTO particles with an insulating barrier-shell before final sintering. This core-shell-like structure has been reported in metal core-polymer shell dielectric composites [159, 160]. The insulation shell can, on the one hand, allow the electrons in the core to tunnel through thereby achieving high dielectric constant. On the other hand, it restricts the electron drift between conductive particles, thus leading to a low dielectric loss.

There are few studies attempted to prepare CCTO core-shell structure. Wang et al [82] reported that CCTO materials coated by SiO₂ (~30 nm thick) exhibited exceptionally low dielectric loss (<0.01) at room temperature. However, the dielectric properties show considerable temperature variation; and the frequency-dependent information was not
reported. Much recently, BaTiO$_3$ partially coated CCTO via complex sol-gel route and oxygen atmosphere annealing were reported by Kim et al [80]. The coated CCTO composites showed both reduced dielectric losses and suppressed leakage currents, which are attributed to the second phases like Ba$_4$Ti$_{12}$O$_{27}$ and CaTiO$_3$ at the grain boundaries. The work on TiO$_2$ shell onto CCTO has been rarely reported, given its excellent electrical performance and potential capability to improve dielectric properties [161, 162]. Since CCTO’s dielectric property mainly relies on the interfaces and grain boundaries, to study the TiO$_2$ shell and its effects on microstructures, second phases and dielectric properties of CCTO would be of both scientific and technological significance.

In this work, TiO$_2$ shells on CaCu$_3$Ti$_4$O$_{12}$ core were attempted by a simple sol-gel precipitation method. The influence of TiO$_2$ shells on the microstructures and dielectric properties of sintered CCTO was investigated. The formation mechanism of barrier layers was discussed.

5.3 Experimental

5.3.1 Materials and preparation

Fine CCTO particles (1–5 μm) were synthesized via a conventional solid state method reported previously [146]. For sol-gel precipitation and deposition process, titanium butoxide (TBOT, Sigma-Aldrich) was used as the starting Ti source according to an adapted procedure [163]. In a standard run, 5 g CCTO powders was firstly dispersed in ethanol (100 mL) with continuous magnetic stirring (300 rpm) to obtain uniform suspension. Secondly, certain amount of TBOT was added into this suspension and stirring continued for 30 min. Water bath was employed to maintain a constant temperature of 40°C. In order to promote the hydrolysis of TBOT and the precipitation of Ti(OH)$_4$, ammonia solution (28 % w/w) was introduced dropwise as per the volume ratio of ammonia to TBOT of 1:2.5. The magnetic stirring continued for another 18 h before the solution was aged for 24 h. On completion of the aging, repeated vacuum pumping filtrations were performed to eliminate the NH$_3$ and excessive Ti$^{4+}$. 
The resultants were collected and then dried at 80°C overnight. Annealing was carried out at 500°C for 2 h. Finally the intact and TiO₂ modified CCTO powders were shaped into tablets separately and sintered at 1075°C for 8 h for further evaluation. Samples were denoted as CCTO, TCCTO-1, TCCTO-2 and TCCTO-3 which represented different TBOT dosage of 0, 0.75, 2.25 and 7.5 mL, respectively.

5.3.2 Characterization

The microstructure of TiO₂ modified CCTO particles after annealing were characterized by transmission electron microscopy (TEM, FEI Tecnai FEG20). Phase constituents of the sintered CCTO and TiO₂ modified ceramics were analyzed by X-ray diffraction (Bruker D2 Phaser). Density of ceramic was calculated using Archimedes principle. A scanning electron microscope (SEM, FEI, XL30 S-FEG) equipped with an energy dispersive X-ray (EDX) spectrometer was used to observe the micromorphology and selected area microanalysis. Elemental mapping of selected area was carried out by another scanning electron microscope (Phenom ProX). Finally, tablet samples were painted with silver paste on both sides for the dielectric properties characterization with an impedance analyzer (Agilent 4294A).

5.4 Results

5.4.1 Morphology of TiO₂ modified CaCu₃Ti₄O₁₂ particles

Figure 5.1 (A) shows the particle morphology of sample TCCTO-3 after calcined at 500°C for 2 h. It is clear that CCTO particle is surrounded by a shell consisting of small crystallites. The selected area electron diffraction (SEAD) pattern of the area 1 within this shell is shown in the inset. It is well identified and confirmed that these crystallites are anatase TiO₂. The high resolution TEM image in Figure 5.1 (B) shows the lattice spacing of 3.52 Å corresponding to the (101) plane of anatase TiO₂. The morphology of other CCTO particles modified with lower TBOT concentrations is also characterized, showing only a few TiO₂
clusters attached to CCTO particles. As such, 5 g CCTO modified with 7.5 mL TBOT (TCCTO-3) is considered to have the optimized TiO$_2$ shell structure in the present case, and used for further evaluation.

![Figure 5.1](image-url) Figure 5.1 (A) TEM image of sample TCCTO-3 particle after calcination at 500°C for 2 h, and the electron diffraction of selected area 1 (inset); (B) high resolution TEM image of anatase TiO$_2$ crystallites within the shell.

### 5.4.2 Phase analysis of TiO$_2$ modified CaCu$_3$Ti$_4$O$_{12}$ ceramics

The CCTO particles modified with different TBOT concentrations were shaped into tablets for sintering at 1075°C for 8 h in ambient atmosphere. The XRD patterns of the un-modified CCTO and modified TCCTO-(1, 2, 3) ceramics are shown in Figure 5.2. The major phase in all samples is CCTO which can be referred to ICSD No. 32002. In samples TCCTO-2 and TCCTO-3, there is a small peak around 2\(\theta\) = 27° matching with the strongest characteristic diffraction peak of rutile TiO$_2$ (ICSD No. 97277). Combining with the TEM analysis, it is concluded that the anatase TiO$_2$ was transformed into rutile TiO$_2$ phase after high temperature sintering, which is consistent with a previous study [128]. No TiO$_2$ peak is observed in the TCCTO-1 sample, probably due to the low TiO$_2$ content. In addition, although some study claimed the observation of CuO in CCTO bulk after sintering at > 1075°C [164],
it should be noted that no evident CuO diffraction peak can be detected in this study which may be due to the amorphous nature of CuO-related phase or the detection limit.

![XRD patterns of CCTO modified with different TBOT concentration](image)

Figure 5.2 XRD patterns of CCTO modified with different TBOT concentration (TCCTO-1, 2, 3) after sintering at 1075°C for 8h.

5.4.3 Morphology of TiO$_2$ modified CaCu$_3$Ti$_4$O$_{12}$ ceramics

In Figure 5.3, the surface and cross sectional morphologies of the sintered TCCTO-3 and CCTO samples are shown comparatively. These SEM images were obtained under backscattering electron mode in order to reflect the compositional contrast. According to Figure 5.3 (a) and (e), the sintered TCCTO-3 and CCTO samples both demonstrate dense microstructure with ripened grains and well-defined grain boundaries. The grain size in these two samples is similar, while the grain boundaries are distinctively different in terms of morphology and composition. For example, in Figure 5.3 (f), grain boundaries of CCTO ceramic are mostly dendritic-like, but in TCCTO-3 (Figure 5.3 (b)), a bunch of crystallite clusters are aggregated and form very unique microstructures, which was reported to result from discontinuous grain growth [42].
Figure 5.3 SEM images on the surface of modified TCCTO-3 sample (a, b, c) and un-modified CCTO sample (e, f, g), and the cross sectional morphology of TCCTO-3 (d) and CCTO (h). Both samples were sintered at 1075°C for 8 h.
Furthermore, the back-scattered images show compositional differences between the grain interiors and grain boundaries in both samples. Upon areas of interests, compositional analysis by EDX has been carried out with standard operational procedures and optimized parameters. Although the absolute accuracy of EDX results is not 100%, the relative ratio among major elements is reasonable for microscopic composition analysis [165]. As shown in Figure 5.3 (c) and (g), several areas upon grains and grain boundary areas were selected and the results are presented in Table 5.1. It can be seen that the ripened grains in both samples (areas 1 and 5) show a mole ratio of Ca/Cu/Ti ≈ 1/3/4 and thus are CCTO. This result is in agreement with the XRD patterns showing that CCTO is the major phase. The grain boundaries, areas 3 and 4, are both Cu enriched, but the unmodified CCTO shows higher relative Cu content (38.53%) than the modified TCCTO-3 (25.70%). This Cu-rich phase is crucial for the formation of barrier layer capacitor structures in CCTO [42, 164].

Table 5.1 Compositions of the selected areas (1–5) in Figure 5.3 (at.%).

<table>
<thead>
<tr>
<th>Elements (at %)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>5.56</td>
<td>2.69</td>
<td>4.02</td>
<td>2.16</td>
<td>5.46</td>
</tr>
<tr>
<td>Cu</td>
<td>17.08</td>
<td>8.27</td>
<td>25.70</td>
<td>38.53</td>
<td>16.58</td>
</tr>
<tr>
<td>Ti</td>
<td>22.56</td>
<td>35.64</td>
<td>15.94</td>
<td>7.99</td>
<td>21.94</td>
</tr>
<tr>
<td>O</td>
<td>54.79</td>
<td>53.40</td>
<td>54.34</td>
<td>51.32</td>
<td>56.02</td>
</tr>
</tbody>
</table>

*For reference, Ca/Cu/Ti=1/3/4 in stoichiometric CCTO.

As shown in Figure 5.3 (b) and (c), the small tetragonal-shape crystallites at the grain boundary in TCCTO-3 were speculated as rutile TiO$_2$. This speculation is made based on the fact that XRD pattern shows the existence of rutile TiO$_2$ phase in TCCTO-3. Besides, the initial anatase TiO$_2$ crystallites around CCTO could be pushed to the grain junctions by the movement of CCTO grain boundaries during sintering. A single crystallite (area 2) was selected for EDX measuring and shows the highest Ti content (35.64%) compared with other
areas. However, a small amount of Cu is also detected (8.27 %), owing to the mix of Cu-rich phase with TiO₂ at high temperature.

Figure 5.3 (d) and (h) show the morphology of the cross-sections. It is clear that both the un-modified CCTO and modified TCCTO-3 samples demonstrate porous interior microstructures (i.e. trapped pores within large grains), which indicates rapid grain growth took place during sintering. The overall mole ratio of Ca/Cu/Ti in these interiors is approximately 1/3/4. The relative sintered density of the CCTO and TCCTO-3 samples is 96.04% and 93.66% respectively, calculated against a theoretical density of 5.05 g/cm³ in the fully solid CCTO ceramic [166]. As such the introduction of TiO₂ would have slightly lowered the relative density of the sintered CCTO ceramics.

5.4.4 Dielectric properties of TiO₂ modified CaCu₃Ti₄O₁₂ ceramics

Figure 5.4 The dielectric constant and dielectric loss of the sintered CCTO samples modified with different TBOT concentrations (TCCTO-1, 2, 3) over the frequency range of 10² – 10⁶ Hz.

The dielectric properties of un-modified CCTO and TiO₂ modified samples (TCCTO-1, 2, 3) were measured over the frequency range of 10² – 10⁶ Hz as shown in Figure 5.4. The TiO₂ modified samples clearly show higher dielectric constant than the un-modified CCTO, and
their dielectric constants remains reasonably stable with a gentle downturn as increasing the frequency. The modified samples TCCTO-2 and TCCTO-3 still keep a relatively high value above $10^4$. The highest dielectric constant of $\sim 5.5 \times 10^4$ was obtained in the TCCTO-3 at $10^2$ Hz, over two times higher than that ($2.16 \times 10^4$) of the unmodified CCTO sample. This high dielectric constant is attributed to the enhanced internal barrier layer capacitor effect which will be interpreted in the following section. Furthermore, the dielectric loss values are less than 0.2, and almost invariant over the frequency range from $10^2$ to $10^5$ Hz. As frequency increases to $10^6$ Hz, the dielectric losses demonstrate a characteristic steep increase due to the Debye relaxation mechanism. Overall, the TiO$_2$ modified CCTO samples show a good combination of high dielectric permittivity and low dielectric loss below $10^5$ Hz.

5.5 Discussions

5.5.1 The role of the TiO$_2$ crystallites in the formation of grain-boundary phase

It is generally believed that the dielectric properties of CCTO ceramic is correlated to the barrier layer capacitor effect which strongly depends on processing parameters [39]. In the present study, the un-modified CCTO is capable of generating CuO enriched grain boundaries by sintering at 1075°C for 8 h in ambient atmosphere (Figure 5.3). This CuO-rich grain boundary has been reported as “one step internal barrier layer capacitor” [14]. In the present case, SEM images and EDX analysis (Table 1) confirm the existence of the CuO-rich phase at grain boundaries. A hypothesis proposed by Subramanian et al [38, 154] is commonly used to interpret the formation of the CuO barrier layer, although the direct in situ evidence is lacking so far. This hypothesis suggests that the key factor lies in the instability of Cu$^{2+}$. During the sintering of CCTO, Cu$^{2+}$ would experience a slight reduction and partial re-oxidization upon heating and cooling, expressed as Cu$^{2+} \rightarrow$Cu$^+ \rightarrow$Cu$^{2+}$. As shown in Figure 5.3 (f), the high CuO content at grain boundaries implies that this valence state change of Cu ion might have also induced the Cu segregation and precipitation. Theoretically, CCTO has a perovskite-related ($ABO_3$) structure, Cu$^{2+}$ ions are sitting at $A$ sites and sharing the corner ‘O’ with TiO$_6$ octahedrons to form CuO$_4$ square planes [30]. The reduction of Cu$^{2+}$ into Cu$^+$.
would lead to a slight increase of ion radii and the crystalline structure of CCTO could be distorted. Therefore, it is assumed that at an elevated temperature a fraction of $\text{Cu}^+$ would jump off the original positions and assemble at the grain boundary area to transform into $\text{Cu}^{2+}$ by re-oxidation. Nevertheless, some argue that the $\text{Cu}^+$ may not be truly presented and the observation of $\text{Cu}^+$ is attributed to measurement factors [167]. They believe the segregation of CuO is ascribed to the intrinsic structure instability and composition non-stoichiometry in CCTO [167-169]. In spite of this argument, the presence of Cu-rich phase at grain boundaries can essentially facilitate the sinterability of CCTO and develops into the barrier layer structures, thereby achieving high dielectric response [135, 170].

![Figure 5.5 (A) SEM image of TCCTO-3 sample and, (B) elemental mapping (Ca, Cu, Ti) of selected area on grains and grain boundaries.](image)

In TiO$_2$ modified CCTO (e.g. TCCTO-3) as shown in Figure 5.5, Cu is still enriched at the grain boundaries (see the mapping results in Figure 5.5 B). But, as shown in Figure 5.5 (A), the initial TiO$_2$ shells have developed into many small crystallites around the ripened CCTO grains. It is well established that the grain growth commences due to the movement of grain boundaries. Hence, because of the grain boundary move of CCTO, the initial TiO$_2$ crystallites have been ‘dragged’ to the grains junctions and developed into rutile TiO$_2$ during sintering. Meanwhile, at high temperature, the segregated CuO phase would mingle with TiO$_2$
crystallites. We assume that no reaction between TiO$_2$ and CuO has occurred as no corresponding phase was found by XRD analysis. Finally, the grain boundaries consisting of rutile TiO$_2$ crystallites mixed with CuO exhibit a very unique grain boundary microstructure in the TiO$_2$ modified CCTO, and such a microstructure plays an important role to the dielectric properties [40, 135].

5.5.2 The effect of microstructures on dielectric properties

Firstly, barrier layer capacitor structures are usually simulated into brick layer model, especially when the grain size is in micron range [171]. According to this model, the effective dielectric permittivity of the microstructure ($\varepsilon$) can be simplified as [43, 135]:

$$\varepsilon = \varepsilon_{gb} t_g / t_{gb}$$

Eq. 5.1

where $\varepsilon$ and $\varepsilon_{gb}$ is the dielectric constant of the barrier layer structure and the grain boundary, and $t_g$ is the average grain size, and $t_{gb}$ is the average thickness of grain boundary. As such, ripened grains coupled with thin grain boundaries are favorable to achieve a high dielectric permittivity. According to SEM images and by using ImageJ software, in sintered CCTO sample the average grains size ($t_g$) is $\sim$125 $\mu$m, and the average thickness of grain boundaries ($t_{gb}$) is $\sim$3 $\mu$m. In the meantime, it is assumed that the value of $\varepsilon_{gb}$ is equal to the intrinsic dielectric permittivity of CCTO, $\sim$100 which is reported by Sinclair et al [14]. The calculated effective $\varepsilon$ equals 4167. This is much smaller than the measured value of $\sim$21000 at 1 kHz. Thus, as pointed out in previous studies [36, 42], there should be other barrier layer mechanism(s) within CCTO grains to account for this giant dielectric permittivity.

It should be noted that a terrace-ledge morphology appears in the CCTO sample (Figure 5.3 g), which is very similar to the structure formed by a spiral growth of crystals via a screw dislocation. Also, there are many bumps inside the grains of TCCTO-3 (Figure 5.3 b and c). It is reported that the surface diffusion determines the formation of those terrace-ledge and
bump microstructures [42]. Therefore it is speculated that the dislocations associated with those distinctive microstructures can act as barrier layers to form more subtle brick layer structures within ripened CCTO grains, thereby contributing to the giant dielectric permittivity.

In the case of TiO₂ modified CCTO samples, we can clearly see there is an obvious bimodal grain size distribution: fine TiO₂ crystallites precipitate around CCTO grains (Figure 5.5 A). In this scenario, TCCTO-3 ceramic could be treated as a bimodal aggregate, or a “composite” that comprises of large (CCTO) and small grain (TiO₂) clusters. According to Lichtenecker’s logarithmic equation [93], the effective dielectric permittivity (εeff) of this composite can be expressed as

\[
\log \varepsilon_{\text{eff}} = \phi_l \log \varepsilon_l + \phi_s \log \varepsilon_s \quad \text{Eq. 5.2}
\]

where \( \phi_l, \varepsilon_l \) and \( \phi_s, \varepsilon_s \) are respectively the volume fraction and dielectric permittivity of large and small grain clusters. Applying brick layer model to large and small crystallites separately, i.e., incorporating Eq. 5.1 into Eq. 5.2, we can obtain

\[
\log \varepsilon_{\text{eff}} = \phi_l \log \left( \frac{\varepsilon_l t_{l,gb}}{t_{l,gb}} \right) + \phi_s \log \left( \frac{\varepsilon_s t_{s,gb}}{t_{s,gb}} \right) \quad \text{Eq. 5.3}
\]

where \( \varepsilon_{l,gb}, t_{l,gb} \) and \( \varepsilon_{s,gb}, t_{s,gb} \) are dielectric permittivity and thickness of grain boundaries in large and small grain clusters, while \( t_l \) and \( t_s \) are the average grains size of large and small grains. In particular, it is reasonable to assume that \( \varepsilon_{s,gb} = \varepsilon_{l,gb} = 100 \), because they should have a very similar composition (CuO-rich).

Moreover, as \( (\phi_l + \phi_s) = 1 \), Eq. 5.3 could be rewritten as

\[
\log \varepsilon_{\text{eff}} = \log \left( \frac{\varepsilon_{l,gb} t_{l,gb}}{t_{l,gb}} \right) + \phi_s \left[ \log \left( \frac{\varepsilon_{s,gb} t_{s,gb}}{t_{s,gb}} \right) - \log \left( \frac{\varepsilon_{l,gb} t_{l,gb}}{t_{l,gb}} \right) \right] \quad \text{Eq. 5.4}
\]

Obviously, in the extreme case of \( \phi_s = 0 \), Eq. 5.4 equals Eq. 5.1 and interprets the dielectric response of pure CCTO. Based on Eq. 5.4, the \( \varepsilon_{\text{eff}} \) in a bimodal TCCTO \( (\phi_s > 0) \) can
only be increased under the circumstance of:

\[
\frac{t_{s,gb}}{t_{s,gb}} > \frac{t_{Lg}}{t_{Lgb}} \quad \text{Eq. 5.5}
\]

In Figure 5.4, TCCTO samples clearly show higher dielectric permittivity than CCTO over the frequency range from $10^2$ to $10^6$ Hz. For example, TCCTO-3 shows dielectric permittivity of 52600 at $10^3$ Hz while CCTO shows a value of 21000. The mean grain size of TiO$_2$ crystallites is ~5 μm. Meanwhile, in CCTO ceramics with bimodal grain size distribution, the volume fraction of $\varphi_s$ could reach up to 50 % [49]. Therefore, the average grain boundary thickness within those small crystallites in TCCTO-3 is around 20 nm. This value is similar as that reported (~3 nm) in previous studies about barrier layer CCTO materials [43, 165].

Furthermore, it is very interesting to notice that the intrinsic dielectric permittivity of TiO$_2$ is also about 100 [172], which is the same as CCTO. Given this good match between TiO$_2$ and CCTO, we may see the whole grain boundary area as a dielectrically continuous phase in the TiO$_2$ modified CCTO to apply the simplified brick layer model. However, the calculated value is much lower than the experimental results, because in this scenario the simplified model does not consider the inhomogeneous or any structural barrier within TiO$_2$-dominant grain boundaries that contributes to the high extrinsic dielectric response.

Based on above discussion, the introduction of initial TiO$_2$ crystallites onto CCTO particles would facilitate the formation of bimodal-distributed microstructure in sintered CCTO and enhance the barrier layer capacitor effect.

5.6 Summary

TiO$_2$ modified CCTO were successfully prepared via a facile sol-gel process and solid-state sintering. During sintering, the initial TiO$_2$ crystallites could be dragged towards grain junctions by grain boundary movement to form a microstructure with bimodal grain size distribution in sintered CCTO. Dielectric properties of CCTO can be improved by the
introduction of those small TiO₂ crystallites and show good stability over the frequency range from $10^2$ to $10^5$ Hz. The grain boundary consisting of small TiO₂ crystallites mixed with CuO phases plays an important role in achieving the enhanced barrier layer capacitor effect in TiO₂ modified CCTO samples. The formation of CuO-rich barrier layers based on the instability of Cu ions has been discussed. The mechanism for the improvement in dielectric permittivity of TiO₂ modified CCTO has been proposed based on a bimodal brick layer model. Large dielectric permittivity ($\sim 5.5 \times 10^4$ at $10^2$ Hz) and low dielectric loss ($<0.2$) could be obtained in the optimized TiO₂ modified CCTO.
Chapter 6. CaCu₃Ti₄O₁₂–PVDF polymeric composites with enhanced capacitive energy density


6.1 Chapter Abstract

CaCu₃Ti₄O₁₂ (CCTO)-PVDF composites were prepared by melt blending and hot molding techniques. The addition of CCTO remarkably enhanced the dielectric properties and the thermal conductivity of PVDF composites. The melting point of the PVDF composites (~170°C) was almost independent of the CCTO addition. Based on the results of dielectric constant and dielectric breakdown voltage, the PVDF composite containing 40 vol.% CCTO fillers shows the optimal capacitive energy storage potential (7.81 J/cm³).

6.2 Introduction

Dielectrics with high capacitive energy storage potential have received great interests due to its fast charge and release ability which is important for portable electronic devices, hybrid electrical vehicles and high energy pulse power applications [19, 129]. Generally, the electrical energy storing density (*U*) of a solid dielectric is defined by $\varepsilon_0 \varepsilon_r E^2/2$, where $\varepsilon_0$ is the permittivity of the vacuum (~8.855×10⁻¹² F/m), $\varepsilon_r$ is the relative permittivity (dielectric constant) of the dielectric material and $E$ is the applied electric field. The maximum energy density is therefore limited by the breakdown voltage ($E_b$). Compared to high dielectric constant, high breakdown voltage is more important for superior energy density as $E$ has quadratic relation with the energy density. Polymers normally have low dielectric constant but show very high breakdown voltage which is favorable for high energy density. Besides,
polymers usually have relatively low processing temperature and good flexibility. Therefore, much interest has been developed to increase the dielectric constant of polymer meanwhile maintaining its high breakdown voltage, in order to achieve a superior energy storing density.

One popular method is to add inorganic dielectrics into polymer matrix. Many ceramics with high dielectric constant have been used, including Pb(Zr,Ti)O₃ (PZT) [88], Pb(Mg₁/₃Nb₂/₃)O₃-PbTiO₃ (PMNT) [89], BaTiO₃ (BTO) [20, 105] and CaCu₅Ti₄O₁₂ [108, 131, 173]. CCTO is a very attractive candidate because of its ultrahigh dielectric constant (~10⁵) which is not sensitive of frequency (20 Hz – 1 MHz) and temperature (100 – 600 K) [11, 12]. As for the matrix, poly(vinylidene fluoride) (PVDF) has been widely studied due to its great breakdown strength, low impedance, and high dielectric constant (~10) among polymers [18, 174]. In order to achieve high dielectric performance, hybrid material with PVDF matrix and CCTO fillers have been investigated recently. For instance, Yang et al [108] have reported that PVDF bulk containing 40 vol.% nanosized CCTO fillers showed giant dielectric constant of 10⁶ at 10² Hz and room temperature, but its considerably high dielectric loss (~48) is not suitable for electrical energy storage. Another study of nano CCTO-PVDF composite thin film showed opposite results that nanocomposite exhibited lower dielectric constant than its micro-sized counterparts, and only demonstrated dielectric constant of <60 even with high nano CCTO particle loading (50 vol.%) [91]. Besides, there is no study on the dielectric breakdown voltage of CCTO-PVDF composites. Furthermore, few studies have investigated the CCTO-PVDF composites’ thermal stability and thermal conductivity, which can strongly influence the breakdown strength.

In this work, we prepared PVDF composites containing different CCTO volume concentration up to 60 vol.%, and systematically studied their thermal stability, thermal conductivity, dielectric properties and energy storing density.

6.3 Experimental

Raw CCTO powders were commercial products from Dianyang LTD, China. In order to minimize the influence of impurities phases, re-calcination of the CCTO product was
performed at 1150°C for 3 h [146]. The as-calcined CCTO powders were subsequently crushed and wet milled into fine particles (2-6 μm) and dried. The density of CCTO powders (4.85 g/cm³) was measured by Archimedes’ principle. The PVDF fine powders (SOLEF 9009) were provided by Solvay Company and used as received (1.75 g/cm³). CCTO-PVDF composites with different CCTO volume concentration (0, 10, 20, 30, 40, 50 and 60 vol.%) were prepared via melt blending and hot molding, which is reported elsewhere [175].

The density (ρ) of synthesized composites was measured by Archimedes’ principle. Differential scanning calorimetry (DSC, NETZSCH, DSC-404-F3) were performed from 25°C to 210°C at a heating rate of 5 K-min⁻¹ in flowing argon atmosphere to study the melting behavior. Environmental scanning electron microscope (ESEM, FEI Quanta 200F) was used for the observation of microstructure. The thermal diffusivity (α, m²·s) and specific heat capacity (Cₚ, J·kg⁻¹·K⁻¹) were measured by LFA 447 Nanoflash (NETZSCH, Germany) at 4 different temperatures (298, 323, 348 and 373 K). Then the thermal conductivity (λ, W·m⁻¹·K⁻¹) was calculated via λ = α·Cₚ·ρ. The dielectric breakdown test was conducted at 50 Hz with a voltage increasing rate of 3 kV/s at Zhuzhou Electrical Locomotive Widget S&T Co., Ltd. The thickness of the tested tablet samples was in the range of 1.7 – 2.5 mm. In order to calculate the energy density (η = ε₀εᵣE²/2), the dielectric constant at 50 Hz of each sample was measured by a precision impedance analyzer (Wayne Kerr 6500B).

6.4 Results and discussion

6.4.1 Density and morphologies

The experimental density and theoretical density of the CCTO-PVDF composites is shown in Figure 6.1. It shows that the experimental density of each PVDF composite is slightly lower than its theoretical density, implying the introduction of fillers may cause voids which would affect the electrical properties of the composite. As the CCTO concentration increasing, the difference between experimental and theoretical densities increases, reflected by the drop down of relative density (experimental density/theoretical density) from 99.89% (pure PVDF) to 98.14% (60 vol.% CCTO). The morphologies of each sample demonstrate
that the CCTO particles were homogeneously dispersed into PVDF matrix, and no obvious pores appear.

![Figure 6.1 Density and morphologies of PVDF composites with different CCTO concentration (each bar stands for 50 μm).](image)

### 6.4.2 DSC and thermal conductivity

The melting temperature is important for polymer dielectrics used in alternative electric field as the heat can be generated due to dielectric loss and accumulated to cause thermal degradation or thermally breakdown. Generally, the melting temperature of polymeric material largely depends on its crystallinity and polymeric chain structure [176]. Figure 6.2 (a) shows the DSC results of CCTO-PVDF composites from 100°C to 200°C. The addition of CCTO fillers did not significantly change the PVDF’s melting point which is in the range of 165.8 to 170.0°C, implying that all polymeric matrixes have similar degree of crystallinity and molecular chain structure.
Figure 6.2 (a) DSC curves of PVDF composites with different CCTO concentration, (b) thermal conductivity of CCTO-PVDF composites at different temperatures.

Figure 6.2 (b) shows the thermal conductivity values of the CCTO-PVDF composites from 298 K to 373 K. At 298 K, pure PVDF shows a thermal conductivity of 0.134 W·m⁻¹·K⁻¹. But the increase of CCTO concentration resulted in remarkable improvement of the thermal conductivity. With 60 vol.% CCTO concentration, the thermal conductivity of PVDF composites reaches 0.788 W·m⁻¹·K⁻¹. On the other hand, temperatures show a limited influence on the thermal conductivity. The top thermal conductivity (0.86 W·m⁻¹·K⁻¹ at 373 K)
can be obtained by 60 vol.% CCTO concentration. The improvement is attributed to the thermally conductive networks formed by high CCTO concentration.

### 6.4.3 Energy density

Figure 6.3 (a) shows the dielectric constant and breakdown voltage of CCTO-PVDF composites at 50 Hz. It is clear that the dielectric constant drastically increases as the CCTO concentration increasing, which is due to the high intrinsic dipole concentration from CCTO and the intensive interfacial polarization from the filler-matrix interface. On the other hand, according to the results, the CCTO concentration shows a complex influence on the dielectric breakdown voltage of PVDF composites. Pure PVDF shows a breakdown voltage of 11.7 kV/mm under the experimental condition, and the addition of CCTO into PVDF matrix instantly lower the breakdown voltage. As the CCTO increasing from 20 to 40 vol.%, the breakdown voltage exhibits an upward trend and reaches the peak value of 11.8 kV/mm. However, when the CCTO concentration is in excess of 40 vol.% (up to 60 vol.%), the breakdown voltage again shows a substantial reduction. It should be noted that the variation of the value of dielectric breakdown voltage is relatively high due to the processing sensitivity of samples. Thin film samples prepared by solution casting with good homogeneity would be desirable to realize high breakdown voltage and show less variation.

We believe there is more than one mechanism that governs the dielectric breakdown voltage in CCTO-PVDF composites. In solid dielectrics, the dielectric breakdown is largely attributed to two mechanisms, electrically breakdown and thermally breakdown. Pure PVDF with homogeneous microstructure possesses uniform inner electrical field, thus, its dielectric breakdown is mainly due to thermally breakdown mechanism. The addition of CCTO fillers into PVDF matrix might, on the one hand, improve the thermal conductivity and transfer away the accumulated heat in alternative field, but on the other hand, introduce electrically inhomogeneity and lower the breakdown strength. Therefore the outcome of CCTO addition largely depends on its loading concentration. Although the thermal conductivity is improved to some extent by low CCTO concentration (10~20 %), the PVDF composites still exhibit
inferior breakdown strength owing to the introduction of imperfections and the limited increase of thermal conductivity.

Figure 6.3 (a) Dielectric constant and dielectric breakdown voltage of CCTO-PVDF composites at 50 Hz, and (b) the energy density of PVDF composites with different CCTO concentration.

When the addition of CCTO is excessive (50–60 %) and results in the highest thermal conductivity, the PVDF composites show decreased breakdown strength because of their
highly electrically inhomogeneity. Therefore, in the present case, the loading of 40 % CCTO can achieve the optimized dielectric breakdown voltage because of its combination of good thermal conductivity and reasonable electrically homogeneity.

Figure 6.3 (b) shows the potential capacitive energy density of CCTO-PVDF composites based on the dielectric constants and breakdown voltages at 50 Hz. The results indicate that the maximum energy density (7.81 J/cm³) can be obtained by PVDF composite with 40 vol.% CCTO concentration, and this value is over two times higher than that of the nano BaTiO₃-PVDF composites (< 3.5 J/cm³) [20, 105]. Pure PVDF can only achieve an energy density of 0.53 J/cm³, even though it has good breakdown voltage. Besides, the PVDF composites with 50 and 60 vol.% CCTO concentration shows a comparable energy density of 7.11 and 5.95 J/cm³, respectively, but their relatively low breakdown voltages are not desirable for application involving high electrical field (>10 kV) [2].

6.5 Summary

Compact and homogeneous PVDF composites containing CCTO up to 60 vol.% have been prepared via melt blending and hot molding techniques. The melting temperature of PVDF composite is in the range of 166 to 170°C, almost independent of CCTO concentration. The thermal conductivity of PVDF composites can be greatly improved with high CCTO concentration (λ = 0.788 W·m⁻¹·K⁻¹ with 60 vol.% CCTO), which is attributed to the inner thermally conductive networks. The highest capacitive energy density (7.81 J/cm³) is obtained in the PVDF composite with 40 vol.% CCTO, because of its optimized combination of dielectric constant and breakdown voltage. Applications such as pulse power supply and other capacitive energy storage devices should be explored with these CCTO-PVDF composites.
Chapter 7. Improving dielectric properties and thermal conductivity of polymer composites with CaCu$_3$Ti$_4$O$_{12}$ and β-SiC hybrid fillers


7.1 Chapter Abstract

In this chapter we report a series of homogeneous polymeric composites with enhanced dielectric properties and thermal conductivity. The composites were constituted of polyvinylidene fluorides (PVDF) matrix and CaCu$_3$Ti$_4$O$_{12}$ (CCTO) singular or β-SiC-CCTO hybrid fillers, and prepared by melt blending and hot molding techniques. The influence of different types of fillers and the composition on dielectric properties and thermal conductivity of the obtained composites was studied. Results show that hybrid loading is preferred and a reasonable combination of thermal conductivity (0.80 W·m$^{-1}$·K$^{-1}$), dielectric constant (~50) and dielectric loss (~0.07) at 10$^3$ Hz was achieved in the PVDF composite containing 40 vol.% CCTO and 10 vol.% β-SiC. The strong dipolar and interfacial polarization derived from the fillers are responsible for the enhancement of the dielectric constant, while the formation of thermally conductive networks/chains by β-SiC whiskers contributes to the improved thermal conductivity. In addition, composite with 40 vol.% singular CCTO addition show the optimal breakdown voltage of 22.58 kV/mm among CCTO-PVDF and β-SiC-CCTO-PVDF composite (40.21 kV/mm for pure PVDF). The introduction of β-SiC whiskers into 40 vol.%-CCTO-PVDF binary composite could reduce the breakdown voltage.

7.2 Introduction

Polymer-matrix composites with functional fillers have drawn considerable attention in
electronic packaging and pulse power applications, because of the flexibility, easy processing, light weight, and tunable electrical/thermal properties. One prevailing strategy is the ceramic/polymer composites because such composites could maintain great breakdown resistance and high dielectric constant if the particles are incorporated with a proper polymer to ceramic ratio and are homogeneously dispersed [19]. A number of conventional dielectric ceramics have been explored, such as TiO₂ [87], barium titanate (BTO) [20], lead zirconate titanate (PZT) [133], and Pb(Mg₁/₃Nb₂/₃)O₃-PbTiO₃ (PMNT) [89].

Recently, much attention has been paid to CaCu₃Ti₄O₁₂ (CCTO) fillers, a perovskite-like ceramic possessing high dielectric permittivity above 10⁴ with weak temperature and frequency dependence [11]. The polymer-based composites with CCTO particles exhibit various dielectric properties depending on different preparation techniques (e.g. in-situ polymerization [177], hot pressing [108], or solution casting [112]) and morphologies (e.g. bulk tablet [108, 178], thin film [131], or sheet [179]). Although there is a dispute about the influence of the particle size [107, 177], it is accepted that the nano CCTO (> 40 vol.%) mixing in polymer matrix could realize very high dielectric constant (~10⁶ at 100 Hz) but with large dielectric loss (~50) [108, 177]. In contrast, the use of micrometer sized CCTO particles can hardly increase the dielectric constant to 100, even with high volume fractions in the composite [132, 179]. Furthermore, as nanoparticles can strengthen the interfacial polarization, they also create serious distortion of electric field in the composites, resulting in inferior breakdown voltage and high dielectric loss.

A hybrid CCTO-polymer composite could mitigate the above mentioned problems, because it is possible to simultaneously achieve high dielectric constant, low dielectric loss and good breakdown field. Yang et al disclosed a dramatic increase in dielectric constant of Ni-CCTO-polymer as the Ni content approached 24 vol.% [180]. It was also reported that the Al-CCTO-epoxy composite could achieve a permittivity of 700 at 100 Hz and room temperature with a low loss [181]. Nonetheless, the initiative of these researches was based on the conductive percolation theory that requires high volume fraction of metal fillers, which would considerably lower the breakdown strengths and harm the performance.

In this study, we select a non-metallic compound, β-SiC whiskers, as the third phase to play a functional part in CCTO-PVDF (polyvinylidene fluoride) composites, because β-SiC
shows high thermal conductivity and good electrical stability, and has wide utilization in corona protection and electric stress control [114]. This work investigated the thermal conductivity and dielectric response of the PVDF composites with different filling fraction of CCTO and β-SiC. The β-SiC-CCTO-PVDF ternary composites demonstrated considerable improvement in dielectric constant and thermal conductivity.

7.3 Experimental

CCTO powders with particle size around 2 – 6 μm were supplied by Dianyang Ltd, China. The β-SiC whiskers (average diameter ~2.5 μm) were purchased from Jiechuang Ltd, China, while the PVDF fine powder (SOLEF 9009) was complimentarily supplied from Solvay, USA. A series of CCTO-PVDF, β-SiC-PVDF and β-SiC-CCTO-PVDF composites (see Table 7.1) were prepared via the simple melt blending and hot molding technique. Firstly, the composite with appropriate ratio was melted and mixed in an extruder (DSE 20, Brabender) for 10 min at 190°C. Then the bulks were milled into powders by ultra-centrifugal mill (ZM 200, Retsch). Finally the powders were shaped into round tablets (d = 25 mm, h = 2 mm) by hot molding at 180°C for 10 min at 20 MPa pressure and followed by 5 min water cooling.

An environmental scanning electron microscope (ESEM, FEI Quanta 200F) was used for observation of micromorphology of the composites. The dielectric properties were tested by Precision Impedance Analyzer (Wayne Kerr 6500B) in the range of $10^2$ to $10^6$ Hz. The thermal diffusivity ($\alpha$, m$^2$·s) and specific heat capacity ($C_p$, J·kg$^{-1}$·K$^{-1}$) were measured with LFA 447 Nanoflash (NETZSCH, Germany) at 25°C. The bulk density of the samples ($\rho$, kg·m$^{-3}$) was measured based on Archimedes’ principle. Thus the thermal conductivity ($\lambda$, W·m$^{-1}$·K$^{-1}$) was calculated as per $\lambda = \alpha \cdot C_p \cdot \rho$.

For the test of dielectric breakdown voltage, Agilent 4294A equipped with high voltage interface (HVI) was used. The tablet samples were hot pressed as thin as possible (0.4 – 0.7 mm) due to the equipment has a voltage limit of 10,000 volts. Both sides of samples were painted with conductive silver paste. The voltage increment is 1 kV/mm with a frequency of 1 Hz.
Table 7.1 Nominal compositions of PVDF composites with different fillers.

<table>
<thead>
<tr>
<th>Composition (vol. %)</th>
<th>CP0</th>
<th>CP1</th>
<th>CP2</th>
<th>CP3</th>
<th>CP4</th>
<th>CP5</th>
<th>CP6</th>
<th>SP2</th>
<th>SP4</th>
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<tr>
<td>β-SiC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>30</td>
<td>40</td>
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<td>60</td>
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<td>80</td>
<td>70</td>
<td>60</td>
<td>50</td>
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<td>98</td>
<td>96</td>
</tr>
<tr>
<td>Composition (vol. %)</td>
<td>SP6</td>
<td>SP8</td>
<td>SP10</td>
<td>SCP2</td>
<td>SCP4</td>
<td>SCP6</td>
<td>SCP8</td>
<td>SCP10</td>
<td></td>
</tr>
<tr>
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<td>10</td>
<td>2</td>
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<td>6</td>
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<tr>
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</table>

7.4 Results and discussion

7.4.1 Thermal conductivity

Figure 7.1 shows the thermal conductivity values of the composites with different fillers and concentration at 25°C. The PVDF matrix shows a thermal conductivity around 0.13 W·m⁻¹·K⁻¹, while the thermal conductivity of the CCTO-PVDF composites increases remarkably with increasing CCTO loading. It reaches to 0.78 W·m⁻¹·K⁻¹ for 60 vol.% CCTO. In comparison with CCTO particles, β-SiC particles prominently contribute more to the increase of thermal conductivity due to its intrinsic high thermal conductivity of ~120 W·m⁻¹·K⁻¹ [182]. When the filler loading is 10 vol.%, the CCTO-PVDF shows the thermal conductivity of 0.22 W·m⁻¹·K⁻¹ whereas the β-SiC-PVDF composite shows a value of 0.28 W·m⁻¹·K⁻¹.
Furthermore, the ternary composites containing both β-SiC whiskers and CCTO particles exhibit a higher thermal conductivity than the binary CCTO-PVDF system with identical solid loading (dashed square in Figure 7.1). For instance, with the same loading at 50 vol.%, β-SiC-CCTO-PVDF and CCTO-PVDF show thermal conductivity values of 0.80 and 0.62 W·m$^{-1}$·K$^{-1}$ respectively. This means that the addition of 10 vol.% β-SiC enhanced the thermal conductivity by 30%. Overall, a higher loading of CCTO and β-SiC leads to a higher thermal conductivity in PVDF composites. At high loading fraction, fillers tend to connect with each other and form thermally conductive pathways, therefore leading to better thermal transfer efficiency compared with low filling fraction.

### 7.4.2 Micromorphology

Figure 7.2 shows the microstructure of the PVDF composites with different fillers. Apparently PVDF shows good compatibility with both CCTO particles and β-SiC whiskers, and results in compact microstructures. The CCTO and β-SiC whiskers are randomly and
uniformly dispersed in the PVDF matrix when the filler loading is low. As the filler loading increases, the particles and whiskers interlace with each other and form networks, which is advantageous for high thermal conductivity.

Figure 7.2 Microstructure of PVDF composites with CCTO and/or β-SiC fillers (each bar stands for 10 μm).

Nielsen model is usually used to evaluate the thermal conductivity of a composite material, which is expressed in Eq. 7.1 [183]:

$$\lambda_c = \lambda_m \frac{1 + AVf}{1 - B(Vf)} \text{ (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$$

Eq. 7.1

where $B = (\lambda_f/\lambda_m - 1)(\lambda_f/\lambda_m + A)$, $\phi = 1 + (1 - Vm)VfVm^{-2}$, and $\lambda_c$, $\lambda_m$, and $\lambda_f$ stands for the thermal conductivity of composites, matrix and filler, respectively; $Vf$ is the volume fraction of the filler while $Vm$ is the maximum packing fraction of the dispersed particles; $A$ is a
constant that depends on the shape and orientation of the filler. Typical values of $A = 3$, $V_m = 0.637$ are assigned to randomly packed aggregates of sphere fillers. According to Eq. 7.1, at a low CCTO and β-SiC concentration (<30 vol.%), the increase of thermal conductivity is less significant, but when the filler loading is higher than 40 vol.%, the thermal conductivity of the composites increases drastically. At a high filler concentration, CCTO particles and β-SiC whiskers easily agglomerates and therefore a conductive chain along the heat flow direction is formed thereby achieving high thermal conductivity. Furthermore, Eq. 7.1 indicates that the thermal conductivity of multi-component materials is dependent not only on the $\lambda_f \lambda_m^{-1}$ (~1000), but also the microstructural feature such as the particle size, concentration, orientation, and the interaction between particles and matrix, which is collectively reflected in the constant $A$.

7.4.3 Dielectric constant and loss

The dielectric property of the composites at different frequency is shown in Figure 7.3. It is clear that the dielectric constant of PVDF materials is enhanced by addition of either CCTO, β-SiC or both. Specifically, the greatest dielectric constant (~55) is obtained by the hybrid loading of 50 vol.% (40 vol.% CCTO and 10 vol.% β-SiC), while singular CCTO just provide a dielectric constant of 45 with the same loading at $10^2$ Hz (see CP5 in Figure 7.3 (a) and SCP10 in Figure 7.3 (c)). The addition of β-SiC whiskers made limited contribution to the dielectric constant due to its small amount (< 10 vol.%). Besides, the dielectric constant of each sample shows a downtrend from $10^2$ to $10^6$ Hz, while the dielectric loss exhibits an opposite trend with a sharp increase over $10^5$ Hz. These frequency dependent properties have an intrinsic relation with the polarization mechanisms.

In general, the polarization of polymer dielectrics is contributed by induced polarization (electron and atomic polarization), dipolar orientation polarization, and interfacial polarization. The characteristic relaxation time ($\tau$) of each polarization is in the order of $\tau_{\text{induced}} < \tau_{\text{orientational}} < \tau_{\text{interfacial}}$. Therefore the interfacial polarization introduced by CCTO and β-SiC fillers becomes negligible at high frequency since the interfacial polarization mechanism needs relatively long relaxation time and cannot keep up with the alternative field, which is reflected
by the reduction of the dielectric constant with frequency (Figure 7.3 (a) and (c)). However, in the relatively low frequency range, interfacial polarization that derives from the CCTO-PVDF and SiC-PVDF interfaces makes a considerable contribution to the effective dielectric constant. So the sample SCP10, with 10 vol.% β-SiC whiskers and 40 vol.% CCTO, shows the highest dielectric constant, largely due to the intensive interfacial polarization. With increasing frequency, the enhancement of dielectric response mainly comes from the intrinsic dipolar polarization of the CCTO, β-SiC and the matrix.

In terms of dielectric loss, there are two typical types: conduction electrons loss, and dipole relaxation loss. In PVDF composites, because of the high concentration of dipoles in CCTO and β-SiC fillers, the dipolar relaxation mechanism is the major factor responsible for the dielectric loss at the lower frequency range. As shown in Figure 7.3 (c) and (d), the dielectric loss increases rapidly at the frequency higher than $10^5$ Hz due to the relaxation of
PVDF. The dielectric loss is tunable over the range from 0.01 to ~ 0.08 below $10^5$ Hz. Such dielectric properties are attractive for electronic applications. Overall, these functional fillers not only give rise to the migration and accumulation of the electrical charge at the interfaces, but also enhance the dielectric constant by their intrinsic high concentration of polar groups which stem from the heterogeneous nano-domain within CCTO materials [36].

7.4.4 Dielectric breakdown voltage

The dielectric breakdown test of PVDF composites containing CCTO and $\beta$-SiC has been carried out and the results are shown in Figure 7.4. According to Figure 7.4 (a), for CCTO-PVDF binary composites, pure PVDF shows the highest breakdown voltage of 40.21 kV/mm. Similar to previous experimental results, the addition of CCTO fillers instantly reduces the overall dielectric breakdown strength in PVDF composites. However, composite with 40 vol.% CCTO still can show a high dielectric breakdown voltage of 22.58 kV/mm.

When introducing $\beta$-SiC whiskers into PVDF composite with 40 vol.% CCTO, an immediate drop of breakdown voltage is shown in Figure 7.4 (b), i.e. from 22.58 to 14.90 kV/mm. Further increase in $\beta$-SiC content results in even lower breakdown voltage and 10 vol.% addition of $\beta$-SiC whiskers leads to the lowest value of 5.70 kV/mm. On the other hand, as for the $\beta$-SiC-PVDF binary composites, the breakdown voltage shows a peak value (~17.20 kV/mm) when the addition of $\beta$-SiC is 6 vol.%. In solid dielectrics, the dielectric breakdown is largely attributed to two mechanisms, electrically breakdown and thermally breakdown. It is clear that the addition of $\beta$-SiC whiskers is not favorable for realizing high breakdown voltage in CCTO-PVDF binary composites, although $\beta$-SiC can effectively enhanced the thermal conductivity. Therefore, same as the results in Chapter 6, PVDF composite with 40 vol.% CCTO has the optimal dielectric breakdown voltage because of its combination of good thermal conductivity and electrically homogeneity.

However, if comparing with the results obtained in Chapter 6, it is worth noting that breakdown voltage is higher in samples with smaller thickness (as shown in Figure 7.4 (a) and
Figure 6.3 (a)), which implies that the preparation technique and extrinsic factors had significant influence onto the dielectric properties. Careful control of the morphology and distribution of fillers is critical to achieve high breakdown voltage in resultant with great energy storing potential.

Figure 7.4 Dielectric breakdown voltages of PVDF composites with different volume fraction of fillers.

7.5 Summary

A series of homogeneous PVDF composites with CCTO and β-SiC fillers have been prepared by simple melt blending and hot molding technique. The study of thermal conductivity and dielectric response showed that the hybrid fillers demonstrate the advantages of high thermal conductivity, high dielectric constant and low dielectric loss within the ternary β-SiC-CCTO-PVDF composites. The enhancement of thermal conductivity is attributed to the formation of thermally conductive networks/chains by CCTO and β-SiC fillers. The
mechanisms governing the frequency-dependent dielectric properties are closely correlated to
the interfacial and dipolar polarization introduced by the fillers. Composite with 40 vol.%
singular CCTO addition shows the optimal breakdown voltage of 22.58 kV/mm among
CCTO-PVDF and β-SiC-CCTO-PVDF composite (40.21 kV/mm for pure PVDF). The
introduction of β-SiC whiskers into 40 vol.%-CCTO-PVDF binary composite could reduce
the breakdown voltage. In addition, the composite containing 40 vol.% CCTO and 10 vol.%
β-SiC showed a reasonable combination of thermal conductivity (0.80 W·m⁻¹·K⁻¹), dielectric
constant (~50) and dielectric loss (~0.07) at 10³ Hz.
Chapter 8. Conclusions, recommendation and further work

This thesis focused on the synthesis, characterization and electrical properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) materials, CCTO-PVDF and β-SiC-CCTO-PVDF composites. Some important findings are summarized in this conclusion chapter. We hope the findings described below could lay a foundation and lead to broader future investigations in these intriguing dielectric materials for use in the next-generation of microelectronic components and energy storage devices.

1) In situ synchrotron X-ray powder diffraction was used to study the high-temperature phase evolution of CCTO solid state and sol-gel precursors. The phase evolution and reaction sequences in both precursors have been established. The CCTO phase forms at a lower temperature (800°C) in the sol-gel precursor than in the solid state precursor (875°C). Intermediate phases such as CaTiO$_3$ appear in the sol-gel precursor but not in the solid state mixture. The crystallite size of the synthesized CCTO powder varies from 200 nm to 2 μm. The resultant sub-micrometric crystallite size is attributable to the fast heating rate of 200 K∙min$^{-1}$ and the short holding time. Real time phase and lattice parameter evolution data reveal that the instability of Cu ions and the segregation of CuO are the origin of the compositional inhomogeneity and defects in CCTO, and eventually responsible for the giant dielectric constant. The formation mechanism of internal barrier layer capacitor is discussed.

2) Microwave-assisted synthesis of CCTO using sol-gel precursor is firstly reported with substantial reduction of preparation time and decreased particle size ($D_{50}=3.826$ μm). The heating rate by microwave radiation is about 100 K∙min$^{-1}$. Comparing with conventional calcination method which required 3 h to obtain 87.6 wt.% CCTO at 1100°C, the 17-min-calcination of microwave heating can achieve 89.1 wt.% CCTO at 950°C. A combination of dielectric constant (~2.5×10$^3$) and dielectric loss (0.161) at 10$^3$ Hz was obtained in the microwave-sintered CCTO at 1050°C for 1 h. In order to realize good dielectric response in the sintered CCTO materials, a reasonably long holding time is necessary. The origin of the dielectric response in the CCTO ceramic is explained. The results
indicated that the microwave technique shows considerable advantages in terms of energy and time efficiency to synthesize CCTO materials or other high performance dielectrics from sol-gel precursors.

3) CCTO was modified with TiO₂ shell via a simple sol-gel precipitation process followed by solid state sintering. The precipitated TiO₂ shells around CCTO particles (core) could transform into small rutile TiO₂ crystallites around CCTO grains to form a very unique bimodal morphology, which plays an important role in achieving the enhanced barrier layer capacitor effect. The mechanism for the improvement in dielectric permittivity of TiO₂ modified CCTO has been proposed based on a bimodal brick layer model. Large dielectric permittivity (~5.5×10⁴ at 10² Hz) and low dielectric loss (<0.2) could be obtained in the optimized TiO₂ modified CCTO.

4) Compact and homogeneous PVDF composites containing CCTO up to 60 vol.% were prepared by melt blending and hot molding techniques. The melting temperature of PVDF composite is nearly independent of CCTO concentration and in the range of 166°C – 170°C. The dielectric constant and thermal conductivity of PVDF composites can be both improved by CCTO addition. The highest capacitive energy density (7.81 J/cm³) is obtained in the composite with 40 vol.% CCTO addition because of the optimal combination of dielectric constant and breakdown voltage. Applications such as pulse power supply and other capacitive energy storage devices should be explored with these CCTO-PVDF composites.

5) A serial of novel polymeric composites constituted of polyvinylidene fluorides (PVDF) matrix, and β-SiC-CCTO functional fillers were also studied. The hybrid fillers largely enhanced the dielectric properties and thermal conductivity of the composites. The formation of the inner thermally conductive networks by β-SiC whiskers contribute to the increase of thermal conductivity, while the strong dipolar and interfacial polarization derived from the fillers are responsible for the enhancement of the dielectric constant. It has been found that the composite with 40 vol.% singular CCTO addition show the optimal breakdown voltage of 22.58 kV/mm among the composites (40.21 kV/mm for pure PVDF), and exhibit a great energy storing potential. The introduction of β-SiC whiskers into 40 vol.%-CCTO-PVDF binary composite, however, would harm the breakdown voltage. Dielectric capacitors based on those composites might hold potential for capacitive energy storage both in large and small
The following recommendation has been made for the future investigations in order to gain comprehensive understanding on CCTO materials and CCTO-polymeric composites, as well as finding new applications for those novel materials.

1) It should be noted that the dielectric property of CCTO is extrinsic and related to its morphology. Thus, it would be very interesting to prepare new types of CCTO nano-fibers or nanowires. It is also worthwhile to study the preparation and electric property of composites containing the CCTO nano-fibers and nanowire additives.

2) According to the present study, optimal dielectric property can be achieved in CCTO-PVDF (40 – 60 vol.%) composite. Hence, it is of technical importance to prepare CCTO composites using other polymer matrix (e.g., P(VDF-TrFE)) in order to develop different composites for various applications. In addition, to use solution casting to fabricate CCTO thin composites might be an effective way to further increase the dielectric breakdown voltage ($E_b$), because higher $E_b$ can be realized in thinner samples in this study.

3) Future investigation on surface properties of CCTO particles is necessary to explore better compatibility between CCTO and polymer matrix. Besides, surface modification via coupling agent (e.g. titanate coupling agent) will improve both the filler distribution and composite workability, and eventually enhance the energy density.
References


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