## CHAPTER 1

#### INTRODUCTION AND OBJECTTIVES

#### **1.1. Introduction**

## 1.1.1. Historical background

Materials exerting a giant dielectric constant have gained a great deal of attention. Since the discovery of ferroelectricity in a single crystal of Rochelle salt in 1921[1], there have been many attempts to find new materials that possess a high dielectric constant (K). Due to the shortage of mica, the most widely used insulator for capacitors during World War II, the urgent demand for ceramic capacitors having high dielectric constants has been a key issue leading to the development of ceramic capacitor technology. However, the most notable achievement in high-K dielectrics (materials having dielectric constants higher than 1000) was not achieved until the unusual dielectric constant of barium titanate (K  $\sim$  1,100) based on the work by Thurnauer [2] was first observed in 1941. Despite the wartime restriction on the circulation of the technical reports by Wainer and Salomon [3], there were analogous results that confirmed barium titanate (BaTiO<sub>3</sub>) as a high-K material by other researchers [4]. With the development of ceramic capacitor technology, the search for high-K materials has continued since the discovery of BaTiO<sub>3</sub>.

Unlike normal dielectric materials with dielectric constants lower than 100, certain types of crystals exhibit high dielectric constants as high as  $10^5$  in specific conditions [5]. Most materials in this category are ferroelectric crystals, and their

ferroelectric behavior is attributed to the appearance of a spontaneous polarization that is tied to a structural phase transition. This spontaneous polarization is realized in the characteristic hysteresis loop and can be reversed by the application of the electric field to the opposite direction. Some examples of high-K ferroelectric crystals are BaTiO<sub>3</sub>, potassium dihydrogen phosphate (KDP, KH<sub>2</sub>PO<sub>4</sub>), and triglycine sulphate (TGS, (C<sub>2</sub>NH<sub>2</sub>COOH)<sub>3</sub>. H<sub>2</sub>SO<sub>4</sub>) [6]. However, the fact that the ferroelectric phenomenon occurs only in a class of materials possessing a non-centrosymmetric crystal structure and a polar axis has attracted great interest in BaTiO<sub>3</sub> and other ferroelectrics having ABO<sub>3</sub>-type perovskite structures.



Figure 1.1 Three-dimensional unit cell structure of the cubic BaTiO<sub>3</sub>

The unit cell structure of BaTiO<sub>3</sub> is shown in Figure 1.1. That BaTiO<sub>3</sub> has a cubic perovskite structure (point group: m3m [7] above a Curie temperature (T<sub>c</sub>) of 123 °C. Below T<sub>c</sub>, the structure changes to tetragonal (point group: 4mm [7]). Inside this cubic unit cell, divalent Ba<sup>2+</sup> ions are located on the corners while a tetravalent Ti<sup>4+</sup> ion is located in the center with the 6 oxygen ions in the centers of the facial planes forming a TiO<sub>6</sub> octahedron. In the tetragonal structure below T<sub>c</sub>, however, the Ti<sup>4+</sup> and Ba<sup>2+</sup> ions are displaced upward by 0.125 Å and 0.067 Å, respectively [8] while O<sup>2-</sup> ions are displaced downward by 0.04 Å [5]. Consequently, this series of ionic displacements in tetragonal BaTiO<sub>3</sub> crystal creates a permanent dipole that gives rise to a spontaneous polarization. As seen in Figure 1.2, BaTiO<sub>3</sub> has a typical dielectric constant of about 10,000 near T<sub>c</sub>, but this value is drastically reduced at T < T<sub>c</sub>. This temperature dependent ferroelectric transition was verified by a simple explanation that combines the Clausius-Mossotti relationship with Lorentz" s internal field formula [9] leading to the well-known Curie-Weiss Law:  $\varepsilon_r' \approx C/(T-T_c)$ .

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Figure 1.2 Dielectric constant of BaTiO3 as a function of temperature [9]

#### 1.1.2. Perovskite Materials

The perovskite structure, written as  $A^{XII}B^{VI}X_3$ , is one of the most versatile crystal structures. The A-site is in 12-fold coordination with large cations, the B-site is in 6-fold coordination with smaller cations, and the X sites are 6-fold coordinated anions. The crystal structure is shown in figure 1.3. Through manipulating composition of each site, it can be used as a catalyst, capacitor, magnetic material, magnetoresistive material, non-linear optical material or even a superconductor [10]. Furthermore, most piezoelectric and ferroelectric materials are derived from the perovskite structure.



Figure 1.3 ABO<sub>3</sub> perovskite-type unit cell and applications

The perovskite structure can tolerate a wide range of compositional variation. The simple ternary perovskite can be divided into  $A^{1+}B^{5+}O_3$ ,  $A^{2+}B^{4+}O_3$ ,  $A^{3+}B^{3+}O_3$ types and oxygen and cation deficient phases. An example for  $A^{1+}B^{5+}O_3$  types perovskite is KNbO<sub>3</sub>. This type oxide is of particular interest due to its ferroelectric properties. The  $A^{2+}B^{4+}O_3$  type probably contains the largest number of perovskite typen compounds. The best compounds known of this type are titanates due to the ferroelectric properties that barium and lead compounds exhibit. The last type of ternary perovskite,  $A^{3+}B^{3+}O_3$ , includes BiFeO<sub>3</sub> and LaAlO<sub>3</sub> which generally possess a lower symmetry structure like rhombohedral or orthorhombic. In addition to the simple ternary perovskite, the perovskite structure can also allow complex charge compensated compositions. Most of the materials in the complex perovskite families are known to be relaxor ferroelectric. The general formula for the complex perovskites can be written as  $(A'A'')^{XII}(B'B'')^{VI}X_3$ . Where the average valence of the A site and B site follows the same rules for simple ternary perovskites.

The discovery revealed by Subramanian *et al.* [12], found out the abnormally high dielectric constant of copper calcium titanate (CCTO), which belongs to the A Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> family known by Deschanvres *et al.* [13] since 1967. They reported that the dielectric constant of CCTO was as high as 10,000 at 1 MHz and showed the temperature dependence. From their expanded data of dielectric constant measured in other ACu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> as well as ACu<sub>3</sub>Ti<sub>3</sub>FeO<sub>12</sub> family, shown in Table 1.1, the unusually high dielectric constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> over 10<sup>4</sup> at 100 kHz is not shown in the rest of compounds. Also, their refinement data via neutron powder diffraction suggested that CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> maintained the same cubic structure at T = 100 K and 35 K, indicating no phase transition. Further study by Ramirez *et al.* [14] confirmed the nearly stable dielectric constant in the temperature range of 100 – 400 K. For the origin of this abnormally high dielectric constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> over the vast temperature range, however, there have been lots of discussions from the different point of views for a few years.

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Compounds	Dielectric constant*	Loss tangent*	Lattiace parameter (Å)
CaCu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	10,286	0.067	7.391
CdCu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	409	0.093	7.384
La <sub>2/3</sub> Cu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	418	0.060	7.427
Sm <sub>2/3</sub> Cu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	1,665	0.048	7.400
Dy <sub>2/3</sub> Cu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	1,633	0.040	7.386
Y <sub>2/3</sub> Cu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	1,743	0.049	7.383
Bi <sub>2/3</sub> Cu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	1,871	0.065	7.413
BiCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	692	0.082	7.445
LaCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	44	0.339	7.454
NdCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	52	0.325	7.426
SmCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	52	0.256	7.416
GdCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	94	0.327	7.409
YCu <sub>3</sub> Ti <sub>3</sub> FeO <sub>12</sub>	33	0.308	7.394

Table 1.1 Dielectric data and the lattice parameter for  $ACu_{3}M_{4}O_{12}$ 

\*measured at 100 kHz

## 1.1.3. Structural studies on CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>

Following the first details on the ACu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> family by a group of French researchers in 1967, Bochu et al. [15] reported the detailed and more precise structural analysis of these compounds in 1979. Based on their study, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> possesses a distorted cubic perovskite (ABO<sub>3</sub>) structure with the space group Im3 and a lattice parameter of 7.391 Å. The extended unit cell structure of  $CaCu_3Ti_4O_{12}$  is shown in Figure 1.4. Here, the  $Ca^{2+}$  ions occupy the corners and the center of the unit cell while Cu<sup>2+</sup> ions are located on the centers of cell edges and planes. The Ti<sup>4+</sup> ions are surrounded by 6 oxygen ions, forming  $TiO_6$  octahedra which are tilted inward in order to make a square planar arrangement for the nearby Cu<sup>2+</sup> ions. Structures with  $Cu^{2+}$  in a square planar configuration are common in compounds with a d<sup>9</sup> electron configuration. This results from d-orbital splitting such that the  $dx^2-y^2$  state shifts to a higher energy state occupied by a single electron while the  $d_z^2$  state takes on a lower energy state with a pair of electrons. This phenomenon, called the Jahn-Teller effect or distortion, is usually achieved by increasing the bond length along the z-axis which consequently causes a reduction in the electron pair repulsion [16] and a tilt of the  $TiO_6$  octahedra in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. Subramanian *et al.* [12] mentioned that the enhanced polarizability and the dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> could be due to the tension of the Ti-O bonds and that the extreme tilt of the TiO<sub>6</sub> octahedra prevents the formation of the ferroelectric state. Although the high dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> can be explained from the structural point of view, there have been many reports that strongly indicate that the other mechanisms are possible.



**Figure 1.4** Three-dimensional unit cell structure of  $CaCu_3Ti_4O_{12}$  [12] [Ca is the largest atom at the corners and the center of a unit cell; Cu atom is located in the center of edges and facial planes in a unit cell; Ti atom is hidden inside of each octahedron, forming TiO<sub>6</sub>; 4 O atoms are bonded to a single Cu atom – CuO<sub>4</sub> square planar structure]

#### 1.2. Research Object

- (1) To study the basic properties of CCTO ceramics.
- (2) To investigate the optimum condition for ceramics processing.
- (3) To study the relationship between dielectric properties and crystal structure.
- (4) To study the ways for improvement both dielectric properties and loss of

ceramics.

(5) To study the effects of additive elements: cesium, cerium, zirconium and germanium on crystals and dielectric properties on CCTO ceramics.

## **1.3. Usefulness of the Research**

- (1) To optimize the processing conditions of CCTO and doped CCTO ceramics.
- (2) To compare the dielectric properties and dielectric loss of CCTO and

cesium, cerium, zirconium and germanium doped CCTO ceramics.

(3) To develop an overall understanding in processing conditions,

microstructure and electrical properties of CCTO ceramics.

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