SYNTHESIS AND CHARACTERIZATION OF BARIUM TITANIUM OXIDE ($BaTiO_3$) AND CALCIUM COPPER TITANIUM OXIDE ($CaCu_3Ti_4O_{12}$) PELLETS AND THIN FILMS

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by

YEOH CHEOW KEAT

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LIST OF SYMBOLS

ε	dielectric constant
T	temperature
γ	diffusivity
tan δ	dielectric loss
e	electron charge
d_g	average grain size
ϕ	potential barrier height
b_e	bulk mobility of electrons
C	capacitance
RH	relative humidity
V	volume
Z	impedance
Y	admittance
M	electric modulus
D	diffusion coefficient
R	resistance
ρ	resistivity
k	Boltzmann’s constant
E_a	activation energy

LIST OF PUBLICATIONS & SEMINARS

1. Yeoh, C. K., Sreekantan, S., Hutagalung, S. D., & Ahmad, Z. A. (2007). Fabrication of $BaTiO_3$ thin films through ink-jet printing of TiO_2 sol and soluble Ba salts. *Materials Letters*. **61(2007):** 4536-4539.

2. Yeoh, C. K., Ahmad, M. F., & Ahmad, Z. A. (2006). Effects of Cu and Ti excess on the dielectric properties of $CaCu_3Ti_4O_{12}$ prepared using a wet chemical method. *Journal of Alloys and Compounds*. **443(1-2):** 155-160.

3. Yeoh, C. K., Sreekantan, S., Hutagalung, S. D., & Ahmad, Z. A. (2006). Microstructure of $CaCu_3Ti_4O_{12}$ prepared through a wet chemical method. Proceedings of the 15th Scientific Conference of the Electron Microscopy Society of Malaysia. Terengganu, Malaysia, December, 2006.

4. Yeoh, C. K., Sreekantan, S., Hutagalung, S. D., & Ahmad, Z. A. (2006). Inkjet printing of $BaTiO_3$ thin films from aqueous solutions. International Conference on X-ray and Related Techniques in Research and Industry (ICXRI 2006). Putrajaya, Malaysia, November, 2006.

5. Yeoh, C. K., Sreekantan, S., Hutagalung, S. D., & Ahmad, Z. A. (2005). Inkjet printing of $CaCu_3Ti_4O_{12}$ films. Proceedings of the 14th Scientific Conference of the Electron Microscopy Society of Malaysia. Penang, Malaysia, December, 2005.

SINTESIS DAN PENCIRIAN PELET DAN FILEM NIPIS BARIUM TITANIUM OKSIDA ($BaTiO_3$) DAN KALSIUM KUPRUM TITANIUM OKSIDA ($CaCu_3Ti_4O_{12}$)

ABSTRAK

$BaTiO_3$ dan $CaCu_3Ti_4O_{12}$ ialah bahan seramik dengan pemalar dielektrik yang tinggi. Pemalar dielektrik tinggi $BaTiO_3$ disebabkan perubahan feroelektrik manakala sebab untuk $CaCu_3Ti_4O_{12}$ belum jelas. Cetakan semburan dakwat (*ink-jet printing*) digunakan untuk menyediakan filem nipis. Kaedah sintesis akueus bersuhu rendah digunakan kerana larutan yang digunakan tidak mengandungi mendakan. Serbuk, yang kemudiannya dibentuk menjadi pelet, dimendakkan daripada larutan dengan mengubah pH. Filem nipis diperoleh dengan mencetak larutan yang disediakan ke atas substrat kaca Corning 1737. Sekurang-kurangnya 5 kali cetakan diperlukan untuk memperoleh filem nipis yang tidak terputus-putus dengan ketebalan 2 μm. Tambahan awal Ba sebanyak 10% lebih daripada nisbah stoikiometri dan larutan pH13 diperlukan untuk mendakan $BaTiO_3$ stoikiometri. Untuk $CaCu_3Ti_4O_{12}$, 10% lebih Ca, 10% kurang Cu dan larutan pH13 diperlukan. XRD menunjukkan mendakan yang diperoleh mengandungi $BaTiO_3$ atau $CaCu_3Ti_4O_{12}$ dan <5% lebihan TiO_2. Spektroskopi galangan (*impedance spectroscopy*) menunjukkan $BaTiO_3$ tidak homogen secara elektrik dan terdiri daripada tiga elemen elektrik: teras berkerintangan rendah, bahagian pukal feroelektrik, dan sempadan butiran berkapasitans tinggi. Hanya teras berkerintangan rendah dan sempadan butiran berkapasitans tinggi diperhatikan dalam $CaCu_3Ti_4O_{12}$. Tenaga pengaktifan, diukur daripada perubahan rintangan apabila suhu dinaikkan, hampir serupa untuk pelet dan filem nipis. Pelet $BaTiO_3$ menunjukkan sifat feroelektrik manakala filem nipis tidak. Pelet dan filem nipis $CaCu_3Ti_4O_{12}$ tidak menunjukkan sifat feroelektrik. Perubahan kecil dalam kapasitans dan rintangan diperhatikan apabila gas oksigen ditambah. Kapasitans untuk campuran $BaTiO_3$-$CaCu_3Ti_4O_{12}$ berada di luar jangkaan model penyambungan siri dan selari mungkin disebabkan tindakbalas antara

$BaTiO_3$ dan $CaCu_3Ti_4O_{12}$. Pemalar dielektrik pelet (>2000) lebih tinggi berbanding filem nipis (<1000).

SYNTHESIS AND CHARACTERIZATION OF BARIUM TITANIUM OXIDE ($BaTiO_3$) AND CALCIUM COPPER TITANIUM OXIDE ($CaCu_3Ti_4O_{12}$) PELLETS AND THIN FILMS

ABSTRACT

$BaTiO_3$ and $CaCu_3Ti_4O_{12}$ are ceramic materials with high dielectric constants. However, the high dielectric constant in $BaTiO_3$ is due to a ferroelectric transition while the reason for $CaCu_3Ti_4O_{12}$ is not yet clear. Ink-jet printing was used to fabricate the thin films. The low temperature aqueous synthesis method was used because the solution form is precipitate-free. Powders, which were later shaped into pellets, were precipitated from the solution by varying pH. Thin films were obtained by printing out the solution on Corning 1737 glass substrates. At least 5 print cycles were required to obtain continuous 2 μm thick thin films. Initial Ba additions 10% in excess of stoichiometry and a pH13 solution was necessary to obtain stoichiometric $BaTiO_3$ precipitates. For $CaCu_3Ti_4O_{12}$, a 10% Ca excess, 10% Cu deficiency and a pH13 solution was necessary. XRD traces show precipitates were mainly $BaTiO_3$ or $CaCu_3Ti_4O_{12}$ with <5% excess TiO_2. Impedance spectroscopy shows the $BaTiO_3$ to be electrically inhomogeneous and made up of three different electrical elements: a low resistivity core, a ferroelectric bulk and a high capacitance grain boundary. Only the low resistivity core and high capacitance grain boundary was observed in the $CaCu_3Ti_4O_{12}$. Activation energies, measured from the change in resistance when temperature was increased, were almost similar for the pellets and thin films. The $BaTiO_3$ pellets showed ferroelectric behavior but the thin films did not. Both $CaCu_3Ti_4O_{12}$ pellets and thin films did not show ferroelectric behavior. Slight changes in the capacitance and resistance were observed when oxygen was introduced. The capacitances of $BaTiO_3$-$CaCu_3Ti_4O_{12}$ mixtures fell outside the prediction of serial and parallel connection models probably due to reaction between the $BaTiO_3$ and $CaCu_3Ti_4O_{12}$. The dielectric constant of the pellets (>2000) was higher than the thin films (<1000).

CHAPTER 1
INTRODUCTION

1.0 Introduction

One of the main drawbacks to widespread research and development of thin films is the high cost of fabrication. This thesis attempts to address this issue by using commonly available ink jet printers to fabricate thin films of $BaTiO_3$ and $CaCu_3Ti_4O_{12}$, two very high dielectric constant materials that have been widely researched. These thin films were then characterized.

1.1 Fabrication of thin films

Thin film fabrication methods may be broadly divided into physical and chemical methods. The physical methods have to be ruled out because they commonly employ very costly vacuum systems, leaving the chemical methods. Chemical methods typically involve solution deposition onto substrates. Lithography processes are then used to pattern the films. Using an ink jet printer bypasses the need for step-by-step lithography methods of patterning as the desired pattern may be printed directly unto the substrate (Figure 1.1). Although there have been custom built ink-jet systems for depositing ceramic inks, the costs for these are prohibitively high. This leaves the common desktop ink-jet printers that can be found in nearly every office worldwide.

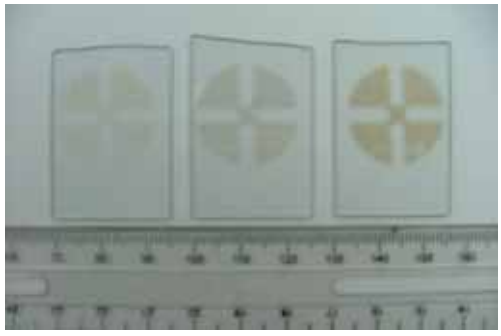


Figure 1.1: A printed design attainable using ink-jet printing without step-by-step photolithography.

The first part of this thesis concerns the preparation of suitable chemical solutions for printing thin films using a common ink-jet printer. A combination of microscopy, elemental spectroscopy and phase analysis was used to understand the synthesis process. The thin films are then heat treated and characterized using impedance spectroscopy. For purposes of comparison, the electrical properties of the pellets were measured as well to determine to what extent ink-jet printing has been able to duplicate the properties of the pellets.

1.2 Materials studied

$BaTiO_3$ and $CaCu_3Ti_4O_{12}$ are high dielectric constant materials of great interest for capacitive applications. Studies about the dielectric properties of $CaCu_3Ti_4O_{12}$ are relatively new compared to $BaTiO_3$, hence the need to have $BaTiO_3$ as a main reference material. $BaTiO_3$ was chosen because of the considerable amount of information already available concerning its fabrication and properties. Historically, $BaTiO_3$ is one of the “classical” high dielectric constant materials developed during World War II (Haertling, 1999). On the other hand, although structural information about $CaCu_3Ti_4O_{12}$ has been known since the 1970s (Collomb et al., 1977), researchers have only begun to study and understand the dielectric properties (Ramirez et al., 2000; Subramanian et al., 2000). It is hoped that the knowledge gained from studying $BaTiO_3$ would help in understanding the fabrication and dielectric properties of $CaCu_3Ti_4O_{12}$.

1.3 Research approach and methodology

This thesis may be broadly divided into three parts (Figure 1.2): the fabrication of the powders, the fabrication of the thin films and the dielectric characterization.

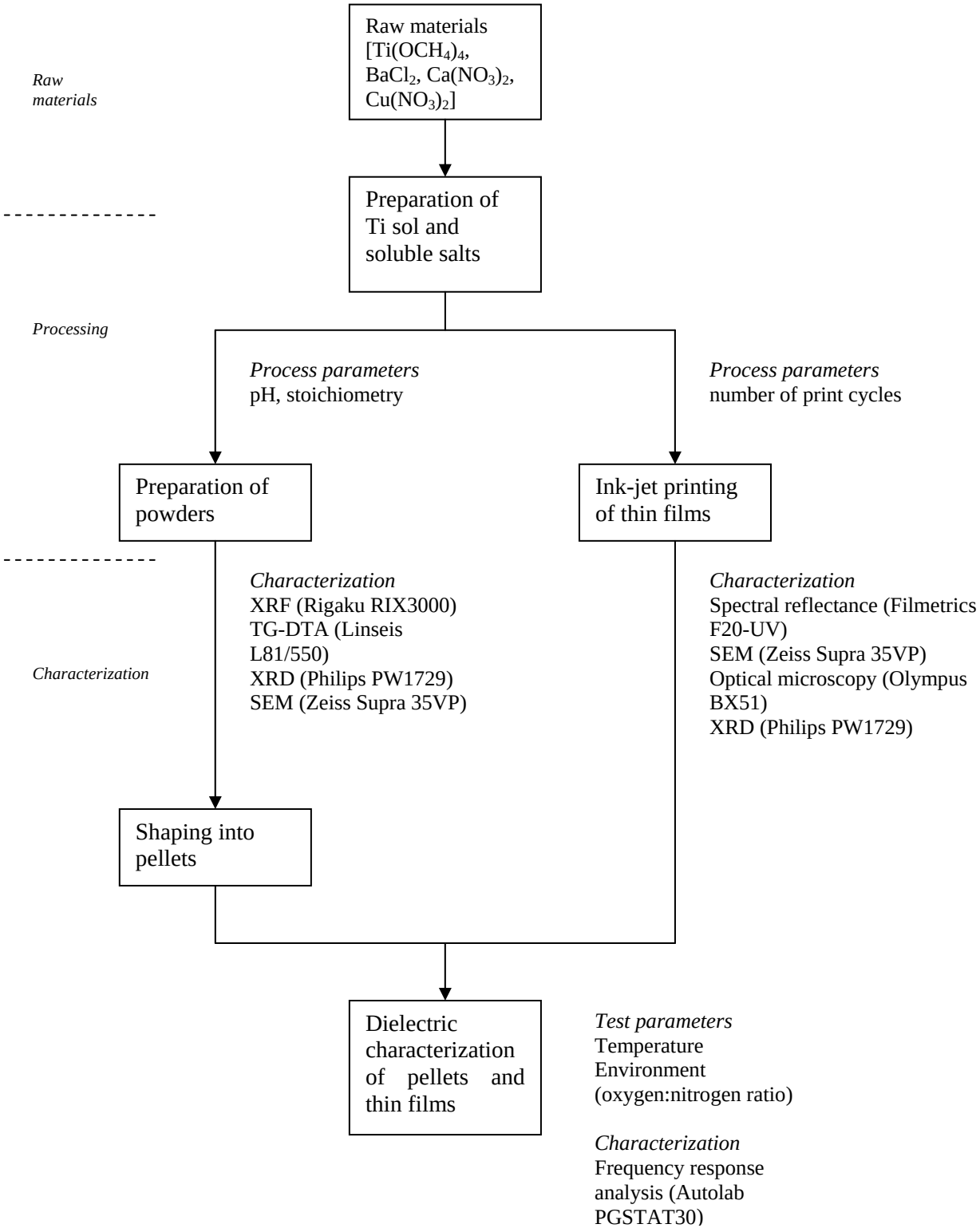


Figure 1.2: A flow chart showing the various stages in this study.

1.3.1 Fabrication and characterization of powders

The powders were fabricated starting from peptized TiO_2 sol, into which was added appropriate amounts of soluble Ba, Ca and/or Cu salts. The preparation of the pellets, in addition to providing a baseline for comparison, also helps in understanding the mechanism by which the compounds form. The powders were characterized using coupled Thermogravimetric and Differential Thermal Analysis (TG-DTA) to observe the stages in the compound formation. X-ray Fluorescence (XRF) analysis was used to determine the elemental composition of the compounds while X-ray Diffraction (XRD) was used to determine the phase content.

1.3.2 Fabrication and characterization of the thin films

The first requirement for the solution is that it must be able to be used in the ink-jet printer. Ink-jet printers have been used to synthesize everything from microcircuits to solar cell metallization to bulk ceramic components. The solution used must have very little or no suspended solids to avoid clogging the ink-jet dispenser. Ink-jet printers are increasingly capable of producing very fine droplets, with some manufacturers claiming picolitre droplets. Therefore, researchers are beginning to use sols, colloids or chemical solutions in place of the ceramic suspensions that have been used previously.

One of the “traditional” methods for producing sol-gel ceramics involves the hydrolysis and condensation of alkoxides. In recent years several other methods (Schwartz et al., 2004) have been advanced such as the metal-organic decomposition processes (Zhu et al., 2004) and the use of short chain carboxylates (Ohya et al., 2004) and other additions to adjust the form of the chemical chains. These different chains are useful in that they might be similar to the final compound and ease the formation of the compound. However, the chemistry is considerably more complex and

the type of reaction more difficult to predict. Therefore, to reduce the number of variables involved, the “traditional” alkoxide approach was selected. After printing, the thin films were characterized using optical and electron microscopy as well as spectral reflectance to determine the thickness and homogeneity of the films. XRD was also used to ensure phase formation in the thin films.

1.3.3 Dielectric characterization of the pellets and thin films

Dielectric characterization of the samples were carried out using impedance spectroscopy (also known as frequency response analysis). Dielectric characterization also helps to determine how successful the ink-jet printing was in replicating the properties of the pellets. During the measurement, temperature was varied from 100 ^{o}C to 500 ^{o}C in 100 ^{o}C intervals to determine the temperature dependence of the dielectric properties. At 500 ^{o}C, oxygen gas was introduced into a pure nitrogen testing atmosphere to determine the effects of different conditions on the dielectric properties.

1.4 Research objectives

The research objectives of this thesis are:

i) To determine the process parameters (i.e. solution pH and initial stoichiometry) to obtain $BaTiO_3$ and $CaCu_3Ti_4O_{12}$ from a wet chemical process.

ii) To fabricate homogeneous thin films of $BaTiO_3$ and $CaCu_3Ti_4O_{12}$ using a desktop inkjet printer.

iii) To compare the effects of temperature and testing environment on the dielectric properties of the pellets and thin films.

CHAPTER 2
LITERATURE REVIEW

2.0 Introduction

The review will be focused initially on the requirements for the fabrication of thin films. The synthesis of the two materials used, $BaTiO_3$ and $CaCu_3Ti_4O_{12}$ are then discussed. Finally, the dielectric properties of $BaTiO_3$ and $CaCu_3Ti_4O_{12}$ are reviewed.

2.1 Fabrication of thin films

Thin films are usually less than a few microns in thickness (Stojanovic et al., 2002). However, the defined thickness is highly dependent on the target application (Schwartz et al., 2004). Historically, one of the pioneers of thin film technology was Thomas Edison (Edison, 1904) who had a patent for a vacuum bell jar-type appratus to metallize objects (Figure 2.1). Since then many advances have been made, with thin films finding application in optical coatings, wear and corrosion resistant coatings, high temperature resistant coatings and even as electronic components. In electronics, the benefits of thin films over the bulk material include a faster response time, a smaller footprint and lower power requirements.

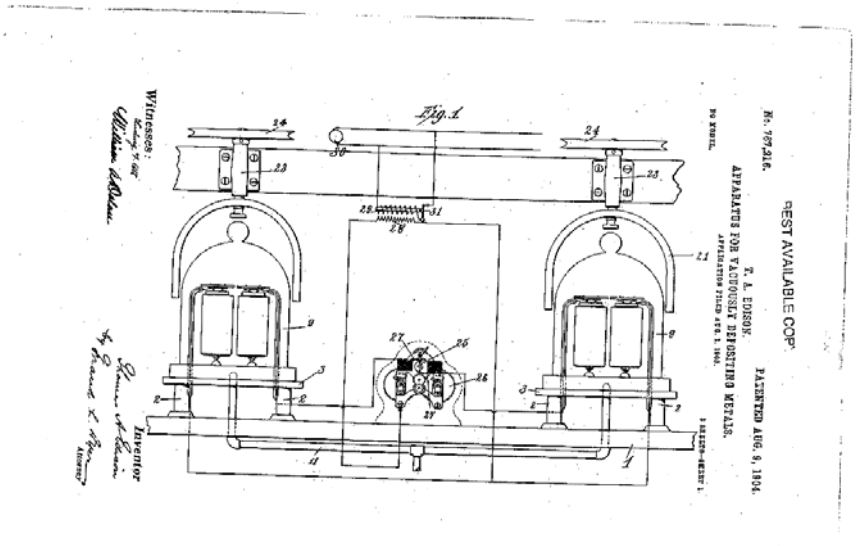


Figure 2.1: A copy of a figure in Edison's patent application (Edison, 1904).

In the production of thin films, it is important to have a controlled flux of material to the substrate so that a homogeneous film is produced. The various methods for producing thin films can generally be separated into physical and chemical methods (Sayer & Sreenivas, 1990). The physical methods usually use a solid of the compound or stoichiometric targets as the source material. An energy source is used to knock atoms out of the source material which is then deposited on the substrate. For example, sputtering uses an electron beam (Wang et al., 2002a), laser ablation uses a laser beam (Lopez et al., 2000; Lu et al., 2003; Miot et al., 1997), while thermal evaporation uses resistive heating as the energy source (Hwang & Souda, 2004). Advantages include compatibility with current semiconductor processes. Disadvantages include the amorphous nature of the deposited films which necessitate higher temperature deposition or post-deposition crystallizing processes (Halder et al., 2002). Line of sight deposition may cause non-uniformity if there is a step or topographic variations on the substrate.

The chemical methods are relatively cheaper because high vacuum systems are not required (Gust et al., 2001). A substrate is coated with a precursor solution which is dried to form a film (Figure 2.2). The required properties of the solution include solubility of the precursors without segregation, easily removed residues, lack of reaction with the substrate, and suitable rheology for deposition (Schwartz et al., 2004). Depending on the process, higher temperature crystallizing treatments may be required if the deposited films are amorphous.

The first well known instances of chemical solution deposition was probably the fabrication of SiO_2 or TiO_2 protective films on glass surfaces during the mid 20^{th} century with electronic applications only being explored in the 1980s (Schwartz et al., 2004). Since this early work, “simple” oxides such as ZnO (Bukowski et al., 1997), $BaTiO_3$ (Phule & Risbud, 1989), $SrTiO_3$ (Jia et al., 1998) as well as complex solid

solutions/compounds such as $Ba_xSr_{1-x}TiO_3$ (Adikary & Chan, 2003), $SrBi_2Ta_2O_9$ (Ricote et al., 2004), $YBa_2Cu_3O_{7-\delta}$ (Sathyamurthy & Salama, 2000) and $Bi_{3.5}La_{0.5}Ti_3O_{12}$ (Zhu et al., 2001), have been fabricated. These methods usually result in thin films approximately 100 nm to 1 μm in thickness although careful process control have resulted in thin films below 100 nm in thickness. Additionally, more viscous solutions have been used to produce films with thicknesses ranging in the tens of microns.

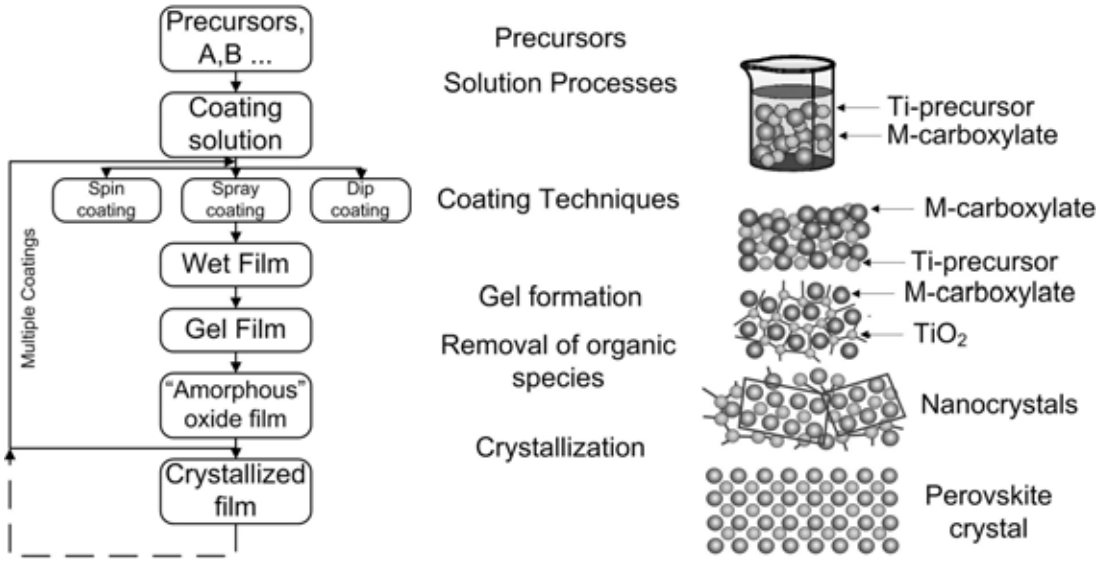


Figure 2.2: An example of the steps in the chemical solution deposition of thin films (Schwartz et al., 2004).

2.1.1 Preparation of chemical precursors

Sol gel methods were originally developed to make ceramics with unique and difficult to process compositions. Advantages of the sol gel techniques include low cost, high purity due to reduced contamination from grinding media, fine grain size, easier compositional control, and short fabrication cycle (Chatterjee et al., 2003; Ries et al., 2003). Sol-gel methods are probably not advantageous for the production of bulk powders because only relatively small quantities of powders are obtainable from large quantities of the solutions. However, the geometry of thin films with its large surface area and low volume is probably best suited for the sol gel process. Usually a

metallorganic compound or metal alkoxide is dissolved in suitable solvents (Zhang et al., 2002). The hydrolysis (Equation 2.1) and subsequent condensation (Equations 2.2 & 2.3) of this solution results in a gel complex or structured solution made up of long chains of metal-organic polymers.

$$M(OR)_x + H_2O \longrightarrow M(OR)_{x-1}(OH) + ROH \quad (2.1)$$

$$2M(OR)_{x-1}(OH) \longrightarrow M_2O(OR)_{2x-3}(OH) + ROH \quad (2.2)$$

$$2M(OR)_{x-1}(OH) \longrightarrow M_2O(OR)_{2x-2}(OH) + H_2O \quad (2.3)$$

Extensive, uncontrolled hydrolysis may lead to hydroxide formation which is undesirable if the final target is the formation of compounds (Schwartz et al., 2004). Controlled hydrolysis leads to the formation of short chains of polymeric species known as oligomers (Schwartz et al., 2004). This is usually accomplished via the addition of chelating agents (Bao et al., 1999) (e.g. ether linkages R-O-R', amine groups $–NH_2$, alcohol –R-OH etc.) which stabilize the compound by forming extra linkages to the metal center of the alkoxide, hindering further complexation.

The "traditional" alkoxide process has undergone modifications to meet different process requirements while new techniques have been explored. For example, metal organic decomposition techniques (Zhu et al., 2004) involve dissolving metallo-organic compounds in suitable solvents. So-called hybrid processes utilize short chain carboxylates and alkoxides (Ohya et al., 2004). The resultant process, although not as chemically complex as the use of chelates (chelation, esterification, hydrolysis, polymerization), is more complex than the simple sol-gel processes (hydrolysis and condensation), thus limiting the control over the precursor structure. Diol and suspension processes (Arscott et al., 1997) are commonly used for thicker films obtainable through fewer deposition steps (approximately 1 - 2 μm per deposition step). This is accomplished by forming crosslinks between the chains thus creating

large oligomer molecules. These large oligomers as well as the non-gelling characteristic allow for thicker film deposits. In addition, the nitrate (Ng & Cima, 1997), citrate (Choy et al., 1998; Zhou et al., 2006) and Pechini (Fang et al., 2002) routes have also been used. In the nitrate routes, metal nitrates are dissolved in deionized water and alcohol before being deposited to form thin films. This method is straightforward without any complicated chemistry. However, drawbacks include the lack of substrate adhesion due to the absence of gelation. Also, the risk of recrystallization of the solid species as nitrates instead of the required oxides must also be addressed. The citrate solution process adds citric acid to the dissolved nitrates to chelate the solution. In the Pechini process, a polyhydroxyalcohol, typically ethylene glycol is added to the nitrate and citric acid solution to form organic ester compounds.

The “traditional” alkoxide route provides simpler chemistry and more predictable precursors compared to the various modifications which make it easier to adapt for ink-jet printing. Therefore, the emphasis from this point forward would be on the use of the traditional alkoxide process for the synthesis of the compounds.

2.1.2 Deposition techniques and film formation

The solution is deposited onto the substrate. After drying, the elemental constituents are held in very close spatial relation. This proximity is such that any chemical reaction is very much easier to initiate and complete, as in the use of very fine particulates in the solid state methods (Ando et al., 2004). The thickness of the film and properties dependent on solution viscosity may be adjusted by controlling the solution pH or type of solvent. On firing, the organic parts are decomposed and, subsequently, the remaining constituents oxidized to form the desired ceramic films. However, the structure of the ceramic films after firing is amorphous or partially crystallized and a subsequent annealing is required to fully crystallize the films.

Commonly used deposition techniques include spin coating, spray coating and dip coating. In spin coating, the substrate is affixed to a platform and flooded with the solution to be coated. The substrate is then spun at speeds between 1000 to 8000 rpms. Film thickness may be controlled by controlling the angular velocity, the solution viscosity, and the duration. Spray coating is accomplished by transforming the solution into an aerosol via an atomizer. The slow settling of the aerosol or electrostatic deposition may be employed. Dip coating only consists of immersing the substrate into the solution, slow withdrawal from the solution to form a film on the substrate and drying of the film. Film thickness is usually controlled by varying the solution concentration and the withdrawal speed. Another, less commonly used technique for ceramic thin films is electrochemical deposition (Guo et al., 2004; Lu et al., 2002; Wu & Lu, 2003).

In addition to these methods, tape casting is also used for processing thick films for multilayer ceramic capacitor applications. The ceramic particles are usually suspended within a polymeric binder to facilitate ease of fabrication (Yoon & Lee, 2004b). The resultant thick films must be subjected to high temperature treatment in order to burn out the polymeric binder.

Drying the film is important because as deposited films still contain a high amount of volatiles and organics. Depending on the precursors, the gelled films may be in the form of polymeric gels, physical aggregates of the polymeric chains or even non-gelling films (Schwartz et al., 2004). Fast heating is preferable to slow heating due to rapid collapse of the gel network before any blisters form (Schwartz et al., 2004).

Oxide or required compounds are usually obtained after heat treatment to remove the volatile organics. The possible types of reaction at this stage include pyrolisis, dehydration, or oxidation of the compounds (Schwartz et al., 2004).

Depending on the compound to be formed, the structure that is formed may help the formation of the desired compound, especially if it is almost similar. For example, in citrate solution combustion for producing $Ba_2Ti_9O_{20}$, the structurally similar Ti-O bonds helps in the formation of the compound during sintering (Zhou et al., 2006). Liu et al. (2005) have also observed the formation of intermediate compounds with similar structure to rutile, when they added sulfonic acid to their alkoxides after hydrolysis with the aim of obtaining nano-sized TiO_2 (rutile) particles. For the processing of $BaTiO_3$ films several steps are observed during heating (Schwartz et al., 2004). At temperatures between 300 – 350 ^oC, the titanium precursor decomposes to form a mixture of amorphous titanium oxide and crystalline titanium carboxylates. At temperatures between 400 – 500 ^oC, barium carboxylates are decomposed. Exact temperatures depend also on the precursor structures and bonds. Intermediate compounds such as $Ba_2Ti_2O_5CO_3$ might be formed as well which shifts the formation of $BaTiO_3$ to even higher temperatures (Duran et al., 2002; Shimooka & Kohiki, 1998). It has also been found that the use of nitrates result in crystalline oxides after combustion compared to the amorphous products from citrates (Zhou et al., 2006). This was believed to be caused by the nitrate precursors having a higher reactivity compared to the citrates, thus helping combustion to occur more completely while residual organics remained in the incompletely combusted samples. This also caused the samples prepared from nitrates to have higher densities than samples prepared from citrates (Zhou et al., 2006).

One of the problems with processing thin films is the high temperature (>600 ^oC) crystallizing heat treatments, which introduces residual thermal stresses within the thin films as well as the risk of diffusion from the substrate to the films. These residual stresses might lead to cracks (Figure 2.3). To overcome this, several processing methods, which involve lasers (Donohue & Todd, 2000) or rapid firing and annealing (Arscott et al., 1997), have been developed. Furthermore, using appropriate buffer

layers between the substrate and the thin films reduce considerably the thermal expansion mismatch (Lipinsky et al., 2005). Lopez et al. (2000) found that the pulsed laser deposited thin films they heat treated at 600 ^{o}C cracked due to the thermal expansion mismatch between the Pt substrates and the $Ba_{0.5}Sr_{0.5}TiO_3$. Other approaches for minimizing the cracks include the introduction of a glassy phase via boron doping of $BaTiO_3$ thin films (Yao & Zhu, 2002).

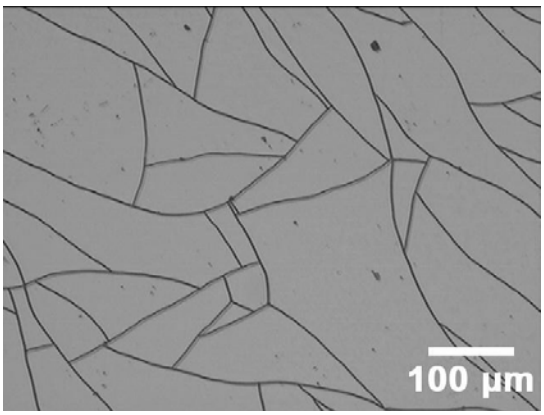


Figure 2.3: Cracks in spin coated $BaTiO_3$ thin films after drying at 100 ^{o}C and heat treatment at 550 ^{o}C.

Thin films may be amorphous/nanocrystalline (Krishna et al., 1997), polycrystalline (Xu et al., 1994), preferentially oriented (Jia et al., 1998) or, very rarely, single crystal structures (Saad et al., 2004). Different structures have different properties. For example, in capacitor applications the crystalline structures generally have higher dielectric constants than the amorphous structures (Xu et al., 1994). This might be due to the increase in tetragonality of the $BaTiO_3$. Preferentially oriented or textured thin films may be better suited for some applications compared to other structures (Schwartz et al., 2004).

Since as-dried films are amorphous or very weakly crystalline, nucleation and growth processes determines the type of film structure that can be expected (Schwartz et al., 2004). Nucleation in the bulk of the film as well as the film-substrate interface

usually leads to polycrystalline thin films (Gust et al., 2001). The remaining organics or precursors influence the nucleation of new crystals and the final structure of the films (Schwartz et al., 1999). Epitaxial thin films develop through a small lattice mismatch between the substrate and the film (Peiying et al., 1995). For these films, the growth depends greatly upon nucleation at the film-substrate interface. The grains which grow from the interface gradually consume the small, randomly oriented grains in the film bulk.

For instance, rf-sputtered $BaTiO_3$ on Pt coated Si substrates exhibited greater crystallinity than uncoated Si substrates, probably due to the lattice mismatch between $BaTiO_3$ (a=0.3994 nm) and Si (a=0.3923 nm) (Wang et al., 2002a). However, this is the subject of some debate with some researchers believing this to be caused by the relative diffusion of Ba and Sr (Gust et al., 2001). These researchers believe that the final grain size in the thin films is the result two competing processes: the nucleation in the bulk and the nucleation at the substrate/thin film interface (Gust et al., 2001). Larger grains might be formed in thin films with extended high temperature treatment, due to the increased nucleation and grain growth. For films with repeated deposition and heating cycles to build up the thickness, grain growth at the substrate-thin film interface might be exaggerated because of the extended high temperature processing of the layers adjacent to the substrate (Gust et al., 2001).

2.1.3 Applications of electronic thin films

Ceramic thin films have found application in many electronic applications which would be very difficult to list completely. Lead zirconate titanate and barium titanate thin films have been studied as ultrasonic transducers (Du et al., 1999; Treu et al., 2004). In electroluminescent displays, lanthanum doped lead zirconate titanate (Sayer & Sreenivas, 1990) and barium titanate (Evangelou et al., 2000; Song et al., 1998) thin films with high breakdown strength and permittivity have been used to limit the amout

of DC current across the device. $BaTiO_3$ has also been studied as potential electrochemical or pH sensors (Wu & Lu, 2003). The gas sensing properties of zinc oxide has been studied (Shen et al., 2005). Yttria stabilized zirconia (Masumoto & Goto, 2004), strontium titanate (Zheng & Sorensen, 1999) and titanium oxide (Li & Chen, 1997) are used in potentiometric oxygen concentration cells or high temperature fuel cells by measuring the emf generated when the thin film is exposed to different oxygen partial pressures.

For capacitive applications, the dielectric constant is very important because it is this parameter that will determine the smallest component possible (Gust et al., 2001; Homes et al., 2003; Kyuho et al., 2002). Some believe that a size reduction is inversely proportional to the square of the relative permittivity (Fechine et al., 2006). The use of thin films also simplify the integration of capacitive elements thus reducing the need for discrete capacitors which take up a lot of space (Ramesh et al., 2003).

2.1.4 Requirements for ink-jet printing thin films

Ink jet printing has been shown to be a low cost alternative for the production of microcircuits (Sirringhaus et al., 2001; Teng & Vest, 1988b) or microlenses (Danzebrink & Aegerter, 1999) and for metallization of solar cells (Teng & Vest, 1987, 1988a), or even the fabrication of small structures such as micrometer-scale walls (Biehl et al., 1998; Guo et al., 2003; Mott & Evans, 2001; Noguera et al., 2005; Zhao et al., 2002). Researchers have also studied the use of ink jet printers for combinatorial research (taking an example from the pharmaceutical industry) with the aim of mining the periodic table for new ceramic compositions (Evans et al., 2001; Wang & Evans, 2005). The advantages of ink jet printing include the possibility of low cost, direct patterning without masking or selective etching (Seo & Lee, 2006), low wastage of materials and close control of the compositions (Ai et al., 2004). Recently, Shen et.al (2005) printed gas sensing ZnO thin films, showing the process to be a simpler, cost effective

processing route amenable to doping by Pd or similar composition variations (Kaydanova et al., 2003). $BaTiO_3$ films have also been printed on a commercial ink-jet using suspensions of the bulk powders (Ding et al., 2004). In ink-jet printing ceramic thin films, solutions with very fine or no suspended solids are needed (Hayes et al., 1999), therefore researchers have utilized very fine suspensions of ceramic particles (Lee & Derby, 2004; MacLaren & Ponton, 2000) and ink-jet systems custom built for delivering these suspensions (Ai et al., 2004). However, with the emergence of printers that deliver increasingly finer droplets, with some claiming picolitre droplets (de Heij et al., 2003; Gooray et al., 2002), it becomes more difficult to have increasingly finer particle suspensions. Therefore, several researchers have begun utilizing sols or colloids as their ceramic inks (Ding et al., 2003; Lewis, 2002).

2.2 Synthesis of $BaTiO_3$ and $CaCu_3Ti_4O_{12}$

To summarize thus far, the "traditional" alkoxide process might be more suitable for ink-jet printing because of the relatively less complicated chemistry and the solid-free solution. This section focuses on the use of the "traditional" alkoxide process to synthesize $BaTiO_3$ and $CaCu_3Ti_4O_{12}$.

2.2.1 Synthesis of $BaTiO_3$

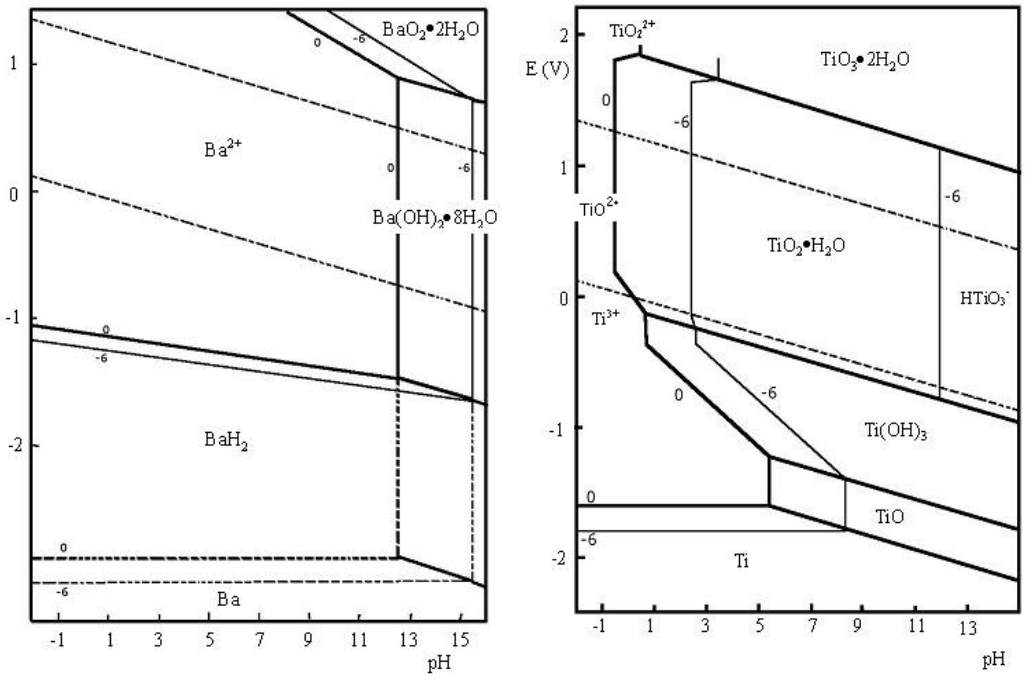
$BaTiO_3$ has been synthesized using a variety of methods including solid state methods, hydrothermal methods and low temperature aqueous methods (MacLaren & Ponton, 2000; Viviani et al., 2001; Viviani et al., 1999; Wada et al., 2001). The benefits of wet chemical synthesis include lower processing temperatures, more uniform grain sizes, higher purity and less risk of contamination by grinding media (Chatterjee et al., 2003; Ries et al., 2003). Since the wet chemical synthesis produces $BaTiO_3$ directly from the solution at relatively low temperatures, there is reduced risk of carbonation of unreacted Ba due to high temperature heat treatment (Kong et al., 2002; Ries et al., 2003). Solid state reactions typically require temperatures of approximately 1000 ^oC

(some researchers suggest 1150 ^{o}C) with higher temperatures necessary for dopants with low diffusivity values (Feteira et al., 2004). In addition, some researchers have noted that the wet chemical method allows for a higher dopant content without the formation of secondary phases compared to solid state methods (Hu et al., 2002). The low temperature aqueous method might hold the greatest promise for ink-jet printing because of the lower processing temperatures and the atmospheric pressure operating conditions. Low temperature aqueous synthesis usually starts from the preparation of a TiO_2 sol prepared from the hydrolysis and condensation of the titanium alkoxides (Qi et al., 2005; Vorkapic & Matsoukas, 1998) as shown in Equations 2.4 and 2.5.

$$Ti(OR)_4 + 4H_2O \longrightarrow Ti(OH)_4 + ROH \quad (2.4)$$

$$Ti(OH)_4 \longrightarrow TiO_2 \cdot xH_2O + (2-x)H_2O \quad (2.5)$$

The addition of acid provides an acidic media for the peptization. During peptization, primary particles and small clusters are removed from the large aggregates. In studying the effects of temperatures and alcohols on the size of the final TiO_2 nanoparticles, Vorkapic and Matsoukas (1998) found that the final size of the TiO_2 particles is determined ultimately by the peptization step. The size of the final particle is determined by the competing processes of peptization and reaggregation with high $[H^+]/[Ti]$ or low pH having a very high rate of peptization. They noted that the presence of residual alcohol, usually added to control the rate of growth during hydrolysis and condensation, promotes the reaggregation thus leading to larger final particles (Hwu et al., 2005). Therefore, it is very important to remove the excess alcohol before peptization. Moderate temperature increase promotes peptization by increasing the breakdown rates of the primary particle bonds. Excessive temperature increase has an adverse effect on the stability of the sol, decreasing the solvent dielectric constant and lowering the electrostatic barrier against reaggregation.



(a) (b)

Figure 2.4: Potential-pH diagrams for (a) Ba and (b) Ti (Pourbaix, 1966) showing the regions of solubility in aqueous solutions.

Barium ions in the form of soluble salts are then added to the peptized solution. Due to the affinity of Ba for CO_2, it is frequently necessary to purge the solution with an inert gas to reduce atmospheric CO_2 (Basca & Dougherty, 1995; Lu et al., 2000). In addition to forming carbonates, the excess CO_2 might react with the Ba and Ti to form intermediate phases which inhibit the crystallization of $BaTiO_3$ below 600 ^oC (Gust et al., 2001). Several researchers have found that the amount of $BaCO_3$ present in commercial $BaTiO_3$ powders vary between 0.6-2.8 wt% (Yoon & Lee, 2004a). Although it is possible to remove the $BaCO_3$ through high temperature calcinations, it is not desirable to do so because of the higher cost. Several researchers have also found that heating in O_2 also can remove the $BaCO_3$ but results in lower surface areas and coarser particles (Demydov & Klabunde, 2004). The potential-pH diagram (Pourbaix, 1966) (Figure 2.4) shows that the Ti species is soluble in aqueous solutions at pH<3, while Ba ions are soluble over a wide range of pH<13. The differences in solubility

cause the leaching of Ba ions from $BaTiO_3$ particles suspended in aqueous solutions leaving a TiO_2 skin on the particles (BlancoLopez et al., 1997; Viviani et al., 1999). One of the methods used to overcome this via the addition of certain polyelectrolytes to passivate the surface of the $BaTiO_3$ particles. However, the drawback is certain salts, for example sodium salts (Wang et al., 2002b), may have detrimental effects on the electrical properties if left in the compound after the synthesis. A better choice might be the use of ammonium salts which are easier to remove via heat treatment (Shen et al., 2004).

Lower pH values frequently lead to the formation of other phases such as BaC_2O_4 and $TiO(OH)_2$ thus requiring higher calcination temperatures to decompose these compounds and form $BaTiO_3$. Increasing the pH value of the solution to pH 13 causes the precipitation of $BaTiO_3$ because it is the only stable phase under these conditions (Kim et al., 2003; Testino et al., 2004). Lowering the pH values of the aqueous solution after the $BaTiO_3$ has been formed usually does not completely cause dissociation into $Ba(OH)_2$ and TiO_2 but the leaching of Ba ions from the particle surface. This causes the formation of a non-water-permeable TiO_2 rich film over the TiO_2 particle that resists further dissolution (Urek & Drofenik, 1998).

Due to the limited solubility of TiO_2 and BaO in $BaTiO_3$ (<0.1 mol%) (Suzuki et al., 2001), an excess of any of these may lead to the formation of secondary phases such as $Ba_6Ti_{17}O_{40}$ (Bomlai et al., 2005) or Ba_2TiO_4. An excess of TiO_2 might lead to abnormal grain growth, due to the formation of a eutectic between $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$ at 1332 ^oC (Lin & Lu, 2002; Proust et al., 1995; Rios et al., 1998) with increasing Ti excess leading to increasingly faceted grains (Cho et al., 2004). A slight excess of TiO_2 has been found advantageous in promoting lower sintering temperatures compared to the pure $BaTiO_3$ (Bomlai et al., 2005). The abnormal grain growth proceeds with increasing temperature with all the nucleation happening at the

beginning of the reaction. Rios et al. (1998) found experimental evidence that suggested the TiO_2 excess suppressed normal grain growth, while allowing for abnormal grain growth in several grains. Normal grain growth could be observed in barium excess samples (Cho et al., 2004). However, excess Ba could lead to the formation of large quantities of $BaCO_3$ after heating at 800 ^oC or the barium rich Ba_2TiO_4 (Hennings et al., 2001).

Urek and Drofenik (1998) compared the use of $Ba(OH)_2$ and $Ba(CH_3COO)_2$ as Ba salt additions. Although using $Ba(CH_3COO)_2$ resulted in samples with less $BaCO_3$, decomposition products from the organic salt delayed the sintering time. These decomposition products usually record a peak in the TG-DTA curves with a corresponding weight loss at approximately 150 ^oC to 600 ^oC. Some of the residual carbonized organic products which cannot be completely removed during washing of the powders are deposited on the surface of the $BaTiO_3$ grains and disintegrate during heating. Excess Ba may form Ba_2TiO_4 during sintering which may inhibit grain growth and degrade the microstructure (Proust et al., 1995; Urek & Drofenik, 1998). Some researchers (Drofenik et al., 2002) have noted that abnormal grain growth is not caused by Ba excess per se, but is more pronounced in the presence of other dopants such as SiO_2 or B_2O_3. The $BaTiO_3$ reacts with the SiO_2 to form a liquid phase, $BaSiTiO_5$, that helps the solution-dissolution process and aids the grain growth (Ueoka & Yodogawa, 1974). These dark blue abnormal grains, in addition to being more resistant to reoxidation, have semiconductive properties compared to the insulating normal light yellow grains. This led the authors (Drofenik et al., 2002) to speculate that oxygen expulsion during the abnormal grain growth is responsible.

There are two possible mechanisms (Eckert et al., 1996) for the formation of $BaTiO_3$ during wet chemical synthesis: a dissolution-precipitation mechanism and an in-situ mechanism. Hertl (1988) and other researchers (Kim et al., 2003; MacLaren &

Ponton, 2000) assumed an in-situ form of reaction where $BaTiO_3$ forms on the surface of the TiO_2 particle and proceeds through continued diffusion of the Ba ions inwards. They frequently point to the formation of a “raspberry-like” surface on the primary TiO_2 as proof of this (Kim et al., 2003). Pinceloup, et al. (1999) submitted what they believed to be evidence of the dissolution-precipitation mechanism when they used the hydrothermal method for the synthesis of $BaTiO_3$. They found smaller grain sizes when the solubility of the constituents was lowered because more particles nucleating at the same time ultimately lead to finer particles. In addition, completely amorphous or completely crystalline precipitates meant no $BaTiO_3$ crystallites were found on top of the amorphous $TiO_2.xH_2O$ particles. Finally, fully reacted particles showed the presence of necks between them, which similar to those found in high temperature sintering, is more likely from a dissolution precipitation compared to an in-situ process. They argue that Ba ions found near the surface of the TiO_2 particles are only temporarily adsorbed and that the composition may still be considered as $TiO_2.xH_2O$. Furthermore, if an in-situ mechanism is involved, the size of the particle would be very close to the initial size of the TiO_2 from which the supply of Ti derives from. This was not observed with TiO_2 nanoparticles very much smaller than the $BaTiO_3$ particles (Pinceloup et al., 1999).

However, other researchers (MacLaren & Ponton, 2000) have observed after prolonged treatment of the precipitates, $BaTiO_3$ grew within and into the amorphous TiO_2. Researchers (Hertl, 1988; MacLaren & Ponton, 2000) seem to agree that the dissolution-precipitation mechanism is dominant during the early stages (i.e. nucleation) with the in-situ mechanism taking over in later stages (i.e. growth of the particle).

As precipitated $BaTiO_3$ particles prepared through wet chemical synthesis is generally cubic without the characteristic splitting of the (002) peak in its tetragonal

form (Feteira et al., 2004). In addition, the presence of any cubic phase may be observed as a cubic to tetragonal phase transition in DTA traces (Kim et al., 2003). The cubic structure is attributed to entrapment of hydroxyl ions within the perovskite lattice (Hennings et al., 2001; Pinceloup et al., 1999; Yan et al., 2005). Hennings et al. (2001) supported this observation using TGA and FTIR data. Although not being able to observe directly the entrapped ions, Qi et al. (2005) indirectly supported this argument with XRD peak broadening measurements that the lattice parameter of their barium strontium titanate nanoparticles were larger than the normal lattice. In addition, TG-DTA curves show weight loss without a corresponding endothermic/exothermic peak which the authors (Qi et al., 2005) attributed to the loss of the entrapped ions from the barium strontium titanate lattice. The lack of any clear endothermic/exothermic peak was believed to be caused by the already crystallized barium strontium titanate (Qi et al., 2005).

In the case of Sr additions, the XRD peak broadening might be due to the variation in lattice parameters of the $SrTiO_3$ solid solution (Bomlai et al., 2005). Some researchers also believe that the $BaTiO_3$ at room temperature is observed as a cubic or tetragonal structure depending on the size of the particles with particles below 0.07 μm being more likely to be observed as cubic through the absence of the XRD peaks splitting (Proust et al., 1995). However, this is also likely due to the broadening of the peaks for very small particles (Gust et al., 2001; Qi et al., 2005). This crystallite size factor is less evident after high temperature heat treatment (Bomlai et al., 2005). Other factors that may induce peak broadening include localized residual stresses that may be induced by deformation or surface grinding (Chen et al., 2005). High temperature heat treatment (>700 ^{o}C) is usually necessary for transformation to a more stable tetragonal form (Yan et al., 2005). The authors (Pinceloup et al., 1999) found the as precipitated powders to be Ba deficient even though XRD traces do not reveal extra phases other than $BaTiO_3$. Some researchers (Bocquet et al., 1999; Yan et al., 2005)

tried to address this problem by recrystallizing the precipitates under low temperature hydrothermal conditions. However, Jiang et al. (2000) in their research into very fine $BaTiO_3$ particles prepared from a stearic acid gel method, suggested that the cubic structure was not size related but rather a bulk property arising from the defects created during the stearic acid synthesis. Similar results were not observed for samples prepared using the more conventional alkoxide based sol-gel method. The crystals they prepared did not revert to the tetragonal form even after sintering at high temperatures (>1000 ^{o}C). Jhung et al. (2004) found cubic $BaTiO_3$ without the characteristic peak splitting in samples prepared from microwave irradiation and hydrothermal methods.

Lee et al. (2004) obtained tetragonal $BaTiO_3$ using a polymeric citrate precursor approach. The presence of Raman peaks indicating the presence of asymmetry within the TiO_6 octahedra was taken to mean that the $BaTiO_3$ was tetragonal. However, this measurement might not completely discount the presence of cubic phase in addition to the tetragonal $BaTiO_3$.

Choi et al. (1999) tried a microwave assisted hydrothermal method to overcome the problems with obtaining tetragonal $BaTiO_3$. They found Ba:Ti ratios of approximately 3 resulted in lower crystallinity compared with particles that were synthesized with particles closer to the stoichiometric ratio of $BaTiO_3$. They suggested that the excess Ba reacted with atmospheric CO_2 to form $BaCO_3$ seeds that promote further crystallization the $BaTiO_3$. They supported this supposition with XRD results which showed greater amounts of $BaCO_3$ for larger initial additions of Ba salts. However, for all their efforts, the degree of tetragonality for $BaTiO_3$ obtained through hydrothermal methods were largely unchanged. A further heat treatment at 250 ^{o}C was necessary to obtain tetragonal $BaTiO_3$.

Miot et al. (1995) found the $BaTiO_3$ they produced through a citric resin method to be a mixture of tetragonal and cubic phases as evaluated from the relative heights in the split of the (400) peaks. By assuming that the cubic phase is located at the surface of spherical tetragonal grains, they calculated the thickness of the cubic layer. They (Miot et al., 1995) also found the amount of cubic phase to decrease with increasing grain size. They believed higher dielectric constants in 1.6 μm grain size samples compared to 0.7 μm grain size samples could be caused by the higher presence of the cubic phase in the 0.7 μm sample which is unaffected by the ferroelectric transition.

Hirata et al. (1996) have found that hot isostatic pressing resulted in less porosity (< 10 %) compared to conventional pressureless sintering (30 – 40%) when powders with fine grain sizes were sintered at 950 ^{o}C and 1100 ^{o}C. However, the effect of this on the dielectric constant was not clear as the samples with higher densities had lower dielectric constants. Furthermore, the effects of porosity on the dielectric constant were almost non-existent for submicrometer sized grains. However, lowering the level of porosity was found to drastically reduce the dielectric loss. They also found that grain sizes below 0.4 μm generally led to cubic structures as revealed in XRD. The *c*-parameter increased with increasing grain size until maximum of approximately 3 μm when the c/a ratio was almost constant. They also observed a slight increase in the lattice parameters of the cubic $BaTiO_3$ for very fine grains. They found the dielectric constant to be greatly dominated by grain size with the maximum dielectric constant obtained when the grain size was approximately 1.4 μm.

Basca and Dougherty (1995) used a hydrothermal method to coat TiO_2 particles with a Ba rich solution thus forming a $BaTiO_3$ film on the particles. They used a similar approach to form $BaTiO_3$ films on Ti metal foils.