HYDROTHERMAL PROCESSING OF BARIUM STRONTIUM TITANATE COMPOSITES ON PRINTED CIRCUIT BOARD FOR THIN FILM VARACTOR APPLICATIONS

By

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Abstract

Thin film $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ has been deposited onto printed circuit boards at low temperatures for low and high frequency applications. The fabrication method involves spin coating sol-gel composites (a mixture of BST powder suspended in an amorphous BST sol), and treating the resultant films at 175°C. The treatment is done in an autoclave in an aqueous environment comprised of barium hydroxide, strontium hydroxide, and water, and is carried out at elevated temperature and pressure. This causes the amorphous BST sol to recrystallize, forming bridges that link the BST powders together, creating a dense network, leading to a higher dielectric constant. Three different types of powders have been explored for the composite. They are low-temperature derived, ceramic derived, and sol-gel derived powder. Low-temperature derived powders are the smallest in size, in the nanometer range. Due to such small sizes, the ferroelectric properties are lost, leading to no tunability and very low dielectric constant. The permittivity ranges from 30 to 55. Sol-gel derived powders are very reactive to the hydrothermal process. The resultant film permittivity is the highest, ranging from 200 to 260, but with a limited tunability of 1%. Ceramic derived powders are compatible with the process. The permittivity is less than that of sol-gel derived, with values from 130 to 140, but the tunability ranges from 4 to 8% at low frequencies (500 kHz to 20 MHz). For high frequency characterization (45 MHz to 1.15 GHz), films containing ceramic derived powder are deposited onto grounded coplanar waveguide capacitors. The dielectric constant significantly reduced, reaching as low as 18, but tunability increased to 18%. 
Acknowledgements

First off, I would like to thank my two supervisors, Dr. Al Freundorfer, and Dr. Michael Sayer for being such great mentors. I want to thank Dr. Freundorfer for his advice and support for the past two years. He has made me work harder, smarter, and more meticulously. The experiences he shared not only helped me grow as a student, but also as a person. And only he has the patience to deal with my lab book. I want to thank Dr. Sayer for his guidance throughout the project. I have learned much from his unconventional methods of running experiments, which made me become more creative. When I first started, I couldn’t make it through a day without him walking me through every detail. Eventually, all his expertise is passed onto me, and I ended up hogging room 260 all to myself. I would also like to thank Chelsea Elliott of the Physics department for putting up with all my urgent (and, sometimes, horribly timed) SEM requests. She couldn’t leave until the end of the day, just before the winter holidays because I, for whatever reason, really needed those SEM images. Without her, this thesis would not have the best looking SEM images. I would like to thank Bernie Ziomkiewicz of the Physics department for helping me out with the evaporator. I would also like to thank Dr. Brad Diak of the Mechanical and Materials Engineering department for letting me constantly bug him during his busiest times just so I can get help with the RTA. I want to thank Charlie Clooney from the Mechanical and Materials Engineering department for putting up with the troubles I have caused from using the carbon coater. I want to thank Dr. Alison Murray and Michael Doutre of the Art Conservation department for helping me out with ATR measurements. Finally, I want to extend my thanks to the graduate students in both the Walter Light and the Stirling offices for making graduate school an amazing time.
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List of Acronyms

AFM  Atomic Force Microscopy
ATR  Attenuated Total Reflectance
BST  Barium Strontium Titanate
BTO  Barium Titanate
BZO  Barium Zirconate
BZT  Barium Zirconate Titanate
CPW  Coplanar Waveguide
CPWG Grounded Coplanar Waveguide
CSD  Chemical Solution Deposition
DR  Dielectric Resonator
DRAM Dynamic Random Access Memory
FWHM Full Width Half Max
MOCVD Metal Organic Chemical Vapour Deposition
PCB  Printed Circuit Board
PLD  Pulsed Laser Deposition
PST  Lead Strontium Titanate
PTO  Lead Titanate
PZT  Lead Zirconate Titanate
RF  Radio Frequency
SEM  Scanning Electron Microscope
SGHP Sol-gel Hydrothermal Processing
STO  Strontium Titanate
VNA  Vector Network Analyzer
XRD  X-ray Diffraction
Chapter 1

Introduction

Ferroelectric materials have been implemented into microwave circuits since the 1940s [1]. The advancements in this area of research are driven by the miniaturization of microelectronic devices, and have been progressively improved in the last 20 years. Ferroelectric materials are used as the dielectric layer in a capacitor and typically have a high relative permittivity, and therefore, giving a high capacitance for a small surface area. The capacitance, $C$, as shown in Fig. 1, is given by the equation [2]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$  \hspace{1cm} (1.1)

Where $\varepsilon_o$ is the permittivity of free space, $8.85 \times 10^{-12}$ F/m, $\varepsilon_r$ is the relative permittivity, $A$ is the area of the electrodes, and $d$ is the separation of the electrodes, or the thickness of the dielectric material.

![Figure 1: Capacitor layout](image-url)
Theoretically, no power is dissipated when energy is stored in the electric field associated with an ideal capacitor. However, this is not the case in practice. Dielectric loss in the capacitor material will lead to power dissipation. Fig. 2 shows that a practical capacitor can be modeled as an ideal capacitor in series or parallel with a resistor. The resistors will have different values depending on the model used.

![Figure 2: Parallel and series equivalent models for a dielectric capacitor][2]

The loss tangent, $\tan \delta$, which represents this energy loss, is given by [2]:

$$
\tan \delta = \omega \cdot C_s \cdot R_s = \frac{1}{\omega \cdot C_p \cdot R_p}
$$

(1.2)

where $\omega$ is the angular frequency, $C_s$ and $C_p$ are the series and parallel capacitances, and $R_s$ and $R_p$ are the series and parallel resistances. Since the series and parallel models the same capacitor, when one set of parameters is found, their counterparts can be calculated using the formulas [2]:

$$
R_s = \frac{\tan \delta^2}{1+\tan \delta^2} \cdot R_p
$$

(1.3)

$$
C_s = (1 + \tan \delta^2) \cdot C_p
$$

(1.4)

Ferroelectrics are of interest for their ability to change their dielectric properties under the presence of an electric field by applying a DC voltage, and hence, allowing circuits to be tuned. By implementing them into tunable circuits, the costs, and sizes of handheld devices can be reduced; matching networks in antennas and amplifiers can be more efficient, and the space and
weight of electronically steerable systems can be minimized [1]. The tunability, \( n \), and the relative tunability, \( n_r \), are given by the equations [1]:

\[
  n = \frac{\varepsilon_r(0)}{\varepsilon_r(E)} \\
  n_r = \frac{\varepsilon_r(0) - \varepsilon_r(E)}{\varepsilon_r(0)}
\]  

(1.5)

(1.6)

Where \( \varepsilon_r(0) \) is the relative permittivity under no external electric field, and \( \varepsilon_r(E) \) is the relative permittivity under a bias in an electric field, \( E \). Under an external bias, the dielectric constant will only decrease, as seen in Fig. 3.

![Figure 3: Effect of bias voltage on relative tunability [1]](image)

1.1 Barium Strontium Titanate

Barium Strontium Titanate (BST, \( \text{Ba}_{x}\text{Sr}_{(1-x)}\text{TiO}_3 \)) is a key ceramic for capacitor applications due to its high relative dielectric constant/relative tunability, and low loss tangent. BST is a solid solution of barium titanate (BTO, \( \text{BaTiO}_3 \)) and strontium titanate (STO, \( \text{SrTiO}_3 \)), and thereby inherits properties from both its parents. Barium titanate has a perovskite tetragonal crystalline structure and strontium titanate has a perovskite cubic structure at room temperature. Strontium atoms displace the barium atoms, changing the crystal structure and properties. BST has an \( \text{ABO}_3 \) perovskite structure, and its high dielectric constant is due to ionic displacements from a centro-symmetric structure [3-5].
BTO has a Curie temperature of 395K, while STO has a Curie temperature of 20K. The Curie temperature, $T_c$, is a transition temperature. A material is in its paraelectric phase at temperatures above $T_c$, and is in its ferroelectric phase at temperatures below $T_c$. In the ferroelectric phase, atoms shift away from their position and the crystal symmetry changes. This is depicted in Fig. 4. Hence, the transition temperature of BST will lie in between the two extremes, depending on the ratio of barium to strontium. The dielectric constants of the ceramics are the highest at the Curie temperature. From Fig. 5, it can be seen that $T_c$ decreases linearly with an increased concentration of strontium [5].

![Figure 4: a) paraelectric phase (centro-symmetric) b) ferroelectric phase (displaced) of BST](image_url)

Figure 4: a) paraelectric phase (centro-symmetric) b) ferroelectric phase (displaced) of BST [4]
The Curie temperature of BST (Ba$_x$Sr$_{1-x}$TiO$_3$) is closest to room temperature when $x = 0.7$, and therefore, the relative permittivity is at a maximum. Overall, barium titanate can achieve the highest dielectric constant, but only at its $T_c$, which is at 120°C. The permittivity is lowered at 25°C. It is reported that bulk ceramic BST can have a dielectric constant of 5000 [6].

BST thin films have lower relative permittivity than their bulk counterpart. However, the range in which $\varepsilon_r$ is a maximum is broader in thin films, as opposed to bulk ceramic, where it is a sharp peak, as shown in Fig. 6. It is speculated that this is because of nonstoichiometry, size effects, and stresses in thin films [1].

Figure 5: BST Curie temperature is linearly dependent on the concentration of Sr [5]
1.2 BST Thin Film Varactors

Varactors are tunable capacitors that change capacitance with an external DC bias. BST thin films have been studied extensively for many electronic applications, particularly in the communications sector, and are typically integrated into circuits as varactors. Applications include filters [1, 4], dynamic random access memory (DRAM) [1, 8], mixers [1, 9], antennas [10], and matching networks [1, 4]. Due to the high permittivity, BST varactors can store large amounts of charge in a small area, which helps reduce varactor sizes. There are four main desirable properties of thin film BST varactors [1]: 1) they have low loss tangent, which can be as low as 0.01, 2) the relative permittivity can be tuned to a quarter of its initial value, 3) they are inexpensive to produce on substrates, and 4) they are reliable and have high reproducibility. Two main competing varactor technologies are semiconductor varactors, and micro-electrical-mechanical systems (MEMS) varactors [1]. MEMS are closest to BST in terms of development maturity; however, the response time is still lacking, and they require larger power consumption. GaAs varactors are very reliable and can operate better than ferroelectrics at higher frequencies, but they are more expensive. Table 1 compares the three different technologies.
Table 1: Comparing different varactor technologies [1]

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>MEMS</th>
<th>BST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunability (n)</td>
<td>~2–6 : 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~1.5–3 : 1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>~2–4 : 1</td>
</tr>
<tr>
<td>RF Loss (Q)</td>
<td>~20–50</td>
<td>Very high</td>
<td>~20–100</td>
</tr>
<tr>
<td>Control voltage</td>
<td>&lt;15 V&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&lt;50 V&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;15 V (parallel plate type)</td>
</tr>
<tr>
<td>Tuning speed</td>
<td>~10&lt;sup&gt;-6&lt;/sup&gt; s</td>
<td>&gt;10&lt;sup&gt;-5&lt;/sup&gt; s</td>
<td>~10&lt;sup&gt;-9&lt;/sup&gt; s&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Reliability</td>
<td>Good&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
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<tr>
<td>Power handling</td>
<td>Poor</td>
<td>Good</td>
<td>Good&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
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</table>

1.2.1 Depositing BST Thin Film Varactors

The four most common techniques of depositing BST thin film varactors are pulsed laser deposition (PLD), RF magnetron sputtering, chemical solution deposition (CSD), and metal organic chemical vapour deposition (MOCVD) [1]. A typical BST film is 500 nm thick.

In PLD, BST is removed from a bulk target using a high intensity UV or infrared laser. The laser is pulsed at small time intervals to ensure that the stoichiometry of the resultant film is the same as that of the target. This process is compatible with many crystalline substrates, including silicon. The processing parameters are substrate temperature, pressure, substrate-to-target distance, pulse rate, and laser energy. Typical BST growth conditions are 750ºC, at 0.1mbar, with the laser energy at 1.5 J/cm<sup>2</sup> [1].

RF magnetron sputtering is very similar to PLD, but is more advantageous since the thin films can be produced over a larger area. It uses a sputtering gas, typically a mixture of argon and oxygen, instead of a laser [1, 4]. The ratio of the composition is optimized for individual scenarios. RF energy is applied to the target. The material on the target is removed, and deposited onto the substrate. The gas pressure directly affects the ferroelectric properties of the film, such as tunability and quality factor. A post-deposition annealing process at 500ºC is generally required to ensure crystallization

CSD is widely used to deposit BST films for DRAM applications [1]. It is low cost, and effective for deposition over a large area. Unlike PLD and sputtering, CSD does not use a target material. Instead, a precursor chemical solution is synthesized and applied onto the substrate via
spin-, or dip-coating, or spraying. It is subsequently dried at 300 – 400°C, forming an amorphous film. Finally, it is treated at a higher temperature (over 500°C) for crystallization and densification. The thermal treatments are slightly different depending on the precursor materials. The disadvantages of this process include non-uniform film thicknesses, high surface roughness, and cracks or voids. Typically, the CSD process is used prior to fabricating integrated circuits.

MOCVD is an extremely effective fabrication technique, and is suitable for depositing multilayer thin films [1, 3, 11]. BST atoms are first combined with gas molecules. This combination is passed over a hot substrate, such as a semiconductor wafer, where the heat splits the molecules, and deposits the desired atoms on the substrate surface. It has good thickness control, produces uniform films, and is very reliable. However, it is costly, and requires high deposition temperatures (650°C) [12], and this limits its practicality.

Tunable phase shifters are simple to construct and are being studied by many research groups to demonstrate the compatibility between device and ferroelectric films [1]. The phase shift of a phase shifter is proportional to the square root of the effective dielectric constant; hence, under an applied electric field, the effective permittivity will decrease, and the phase shift will become tunable. BST thin films are loaded into tunable filters through interdigital capacitor or parallel plate thin film configurations. Certain configurations give different tunable percentages, and can go as high as 57% in the megahertz region.

1.3 Embedded Capacitors

Embedded capacitor technology utilizes ferroelectric thin films and is being explored by many printed circuit board (PCB) manufacturers. There is a growing interest in increasing the number of passive devices on a given circuit board [13-16]. In a typical cell phone application, the ratio of passive to active components is 20:1 [13]. Discrete passive devices such as capacitors, inductors, and resistors have high parasitics, low reliability, and require large attachment areas [13]. To improve the efficiency of electronic packaging, these devices are preferably contained within the substrates themselves. The largest contribution of passives in a typical device is from capacitors [14]; therefore, they should be the first to be built within circuit boards. This, in turn, will 1) reduce the number of necessary interconnects from device to substrate, 2) improve electrical performance, 3) reduce costs, and 4) ease assembly processes. Currently, both resistors and capacitors are being embedded into PCB substrates [14]. The criteria for embedded capacitor materials are the same for that of varactors: high dielectric constant, low loss tangent, and low production costs. The only parameters of the capacitor which are flexible with design are the relative permittivity, and the thickness of the dielectric material. The area is restricted due to
space limitations on a densely packed PCB. Thick film barium titanate is typically chosen for capacitor purposes. It has a dielectric constant of 3000 [15, 16]. Quoted capacitances range from 0.5 - 30 nF/in², based on the permittivity range of 14 to 22 depending on the manufacturers. However, barium titanate capacitors are brittle, have poor adhesion with copper, and need to be sintered at temperatures above 1000°C [16]. Epoxy-based PCB substrates will thermally degrade above their glass transition temperatures, Tg, which range from 150°C to 250°C. Thick films are created by mixing ceramic nanoparticles into specialty epoxy, which has a dielectric constant of 3 to 4. The composite is screen printed as a thick film onto the circuit boards and cured at a low temperature (150°C – 180°C). The combination of powder and epoxy lowers the dielectric constant [16]. The top of the dielectric is covered by a metal, and finally finished with the substrate material. The embedded capacitor is connected to other components or packaged integrated circuits using through vias.

1.4 Competing Materials

Research is also being done on other materials for tunable microwave devices. Strontium Titanate thin films demonstrate high tunability at low operating temperatures (Curie temperature of about 77K), and are incorporated with high temperature superconductors, which becomes superconductive at 135K, to improve loss performances [1]. Incorporating STO requires annealing in oxygen at 830°C [17].

Na0.5K0.5NbO3 (NKN) films demonstrate tunability greater than 10% under a bias of 200KV/cm at 50 GHz [1]. It is deposited onto silicon using PLD at a temperature reaching 600°C [18]. A higher tunability is observed at frequencies below 10 GHz. This material is of interest due to its decrease in loss tangent with increasing frequency.

Pb0.3Sr0.7TiO3 (PST30) can be deposited as thin films using common fabrication techniques, including CSD (530°C to 630°C) [19], and MOCVD (600°C) [20]. It is found that PST has better loss performance than BST at high frequencies, but with comparable εr and tan δ. Low lead content PST have a close lattice match with cubic substrates, to produce better quality films. The main disadvantages to using PST are the negative environmental effects and health hazards associated with lead-based materials [1].

1.5 Thesis Goals

The objective of this project is to grow high quality BST thick film varactors onto low cost epoxy-based PCB substrates, for applications in the frequency range between 500 kHz to 1.15 GHz. There are four goals that must be met:
1. The process must be compatible with the low glass transition temperatures of the PCB. The chosen temperature is 175°C.

2. The BST thin films must have suitable dielectric constants and losses for practical applications.

3. The BST must demonstrate 5 to 10% tunability under an external voltage bias of under 10V.

4. The films must be grown using sol-gel composite thin film fabrication techniques.

The motivation for this research is to allow direct fabrication of ceramic capacitors directly onto circuit boards for realizing three-dimensional PCB circuits.

To satisfy the project objectives, hydrothermally processed BST sol-gel composites [3] are chosen. BST is a widely used tunable ferroelectric material with a high dielectric constant, and low loss tangent. BST is the material of choice because it is intensively studied for ferroelectric applications compared to other materials. It is typically implemented in industry applications as thin film varactors, generally processed at >750°C. To achieve low processing temperatures, the hydrothermal technique is currently the only known method with this capability. It is carried out at temperatures under 175°C, making it an ideal process to be compatible with PCB with low glass transition temperatures. Hydrothermal synthesis involves heating an amorphous material in a high pressure aqueous environment. Both the water and the high pressure play a role in inducing crystallization of amorphous structures at low temperatures. Amorphous sol-gel derived thin films have been previously demonstrated to crystallize using this method [3, 10]. BST sol-gel composites are BST powder suspended in an amorphous BST sol matrix. Since a composite is sol-gel based, sol-gel thin film fabrication methods will also be applicable to composite thin films. In a composite film, the amorphous sol is situated within the pores between the powder particles. After hydrothermal processing, crystalline sol-gel derived BST will create a coating around existing ceramic powder. Coatings on adjacent particles link up with each other, forming a dense matrix of interconnected BST powder, leading to a higher dielectric constant after hydrothermal processing. The thickness and density of films made in this way are dominated by the particle size of the ceramic BST powder as the thickness of the crystallized gel is negligible. Small particles will provide the best control because they have a higher packing density. A high packing density reduces pore size, which increases the effective dielectric constant of the thick films.

The contribution of this work includes modifying the formula for the BST sol, previously developed at Queen’s University. Acetic acid is introduced into the sol-gel composites to make the liquid less viscous for ease of application. Three different BST powder types are made to
explore the effects of nanostructures and ferroelectricity. The sol-gel composites are tested by using parallel plate capacitors for low frequencies, and coplanar waveguide capacitors for high frequencies. The novelty of this is that the capacitors are made on printed circuit boards. Thin films have never been grown in printed circuit board materials.

1.6 Outline of Thesis

This thesis contains 5 chapters. The literature review of different BST fabrication techniques, thin films fabricated via hydrothermal methods, and the theory behind hydrothermal synthesis is presented in Chapter 2. Chapter 3 contains the experimental methods carried out in this work. This includes three different BST powder fabrication methods, the chemical composition of the BST sol, and the design of capacitors for both low and high frequency applications. Chapter 4 presents the results, and is divided into three main sections. The first includes the findings from the powders. The second section includes the results for capacitor measurements at low frequencies. The third, and final, section contains the high frequency results. Conclusions and future work are outlined in Chapter 5.
Chapter 2

Literature Review

2.1 BST Fabrication Techniques

BST has been extensively studied for its good electrical and ferroelectric properties. Much research done on fabricating the powder has focused on the reduction of processing temperature and sizes, and achieving better control of the barium to strontium ratio. It is of particular interest to produce nano-sized materials because they have better chemical and physical properties compared to that of the bulk counterparts. Nanoparticles exhibit larger surface to volume ratio, and quantum size effects, both of which contribute to better properties. Different fabrication methods produce different shapes and sizes, including spheres, rods, cubes, and wires with the addition of chemical agents [1]. These are useful for different applications.

The most common powder fabrication technique is by solid-state reaction. It involves high temperature calcination of barium carbonate (BaCO₃), strontium carbonate (SrCO₃), and titanium dioxide (TiO₂) to produce Ba₁₋ₓSrₓTiO₃ [3]. The as-prepared solid solution is broken down into smaller sizes via repeated milling or grinding, which is prone to contamination from the wear of the milling media. The resultant particle sizes are usually large, and in randomly distributed shapes.

Sol-gel technique can produce nanoparticles [1, 3, 5]. The procedure involves mixing and aging of chemicals. Over time, the liquid state, known as the sol, will undergo gelation, forming the gel. The gel is then dried and ground to form a very fine amorphous powder. It then needs to be sintered to crystallize, and to remove unwanted organic contaminants.

Wet-chemical methods are advantageous over the previous two procedures because they can produce nanostructured powders at temperatures as low as 60ºC [21]. The starting materials are inexpensive, the particle sizes are small, and size distribution is relatively uniform. However, the final stoichiometry is hard to control, and the final powders are prone to contamination. The entire process is carried out in water, where the chemicals react, and precipitate out BST. It is suggested that, due to the aqueous environment, interstitial hydrogen in the form of H⁺ and OH⁻ radicals are introduced with the lattice, which will contribute to negative effects for ferroelectricity. Low synthesis temperature is the major factor in forming lattice dislocations. The molarity of the solution, the mixing rate, and the synthesis temperature are all factors which dictate the final particle size.
2.2 Sol-gel Thin Films

The sol-gel process describes a method where materials are derived from very small molecules. This technology became of considerable interest in the late 1800s to the 1920s [22]. It had great potential of achieving high chemical homogeneity, and is capable of producing many ceramic oxides that could not be achieved with traditional powder methods. BST sol-gel coatings have been employed mainly in DRAM applications due to its advantages for stoichiometry control, homogeneity, ease of processing, and the ability to coat large and complex area substrates. Unlike other deposition techniques, sol-gel coatings do not require a vacuum [23].

The sol is an organic dispersion of extremely small particle regions of diameters ranging from 1 to 100 nm, in a liquid. The gel is an interconnected network of porous polymer chains, which forms upon drying [22, 23]. The sol-gel process can be split up into three main stages [22]. The first is mixing. A sol is produced by mixing precursor material in water. The chemicals are broken down, and OH bonding occurs with the parent materials. The second stage is gelation. Over time, the bonding of the small particles eventually cross link with each other. Longer chains are produced, and eventually, this becomes a large three-dimensional network. The viscosity increases, and the liquid eventually solidifies. The third, and final, stage is drying. The liquid will eventually be removed, which is followed by densification and shrinkage. The resultant stresses can cause the gel to crack.

The two main methods of applying a sol-gel coat are dip coating and spin coating [24]. In dip coating, the substrate is pulled out vertically at a constant speed from a liquid bath, leaving behind a thin layer of coating. While the pull is occurring, the coating is simultaneously evaporating. The thickness is proportional to the square root of the product of the liquid viscosity, and the speed at which the substrate is pulled out. In spin coating, the film is deposited by centrifugal draining and evaporation. There are four stages to this coating procedure: deposition, spin-up, spin-off, and evaporation. The substrate is covered by the sol in the deposition stage. The liquid is then spread outwards due to the centrifugal force during spin-up. The excess is spun off the substrate surface as droplets [3, 24]. Evaporation overlaps with the other stages, where volatile components are removed, thinning the sol. The thickness is inversely proportional to the spin rate. Spin-coating is the better of the two coating methods since the thickness becomes more uniform during spin-off.
2.3 Low Temperature Derived BST Thin Films

2.3.1 Hydrothermal Processing

Many research groups have successfully grown perovskite ABO$_3$ ceramic thin films onto metallic substrates at very low temperatures via hydrothermal processing. The overall process involves a B-metal substrate immersed in an A-cation solution at temperatures ranging from 80°C to 250°C and pressures above 1 bar. Successfully fabricated ceramic films include BTO $^{[25-28, 30-35]}$, STO $^{[25-27, 35]}$, BST $^{[25-26, 31]}$, BZO (BaZrO$_3$) $^{[25-26]}$, PTO (PbTiO$_3$) $^{[29]}$, and PZT (Pb(Zr$_x$Ti$_{1-x}$)O$_3$) $^{[25, 36]}$. Low temperature growth leads to high dielectric losses due to high levels of hydroxyl defects in the lattice structure. Oxygen plasma and heat treatments can improve dielectric loss $^{[28]}$. In the case of BST, both barium hydroxide (Ba(OH)$_2$) and strontium hydroxide (Sr(OH)$_2$) are used as aqueous reactants with titanium as the substrate. The substrates are heated in an autoclave to a suitable temperature for several hours. The setup for hydrothermal processing is shown in Fig. 7.
Figure 7: Hydrothermal pressure vessel setup: A) thermocouple, B) Teflon beaker, C) substrate, D) alkaline solution, E) heating element [35]

The result is a ceramic thin film tightly bonded with the substrate. Barium and strontium hydroxides are extremely reactive to carbon dioxide, and can react with the slightest carbon content in the atmosphere to produce carbonate [3, 25-28, 30-35]. The carbonates do not come off with water, but are removable through the use of high energy argon gas bombardment [25], wiped off with tissue paper [26], or dissolved with ethanol and weak acid [37]. The hydrothermal processing parameters are governed by temperature and time, where an increase in either or both will yield a much denser film. Prolonged exposure will cause the hydroxide to erode the existing film. The limitation to this fabrication technique is the small penetration depth of the hydroxide to the metallic film. Ceramic is produced on the top layer, but much of the bottom is unreacted.
When the first layer of dielectric is formed, the process is now diffusion-limited. The grains and grain-boundaries are impermeable. Cations now have limited paths to diffuse into the titanium. Parallel plate capacitors are made to measure the electrical properties of the thin films, where an evaporated metal acts as the top electrode, and the unreacted Titanium acts as the bottom electrode. A photograph of such a film is shown in Fig. 8. Successfully fabricated films are summarized in Table 2. Some materials are made for purely material analysis, and no electrical data is available.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Material</th>
<th>Frequency</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilleux et al [25, 26]</td>
<td>BTO</td>
<td>10 kHz</td>
<td>135</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 MHz</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>BZO</td>
<td>1 MHz</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>BST</td>
<td>1 MHz</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tan et al [28]</td>
<td>BTO</td>
<td>100 MHz – 3 GHz</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td>Cho et al [29]</td>
<td>PTO</td>
<td>1 kHz</td>
<td>215</td>
<td>-</td>
</tr>
<tr>
<td>Hou et al [31]</td>
<td>BTO/BST</td>
<td>100 kHz</td>
<td>0.44 μF/cm²</td>
<td>0.04</td>
</tr>
<tr>
<td>Bacsa et al [32]</td>
<td>BTO</td>
<td>10 – 50 kHz</td>
<td>450 – 500</td>
<td>0.04 – 0.1</td>
</tr>
<tr>
<td>Balaraman et al [33]</td>
<td>BTO</td>
<td>100 kHz</td>
<td>900</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 2: Summary of successfully fabricated thin films via low temperature hydrothermal processing. Hou et al [31] provided results for capacitance/area, and is denoted with units.

Because of the above inherent limitation in film thickness, the present work will examine the rate of hydrothermal processing and recrystallization of an amorphous BST matrix rather than direct reaction with a metal.

2.3.2 Sol-gel Hydrothermal Processing (SGHP)

There have been efforts to improve hydrothermal processing techniques since the resultant films are too thin for practical applications. The thicknesses for a usable thin film are between 0.4 and 2 μm [37]. Low temperature hydrothermal processing of coatings on metallic substrates creates thin films of thicknesses less than this usable range. Sol-gel-hydrothermal (SGHT) processing has been developed to address this issue. This method involves recrystallizing amorphous sol-gel derived thin films on Pt/Ti/SiO₂/Si substrates [37–43]. The sol-gel composition includes BTO [37–40], BST [41, 42], BZT [43], and PZT [44]. The procedures are very similar to hydrothermal processing, but instead of using titanium metal as a starting material, an amorphous structure in the form of a dried gel is used. The alkaline solution is not used for a reaction process, but as a catalyst to drive crystallization. Much of the starting structure exists within the amorphous films. It only needs to rearrange itself to become crystalline. The sol is spun onto the chosen substrate and allowed to gel. A thicker film can be derived by adjusting the spin rate or by multiple coatings, and is not limited by the penetration depth of the hydroxide solution. The film is annealed at 400°C for several minutes, before being processed in the autoclave. Processing in the autoclave is the same as before, where the substrate is submerged and reacts with an alkaline solution. In the case of PZT, the alkaline solution is composed of potassium hydroxide (KOH) and lead hydroxide (Pb(OH)₂). During this time, amorphous sol-gel derived films form crystalline ceramic. The films are then annealed at 500°C after processing to remove hydroxyl groups. It has been demonstrated that post-process annealing will increase not only the dielectric constant but also the loss tangent. There are two kinds of hydroxyl groups that get incorporated into the ceramic lattice during hydrothermal processing [38]. They are surface-absorbed OH⁻, and lattice OH⁻. Surface OH⁻ occurs in the interface between the thin film surface,
and the top electrode. This changes any external electric fields, and decreases polarization. Post-processing annealing has been shown to increase the polarization response of BTO [38] and PZT [44] thin film. Tunability increased from 17% to 25%. OH⁻ groups embedded in the lattice structure distort the ferroelectric hysteresis loops and make them asymmetrical.

The annealing process can cause an increase in dielectric loss. It is speculated that this is a result of generating a denser space charge [38]. At high temperatures, OH⁻ groups undergo a reaction process: 2OH⁻ → H₂O + O²⁻. Instead of a single negative charge, the negatively charged oxygen ions provide two. They accumulate near the electrode-to-film interfaces or in grain boundaries which may consume energy. A summary of the results are presented in Table 3.

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Material</th>
<th>Frequency</th>
<th>Post-process No annealing</th>
<th>Post-process Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>εᵣ</td>
<td>tan δ</td>
<td>εᵣ</td>
</tr>
<tr>
<td>Xu et al</td>
<td>BTO [37]</td>
<td>1 MHz</td>
<td>80</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>BTO [38]</td>
<td>10 kHz</td>
<td>80</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>BST [41]</td>
<td>1 MHz</td>
<td>42</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>BZT [43]</td>
<td>1 kHz</td>
<td>247</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 MHz</td>
<td>87</td>
<td>0.01</td>
</tr>
<tr>
<td>Zeng et al</td>
<td>BTO [39]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wei et al</td>
<td>BTO [40]</td>
<td>66 Hz</td>
<td>21</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td></td>
<td>BST [42]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PZT [44]</td>
<td>1 Hz</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3: Summary of successfully fabricated thin films via sol-gel hydrothermal processing. Wei et al [44] provided results for capacitance and is denoted by the units.

An extension of the SGHT process was explored by Zelonka [3, 45], where a sol-gel composite is used to produce denser ceramic thin film structures. Composites were fabricated by mixing high dielectric BST ceramic powder into amorphous BST sol. Composites are gelled after spin coating onto a substrate. The hydrothermal process allowed the crystallization of the gel, causing the BST powder to be trapped within a dense, crystalline sol-gel derived BST thin film. Aside from the crystallization of the amorphous matrix, another phenomenon occurred when processing composite films. AFM images in Fig. 9 and Fig. 10 show bridges linking the ceramic
powder together, forming a well-connected electrical network. These bridges are about 100 nm in length.

![BST bridges formed between BST particles as an electrical network](image)

**Figure 9: BST bridges formed between BST particles as an electrical network [3]**

The films are no longer comprised of individual particles, but instead, a well linked ceramic matrix. The resultant dielectric constant is higher than that reported in Tables 2 and 3. An increase in concentration of hydroxides in the alkaline solution was found to increase the film permittivity, but caused poor adhesion to the substrate. Films processed in a 1M solution resulted in a dielectric constant and loss tangent of 1400 and 0.6 at 1 kHz, and 1000 and 0.1 at 100 kHz.

Bijumon et al [10] employed Zelonka’s [3] technique to incorporate ceramic resonators in microwave integrated circuits, which gives the added advantage of decreasing size and weight of devices. Since the dielectric resonators (DRs) have dimensions smaller than 1 mm, common coupling materials such as ceramic glue can largely affect the effective permittivity and the operating frequency. A sol-gel composite with the same material as the DR can enhance the radiation energy by focusing the fringing fields away from the lossy substrate, and into the DR. The chosen DR and sol-gel composite was BTO. The sol-gel composite formed electrical bridges between the bulk DR material and the thin film which eliminated grain boundary defects and the
dielectric properties are enhanced. At 31.60 GHz, the reported dielectric constant was 38, an increase from the pre-processing value of 34.

![Interconnected microstructure with crystallized sol-gel](image)

**Figure 10: Crystallized sol-gel interconnected microstructure [10]**

### 2.4 Theory of Hydrothermal Synthesis

In hydrothermal synthesis, three major components affect crystallization. The first two are heat and water, which the term hydrothermal suggests. The third component, which is also crucial, is pressure. The three work in conjunction with each other, and are responsible for forming many natural minerals, especially in the ocean floor. Needless to say, many materials are formed in laboratories using this method for scientific applications.

#### 2.4.1 Aqueous and Thermal Models

Two main mechanisms are often suggested when understanding the thermal and aqueous dependence of hydrothermal synthesis/processing. In the models presented by Eckert Jr. et al, the two transformation mechanisms are in-situ transformation [46, 47], and dissolution-precipitation [27, 47]. Barium titanate will be used as the example as most hydrothermal research has been done using BTO. The reaction that occurs is given as [46]:

\[
Ba(OH)_2 + TiO_2 \rightarrow BaTiO_3 + H_2O
\]  

(2.1)
The in-situ transformation is diffusion driven. TiO$_2$ reacts with dissolved Ba$^{2+}$ atoms, where the barium diffuses into the TiO$_2$ atom and reaction occurs until the titania is exhausted, as shown in Fig. 11. As the reaction is taking place, the area of unreacted titania decreases, and the thickness of the BTO product increases. The rate is governed by how fast barium diffuses into titania, and how long the reaction takes. Generally, the reaction rate is fast, hence, the rate-determining step is the diffusion of atoms [46].

![Diagram of in-situ transformation of BTO](image)

**Figure 11: In-situ transformation of BTO [47]**

The fraction of total reaction, $\alpha$, is given by the equation [46]:

$$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = \frac{kt}{r_0^2}$$

(2.2)

where $k$ is a rate constant, $t$ is the time, and $r_0$ is the initial radius of the particle. The rate constant is given as [46]:

$$\frac{dr}{dt} = k$$

(2.3)

Hence it takes into account any change in the final particle size. In an alkaline solution where the concentration of Ba(OH)$_2$ is greater than 1M, the reaction rate becomes independent of the concentration, but dependent on the temperature. The surface area variation of the final product is
insignificant at concentrations above 2M, but at low Ba(OH)₂ concentrations, surface areas can be 4 to 5 times smaller.

In the dissolution-precipitation model, shown in Fig. 12, Ti-O bonds get broken to form hydroxytitanium structures (Ti(OH)ₓ⁺). These structures can dissolve and react with Ba²⁺ ions or BaOH⁺ ions to produce BaTiO₃. Two types of nucleation are present, and are classified as either homogeneous, or heterogeneous. Barium titanate nuclei can form in the solution, which is the homogeneous case, or the nuclei can form on the titanium dioxide substrate, which is classified as heterogeneous. Heterogeneous transformation is very similar to in-situ transformation, and is diffusion driven. The diffusional barrier is said to slow the hydrothermal reaction.

![Diagram of dissolution-precipitation transformation of BTO](image)

Figure 12: Dissolution-precipitation transformation of BTO [47]

Wu et al [27] speculates that the titanium film dissolves upon contact with the alkaline solution. In the case of BTO, Titanium hydroxyl species (HTiO₃⁻) and BaTiO₃ atoms form simultaneously.
In hydrothermal process, BaTiO$_3$ crystals nucleate from the solution, covering the top surface of the titanium film. Pores and fissures will be present. Ba$^{2+}$ ions diffuse to the inner titanium atoms through cracks, and continue to react with unreacted titanium films until the newly formed BTO becomes impenetrable to floating Ba$^{2+}$ ions.

In-situ transformation is the most probable mechanism than dissolution-precipitation transformation in recrystallization of BST sol-gel thin films. Dissolution-precipitation suggests a partial, if not complete, disintegration of the structure. However, no disintegration is seen in this work.

### 2.4.2 High Pressure Crystallization (HPC) / High Pressure Annealing

Pressure plays a significant role in both hydrothermal processing and sol-gel hydrothermal processing. The crystallization occurs in a sealed autoclave, where the pressure increases as the temperature increases. Titanium dioxide (TiO$_2$) has been demonstrated to crystallize under high pressure environments [48]. Titanium dioxide precursor films are deposited onto Silicon wafers as the starting material, which are pyrolyzed at 325°C for 30 minutes to remove organic components. This temperature is insufficient for any crystallization. Two different crystallization methods are compared in this study. The first is heating the as-deposited film in a furnace at temperatures ranging from 350°C to 600°C, carried out under atmospheric pressure (1.01 x 10$^5$ Pa) for 2 hours. The second film is crystallized in a sealed autoclave filled with deionized water to create high-pressure saturated steam at temperatures over 100°C. Unlike traditional hydrothermal methods, no additional chemicals are added to the water, and the films are situated on the water surface, and not submerged. The pressure reaches up to 4.05 x 10$^6$ Pa at temperatures ranging from 150°C to 250°C for 2 hours. Fig. 13 compares the x-ray diffraction peaks of the titanium dioxide films produced by both methods.
Figure 13: a) TiO\textsubscript{2} films annealed at atmospheric pressure; b) TiO\textsubscript{2} films annealed at high pressure [48]

X-ray diffraction (XRD) shows that TiO\textsubscript{2} fully crystallizes at 600°C under normal circumstances. At much higher pressures, full crystallization occurs at 250°C. A nucleation process is considered to be the mechanism behind crystallization under high pressures. Under high pressure environments, the critical free energy required to form a stable nuclei is significantly reduced [49]. The nucleation rate, \( I \), is given by the equation [49]:

\[
I = I_o \exp \left( -\frac{\Delta G + \Delta E}{RT} \right) = I_o \exp \left( -\frac{G}{RT} \right) \tag{2.4}
\]

where \( I_o \) is a constant, \( \Delta G \) is the thermodynamic potential barrier of nucleation, \( \Delta E \) is the diffusion activation energy, \( R \) is the universal gas constant, and \( T \) is the temperature. Note that in Eqn. 2.4, \( G = \Delta G + \Delta E \), and is known as the nucleation energy. \( \Delta G \) is given as:

\[
\Delta G = \frac{16\pi\sigma^3}{3\Delta G_v^2} = \frac{16\pi\sigma^3}{3(G_c - G_a)^2} \tag{2.5}
\]
where $\sigma$ is the interfacial activation energy of the amorphous phase and the crystallized phase of a structure, and $G_a$ and $G_c$ are the Gibb’s free energies of the amorphous phase and the crystallized phase. The change in $G$ with respect to changing pressure, at a constant temperature is given by:

$$\left(\frac{\delta G}{\delta P}\right) = -\frac{32\pi\sigma^3}{3(G_c-G_a)^3}(v_c - v_a) + \left(\frac{\delta\Delta E}{\delta P}\right)$$

(2.6)

where $v_a$ and $v_c$ are mole volumes of the amorphous and crystallized phase respectively. In an amorphous material (or mostly amorphous), $v_c - v_a < 0$, and $G_c - G_a < 0$. The first term represents crystallization promotion, and the second term represents crystallization retardation. The crystallization retardation term increases with pressure, but only slightly. $G_c - G_a$ is also pressure dependent, and can be expanded as:

$$(G_c - G_a) = -k(v_c - v_a)p^2 + (v_c - v_a)p - C$$

(2.7)

where $k$ and $C$ are constants. As long as the first term is larger than the second term in Eqn. 2.6, the nucleation activation energy decreases with increasing pressure, favoring crystallization.

2.5 Chapter Summary

There are three common methods of producing BST powder. They are solid-state reaction, sol-gel techniques, and wet-chemical methods. For solid-state reaction to take place, high temperatures are necessary in producing the powders. They are then broken down into smaller pieces through milling or grinding methods, which results in particles with randomly distributed shapes. The sol-gel process takes time for the sol to undergo gelation and requires a sintering stage; however, nanoparticles can be produced this way. Wet-chemical methods can produce nanosized particles at temperatures as low as 60°C. It is the most advantageous technique since the starting materials are inexpensive, resultant particle sizes are small and uniform. However, since the fabrication process is carried out under aqueous environments, and so, interstitial hydrogen may contribute to negative effects for ferroelectricity. An objective explored with this thesis has been to compare the ferroelectric nature of nano-particles compared to that of powders prepared by conventional grinding.

Hydrothermal processing is the only known process to synthesize thin films onto substrates at temperatures ranging from 80°C to 250°C. This involves submerging a sol-gel
derived thin film in the hydrothermal solution, and heating the solution in a sealed autoclave at elevated temperatures and pressure. Sol-gel composites are more advantageous than purely sol-gel derived thin films. Composites are mixtures of powder and an amorphous sol. The sol will recrystallize during hydrothermal processing, forming interconnects between the powders. This leads to a higher dielectric constant.

The parameters behind hydrothermal processing are temperature and pressure. There are two transformation mechanisms: 1) in-situ transformation and 2) dissolution-precipitation. In-situ transformation involves the diffusion of metallic ions (barium) into a base material (titanium dioxide). As the barium diffuses into the structure, it reacts with the titanium, producing barium titanate. In the dissolution-precipitation model, the titanium dioxide is pulled into the aqueous solution containing barium ions. Reactions occur as the titanium is pulled out, producing barium titanate.
Chapter 3

Experimental Methods

3.1 BST Powder Fabrication

Three different powder fabrication techniques have been explored to produce Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. As mentioned in Section 2.1, different production processes have their own advantages and disadvantages. The two major differences between the three methods are particle size and hydration. The powder fabrication methods explored are: 1) ceramic derived, 2) sol-gel derived, and 3) low temperature wet chemical derived.

3.1.1 Ceramic Derived Powder

Appropriate amounts of barium and strontium carbonate powders are mixed with titanium dioxide and dry-milled for four hours to promote good mixing. The mixture is then calcined at 600°C for 24 hours. The powder is reground in the mill to break the agglomeration. It is then sintered in the furnace by ramping from 25°C to 600°C in 2 hours, and ramped from 600°C to 1100°C in another 2 hours. Finally, the powder is held at 1100°C for 20 hours [3]. The final product is dry-milled for 2 days to break the agglomeration, and washed out with water. It is dried for 8 hours at 100°C.

3.1.2 Sol-gel Derived Powder

Deionized water is first boiled to remove any dissolved carbon. Barium acetate ((CH$_3$COO)$_2$Ba) and strontium acetate ((CH$_3$COO)$_2$Sr) are mixed, stirred, and ultrasonically agitated until the solution becomes clear. Titanium butoxide (Ti(OCH$_2$CH$_2$CH$_3$)$_4$), methanol (CH$_3$OH), and acetic acid (CH$_3$CO$_2$H) form the basis of a second solution. The three ingredients for the second solution are mixed in a separate beaker, and are ultrasonically agitated until clear. Finally, the two solutions are mixed together. A reaction will take place, and the liquid produces bubbles, and the color turns milky. The final solution is agitated until it becomes clear. It then sits in air, and is allowed to gel [3]. Once gelled, it is placed in an oven at 100°C for 24 hours to speed up the evaporation process, hand ground, and dried again for 24 hours. While in a “soft” powder state, it is dry-milled for 8 hours, and sintered afterwards at 750°C for 24 hours. The final product is dry milled again to break up agglomeration.
3.1.3 Low-temperature Wet-Chemical Derived Powder

For this fabrication process, the deionized water is not boiled. The two hydroxide-octahydrates (Ba(OH)$_2$·8H$_2$O and Sr(OH)$_2$·8H$_2$O) are mixed with room-temperature deionized water, and stirred vigorously using a magnetic stirrer. While mixing, the temperature of the base solution is heated and held at 60°C. During the heating process, a titanium solution, comprised of titanium butoxide and ethanol (CH$_3$CH$_2$OH), is made in a separate beaker. The mixture is ultrasonically agitated for 20 minutes to ensure a thorough mix. Once the base solution reaches 60°C, the titanium solution is slowly dripped into the magnetically stirred hydroxide solution [21]. Upon contact between the two solutions, white precipitates can be seen to form immediately. Once the titanium solution is used up, the stirring and heating is continued for another 15 minutes, after which, the newly formed solution is aged for 10 hours. The precipitates, which settle at the bottom, are BST nano-particles, and are retrieved using filter paper. The powder is dried at 100°C for 24 hours, and washed in formic acid before annealing at 500°C for 8 hours. The formic acid wash is to remove carbonate residue from the hydroxide precursors. The amounts of barium hydroxide and strontium hydroxide have been adjusted for purity. Barium hydroxide octahydrate and strontium hydroxide octahydrate have purity levels of 98%, and 95% respectively.

3.2 Sol Fabrication for Sol-gel Composite Application

The chemicals used to fabricate the sol for sol-gel composites is the same as those used to produce sol-gel derived powder. However, the amount used is less, and the ratio of water, methanol, and acetic acid to barium, strontium, and titanium is significantly reduced. The reduction in water, methanol, and acid is to ensure sols used for composites are highly concentrated with barium, strontium, and titanium. The sol described in this section, along with the powders produced in Chapter 3.1, form the basis of sol-gel composites.
3.2.1 Sol

<table>
<thead>
<tr>
<th></th>
<th>Chemical</th>
<th>Formula</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solution 1</strong></td>
<td>Barium Acetate</td>
<td>(CH$_3$COO)$_2$Ba</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>Strontium Acetate</td>
<td>(CH$_3$COO)$_2$Sr</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>Deionized Water</td>
<td>H$_2$O</td>
<td>5.40</td>
</tr>
<tr>
<td><strong>Solution 2</strong></td>
<td>Titanium Butoxide</td>
<td>Ti(OCH$_2$CH$_2$CH$_2$CH$_3$)$_4$</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td>Acetic Acid</td>
<td>CH$_3$CO$_2$H</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4: Material for fabricating the sol used in sol-gel composites

Solutions 1 and 2 are made in separate beakers, and ultrasonically agitated individually for a thorough mix. The two are then mixed into each other and agitated further for 15 minutes. Afterwards, the final solution is sealed and refrigerated for a minimum of 8 hours before use. Due to the reduction in water, methanol, and acetic acid, the gelation rate increases. For composite applications, the solution gels in 2 to 3 days, making them unusable. The quantities of the chemicals are shown in Table 4.

3.2.2 Sol-gel Composites

The basis of a composite involves mixing BST powder into a BST sol, diluted with acetic acid. For composites involving the mix of ceramic derived powder + sol, and sol-gel derived powder + sol, the ratio is 1:1:0.5 – powder: sol: acetic acid. For composites involving the mix of low-temperature derived powder + sol, the ratio is 1:1:1.7 – powder: sol: acetic acid. The three components are mixed, and ultrasonically agitated until the solution becomes milky. The ratios have been formulated to reduce film cracking, and particle agglomeration in a sol-gel composite thin film. Adding acetic acid does two things. First, it thins out the sol. The sol is very viscous; hence it is difficult to create a thin film. Second, particles clump together without the acid, which affects the uniformity of the as-deposited film. Particle clumping is due to the solution having a zeta potential near 0 mV, and is found to disappear at potentials ±30 mV [50]. The pH level governs zeta potential, where low pH (acidic) increases, and high pH (basic) decreases the potential level. A net 0 potential level indicates some particles are positively charged, while some are negatively charged. Since opposites attract, particles with different charges will group together, forming particle clumps. A net positive or net negative potential...
indicates that the particles are of the same charge, and will repel each other. Since the sol is acetic-acid-based, acetic acid is used as the agent to increase the overall zeta potential.

3.3 Devices for Electrical Measurements

Devices were designed to both utilize and characterize the materials made in this project. They are separated into two categories: low frequency devices, and high frequency devices. Low frequencies range from 0 to 20 MHz, and are characterized by parallel plate capacitors. High frequencies range from 45 MHz to 1.15 GHz, and are characterized by grounded coplanar waveguide capacitors. The substrate used is Panasonic R-1755v. It has a glass transition temperature of 190°C. The dielectric constants and loss tangents are 4.7 and 0.013 at 1 MHz, and 4.4 and 0.016 at 1 GHz, respectively. The substrate is plated with 17.5 μm thick copper (½ oz), and finished with a nickel coating. For the experiments in this project, hydrothermal processing is carried out at 170°C - 175°C (temperature varies slightly due to temperature controller). Having a glass transition temperature of 190°C allows a larger margin of error with temperature control. The nickel finish on the copper plating is to protect the copper in the alkaline environment associated with hydrothermal processing, which will produce copper oxide.

3.3.1 Parallel Plate Capacitors

Parallel plate capacitors are made by spin coating either the sol, or the sol-gel composites onto the substrates. The spin rate dictates the overall film thickness. For this project, the spin rate is 2500 rpm, which gives a thickness ranging from 3 μm to 5 μm depending on the composite used. After each layer is spun on, it is dried in the oven at 160°C for 30 minutes to remove any volatile organic components. Two layers of sol or sol-gel composite are deposited for each structure. The film is then hydrothermally processed (explained in Section 3.4), and finished by evaporating aluminum dots as the top electrode. The aluminum dot size is 1.6 mm in diameter. The capacitors are shown in Fig. 14. To obtain accurate thickness measurements, the composites are spun onto silicon substrates. Printed circuit boards are not perfectly flat, and will have slight bends on the boards themselves, which will affect surface profile measurement readings, whereas high quality silicon is perfectly flat. Since the materials have the same consistency, and the spin rates are the same, the thicknesses measured on silicon should be very similar to that on PCB.
3.3.2 Grounded Coplanar Waveguide Capacitors

Grounded coplanar waveguides are fabricated on the same Panasonic substrates with nickel finish. A 50 ohm signal line was designed, with the line width being 40 mils, and the gap size of 35.12 mils. The dimensions are shown in Fig. 15. A line width of 40 mils is chosen because the center pin of gold connectors is the same size, making soldering easier. The length of the transmission line is 587 mils. A 3 mil gap is used to separate the end of the signal line with the ground plane. Through-vias are used to connect the surface ground plane with the bottom ground plane, which is depicted in Fig. 16.
Sol and sol-gel composites are spun onto the large ground plane of the waveguide structures (the area where the end of the transmission line is separated by the 3 mil gap). The
remainder of the circuit is protected by a piece of tape when spin coating, to avoid BST from covering the transmission line area. The tape is subsequently removed after the coating process. The coating is hydrothermally processed (Section 3.4), and a large aluminum dot (diameter of 6.3 mm) is evaporated onto the thin film. Nail polish is used to cover the 3 mil gap, and silver paint is used to connect the dot with the transmission line. SMA gold connectors are soldered onto the start of the transmission line for measurement purposes, as shown in Fig. 17.

Figure 17: Fully connected and fabricated grounded coplanar waveguide BST capacitor

3.4 Hydrothermal Processing

Hydrothermal processing starts by preparing the hydrothermal solution. Experiments have been conducted using different molarities, and different ratios of barium to strontium. These parameters affect the bridging between the particles, dielectric constants, and tunability. Appropriate amounts of hydroxides are dissolved in boiled deionized water. Insoluble powder-like substances will separate upon mixing. These are the impurities, and are filtered out under nitrogen using coarse filter paper. The filtered solution is poured into a teflon cup, where the circuits are placed. The cup is sealed in an autoclave (similar to the one in Fig. 7) and flushed out with nitrogen for 20 minutes. This is to prevent the hydroxides from forming their respective carbonates due to reaction with atmospheric carbon dioxide. Once fully flushed, the valves are
tightly sealed, allowing the internal pressure to increase as the temperature is increased. The heating rate is 1.3°C/minute. It takes about 2 hours to ramp from 25°C to 175°C (ramp time). The temperature is held for another 2 hours (hold time). After the process is completed (total of 4 hours), the system is air cooled for 1 hour, until the internal temperature is between 80°C and 90°C. At this temperature, the internal pressure is atmospheric pressure, and is safe to handle. The removal process is done at elevated temperatures to prevent the hydroxides from solidifying on the circuits. The processed circuits are washed in boiling water to remove the hydroxide solution to stop future carbonation. They are dried at 160°C for a minimum of 10 hours before evaporating aluminum dots and measuring. Dots are evaporated using an Edwards E306A Coating System.

3.5 Analysis Techniques

3.5.1 Powder Analysis

Powders fabricated using the methods listed in Chapter 3.1 were analyzed using a Rigaku Miniflex x-ray diffraction (XRD) analyzer with CuKα radiation. Attenuated total reflectance (ATR) is carried out using Nicolet FTIR spectrometer. High magnification images were taken using a JEOL 740 scanning electron microscope (SEM).

3.5.2 Thin Film Capacitor Analysis

A Hewlett Packard 4396B network analyzer was used to measure frequencies from 500 KHz to 20 MHz. The analyzer was used with a HP 43961A RF impedance test adapter, and a HP E3630 triple outlet DC power supply. For high frequency measurements (45 MHz to 1.15 GHz), a HP 8510C vector network analyzer is used. To calibrate the grounded coplanar structures, a self-made calibration kit is used, which is used for open, short, and load calibrations. This is shown in Fig. 18 and Fig. 19. The calibrations are tested by measuring a standard capacitor to determine whether the measured results matched the expected value. The thickness of the thin film is measured using a Dektak XT surface profiler.
Figure 18: Self-made calibration for short circuit. No vias are present in the large ground plane on the right side, therefore, solder is used. This provides better and more efficient ground connection from top to bottom metal.

Figure 19: Calibration for open circuit on the left. 50Ω load calibration on the right.
4.1 BST Powder Results

4.1.1 X-ray and Infrared Characterization

The XRD peaks indicate that all three fabrication methods produce crystalline BST ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$). They are shown in Fig. 20 to Fig. 22.

![X-ray diffraction peaks](image)

Figure 20: X-ray diffraction peaks for ceramic derived $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ powder
Figure 21: X-ray diffraction peaks for sol-gel derived powder

Figure 22: X-ray diffraction peaks for low-temperature derived powder
The stars above the small peaks at 23° - 25° indicate that small traces of Ba/Sr carbonates are present. This is due to residual organics from the precursor materials. Attenuated total reflectance (ATR) analysis, shown in Fig. 23, further characterizes the three fabrication methods, particularly with impurity content.

![Figure 23: ATR comparison of powders made from the three fabrication methods](image)

Even with significant efforts to remove carbonates using a formic acid wash, they are still prominent under ATR analysis. Ceramic derived powder contains no carbonate. The extremely high fabrication temperature with the presence of oxygen causes all precursor carbon to be released as CO₂, leaving behind pure BST.

The fabrication temperature has an enormous effect on the properties of the powders, which cannot be seen in XRD. Since the x-rays show the same diffraction peaks, one would assume the three fabrication methods produce the exact same material. However, as seen under ATR, BST with three different properties are produced in each of the three cases.

At higher wavenumbers, the total infrared transmittance is much less in the ceramic derived and sol-gel derived powder. This is attributed to the high temperatures required to fabricate the powders. They are sintered at 1100°C and 750°C respectively. The denser and better crystalline particles absorb more of the infrared, leading to a lower transmittance percentage. The low temperature derived powder is fabricated at 60°C and heated at 500°C, which may explain
why the infrared transmittance is at almost 100%. Carbonates from the sol-gel derived powder are produced as a by-product. The barium, strontium, and titanium react to form BST. The remaining elements will either be burned off at 750°C, or rearrange to produce barium/strontium carbonate. The carbonate residue from the low temperature derived powder is due to the initial hydroxides that reacted with carbon dioxide in the ambient atmosphere, and remained throughout the entire fabrication process. When the wave number is under 500 cm\(^{-1}\), the IR spectrum of both the ceramic and sol-gel derived powder exhibit a sharp increase in IR transmittance, almost to 60%, whereas low temperature derived only goes to 40%. This indicates that certain elements are removed from the system, whereas 500°C is insufficient to remove this unknown element. The sharp peak at 500 cm\(^{-1}\) is most prominent for ceramic derived BST. This is likely a characteristic of the ferroelectric properties of the lattice.

Since the low temperature method produces nano-sized BST, it is further examined. Washing the low-temperature derived powder with formic acid, and heating it to 500°C are necessary to improve the quality of the BST powder. The properties can be seen in their respective infrared spectra. When fabricated at 60°C, water and carbonate is incorporated into the system. The water component is the result of the aqueous environment. They are tightly bonded into the lattice structure as O-H groups. From Fig. 24, drying the powder at 100°C does not remove it. When the hydroxides are dissolved in water, the initial carbonate impurities are separated instantly. As the production is carried out, part of the hydroxide solution will react with ambient carbon dioxide producing carbonates. These are the two reasons for to the carbonate component shown in the infrared spectra.
Figure 24: Low temperature derived powder without post-processing. It is full of unwanted byproducts such as water and carbonates.

The powder is then annealed at 500°C for 3 hours. 500°C is chosen because this temperature is not high enough to promote grain growth, which would defeat the purpose of producing nano-sized particles. The O-H groups incorporated in the lattice structure disappear. The carbonate still remains. The ATR of this is shown in Fig. 25.

To remove the carbonates, the powder is washed using formic acid. The acid only partially dissolves the carbonates, and the powder remains unaffected. Traces of carbonates still remain, which can be seen in the infrared spectrum from Fig. 26.
Figure 25: Firing the low temperature derived powder at 500°C eliminates water content, but does not remove carbonate residue.

Figure 26: Formic acid helps reduce carbonate content in the system.
Heating the powder to 1100°C completely changed the material as shown by the x-ray patterns in Fig. 27. It contains unusual peaks which may be other derivatives of titania. This indicates that the low-temperature derived powder is very sensitive to its fabrication criteria, and can only be made following specific procedures.

Figure 27: Unlike ceramic derived powder, sintering low temperature derived powder does not remove carbonate content. It changes the structure completely.

4.1.2 Powder Morphology

Not only does temperature have an effect on the intrinsic properties of the powder, it also affects the extrinsic properties. Solid-state reaction, which requires the highest temperature, promotes grain growth, and yields the largest particle sizes. This is shown in Fig. 28. Even after ball milling, particles can be greater than 2µm. As seen in Fig. 29, sol-gel derived powder is produced at a slightly lower temperature, hence, slightly smaller particle sizes. Low temperature derived powder is made at the lowest temperature of the three, and yields the smallest particle size. When dried, the BST nanoparticles are clumped together due to electrostatic forces. This is
shown in Fig. 30 and Fig. 31. However, they can be separated by adding acids to alter the net pH level. This is done when making composite thin films to separate the BST into individual particles. It is interesting to note that only the low temperature synthesis produces powders with uniform shape and size.

Figure 28: SEM image of ceramic derived powder. The size of the powder is the largest of the three fabrication methods.
Figure 29: SEM image of sol-gel derived powder. Much like ceramic derived powder, the sizes are relatively large, non-uniform, and are in various shapes.
Figure 30: SEM image of low temperature derived powder. The particles are clumped together due to electrostatic forces.
4.1.3 Low Temperature Recrystallization

To demonstrate that hydrothermal processing will produce crystalline BST, dried amorphous BST sol-gel powder (powder not sintered at 750°C) has been processed. The XRD shows no definite peaks prior to processing, indicating an amorphous structure.

For comparison, amorphous gel powder is sintered at 750°C for 3 hours. The XRD patterns show definite XRD peaks which indicate that crystalline BST is produced. The same pattern can be seen in hydrothermally processed amorphous powder. The XRD patterns are the same, with the exception of the XRD intensities. This shows that hydrothermally processing will generate crystalline powder, but the trade-off is between crystallinity and temperature. Higher temperatures will produce more crystalline structures. Fig. 32 shows the comparison of the XRD peaks.
Figure 32: Comparing the effects of hydrothermal processing with traditional sintering. Amorphous structures recrystallize in both cases, but hydrothermal processing yields smaller particle sizes.

The widths of the peaks produced via hydrothermal processing are broader than that from firing at 750°C. The Scherrer equation states that the size of a particle is inversely proportional to the full width half max (FWHM) of the XRD peaks [51]. This indicates that BST particles formed this way are much smaller than traditional sintering. However, because this set of BST is produced at very low temperatures, it is expected to have very poor ferroelectric properties, similar to that of low temperature derived powders. This is as expected since the fabrication is carried out under a highly aqueous environment. Water will definitely be incorporated into the lattice. Carbonates are present because of the hydroxides dissolved in the water. It is unnecessary to attempt to remove the unwanted byproducts since these procedures cannot be used for thin film applications.

The result can be applied to thin films. In a thin film comprised of only amorphous gel, it will crystallize, behaving similarly to the powder. With regards to the composite films, where powder is submerged in an amorphous gel matrix, the gel will crystallize after processing, resulting in an extremely dense film, where BST powder is locked in a crystalline BST gel.
matrix. Images in section 4.2 easily show small particles produced from recrystallizing amorphous sol-gel structures.

4.2 Thin Film Results

4.2.1 Film Characteristics and Low Frequency Measurements

Prior to hydrothermal processing, both the powder and the amorphous sol-gel components of the film can be seen under the SEM, as well as cracks propagating throughout the structure. This is easily seen in Fig. 33. These cracks contribute to short circuiting when evaporating aluminum dots on top, therefore, only qualitative data is available. As shown in Fig. 34, amorphous sol-gel derived thin films (non-composites) are smooth in structure, and have significantly more cracks. In typical sol-gel thin film fabrications, additives such as propylene glycol, is added to make the solution less volatile, reducing the number of cracks [23]. They are then sintered at elevated temperatures to be removed. In this case, additives cannot be used since they will not be removed during processing.

Figure 33: Structure of unprocessed sol-gel composite thin films. Powder and amorphous component can be easily distinguished. Cracks are present in the structures.
Figure 34: Purely amorphous sol-gel derived thin films. There are more cracks only gel-like sheets are present.

Much like recrystallization of amorphous sol-gel derived powder, hydrothermal processing also causes the amorphous structures of the thin films to recrystallize. From Fig. 34 and Fig. 36, it is clear that the smooth structure in a purely amorphous sol-gel thin film transforms into small BST particles. Cracks are slightly mended, which is seen in Fig. 35. The initial crack sizes prior to processing are quite large. Expansions must have occurred during processing to shrink the gap sizes, but is still insufficient to close them up. As mentioned in Chapter 2, in-situ transformation is the obvious mechanism of sol-gel recrystallization. If dissolution-precipitation is to happen, the film will disappear. However, the film remains intact post processing, indicating no dissolution has occurred. The films also changed colors, from a semi-transparent white to an opaque white film. Therefore, the only plausible explanation for the transformation is in-situ.
Figure 35: Purely amorphous sol-gel derived thin film after hydrothermal processing. The spikes are carbonates, which are derived from residue hydroxides trapped in the cracks. The cracks are present, but are smaller in width. This suggests expansion of the film occurs during recrystallization.
No electrical measurements can be made due to these cracks. Cracks cause short circuiting between the top and bottom electrodes. One of the advantages of hydrothermal processing is that cracks in composite films will mend since they are smaller to begin with. In Fig. 35, the cracks are filled with spike-like structures. These are carbonate byproducts resulting from the process. Hydroxides from the hydrothermal solution are trapped within the gaps, and are difficult to wash off. They will react with ambient carbon dioxide and form their respective carbonate structures.

The material properties of low temperature derived powder are very poor based on the ATR, as it is drastically different from that of ceramic-derived powder. As a result, composite thin films made using these powders are also very poor, both physically and electrically. Qualitatively, the BST powder is extremely reactive under hydrothermal conditions. Large amounts of spikes grow on the film surface as shown in Fig. 37 and Fig. 38. The spikes are barium and strontium carbonates as determined using Energy-dispersive X-ray spectroscopy (EDS) from the SEM. These are unwanted byproducts because they will affect the dielectric
constant of the films. They can be washed away with weak formic acid, but the acid will also etch away parts of the film. The formation of carbonate spikes is not solely due to hydroxide residue. The spike occurrence is more than usual, compared with pure sol-gel derived films, as well as films containing the other two types of powders, which are discussed below. The carbonates are produced as a reaction between the initial powders and the process. Parallel plate capacitors made from these films resulted in low dielectric constant and no tunability as shown in Fig. 39. The loss tangent in Fig. 40 is also very high, which can be explained by the excess of carbonate, and poor material properties of the starting powder.

Figure 37: Post-processing of composite thin films containing low-temperature derived powder. Unusually large amounts of carbonate cover the surface of the film, which is attributed to the material properties of the starting powder.
Figure 38: Magnified view of the composite thin film from Fig. 37. Cracks are slightly mended. The spike-like structures are carbonate.
Figure 39: The poor material properties of the low temperature derived powder, along with the surface carbon containments lead to a low dielectric constant film.

Figure 40: The loss of the film is also very high.
SEM images for composite films made from ceramic-derived powder, and sol-gel derived powder are similar in structure. The structures are shown in Fig. 41 to Fig. 44. Limited carbonates are present, and the particle sizes are 2μm and under in diameter. The shrinkage in particle sizes is attributed to the addition of formic acid when making the composite solutions, where the acid eats away a portion of the powders.

Figure 41: Overview of a composite film using ceramic derived powder. Carbonate spikes are not dominant on the film surface. Surface cracks and voids are still present.
Figure 42: Closer look at the film shown in Fig. 41.
Figure 43: Overview of a composite film using sol-gel derived powder.
Composites made using sol-gel derived powder have a higher dielectric constant than composites made using ceramic derived powder, as compared in Fig. 45. Fig. 46 shows that the dielectric constant is very high, but has a higher loss tangent. This is often the case, where a high permittivity is associated with a dielectric loss. Composite films made using sol-gel derived powder exhibit 1% tunability, but films containing ceramic-derived powder give a tunable range of 4 to 8%. They are shown in Fig. 47 and Fig. 48 respectively. For good capacitor material, sol-gel derived powder is the material of choice, but will not be useful for varactor applications.
Figure 45: Comparison between sol-gel composite films made from the two different powders: sol-gel derived and ceramic derived. Sol-gel derived powder produces films with a much higher dielectric constant, which is ideal for high capacitance applications.
Figure 46: The losses associated with each powder for composite films. Sol-gel derived powder films have higher dielectric loss, which is associated to a higher dielectric constant.

The high dielectric constant resulted from using sol-gel derived powder must be the positive reactivity between the powder with the process. Negative reactivity would result in unwanted products, as seen from low temperature powders. Positive reactivity represents a strong ability to bond with neighboring particles to form a strong electrical network. Zelonka [3] showed that small bridges are seen to grow between particles; therefore, the bridge permittivity must also be small (but still greater than air). This is the same for the case of composite thin films containing ceramic-derived powder. High dielectric powder with a low dielectric bridge will result in a mediocre effective dielectric constant film. Since the sol-gel derived powder is more reactive, during processing, the sol-gel crystallization is encouraged to strongly grow together with the highly reactive powder. The bonding between gel and powder is much easier, and the bridges are speculated to be much larger than that in a ceramic-derived composite. This leads to a stronger electrical network, and an overall higher effective dielectric constant. Based on the SEM
images alone, films using sol-gel derived powder are denser. Voids and pores are more obvious in films containing ceramic derived powder.

**Figure 47:** The tunability of a composite film is 1%. It does not tune beyond 3V. The trade-off for using this type of powder is between dielectric constant and tunability.
Figure 48: The tunability of a composite film using ceramic derived powder ranges from 4 to 8%. It does not tune beyond 8V. A lower film permittivity leads to a larger tuning range.

The maximum dielectric constant occurs at -2V for the ceramic sample, shown in Fig. 49, which is counter intuitive as an external bias causing only a decrease in dielectric constant in BST capacitors. This only holds true for materially symmetrical devices [53]. In this case, the device is asymmetric, with a top electrode as aluminum, and the bottom being nickel. Silver paint is applied on the aluminum dot to protect it from being damaged by measurement probes. The physical layout was depicted in Fig. 14. Charges accumulate near the asymmetric interfaces of the Al/BST/Ni structures is responsible for the asymmetric bias tunability.
The losses of the capacitors increases significantly at very low frequencies with increasing applied voltages. This is shown in Fig. 50. However, as the frequencies increase, the losses decrease. Negative voltages increase the losses faster than positive voltages. Again, this can be due to charge effects from asymmetric interfaces.
Figure 50: Applying an external bias increases the loss tangent of a composite film using ceramic powder sharply at low frequencies.

The processing conditions have been varied to determine the effects on the tunability and the overall dielectric constant of the thin films. This is done by changing the molarity of the hydrothermal solution, and altering the ratio of Ba to Sr in the solution.

Tunability remains relatively constant when the ratio of the hydrothermal solution is varied, as shown in Fig. 51. This suggests that the tunability effect is dominated by the initial powder, and the recrystallized of amorphous sol-gel component plays an insignificant role. However, there is a drastic difference in the permittivity of the composite films when the ratio is altered. Solutions containing only barium hydroxides yield the lowest results, whereas, solutions optimized using 80% barium- and 20% strontium- hydroxides produced films with the best electrical properties. The finding holds true for both ceramic composites and sol-gel composites, as shown in Fig. 52 and Fig. 53. An increase in strontium above 20% will have a negative effect, but more prominent on the composites with sol-gel derived powder. This further proves that sol-gel derived powder is much more sensitive to the parameters of hydrothermal processing.
Figure 51: Normalized tunability curve of a composite film using ceramic derived powder at 2 MHz. The ratio of barium to strontium in the hydrothermal solution has no profound effect.

Figure 52: Altering the ratio of barium to strontium in the hydrothermal solution changes the dielectric constant of the composite film. In this case, ceramic powder is used. 80/20 is the optimal ratio.
Figure 53: 80/20 is the optimal ratio between barium and strontium hydroxide for processing composite films using sol-gel derived powder.

Altering the concentration of the hydrothermal solution affected both the tunability and the film permittivity. From Fig. 54 to Fig. 56, a decrease in concentration is shown to improve one of the properties, and worsen the other. Tunability increased with increasing molarity of the hydrothermal solution, but the film dielectric constant decreased. For ceramic-composites, 0.15M and 0.2M yield similar results. 0.1M consistently produces the best results, and 0.3M consistently produces the worst results. For sol-gel composites, concentrations beyond 0.15M damaged the thin films, and no electrical measurements could be made. The general trend is that 0.1M is the optimal concentration for producing the highest dielectric constant films for both types of powder.
Figure 54: Normalized tunability curve of a composite film using ceramic derived powder at 2 MHz. The concentration of ions in the hydrothermal solution has a slight effect of tunability, with 0.3M being the most optimal.

Figure 55: Decreasing the concentration of the hydrothermal solution increases the dielectric constant of the composite films.
Figure 56: 0.1M is the optimal concentration to process composite films using sol-gel derived powder. Concentrations beyond 0.15M damaged the initial film.

The Curie temperature of BST is closest to room temperature at a ratio of 70:30:100 Ba:Sr:Ti, yet from the ratio adjustment experiments, the best results are from ratios of 80:20 Ba:Sr. The ratios from the hydrothermal solution is relative to the total amount of Ba and Sr in the solution, and not relative to the amount of titanium. That is, \( \frac{Ba}{(Ba+Sr)} = 0.8 \). For all cases containing both barium and strontium hydroxides, there is an excess of atoms in the system compared to the titanium present in each composite film. The likely explanation is that the 80:20 ratios are the most chemically favorable for forming BST bridges and recrystallization of amorphous sol-gel regions. The dominant effect of high dielectric constant comes from the initial starting powder.

As the molarity increases, the hydrothermal solution becomes more basic. When the pH level increases, bridge formation increases, and the amorphous components are recrystallizing, while simultaneously being etched away by the basic solution. The ceramic-derived powder is less reactive and therefore, it is able to sustain the damage. This is shown by the drop in film permittivity, but electrical measurements can still be made because no underlying metal layer is
exposed. The sol-gel derived powder is more reactive. Therefore, 0.15M is the threshold for the concentration of hydroxides.

It is also more chemically favorable to use a hydrothermal solution with more water than alkaline material, which stresses on why 0.1M is optimal for the experiments. In the results done by Wang and Ying [52], titania particles are synthesized hydrothermally. Treatments with high water to alkoxide ratios in the reaction favored nucleation versus particle growth. This is a key concept since the basis of good electrical properties in composite thin films is the nucleation of sol-gel bridges between particles.

The lack of or low tunability in the three different composite thin films can be made clear from the SEM images from Fig. 57 and Fig. 58. The same explanation is applied to a lower dielectric constant compared to its high-temperature-processed counterparts. Composite films are unlike traditional thin films because it has three distinct components, as opposed to two. In traditional thin films, nano-sized particles are used for its high packing factor. After deposition, the film is annealed at temperatures over 700°C to sinter. The two components of such films are the powders and the interconnected bridges resulted from the high temperature growth. In post-hydrothermally processed composite films, the three components are the powders, the interconnected bridges, and the nano-crystallized sol-gel derived particles.
Figure 57: Amorphous sol-gel components in a composite film recrystallize during hydrothermal processing. Small BST particles are grown on the initial powder.
It has been found that small particle sizes will decrease both the dielectric constant and the tunability of ferroelectric materials [54]. Fine-grained ferroelectric materials undergo a relaxor behavior, which shifts the Curie temperature of the ceramic, the temperature where dielectric constant is at a maximum. Coarse-grained BST has a Curie temperature near 25°C, but due to this relaxor behavior, the \( T_c \) of fine-grained BST will change. The relaxor behavior is still not fully understood. This criterion has been proven by the results of the three types of composite thin films from this project. After traditional high temperature processing, the particles in thin films are connected together by interconnected bridges resulted from grain growth. Due to this linkage, the overall size of the particle is no longer a single particle, but will be the combination of all the particles linked together, as well as the sizes of these bridges. From Fig. 59, BZT particles of 2 μm have a tunable range up to 22%. Particles of 15 μm have a tunable range 73%.
Figure 59: The grain sizes of BZT ceramic affects both the maximum dielectric constant and the tunability range of the material [54].

Applying this concept to the composite films, it is understandable why low-temperature derived powder show no tunability. Individual particles are 100 nm. The bridges from [3] are nano-scaled, and the formation of bridges from hydrothermal processing won’t be as prominent as high temperature annealing. The recrystallized sol-gel is also nano-sized particles that may not be connected to each other. Fully linked networks are likely to still be in the nano-scale range, since not all individual networks are linked together. Therefore, in a low-temperature composite film, it is comprised of several linked networks, all very small, as well as unconnected recrystallized sol-gel derived powder.

Based upon the results from [54], in a ceramic-composite film, the bridges are larger, yielding a higher dielectric constant. Tunability of fewer than 10% suggests the linked networks are likely to be less than 2 μm. The small linked networks, and the distribution of nano-sized sol-gel derived particles leads to a smaller dielectric constant than that of a traditional annealed thin film. The film permittivity is smaller than composites of sol-gel derived powder because these
films have more voids. The voids, comprised of air with a permittivity of 1, are seen on the surface (Fig. 60), which indicates that they are present throughout the entire structure.

Figure 60: Surface topology of a composite film using ceramic derived powder. Surface voids and cracks can be seen.
In a composite film comprised of sol-gel derived powder, the bridges created via hydrothermal processing must be the most prominent, if not the largest, of the three composite cases. This explains why the dielectric constant is consistently the highest. Unlike ceramic films, the air voids are filled with smaller BST powder recrystallized from the sol-gel components. Fig. 61 shows how dense the film is. However, this is counterintuitive as to why the tunability is significantly less than its ceramic derived counterpart. A denser material should result in better tunability. From the SEM image (Fig. 58), it can be seen that small particles are grown on the initial powder surfaces, as it is extremely reactive under hydrothermal conditions. When an electric field is applied to the film, the field gets distributed to both the initial large powder, and the small powders. When a particle is large, less stress is induced as a result of a voltage, leading to a high tune [55]. Since the field is distributed to the many small particles on the surface of the powder, this results in a high stress region, resulting in a very small tunability range. In the case of a ceramic composite, the electric field does not distribute itself into the air voids as this is not electrically favorable.
The temperature used to fabricate the starting powder for composite films is a key parameter for quality composite film synthesis. It changes the surface structure of the starting powder, which yields different results. Ceramic powders show limited react-ability with the gel, and have less surface particles. Sol-gel derived powders sintered at 750°C show a strong react-ability with the gel, resulting in a denser film. As a result, sol-gel derived powders are sintered to 1100°C to verify the relationship between powder fabrication temperature, and surface reactivity.

Composite films were made using 1100°C sintered sol-gel powder as shown in Fig. 62. The composite films are processed using a 0.1M hydroxide solution with the ratio 80:20 barium to strontium hydroxide to maximize dielectric constant. Examining the powder structures post processing in Fig. 63, it can be seen that limited to no growth of smaller BST particles on the starting powders. This is very similar to that of ceramic derived powder. Tunability of the sintered powder increased compared to its non-sintered sol-gel counterpart. The film dielectric constant and tunable range is comparable to that of ceramic derived powder. The two plots are shown in Fig. 64 and Fig. 65.

Figure 62: Surface topology of composite films using sintered (1100°C) sol-gel derived powder.
Figure 63: Limited growth of recrystallized BST particles is shown on the surface of the sintered powders. This proves that the fabrication temperature of the starting powder is an important parameter when making sol-gel composites for hydrothermal processing.
Figure 64: Dielectric constant of a composite film using sintered sol-gel derived powder.

Figure 65: Tunable range of sintered sol-gel derived powder at 2 MHz. It is comparable to that of ceramic derived powder.
4.2.2 High Frequency Characteristics

To make high frequency measurements, coplanar capacitor structures must be used for measurement machine compatibilities. A larger aluminum dot is evaporated on to the BST surface. Due to the larger top electrode, more surface and lattice defects such as surface cracks and interstitial OH\(^{-}\) are contained within the given area. This is obvious when measuring the enlarged dots at low frequencies, where the electrical behavior is different from that of using small dots. The film permittivity drops sharply (Fig. 66 and Fig. 68), and the loss tangent rises (Fig. 67 and Fig. 69).

![Graph showing dielectric constant vs. frequency](image-url)

**Figure 66:** At low frequencies, the dielectric constant of a ceramic-composite film with a large top electrode decreases much faster than that with a smaller top electrode. The larger area incorporates more defects in the film.
Figure 67: The loss tangent of a ceramic-composite film with a larger top electrode increases faster than films with smaller top electrodes at low frequencies.
Figure 68: The dielectric constant of a composite film using sol-gel derived powder. Larger dot size causes the permittivity to decrease sharply due to incorporation of more defects.
Figure 69: The loss tangent of a composite film using sol-gel derived powder. Larger dot size causes the losses to be more significant.

At high frequencies, the data is represented using smith charts, displaying both the resistances and reactance of the device. This is shown in Fig. 70 and Fig. 71. Fig. 71 shows how applying an external bias will affect the data on the Smith chart. The circuit can be modelled as a resistor, a single inductor and a single capacitor, as shown in Fig. 72. The resistor represents the total loss from the silver paint, and the dielectric. An inductor is used because at high frequency, the signal line looks very long, and becomes an inductive component. The capacitor is the parallel sum of the dielectric, and the parasitics. The model smooths the actual curve, which can be further broken down for analysis.
Figure 70: High frequency data is read off a Smith chart. A model is used to fit the actual data for further analysis.
Figure 71: Applying different bias voltages will shift the curve left or right.

Figure 72: A simplified model to represent data taken from a Smith chart. A resistor, inductor, and a capacitor are used.
To properly model the circuit to determine the capacitance of the BST capacitor, a distributed element model or transmission line model is used. The simplified model helps demonstrate where the transmission line model should fit. A transmission line model consists of two parallel capacitors, $C_T$, and a series inductor, $L_T$, as shown in Fig. 73.

Figure 73: Transmission line model or lumped element model

The circuit can be split into three different regions, to two of which the transmission line model is applied. The physical breakdown depicted in Fig. 74. The side and front cross sections of this are shown in Fig. 75a and 75b respectively, and the equivalent model is shown in Fig. 75c. Region 1 covers the parasitics due to a “nail polish transmission line”, where the dielectric is from a lacquer. Region 2 accounts for the parasitics of a small BST transmission line, which is the result of connecting the signal line to the actual BST capacitor. Because of the direct connection to the BST, the parasitics will change from an applied bias voltage. Region 3 is the BST capacitor of interest.
Figure 74: High frequency circuit physically broken down into 3 regions. Region 1 is a “nail polish transmission line”, region 2 is a small BST transmission line, and region 3 is the BST capacitor under test.
Figure 75: a) Cross section of the capacitor. b) Region 1 is in a coplanar waveguide configuration (CPW), and region 2 is in a microstrip configuration. c) Modelling of the high frequency circuit.
The initial values of parasitic inductance and capacitance are determined using the LineCalc function on Advanced Design Systems (simulation software), where the characteristic impedance, $Z_o$ and effective dielectric constant, $\varepsilon_{eff}$, is given. Two different sets of values are given for regions 1 and 2. From $Z_o$ and $\varepsilon_{eff}$, the respective $L_T$ and $C_T$ can be found based on the formulas:

$$v = \frac{c}{\sqrt{\varepsilon_{eff}}} \quad (4.1)$$

$$C_T = \frac{1}{Z_0 v} d \quad (4.2)$$

$$L_T = \frac{Z_0}{v} d \quad (4.3)$$

where $v$ is the speed of the traveling wave, $c$ is the speed of light, and $d$ is the length of the transmission line. The parameters for regions 1 and 2 are summarized in Table 5.

<table>
<thead>
<tr>
<th>Region</th>
<th>Configuration</th>
<th>$Z_o$ (Ω)</th>
<th>$v$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CPW</td>
<td>97.86</td>
<td>1.8*10⁸</td>
</tr>
<tr>
<td>2</td>
<td>microstrip</td>
<td>0.2</td>
<td>5.5*10⁷</td>
</tr>
</tbody>
</table>

Table 5: $Z_o$ and $v$ for regions 1 and 2 taken from LineCalc

The end points of the changes with respect to applied voltage are given in Table 6. $C_1$ and $L_1$ do not change because they are not in contact with the BST.
<table>
<thead>
<tr>
<th>Region</th>
<th>Voltage</th>
<th>0V</th>
<th>12V</th>
<th>-12V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (Ω)</td>
<td>2.14</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>1</td>
<td>C₁ (fF)</td>
<td>165</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>L₁ (nH)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>C₂ (nF)</td>
<td>300</td>
<td>1250</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>L₂ (pH)</td>
<td>28</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>C₃ (nF)</td>
<td>2.6</td>
<td>2.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 6: Changes in parasitics and capacitance of the device

The capacitance (region 3) from 45 MHz to 1.15 GHz remains constant, indicating that the dielectric constant of the film has saturated at high frequencies. The percentage of tunability increased significantly. At low frequencies, the tunable range is between 4 to 8%. At high frequency, the tunability can be as high as 18%. This is because the initial dielectric constant is so small, such that a small dielectric change equates to a large percentage change. The full data is shown in Fig. 76 and Fig. 77.

Figure 76: The change in dielectric constant with respect to voltage from 45 MHz to 1.15 GHz.
Figure 77: The tunability increases at high frequencies because small dielectric changes equate to large tunability changes.

4.3 Chapter Summary

Ceramic-derived, sol-gel derived, and low temperature derived BST show the same XRD patterns, indicating that the resultant powders are crystalline. However, based on ATR analysis, the three powders have different material properties. Both the sol-gel derived and low temperature derived powders contain carbonate. Low temperature derived powder is full of water, and must be heated at 500°C to remove this. It is also shown that low temperature methods is the only method of producing nanosized particles. Amorphous sol-gel derived powder is hydrothermally processed, and the resultant XRD peaks show the same pattern as that of the above three powders, proving that hydrothermal processing is a technique capable of producing BST at temperatures under 175°C.

The three different powders are used to make sol-gel composite thin films. Low temperature powder films yield the worst results, with the lowest dielectric constants and the highest loss tangent. No tunability is exhibited. Carbonates cover the film surface, suggesting that the powder is very reactive to the process. It is also found that due to the extremely small particle sizes, the BST powder loses its ferroelectricity due to relaxor behavior, hence affecting the
electrical properties. Composite films containing ceramic derived powder showed much better dielectric constant and smaller loss tangents. Films using this type of powder exhibited a tunable range of 4 to 8% and had dielectric constants of 130 to 140. Sol-gel derived powders produced composite films with the highest dielectric constants, ranging from 200 to 260, but with a tunability of only 1%. However, using a hydrothermal solution of 0.1M, with barium to strontium ratio of 80:20 increased the overall dielectric constant, and has no effect on tunability. Composite films are finally made using sol-gel derived powder sintered at 1100°C. The electrical and tunable properties are comparable to that of ceramic derived powder, indicating that the temperature used to fabricate powders has a strong effect on the properties of the composite thin films.

At high frequencies, the dielectric constant is reduced to as low as 18. Parasitics play a large role and are modeled as two parallel capacitors in series with an inductor. Tunability is seen to increase up to 18%.
Chapter 5

Conclusions and Future Work

Different fabrication methods for barium strontium titanate produce BST of different material properties. Low temperature chemical methods produce powders in the nano-range, but have very poor material characteristics. Sol-gel derived and ceramic derived powders are of higher quality, and are very compatible with hydrothermal processing.

Hydrothermal processing is a proven technique to fabricate thin films at temperatures less than 175°C, and using different derivations of BST will lead to different results. Sol-gel derived powder is very reactive under high pressure and low temperatures, promoting growths of interconnecting BST bridges. Strong connections increase the film permittivity, but simultaneously diverges any external electrical fields, decreasing tunable performance. Ceramic derived powder is less reactive, but interconnecting bridges are still formed. Less bridging hinders dielectric constant, but gives a tunable range of 10% at frequencies ranging from 500 kHz to 20 MHz. Tunability is asymmetrical due to different top and bottom electrodes.

Altering the ratios of the hydrothermal solution has no effect on tunability, but a profound effect on film permittivity. 80/20 is the optimal ratio of barium hydroxide to strontium hydroxide in the liquid to produce highest quality thin films. A low molarity concentration such as 0.1M solution is also chemically favorable for high performance films. Low alkaline concentration limits the pH level, and prevents self-etching. Also, higher water content in the solution promotes bridge nucleation.

At high frequencies, losses are more prominent. A grounded coplanar capacitor is modelled using a resistor to account for losses, an inductor for the long distances the current travels, and a capacitor for the ceramic and parasitic capacitances. It is shown that capacitance increase with applied bias voltage as opposed to decrease. This can be attributed to high frequency parasitics, and device structures.

The contributions of this work includes reducing excess organics within the BST sol, previously developed at Queen’s University, an exploration of the difference in ferroelectricity between the three types of powders, method of depositing sol-gel composites onto PCB circuits, and testing them at both low and high frequencies.

Future works can be divided into two categories. The first is to further investigate the material characteristics of the thin films recrystallized via hydrothermal processing. Since the bridging between particles only act as a network of connectors, and have no effect on tunability,
titanium dioxide can be used. This involves reducing the hydrothermal solution to pure water, hence eliminating possible carbonate contamination.

To improve the existing thin films, a combination of powders can be used to achieve an optimal point for high dielectric constant and tunability. Sol-gel powders are great for high dielectric constant films, while ceramic powders provide a good tunable range. Composites containing both powders will have the two benefits. The effect of the overall film permittivity will need to be studied.

Enhancing the electrical properties of current composite thin films can also be done. Doping BST with materials such as Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$, and Fe$^{2+}$ is said to increase the tunability and decrease the dielectric loss as these materials change the film stress and orientation [56].

The second extension of this project is to apply the tunable capacitors into tunable filter applications. Transmission line bandpass filters can be designed onto PCB substrates such as the one shown in [57]. Loading the ends of the transmission lines with BST varactors will alter the effective lengths under an external bias voltage. However, instead of using surface mount devices, thin films can be synthesized onto the structure via hydrothermal processing.
Bibliography


