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Negative Thermal Expansion and Ferroelectric Oxides in Electronic Device Composites

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Negative Thermal Expansion and Ferroelectric Oxides

in Electronic Device Composites

A dissertation submitted in partial satisfaction of the

requirements for the degree Doctor of Philosophy

in Materials Science and Engineering

by

Joy Elizabeth Trujillo

2017
ABSTRACT OF THE DISSERTATION

Negative Thermal Expansion and Ferroelectric Oxides

in Electronic Device Composites

by

Joy Elizabeth Trujillo

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2017

Professor Bruce S. Dunn, Chair

Electronic devices increasingly pervade our daily lives, driving the need to develop components which have material properties that can be designed to target a specific need. The principle motive of this thesis is to investigate the effects of particle size and composition on three oxides which possess electronic and thermal properties essential to designing improved ceramic composites for more efficient, high energy storage devices. A metal matrix composite project used the negative thermal expansion oxide, ZrW$_2$O$_8$, to offset the high thermal expansion of the metal matrix without sacrificing high thermal conductivity. Composite preparation employed a powder mixing technique to achieve easy composition control and homogenous
phase distribution in order to build composites which target a specific coefficient of thermal expansion (CTE). A tailorable CTE material is desirable for overcoming thermomechanical failure in heat sinks or device casings.

This thesis also considers the particle size effect on dielectric properties in a common ferroelectric perovskite, Ba$_{1-x}$Sr$_x$TiO$_3$. By varying the Ba:Sr ratio, the Curie temperature can be adjusted and by reducing the particle size, the dielectric constant can be increased and hysteresis decreased. These conditions could yield anomalously large dielectric constants near room temperature. However, the ferroelectric behavior has been observed to cease below a minimum size of a few tens of nanometers in bulk or thin film materials. Using a new particle slurry approach, electrochemical impedance spectroscopy allows dielectric properties to be determined for nanoparticles, as opposed to conventional methods which measure only bulk or thin film dielectric properties. In this manner, Ba$_{1-x}$Sr$_x$TiO$_3$ was investigated in a new size regime, extending the theory on the ferroelectric behavior to < 10 nm diameter. This knowledge will improve the potential to incorporate high dielectric constant, low loss ferroelectric nanoparticles in many complex composites.

Finally, powder composite processing and impedance spectroscopy techniques were combined to investigate the SrTiO$_3$/(Y$_2$O$_3$)$_x$(ZrO$_2$)$_{1-x}$ (STO/YSZ) oxide system. Thin film heterostructures of STO/YSZ are used in electrochemical energy devices due to their enhanced interfacial ionic conductivity. This work investigated whether this ionic conductivity enhancement could be observed in bulk sintered architectures, which may lead to new device designs for energy storage needs.
The dissertation of Joy Elizabeth Trujillo is approved.

Yongho Ju

Qibing Pei

Bruce S. Dunn, Committee Chair

University of California, Los Angeles

2017
# Table of Contents

LIST OF FIGURES ........................................................................................................... viii
LIST OF TABLES ............................................................................................................... xiv
Acknowledgements ......................................................................................................... xvi
Vita ..................................................................................................................................... xviii
Chapter 1: Introduction and Objective .......................................................................... 1
Chapter 2: Metal Matrix Composites .............................................................................. 3
  2.1 Introduction .............................................................................................................. 3
  2.2 Experimental .......................................................................................................... 6
    2.2.1 Initial Concept Composites .............................................................................. 6
    2.2.2 ZrW₂O₈ .......................................................................................................... 7
    2.2.3 Silver ............................................................................................................. 8
    2.2.4 NTE Metal Matrix Composites ................................................................. 8
    2.2.5 Characterization and Instrumentation ..................................................... 9
    2.2.6 Calculations .................................................................................................. 12
  2.3 Results ................................................................................................................... 12
    2.3.1 Ag/ZrW₂O₈ Composites ............................................................................ 12
    2.3.2 Cu Composites ............................................................................................ 20
  2.4 Discussion ............................................................................................................ 23
    2.4.1 Effect of Composition and Particle Size on Ag/ZrW₂O₈ Properties ........ 23
    2.4.2 Successes and Failures of Cu Composites .............................................. 25
  2.5 Future Work ......................................................................................................... 26
  2.6 Conclusions .......................................................................................................... 27
Chapter 3: Ferroelectric Nanoparticles ........................................................................... 28
  3.1 Introduction .......................................................................................................... 28
  3.2 Current Particle Size Effect Theories ................................................................... 31
  3.3 Experimental ........................................................................................................ 33
    3.3.1 Ba₁₋₃Sr₃TiO₃ ................................................................................................ 33
    3.3.2 Powder Dispersions for Polymer Chemistry .......................................... 33
    3.3.3 Characterization and Instrumentation .................................................... 34
3.3.4 EIS Modeling and Calculations ............................................................... 36
3.4 Results ............................................................................................................ 38
3.5 Discussion ....................................................................................................... 53
3.6 Future Work ................................................................................................... 58
3.7 Conclusions .................................................................................................... 58

Chapter 4: Enhanced Ionic Conductivity with Mixed Nanoparticles .................. 60
4.1 Introduction ..................................................................................................... 60
4.2 Experimental ................................................................................................ 60
  4.2.1 SrTiO$_3$ and YSZ Powders ............................................................... 60
  4.2.2 Powder Pressing and Sintering .......................................................... 62
  4.2.3 Preparing Samples for EIS Measurements .......................................... 62
  4.2.4 Phase Analysis of SEM Images ............................................................. 64
  4.2.5 Characterization and Instrumentation .................................................. 65
  4.2.6 Calculations ............................................................................................. 66
4.3 Results ............................................................................................................ 68
4.4 Discussion ...................................................................................................... 74
4.5 Conclusions and Suggestions for Future Work .......................................... 76

Chapter 5: Conclusions ....................................................................................... 78
Appendix ............................................................................................................. 80
References .......................................................................................................... 82
LIST OF FIGURES

Figure 2.1: XRD pattern showing as-synthesized cubic α-ZrW₂O₈ powder (referenced to JCPDS 50-1868) and oxide powders recovered from sintered composites. The (012) peak used for Scherrer’s equation calculations is approximately at 21.9°. ..............................................................13

Figure 2.2: (Left) XRD pattern showing pure as-synthesized Ag (referenced to JCPDS 3-065-871) with a calculated crystallite size of 10.5 nm based on the (111) peak at 38.1°. (Right) TEM image of oleylamine-capped synthesized Ag nanoparticles with an average diameter of 4.2 ± 0.4 nm. ..........................................................................................................................14

Figure 2.3: Secondary electron SEM micrographs at (a) high magnification and (b) low magnification of a 54v/46v commercial nano Ag/ZrW₂O₈ composite and (c) high magnification and (d) low magnification of a 54v/46v synthesized nano Ag/ZrW₂O₈ composite. The broad, flat dark regions are segregated phases of ZrW₂O₈ within the metal matrix, although charging effects brighten some of these regions in (d). All samples were hot pressed at 500 °C for 3 hrs and prepared using standard metallographic polishing.................................................................16

Figure 2.4: Measured dilatometry data plotting change in length vs. temperature of commercial nano Ag, ZrW₂O₈, and a 54v/46v commercial nano Ag/ZrW₂O₈ composite. The slope of each line is the CTE, α .........................................................................................................................17

Figure 2.5: Measured CTE vs. composition of commercial nano Ag/ZrW₂O₈ composites as compared to the calculated ROM prediction. Only samples > 5 mm thick are plotted here to achieve greatest accuracy and consistency. .................................................................18

Figure 2.6: XRD pattern showing pure as-synthesized cubic α-ZrW₂O₈ powder (pattern at bottom) and Cu/ZrW₂O₈ composites hot pressed under 72 MPa and various time and
temperature conditions. The two peaks near 43° and 50° match main Cu peaks while the remaining minor peaks correspond to main peaks of the indicated oxides. There is little to no indication that any ZrW$_2$O$_8$ remains in the samples.

Figure 2.7: CTEs of hot pressed 325 mesh Cu/Pyrex and Cu/ZrW$_2$O$_8$ composites as compared to the calculated ROM predictions for each.

Figure 3.1: Nyquist plot of real vs. imaginary impedance of measured data (solid line) with applied modeling fit (circle line) and two hypothetical semicircles (dashed lines) illustrating the extraction of separate contributions of the liquid and oxide components. The low frequency tail results from the double layer capacitance of the electrodes and is excluded from the data modeling. [102]

Figure 3.2: (Left) XRD patterns of Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles highlighting composition. (Upper right) Focus on the (110) peak near 31° illustrating the peak shift to higher 2θ with increasing Sr content, as expected due to decreasing lattice spacing. (Lower right) TEM micrograph of as-synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ nanoparticles.

Figure 3.3: XRD 2θ averages vs. mol % Sr for all as-synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles. Solid lines represent the trend plotted from five JCPDS references.

Figure 3.4: TEM micrograph of Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ nanopowders from Figure 3.2 following heat treatments at (left) 800 °C, (middle) 900 °C, and (right) 1000 °C for 1 hr.

Figure 3.5: Plot of temperature vs. average XRD crystallite diameter highlighting post-synthesis heat treatments to control particle diameters.

Figure 3.6: XRD crystallite diameter vs. TEM measured diameters for as-synthesized and heat treated nanopowders.
Figure 3.7: HR-TEM micrographs of Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ nanopowders with rotated and zoomed insets.

Figure 3.8: (Left) Raman spectra comparing commercial Ba$_{1-x}$Sr$_x$TiO$_3$ compositions with four characteristic tetragonal active modes. The 67:33 prominently displays tetragonal modes while the 50:50 lacks these modes indicating it is cubic. The 80:20 shows some mix of the two. This assessment agrees with XRD patterns collected (data not shown) and the phase information provided by the manufacturer. (Right) Raman spectra comparing heat treated synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ samples. Black bars represent the 4 characteristic tetragonal phonon modes. The XRD crystallite diameters are listed with each corresponding line color.

Figure 3.9: Raman spectra comparing synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ compositions displaying four characteristic tetragonal active modes. The average crystallite diameters for all samples are $\sim$ 10 nm. The 80:20 and 75:25 are characterized as tetragonal while the 65:35 and 50:50 are mixed cubic with tetragonal.

Figure 3.10: (Left) Plot of dielectric constant vs. temperature comparing (solid) direct EIS measurements of pure PEG, (long dash) PEG contributions in mixed slurries of 5 vol % Ba$_{1-x}$Sr$_x$TiO$_3$ in PEG extracted by modeling, and (short dash) the pure PEG value as reported in literature. [117] Both commercial and synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ powders are represented in the mixed slurry data. Line colors are only to visually distinguish multiple experimental runs. (Right) Plot of dielectric constant vs. time for 5 vol % commercial Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ powder dispersed in PEG and held at constant temperature.

Figure 3.11: Comparison of the experimental dielectric constant for commercial BaTiO$_3$ to various values reported in literature. (Left) Data collected using similar measurement
methods of BaTiO\textsubscript{3} powder at room temperature between $10^2$ to $10^6$ Hz with dispersions between 5 and 20 vol % in BOE and PC. (Right) BaTiO\textsubscript{3} data reported from literature and collected using different processing and measurement methods. The “powders” data points in the right graph are the same “literature” data points in the left graph. [11, 12, 14, 15, 17, 18, 27, 83, 84, 100, 118-125].........................48

Figure 3.12: Plots of dielectric constant vs. temperature for four compositions of synthesized Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3} powders (< 10 nm) suspended by 5 vol % in PEG. Each line represents an EIS analysis of different batches of each composition. Literature $T_c$ values for sintered bulk samples of each composition are as follows: 50:50 (-23 °C), 65:35 (25 °C), 75:25 (59 °C), 80:20 (74 °C). [77].................................49

Figure 3.13: EIS data compiled on synthesized Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3}: (Top) dielectric constant vs. temperature sorted by particle size and (Bottom) dielectric constant vs. average crystallite diameter sorted by temperature. The data in the bottom graph is expanded in separate temperature graphs in the appendix. ..........................................................50

Figure 3.14: (Left) Plot of dissipation vs. frequency for synthesized Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3} particles with an average crystallite diameter by XRD of 16.1 nm. Temperature increases 10 °C with each successive line, from 0 – 50 °C. (Inset) Plot of ln (frequency at $D_{\text{max}}$) vs. 1/T for activation energy comparing synthesized Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3} and commercial BaTiO\textsubscript{3}. (Right) Plot of dissipation vs. temperature at 10 kHz for synthesized Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3} particles comparing crystallite diameters..................................................51

Figure 3.15: (Left) Dispersion solutions having about 0.8 wt % synthesized BaTiO\textsubscript{3} particles suspended in 1 M surfactant in MEK. Surfactants are B2-MEP left and PA2-HME right.
Stability after 3 days. (Right) Solution having about 5 wt % BaTiO₃ particles suspended in 0.5 M B₂-MEP. Stability after 10 days. ...........................................................52

Figure 4.1: Sintered YSZ 8601 sample with Ag paste cured on the surface. .........................63

Figure 4.2: (Left) Sintered sample with Ag electrode coating cradled in Macor holder and sandwiched between Pt mesh. (Right) Sample assembly clamped between two Macor planks and secured in place on the alumina stage.................................................................64

Figure 4.3: (a) Equivalent circuit model for EIS measurements taken on YSZ and STO samples. (b) Nyquist plot of EIS data taken between 500 and 600 °C for a sintered YSZ 8601 sample. The model fit semicircle overlapping the 500 °C data was generated using the equivalent circuit model from (a). .......................................................................................67

Figure 4.4: XRD patterns showing phase pure YSZ (provided and synthesized) and STO powders. Main peak labels for YSZ are given above and match JCPDS 48-0224. Main peak labels for STO are given below and match JCPDS 35-0734. .................................68

Figure 4.5: (Left) Secondary electron SEM micrograph of commercial STO powder following ethanol suspension and drying. (Right) TEM micrograph of as-synthesized YSZ 5% nanoparticles, taken by Enrico Della Gaspera. .................................................................69

Figure 4.6: Secondary electron SEM micrograph of 50w/50w STO/YSZ 5933 sintered at 1400 °C for 1 hr and etched in phosphoric acid. ........................................................................70

Figure 4.7: Backscatter electron SEM micrographs of (Left) 50w/50w STO/YSZ 5933 and (right) 80w/20w STO/synth YSZ 8%. ................................................................................................71

Figure 4.8: Plot of measured resistivity vs. temperature between 400 and 600 °C for synthesized YSZ (solid), Airforce YSZ (short dash), 80w/20w STO/synthesized YSZ (dot-dash), and 50w/50w STO/Airforce YSZ (long dash) from data listed in Table 4.6. .......................72
Figure 4.9: Zoomed region plot of Figure 4.8. Measured resistivity vs. temperature between 400 and 600 °C for synthesized (solid) and Airforce (short dash) YSZ..........................73

Figure 4.10: Plot of log ρ vs. inverse temperature for two sintered samples. Slope from a best fit line is used to calculate the given activation energies, E (eV)................................73

Figure A1: Distinct temperature plots for every 5 °C between 0 – 50 °C of dielectric constant vs. average crystallite diameter for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$, presented as accompaniment to the data compiled in Figure 3.13. .................................................................80-81
# LIST OF TABLES

Table 2.1. CTE of Composite Components and Target Semiconductors .........................4
Table 2.2. Experimental Volume % of Metal/ZrW\textsubscript{2}O\textsubscript{8} with Corresponding Weight % .........9
Table 2.3. Measured % theoretical density and % open porosity averages for various compositions of commercial nano Ag/ZrW\textsubscript{2}O\textsubscript{8} composites ................................15
Table 2.4. Average measured CTE and % open porosities of micron and commercial nano Ag composites (> 2 mm thick) as compared to the calculated ROM CTE .........................19
Table 2.5. Thermal and electrical conductivities of 54\textsubscript{v}/46\textsubscript{v} nano Ag/ZrW\textsubscript{2}O\textsubscript{8} composites ......19
Table 2.6. Measured % theoretical density and % open porosity averages for various compositions of Cu/Pyrex (325 and 60 mesh) and Cu/ZrW\textsubscript{2}O\textsubscript{8} composites ...............21
Table 3.1. Average crystallite diameter (XRD) and particle size (TEM) for as-synthesized Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3} ...........................................................................................................................................39
Table 3.2. Calculations for relative surface area coverage by benzyl alcohol (b.a.) ligands on Ba\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3} nanoparticles as-synthesized and after heat treatment ..........................42
Table 3.3. D-spacing calculations from JCPDS references and experimental TEM measurements to correlate crystal structure .................................................................................................44
Table 3.4. Calculated activation energies for synthesized Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3} and commercial BaTiO\textsubscript{3} .............................................................................................................................................52
Table 4.1. YSZ powders as provided by the Airforce ................................................................61
Table 4.2. Calculated grams of precursors used in YSZ synthesis ......................................62
Table 4.3. Calculations for ideal weight % of STO:YSZ dependent on YSZ particle diameter .........................................................................................................................................66
Table 4.4. Measured % theoretical density and % open porosity averages for various compositions of STO and YSZ samples comparing sintering conditions ....................70

Table 4.5. Phase analysis by dark/light pixel ratios.................................................................71

Table 4.6. Measured resistivities, calculated activation energies, and measured % theoretical densities of samples sintered 1400 °C for 1 hr .................................................................74
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Publications


Conference Presentations


Chapter 1: Introduction and Objective

Ceramic composite materials are pivotal to the advancement of many electronic devices as demand continues for ever smaller components, more efficient energy storage, higher power consumption, and even to develop electronic devices which are flexible, wearable, or bio-compatible. However, in the materials design of many composites, components behave and interact non-ideally resulting in complications such as catalyzed decomposition or interfacial mechanical failure. Designing effective composites requires a materials study of individual components and the interaction of the components when assembled together. This thesis considers the effects of particle size and composition in the study of three classes of ceramics of interest for use in electronic device composites.

First, metal matrix composite (MMC) materials are an important class of engineering materials which have been widely researched since the 1980’s, proving revolutionary to many industries including automotive, aerospace, structural, energy, and electronics. [1-7] The research interest here in MMCs is to use a metal matrix for its high thermal and electrical conductivities in combination with a low or negative coefficient of thermal expansion (CTE) oxide filler to produce a low and tailorable CTE composite with high thermal and electrical conduction. Composite properties will be improved by working with intimately mixed homogenous powder composites and by reducing the initial metal matrix particle diameter.

Second, ferroelectric nanoparticles possess dielectric properties which are of great interest to many complex electronic material systems such as flexible polymer matrix-ceramic nanoparticle filler composites [8-10] and ceramic capacitors. [11-13] Many dielectric behaviors at the nanometer scale are distinct from those observed in bulk or micrometer scales. [8, 14-20]
The research interest here in ferroelectric oxides is in characterizing the dielectric properties of barium strontium titanate (BST, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) nanoparticles below 10 nm diameter, which is below an observed superparaelectric (SPE) size range where ferroelectric properties cease. [12, 18, 21-23] Reducing the particle size to the order of 10 nm may reduce the hysteresis loop or remnant polarization to a point where hysteresis disappears [8, 24] yielding extremely high dielectric constants. [25-27]

Third, improving efficiency in electrochemical energy storage devices is limited by the electrolytic efficiency of transporting oxygen anions. [28] Yttria-stabilized zirconia (YSZ, $(\text{Y}_2\text{O}_3)_(x)(\text{ZrO}_2)_(1-x)$) is ideal as an electrolyte for its mechanical and chemical stability. Building layered film heterostructures of YSZ with strontium titanate (STO, $\text{SrTiO}_3$) greatly enhances the interfacial ionic conductivity. [28] The research goal here is to use powder processing to prepare bulk sintered pellets of pure and mixed STO and YSZ, testing the effect particle size has on composite sintering, density, resistivity, and activation energy.
Chapter 2: Metal Matrix Composites

2.1 Introduction

Many electronic packaging materials suffer from significant thermal strain and thermal fatigue failure due to differences in adjoining component coefficients of thermal expansion (CTE). A materials solution is to design metal matrix composites (MMCs) which combine the high ductility, toughness, and thermal conductivity of metals with the high strength, high modulus, and low thermal expansion of ceramics. Prominent examples of MMCs include WC/Co which is known for its high strength, toughness, hardness, and melting temperature and Al/SiC which is known for having high strength, low density, and low but difficult to predict CTEs. [3, 7, 29] A MMC system like Al/SiC requires relatively high vol % ceramic particulates (> 55%) for CTEs below $10 \times 10^{-6}/\degree C$, which contributes to complex internal structures and stresses. [3]

Differences in CTE can result in significant strain, reducing the thermomechanical reliability and often resulting in structural and material failure. Table 2.1 lists the CTE and, where applicable, the thermal conductivity of several key materials considered in this research. Specifically Ag is known to have the highest thermal conductivity of these pure metals (429 W/m·K) but also has a high CTE of about $20 \times 10^{-6}/\degree C$. This research selected to use a negative thermal expansion (NTE) ceramic filler material in order to significantly reduce the overall MMC CTE while maintaining the highest possible volume ratio of the metal matrix. The target composite CTE is to match that of GaAs.
Table 2.1. CTE of Composite Components and Target Semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE ($10^{-6}/\degree{}C$)</th>
<th>Thermal conductivity (W/m·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>19.7</td>
<td>429</td>
</tr>
<tr>
<td>Cu</td>
<td>16.6</td>
<td>401</td>
</tr>
<tr>
<td>Au</td>
<td>14.2</td>
<td>318</td>
</tr>
<tr>
<td>Al</td>
<td>23.6</td>
<td>222</td>
</tr>
<tr>
<td>Vycor</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Pyrex</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>ZrW$_2$O$_8$</td>
<td>-8.7*</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

*Value listed is specific for the cubic-α phase of the ceramic.

Negative thermal expansion (NTE), the phenomenon where material structures contract with increasing temperature, occurs in many materials including Si, Ge, perovskite oxides such as BaTiO$_3$ and PbTiO$_3$, and other oxides such as β-quartz and Cu$_2$O. [30-32] For most NTE materials, this behavior occurs over a short temperature range, yields relatively small negative expansion, or results in an anisotropic NTE. [30-32] Zirconium tungstate (ZrW$_2$O$_8$) is an unusual material where a relatively large, isotropic NTE occurs over a wide temperature range (about -273 to 777 °C). [30-33] This ceramic is comprised of corner sharing WO$_4$ tetrahedra and ZrO$_6$ octahedra; the mechanism for the large, wide temperature range NTE is related to the
angles of the Zr-O-W bridging oxygen groups and relative rotations of the structural polyhedra. [30-33] A cubic α-phase (CTE: \(-8.7 \times 10^{-6}/\text{°C}\)) is stable to about 160 °C and ~0.4 GPa, a cubic β-phase (CTE: \(-4.9 \times 10^{-6}/\text{°C}\)) is stable between 160 ~ 680 °C and ~0.5 GPa, and an orthorhombic γ-phase (CTE of \(-1.0 \times 10^{-6}/\text{°C}\)) forms at > 0.5 GPa. [31, 34, 35] The cubic-α CTE can vary, however, with some reports as low as \(-12 \times 10^{-6}/\text{°C}\) between 50 and 150 °C. [31, 34-36]

Many low thermal expansion MMCs have been investigated which combine NTE materials in a metal matrix. Composites of Ni-Ti core rods clad with a Cu matrix produced an anisotropic low CTE MMC; however, after multiple thermal cycles these composites lost their low CTE due to structural degradation at the interface. [37] Cyclic thermal stresses inducing metal matrix yielding and loss of mechanical integrity are known to be a common problem in fiber-reinforced and laminate MMCs. [7] The NTE ceramic ZrW₂O₈ has been investigated as a filler material with both metal (Cu, Al) and ceramic based matrices (ZrO₂, WO₃, Al₂O₃, cement). [38-42] MMCs of Cu/ZrW₂O₈ micron-powder composites were hot or cold isostatically pressed to at least 100 MPa and had larger than expected CTEs due to a pressure induced phase change [35, 43] or Cu induced decomposition. [44] Characterizations of these composites also show distinct separate phases of the metal and ceramic with visible porosity. Similarly, MMCs of Al/ZrW₂O₈ using pulse current sintering demonstrated a pressure induced γ-phase which required heat treatment to convert back to the desired phase. [42] ZrW₂O₈ has been modeled using finite element analysis to characterize its response when used in composites with Cu and ZrO₂, finding that thermal stress and phase transformations were definite issues. [45]

In this project powder components are intimately mixed to reduce the loss of interfacial structural integrity and minimal temperature and pressure processing conditions, accomplished
by reducing the initial particle size of the matrix, are used to avoid the phase change and decomposition of the NTE ceramic material. The higher surface to volume ratio of smaller nanoparticles maximizes the interphase regions between the components and improves the ceramic particle dispersion within the metal matrix. This improved uniformity also carries the benefit of more uniform material properties across the entire dimension of the samples and aids in reducing or even eliminating losses in structural integrity during repeated thermal cycling. [4, 5] Furthermore, nano-scale powders require lower temperatures and pressures to form fully dense sintered materials [46] which helps avoid the formation of pressure induced phase changes and decomposition of the NTE ZrW$_2$O$_8$ ceramic.

The research objectives here are to develop a MMC material system having high thermal and electrical conductivities suitable for electronic packaging and heat transfer applications but a low and tailorable CTE – a CTE designed to match that of the common semiconductor material GaAs (6.5 x 10$^{-6}$/°C). These MMCs will also be designed to exhibit full density since a porous microstructure degrades the thermal conductivity of the material and produces inconsistencies in the CTE across the material. To the best possible knowledge, this is the first research to use Ag as the metal matrix material in the development of MMC with the NTE ceramic ZrW$_2$O$_8$.

2.2 Experimental

2.2.1 Initial Concept Composites

Vycor and Pyrex powders (60 and 325 mesh) were obtained from Corning Inc. Cu powder (325 mesh) was obtained from Cerac Inc. For all pellets fired under ambient pressure, between 1 to 2 g of mixed powder was pressed in a 1.5 ID stainless steel die to 365 MPa using a Carver Model M hydraulic press, then fired at 5 °C/min to 800 – 1000 °C under N$_2$ atmosphere
for 2 – 6 hrs. Cu/Vycor powder composites were ball mill tumbled in 50v/50v, 70v/30v, 75v/25v, and 90v/10v ratios and Cu/Pyrex composites in 8v/92v, 20v/80v, 35v/65v, 50v/50v, and 65v/35v ratios. A series of Cu/Pyrex pellets were hot pressed in isomolded GR001CC grade graphite dies (1.27 cm ID) under Ar atmosphere using a hydraulic press (Elatec Inc.) at 13 °C/min to 700 °C held at 70 MPa for 45 min. Analyses used powder X-ray diffraction (XRD) and dilatometry taken between 40 and 170 °C.

### 2.2.2 ZrW₂O₈

Zirconium (IV) oxychloride octahydrate (ZrOCl₂·8H₂O) was obtained from Fluka Analytical. All other chemicals were obtained from Sigma Aldrich. ZrW₂O₈ was sol-gel synthesized by mixing ZrOCl₂·8H₂O, ammonium metatungstate hydrate ((NH₄)₆H₂W₁₂O₄₀·xH₂O), and citric acid in a 1:2:6 ratio then adjusting the solution pH to 7 with ammonium hydroxide. [47] This was aged at 60 °C for 20 – 22 hrs to form a viscous gel then calcined at 800 °C for 12 hrs. The resulting powder was sintered at 1180 °C for 2 hrs and quenched in liquid nitrogen to preserve the desired oxide phase. Quenched pellets were ground and the powder analyzed using dilatometry measurements made between 40 and 500 °C and XRD.

No attempts were made to control for particle size of the ZrW₂O₈ powder since the oxide filler has no bearing on the sintering of the composite. Furthermore, ZrW₂O₈ nanopowders with a crystallite size of 30 nm or less have been observed to undergo autohydration in ambient conditions, disrupting the NTE nature of the material. [48]
2.2.3 Silver

Two grades of commercial nano (< 100 nm) and micron (2 – 3.4 µm) Ag powder and all synthesis precursors were obtained from Sigma Aldrich. Ag nanopowder (~ 5 nm) was synthesized by first dissolving silver acetate (AgC₂H₅O₂) and oleylamine (C₁₈H₃₅NH₂) in toluene at 60 °C then slowly adding phenylhydrazine (C₆H₅NHNH₂) while stirring. [49-51] Ag particles are precipitated using a 50/50 volume methanol/acetone solution, washed, and filtered. In this thesis, micron Ag refers to the 2 – 3.4 µm diameter particles, commercial nano Ag refers to < 100 nm diameter particles, and synthesized nano Ag refers to the ~ 5 nm diameter particles. Synthesized nano Ag was prepared and analyzed with the assistance of Jong Woung Kim using XRD, thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), UV-visible spectroscopy (UV-Vis), and transmission electron microscopy (TEM).

2.2.4 NTE Metal Matrix Composites

Metal and ZrW₂O₈ powders of various wt % ratios (Table 2.2) were ball mill mixed overnight. Hot pressed composites were prepared in graphite dies (1.27 cm ID) under applied pressures of 70 – 80 MPa at a ramp rate of 13 °C/min to 500 – 700 °C for 2 – 4 hrs in Ar atmosphere. The standard hot pressing condition was 80 MPa at 500 °C held for 3 hrs. The hydraulic pressure and Ar gas flow were left on during the cooling phase until temperatures reached 100 °C or less. Composites were analyzed using XRD, SEM, dilatometry cycled 2 to 3 times between 40 and 150 °C, Archimedes density principles, isothermal parallel-plate method, and four-point van der Pauw method.
### Table 2.2. Experimental Volume % of Metal/ZrW₂O₈ with Corresponding Weight %

<table>
<thead>
<tr>
<th>Volume % Ag</th>
<th>Volume % ZrW₂O₈</th>
<th>Weight % Ag</th>
<th>Weight % ZrW₂O₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>67</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>42</td>
<td>58</td>
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<td>40</td>
</tr>
<tr>
<td>54</td>
<td>46</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>66</td>
<td>34</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>82</td>
<td>18</td>
<td>90</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Volume % Cu</th>
<th>Volume % ZrW₂O₈</th>
<th>Weight % Cu</th>
<th>Weight % ZrW₂O₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>17</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>63</td>
<td>37</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>55</td>
<td>45</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>46</td>
<td>54</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>36</td>
<td>64</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

#### 2.2.5 Characterization and Instrumentation

Powder XRD was performed on an X'Pert Pro (PANalytical B.V) (CuK\(_\alpha\), \(\lambda = 1.54 \text{ Å}\)) using a Gonio (\(\theta/\theta\)) scan mode under ambient temperature and pressure. The scanning step size was 0.017 in 2\(\theta\) and a counting time was about 0.75 s per step. Estimates of apparent crystallite size, \(\varepsilon\), were calculated using Scherrer’s equation as expressed in Equation 1,
\[
\varepsilon = \frac{0.89\lambda}{B \cos \theta}
\]  

(1)

where \(\lambda\) is the wavelength of radiation, \(B\) is the peak broadening at full width half maximum (FWHM), and \(\theta\) is the Bragg angle. The ZrW\(_2\)O\(_8\) phase was recovered from sintered MMCs by dissolving the Ag matrix in concentrated HNO\(_3\) overnight and washing the remaining ZrW\(_2\)O\(_8\) powder in deionized water.

Dilatometry was performed under Ar atmosphere using a DIL 402 PC (Netzsch Instruments N.A. LLC.) with a ramp rate of 5 °C/min. Dilatometry data were analyzed using Netzsch Proteus Thermal Analysis software with alumina holder and push rod corrections applied. CTE, \(\alpha\), is given in Equation 2 where \(L_0\) is initial sample length and \(T\) is temperature. The value of \(\alpha\) is readily determined as the slope of the line from a \(dL/L_0\) vs. temperature plot.

\[
\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T}
\]  

(2)

Initial sample thickness can affect the reliability and accuracy of the relative measured \(\Delta L\) value; therefore, only MMC samples with a minimum thickness of 1.5mm were used. [52] All MMC samples were polished to ensure each disc had smooth and parallel surfaces, since uneven sample thicknesses can reduce the accuracy of the measured \(\Delta L\). [52]

SEM was performed using a JSM-67 Field Emission SEM (JEOL) operating at 5 kV in secondary electron mode. Sintered samples were cross-sectioned on a Model 650 low speed diamond saw (South Bay Technology) and polished by standard metallographic polishing procedures. Silver grain boundaries were etched by a 10 sec dip in a 50/50 vol mixture of concentrated HCl/HNO\(_3\) and rinsed with DI water and ethanol.
Density was measured using an Excellence XP/XS precision balance density kit (Mettler Toledo). TEM was collected on a JEM1200-EX (JEOL) with samples prepared on a copper mesh grid (Ted Pella). TGA was measured on a Pyris Diamond TG/DTA (PerkinElmer Inc.) under Ar atmosphere. FT-IR was performed using KBr pellets in an FT-IR-670 (JASCO). UV-Vis analysis was done in a Varian Cary 100 (Biosystem).

Thermal conductivity measurements were performed using the parallel plate method on samples about 5 mm thick with two 0.5 mm diameter holes drilled into the sides spaced 2 – 3 mm apart. K-type thermocouples pre-coated with a high-thermal conductivity paste (TC-5025, Dow Corning) were inserted into the holes and secured with an epoxy. Each sample was clamped between hot and cold plates. The heat flux applied to the hot plate was measured using a series of four K-type thermocouples spaced 1 cm apart along the plate. A steady-state was assumed when the fluctuations in the measured temperature difference across the sample were less than 0.5%. The reported average thermal conductivity is calculated from 75 measurements taken at a frequency of 5 Hz. Thermal conductivity measurement and analysis was accomplished with the aid of Stephen Sharratt.

Electrical conductivity was measured on sintered samples ranging between 0.34 to 2 g and polished to achieve uniform thickness and parallel surfaces. The four-point van der Pauw apparatus was based on a design by McCormack and Fleurial [53] to measure resistivity in Ω·cm. This data was collected with the aid of Kurt Star.

Hermetic sealing testing was performed for H₂ gas leakage from vapor chambers held at 100 °C. This testing was done with the aid of Jon Zuo and Pete Dussinger at Advanced Cooling Technologies, Inc.
2.2.6 Calculations

For many powder composites the linear rule of mixtures (ROM) is a reasonable predictor for density and CTE. [54] All the density and CTE predictions used in this work follow the ROM calculation given in Equation 3.

\[
\text{ROM Property} = \sum (\text{Vol}\%_i \times \text{Property}_i) \quad (3)
\]

Density calculations follow the Archimedes principle as given in Equations 4, 5, and 6 where \( W_{dry} \) is the dry sample weight, \( W_{sat} \) is the saturated sample weight, and \( W_{sub} \) is the submerged sample weight.

\[
\text{Bulk density} = \frac{W_{dry} - \rho_{water}}{W_{sat} - W_{sub}} \quad (4)
\]

\[
\% \text{ theoretical density} = \frac{\text{bulk density}}{\text{ROM density}} \times 100 \quad (5)
\]

\[
\% \text{ open porosity} = \frac{W_{sat} - W_{dry}}{W_{sat} - W_{sub}} \times 100 \quad (6)
\]

2.3 Results

2.3.1 Ag/ZrW\textsubscript{2}O\textsubscript{8} Composites

XRD and dilatometry verified the phase and NTE for each synthesized batch of cubic \( \alpha \)-ZrW\textsubscript{2}O\textsubscript{8}. The overall average CTE is \(-13.6 \times 10^{-6}/\text{°C} \) and the Scherrer’s equation average crystallite diameter is 63.9 ± 12.1 nm. Figure 2.1 shows the XRD pattern of as-synthesized phase pure cubic \( \alpha \)-ZrW\textsubscript{2}O\textsubscript{8} along with ZrW\textsubscript{2}O\textsubscript{8} powders recovered from sintered composites. ZrW\textsubscript{2}O\textsubscript{8} decomposition just begins at 650 °C with the formation of WO\textsubscript{x} and ZrO\textsubscript{2} peaks; their peak intensity increases with temperature to 700 °C.
Figure 2.1: XRD pattern showing as-synthesized cubic $\alpha$-ZrW$_2$O$_8$ powder (referenced to JCPDS 50-1868) and oxide powders recovered from sintered composites. The (012) peak used for Scherrer’s equation calculations is approximately at 21.9°.

XRD also confirms phase purity of the synthesized Ag nanoparticles with a calculated crystallite size of 10.5 nm based on the (111) peak as shown in Figure 2.2. FT-IR and TGA (not shown) confirm the presence of oleylamine as a capping agent at about 1.4 weight % with total oleylamine decomposition occurring at approximately 330 °C. UV-Vis (not shown) absorption spectra exhibit a single surface plasmon resonance peak as expected at 417 nm [55] indicating there are no anisotropic particles such as rods and plates. TEM analysis (Figure 2.2) further confirms the Ag nanoparticles are uniformly spherical with average diameters of 4.2 ± 0.4 nm.
Figure 2.2: (Left) XRD pattern showing pure as-synthesized Ag (referenced to JCPDS 3-065-871) with a calculated crystallite size of 10.5 nm based on the (111) peak at 38.1°. (Right) TEM image of oleylamine-capped synthesized Ag nanoparticles with an average diameter of 4.2 ± 0.4 nm.

Sintered Ag/ZrW$_2$O$_8$ samples with compositions as listed in Table 2.2 were successfully produced having 1.25 cm diameters and ranging from 0.6 to 5 mm in thickness. The calculated average values of % theoretical density and % open porosity (% op) for Ag/ZrW$_2$O$_8$ composites of various compositions that used commercial nano Ag (< 100 nm) are listed in Table 2.3. Data and discussion on the particle size difference affected by the Ag metal matrix (micron vs. nano) are given later in this section.
Table 2.3. Measured % theoretical density and % open porosity averages for various compositions of commercial nano Ag/ZrW₂O₈ composites

<table>
<thead>
<tr>
<th>Vol % nano Ag/ZrW₂O₈</th>
<th>% theoretical density</th>
<th>% open porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>33/67</td>
<td>80.4 ± 2.7</td>
<td>9.6 ± 8.0</td>
</tr>
<tr>
<td>40/60</td>
<td>86.4 ± 5.9</td>
<td>8.7 ± 5.1</td>
</tr>
<tr>
<td>42/58</td>
<td>84.8 ± 0.3</td>
<td>9.5 ± 1.2</td>
</tr>
<tr>
<td>54/46</td>
<td>87.1 ± 4.0</td>
<td>5.1 ± 3.2</td>
</tr>
<tr>
<td>66/34</td>
<td>89.8</td>
<td>0.1</td>
</tr>
<tr>
<td>82/18</td>
<td>86.7 ± 2.2</td>
<td>0.2 ± 0.2</td>
</tr>
<tr>
<td>100/0</td>
<td>90.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

SEM in Figure 2.3 directly compares sintered commercial (a and b) and synthesized (c and d) nano Ag matrices. The commercial 54v/46v nano Ag/ZrW₂O₈ composite (< 100 nm Ag) has 3 % op and 83 % theoretical density. The synthesized 54v/46v nano Ag/ZrW₂O₈ (~5 nm Ag) has 0 % op and 98 % theoretical density. Some closed porosity is observed in both samples. Ag grain diameters are 0.25 ± 0.06 μm for the commercial nano Ag composite and 0.21 ± 0.05 μm for the synthesized nano Ag composite. Low magnification images compare the relative ZrW₂O₈ phase distribution between the commercial (b) and synthesized (d) nano Ag matrices. By standard image analysis, the synthesized nano Ag matrix has smaller average ZrW₂O₈ areas.
by 55% and the standard deviation of these areas is lower by 70% versus the commercial nano Ag matrix.

Figure 2.3: Secondary electron SEM micrographs at (a) high magnification and (b) low magnification of a 54v/46v commercial nano Ag/ZrW$_2$O$_8$ composite and (c) high magnification and (d) low magnification of a 54v/46v synthesized nano Ag/ZrW$_2$O$_8$ composite. The broad, flat dark regions are segregated phases of ZrW$_2$O$_8$ within the metal matrix, although charging effects brighten some of these regions in (d). All samples were hot pressed at 500 °C for 3 hrs and prepared using standard metallographic polishing.
Figure 2.4 compares the measured dilatometry data as a function of temperature for as-synthesized ZrW\textsubscript{2}O\textsubscript{8}, hot pressed commercial nano Ag, and hot pressed 54v/46v commercial nano Ag/ZrW\textsubscript{2}O\textsubscript{8}. The slope of these lines is the CTE. CTE values of commercial nano Ag/ZrW\textsubscript{2}O\textsubscript{8} composites are plotted in Figure 2.5 against calculated CTE values based on the rule of mixtures (ROM). The plotted data points of CTE vs. composition represent the measured slope from a single 100 – 150 °C segment from multiple heating and cooling segments taken during the dilatometry measurement cycle of one sample. The average measured CTE (cycled 2 to 3 times between 40 and 150 °C) and % op values for sintered Ag/ZrW\textsubscript{2}O\textsubscript{8} composites are given in Table 2.4.

![Dilatometry Data Plot](image)

Figure 2.4: Measured dilatometry data plotting change in length vs. temperature of commercial nano Ag, ZrW\textsubscript{2}O\textsubscript{8}, and a 54v/46v commercial nano Ag/ZrW\textsubscript{2}O\textsubscript{8} composite. The slope of each line is the CTE, \( \alpha \).
Figure 2.5: Measured CTE vs. composition of commercial nano Ag/ZrW$_2$O$_8$ composites as compared to the calculated ROM prediction. Only samples > 5 mm thick are plotted here to achieve greatest accuracy and consistency.

Table 2.5 lists thermal ($\kappa$) and electrical ($\sigma$) conductivities for sintered 54v/46v nano Ag/ZrW$_2$O$_8$ composites highlighting improved conductivities with reduced initial particle sizes of the Ag matrix. Under similar sintering conditions, the synthesized Ag silver matrix (~ 5 nm dia.) gives about 35% improvement in $\kappa$ and about 50% improvement in $\sigma$ over commercial nano Ag (> 100 nm dia.) for the same composite composition. The measured $\kappa$ of the 54v/46v synthesized nano Ag/ZrW$_2$O$_8$ composite is nearly 50% of the measured $\kappa$ of a pure nano Ag sample processed under similar conditions. [56]
Table 2.4. Average measured CTE and % open porosities of micron and commercial nano Ag composites (> 2 mm thick) as compared to the calculated ROM CTE

<table>
<thead>
<tr>
<th>Vol % Ag/ZrW₂O₈</th>
<th>Micron Ag</th>
<th>Commercial Nano Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM CTE (x 10⁻⁶/°C)</td>
<td>Average CTE (x 10⁻⁶/°C)</td>
</tr>
<tr>
<td>54/46</td>
<td>6.6</td>
<td>15.7</td>
</tr>
<tr>
<td>66/34</td>
<td>10.0</td>
<td>16.4</td>
</tr>
<tr>
<td>82/18</td>
<td>14.6</td>
<td>16.0</td>
</tr>
<tr>
<td>100/0</td>
<td>19.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5. Thermal and electrical conductivities of 54v/46v nano Ag/ZrW₂O₈ composites

<table>
<thead>
<tr>
<th></th>
<th>Average Thermal Conductivity (W/m-K)</th>
<th>Electrical Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial nano Ag</td>
<td>76</td>
<td>1.1 x 10⁵</td>
</tr>
<tr>
<td>Synthesized nano Ag</td>
<td>117</td>
<td>2.0 x 10⁵</td>
</tr>
</tbody>
</table>

* For pure bulk Ag, standard κ is 428 W/m·K and standard σ is 6.8 x 10⁵ S/cm
2.3.2 Cu Composites

All the Cu/Vycor composites which were prepared to evaluate the CTE concepts on MMCs failed to sinter. XRD of these samples (not shown) confirmed phase pure Cu showing no interphase reactions occurred and all Cu oxidation was suppressed. Samples ranged from 1 to 3 mm thick. The Cu/Pyrex composites of both 325 and 60 mesh Pyrex successfully sintered under both ambient and hydraulic pressure. Samples ranged between 1 to 4 mm thick. Hot press sintered Cu/ZrW$_2$O$_8$ composites were produced ranging between 1 to 2 mm thick. XRD confirmed the Cu matrix undergoes no oxidation; however, ZrW$_2$O$_8$ decomposes into tungsten and zirconium oxides regardless of composition and hot pressing conditions as shown in Figure 2.6. Calculated average values of % theoretical density and % op are given in Table 2.6 comparing pressure conditions for the Cu/Pyrex samples (325 and 60 mesh) and listing data for hot pressed Cu/ZrW$_2$O$_8$ composites. CTE was taken from 40 – 170 °C on hot pressed 325 mesh Cu/Pyrex samples between 1.1 to 2.1 mm thick with data reported from segments between 100 and 150 °C and averaged from at least 3 individual experimental runs. The CTE cycles for Cu/ZrW$_2$O$_8$ composites were run 2 to 3 times between 40 – 160 °C with data averaged and reported from segments between 100 and 150 °C. The CTE data for both 325 mesh Cu/Pyrex and Cu/ZrW$_2$O$_8$ is plotted in Figure 2.7 and compared to the calculated ROM for both composites.
Table 2.6. Measured % theoretical density and % open porosity averages for various compositions of Cu/Pyrex (325 and 60 mesh) and Cu/ZrW$_2$O$_8$ composites

<table>
<thead>
<tr>
<th>Vol/Vol</th>
<th>Ambient Pressure</th>
<th></th>
<th>Hydraulic Pressure</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% theoretical</td>
<td>% open porosity</td>
<td>% theoretical</td>
<td>% open porosity</td>
</tr>
<tr>
<td></td>
<td>density</td>
<td></td>
<td>density</td>
<td></td>
</tr>
<tr>
<td>Cu/Pyrex</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/92</td>
<td>62.58</td>
<td>26.55</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>20/80</td>
<td>61.90</td>
<td>22.71</td>
<td>98.51</td>
<td>0.37</td>
</tr>
<tr>
<td>35/65</td>
<td>64.77</td>
<td>17.01</td>
<td>98.99</td>
<td>0.50</td>
</tr>
<tr>
<td>50/50</td>
<td>71.33</td>
<td>17.72</td>
<td>98.37</td>
<td>0.54</td>
</tr>
<tr>
<td>65/35</td>
<td>76.73</td>
<td>14.85</td>
<td>98.24</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu/ZrW$_2$O$_8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36/64</td>
<td>--</td>
<td>--</td>
<td>120.25</td>
<td>0.40</td>
</tr>
<tr>
<td>46/54</td>
<td>--</td>
<td>--</td>
<td>104.87</td>
<td>6.17</td>
</tr>
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<td>55/45</td>
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<td>--</td>
<td>96.93</td>
<td>10.01</td>
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<td>63/37</td>
<td>--</td>
<td>--</td>
<td>99.30</td>
<td>6.93</td>
</tr>
</tbody>
</table>
Figure 2.6: XRD pattern showing pure as-synthesized cubic $\alpha$-ZrW$_2$O$_8$ powder (pattern at bottom) and Cu/ZrW$_2$O$_8$ composites hot pressed under 72 MPa and various time and temperature conditions. The two peaks near 43° and 50° match main Cu peaks while the remaining minor peaks correspond to main peaks of the indicated oxides. There is little to no indication that any ZrW$_2$O$_8$ remains in the samples.

Figure 2.7: CTEs of hot pressed 325 mesh Cu/Pyrex and Cu/ZrW$_2$O$_8$ composites as compared to the calculated ROM predictions for each.
2.4 Discussion

2.4.1 Effect of Composition and Particle Size on Ag/ZrW₂O₈ Properties

This research has successfully combined positive and negative CTE components to yield tailorable composite CTEs. In Figure 2.5 and Table 2.4 good agreement is shown for the CTE of all compositions of the commercial nano Ag composites with the calculated ROM CTE. Therefore Vegard’s law, which has predicted many material properties as functions of composition for other powder processed MMCs [54, 57, 58], is also a reasonable predictor of CTE for these composites. This indicates that the lattice parameters of the Ag/ZrW₂O₈ composites vary linearly with respect to the relative ratio of each component [59] and that the desired cubic α-ZrW₂O₈ phase is retained within the composite (Figure 2.1). Preserving the thermal stability of the NTE phase of the synthesized ZrW₂O₈ powder is crucial to achieving the target CTE of the overall composite. Although the average CTE for the synthesized ZrW₂O₈ (-13.6 x 10⁻⁶/°C) is more negative than anticipated, it is in close agreement with other experimentally measured CTE values for the same temperature range and does not appear to interfere with the ROM CTE predictions. [36] Porosity may affect the accuracy of dilatometry, possibly by contributing to some hysteresis between heating and cooling cycles. [60] However, corrections for push rod dilatometry, beyond accounting for holder and push rod expansion, are rare and very system specific with none being found for ZrW₂O₈. [61, 62]

The Ag/ZrW₂O₈ composites do not sacrifice thermomechanical stability. After being subjected to repeated thermal stress cycles (during dilatometry experiments), the cross-sectioned Ag/ZrW₂O₈ microstructures in Figure 2.3 are uniform with low intergranular porosity indicating there is strong interfacial phase bonding, which is vital to achieving optimal mechanical properties. [4, 5, 37] Furthermore, Figure 2.3 proves that reducing the initial particle size of the
matrix improves the overall phase distribution as evidenced by the smaller and more uniform oxide areal regions within the synthesized nano Ag matrix. The even phase distribution by the powder mixing process maximizes interfacial contact and more evenly distributes thermal stress across the entire composite. While the large difference in CTE between the utilized components can cause significant thermal stress, it is accommodated by localized deformation of the Ag matrix. [63] FCC metals such as Ag can withstand large plastic deformation [64-66] and Ag exhibits increased yield strengths and reduced hardening rates with decreasing grain size. [67, 68] It has also been shown that recovery from structural defects in Ag occurs even at room temperature. [69, 70]

Reducing the initial Ag matrix particle diameter improves all measured material properties. Composites made with nano Ag demonstrate higher thermal and electrical conductivities (Table 2.5) and lower % op (Table 2.4) than those made with micron Ag. The poor conductivity of the ZrW₂O₈ phase and the presence of electron and phonon scattering at phase interfaces does reduce the overall composite conductivity. Still, the 54v/46v Ag/ZrW₂O₈ composites return a κ comparable to pure Zn and several Cu alloys and an σ on the same order of magnitude as pure bulk Ag. This is likely due to a continuous, sintered Ag matrix being maintained in the composites.

The measured property improvements are primarily achieved through a combination of more homogenous phase mixing and more complete sintering of the nanoparticle matrix. Metal nanoparticles are known to have much lower melting and sintering temperatures than their bulk counterparts [46] and reducing the particle size of the Ag packed around the ZrW₂O₈ improves the composite packing density during sintering. From Table 2.4 it is clear that the nano Ag composites have lower % op across all compositions and the micron Ag composites are
completely inconsistent with the calculated ROM. This is likely due to the poor sinterability of the micron Ag at 500 °C. In fact, the micron Ag composites failed to sinter at all when the vol % of ZrW₂O₈ exceeded that of Ag (40v/60v Ag/ZrW₂O₈). This is expected since hard ZrW₂O₈ powder is less accommodating to any shifting and packing that occurs as the Ag matrix is trying to sinter around it. Finally, some electronic packaging applications require full density to promote hermetic sealing against fluids. The hermeticity testing found only those samples with < 1% op satisfied the requirements of negligible fluid loss against H₂ gas at 100 °C for > 1500 hrs.

2.4.2 Successes and Failures of Cu Composites

The measured CTE values of the hot pressed 325 mesh Cu/Pyrex composites mirror the general trend predicted by the ROM, proving that combining low-CTE ceramic powder with high-CTE metal powder can yield composites with tailorable CTE (Figure 2.7). However, the measured CTE values are consistently high relative to the ROM predictions. The samples prepared were only 1 to 2 mm thick which may have increased uncertainty in the measured CTE values. [52] The high CTEs may also be due to the relatively large and inconsistent particle size of the initial powders. A 325 mesh particle corresponds to diameters of 44 microns or less. Larger micron-sized particles for both the ceramic and metal phases reduce uniform phase mixing, inhibit efficient powder packing, and increase the required temperature to achieve complete sintering. Samples prepared with 60 mesh (250 micron or less) Pyrex exhibited sintering and density properties comparable to the 325 mesh Pyrex composites but were not included in the CTE analyses. Since it was intended to use NTE ZrW₂O₈ for this MMC design,
further microstructural and particle size analyses were not pursued for Cu/Pyrex composites in this work.

Initial experiments with the NTE oxide ZrW$_2$O$_8$ used a Cu matrix due to the relatively low cost and high thermal conductivity of Cu. However, the experimental Cu/ZrW$_2$O$_8$ composites returned average CTEs of 14.6 x 10^{-6}/°C, regardless of composition (Figure 2.7). This is approximately the CTE of pure Cu (16.6 x 10^{-6}/°C). XRD verified ZrW$_2$O$_8$ decomposes into separate zirconium and tungsten oxides, even as low as 500 °C when in composite with Cu (Figure 2.6). It is also noted the oxides present after decomposition are denser than ZrW$_2$O$_8$. (ZrW$_2$O$_8$: 5.08 g/cm$^3$, ZrO$_2$: 6.21 g/cm$^3$, WO$_2$: 11.03 g/cm$^3$, WO$_3$: 6.42 g/cm$^3$) This artificially inflates the measured density of the Cu/ZrW$_2$O$_8$ composites, with several samples exhibiting > 100 % theoretical density in Table 2.6. It was not possible to sufficiently sinter the Cu matrix and avoid ZrW$_2$O$_8$ decomposition by hot pressing and so research shifted to develop composites with Ag as discussed in the prior section. Silver has a lower melting temperature relative to Cu (961 °C vs. 1085 °C) and a lower CTE and higher thermal conductivity relative to Al (Table 2.1).

2.5 Future Work

The thermal stability of single phase ZrW$_2$O$_8$ does not carry through when used in a MMC. Previous work using a Cu matrix with ZrW$_2$O$_8$ [35, 43, 44] and the initial work here with Cu powders revealed Cu catalyzed premature decomposition of ZrW$_2$O$_8$ at temperatures and pressures as low as 500 °C and 72 MPa regardless of composition. Separate research has begun investigating processing methods to make lower cost Cu a feasible matrix for ZrW$_2$O$_8$ MMCs through Cu particle size reduction. [71]
2.6 Conclusions

The MMC Ag/ZrW$_2$O$_8$ materials developed in this work achieve high thermal conductivity with easily tailored CTEs, combining positive and negative CTE materials and avoiding ZrW$_2$O$_8$ decomposition. Reducing the initial matrix particle size from micron to nano Ag improves CTE predictability, lowers sintering temperatures, decreases % open porosity, and improves thermal and electrical conductivities for sintered composites of the same composition. Several 54v/46v commercial nano Ag/ZrW$_2$O$_8$ samples matched the target CTE of GaAs by < 5% with the overall composition average CTE matching GaAs by 8.7%.
Chapter 3: Ferroelectric Nanoparticles

3.1 Introduction

The future of many complex electronic composites hinges on continued development of ferroelectric nanoparticles having high dielectric constants, large polarizations, low hysteresis losses, high dielectric field breakdown strengths, and tailorable Curie temperatures ($T_c$). Making these material advances requires a clear understanding of each material component, often under different size regimes. While the properties of one common high dielectric constant ceramic, BaTiO$_3$, have been studied extensively in bulk, single crystal, polycrystalline, thin film, and even nanocrystalline forms, studies on a related material, Ba$_{1-x}$Sr$_x$TiO$_3$ where $T_c$ depends on the value of $x$, have largely focused on bulk and thin film structures. Since many electrical properties vary between the grain and the grain boundaries [72], nanoparticles of Ba$_{1-x}$Sr$_x$TiO$_3$ are of great interest for developing electronic composites which can be designed for a target $T_c$.

Dielectric materials are polarized under an applied electric field via the short range motion of charge carriers. A subset under dielectric materials, ferroelectrics (FE), exhibit a temperature dependent, spontaneous, and reversible polarization between the paraelectric (PE) and FE phases. The spontaneous dipole alignment of the FE phase induces very large polarization ($P$) changes at $T_c$. The net dielectric displacement ($D$) is related to polarization by equation 7 where $\varepsilon_0$ is permittivity of a vacuum and $E$ is the applied external electric field.

$$D = \varepsilon_0 E + P$$  (7)

Relative permittivity is more commonly called dielectric constant, $\varepsilon_r$, and is related to the permittivity of a material, $\varepsilon$, by equation 8.
\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \]  

(8)

In general, the energy density capacity of FE materials is most closely related to the E, P, dielectric breakdown strength (\(E_b\)), and remnant polarization or hysteresis. [13] An ideal FE material would be designed to have low hysteresis, low elastic strain, low thermal losses, high \(E_b\), and high \(\varepsilon_r\) in order to accommodate efficient device operation in higher electric fields with large polarization changes.

One of the most common and extensively studied ferroelectrics is the perovskite BaTiO\(_3\) which is known to be cubic above 120 °C, tetragonal from 120 to 5 °C, orthorhombic from 5 to –90 °C, and rhombohedral below –90 °C. [20, 27, 73, 74] The perovskite structure exhibits FE behavior as the Ti atom displaces relative to the O octahedra it is centered in, either by applied electric field or structural deviations from cubic. The FE behavior of BaTiO\(_3\) is most often modeled using Devonshire’s free energy analysis as a basis. [75] The peak FE behavior near \(T_c\) is characterized by the Curie-Weiss Law, which relates the dielectric constant, \(\varepsilon\), to a Curie-Weiss constant, \(A\), according to Equation 9. [75-77]

\[ \varepsilon = \frac{A}{T - \theta_c} \]  

(9)

The temperature \(\theta_c\) is a near but not exactly \(T_c\) and \(T > T_c\). Research has shown Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) can deviate from Curie-Weiss Law behavior. [78-80] Experimental data is commonly used to determine parameters to fit Devonshire-based energy models, regularly returning \(A\) values on the order of \(10^5\) degrees for Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\). [19, 75, 77, 79] It is not clear if the free energy models developed for Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) could predict a theoretical maximum for \(\varepsilon\).
The particle size of a FE has been proven to have a profound effect on the dielectric properties. Simply decreasing the particle size decreases the $T_c$ [22, 25, 26, 81, 82], increases the dielectric constant [19, 26, 83], and decreases the hysteresis [8, 13, 84] in several titanate systems. Modeling of $\text{PbZr}_{0.6}\text{Ti}_{0.3}\text{O}_3$ predicts that hysteresis completely disappears below a critical radius on the order of a few nanometers. [24] To this end, synthesizing $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ nanoparticles with diameters equal to a single ferroelectric domain could result in anomalously high dielectric constant with minimum hysteresis and dielectric losses. The transition from single to multi-FE domain occurs at crystallite diameters of 100 nm in calcined $\text{BaTiO}_3$. [85]

A compositional effect on $T_c$ occurs by forming a solid solution, where Sr replaces some of the Ba in the lattice to create $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$. Increased addition of smaller Sr atoms ($r = 1.90 \, \text{Å}$) in place of Ba atoms ($r = 2.06 \, \text{Å}$) induces the shift from the cubic to tetragonal structure at lower temperatures. [73, 77, 86] Sr substitution lowers the $T_c$ to room temperature at about $x = 0.3$ to 0.4. [77, 86-88] A relatively simple solvothermal synthesis for nanoparticle preparation [89, 90] exists which is similar to the industry standard Bayer process route used for production of crystalline alumina. This will facilitate easier large scale production of these materials. [91] It should be noted that the very methods used for synthesis and preparation of the powders affect the ferroelectric properties of $\text{BaTiO}_3$. [11, 14, 18, 92, 93] Therefore, great care was taken to first confirm the crystal structure and ferroelectric response of the synthesized $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$. 


3.2 Current Particle Size Effect Theories

Theories explaining the particle size effect on dielectric properties focus on multiple factors including grain boundaries, ferroelectric domains and domain walls, internal elastic stresses, and surface charges. For “bulk” particles > 10 μm, 90° domain twinning between grains helps to relieve internal stresses by distributing the c-axis elongation of the tetragonal structure in all three dimensions of the crystal. [83, 93] The total dielectric constant is a volume weighted sum of each crystal and the FE domain walls; for bulk materials the relative contribution of each is essentially constant. However, as particle sizes decrease to about 1 μm the contribution of the domain walls relative to the grain volume greatly increases. [94] Smaller grains with fewer domains also experience increased domain wall pinning which leads to reduced dielectric loss effects. [93, 95] For these particles between 10 to 1 μm, the increase in dielectric constant originates from the reduction of 90° twinning and increasing internal stress. Below 1 μm, twinning is reduced to the point of disappearing [83, 94] since few 0.4 μm thick domain walls can fit within < 1 μm grains. Even if 90° domain walls scale with respect to grain size and persist in grains < 1 μm, it has been extrapolated that domain walls will disappear altogether below 0.4 μm diameter. [94] The density and structure of FE domains and the related internal stress has been shown to be dependent on grain size. [93, 95] In a single domain grain, the unrelieved internal stress would be maximized and is expected to prod the strained tetragonal BaTiO₃ structure towards the unstrained cubic state mimicking the cubic-tetragonal transition state of peak dielectric constant. [83] A high stress state is correlated to the unusually high dielectric constant observed in fine-grained titanates. [27, 83, 94, 96] Externally applied pressure on 1 μm BaTiO₃ has been shown to increase the measured dielectric constant, indicating that structural stress indeed triggers an increase in dielectric constant. [96] The stress distribution of fine
grained BaTiO$_3$ is highly complex and attempts at modeling the values of dielectric constants use modified free energy equations with several broad simplifications. [83, 96]

In both bulk and nano particle studies on BaTiO$_3$, a structurally distinct surface layer has been identified which contributes different dielectric characteristics than the interior “bulk”. [23, 27, 79, 92] A thin insulating region or surface layer may induce enhanced interfacial polarization by acting as a barrier layer capacitor between more conductive core regions. [27, 92] A common model of BaTiO$_3$ is as a “core shell” sphere of a tetragonal core with a cubic surface shell about 0.1 to 1 μm thick which behaves as a non-ferroelectric with a lower ε$_r$, higher hysteresis loss, and has electron trapping surface states which may impede polarization switching. [8, 26, 27] As the particle size decreases, this surface layer contributes more to the overall material dielectric properties. [27] Furthermore, in the range of tens of nanometers, a size induced loss of ferroelectric properties, called a superparaelectric (SPE) limit, has been observed and modeled in several perovskite systems. [8, 12, 18, 22-26, 94, 97, 98] Theoretically, this involves the gradual reduction of the tetragonal core of a particle while the cubic shell persists with a constant thickness. The tetragonal core gives way to a pseudo-cubic phase before vanishing below a certain particle size, usually on the order of tens of nanometers, and leaving only a cubic PE phase material. However, BaTiO$_3$ has been found to display localized tetragonal distortions < 40 nm in a regime believed to be completely cubic. [20, 21, 99] Considering the possible disappearance of hysteresis in this size regime, this research project elected to investigate dielectric properties of < 10 nm Ba$_{1-x}$Sr$_x$TiO$_3$ for high dielectric constant nanoparticles near room temperature.
3.3 Experimental

3.3.1 Ba$_{1-x}$Sr$_x$TiO$_3$

Commercial powders of BaTiO$_3$ (100 nm) and Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (< 100 nm), Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ (200 nm), and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ (< 100 nm) were obtained for reference. Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles (< 10 nm) were synthesized by a sol-gel approach. Ba metal (99+ %) was obtained from Acros Organics. Sr metal (99 %), titanium (IV) isopropoxide (Ti[OCH(CH$_3$)$_2$)$_4$), diethyl ether, benzyl alcohol, and ethanol were obtained from Sigma Aldrich. The synthesis involved dissolving the desired molar ratios of Ba and Sr metal separately in benzyl alcohol under Ar atmosphere at 60 to 90 °C then mixing the cooled alkoxides with titanium (IV) isopropoxide [89, 90]. The solution was heated at 200 °C for 48 hrs in a Teflon lined acid digestion reaction vessel (Parr Instrument) in open atmosphere. Ba$_{1-x}$Sr$_x$TiO$_3$ precipitates were washed with ethanol and diethyl ether and then dried at room temperature. Ba$_{1-x}$Sr$_x$TiO$_3$ powders were characterized using XRD, TEM, SEM, TGA, Raman spectroscopy, and electrochemical impedence spectroscopy (EIS).

3.3.2 Powder Dispersions for Polymer Chemistry

Solvents dimethylformamide (DMF) and methyl ethyl ketone (MEK) were tested with surfactants phosphoric acid 2-hydroxyethyl methacrylate ester (PA2-HME) or bis[2-(methacryloyloxy)ethyl]phosphate (B2-MEP). All chemicals were acquired from Sigma Aldrich. Stock solutions were mixed by weighing the grams of the surfactant in a vial and adding mL of solvent for the desired molarity. Solutions were mixed in 0.01, 0.5, 1, and 2 M
concentrations and then agitated until complete dissolution of the surfactant. $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders were dispersed in these solutions at 0.8 to 5 wt% by sonicating for 10 – 90 min. Samples were observed visually for solution clarity and particle settling and characterized using dynamic light scattering (DLS).

### 3.3.3 Characterization and Instrumentation

Powder XRD was gathered using a MiniFlex II, (Rigaku) $(\text{CuK}_{\alpha}, \lambda = 1.54 \text{ Å})$ with a Gonio $(\theta/2)$ scan mode at ambient temperature and pressure. The scanning step size was 0.05 in $2\theta$. Scherrer’s equation calculations gave estimates of apparent crystallite size, $\varepsilon$, according to Equation 1.

$\text{SEM}$ was performed using a JSM-67 Field Emission SEM (JEOL) operating between 5 and 15 kV in secondary electron mode. TEM was performed with a JEM 1200-X (JEOL) operating at 80 kV. High resolution TEM (HR-TEM) was conducted with a Titan S/TEM (Titan) operating at 300 kV with the aid of Matt Mecklenburg at the California NanoSystems Institute (CNSI). All TEM samples were prepared on copper mesh grids (Ted Pella). Lattice d-spacings from HR-TEM were measured using image processing software to measure the distance between adjacent “valley” positions of each line at multiple points across the image. Unit cell geometry calculations used JCPDS reference values and measured d-spacing values with $a = b = d_{100}$ and $1/3(\text{body diagonal}) = d_{111}$ to determine a calculated value for $c$ and concluded by calculating the $c/a$ ratio.

$\text{TGA}$ was run in air using a SDT Q600 (TA Instruments) with alumina sample pans. The program first equilibrated at 40 °C then ramped to 800 °C at a rate of 10 °C/min. Calculations
related the weight % lost measured data to relative surface area ligand coverage on as-synthesized and heat treated Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles. These calculations assumed spherical Ba$_{1-x}$Sr$_x$TiO$_3$ particles and benzyl alcohol as the residual ligand and yield a mole ratio of benzyl alcohol to Ba$_{1-x}$Sr$_x$TiO$_3$. From this molar ratio, the number of benzyl alcohol molecules per Å$^2$ of Ba$_{1-x}$Sr$_x$TiO$_3$ is determined.

Raman spectroscopy was performed in a Renishaw In-Via micro-Raman spectrometer (Renishaw PLC) using a 514 nm argon ion laser at 25 mW. Samples were prepared by mixing a 50 μg polystyrene/μL toluene solution then dispersing the oxide powders in a 50 μg/μL concentration. The solution was drop cast onto Si substrates and air dried. Raman spectra were taken in 10-second accumulations averaged from 3 collections taken at 5 to 10 locations on each sample. These were combined in a sample average in order to minimize inconsistencies in powder concentration across the sample. Reference spectra were collected for Si substrates and polystyrene.

EIS samples were prepared by dispersing 5 vol % powder in polyethylene glycol (PEG) 300 and vortexing the solution for two 15 sec intervals immediately prior to loading the 16452A liquid test fixture (Agilent). System temperature control was handled by immersing the liquid test fixture into a 9106 circulating temperature bath (PolyScience) filled with silicone oil (type 200.10, ThermoWorks, Inc.). EIS measurements were taken as ZTR (Z = impedance in Ω, TR = θ in radians) as a function of frequency ($10^2$ to $10^6$ Hz) at 5 °C intervals between 0 and 50 °C with a HP 4284A LCR meter (Hewlett-Packard). Initial tests to record minimum time to equilibrate between each temperature step (+/- 0.5 °C) used a test slurry of 5 vol % commercial Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ and an external thermocouple probe inserted into the center of the liquid test
fixture. The collected ZTR data are converted to yield $Z_{\text{real}}$ and $Z_{\text{img}}$ as a function of frequency. EIS data were analyzed using ZView software (Scribner Associates, Inc).

Differential scanning calorimetry (DSC) was collected using a Diamond DSC (Perkin Elmer) from -10 to 150 °C ramped at 5 °C/min with samples held under nitrogen atmosphere. Dynamic light scattering (DLS) was run with an N4 Plus (Beckman Coulter) on samples ranging between 0.01 to 2 wt % BaTiO₃ dispersed in DMF, MEK, or ethanol/acetone using 0 – 6 wt % surfactants PA2-HME or B2-MEP.

### 3.3.4 EIS Modeling and Calculations

EIS was mathematically modeled as two equivalent RC circuits in series (Figure 3.1a). The dielectric contributions of the solvent (high frequency) and oxide (low frequency) can be separately modeled from a Nyquist plot as demonstrated in Figure 3.1-b. Some overlap of the impedance spectra is expected and is related to the uniformity of the slurry dispersion. The modeling fit generates a $T$ (magnitude), $P$ (phase angle), and $R$ (resistance) for each component yielding capacitance, $C_p$, according to equation 10.

$$C_p = T^{1/p} \times R^{1-p/p}$$  \hspace{1cm} (10)

This capacitance is related to relative dielectric constant, $\varepsilon_r$, by Equation 11 where $A$ is the area of the parallel plate capacitors and $d$ is the separation distance of the capacitor plates.

$$\varepsilon_r = \frac{C_p d}{\varepsilon_0 A}$$  \hspace{1cm} (11)
Plotting this calculated $\varepsilon_r$ as a function of temperature yields a $T_c$ peak for the Ba$_{1-x}$Sr$_x$TiO$_3$ nanopowder. This modeling method has also been used to successfully characterize micron and mm particles of TiO$_2$, CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ and shows good agreement with dielectric constants measured on bulk materials of each oxide. [11, 14, 15, 100-103]

Figure 3.1: Nyquist plot of real vs. imaginary impedance of measured data (solid line) with applied modeling fit (circle line) and two hypothetical semicircles (dashed lines) illustrating the extraction of separate contributions of the liquid and oxide components. The low frequency tail results from the double layer capacitance of the electrodes and is excluded from the data modeling. [102]
The dissipation loss (D) or tan delta (tan δ) is equal to the ratio of the measured $Z_{\text{real}}$ to $Z_{\text{img}}$ as given in equation 12. It is also possible to calculate δ as the complementary angle to θ. Values for D were identical using either calculation. The activation energy for loss, $E_a$, was determined from the slope of frequency ($f$) at $D_{\text{max}}$ vs. inverse temperature ($1/T$) according the Equation 13, where $f_o$ is the pre-exponential factor and $k$ is the Boltzmann constant.

$$D = \frac{Z_{\text{real}}}{Z_{\text{img}}}$$ \hspace{1cm} (12)

$$f_{D_{\text{max}}} = f_o \exp\left(-\frac{E_a}{kT}\right)$$ \hspace{1cm} (13)

### 3.4 Results

Phase pure Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles are verified with XRD (Figure 3.2) having crystallite diameters consistently < 10 nm (Table 3.1). The peak shift to higher 2θ with increasing Sr can be observed in the (110) peak focus in Figure 3.2-right. As plotted in Figure 3.3, the average measured 2θ shift with increasing Sr agrees well with expected literature values for three primary XRD peaks. TEM in Figure 3.2 shows consistent size and shape with measured diameters closely matching the XRD calculated crystallite diameters.
Figure 3.2: (Left) XRD patterns of $\text{Ba}_1-x\text{Sr}_x\text{TiO}_3$ nanoparticles highlighting composition. (Upper right) Focus on the (110) peak near 31° illustrating the peak shift to higher 2θ with increasing Sr content, as expected due to decreasing lattice spacing. (Lower right) TEM micrograph of as-synthesized $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ nanoparticles.

Table 3.1. Average crystallite diameter (XRD) and particle size (TEM) for as-synthesized $\text{Ba}_1-x\text{Sr}_x\text{TiO}_3$

<table>
<thead>
<tr>
<th></th>
<th>XRD (nm)</th>
<th>TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST 50:50</td>
<td>4.6 ± 0.7</td>
<td>--</td>
</tr>
<tr>
<td>BST 65:35</td>
<td>5.0 ± 1.3</td>
<td>4.3 ± 1.1</td>
</tr>
<tr>
<td>BST 75:25</td>
<td>3.4 ± 0.7</td>
<td>--</td>
</tr>
<tr>
<td>BST 80:20</td>
<td>4.3 ± 0.6</td>
<td>--</td>
</tr>
<tr>
<td>BT</td>
<td>4.0 ± 0.4</td>
<td>6.9 ± 3.1</td>
</tr>
</tbody>
</table>
Figure 3.3: XRD 2θ averages vs. mol % Sr for all as-synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles. Solid lines represent the trend plotted from five JCPDS references.

TEM micrographs in Figure 3.4 reflect the induced particle size growth of heat treated Ba$_{0.65}$Sr$_{0.35}$TiO$_3$. Particle size control was achieved by post-synthesis heat treating between 500 and 1000 °C as tracked in Figure 3.5. Retaining particle diameters of 10 nm or less requires heat treatments of 700 °C for 10 min. Diameters were achieved of ~ 15 nm after 800 °C for 1 hr, 20 to 25 nm after 900 °C for 1 hr, and ~ 30 nm after 1000 °C for 1 hr, all as measured by XRD. Particle sizes of as-synthesized and heat treated powders are graphed in Figure 3.6, comparing XRD and TEM measurements and showing consistency between the methods up to ~ 20 nm diameter. Heat treatments were also tested as a means to remove residual ligands, which can affect the measured dielectric properties on nanoparticles in slurry [18, 104]. Using TGA
(calculations in Table 3.2), it was determined that 700 °C for 10 min gives the ideal balance between maintaining particles < 10 nm diameter and sufficiently removing ligands.

Figure 3.4: TEM micrograph of Ba_{0.65}Sr_{0.35}TiO_3 nanopowders from Figure 3.2 following heat treatments at (left) 800 °C, (middle) 900 °C, and (right) 1000 °C for 1 hr.

Figure 3.5: Plot of temperature vs. average XRD crystallite diameter highlighting post-synthesis heat treatments to control particle diameters.
Figure 3.6: XRD crystallite diameter vs. TEM measured diameters for as-synthesized and heat treated nanopowders.

Table 3.2. Calculations for relative surface area coverage by benzyl alcohol (b.a.) ligands on Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ nanoparticles as-synthesized and after heat treatment

<table>
<thead>
<tr>
<th>BST 80:20</th>
<th>Dia. (Å)*</th>
<th>Wt % lost</th>
<th>Mole ratio</th>
<th>Molecules of b.a./Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As synthesized</td>
<td>38</td>
<td>17.02</td>
<td>0.4</td>
<td>4.06E-02</td>
</tr>
<tr>
<td>HT 500 °C 1 hr</td>
<td>50</td>
<td>4.55</td>
<td>0.1</td>
<td>1.24E-02</td>
</tr>
<tr>
<td>HT 600 °C 1 hr</td>
<td>65</td>
<td>1.21</td>
<td>0.03</td>
<td>4.14E-03</td>
</tr>
<tr>
<td>HT 700 °C 10 min</td>
<td>90</td>
<td>0.43</td>
<td>0.009</td>
<td>2.02E-03</td>
</tr>
<tr>
<td>HT 700 °C 10 min</td>
<td>95</td>
<td>0.38</td>
<td>0.008</td>
<td>1.89E-03</td>
</tr>
<tr>
<td>HT 700 °C 1 hr</td>
<td>112</td>
<td>0.17</td>
<td>0.004</td>
<td>9.93E-04</td>
</tr>
</tbody>
</table>

*Crystallite diameter as measured by XRD
HR-TEM determined whether the lattice spacing of the synthesized nanoparticles is more consistent with the cubic or tetragonal phase. Figure 3.7 shows images of two distinct particles of synthesized $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ with insets of rotated and zoomed regions. The measured average lattice spacing is $2.35 \pm 0.04 \text{ Å}$, consistent across the entire left image, while three distinct lattice parameters were measured from different regions of the right image: $2.39 \pm 0.48$, $2.86 \pm 0.30$, and $4.10 \pm 0.67 \text{ Å}$. Using JCPDS references these measured d-spacings were correlated to crystallographic directions as given in Table 3.3. From unit cell geometry calculations, the c/a ratio of the synthesized powder is $\sim 1.01$, indicating tetragonal structure. A c/a value of $\sim 1.01$ is commonly reported for bulk tetragonal $\text{BaTiO}_3$ at room temperature [22, 105, 106], for tetragonal $\text{BaTiO}_3$ nanoparticles [106], and for modeled tetragonal core shell structures of nanoparticles. [23]

Figure 3.7: HR-TEM micrographs of $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ nanopowders with rotated and zoomed insets.
Table 3.3. D-spacing calculations from JCPDS references and experimental TEM measurements to correlate crystal structure

<table>
<thead>
<tr>
<th></th>
<th>BST 50:50 39-1395 (cubic)</th>
<th>BST 60:40 34-0411 (cubic)</th>
<th>BST 67:33 1-089-0274 (tetragonal)</th>
<th>BST 77:23 44-0093 (tetragonal)</th>
<th>Measured TEM from Figure 3.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>{100}</td>
<td>3.949</td>
<td>3.966</td>
<td>3.972</td>
<td>3.977</td>
<td>4.10 ± 0.67</td>
</tr>
<tr>
<td>{110}</td>
<td>2.792</td>
<td>2.806</td>
<td>2.808</td>
<td>2.816</td>
<td>2.86 ± 0.30</td>
</tr>
<tr>
<td>{111}</td>
<td>2.280</td>
<td>2.290</td>
<td>2.293</td>
<td>2.298</td>
<td>2.39 ± 0.48</td>
</tr>
<tr>
<td>Body diagonal from {111}</td>
<td>6.84</td>
<td>6.87</td>
<td>6.88</td>
<td>6.89</td>
<td>7.17</td>
</tr>
<tr>
<td>Cube side calculated from body diagonal</td>
<td>3.948</td>
<td>3.966</td>
<td>3.972</td>
<td>3.981</td>
<td>4.140</td>
</tr>
<tr>
<td>% difference from {100}</td>
<td>0.025</td>
<td>0.010</td>
<td>0.018</td>
<td>0.095</td>
<td>0.961</td>
</tr>
<tr>
<td>c/a ratio</td>
<td>1.0002</td>
<td>1.0001</td>
<td>1.0002</td>
<td>1.0009</td>
<td>1.0098</td>
</tr>
</tbody>
</table>

Raman spectroscopy was first performed on the commercial powders to establish a baseline comparison between known cubic and tetragonal commercial Ba$_{1-x}$Sr$_x$TiO$_3$ particles as given in Figure 3.8-left. A single sharp Si peak located at 514 cm$^{-1}$ and two sharp polystyrene peaks at 994 and 1596 cm$^{-1}$ (data not shown) were also initially identified. Four characteristic Raman peaks located at 180, 218, 514, and ~730 cm$^{-1}$ are specific to tetragonal Ba$_{1-x}$Sr$_x$TiO$_3$ modes [107-111] and are prominently observed in a tetragonal powder but significantly muted or absent in the cubic powders. These tetragonal phonon modes can be distinguished regardless of particle diameter, even down to ~10 nm, as evidenced in Figure 3.8-right with a series of synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ following heat treatments for particle size control. It is noted that the Si peak overlaps one tetragonal Ba$_{1-x}$Sr$_x$TiO$_3$ peak; however, Si was not detected and did not interfere...
with the spectra when sufficiently covered with Ba$_{1-x}$Sr$_x$TiO$_3$ particles dispersed in polystyrene, regardless of whether the Ba$_{1-x}$Sr$_x$TiO$_3$ was tetragonal or cubic.

Figure 3.8: (Left) Raman spectra comparing commercial Ba$_{1-x}$Sr$_x$TiO$_3$ compositions with four characteristic tetragonal active modes. The 67:33 prominently displays tetragonal modes while the 50:50 lacks these modes indicating it is cubic. The 80:20 shows some mix of the two. This assessment agrees with XRD patterns collected (data not shown) and the phase information provided by the manufacturer. (Right) Raman spectra comparing heat treated synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ samples. Black bars represent the 4 characteristic tetragonal phonon modes. The XRD crystallite diameters are listed with each corresponding line color.

When characterizing the synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ powders (~ 10 nm dia.), the same distinguishing tetragonal phonon lines are observed (Figure 3.9). The phonon peak near 730 cm$^{-1}$ shifts to higher wave number with increasing Sr content due to the stronger interaction of the Sr$^{2+}$ ions with the surrounding TiO$_6$ octahedron. [107, 110] The peak near 615 cm$^{-1}$ may be related to disorder-activated scattering observed with Sr addition in Ba$_{1-x}$Sr$_x$TiO$_3$. [112] Asymmetric broadening of the Raman peaks with decreased particle size is also observed. [113-
The slight peaks near 138 and 298 cm\textsuperscript{-1} are attributed to E(TO\textsubscript{1}) and E(TO\textsubscript{2}) modes respectively and are both associated with the cubic to tetragonal phase shift. [107] The flattening of the regions centered near 220 and 585 on the 65:35 and 50:50 is characteristic of cubic Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3}. [107, 112, 116]

Figure 3.9: Raman spectra comparing synthesized Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3} compositions displaying four characteristic tetragonal active modes. The average crystallite diameters for all samples are ~ 10 nm. The 80:20 and 75:25 are characterized as tetragonal while the 65:35 and 50:50 are mixed cubic with tetragonal.
The EIS method employed here measures the ferroelectric properties directly from individual nanoparticles. This distinguishes this research from prior work on Ba$_{1-x}$Sr$_x$TiO$_3$ sintered bulk ceramics and thin films because processing methods can greatly affect the measurement results. Establishing confidence in the EIS method began by first selecting a suitable host liquid. Butoxyethanol (BOE), propylene carbonate (PC), and polyethylene glycol (PEG) were tested with PEG selected as an ideal lossy liquid solvent to stably suspend the Ba$_{1-x}$Sr$_x$TiO$_3$ powders. In the temperature range of 0 – 50 °C, a consistent dielectric constant was measured for PEG, comparable in value with another method [117] (Figure 3.10-left) and showing negligible change in measured dielectric properties for > 4 hrs, which is sufficient time to complete each experiment. These dielectric constants, reported in Figure 3.10-right, were measured at about 30 minute intervals with fluctuations averaging 2.1 % difference at room temperature (no temperature control, ~22 °C) and 0.9 % difference at 50 °C. Furthermore, as presented in Figure 3.11, the dielectric constant relative to particle size measured using the commercial BaTiO$_3$ in slurry is within the range of literature values reported using a similar evaluation method. [11, 12, 14, 17, 18, 100, 102, 103] It should be noted that different vol % and suspension solvents are shown to have a negligible effect on the measured BaTiO$_3$ dielectric constant for this method; therefore, it is reasonable to make this relative comparison based primarily on particle size. The measured T$_c$ of commercial Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ is about 25 °C as expected. The measured commercial Ba$_{1-x}$Sr$_x$TiO$_3$ powder EIS data is not shown.
Figure 3.10: (Left) Plot of dielectric constant vs. temperature comparing (solid) direct EIS measurements of pure PEG, (long dash) PEG contributions in mixed slurries of 5 vol % Ba$_{1-x}$Sr$_x$TiO$_3$ in PEG extracted by modeling, and (short dash) the pure PEG value as reported in literature. [117] Both commercial and synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ powders are represented in the mixed slurry data. Line colors are only to visually distinguish multiple experimental runs. (Right) Plot of dielectric constant vs. time for 5 vol % commercial Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ powder dispersed in PEG and held at constant temperature.

Figure 3.11: Comparison of the experimental dielectric constant for commercial BaTiO$_3$ to various values reported in literature. (Left) Data collected using similar measurement methods of BaTiO$_3$ powder at room temperature between $10^2$ to $10^6$ Hz with dispersions between 5 and 20 vol % in BOE and PC. (Right) BaTiO$_3$ data reported from literature and collected using different processing and measurement methods. The “powders” data points in the right graph are the same “literature” data points in the left graph. [11, 12, 14, 15, 17, 18, 27, 83, 84, 100, 118-125]
An EIS comparison of the synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ compositions is shown in Figure 3.12 for < 10 nm powders (either as-synthesized or minimally heat treated to 700 °C). Focusing on the synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$, the effects of both heat treatment controlled particle size and temperature are plotted in Figure 3.13. Separated temperature graphs from Figure 3.13 are given in the appendix for extended clarity.

Figure 3.12: Plots of dielectric constant vs. temperature for four compositions of synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ powders (< 10 nm) suspended by 5 vol % in PEG. Each line represents an EIS analysis of different batches of each composition. Literature $T_c$ values for sintered bulk samples of each composition are as follows: 50:50 (-23 °C), 65:35 (25 °C), 75:25 (59 °C), 80:20 (74 °C). [77]
Figure 3.13: EIS data compiled on synthesized $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$: (Top) dielectric constant vs. temperature sorted by particle size and (Bottom) dielectric constant vs. average crystallite diameter sorted by temperature. The data in the bottom graph is expanded in separate temperature graphs in the appendix.
Dielectric dissipation loss (D) is a ratio of energy lost/energy stored. Data for D vs. frequency as a function of temperature for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ particles ~ 16 nm diameter are given in Figure 3.14-left, with the inset showing a plot of ln (frequency at D$_{\text{max}}$) vs. inverse temperature for the determination of activation energy. The low frequency noise (< 10$^{3}$ Hz) is typical for measurements taken below 20 °C, particularly the large divergent peaks at the system resonance frequency of 300 Hz. Figure 3.14-right plots D vs. temperature at the frequency of 10 kHz for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ particles, comparing the effect of particle size. The activation energies from plots of frequency at D$_{\text{max}}$ vs. 1/T between 10 – 50 °C are listed in Table 3.4 for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ and commercial BaTiO$_3$.

Figure 3.14: (Left) Plot of dissipation vs. frequency for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ particles with an average crystallite diameter by XRD of 16.1 nm. Temperature increases 10 °C with each successive line, from 0 – 50 °C. (Inset) Plot of ln (frequency at D$_{\text{max}}$) vs. 1/T for activation energy comparing synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ and commercial BaTiO$_3$. (Right) Plot of dissipation vs. temperature at 10 kHz for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ particles comparing crystallite diameters.
Table 3.4. Calculated activation energies for synthesized $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ and commercial $\text{BaTiO}_3$

<table>
<thead>
<tr>
<th>XRD Crystallite Dia. (nm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>synth BST 65:35</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>26.6</td>
</tr>
<tr>
<td>comm BT ~100*</td>
<td>~100*</td>
</tr>
<tr>
<td></td>
<td>~100*</td>
</tr>
</tbody>
</table>

* Manufacturer reported particle diameter

Several surfactant/solvent systems were tested to produce stable monodispersions of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ particles for possible incorporation of synthesized particles into thin film polymer chemistry. [126] The surfactant/solvent system of 0.5M B2-MEP/MEK dispersed up to 5 wt% $\text{BaTiO}_3$ successfully as demonstrated in Figure 3.15. No ideal surfactant/solvent system was identified for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ particles.

Figure 3.15: (Left) Dispersion solutions having about 0.8 wt % synthesized $\text{BaTiO}_3$ particles suspended in 1 M surfactant in MEK. Surfactants are B2-MEP left and PA2-HME right. Stability after 3 days. (Right) Solution having about 5 wt % $\text{BaTiO}_3$ particles suspended in 0.5 M B2-MEP. Stability after 10 days.
Data on particle size and $T_c$ were initially collected using dynamic light scattering (DLS) and differential scanning calorimetry (DSC); however, the results from DLS were all inconclusive and are not presented here. The DSC results (data not shown) gave unreliable and very low intensity $T_c$ peaks, often undetectable for many samples. A $T_c$ near 127 °C for the commercial BaTiO$_3$ was observed which agrees with the literature [27]. The synthesized BaTiO$_3$ powders (~ 40 nm) returned a $T_c$ peak near 115 °C, suggesting that reducing the particle size depresses the $T_c$. However, this isolated result could not be repeated across other synthesized samples. It was elected to abandon this technique in favor of other more reliable characterization methods for $T_c$.

3.5 Discussion

The particle size effects on $\varepsilon_r$ are clearly seen in Figure 3.13. (Refer also to the appendix.) Decreasing the particle size consistently increases $\varepsilon_r$ for Ba$_{0.65}$Sr$_{0.35}$TiO$_3$. Especially noted are those particles < 10 nm having the highest $\varepsilon_r$, regardless of temperature, with $\varepsilon_r > 2500$ at room temperature and values exceeding even 8000 at > 40 °C. This compares well to 1 μm BaTiO$_3$ at room temperature where $\varepsilon_r$ commonly measures near 3000 – 4000 [94] and contrasts with Ba$_{1-x}$Sr$_x$TiO$_3$ for x ~ 0.35, where $\varepsilon_r$ ranges between 100 for a pressed pellet [127] to 600 for a thin film [128] at room temperature. Knowing the slurry measurement method compares well to literature for the commercial BaTiO$_3$, this indicates that under the right processing conditions Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ nanocrystals < 10 nm have a $\varepsilon_r$ comparable to micron BaTiO$_3$. The relative broadness of the $T_c$ and dissipation peaks presented here has been observed in other Ba$_{1-x}$Sr$_x$TiO$_3$ measurements and is attributed to small grain sizes. [129, 130]
The $\varepsilon_r$ measured in this work increases below the superparaelectric (SPE) size limit and this likely is related to the crystallinity in two manners. First, despite the predictions that tetragonality vanishes as the cubic core remains, the HR-TEM and Raman spectroscopy experiments in Figures 3.7, 3.8, and 3.9 prove tetragonal characteristics persist in Ba$_{1-x}$Sr$_x$TiO$_3$ below 10 nm. Second, the divergence of XRD (crystalline diameter) from TEM (particle diameter) in Figure 3.6 suggests that the nanoparticles synthesized here are single crystalline below 20 nm and polycrystalline above 20 nm. Consider the EIS measurements in Figure 3.13-top, which record the highest PE to FE transition $T_c$ peaks below 10 nm; yet as the particle size increases to 20 - 30 nm, the presence of a definite $T_c$ peak disappears. Moreover, a shift in $\varepsilon_r$ is noted in Figure 3.13-bottom, where $\varepsilon_r$ tends to plateau to 1000 - 2000 near diameters of > 15 to 20 nm for every temperature. This plateau is especially evident in the temperature separated graphs presented in the appendix. However, a visual analysis by TEM suggests all the synthesized nanoparticles, even those below 20 nm diameter, may be polycrystalline. A complete diffraction analysis to ascertain the single or poly-crystallinity of the synthesized particles has not been pursued at this time.

The highest dielectric constants are consistently achieved with potentially single crystal nanoparticles < 10 nm. In part, this may be due to increased transformation stress [83] as the elongation between cubic and tetragonal is constrained to one or few crystallographic directions in < 10 nm nanoparticles. This mechanism would be similar to how the lack of 90° twinning in single FE domain nanoparticles induces increased stress. Furthermore, this thesis hypothesizes that a < 10 nm single FE domain, single crystal nanoparticle will have relatively few unit cells in which to induce polarization, thereby reducing or eliminating hysteresis and maximizing the efficiency of the polarization response. Using the unit cell geometry for Ba$_{1-x}$Sr$_x$TiO$_3$ from
Table 3.3 and assuming ideal packing, it can be estimated a 10 nm particle would contain on the order of $10^3$ unit cells compared to a 1 μm particle which would contain $10^9$ unit cells. Current theory for 1 μm ideal, single FE domain crystals suggests the absence of adjacent antiparallel domains would permit bulk BaTiO$_3$ to feel higher local field effects, favoring complete polarization reversal; however, particles of this size are theorized to experience maximum hysteresis. [27] Still, it is known that any mechanism which restricts domain wall motion or domain wall nucleation decreases the dielectric loss, D. [93, 95, 129, 130] Decreasing the size of the particle reduces the motion of domain walls by increasing the relative ratio of grain boundaries to total grain volume. Further, reducing particle size limits the number of FE domains which can physically fit within each particle, so the < 10 nm particles are severely hampered in the nucleation of new domain walls.

This work had initially tested several nanoparticle syntheses for crystalline tetragonal Ba$_{1-x}$Sr$_x$TiO$_3$ nanoparticles. However, many of these approaches yielded cubic or amorphous powders which required post synthesis heat treatments, nullifying the small initial diameters. [99, 131, 132] The low temperature sol-gel synthesis [89, 90] successfully yields ferroelectric crystalline Ba$_{1-x}$Sr$_x$TiO$_3$ having the expected Ba:Sr ratio based on molar mixing calculations as evidenced by the recorded 2θ peak shift in Figures 3.2 and 3.3. Some of the observed $T_c$ peaks in Figure 3.12 do not agree with the recorded literature values for Ba$_{1-x}$Sr$_x$TiO$_3$. [77] The 50:50, the 75:25, and the 80:20 compositions are expected to fall outside the 0 – 50 °C measurement range, so a real $T_c$ peak is not expected. The 65:35 composition is within the measured temperature range but returns a $T_c$ slightly higher than expected (measured $T_c$ ranges between 30 to 40 °C versus expected 25 °C). Since processing methods are known to affect dielectric properties of BaTiO$_3$ (Figure 3.11), it is noted that measurements here are taken directly from
dispersed, individual < 10 nm particles while reported literature values are taken from sintered solids and thin films. Furthermore, \( T_c \) variations on the order of 10 °C are common for BaTiO\(_3\) with higher \( T_c \) values being attributed to higher purity samples. [92]

When selecting PEG as the host liquid for EIS, possible effects the suspension medium can have on the measurement were considered, knowing higher dielectric response from the host liquid contributes to a higher overall dielectric constant. [102] Because the ratios of the high and low frequency dielectric responses are not affected [102], the relative contributions extracted for the oxide and liquid using the given modeling technique can be considered independent of the chosen suspension medium. [14, 17, 100, 102] Still, it has been found that low frequency responses (the oxide contribution) are more accurate for systems with higher dielectric contrast between the components. [133] Therefore, the relatively low values of \( \varepsilon_r \) for PEG (~ 20) relative to BOE (~ 50) and PC (~ 100) over the same temperature range proved ideal for measuring and extracting separate capacitance and dielectric constants for each slurry component. (See Figure 3.10; BOE and PC data are not shown.) However, the host liquid prevents the extraction of meaningful values for D from the slurries. Over all measured frequencies, the dielectric losses in the slurry are dominated by the lossy nature of the liquid [15] and relative overwhelming quantity (95 vol %). This is especially evident from the high magnitude of the calculated values for D as seen in Figure 3.14. Reported values for D at 10 kHz for BaTiO\(_3\) are orders of magnitude lower, usually ~0.09. [124] Furthermore, the values calculated here for D increase as particle size decreases. This is opposite of what was anticipated. The theory proposed in this thesis ties an increase in dielectric constant with a reduction or elimination of hysteresis and dielectric losses as the particle sizes and FE domains are reduced to < 10 nm. The observed inverse behavior of D with particle size is likely due to the increased surface to volume ratio of
the smaller nanoparticles. The smaller nanoparticles experience the greatest relative influence of the surrounding lossy liquid, leading to an overall increase in D as particle size decreases.

The presence and ease of motion of oxygen vacancies and domain walls are mechanisms for dielectric loss in BaTiO$_3$ and Ba$_{1-x}$Sr$_x$TiO$_3$. [95, 129, 130] The calculated activation energies are consistent with each other, regardless of particle size (~ 0.30 eV), but lower than other reported dielectric loss activation energies with 0.41 eV reported for BaTiO$_3$ in polymer composite [134] and 0.47 eV for bulk BaTiO$_3$ [95]. Once again, this may be due to the nature of taking EIS measurements on nanoparticles in the slurry medium. The liquid contribution to D overwhelms the total system losses, lowering the energy necessary to activate measured dielectric loss. The larger (~ 100 nm) commercial BaTiO$_3$ particles have the same activation energy as the smaller (~ 10 – 30 nm) synthesized Ba$_{1-x}$Sr$_x$TiO$_3$ in Table 3.4 despite knowing the mechanisms behind dielectric loss have particle size dependence. This can be explained through their similar loss environments. Since the lossy liquid makes up a majority (95 vol %) of all measured slurries, similar losses are activated and measured for the total system regardless of oxide particle size.

Despite the relative success in producing stable monodisperse suspensions of BaTiO$_3$ particles in the B2-MEP/MEK system (Figure 3.15), all tested suspensions failed to lead to polymer/ceramic composites. Attempts to incorporate BaTiO$_3$ particle suspensions into ferroelectric polymer films (work done by Chaokun Gong) indicated the ceramic particles did not stabilize uniformly within the polymer network but settled out during polymerization. This resulted in a layer of BaTiO$_3$ particles on one surface of the films rendering them unsuitable for dielectric measurements. Introducing Sr into BaTiO$_3$ particles altered their zeta potential, making the B2-MEP/MEK system ineffective for stably suspending Ba$_{1-x}$Sr$_x$TiO$_3$. Given the
insufficiency of these dispersions to incorporate BaTiO\(_3\) with polymer chemistry, designing a surfactant/solvent system for Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) was not pursued.

### 3.6 Future Work

A theory for ferroelectric properties for Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) particles below 10 nm, especially as it relates to reduced hysteresis and single crystallinity, is not yet complete. Further work to clarify the mechanisms behind the high dielectric constant observed in < 10 nm particles should take how stresses behave in this size regime into consideration. Collecting diffraction data on the synthesized Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) nanoparticles would establish their crystalline nature – single or poly – with respect to particle size. Measurements that could determine hysteresis or dielectric loss directly from the nanoparticles without interference from a lossy suspension fluid would prove illuminating; particularly for comparison to losses in sintered bulk or thin film Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) structures.

### 3.7 Conclusions

Tetragonal structure and ferroelectric characteristics have been observed in Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) nanoparticles < 10 nm, below the well-known superparaelectric limit, using Raman and EIS spectroscopy taken directly on individual nanoparticles. Decreasing the particle size of Ba\(_{0.65}\)Sr\(_{0.35}\)TiO\(_3\) below 20 nm tends to increase the measured \(\varepsilon_r\) up to 50 °C, with the highest \(\varepsilon_r\) exceeding even 10000 above 40 °C and having a \(\varepsilon_r > 2500\) at room temperature, which is comparable to “bulk” BaTiO\(_3\). A proposed mechanism relates the increased \(\varepsilon_r\) to increased
structural stress. Furthermore, reducing the diameter < 10 nm restricts domain wall motion and nucleation therefore minimizing dielectric losses. Nanoparticles < 10 nm may even be single crystalline having a single FE domain which would theoretically eliminate hysteresis losses due to lack of adjacent antiparallel domains.
Chapter 4: Enhanced Ionic Conductivity with Mixed Nanoparticles

4.1 Introduction

Making improvements in electrochemical energy storage devices, such as solid oxide fuel cells (SOFC), may be accomplished by enhancing ionic conductivity through the oxide components. A common electrolyte material used in SOFCs is yttria-stabilized zirconia (YSZ). It has been well documented that epitaxial heterostructures of SrTiO$_3$ (STO) with YSZ result in large increases in interfacial ionic conductivity — up to eight orders of magnitude at room temperature. [28] Although significant work has been done with STO/YSZ thin films, the question remains whether the interfacial conductivity enhancement persists in other composite structures. Using the well-mixed powder processing techniques developed during the MMC project from Chapter 2, powder pellets of STO and YSZ, both pure and mixed, are pressed and sintered. An electrochemical impedance spectroscopy (EIS) procedure was developed to reliably measure resistivity and activation energy of these bulk materials between 250 – 600 °C, especially in order to compare particle size effects of YSZ nanoparticles from ~30 to < 5 nm diameter.

4.2 Experimental

4.2.1 SrTiO$_3$ and YSZ Powders

Commercial STO powder (~100 nm, 99.95 %) was obtained from Inframat. Several batches of YSZ were provided by the Airforce (AF) as designated in Table 4.1. As needed, the
relative mole % of Y$_2$O$_3$ to ZrO$_2$ in YSZ will be reported as the “x” in “YSZ x %” in this thesis. Synthesized YSZ nanoparticles were prepared following a solvothermal process [135] for 2.5, 5, and 8 mol% yttria compositions. Zirconyl chloride octahydrate (ZrOCl$_2$·8H$_2$O) was obtained from Alfa Aesar, yttrium chloride (YCl$_3$) from Acros Organic, and ethanol and isopropanol from Sigma Aldrich. ZrOCl$_2$ is dissolved in an 80v/20v solution of ethanol/isopropanol in a 0.05M concentration. YCl$_3$ is also dissolved in the solution, calculated based on the desired mol% of Y$_2$O$_3$ relative to the ZrO$_2$ in the final product. The solution was stirred at room temperature for 24 hrs and then heated at 200 °C for 24 hrs in a Teflon lined acid digestion reaction vessel (Parr Instrument) in open atmosphere. YSZ precipitates were washed twice with ethanol and then dried at room temperature. This synthesis is easily scaled up by adjusting the initial mL of ethanol/isopropanol solution and limited only by the size of the Teflon reaction vessel (45 or 125 mL). Several batch calculations are given in Table 4.2. All STO and YSZ powders were characterized using XRD, SEM, and Archimedes density principles.

Table 4.1. YSZ powders as provided by the Airforce

<table>
<thead>
<tr>
<th>As-Received Designation</th>
<th>Abbreviation Used</th>
<th>Crystallite dia. by XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ 3% 40390N-9502 Inframat 30 – 60 nm</td>
<td>YSZ 9502</td>
<td>10.0 ± 2.2</td>
</tr>
<tr>
<td>YSZ 8% MKN-8Y5Z-050 MKNano 50 nm</td>
<td>YSZ MKN</td>
<td>21.8 ± 2.5</td>
</tr>
<tr>
<td>YSZ 8% 40390N-8601 Inframat 30 – 60 nm</td>
<td>YSZ 8601</td>
<td>12.8 ± 1.6</td>
</tr>
<tr>
<td>YSZ 8% 5933ZS nanostructured 20 – 30 nm</td>
<td>YSZ 5933</td>
<td>12.8 ± 0.9</td>
</tr>
</tbody>
</table>
4.2.2 Powder Pressing and Sintering

STO and YSZ mixed powders were prepared by hand mixing and grinding dry powder for 10 minutes in 50w/50w and 80w/20w ratios, depending on the YSZ particle diameter. See section 4.2.6 for ratio calculations. Ball mill tumbling resulted in immediate agglomeration and compacting against the vial walls and was not used for this preparation. Pure STO, YSZ and mixed powders were pressed in a 7.93 mm ID stainless steel die to 900 MPa using a Carver Model M hydraulic press at 0.2 to 0.4 g powder each, then fired at 5 °C/min to 1000 °C for 30 min (for YSZ) or 1400 °C for 1 hr (for STO). All sintered samples were characterized by Archimedes density principles and ionic conductivity. Some samples were cross-sectioned and analyzed using SEM.

4.2.3 Preparing Samples for EIS Measurements

High service temperature Ag paste (16047, Ted Pella) was spread over both sides of a sintered sample and cured at 100 °C for 2 hrs as shown in Figure 4.1. Covering the entire cylindrical surface ensured unhindered conductivity across a known geometry. Care was taken
to ensure Ag paste did not overflow the edges. These samples were loaded into the furnace stage assembly shown in Figure 4.2, where the sample is sandwiched between two Pt mesh sheets and cradled within a non-conducting Macor holder (McMaster-Carr) to prevent shorting across the Pt mesh layers. A non-conducting ceramic adhesive (16026-10, Ted Pella) was spread and cured over key parts of the stage assembly to prevent shorts. The Pt mesh sheets were soldered to two Pt wire leads which are fed to the outside of the furnace assembly and attached to the impedance analyzer. The whole assembly was clamped to an alumina stage with two Macor planks and lowered into a top loading tube furnace. This set up allows for a complete electrical circuit to be run through the sintered samples under controlled temperature. The Pt wire lead and mesh sheets preparation was accomplished with aid from Nicholas Ware.

Figure 4.1: Sintered YSZ 8601 sample with Ag paste cured on the surface.
Figure 4.2: (Left) Sintered sample with Ag electrode coating cradled in Macor holder and sandwiched between Pt mesh. (Right) Sample assembly clamped between two Macor planks and secured in place on the alumina stage.

4.2.4 Phase Analysis of SEM Images

Backscatter SEM images were analyzed using image processing software for relative phase ratios. For each sample 11 images were collected from different regions of the sample with magnifications ranging between 1.3k and 40k. For each image a pixel selection tolerance was set to produce an ideal dark/light pixel histogram, giving a total count for dark (STO phase) and light (YSZ phase) pixels. This procedure was repeated for each image 2 – 4 times to balance out pixel selection differences. All image pixel count analyses were averaged for each sample image and these averages combined to yield a total sample dark/light pixel ratio average. The tolerance was set to avoid selecting pore regions in the dark pixel count.
4.2.5 Characterization and Instrumentation

Powder XRD was performed on a MiniFlex II, (Rigaku) (CuKα, λ = 1.54 Å) using a Gonio (θ/2) scan mode under ambient temperature and pressure. The scanning step size was 0.05 in 2θ. Estimates of apparent crystallite size, ε, were calculated using Scherrer’s equation as expressed in Equation 1.

SEM was performed using a Nova Nano 230 SEM (FEI) operating at 10 to 15 keV in secondary electron or backscatter modes. Sintered samples were cross-sectioned on a Model 650 low speed diamond saw (South Bay Technology) and polished by standard metallographic polishing procedures. Grain boundary etching was attempted by a 2 – 5 min dip in concentrated phosphoric acid at 180 °C [136] and rinsed with either water or acetic acid. SEM was collected with the aid of Danielle Casillas.

Density was measured using an Excellence XP/XS precision balance density kit (Mettler Toledo) following the same procedure outlined in section 2.2.6 with Equations 4, 5, and 6. TEM was collected on a JEM1200-EX (JEOL) operating at 80 kV with samples prepared on a copper mesh grid (Ted Pella).

EIS was collected using a Solartron 1287 potentiostat and Solartron 1252a function generator (Solartron Analytical) or a VMP3 Multi Potentiostat (Bio Logic). The potenti EIS program sweeps frequencies from $10^{-1}$ to $10^{5}$ Hz under controlled voltage (10 mV). A base EIS measurement was taken at room temperature, then at 50 °C increments between 250 – 600 °C with temperatures equilibrating for 30 min before each measurement. Data were analyzed using ZView software (Scribner Associates, Inc).
4.2.6 Calculations

Determining ideal starting ratios for mixing STO and YSZ powder assumes spherical particles and perfect packing density of a single layer of YSZ on the STO surface. As given in the results, the particle diameters are 70 nm for STO by SEM and 4 or 13 nm for YSZ by XRD. The number of YSZ particles on the STO was first estimated by dividing the surface area of the STO by the cross sectional area of the YSZ and rounding to the nearest whole number. The volume ratio of the single STO particle to the total number of YSZ particles was then calculated and converted to a volume % and finally to a weight %. Calculation results are given in Table 4.3.

Table 4.3. Calculations for ideal weight % of STO:YSZ dependent on YSZ particle diameter

<table>
<thead>
<tr>
<th>STO dia. (nm)</th>
<th>YSZ dia. (nm)</th>
<th># YSZ particles on STO surface</th>
<th>Vol % STO</th>
<th>Vol % YSZ</th>
<th>Wt % STO</th>
<th>Wt % YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>4</td>
<td>1225</td>
<td>81.4</td>
<td>18.6</td>
<td>78.9</td>
<td>21.1</td>
</tr>
<tr>
<td>70</td>
<td>13</td>
<td>116</td>
<td>57.4</td>
<td>42.6</td>
<td>53.5</td>
<td>46.5</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>22</td>
<td>36.6</td>
<td>63.4</td>
<td>33.0</td>
<td>67.0</td>
</tr>
<tr>
<td>70</td>
<td>50</td>
<td>8</td>
<td>25.5</td>
<td>74.5</td>
<td>22.6</td>
<td>77.4</td>
</tr>
</tbody>
</table>

In modeling EIS data, the circuit diagram shown in Figure 4.3 was used to output values of primary resistance (R1) and secondary resistance (R2). R1 accounts for resistance across the sample while R2 accounts for contact resistance between the sample and the analyzer.
Figure 4.3: (a) Equivalent circuit model for EIS measurements taken on YSZ and STO samples. (b) Nyquist plot of EIS data taken between 500 and 600 °C for a sintered YSZ 8601 sample. The model fit semicircle overlapping the 500 °C data was generated using the equivalent circuit model from (a).

The sum resistance, $R_1 + R_2$, returns the total resistivity $\rho$ (in $\Omega\cdot m$) using the calculation shown in Equation 14 where $A$ is the surface area and $t$ is the thickness of the sample.

$$\rho = \frac{R \times A}{t} \quad (14)$$

Activation energy, $E_a$, for ionic conduction was determined from the slope of log $\rho$ vs. inverse temperature ($1/T$) as determined from Equation 15, where $\rho_0$ is the pre-exponential factor and $k$ is the Boltzmann constant.

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \quad (15)$$
4.3 Results

All STO and YSZ powders are confirmed phase pure by XRD as given in Figure 4.4. The commercial STO powder has uniform spherical particles of 70 ± 16 nm as shown in Figure 4.5. Ethanol suspensions of STO, sonicated for 1.5 hrs, remained stable for up to 3.5 hrs. The Airforce (AF) provided YSZ powders have crystallite diameters about 10 – 20 nm by XRD as listed in Table 4.1. All batches of the synthesized YSZ have average crystallite diameters of 4.0 ± 0.3 nm by XRD and 5.0 ± 0.8 nm diameter by TEM as shown in Figure 4.5. All synthesized batches gave between 60 – 90 % theoretical yields.
Figure 4.5: (Left) Secondary electron SEM micrograph of commercial STO powder following ethanol suspension and drying. (Right) TEM micrograph of as-synthesized YSZ 5% nanoparticles, taken by Enrico Della Gaspera.

Pressed and sintered pellets of 1.2 – 2.2 mm thickness were produced with % theoretical density and % open porosities as given in Table 4.4. Only samples > 1mm thick were determined to be suitable for measurement purposes since thinner pellets shorted through the thickness of the sample.

Secondary electron SEM of a 50w/50w STO/YSZ 5933 sample sintered at 1400 °C and etched in phosphoric acid is shown in Figure 4.6. The lighter textured regions are identified as STO and the darker blurred regions as YSZ based on comparison to surfaces of etched samples of pure STO and pure YSZ (not shown). Unetched 50w/50w and 80w/20w samples were analyzed by backscatter electron SEM for phase distribution comparisons in Figure 4.7. Here light regions are YSZ phase and dark regions STO phase as confirmed by an electron dispersive X-Ray spectroscopy (EDS) detector. The phase distribution determined by image analysis is reported in Table 4.5.
Table 4.4. Measured % theoretical density and % open porosity averages for various compositions of STO and YSZ samples comparing sintering conditions

<table>
<thead>
<tr>
<th></th>
<th>1000 °C 30 min</th>
<th></th>
<th>1400 °C 1 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% theoretical</td>
<td>% open porosity</td>
<td>% theoretical</td>
</tr>
<tr>
<td>density</td>
<td>density</td>
<td></td>
<td>density</td>
</tr>
<tr>
<td>Commercial STO</td>
<td>--</td>
<td>--</td>
<td>84.8 ± 2.9</td>
</tr>
<tr>
<td>Airforce YSZ</td>
<td>56.6 ± 7.0</td>
<td>40.6 ± 7.6</td>
<td>--</td>
</tr>
<tr>
<td>Synthesized YSZ</td>
<td>79.0</td>
<td>12.1</td>
<td>91.9</td>
</tr>
<tr>
<td>50w/50w</td>
<td>54.4</td>
<td>38.3</td>
<td>87.2 ± 0.6</td>
</tr>
<tr>
<td>Comm STO/AF YSZ</td>
<td>--</td>
<td>--</td>
<td>86.8</td>
</tr>
</tbody>
</table>

Figure 4.6: Secondary electron SEM micrograph of 50w/50w STO/YSZ 5933 sintered at 1400 °C for 1 hr and etched in phosphoric acid.
Figure 4.7: Backscatter electron SEM micrographs of (Left) 50w/50w STO/YSZ 5933 and (right) 80w/20w STO/synth YSZ 8%.

Table 4.5. Phase analysis by dark/light pixel ratios

<table>
<thead>
<tr>
<th>STO/YSZ w/w</th>
<th>Ideal STO/YSZ volume ratio</th>
<th>SEM dark/light pixel average</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>1.20</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>80/20</td>
<td>4.56</td>
<td>6.1 ± 1.4</td>
</tr>
</tbody>
</table>

EIS measurements yielded resistivity, $\rho$, as measured between 250 – 600 °C and plotted in Figures 4.8 and 4.9. Figure 4.10 demonstrates the determination of activation energy by plotting log $\rho$ vs. inverse temperature. Values for resistivity, activation energy, and % theoretical density are given in Table 4.6. All ranges for activation energy are 250 – 600 °C except where noted.
Figure 4.8: Plot of measured resistivity vs. temperature between 400 and 600 °C for synthesized YSZ (solid), Airforce YSZ (short dash), 80w/20w STO/synthesized YSZ (dot-dash), and 50w/50w STO/Airforce YSZ (long dash) from data listed in Table 4.6.
Figure 4.9: Zoomed region plot of Figure 4.8. Measured resistivity vs. temperature between 400 and 600 °C for synthesized (solid) and Airforce (short dash) YSZ.

Figure 4.10: Plot of log $\rho$ vs. inverse temperature for two sintered samples. Slope from a best fit line is used to calculate the given activation energies, E (eV).
Table 4.6. Measured resistivities, calculated activation energies, and measured % theoretical densities of samples sintered 1400 °C for 1 hr

<table>
<thead>
<tr>
<th></th>
<th>Resistivity (Ω·m)</th>
<th>Activation Energy (eV)</th>
<th>% Theo. Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 °C</td>
<td>350 °C</td>
<td>400 °C</td>
</tr>
<tr>
<td>YSZ 5933 (red)</td>
<td>7.1E+04</td>
<td>9.5E+03</td>
<td>3.5E+03</td>
</tr>
<tr>
<td>YSZ 8601 (orange)</td>
<td>3.5E+04</td>
<td>1.3E+04</td>
<td>3.6E+03</td>
</tr>
<tr>
<td>YSZ MKN (purple)</td>
<td>2.8E+04</td>
<td>7.6E+03</td>
<td>2.9E+03</td>
</tr>
<tr>
<td>50/50 STO/YSZ 8601 (green)</td>
<td>3.6E+04</td>
<td>1.7E+04</td>
<td>6.0E+03</td>
</tr>
<tr>
<td>50/50 STO/YSZ 5933 (blue)</td>
<td>2.9E+04</td>
<td>4.9E+04</td>
<td>6.9E+03</td>
</tr>
<tr>
<td>Synth YSZ 8% (blue)</td>
<td>1.2E+03</td>
<td>2.0E+02</td>
<td>8.6E+01</td>
</tr>
<tr>
<td>Synth YSZ 8% (green)</td>
<td>1.2E+03</td>
<td>2.9E+02</td>
<td>8.9E+01</td>
</tr>
<tr>
<td>80w/20w STO/synth YSZ 8% (purple)</td>
<td>3.2E+04</td>
<td>1.3E+04</td>
<td>6.5E+03</td>
</tr>
<tr>
<td>80w/20w STO/synth YSZ 8% (red)</td>
<td>5.2E+03</td>
<td>3.1E+03</td>
<td>1.5E+03</td>
</tr>
</tbody>
</table>

(Line colors corresponding to Figures 4.8 and 4.9 are given in parenthesis.)

*Activation energy slope taken between 300 to 600 °C

4.4 Discussion

Peak ionic conductivity for YSZ has been identified for the 8 mole % composition [137] with reported activation energies generally on the order of 1.1 eV for pure bulk YSZ. [28] Typical activation energies for pure bulk STO are reported as 0.85 to 1.2 eV and values of 0.6 to 0.7 eV are reported for STO/YSZ thin films. [137-139] From Table 4.6, the calculated activation energies are ~ 50 - 70 % lower than the reported STO/YSZ literature values. The increased and more homogenously distributed interphase contact between STO and YSZ of these
mixed powder samples versus the layered heterostructures of the STO/YSZ thin films may be contributing to the reduced activation energies. The mixed powder samples also show lower activation energies relative to the pure YSZ samples, ~ 15% lower for the AF YSZ and ~ 47% lower for the synthesized YSZ. This indicates that bulk sintered structures of mixed STO/YSZ powders retain the enhanced ionic conductivity of STO/YSZ thin film structures and that reducing the particle size improves this effect.

Reducing the particle size of pure YSZ leads to lower resistivities at all temperatures. The synthesized YSZ samples (~ 4 nm) have resistivities 1 to 2 orders of magnitude lower compared to the AF YSZ samples (≥ 13 nm) as seen in Table 4.6 and Figures 4.8 and 4.9. The incongruity of measured resistivity for the 80w/20w STO/YSZ samples is likely related to incomplete phase mixing and closed porosity. Sample density and degree of sintering affect ionic conductivity, especially the grain boundary conductivity [140], since structural defects like pores interrupt the ionic conduction path through the material. [141]

Reducing particle size also improves sintering. While typical sintering temperatures are > 1200 °C for bulk YSZ, nanometer diameters have been shown to sinter as low as 1000 °C [141, 142], which was confirmed here. From the density data in Table 4.4, at 1000 °C the pure YSZ samples sintered with higher % theoretical density and lower % op using the smaller diameter synthesized YSZ. Increasing the sintering temperature improved density properties of both pure and mixed powder samples due to more complete sintering. However, particle size reduction between the mixed STO/YSZ composites appears to have no effect on measured density when sintering at 1400 °C. Again, this may be due to the inhomogeneous phase mixing in the 80w/20w STO/YSZ.
The backscatter images in Figure 4.7 show the phases are homogeneously distributed in the 50w/50w STO/YSZ sample while significant phase agglomeration is observed in the 80w/20w STO/YSZ sample. This agglomeration detrimentally affects the density and sintering of YSZ [143] and is known to be more prevalent with reduced particle size. The phase ratio analysis in Table 4.5 shows a relatively low standard deviation in the calculated pixel ratio of the 50w/50w STO/YSZ sample versus the 80w/20w STO/YSZ sample. This implies a relative increase of inhomogeneity between different regions analyzed from the 80w/20w sample. For both compositions the pixel ratio is high relative to the calculated volume ratio ideal, both by ~ 33%. However, this does not necessarily indicate that more STO phase is present than expected. The pixel ratio analysis is hindered in part by the prevalence of dark pore regions and by the limitations of using a cross-sectional analysis in comparison to a volume ratio. From SEM in Figures 4.6 and 4.7, it is also clear that significant closed porosity persists in all sintered materials. Although the STO surfaces visibly etched in phosphoric acid, no grain boundaries can be clearly identified in the resulting texture for either phase. Furthermore, no rinsing technique consistently rid the surface of epoxy residue which dissolved into the etching solution and redeposited on the sample. Efforts to reveal the YSZ and STO grain boundary structures were abandoned in favor of the phase information yielded by backscatter SEM.

4.5 Conclusions and Suggestions for Future Work

EIS measurements suggest the ionic conductivity enhancement from mixing STO/YSZ persists in mixed powder bulk materials. Particle size reduction also contributes to a lower activation energy. The presented results are preliminary, with only 2 – 3 samples of each
composition measured for EIS. Repeating the measurements with a larger sample set is recommended. However, the current powder mixing and sintering process used here results in significant closed porosity in all materials and phase agglomeration with reduced particle size. Extremely high pressure sintering methods are being investigated by colleagues at the Airforce in order to produce fully dense, transparent sintered samples. These would have been ideal samples for EIS testing based on the original scope of the project. Furthermore, powder mixing and de-agglomeration may be improved by testing various solvents for dispersion and mixing of the STO and synthesized YSZ nanopowders. [143] The EIS procedure developed here should proceed with further testing on bulk STO/YSZ mixed powder composites after steps have been taken to reduce sample porosity and improve phase mixing.
Chapter 5: Conclusions

Effects of particle size and composition have been evaluated for three ceramic material systems. First, this research has shown that positive and negative thermal expansion materials can form composites having high thermal and electrical conductivities with predictable, low CTEs controlled easily by composition design. The powder processing and low temperature sintering methods used here, improved by reducing the particle diameter of the metal matrix, take advantage of homogenous, intimate phase mixing and more complete sintering to give more uniform material properties. These results with the Ag/ZrW₂O₈ system might be applicable to other MMC systems and could overcome common issues of thermomechanical stability in electronic device casings and heat transfer architectures.

Second, theories relating particle size to mechanisms of ferroelectric behavior in a common perovskite class ceramic has been extended to a new nanoparticle diameter threshold. Ba₁₋ₓSrₓTiO₃ nanoparticles < 10 nm diameter have been proven to retain their ferroelectric behavior below a previously defined superparaelectric size limit. These nanoparticles can be compositionally selected to have their peak dielectric constant (at T_c) near room temperature. Making high dielectric constant nanoparticles with reduced polarization losses will be crucial in developing high efficiency energy storage capacitors, especially as device applications require ever smaller components.

Third, a common solid electrolyte for electrochemical energy, STO/YSZ, which exhibits enhanced interfacial ionic conductivity for thin film heterostructures also displays improved ionic conductivity for mixed powder sintered pellets. Reducing the particle size of YSZ lowers activation energy for ionic conductivity in mixed powder composites and increases the sintered
density in pure phase composites. Expanding the architecture of this composite from thin film to mixed powder bulk pellets will expand potential for device applications. The advances made in understanding all of these three ceramic systems will contribute to improving ceramic composite design for many electronic device and energy storage applications.
Appendix

This appendix contains the EIS data in Figure 3.13 on synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$.

These plots of dielectric constant vs. average crystallite diameter separate the EIS data by every 5 °C for improved visualization.

Figure A1: Distinct temperature plots for every 5 °C between 0 – 50 °C of dielectric constant vs. average crystallite diameter for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$, presented as accompaniment to the data compiled in Figure 3.13
Figure A1 - Continued: Distinct temperature plots for every 5 °C between 0 – 50 °C of dielectric constant vs. average crystallite diameter for synthesized Ba$_{0.65}$Sr$_{0.35}$TiO$_3$, presented as accompaniment to the data compiled in Figure 3.13.
References


87