DEVELOPMENT AND CHARACTERIZATION OF HIGH TEMPERATURE, HIGH ENERGY DENSITY DIELECTRIC MATERIALS TO ESTABLISH ROUTES TOWARDS POWER ELECTRONICS CAPACITIVE DEVICES
A Dissertation in
Materials Science and Engineering

By
Dennis P. Shay
© 2014 Dennis P. Shay

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2014
The dissertation of Dennis P. Shay was reviewed and approved* by the following:

Clive A. Randall  
Professor of Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Michael A. Lanagan  
Professor of Engineering Science and Mechanics

Gary L. Messing  
Distinguished Professor of Materials Science and Engineering  
Head, Department of Ceramic Science and Engineering

Nikolas J. Podraza  
Assistant Professor of Physics, The University of Toledo  
Special Member

Susan Trolier–McKinstry  
Professor of Ceramic Science and Engineering

Suzanne Mohney  
Chair, Intercollege Graduate Degree Program in Materials Science and Engineering  
Professor of Materials Science and Engineering and Electrical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The maximum electrostatic energy density of a capacitor is a function of the relative permittivity ($\varepsilon_r$) and the square of the dielectric breakdown strength ($E_b$). Currently, state–of–the–art high temperature (>200 °C), SiC–based power electronics utilize CaZrO$_3$–rich NP0/C0G–type capacitors, which have low relative permittivities of $\varepsilon_r$ ~ 30–40, high breakdown strengths (> 1.0 MV/cm), and are chosen for their minimal change in energy storage with temperature. However, with operating temperatures exceeding the rated temperatures for such capacitors, there is an opportunity to develop new dielectric ceramics having higher energy densities and volumetric efficiencies at high temperatures (>200 °C) by utilizing higher permittivity dielectrics while maintaining high breakdown strengths via doping. The development strategy involves identifying binary linear dielectric compositions that combine medium permittivities with large band gaps, and either substituting end members or identifying doping strategies to minimize high temperature ionic conductivity, achieving large energy densities at elevated temperatures.

The solid solution behavior of Ca(Ti$_x$Zr$_{1-x}$)O$_3$ was characterized in order to determine the optimal composition for balancing permittivity and dielectric breakdown strength to obtain high energy densities at elevated temperatures. Characterization by X–ray diffraction (XRD) showed Vegard’s law behavior across the solid solution with minimal 2nd phases. Microstructural analysis showed little variation in grain size across the solid solution, with grain sizes on the CaTiO$_3$ – rich end of the composition range being ~2.0 – 3.0 μm. Room temperature relative permittivities also showed a linear trend across the solid solution, with permittivities increasing with increasing CaTiO$_3$ content. In order to mitigate ionic conduction, an investigation into various Mn doping concentrations on the Ti$^{4+}$ site using Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) was conducted to determine the optimum doping concentration for minimizing dielectric loss at elevated temperatures. It was determined that doping with 0.5 mol% Mn shows the earliest onset of densification during sintering in air and the lowest dielectric losses with increasing temperature.

To determine a Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition that will also minimize electronic or band conduction, the optical properties of the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ solid solution were investigated to identify a composition on the CaTiO$_3$ – rich end of the solid solution with a large band gap. Both ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis) and spectroscopic ellipsometry were utilized to determine the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ band gaps and optical properties. Both techniques yield an asymmetric Vegard’s law trend in the band gaps across the solid solution, with larger
band gaps weighed towards the CaZrO$_3$ – rich end of the solid solution. Band gaps on the CaTiO$_3$ – rich end of the solid solution ranged from 3.7 to 3.8 eV. Divided special range analysis of spectroscopic ellipsometry data was utilized to less ambiguously determine band gaps compared to UV–Vis, for which the analysis contains several assumptions. Additionally, the refractive index and optical dielectric constants were determined via ellipsometry and showed good agreement with calculated values.

The resistivity at 250 °C scaled with the band gap energy across the solid solution. Comparing the current–voltage (I–V) behavior at 250 °C for Ca(Ti$_{1-y}$Mn$_y$Zr$_{0.2}$)O$_3$ (CTZ + Mn) where $x = 0.7, 0.8, 0.9$, and $y = 0.005$, it was found that the Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ composition showed the lowest current density and a decrease in current density of 5 orders of magnitude compared to the un–doped composition. The Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ composition was selected for single layer, Pt buried electrode capacitor prototyping to evaluate high temperature electrical characteristics. Capacitors of un–doped CTZ were also prototyped to compare the high temperature electrical properties and to determine the effects of Mn doping on high temperature electrical performance.

Polarization–field (P–E) hysteresis measurements of CTZ showed a large increase in dielectric loss with increasing temperature, limiting the dielectric breakdown strength and recoverable energy density. When doped with Mn, CTZ + Mn showed a minimization of the temperature dependence of the breakdown strength, and maximum energy densities of 7.00 J/cm$^3$ at a $E_b$ of 1.1 MV/cm at room temperature and 5.36 J/cm$^3$ at $E_b$ = 1.0 MV/cm at 300 °C were observed. Impedance spectroscopy of the CTZ and CTZ + Mn dielectrics showed that doping with Mn resulted in a decrease in ionic conductivity and a subsequent decrease in electronic conductivity. To further increase the high temperature resistivity of the CTZ + Mn system, Zr was replaced with Hf to determine the effects of a heavier ion and higher band gap end member on the high temperature electrical properties.

Basic characterization of Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) showed similar characteristics compared to the CTZ system. High temperature impedance spectroscopy of CTH and CTH + Mn showed similar behavior to the CTZ and CTZ + Mn systems, but with overall decreases in ionic and electronic conductivity. Coupled with thermally stimulated depolarization current measurements (TSDC), oxygen vacancy migration and space charge conduction are dominant and could be minimized with Mn doping. Compared to CTZ +
Mn, CTH + Mn showed an additional decrease in current density at 250 °C by an order of magnitude. Systematic energy density characterization showed minimization of the temperature dependence of the dielectric breakdown strength in CTH + Mn, with a maximum energy density of 6.5 J/cm³ and 1.1 MV/cm observed at 300 °C.

To gain further insight into how aliovalent Mn controls high temperature conduction in the CTH + Mn system, capacitors were quenched from the sintering temperature and an impedance study was performed. It was observed that ionic conductivity was quenched in due to oxygen vacancies compensating Mn³⁺, and interfacial features were observed in impedance spectra due to double back–to–back Schottky barriers (depletion layers). As capacitors were re–oxidized, bulk resistivity increased while interfacial resistivity decreased. The hypothesis was supported by the application of dc bias during impedance measurements, which showed similar impedance behavior to the re–oxidation study with a redistribution of oxygen vacancies to the interfaces after the bias was removed.

In a final attempt to optimize the CTH + Mn system, a rare earth co–doping study with Mn and Mg was investigated to further minimize ionic conductivity and maximize high temperature energy densities. Co–doping CTH with Mg and Dy yielded the lowest conductivities observed in this work, and the least temperature dependence of conductivity up to 250 °C. Room temperature energy densities of ~10 J/cm³ were observed. However, due to grain sizes approaching 9.0 μm, prototyped single layer capacitors showed a large increase in dielectric loss with increasing temperature due to the minimal number of insulating grain boundaries per dielectric layer.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... ix

LIST OF TABLES ............................................................................................................... xxii

ACKNOWLEDGEMENTS ............................................................................................... xxiv

CHAPTER 1 MOTIVATION AND OBJECTIVES ............................................................... 1

1.1 Introduction ................................................................................................................... 1
1.2 Background .................................................................................................................. 1
1.3 Applications ............................................................................................................... 2
  1.3.1 Automotive .......................................................................................................... 3
  1.3.2 Aircraft ................................................................................................................ 3
  1.3.3 Deep Oil/Gas Extraction ...................................................................................... 4
  1.3.4 Renewable Energy .............................................................................................. 4
1.4 Capacitors for Power Electronics ............................................................................... 4
1.5 Materials for High Temperature, High Energy Density Capacitors ......................... 7
1.6 Material Development Rationale ............................................................................... 10

CHAPTER 2 EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES ................................................................................................................................. 19

2.1 Introduction ................................................................................................................ 19
2.2 Mixed Oxide Powder Processing .............................................................................. 19
2.3 Capacitor Quenching ................................................................................................. 25
2.4 X–Ray Diffraction .................................................................................................... 27
2.5 Dilatometry ............................................................................................................... 27
2.6 Scanning Electron Microscopy ................................................................................. 28
2.7 Transmission Electron Microscopy .......................................................................... 29
2.8 Capacitance and Dielectric Loss ............................................................................. 29
2.9 Optical Properties and Band Gap Determination .................................................. 29
  2.9.1 Ultraviolet–Visible Diffuse Reflectance Spectroscopy ........................................... 29
  2.9.2 Spectroscopic Ellipsometry ............................................................................... 30
2.10 Current – Voltage and Conductivity Measurements ............................................. 34
2.11 Polarization – Field Hysteresis Loops ................................................................... 36
2.12 Impedance Spectroscopy ....................................................................................... 39
  2.12.1 Measurement and Equivalent Circuit Modeling .................................................. 41
2.13 Thermally Stimulated Depolarization Current ...................................................... 47

CHAPTER 3 STRUCTURE – PROPERTY RELATIONSHIPS, SOLID SOLUTION TRENDS, AND ELECTRICAL CHARACTERIZATION OF Ca(Ti$_{1-x}$Zr$_x$)$_3$O$_9$ (CTZ) AND Ca(Ti$_{1-x}$Mn$_x$Zr$_{0.5}$)$_3$O$_9$ (CTZ + Mn) .................................................................................. 50

3.1 Introduction ................................................................................................................ 50
3.2 Background ............................................................................................................... 50
3.3 Ca(Ti$_{1-x}$Zr$_x$)$_3$O$_9$ (CTZ) and Ca(Ti$_{1-x}$Mn$_x$Zr$_{0.5}$)$_3$O$_9$ (CTZ + Mn) Crystal Structure and Microstructure ................................................................. 54
3.4 Electrical Characterization ........................................................................64
3.5 Optical Characterization and Band Gap Energy Determination ..................66
  3.5.1 Ultraviolet–Visible Diffuse Reflectance Spectroscopy Results ...............68
  3.5.2 Spectroscopic Ellipsometry Results .................................................73
3.6 Conductivity Measurements ......................................................................87
3.7 Polarization – Field Loops and Energy Density Evaluation .......................91
3.8 Impedance Spectroscopy ............................................................................94
3.9 Summary ..................................................................................................105

CHAPTER 4 INFLUENCE OF Hf SUBSTITUTION FOR Zr AND 0.5 MOL% Mn
DOPING ON THE ELECTRICAL PROPERTIES OF Ca(Ti0.8Hf0.2)O3 FOR HIGH
TEMPERATURE, HIGH ENERGY DENSITY APPLICATIONS ..............................108

4.1 Introduction .............................................................................................108
4.2 Background .............................................................................................108
4.3 Structure – Property Characterization of Ca(Tio.2Hfo.8)O3 (CTH) and
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................110
4.4 Electrical Characterization of Ca(Tio.2Hfo.8)O3 (CTH) and
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................116
4.5 Energy Density Evaluation of Ca(Tio.8Hfo.2)O3 (CTH) and
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................129
4.6 Summary ..................................................................................................134

CHAPTER 5 IMPEDANCE SPECTROSCOPY AND HIGH TEMPERATURE
CONDUCTIVITY IN QUENCHED AND SLOW–COOLED
Ca(Tio.795Mn0.005Hfo.2)O3 ..............................................................................137

5.1 Introduction .............................................................................................137
5.2 Background .............................................................................................137
5.3 Effect of Oxygen Vacancies on Conductivity in Ca(Tio.8Hfo.2)O3 (CTH) and
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................140
5.4 Effects of High Temperature Quenching on High Temperature Conductivity in
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................148
5.5 Effects of Re–Oxidation on Impedance Spectra of Quenched
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................154
5.6 Microstructural Analysis of Quenched and Slow–Cooled
  Ca(Tio.795Mn0.005Hfo.2)O3 (CTH + Mn) ................................................170
5.7 Summary ..................................................................................................177

CHAPTER 6 CHARACTERIZATION OF RARE EARTH AND Mn, Mg, or Mn + Mg
– DOPED Ca(Ti,Hf)O3 ..................................................................................180

6.1 Introduction .............................................................................................180
6.2 Background .............................................................................................180
6.3 Structure–Property Characterization of (Ca0.99RE0.01)(Ti0.795Mn0.005Hfo.2)O3 (CTH
  + X + RE) ..............................................................................................184
6.4 Electrical Characterization of (Ca0.99RE0.01)(Ti0.795Mn0.005Hfo.2)O3 (CTH + Mn +
  RE) ........................................................................................................189
6.5 Modification of Acceptor Dopants and Effects on Dielectric Properties in 
(Ca$_{0.99}$Dy$_{0.01}$)(Ti$_x$Hf$_{0.2}$)O$_3$ (CTH + X + Dy) ......................................................... 193
6.6 Summary ......................................................................................................................... 206

CHAPTER 7  FUTURE WORK AND SUMMARY OF DISSERTATION ................................. 209

7.1 Introduction ..................................................................................................................... 209
7.2 Chemical Powder Synthesis ......................................................................................... 209
  7.2.1 Oxalate and Hybrid Oxalate Processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ......................... 211
  7.2.2 Sol–Gel Processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ............................................................ 215
  7.2.3 Polymerized Complex Processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ................................. 220
7.3 Development of Non–Reducible, Non–Linear Dielectrics ............................................. 223
7.4 Further Optimization of Existing Compositions ............................................................. 226
7.5 Summary of Dissertation ............................................................................................... 227

REFERENCES ...................................................................................................................... 235

Appendix A  OPTICAL PROPERTIES BACKGROUND .................................................. 251
Appendix B  ELLIPSOMETRY MODELING PARAMETERS .............................................. 258
LIST OF FIGURES

Figure 1–1: Thermal image of high temperature low-temperature co-fired ceramic (LTCC) gate driver board used in SiC–based power electronics modules (Losetter et al., 2009). ..................................................................................................................2

Figure 1–2: Schematic diagram of common power electronics circuit (Mohan et al., 1989). Direct current bus capacitors = $C_{b}$, snubber capacitors = $C_{c}$, filter capacitors = $C_{r}, C_{f}$. .................................................................................................................................5

Figure 1–3: Field experience of a 3.5–MW photovoltaic (PV) plant separated into a) unscheduled maintenance events by subsystem and b) unscheduled maintenance costs by subsystem. PV = photovoltaic, ACD = anti-coincidence system, and DAS = data acquisition system (Wang et al., 2013; Moore et al., 2008). ..................................................6

Figure 1–4: Surveys on failures in power electronics systems among major components (Wang et al., 2013; Wolfgang, 2007). .................................................................................................................................6

Figure 1–5: Comparisons of non-linear dielectric materials, in terms of their polarization–electric field dependence .................................................................................................................................8

Figure 1–6: Thermochemical model prediction of breakdown strength as a function of dielectric constant ($k$) for materials having various values of $k$ (McPherson et al., 2003). ..................................................................................................................................................11

Figure 1–7: Trend in breakdown strength as a function of dielectric (relative) permittivity for various polymer and ceramic materials (Tuttle et al., 2008; Jain et al., 2002). The star indicates the region of dielectric breakdown and dielectric permittivity explored in this dissertation. Image courtesy of Srowthi Bharadwaja. .................................................12

Figure 1–8: Trend in breakdown strength with increasing band gap energy for various covalent, ionic–covalent, and polymer dielectric materials (Tan et al., 2007). .................................................................13

Figure 1–9: Temperature dependence of insulation resistance for base metal electrode (BME) C0G CaZrO3 – based multilayer ceramic capacitor (MLCC) compared to X8R MLCC (Xu et al., 2009). ..............................................................................................................14

Figure 1–10: Energy density at breakdown strength with increasing temperature for CaZrO3–based NP0/C0G CaZrO3 – based multilayer ceramic capacitor (MLCC) (Xu et al., 2009). ..................................................................................................................15

Figure 1–11: Schematic of state–of–the–art reliability design procedure for power electronic systems (Wang et al., 2013). ..........................................................................................................................16
Figure 1–12: Flow chart for developing new linear dielectric ceramics for optimized
energy densities at temperatures up to 300 °C, where \( E_g \) = band gap energy (eV), I–V = current–voltage, P vs. E = polarization vs. field, and \( \sigma \) = conductivity.

Figure 2–1: Thermal profile for determining calcination and sintering temperatures for
powders prepared by the mixed oxide method.

Figure 2–2: Flow chart for mixed oxide processing of bulk ceramic disks.

Figure 2–3: Flow chart for ceramic slurry preparation, tape casting, and single layer
capacitor with Pt internal electrode fabrication. MEK: methyl ethyl ketone, PVB:
polyvinyl butyral, BBP: butyl benzyl phthalate.

Figure 2–4: Capacitor process schematic for green body forming (left) and high
temperature processing (right) (Johanson Dielectrics, 2013).

Figure 2–5: Scanning electron microscope (SEM) images of electrodes and single layer
thicknesses for all capacitors prototyped in this research where CTH + Mn is
\( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Zr}_{0.2})\text{O}_3 \), CTH + Mn is \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) and CTH + Mg +
Dy is \( \text{(Ca}_{0.99}\text{Dy}_{0.01})\text{(Ti}_{0.795}\text{Mg}_{0.005}\text{Hf}_{0.2})\text{O}_3 \). The lighter contrast in the image
corresponds to the electrode and the darker contrast corresponds to the dielectric.

Figure 2–6: Quenching furnace used for quenching \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) with main
components labeled.

Figure 2–7: Precise rate – controlled high temperature dilatometer equipped with a
computer – aided design and gas control system.

Figure 2–8: \( \Delta \), \( \psi \), \( \epsilon_1 \) and \( \epsilon_2 \) for \( x = 0.8 \) \( \text{Ca(Ti}_{x}\text{Zr}_{1-x})\text{O}_3 \) derived from low and high photon
energy parameterizations using Sellmeier and CPPB oscillators respectively.

Figure 2–9: Experimental setup for high measuring high temperature current – voltage (I–V) and conductivity. DMM = digital multimeter.

Figure 2–10: Schematic of the circuit used in I–V measurements. The S is the switch, R is
resistor, \( I_m \) is the current measured, V is voltage, and C is the capacitor.

Figure 2–11: Example of bulk, Pt–electroded sample bottom (left) and masked top (right)
for multiple electrical measurements on a single sample. Samples had electrode
areas of 3.0 mm\(^2\) and thicknesses of 0.2 to 0.5 mm.

Figure 2–12: Experimental setup for measuring high temperature polarization – field (P–E) hysteresis loops.

Figure 2–13: Schematic of modified Sawyer – Tower circuit used for P–E measurements,
where V is voltage, C is capacitor, E is electric field, and R is resistor.

Figure 2–14: Schematic of how energy density and dielectric loss are quantified for linear
dielectrics.
Figure 2–15: Amplitude and phase relation between voltage ($U(t)$) and current ($I(t)$) of a dielectric material (After Alpha High Resolution Dielectric Analyzer User’s Manual). .................................................................40

Figure 2–16: Complex impedance and first step in the equivalent circuit model fitting for the high frequency feature of the un–doped $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) composition at 650 °C. $R =$ resistance and $C =$ capacitance ........................................42

Figure 2–17: Complex impedance and second step in the equivalent circuit model fitting for the high frequency feature of the un–doped $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) composition at 650 °C. $R =$ resistance, $C =$ capacitance, G.B. = grain boundary/interface, and C.P.E = constant phase element .........................43

Figure 2–18: Complex impedance and final step in the equivalent circuit model fitting for the high frequency feature of the un–doped $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) composition at 650 °C. $R =$ resistance, $C =$ capacitance, G.B. = grain boundary/interface, D.L = double layer and C.P.E = constant phase element ..................44

Figure 2–19: Complex impedance and first step in the equivalent circuit model fitting for the high frequency feature of the quenched $\text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CTH + Mn) composition at 675 °C. $R =$ resistance and C.P.E = constant phase element ..........45

Figure 2–20: Complex impedance and second step in the equivalent circuit model fitting for the high frequency feature of the quenched $\text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CTH + Mn) composition at 675 °C. $R =$ resistance, C.P.E = constant phase element, and G.B = grain boundary/interface ........................................46

Figure 2–21: Complex impedance and final step in the equivalent circuit model fitting for the high frequency feature of the quenched $\text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CTH + Mn) composition at 675 °C. $R =$ resistance, C.P.E = constant phase element, D.L = double layer and G.B = grain boundary/interface .................47

Figure 2–22: Graphical depiction of the temperature and electric field profile for the thermally stimulated depolarization current (TSDC) measurement. $T_p =$ poling temperature and $E_p =$ poling field .........................................................48

Figure 3–1: Schematic representation of objectives to establish routes towards high energy density linear dielectric materials..........................................................53

Figure 3–2: Indexed X–ray diffraction (XRD) patterns for $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) and $x = 0.7 \text{, 0.8, 0.9, } y = 0.005 \text{Ca(Ti}_{x-y}\text{Mn}_y\text{Zr}_{0.2})\text{O}_3$ (CTZ + Mn). The star in the $x = 0.7$ pattern denotes a $\text{ZrO}_2$ 2nd phase peak .........................................................55

Figure 3–3: Unit cell volumes across the entire un–doped $\text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) composition range measured from sintered and crushed bulk samples. The error bars were ± 0.01 Å and could not be seen on the plot .........................................................56

Figure 3–4: Schematic of an orthorhombic $\text{ABO}_3$ perovskite having the $\text{Pbnm}$ space group. Red spheres represent the A cation, yellow spheres represent B cations, and gray shaded planes represent oxygen octahedra ...........................................56
Figure 3–5: Scanning electron microscope (SEM) images of thermally etched grain microstructures for several un–doped, air–fired Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) compositions across the composition range..................58

Figure 3–6: Dilatation (shrinkage) curves for un–doped x = 0.8 Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) and x = 0.8, y = 0.005, 0.02, 0.03, and 0.04 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ (CTZ + Mn) in air and without glass frits as a sintering aid..................59

Figure 3–7: SEM images of thermally etched x = 0.8, y = 0.005, 0.02, 0.03, and 0.04 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ (CTZ + Mn) samples fired in air at 1300 °C..................61

Figure 3–8: SEM images of thermally etched x = 0.8, y = 0.005, 0.02, 0.03, and 0.04 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ (CTZ + Mn) fired at 1300 °C at pO$_2$ = 10$^{-11}$ atm..................62

Figure 3–9: Energy dispersive X–ray spectroscopy (EDS) images of air–fired x = 0.8 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ with a) y = 0.05 (0.5 Mn CTZ) b) y = 0.4 (4 Mn CTZ)..................63

Figure 3–10: Temperature coefficient of capacitance (TCC) and dielectric loss (tanδ) for x = 0.8 Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) and x = 0.7, 0.8, and 0.9, y = 0.005 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ (CTZ + Mn), from −50 to 150 °C at 1 kHz..................64

Figure 3–11: Room temperature relative permittivities a) across the un–doped Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ composition range with linear fit to show Vegard’s Law behavior and b) room temperature relative permittivities for x = 0.7, 0.8, and 0.9, y = 0.005 Ca(Ti$_{x}$Mn$_{y}$Zr$_{0.2}$)O$_3$ and compared to the un–doped compositions..................65

Figure 3–12: Tauc plots constructed to extract the indirect band gaps, $(F(R)hv)^{0.5}$, and direct band gaps, $(F(R)hv)^{2}$, from the zero–intercept of the linear portion of the curve at energies above the defect/Urbach tail for x = 0.7, 0.8, and 0.9 Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$. ........9

Figure 3–13: Direct and indirect band gap summary across the Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) composition range as extracted from Tauc plots constructed from UV–Vis measurements. Error bars for the direct band gap energy were included but were typically 0.01 eV and were smaller than the data points..........................70

Figure 3–14: a) Reflectance vs. photon energy and b) Tauc plot for un–doped x = 0.8 Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ and x = 0.8 Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ + 0.5 mol% Mn obtained from UV–Vis measurements.................................................................72

Figure 3–15: a) Absorption coefficient (α) vs. photon energy across the Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ composition range with emphasis on the defect tail trend and b) absorption coefficient vs. photon energy for the CaTiO$_3$ – rich compositions of the CTZ solid solution, with emphasis on the defect tails.............................73

Figure 3–16: Schematic of probable energy band gap and defect tail origin for a recombination process such that observed in CaTiO$_3$ and the Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) system as proposed by Pontes et al. (Pontes et al., 2002). .................................................................75
Figure 3–17: Absorption coefficient ($\alpha$) vs. photon energy for $x = 0.8$ Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ and $x = 0.8$, $y = 0.005$ Ca(Ti$_{1-y}$Mn$_y$Zr$_{0.2}$)O$_3$ with an inset plot of the same focusing on the comparison of absorption tails. ................................................................. 77

Figure 3–18: a) Modeled and inverted ellipsometry data for extinction coefficient $k$ (top) and refractive index $n$ (bottom) for $x = 0.8$ Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ (CTZ) and b) extinction coefficient $k$ (top) and refractive index $n$ (bottom) vs. photon energy across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range................................................................. 78

Figure 3–19: a) Refractive index vs. photon energy in the low energy transparent region across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range with model overlaid for several compositions and b) refractive index at 633nm (1.95eV) across Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range. Error bars were typically ± < 0.001 and could not be visible on the plot in b). ................................................................. 79

Figure 3–20: Calculated refractive index from the Gladstone–Dale relation and measured refractive index at 588 nm (helium arc) across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range. Error bars were typically ± < 0.001 and could not be visible on the plot in b). ................. 80

Figure 3–21: Comparison of optical relative permittivity obtained from ellipsometry and relative permittivity under dc bias at 1 kHz for Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ (CTZ).................................. 81

Figure 3–22: a) Absorption coefficient ($\alpha$) from which direct ($\alpha^0$) and indirect ($\alpha^{0.5}$) band gaps were determined across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ (CTZ) composition range and b) examples of linear regions from which the band gap was determined for $x = 0.8$ CTZ via ellipsometry................................................................. 82

Figure 3–23: Summary of direct and indirect band gaps, first direct transition obtained from the CPPB fit, and indirect band gaps from UV–Vis and ellipsometry across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range. Error bars are plotted but are not visible due to scaling. Standard deviations are found in Table 3–4. ................................................................. 83

Figure 3–24: Indirect band gaps obtained via UV–Vis diffuse reflectance spectroscopy and spectroscopic ellipsometry across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ solid solution with calculated asymmetric Vegard’s Law fits. ................................................................. 86

Figure 3–25: Resistivity at 250 °C and 1 kV/cm for several compositions across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range measured on bulk samples................................. 88

Figure 3–26: Calculated room temperature polarizabilities across the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ composition range using Eqns. 3–3 and 3–4. Error bars were on the order of ± 10$^{-3}$ and were smaller than the size of the data point. ................................................................. 89

Figure 3–27: Steady state resistivity at 250 °C and 1 kV/cm versus direct and indirect band gap energies for the Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ system measured on bulk samples............. 90

Figure 3–28: Ln(current density, $J$) vs. Ln(electric field) for $x = 0.8$ Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ and $x = 0.7$, 0.8, and 0.9, $y = 0.005$ Ca(Ti$_{1-y}$Mn$_y$Zr$_{0.2}$)O$_3$ at 250°C and a maximum electric field of 25 kV/cm measured on bulk samples................................................................. 91
Figure 3–29: Temperature evolution of P–E hysteresis loops for a) \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \) at 0.25\( E_b \) and b) \( x = 0.8, y = 0.005 \text{Ca(Ti}_{x-0.2}\text{Mn}_y\text{Zr}_{0.2})\text{O}_3 \) at 0.25\( E_b \) ............................................. 92

Figure 3–30: P–E hysteresis loops for single layer, air fired, Pt internal electrode capacitors of \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Zr}_{0.2})\text{O}_3 \) measured at room temperature and 300 °C having the highest energy densities ................................................................. 93

Figure 3–31: Room temperature P–E hysteresis loops for \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Zr}_{0.2})\text{O}_3 \) capacitors with Ni electrodes fired at 1200 °C in \( pO_2 = 10^{-11} \text{atm} \) followed by re-oxidation at 900 °C in \( pO_2 = 10^{-9} \text{atm} \) for a) 9 hours and b) 12 hours. .......................... 94

Figure 3–32: High temperature impedance spectra for a) \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \) (CTZ) and b) \( x = 0.8, y = 0.005 \text{Ca(Ti}_{x-0.2}\text{Mn}_y\text{Zr}_{0.2})\text{O}_3 \) (CTZ + Mn) measured from 600 to 700 °C. Samples were buried Pt electrode, single layer, air – fired capacitors ....... 95

Figure 3–33: Total ionic and electronic conductivity vs. 1000/\( T \) (K\(^{-1}\)) for \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \) (CTZ) (top) and electronic conductivity vs. 1000/\( T \) (K\(^{-1}\)) for \( x = 0.8, y = 0.005 \text{Ca(Ti}_{x-0.2}\text{Mn}_y\text{Zr}_{0.2})\text{O}_3 \) (CTZ + Mn) (bottom). ................................................. 97

Figure 3–34: Overlap of the imaginary part of the complex impedance (\( Z'' \)) and complex modulus (\( M'' \)) at 600, 625, 650, 675, and 700 °C for \( \text{Ca(Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3 \) (CTZ). The blue data represents the \( Z'' \) plot while orange data represents \( M'' \). ............................................. 98

Figure 3–35: Effective permittivity and dielectric loss (\( \text{Tan}\delta \)) vs. frequency for \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \) (CTZ) at 600, 625, 650, 675, and 700 °C. .................................................. 100

Figure 3–36: Grain boundary and double layer (electrode interface) thicknesses vs. temperature for \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \). .................................................................................. 102

Figure 3–37: Effect of dc bias on impedance spectra of a) \( \text{Ca(Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3 \) (CTZ) at 700 °C from 0.0 V to 1.0 V and b) 0.0 V comparison before and after all voltages were applied to \( x = 0.8 \text{Ca(Ti,Zr}_{1-x})\text{O}_3 \) (CTZ) ........................................... 104

Figure 4–1: X-ray diffraction patterns for \( \text{Ca(Ti}_{0.8}\text{Hf}_{0.2})\text{O}_3 \) (CTH) and \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) (CTH + Mn). Main diffraction peaks are indexed and the star denotes the location of the ZrO\(_2\) 2\(^{nd}\) phase peak. A more thorough indexing of all peaks can be found in reference to the \( \text{Ca(Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3 \) in Fig. 3–2. .................. 111

Figure 4–2: Grain microstructures from scanning electron microscopy for \( \text{Ca(Ti}_{0.8}\text{Hf}_{0.2})\text{O}_3 \) (CTH) (left) and \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) (CTH + Mn) (right). .............. 112

Figure 4–3: Absorption coefficient (\( \alpha \)) vs. photon energy for \( \text{CaZrO}_3 \) (CZ) and \( \text{CaHfO}_3 \) (CH) obtained from spectroscopic ellipsometry. ................................................................. 113

Figure 4–4: Defect tails in the absorption coefficient of \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) (CTH + Mn) and \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Zr}_{0.2})\text{O}_3 \) (CTZ + Mn) from spectroscopic ellipsometry. ........... 114

Figure 4–5: Comparison of \( \alpha^{0.5} \) and \( \alpha^2 \) from which the indirect and direct band gaps were determined for CTH, CTH + Mn, and comparison between \( \alpha^{0.5} \) and \( \alpha^2 \) for CTH + Mn and CTZ + Mn from spectroscopic ellipsometry. ......................... 115
Figure 4-6: Comparison of extinction coefficient and refractive index from spectroscopic ellipsometry for the CTH + Mn and CTZ + Mn compositions. ..............................................116

Figure 4-7: Temperature coefficient of capacitance (TCC) and dielectric loss (Tanδ) for Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) from −50 to 150 °C. ...............................................................117

Figure 4-8: Frequency dependence of the temperature coefficient of capacitance for Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) from −50 to 150 °C. ...............................................................118

Figure 4-9: Impedance spectra from 600 to 700 °C for a) Ca(Ti0.8Hf0.2)O3 (CTH) and b) Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn). ...............................................................118

Figure 4-10: Specific conductivities extracted from fitting the impedance spectra for Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn). ...............................................................119

Figure 4-11: Z’” and M” vs. frequency for un–doped Ca(Ti0.8Hf0.2)O3 (CTH) from 600 to 700 °C. ........................................................................................................121

Figure 4-12: Comparison of Z’” and M” vs. frequency for un–doped Ca(Ti0.8Zr0.2)O3 (CTZ) and Ca(Ti0.8Hf0.2)O3 (CTH) at 625 °C. ...............................................................121

Figure 4-13: Effective permittivity and dielectric loss (Tanδ) vs. frequency for Ca(Ti0.8Hf0.2)O3 (CTH) from 600 to 700 °C ...............................................................122

Figure 4-14: Grain boundary and double layer (electrode interface) thicknesses vs. temperature for Ca(Ti0.8Hf0.2)O3 (CTH). ...............................................................123

Figure 4-15: Comparison of the effective permittivity and dielectric loss (tanδ) vs. frequency from impedance spectroscopy for Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.8Zr0.2)O3 (CTZ) at 650 °C. ...............................................................124

Figure 4-16: Comparison of the conductivities extracted from impedance spectroscopy fitting between Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.8Zr0.2)O3 (CTZ) ...............................................................125

Figure 4-17: Thermally stimulated depolarization current (TSDC) measurements at 250 °C for Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) ...............................................................126

Figure 4-18: 250 °C current–voltage (I–V) leakage current results for a) Ca(Ti0.8Hf0.2)O3 (CTH) and b) Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn). ...............................................................127

Figure 4-19: Current density with increasing electric field at 250 °C for Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) and Ca(Ti0.795Mn0.005Zr0.2)O3 (CTZ + Mn) ...............................................................128

Figure 4-20: Summary of the polarization–field (P–E) loops for capacitors having the highest energy density at each temperature in a) Ca(Ti0.8Hf0.2)O3 (CTH) and b) Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn). ...............................................................129
Figure 4-21: Trend in energy density with increasing field for Ca(Ti$_{0.8}$Hf$_{0.2}$)$_2$O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) with the highest energy density at the breakdown strength. .......................................................... 131

Figure 4-22: Weibull breakdown plots for Ca(Ti$_{0.8}$Hf$_{0.2}$)$_2$O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) for a number of isothermal breakdown tests. Weibull parameters for CTH were 13.89, 8.15, 8.46, and 2.70 for 25, 100, 200, and 300 °C respectively. Weibull parameters for CTH + Mn were 24.49, 18.59, 17.02, and 17.87 for 25, 100, 200, and 300 °C respectively. .......................................................... 132

Figure 4-23: Comparison of P–E loops yielding the highest energy densities for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) and Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.02}$)$_2$O$_3$ (CTZ + Mn) at room temperature and 300 °C. .......................................................... 133

Figure 5-1: a) Temperature dependence of impedance spectroscopy for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) sintered at 1250 °C and pO$_2$ = 10$^{-11}$ atm followed by 6 hr reoxidation at 900 °C and pO$_2$ = 10$^{-9}$ atm and b) thermally stimulated depolarization current (TSDC) spectra at 250 °C for CTH + Mn fired under similar conditions. .......................... 141

Figure 5-2: Schematic of the procedure used to estimate TSDC peak activation energies, $E_a$ (after Levi, 2003). .......................................................................................................................... 142

Figure 5-3: Hypothetical temperature dependence of Mn$^{3+}$, Mn$^{4+}$, oxygen vacancies, and hole concentrations upon cooling from the sintering temperature based off of mass action equations derived for Fe–doped SrTiO$_3$ (Calculated plot courtesy of Russell Maier, Penn State, 2013 using the mass action constants of Moos et al., 1997). .............. 147

Figure 5-4: a) Impedance spectroscopy for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) quenched from 1250 °C and b) equivalent circuit modeling used to fit the data in a) at 675°C °C. R = resistivity, C.P.E. = constant phase element, G.B. = grain boundary/interface, D.L. = double layer. ........................................ 148

Figure 5-5: Schottky depletion model for the description of grain boundary interfaces in $p$–type SrTiO$_3$ (after Denk et al., 1997). .................................................. 150

Figure 5-6: Temperature dependence of $\varepsilon''$ and $\varepsilon''$ vs. frequency from 600 to 700 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) quenched from 1250 °C ........................................... 151

Figure 5-7: Conductivity summary obtained from fits to data in Fig. 3 for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) quenched from 1250 °C ........................................ 152

Figure 5-8: Evolution of impedance spectra over 12 hours in air of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) quenched from 1250 °C at a) 700 °C, b) 725 °C, and c) 750 °C. .......................................................... 156

Figure 5-9: Evolution of $\varepsilon''$ and $\varepsilon''$ vs. frequency at 725 °C over 12 hours during reoxidation for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.02}$)$_2$O$_3$ (CTH + Mn) quenched from 1250 °C. ............ 157
Figure 5–10: Bulk and grain boundary conductivity extracted from fitting the impedance model in Fig. 5–4b at a) all temperatures and b) 700 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C. .............................................................. 158

Figure 5–11: a) Normalized bulk ionic conductivity extracted from fitting impedance spectra over 12 hours during re–oxidation and b) effective diffusivities calculated from the normalized bulk ionic conductivity for quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn). .......................................................... 160

Figure 5–12: a) Impedance spectroscopy at 0 hours for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C contrasted with the spectra for the same samples heated to 1250 °C and slowly cooled to room temperature and b) comparison of impedance spectroscopy at 0 hours for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched and slow–cooled with un–doped Ca(Ti$_{0.8}$Hf$_{0.2})$O$_3$ at 700 °C. .......................................................... 161

Figure 5–13: Temperature dependence of $Z''$ and $M''$ vs. frequency for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) originally quenched from 1250 °C, then heated to 1250 °C in air and slowly cooled to room temperature. .................................................. 162

Figure 5–14: a) Voltage dependence of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C and b) comparison of 0.0 bias impedance spectra before collecting data with applied dc bias and after all voltages had been applied. ........................................... 163

Figure 5–15: a) Voltage dependence of conductivity from impedance modeling of dc bias impedance spectroscopy for grain boundary and bulk and b) voltage dependence of bulk capacitance with capacitances extracted from impedance modeling of dc bias impedance spectroscopy of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn). .................................................................................. 164

Figure 5–16: Voltage dependence at 0, 0.2, 0.4, 0.6, 0.8, and 1.0V of $Z''$ and $M''$ vs. frequency for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C measured by dc bias impedance spectroscopy at 700 °C. .......................................................... 166

Figure 5–17: a) TSDC of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C measured at 250 °C and b) current density during the poling time for the TSDC measurement. .................................................................................. 166

Figure 5–18: Comparison of 250 °C TSDC spectra for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C (green) and the same samples heated to 1250 °C and slow cooled in air (blue). Poling fields were 5, 10, and 15 kV/cm. ........................................... 168

Figure 5–19: Polarization – Field (P–E) loops at various temperatures for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C. Loops shown were measured at the last field sustained before breakdown. ........................................... 169

Figure 5–20: Transmission electron microscope (TEM) image of a single grain of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2})$O$_3$ (CTH + Mn) quenched from 1250 °C. The red circle denotes an inclusion or pseudo core–shell feature. Image courtesy of collaboration with Dr. Weiguo Quo, Penn State (2013). .......................................................... 171
Figure 5–21: Energy dispersive X-ray spectroscopy (EDS) of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) for the inclusion (core) and shell (main grain). ..172

Figure 5–22: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn). ......................................................... 173

Figure 5–23: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), zoomed in to emphasize the Mn peak................................................................. 173

Figure 5–24: TEM image of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) slowly cooled from 1250 °C. The red circles denote A) in grain and B) an inclusion or pseudo core–shell feature. Image courtesy of collaboration with Dr. Weiguo Quo, Penn State (2013). ...... 174

Figure 5–25: EDS analysis of slow–cooled Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) for the inclusion (area A) and shell (area B).................................................................................. 175

Figure 5–26: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of slow–cooled Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), zoomed in to emphasize the Mn peak................................................................. 175

Figure 5–27: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of slow–cooled Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), zoomed in to emphasize the Mn peak................................................................. 176

Figure 6–1: Goldschmidt tolerance factor calculations for A or B site occupation of rare earths in Ca(Ti$_{0.9}$Hf$_{0.2}$)O$_3$........................................................................................................ 181

Figure 6–2: Local atomic structures around dopants and VO in BaTiO$_3$. (a) GdBa–MgTi–VO, (b) GdBa–VO and (c) MgTi–VO. Arrows denote the shifts of GdBa (u1) and O neighboring to both MgTi and VO (u2) (after Honda et al., 2011)............................. 184

Figure 6–3: X-ray diffraction (XRD) patterns for (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm compared to Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn). ................................................................. 185

Figure 6–4: Calculated theoretical densities for (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm compared to Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn). ................................................................. 186

Figure 6–5: Scanning electron microscope (SEM) images of the grain microstructures of CTH + Mn + RE. Average grain sizes were measured to be 8.9, 8.7, and 7.7 μm for RE = Dy, Gd, and Sm respectively. ................................................................. 187

Figure 6–6: Absorption (α) spectra for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm obtained from spectroscopic ellipsometry. ................................................................. 188
Figure 6–7: Temperature coefficient of capacitance (TCC) and dielectric loss (tan\(\delta\)) from –50 to 150 °C for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)RE\(_x\)O\(_3\)) (CTH + Mn + RE) where RE = Dy, Gd, or Sm ...... 190

Figure 6–8: Variation in relative permittivity from –50 to 200 °C for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)RE\(_x\)O\(_3\)) (CTH + Mn + RE) where RE = Dy, Gd, or Sm ...... 191

Figure 6–9: Electric field dependence of current density obtained from current–voltage measurements (I–V) at 250 °C for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)RE\(_x\)O\(_3\)) (CTH + Mn + RE) where RE = Dy, Gd, or Sm. All currents were measured at steady state after 10 minutes of applied electric field. ..192

Figure 6–10: XRD patterns for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)) with major reflections indexed. A complete indexing can be found in Fig. 6–3. ........................................................................................................... 194

Figure 6–11: Comparison of refractive index for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)) from spectroscopic ellipsometry. ........................................ 194

Figure 6–12: Absorption spectra obtained from spectroscopic ellipsometry for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)). .................................................. 195

Figure 6–13: Temperature dependence of the relative permittivity and dielectric loss (tan\(\delta\)) from 0 to 150 °C for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)). .................................................. 196

Figure 6–14: Field dependence of current density at 250 °C for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)). .................................................. 197

Figure 6–15: Log conductivity vs. 1000/T for Ca(Ti\(_{1-x}\)Mn\(_x\)O\(_3\)) (CTH + Mn) compared to Ca(Ti\(_{1-x}\)Dy\(_x\)O\(_3\)) (CTH + Mn) where X = Mn\(_0.005\), Mn\(_0.005\), or (Mn\(_0.005\) + Mg\(_0.005\)) at 25 kV/cm for bulk samples. .................................................. 198

Figure 6–16: SEM image of single layer, Pt–electrode, air–fired, polished, and thermally etched (Ca\(_{1-y}\)Mg\(_y\)O\(_3\)) (CTH + Mg + Dy) single layer capacitor. Dielectric layer thicknesses ranged from 10–15 μm. .................................................. 199

Figure 6–17: Polarization vs. field loops for Ca\(_{0.99}\)Mg\(_{0.005}\)Hf\(_{0.005}\)O\(_3\) (CTH + Mg + Dy) single layer capacitors with increasing temperatures. Loops shown for capacitors yielding the highest energy density at each temperature. .................................................. 199

Figure 6–18: Weibull breakdown statistics for the Ca\(_{0.99}\)Mg\(_{0.005}\)Hf\(_{0.005}\)O\(_3\) (CTH + Mg + Dy) system for a number of isothermal breakdown tests. Weibull parameters ranged from 6.32 to 6.79. .................................................. 201
Figure 6–19: Temperature dependence of impedance spectroscopy for single layer, air-fired, Pt–electrode capacitor of Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy)......203

Figure 6–20: Equivalent circuit model used to fit high temperature impedance spectra for Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy). An offset resistivity was utilized when the data collection began at a non–zero value. G.B. = grain boundary/interface. ..203

Figure 6–21: High temperature conductivities obtained from equivalent circuit modeling of impedance spectroscopy data for Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy). Double layer = D.L. .................................................................204

Figure 6–22: Thermally stimulated depolarization current (TSDC) measurements at 250 °C with a 3 °C/min heating rate for a) Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy) with 5 and 10 minute poling times and b) CTH + Dy + Mg with 5 and 10 minute poling times compared to un–doped Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn). .................................................................205

Figure 7–1: Schematic of hypothetical increase in energy density achieved by producing capacitors having submicron grain sizes using starting particle sizes of ~0.1 μm compared to ~1.0 μm. The recoverable energy density of > 30 J/cm$^3$ is estimated and has not been experimentally verified. .................................................................210

Figure 7–2: Flow chart for hybrid oxalate–mixed oxide processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ........212

Figure 7–3: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for hybrid oxalate–mixed oxide prepared Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ and b) indexed XRD spectrum for a pulverized disk of the same powder sintered at 1300 °C for 3 hours.................................................................213

Figure 7–4: a) Scanning electron microscopy (SEM) microstructure of sintered disk of hybrid oxalate–mixed oxide processed Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) and b) elemental distribution analysis from energy dispersive X–ray spectroscopy (EDS). ..................214

Figure 7–5: Transmission electron microscopy (TEM) image of hybrid oxalate–mixed oxide processed Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ). ..........................................................................................214

Figure 7–6: Flow chart for sol–gel processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ)..........................................216

Figure 7–7: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for sol–gel–prepared Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ and b) indexed XRD spectrum for a pulverized disk of the same powder sintered at 1300 °C for 3 hours..............................217

Figure 7–8: Microstructure of sintered, thermally etched disk of sol–gel–derived Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) from scanning electron microscopy..................................................217

Figure 7–9: a) TEM image of rod–like morphology in Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) obtained from sol–gel processing and b) TEM image of a large rod observed in sol–gel–derived CTZ. ..................................................................................218
Figure 7–10: XRD patterns for sol–gel–derived Ca(Ti0.8Zr0.2)O3 (CTZ) taken with increasing temperature and compared to the final phase pure spectrum obtained from a dense sintered disk of sol–gel CTZ. The stars indicate peaks associated with anatase (TiO2).

Figure 7–11: Flow chart for polymerized complex processing of Ca(Ti0.8Zr0.2)O3 (CTZ).

Figure 7–12: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for polymerized complex–prepared Ca(Ti0.8Zr0.2)O3 and b) indexed XRD pattern for a pulverized disk of the same powder sintered at 1300 °C for 3 hours.

Figure 7–13: TEM particle morphology of CTZ powders synthesized by the polymerized complex method and calcined at 900 °C for 3 hours.

Figure 7–14: a) Temperature dependence of the dielectric constant at 1 kHz and b) P–E hysteresis loops of the Na1–xBaxBa1–xTi3O3 ceramics at room temperature (right) (Zeng et al., 2006).

Figure 7–15: Comparison of 250 °C bulk current density up to 25 kV/cm for Ca(Ti0.795Mn0.005Zr0.2)O3 (CTZ + Mn), Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn), and Ca0.99Dy0.01(Ti0.795Mg0.005Hf0.2)O3 (CTH + Dy + Mg) that were eventually prototyped into single layer capacitors for energy density evaluations.

Figure 7–16: Comparison of the temperature evolution of maximum energy density and average power dissipation factor for Ca(Ti0.795Mn0.005Zr0.2)O3 (CTZ + Mn), Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn), and Ca0.99Dy0.01(Ti0.795Mg0.005Hf0.2)O3 (CTH + Dy + Mg) prototyped into single layer, Pt–electrode, air–fired capacitors.

Figure 7–17: Trend in breakdown strength with increasing band gap energy for various covalent, ionic–covalent, and polymer dielectric materials (Tan et al., 2007). The star designates the breakdown strengths and band gaps achieved in this work. It is important to note that the materials compared to are nanostructured.

Figure A–1: Diagram of the electromagnetic spectrum.

Figure A–2: Schematic diagram of standard illuminating and viewing geometries in an integrating sphere (Torrent et al., 2008).

Figure A–3: Cross–sectional diagram of a powder sample as assumed by Kubelka – Munk theory (Torrent et al., 2008).

Figure A–4: (Left): Schematic of the plane of incidence along with propagation wave vectors k’ and k’ where i and r refer to the incident and reflected beams respectively and (right): cross–sectional amplitudes and phase angels of s and p polarized light in the xy plane (Ferreira, (2004); Ferlauto, (2001).
LIST OF TABLES

Table 1–1: Room temperature relative permittivities (\(\varepsilon_r\)), breakdown strengths (\(E_b\)), and energy densities (\(U_{vol}\)) of several polymer and ceramic dielectrics. PVDF: polyvinylidene fluoride, PP: polypropylene. ................................................................. 8

Table 2–1: Equations for complex optical constants, where \(n\) is the refractive index and \(k\) is the extinction coefficient (Pankove, 1971)............................................................................................................ 31

Table 3–1: Densification onset temperature and % theoretical density in air for \(x = 0.8\) Ca(Ti\(_{3x}\)Zr\(_{1-x}\))O\(_3\) (CTZ) and \(x = 0.8, y = 0.005, 0.02, 0.03, 0.04\) Ca(Ti\(_{x}\)Mn\(_y\)Zr\(_{0.2}\))O\(_3\) (CTZ + Mn)................................................................................................. 60

Table 3–2: Direct or indirect band gap data for various calcium zirconates and titanates obtained by several methods. ................................................................. 67

Table 3–3: Indirect band gaps obtained from UV–Vis diffuse reflectance with range of \((F(R)^*h\nu)^{0.5}\) that was used to obtain \(E_g\) from the zero–intercept of \((F(R)^*h\nu)^{0.5}\) vs. photon energy and direct band gaps obtained from UV–Vis diffuse reflectance with the range of \((F(R)^*h\nu)^2\) that was used to obtain \(E_g\) from the zero–intercept of \((F(R)^*h\nu)^2\) vs. photon energy across the Ca(Ti\(_{3x}\)Zr\(_{1-x}\))O\(_3\) composition range. ...................... 71

Table 3–4: Direct band gap (\(E_g\)) and range of absorption (\(\alpha^2\)), where \(AU\) is absorbance units, that was used to obtain \(E_g\) from the the zero–intercept of \(\alpha^2\) vs. photon energy, indirect band gap (\(E_g\)) and range of absorption (\(\alpha^{0.5}\)) that was used to obtain \(E_g\) from the zero–intercept of \(\alpha^{0.5}\) vs. photon energy, and energy of the first direct transition obtained from the first high energy CPPB oscillator for Ca(Ti\(_{3x}\)Zr\(_{1-x}\))O\(_3\) where Composition = \(x\)........................................................................................................ 84

Table 3–5: Transference numbers (\(t\)) for un–doped \(x = 0.8\) Ca(Ti\(_{3x}\)Zr\(_{1-x}\))O\(_3\) extracted from conductivities modeled with impedance spectra. ......................................................... 98

Table 4–1: Transference numbers for un–doped Ca(Ti\(_{0.8}\)Hf\(_{0.2}\))O\(_3\) (CTH) calculated from impedance spectroscopy fitting................................................................. 120

Table 4–2: Comparison of basic dielectric properties between Ca(Ti\(_{1-0.795}\)Mn\(_{0.005}\)Hf\(_{0.2}\))O\(_3\) (CTH + Mn) and Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Zr\(_{0.2}\))O\(_3\) (CTZ + Mn). TCC = temperature coefficient of capacitance.......................................................... 128

Table 4–3: Summary of average values extracted from room and high temperature polarization vs. field loops for Ca(Ti\(_{0.8}\)Hf\(_{0.2}\))O\(_3\) (CTH) and Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Hf\(_{0.2}\))O\(_3\) (CTH + Mn). ............................................................... 130

Table 4–4: Comparison of energy densities, breakdown strengths, and volumetric power dissipations for Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Hf\(_{0.2}\))O\(_3\) (CTH + Mn) and Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Zr\(_{0.2}\))O\(_3\) (CTZ + Mn)........................................................................................................ 134

Table 6–1: Summary of properties obtained from P–E loops for CTH + Dy + Mg from room temperature to 200 °C. Energy density = \(U_{vol}\), \(E_b\) = breakdown strength, and \(P/V\) = power dissipation energy. ........................................... 202
Table 7-1: Characteristic properties of (Na_{0.5}K_{0.5})NbO_3–LiF ceramics fired in reduced and air atmospheres (Kobayashi et al., 2012). .................................................................224

Table 7-2: Property summary for Ca(Ti_{0.795}Mn_{0.005}Zr_{0.2})O_3 (CTZ + Mn), Ca(Ti_{0.795}Mn_{0.005}Hf_{0.02})O_3 (CTH + Mn), and Ca_{0.99}Dy_{0.01}(Ti_{0.795}Mg_{0.005}Hf_{0.02})O_3 (CTH + Dy + Mg) prototyped into single layer, Pt–electrode, air–fired capacitors for energy density evaluations. .................................................................231

Table 7-3: Activation energies extracted from Arrhenius behavior of conductivity determined from modeling of impedance spectra with the appropriate equivalent circuit for x = 0.8 Ca(Ti_xZr_{1-x})O_3 (CTZ), x = 0.8, y = 0.005 Ca(Ti_{x-y}Mn_xZr_{0.2})O_3 (CTZ + Mn), Ca(Ti_{0.8}Hf_{0.2})O_3 (CTH), Ca(Ti_{0.795}Mn_{0.005}Hf_{0.02})O_3 (CTH + Mn), and (Ca_{0.99}Dy_{0.01})(Ti_{0.795}Mg_{0.005}Hf_{0.02})O_3 (CTH + Mg + Dy). G.B. = grain boundary........232

Table B-1: Sellmeier oscillator energies and magnitudes for the low energy (transparent region) across the Ca(Ti_xZr_{1-x})O_3 composition (comp.) range. Surface roughness layer thickness as represented by a Bruggeman effective medium approximation (EMA) is also listed. The low energy range was 0.732 – 3.00 eV for all samples. The 0.80 Mn composition was doped with 0.5 mol% Mn. EMA: Effective Medium Approximation.................................................................258

Table B-2: Sellmeier oscillator energies and magnitudes for the high energy (absorbing region) oscillators across the Ca(Ti_xZr_{1-x})O_3 composition range.................................259

Table B-3: First high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti_xZr_{1-x})O_3 composition range.................................................................260

Table B-4: Second high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti_xZr_{1-x})O_3 composition range.................................................................261

Table B-5: Third high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti_xZr_{1-x})O_3 composition range.................................................................262
ACKNOWLEDGEMENTS

First, I would like to extend sincere thanks to my advisor, Prof. Clive Randall, for all of the guidance and support he provided not only during my Ph.D. research, but as an undergraduate as well. He has been an incredible mentor, providing me with significant praise for my successes, support and direction through my failures, and amazing opportunities to travel the world to present my research to the scientific community. I am also very grateful for the guidance I received from Prof. Elizabeth Dickey and Dr. Anton Polotai, who first introduced me to electronic ceramics research as an undergraduate. Through my research with them, I gained invaluable research experience and solidified my decision to pursue a doctorate in materials science and engineering. I would also like to thank Prof. Nikolas Podraza, a great scientist and friend, for his collaborative work with my research and above all, his patience. Additionally, I would like to thank my other Ph.D. committee members, Prof. Gary Messing, Prof. Mike Lanagan, and Prof. Susan Trolier–McKinstry for their valuable advice and support for this research.

Much of this research would not have been possible without the aid of the talented technical staff at the Materials Research Institute. I would like to thank Amanda Baker and Beth Jones for their assistance with material processing and providing me with tips and tricks for developing optimized materials and devices. I would also like to thank Jeff Long, Steve Perini, and the late Paul Moses for their patience and valuable assistance with setting up and performing electrical measurements. Additionally, I would like to thank Maria Dicola, Nichole Wonderling, Maria Klimciewicz, and Josh Stapleton for their assistance with measurements and research guidance. I also cannot thank Joanne Aller enough for her administrative support and friendship over the years.

I would also like to thank Niall Donnelly for his extensive advice on impedance spectroscopy and assistance with data interpretation and modeling. This thanks also extends to Russell Maier and Soonil Lee, who were always helpful with bouncing ideas back and forth with and attempting to explore every possibility associated with interpretation of results. My thanks also goes out to my fellow lab group members, both in the Randall group and the Trolier–McKinstry group for their advice and camaraderie. I am also grateful for the funding provided to me through the Center for Dielectric Studies (CDS) and the National Defense Science and
Engineering Graduate Fellowship (NDSEG) for providing me with the financial means to perform this research.

Lastly, I would like to extend a sincere thanks to all the friends and family who have supported me through the good times and the bad during my Ph.D. research. I have made many amazing friends over my 10+ years at Penn State, and I am eternally grateful for their involvement in my life. My parents and brother, Diane, Charley, and Andrew are the best family a guy could ever ask for and their love and support has without doubt been the most important proponent for the completion of this dissertation.
CHAPTER 1
MOTIVATION AND OBJECTIVES

1.1 Introduction

This chapter will provide a background on the power electronics technologies affected by this work, examples of types of materials utilized in such applications, and the material design approach taken in this dissertation for developing such materials. The fundamentals of dielectric materials, multilayer ceramic capacitors, and other basic materials science concepts related to this research have been summarized in detail by numerous authors (Moulson et al., 2003; Lee, 2006; Levi, 2009; Liu, 2009). For this dissertation, each chapter provides an introduction with the relevant scientific background related to the presented data. The purpose of this chapter is to outline the core technologies affected by this work.

1.2 Background

At the core of all power electronics systems, power electronics modules are pivotal for converting electrical energy from one form, provided by the source, to another form, consumed by a load. With the emergence of SiC power modules capable of operating at temperatures > 400 °C, improvements in the efficiency of power conversion in hybrid vehicle, aircraft, deep oil/gas extraction, and renewable power distribution technologies are possible through size and volume reduction of the modules (Losetter et al., 2009). Additionally, for these high temperature applications, opportunities arise for improving efficiency through developing multilayer ceramic capacitors (MLCCs) having higher energy densities and volumetric efficiencies at these elevated temperatures.

Recently, power electronic modules based on SiC have become commercialized, reducing the size and volume of current power electronic modules by an order of magnitude relative to state–of–the–art silicon–based solutions while simultaneously reducing energy loss by > 50%, offering the potential to save $100s of millions (Losetter et al., 2009). Theoretically, SiC can operate at temperatures > 600 °C, whereas standard silicon–based technologies are limited to 150 °C. Recently commercialized SiC–based technologies are capable of operating at
temperatures > 250 °C as shown in Fig. 1–1 for a low temperature co–fired ceramic (LTCC) gate
driver board operating at high temperature.

As seen in Fig. 1–1, the gate driver board can sustain temperatures > 260 °C. As a result,
all components on the board must also be able to operate efficiently at these elevated
temperatures. As will be elaborated upon shortly, the gate driver board currently utilizes
NP0/C0G–type capacitors, which are typically specified for maximum operating temperatures of
120 °C to 150 °C. As a result, there is substantial opportunity to develop new ceramic dielectric
compositions that further increase high temperature efficiency of SiC–based power inversion
modules by having higher energy densities at high temperatures compared to the state–of–the–art
capacitor materials.

1.3 Applications
Since the SiC–based power module can operate at significantly higher temperatures
compared to Si–based systems, a number of important high temperature power electronics
applications become available. Typically, power electronics modules are used to drive electric
motors (motors for electric and hybrid vehicles), convert energy from renewable sources (solar,
wind, etc.), and provide power for electronic systems (dc power supplies) (Losetter et al., 2009). Additional high temperature applications exist in aircraft and deep oil/gas extraction.

**1.3.1 Automotive**

In general, high-energy efficiency in hybrid–electric vehicles saves the automotive owner money through the reduction in energy losses. At high temperatures, the long-term reliability of “under the hood” power electronics reduces the thermal management system requirements, resulting in improved performance and long-term cost savings (Buttay et al., 2011). In general, under the hood temperatures can exceed 140 °C, an example being the rectifier diodes at the back of the alternator, which operate above 160 °C (Buttay et al., 2011). Specifically in hybrid vehicles, it is possible to take advantage of the cooling loop to extract heat from power electronics systems, but the water temperature can exceed 120 °C, which approaches the limit of Si-based devices and NP0/C0G-type capacitors, which are commonly limited to 150 °C operation (Buttay et al., 2011).

**1.3.2 Aircraft**

The main target for the aircraft industry as related to power electronics modules is the need to reduce aircraft maintenance costs and operation weights while improving fuel efficiency (Lotsetter et al., 2009). As a result, aircraft system designers are moving towards More Electric Aircraft (MEA) solutions, which aim to replace conventional hydraulic design methods with electric and electronic replacements (Buttay et al., 2011). One example is the replacement of hydraulic systems with electric motors and electronic motor drives, which must be lightweight and able to withstand extreme temperatures with minimal cooling (Lotsetter et al., 2009). To achieve the desired efficiency, electrical actuators are driven through power electronics converters in a distributed fashion (Mehdi et al., 2006). Such converters are placed as close to the actuator as possible, implying that some converters will be subject to harsh environments. When placed close to the jet engine, for example, temperatures can range from −55 to 225 °C (Mehdi et al., 2006).
1.3.3 Deep Oil/Gas Extraction

Unlike automotive and aircraft applications, deep oil/gas extraction applications are expected to run continuously at high temperatures for 5 years or more, but without significant thermal cycling (Buttay et al., 2009). Reliability of the power electronics systems in these applications is crucial due to the high cost of stopping the gas/oil extraction, where power systems are typically located several kilometers below ground. One example of such a power system for such systems is an electrical down-hole gas compressor, which is designed to increase production of gas wells by putting a compressor close to the gas reservoir (Buttay et al., 2009). For deep oil wells, temperatures are expected to reach as high as 225 °C, with a system lifetime of 5 years (Buttay et al., 2009).

1.3.4 Renewable Energy

Every renewable energy source requires power electronic converters in order to output energy in a form that can be utilized by an end user. Typically, such conversion systems require a power inverter that outputs power in a single or three-phase alternating current (ac) configuration, and are often tied directly to the power utility grid (Lotsetter et al., 2009). Essential to the power inverter is the power module, which performs the energy conversion process and determines the energy efficiency of the inverter system.

Overall, there are numerous applications for high temperature SiC–based power electronics for which the high temperature efficiency can be further improved upon by developing dielectric capacitor materials having higher energy densities at elevated temperatures compared to the state–of–the–art materials. As seen in Fig. 1–1, the capacitors are some of the largest components on the board, so there are opportunities to further reduce the size of the boards while yielding better volumetric efficiency at these high operating temperatures.

1.4 Capacitors for Power Electronics

One of the most important roles of capacitors in power electronics modules and technologies lies in the conversion of electric power from one form (dc) into another (ac).
Capacitors are critical components in the power electronics circuit, as shown in Fig. 1–2.

Figure 1–2: Schematic diagram of common power electronics circuit (Mohan et al., 1989). Direct current bus capacitors = $C_E$, snubber capacitors = $C_C$, filter capacitors = $C_R, C_F$.

Direct current bus capacitors ($C_E$) are critical components for enabling energy storage, electrical discharge, and voltage smoothing. The bus capacitors typically require a large capacitance (100–2000 μF) and energy density. Snubber capacitors ($C_C$) are required to reduce power dissipation in solid–state inverters, and tend to have capacitances of 10–1000 nF. Filter capacitors ($C_R$ and $C_F$) remove unwanted frequencies and harmonics from the output ac signal, so their capacitances depend strongly on the output frequency (Mohan et al., 1989).

At the component level, semiconductor switching devices and capacitors are the two types of reliability–critical components. Using renewable photovoltaic power grid as an example, a survey showing the failure distribution among power electronics components is shown in Fig. 1–3 where PV = photovoltaic, ACD = anti–coincidence system, and DAS = data acquisition system.
As seen in Fig. 1–3, the inverter technologies, which rely heavily on the efficiency and reliability of capacitors, show the largest percentage of both failure sources and cost. The failures associated with major components are shown in Fig. 1–4.

Figure 1–3: Field experience of a 3.5–MW photovoltaic (PV) plant separated into a) unscheduled maintenance events by subsystem and b) unscheduled maintenance costs by subsystem. PV = photovoltaic, ACD = anti–coincidence system, and DAS = data acquisition system (Wang et al., 2013; Moore et al., 2008).

As seen in Fig. 1–3, the inverter technologies, which rely heavily on the efficiency and reliability of capacitors, show the largest percentage of both failure sources and cost. The failures associated with major components are shown in Fig. 1–4.

Figure 1–4: Surveys on failures in power electronics systems among major components (Wang et al., 2013; Wolfgang, 2007).

From Fig. 1–4, it can be seen that the capacitors are responsible for the largest percentage of
failures in power electronics systems. For power electronics systems, electrolytic and polymer
dielectrics are most commonly used for capacitor materials, with newer technologies moving
towards NP0/C0G–type materials. While NP0/C0G–type materials show good performance up to
150 °C, they are below the temperature specification for many of the applications discussed for
this dissertation. The actual lifetime of capacitors used in power electronics applications depends
on a number of factors in addition to their rated lifetimes including vibration/shock, steady state
and cyclical temperatures, humidity/moisture, and contaminants/dust (Wang et al., 2013).
Additionally, all of these materials show poor volumetric efficiency for high temperature power
electronics applications. As a result, it is crucial to develop materials that can improve the high
temperature performance of capacitors used in power electronics applications.

1.5 Materials for High Temperature, High Energy Density Capacitors

Polymers and ceramics dominate the dielectric materials that are currently used in solid–
state capacitors. However, with the exception of fluorine–based polymers, most polymer–based
dielectrics are limited to operating temperatures < 105 °C (Chu et al., 2006). Therefore, only
revolutionary new polymer/polymer composite film materials or new ceramic materials are
options for obtaining high voltage–capable, high energy density capacitors at elevated
temperatures. Numerous dielectric compositions for high energy density applications, such as
linear dielectrics, ferroelectrics, and antiferroelectrics have been investigated, some examples of
which are shown in Table 1–1. While polyvinylidene fluoride (PVDF) shows the highest energy
densities of the materials listed in Table 1–1, their operating temperatures are typically rated for
temperatures < 100 °C and restrict their applicability for this dissertation.
Table 1-1: Room temperature relative permittivities ($\varepsilon_r$), breakdown strengths ($E_b$), and energy densities ($U_{vol}$) of several polymer and ceramic dielectrics. PVDF: polyvinylidene fluoride, PP: polypropylene.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_r$</th>
<th>$E_b$ (MV/cm)</th>
<th>$U_{vol}$ (J/cm$^3$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>13</td>
<td>5.8</td>
<td>17</td>
<td>Chu et al., 2006</td>
</tr>
<tr>
<td>Nanocomposite PVDF</td>
<td>11-13</td>
<td>7.8</td>
<td>19</td>
<td>Tomer et al., 2011</td>
</tr>
<tr>
<td>PP</td>
<td>2.2</td>
<td>5.5</td>
<td>2.6</td>
<td>Wisken et al., 2001</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>165-200</td>
<td>0.40</td>
<td>1.3</td>
<td>Burn et al., 1972</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>2000</td>
<td>0.80</td>
<td>5</td>
<td>Love, 1990</td>
</tr>
<tr>
<td>La, Ca Doped PbZrO$_3$</td>
<td>700</td>
<td>0.50</td>
<td>12</td>
<td>Brodeur et al., 1994</td>
</tr>
<tr>
<td>0.7BaTiO$_3$ – 0.3BiScO$_3$</td>
<td>1000</td>
<td>0.73</td>
<td>6.1</td>
<td>Ogihara et al., 2009</td>
</tr>
</tbody>
</table>

Figure 1-5 shows a schematic of the polarization as a function of electric field for three types of non–linear dielectrics that can be investigated for high temperature, high energy density applications. The recoverable energy density, in red, is indicated for each type (Burn et al., 1972).

Figure 1–5: Comparisons of non–linear dielectric materials, in terms of their polarization–electric field dependence.
In the case of ferroelectrics, the origin of high permittivity is long-range order of spontaneous polarization. BaTiO$_3$, the most important commercial ferroelectric dielectric, has a major limitation as a high energy density dielectric: the permittivity decreases significantly with high fields. One method to minimize the field dependence and increase the electrostatic energy density is to frustrate the long–range order and provide a so–called weakly coupled relaxor ferroelectric with re–entrant polarization behavior. Examples of this include solid solutions of BaTiO$_3$ with BiScO$_3$ or Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (Ogihara et al., 2009; Kwon et al., 2012). Such materials have demonstrated to be effective up to 17 to 20 J/cc and temperatures above 100 °C in the form of high voltage capacitors ~10 kV, and demonstrated pulsing for at least 8,000 cycles. Sandia National Laboratories have also demonstrated prototypes based on 0.8BaTiO$_3$–0.2Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$, which charge and discharge in a nanosecond time scale (Raengthon et al., 2012). Overall, however, despite having large permittivities (\(\varepsilon_r > 1000\)), recoverable energy densities in ferroelectrics are limited due to their hysteretic and non–linear behavior in which low breakdown strengths (\(< 1000 \text{ kV/cm}\)) and large high field losses restrict their applicability.

Antiferroelectric materials (e.g. PbZrO$_3$) have antiparallel spontaneous polarization, and the application of a sufficiently strong field induces the transformation to a ferroelectric state. The process involves a first–order phase transition and the nucleation of ferroelectric phases in an antiferroelectric matrix at a critical field (Gachigi, 1992). The permittivity increases with the applied field strength during this process, thereby increasing the energy density. Antiferroelectric compositions are typically lead–based and new lead–free compositions need to be investigated. While antiferroelectrics show large permittivities (\(\varepsilon_r > 500\)), the possible high field polarization dependence, high field losses due to hysteresis, strains as high as 0.6%, and lead–based chemistries make them less attractive for these new opportunities (Brodeur et al., 1994).

Paraelectric materials (e.g. SrTiO$_3$) are the third class of non–linear dielectrics and are the high temperature form of both ferroelectric and antiferroelectric phases. In the high temperature regime, the spontaneous polarization is absent. This is true in many perovskite materials, but not strictly required. However, the permittivity–electric field dependence remains non–linear in the paraelectric phase. The permittivity is also strongly temperature dependent, following the Curie–Weiss relation, and the voltage dependence seen in the ferroelectric phase is retained.
Linear dielectrics (CaTiO$_3$, CaZrO$_3$), which are the focus of this dissertation, have a similar dielectric response to paraelectrics, but with no hysteresis, linear polarization–field dependence, moderate permittivities ($\varepsilon_r \sim 30–300$), and low losses ($\tan\delta < 0.001$) within the working temperature range. In an ideal linear dielectric, the dielectric displacement increases linearly with increasing applied electric field, which allows for all stored energy to be recovered upon discharge while experiencing minimal dielectric loss as desired for these applications.

In summary, there are several classes of materials that can be used to develop new non-linear dielectrics for high-voltage and high-power applications. A major need is to better understand their individual limitations at high electric field strengths in terms of the high-field conductivity and electrical breakdown. The phenomena that lead to failure are complex and need more extensive scientific understanding, particularly in regard to polarization and conduction at interfaces, the specific charge transfer process, and point defect (and thus field) distributions in the vicinity of microstructural features and electrodes, how these are coupled, and how they evolve with time under electrical bias. Despite substantial work in non-linear dielectrics, such knowledge remains unknown and limits current strategies for improving high-temperature and high-field performance dielectrics.

### 1.6 Material Development Rationale

As mentioned previously, the intrinsic energy density of a lossless linear capacitor is defined by $U_{\text{vol}}$ (J/m$^3$),

$$U_{\text{vol}} = \frac{\varepsilon_r \varepsilon_0 E_b^2}{2}$$  \hspace{1cm} (Equation 1–1)

where $\varepsilon_r$ is the relative dielectric permittivity, $\varepsilon_0$ is the free-space permittivity ($8.85 \times 10^{-12}$ F/m), and $E_b$ is dielectric breakdown strength (V/m) (Love, 1990). As seen in Eq. 1–1, material development for achieving high energy densities relies on the optimization of relative permittivity and dielectric breakdown strength. The optimization depends on a balance of the two material properties, since materials with high relative permittivities tend to have lower breakdown strengths and materials having high breakdown strengths tend to have lower relative permittivities (McPherson et al., 2003).
It was found by McPherson et al. that for materials of increasing dielectric constant ($k$), or relative permittivity ($\varepsilon_r$), the breakdown strength follows a $\sim k^{-1/2}$ dependence, as shown in Fig. 1–6.

![Thermochemical model prediction of breakdown strength as a function of dielectric constant (k) for materials having various values of k (McPherson et al., 2003).](image)

Figure 1–6: Thermochemical model prediction of breakdown strength as a function of dielectric constant ($k$) for materials having various values of $k$ (McPherson et al., 2003).

It was suggested that the very high local electric field in high $k$ materials is important and drives the observed behavior. The local field distorts polar molecular bonds, making them susceptible to breakage by Boltzmann processes and/or hole capture, thus lowering the breakdown strength (McPherson et al., 2003). This trend would suggest that by choosing materials with increasing relative permittivities, minimal increases in breakdown strength, and thus energy densities, would be achieved. However, there are numerous contributions to dielectric breakdown strength, and the ultimate $E_b$ is also dependent on the frequency of the applied field and temperature. More recently, it has been suggested by compiling breakdown strengths as a function of dielectric constant for a broader range of materials, the trend suggested by McPherson et al. may not be so severe and may not reach such a drastic saturation point with increasing permittivity, especially in binary systems as shown in Fig. 1–7 (Tuttle et al., 2008; Jain et al., 2002).
From Fig. 1–7, it can be seen that when comparing many material types, the trend in breakdown field with increasing dielectric permittivity follows more of a weak linear trend compared to that observed by McPherson et al. The materials investigated by McPherson et al. were undoped oxides and SrTiO$\text{\textsubscript{3}}$. As seen in Fig. 1–7, forming binary or ternary dielectric compositions involving a material having a lower dielectric constant and one with high breakdown strength can increase the overall breakdown strengths of medium permittivity materials. It is important to note that many of the compositions in Fig. 1–7 are in thin film form and typically have higher breakdown strengths compared to the bulk form. Additionally, by developing doping strategies that mitigate high temperature dielectric losses and conduction, the breakdown strength can be increased relative to the undoped case (Kishi et al., 2001; Cha et al., 2006; Jeong et al., 2006; Jeong et al., 2007; Honda et al., 2011; Cai et al., 2010).

It has also been observed that by selecting materials having larger electronic band gaps, band conduction can be reduced and high dielectric breakdown strengths can be achieved as shown in Fig. 1–8.
It is expected that the materials of interest in this research will have band gap energies of ~3.5 – 4.0 eV, and the trend in breakdown strength emphasizes the importance of identifying materials within solid solutions which have the best combination of large band gap and medium relative permittivity.

As mentioned previously, solid-state capacitors used in state–of–the–art power electronics modules are of the NP0/C0G capacitor type, which are commonly based on low dielectric constant ($\varepsilon_r \approx 35$), high breakdown strength (> 1.0 MV/cm) materials such as CaZrO$_3$. In order to increase the energy density, binary compositions are typically paired with materials such as CaTiO$_3$ to form compositions such as Ca(Ti$_{0.2}$Zr$_{0.8}$)O$_3$ with a variety of dopants to mitigate high temperature conduction (Pinceloup et al., 2006; Xu et al., 2009). The NP0/C0G capacitor class utilizes dielectric materials that show near zero capacitance change from the room temperature value over a range of temperatures, typically −55 to 125 °C, and minimal temperature dependence of resistivity, as shown in Fig. 1–9 compared to a high permittivity X7R dielectric (typically BaTiO$_3$–based).

Figure 1–8: Trend in breakdown strength with increasing band gap energy for various covalent, ionic–covalent, and polymer dielectric materials (Tan et al., 2007).
Unlike NP0/C0G compositions, the binary stoichiometries in this dissertation will contain more titanate than zirconate. Due to the higher permittivity of CaTiO$_3$–based materials, it is likely that the temperature independence of the insulation resistance and capacitance will be sacrificed to a degree. However, provided substantially larger energy densities can be achieved at temperatures up to 300 °C, the payoff in volumetric efficiency is worth the loss of completely temperature independent properties.

With the push away from electrolytic and polymer capacitors in state–of–the–art power electronics modules, development has shifted to solid–state ceramic dielectric materials. Currently, NP0/C0G–type capacitors are being used on recently commercialized SiC–based gate drive boards for use in power electronics modules, a common composition of which is doped Ca(Ti$_{0.2}$Zr$_{0.8}$)O$_3$. While typically selected due to their temperature independent dielectric properties (up to 150 °C), such CaZrO$_3$–based materials are being investigated for their recoverable energy densities at temperatures > 150 °C as shown in Fig. 1–10 (Losetter et al., 2009; Xu et al., 2009).

Figure 1–9: Temperature dependence of insulation resistance for base metal electrode (BME) C0G CaZrO$_3$–based multilayer ceramic capacitor (MLCC) compared to X8R MLCC (Xu et al., 2009).
As seen in Fig. 1–10, the CaZrO$_3$–based material shows energy densities of ~5 J/cm$^3$ at 20 °C and 200 °C, but the energy density is limited to ~3 J/cm$^3$ at 300 °C. It is possible that by using higher relative permittivity materials and adopting doping strategies that mitigate high temperature dielectric loss and conduction, high breakdown strengths can be coupled with the increased permittivity to yield even higher energy densities compared to C0G/NP0–type materials (Xu et al., 2009). Overall, the material development strategy for new dielectric capacitor materials is similar to approaches used in the design stages for power electronics systems as a whole, as shown in Fig. 1–11.
The initial concept for materials developed in this research is to utilize existing compositions such as Ca(Ti$_{0.2}$Zr$_{0.8}$)O$_3$, for which minimal literature exists due to the proprietary nature of capacitor material technologies. Since little literature exists on the solid solution behavior of such linear dielectric systems, the initial analysis phase consisted of a study of the full composition range of Ca(Ti$_x$Zr$_{1-x}$)O$_3$ (CTZ) to identify compositions having the best combination of medium permittivity (to maximize polarization) and large band gap (to minimize band/electronic conduction). In the initial design phase, an optimal acceptor dopant (Mn) concentration was identified by measuring the high temperature, high field properties on several isolated CTZ compositions. The verification stage was then approached by prototyping single layer capacitors and measuring the temperature dependence of breakdown strength and energy density. Based on the results of the verification stage, additional binary end members and acceptor/donor strategies were evaluated until an optimized design (capacitor material) was identified. Experimentally, the material selection and optimization process was approached as shown in Fig. 1–12.

Figure 1–11: Schematic of state-of-the-art reliability design procedure for power electronic systems (Wang et al., 2013).
Overall, the main goals of this dissertation were to identify linear dielectric materials having medium permittivities and large band gaps to optimize the recoverable energy density through high breakdown strengths and corresponding polarizations. By identifying base compositions and analyzing their high temperature dielectric behavior, doping strategies such as acceptor doping with Mn or co–doping with rare earths and Mn or Mg were developed to minimize high temperature ionic conductivity that may arise due to the use of titanate–rich compositions, hence minimizing the temperature dependence of the breakdown strength. While the focus of this research was the development of linear dielectric materials, as a whole this dissertation serves as a comprehensive template for developing any dielectric material, whether linear, ferroelectric, or antiferroelectric, for high temperature, high energy density applications. The proposed design methods are crucial for optimizing the performance and high temperature efficiency of important emerging power electronics systems through conceptualization, development, and optimization of new capacitor materials.

Figure 1–12: Flow chart for developing new linear dielectric ceramics for optimized energy densities at temperatures up to 300 °C, where $E_g =$ band gap energy (eV), I–V = current–voltage, $P$ vs. $E$ = polarization vs. field, and $\sigma$ = conductivity.
Specifically, we outline a number of strategies for developing high temperature dielectrics through selected systems. The objectives of this dissertation can be summarized into the following:

1. Characterize the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ solid solution to identify a composition having the optimal combination of medium permittivity to optimize polarization, and large band gap to minimize electronic conductivity and optimize breakdown strength.

2. Identify an optimum doping concentration of Mn in order to minimize dielectric loss and ionic conductivity at elevated temperatures.

3. Determine whether substitution of CaZrO$_3$ with CaHfO$_3$ can yield improvements in high temperature energy density due to the higher band gap of CaHfO$_3$ and heavier atomic weight of Hf to minimize thermal vibration of atoms.

4. Understand the role of Mn in controlling high temperature ionic conductivity by coupling high temperature quenching with various impedance spectroscopy techniques and thermally stimulated depolarization current measurements.

5. Determine whether rare earth co–doping of Ca(Ti$_x$Hf$_{1-x}$)O$_3$ with either Mn or Mg can further mitigate high temperature conductivity and improve high temperature recoverable energy densities.
CHAPTER 2
EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

This chapter outlines the experimental methods and characterization techniques utilized to maximize recoverable energy density in the Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) and Ca(Ti$_{x}$Hf$_{1-x}$)O$_3$ (CTH) binary systems. This maximization was done by identifying compositions and doping chemistries that yield materials with high breakdown strengths, low dielectric loss and conductivity, and medium relative permittivities at high temperatures. In addition to processing and basic material characterization, methods for understanding structure–property relationships, characterizing high temperature electrical properties, and understanding how Mn doping affects high temperature conductivity are addressed to aid future researchers in repeating and expanding upon this research.

2.2 Mixed Oxide Powder Processing

Powders for characterization of undoped CTZ and CTH and the same materials with Mn, Mg, or rare earth (Dy, Gd, Sm) dopants were synthesized using solid state ceramic processing. For powder batching, Mn and Mg were assumed to occupy the Ti$^{4+}$ site, while rare earths were assumed to occupy the Ca$^{2+}$ site. Starting powders of CaCO$_3$ (Sigma–Aldrich, 99+% A.C.S. reagent), TiO$_2$ (Ishihara Sangyo Kaisha LTD., ultra high purity), HfO$_2$ (Alfa Aesar, tech.), ZrO$_2$ (MEL Chemicals, Flemington, NJ), MnO$_2$ (Cerac, 99%), and RE$_2$O$_3$ (Alfa Aesar, 99.9) where RE = Dy, Gd, or Sm were combined stoichiometrically and ball–milled in ethanol for 24 hours.

To determine the calcination conditions for processing, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed. For DSC, the difference between the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. A DSC system (DSC2920, TA Instruments) was used for the measurements. The measurements were taken under a nitrogen atmosphere with a heating rate of 10 °C/min. For TGA, changes in the mass of a sample were studied while the sample was
subjected to a controlled temperature program. The losses in weight were indicative of decomposition reactions, so the necessary holding temperatures for ensuring full decomposition of the starting powders can be determined. The results for DSC and TGA for CTZ are shown in Fig. 2–1.

![Graph](image.png)

Figure 2–1: Thermal profile for determining calcination and sintering temperatures for powders prepared by the mixed oxide method.

Milled powders were dried, sieved, and calcined at 1100 °C for 6 hours with a 6 hour hold at 800 °C to fully decompose CaCO$_3$. While powders were of mixed CaTiO$_3$ and CaZrO$_3$ or CaHfO$_3$ phases after calcining, a single perovskite phase was observed after sintering to dense, bulk samples. To aid in densification, 1.0 wt.% borosilicate glass frits were added post–calcining and ball milled in ethanol for 6 hours. Final powders were dried and sieved. A general flow chart for the mixed oxide processing used in this research is shown in Fig. 2–2.
To assess the high field behavior of the CTZ and CTH systems, single layer capacitors with Pt internal electrodes were processed via tape casting. A general flow chart for preparing slurries for tape casting and the casting and prototyping of capacitors is shown in Fig. 2–3. A more detailed description of the slurry formation and capacitor prototyping utilized in this research are described elsewhere (Ogihara et al., 2009).

Figure 2–2: Flow chart for mixed oxide processing of bulk ceramic disks.
Tape thicknesses after casting were 16–19 μm for active layers and 50–60 μm for bulk layers. To remove organic components, the capacitors were heated to 270°C at 0.5 °C/min, then heated to 600 °C at 0.5 °C/min while holding for 6 hours at both temperatures. A pictorial description of the capacitor prototyping process is shown in Fig. 2–4.

Figure 2–3: Flow chart for ceramic slurry preparation, tape casting, and single layer capacitor with Pt internal electrode fabrication. MEK: methylethylketone, PVB: polyvinyl butyral, BBP: butyl benzyl phthalate.
In addition to Pt electrodes, Ni electrodes were also prepared to assess the base–metal electrode (BME) compatibility of the CTZ + Mn system. To prepare Ni electrode ink, 6.32 g of dihydro terpineol (DHT), 0.6 g Emphos (C_{11}H_{10}F_{3}NO_{2}), 10 g Ni powder, and 1.99 g of calcined CTZ + Mn powder were mixed and milled for 24 hours. Once milled, 5.97 g of ethyl cellulose N–4 was added in a 10/90 mixture and milled for another 24 hours. Capacitors with Ni internal electrodes were fired at the same temperatures, but at \( pO_2 = 10^{-12} \text{ atm} \) followed by re–oxidation at \( pO_2 = 10^{-9} \text{ atm} \) for 9 hours and 12 hours to determine the effect of re–oxidation time on dielectric loss. The atmosphere was controlled using dry nitrogen, wet nitrogen, and a 0.1% \( \text{H}_2–\text{N}_2 \) mixture.

Bulk disk samples for determining sintered phase purity and percent theoretical density (T. D.) were prepared by cold isostatic pressing (CIP) using an Autoclave Engineers Inc. CIP (Erie, PA) at 30,000 psi. All samples were sintered by heating at 10 °C/min to 800 °C, held for one hour, then heated at 3 °C/min to 1250 to 1300 °C and held for 3 hours. Final capacitor dimensions had thicknesses of ~ 9 – 12 μm and electrode areas of ~ 3 mm². Percent theoretical densities were determined via the Archimedes method. Scanning electron microscope (SEM) images of the single layer capacitors for the systems prepared in this research are shown in Fig. 2–5.

Figure 2–4: Capacitor process schematic for green body forming (left) and high temperature processing (right) (Johanson Dielectrics, 2013).
Figure 2–5: Scanning electron microscope (SEM) images of electrodes and single layer thicknesses for all capacitors prototyped in this research where CTH + Mn is Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$, CTH + Mn is Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ and CTH + Mg + Dy is (Ca$_{0.99}$Dy$_{0.01}$)(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$. The lighter contrast in the image corresponds to the electrode and the darker contrast corresponds to the dielectric.
Silver ink (Dupont 6160, Dupont, Wilmington, DE) was applied to both ends of the samples as termination electrodes and fired on at 850 °C for 30 minutes. Stacked and laminated tapes were also used to prepare sintered samples without electrodes for bulk electrical characterization. It is worth noting that the prototyped capacitors are not of commercial device quality, but are sufficient for evaluating the dielectric performance in a single layer buried capacitor form.

2.3 Capacitor Quenching

The roles of multivalent acceptor dopants such as Fe and Mn have been studied extensively in SrTiO$_3$ (Merkle et al., 2003). At temperatures below 1200 °C, the ratio of Sr / Ti can be considered constant. At higher temperatures, such as those in this research, this ratio is no longer constant and partial Schottky defects can be present, leading to the formation of Sr vacancies. Similar to the behavior of Sr in SrTiO$_3$, the formation of Ca vacancies is energetically unfavorable, yielding the partial Schottky relations (Moos et al., 1997),

$$O_{O}^{x} + Ca_{Ca}^{x} \leftrightarrow V_{O}^{**} + V_{Ca}'' + CaO_{surface}$$ \hspace{1cm} (Equation 2–1)

with the notation according to Kröger and Vink (Kröger et al., 1956). At the sintering temperature of 1250 °C, it is expected that the following electroneutrality condition exists:

$$2[V'_{Ca}''] = 2[V_{O}^{**}] + p$$ \hspace{1cm} (Equation 2–2)

where $p$ is the concentration of holes. When the sample is cooled to room temperature, the oxygen vacancy concentration is frozen in, leading to high ionic conductivity. Additionally, while there is little experimental evidence for support, it is also theoretically possible for Ca$^{2+}$ to substitute for Ti$^{4+}$ if Ca / Ti $> 1.0$ by

$$Ca_{Ca}^{x} + Ti_{Ti}^{x} \leftrightarrow Ca_{Ti}'' + V_{O}^{**}$$ \hspace{1cm} (Equation 2–3)

Manganese is a multivalent ion depending on oxygen partial pressure and temperature, with Mn$^{3+}$ and Mn$^{4+}$ being the expected valence states when fired in air (Jeong et al., 2007). The defect reactions for Mn$^{3+}$ and Mn$^{4+}$ are, respectively,
2\text{Mn}_{Ti}' + 2\text{V}_{O}^{**} + \frac{1}{2}O_2 \rightarrow 2\text{Mn}_{Ti}' + \text{V}_{O}^{**} + O_O \quad \text{(Equation 2–4)}

2\text{Mn}_{Ti}' + \text{V}_{O}^{**} + \frac{1}{2}O_2 \rightarrow 2\text{Mn}_{Ti}^{X} + O_O \quad \text{(Equation 2–5)}

Similarly to Fe–doped SrTiO$_3$, it is expected that at high temperatures and slightly reducing atmospheres Mn$^{3+}$ is dominant, acting as an acceptor on the Ti site, which creates a corresponding amount of oxygen vacancies according to

\[ [\text{Mn}_{Ti}'] = 2[\text{V}_{O}^{**}] + p \quad \text{(Equation 2–5)} \]

However, as the sample is cooled, Mn$^{4+}$ becomes the dominant state and the concentration of compensating oxygen vacancies is decreased, minimizing ionic conductivity. To verify this, single layer capacitors of CTH + Mn were heated to 1250 °C (sintering temperature) in air and held for 3 hours using the quenching furnace shown in Fig. 2–6.

Figure 2–6: Quenching furnace used for quenching Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ with main components labeled.
This allowed for the samples to be cooled within seconds, resulting in the Mn$^{3+}$ valence state and corresponding oxygen vacancies being present in the structure.

### 2.4 X–Ray Diffraction

X–ray diffraction (XRD) was used to identify phase purity and obtain lattice parameters on crushed, sintered, non–electroded ceramics using a PANalytical X’Pert Pro MPD θ/θ goniometer with Cu–Kα radiation, and fixed slit incidence (0.5° divergence, 1.0 deg. anti–scatter, specimen length 10 mm) and diffracted (0.5° anti–scatter, 0.02 mm nickel filter) optics. Samples were prepared by the back–loading method in which a powder sample is pressed into the cavity of a quartz low–background support. Data were collected at 45 kV and 40 mA from 10–70 °2θ using a PIXcel detector in scanning mode with a PSD length of 3.35 °2θ, and 255 active channels for a duration time of approximately an hour. Resulting patterns were corrected for both °2θ position and instrumental peak broadening using NIST 640c silicon and analyzed with Jade+9 software (MDI, Livermore, CA).

### 2.5 Dilatometry

Previous researchers investigated densification trends in similar materials, but focused on the CaZrO$_3$ – rich end of the binary (Pinceloup et al., 2006). To investigate densification trends and determine the optimum mol% doping of Mn for the CaTiO$_3$ – rich end of the binary, preliminary sintering was performed for $x = 0.8$ CTZ with 0.5, 2, 3, and 4 mol% Mn substituted for Ti in a precise rate – controlled high temperature dilatometer equipped with a computer – aided design and gas control system designed within the Center for Dielectric Studies at Penn State (Polotai et al., 2005), shown in Fig. 2–7.
Samples without glass frits added were heated in air at 10 °C/min to 1400 °C and held at temperature for 2 hours. The temperature at the onset of densification and final % T. D. were determined.

2.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using a Hitachi S–3000N SEM (Tokyo, Japan) using secondary electron imaging at an operating voltage of 5 kV. Samples for SEM were polished to 1 μm using diamond slurry then thermally etched at a temperature 10% below the sintering temperature for 30 minutes. Grain size measurements were obtained using the line intercept method (ASTM Standard E 112–10, 1955 (2006)). Energy dispersive X–ray spectroscopy (EDX) was used in the same SEM to assess the homogeneity of elemental distribution in the samples.
2.7 Transmission Electron Microscopy

To observe the presence of microstructure and microchemical features of CTH + Mn in terms of whether Mn was located with grains, grain boundaries, or all three, transmission electron microscopy (TEM) and EDS were performed. Samples for TEM were prepared using a focused ion beam (FIB) system (Quanta 200 3D Dual Beam, FEI). The microstructure and microchemistry were studied using a JEOL 2010F transmission electron microscope operated at 200kV. Bright field images were recorded by CCD camera and analyzed with Gatan Digitalmicrograph software (Gatan, Pleasanton, CA). EDS was performed with an Oxford Systems EDS detector attached to the JEOL 2010F microscope and the data were analyzed with Emispec ESVision software (Emispec, Clackamas, OR).

2.8 Capacitance and Dielectric Loss

Capacitance and dielectric loss measurements were made on bulk disk samples with Pt sputtered electrodes using a Hewlett Packard 4284A Precision LCR meter (HP, Santa Clara, CA) with a Hewlett Packard 3478A multimeter in Delta ovens (Delta Technologies, Conway, AR) with custom–designed multiple sample holders over the temperature range of 150 to −50 °C with a 3 °C/min cooling rate at frequencies of 100 Hz to 1 MHz. From these measurements and dimensions of the samples, relative permittivity and the temperature coefficient of capacitance (TCC), which determines the percent the capacitance strays from the room temperature value, were measured.

2.9 Optical Properties and Band Gap Determination

A background of both ultraviolet – visible diffuse reflectance spectroscopy (UV–Vis) and spectroscopic ellipsometry can be found in Appendix A.

2.9.1 Ultraviolet–Visible Diffuse Reflectance Spectroscopy

Ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis) was first used to determine band gaps for sintered, crushed samples for the CTZ system. Reflectance spectra were collected
using a diffuse reflectance spectrophotometer (Perkin–Elmer 950 UV–visible spectrophotometer) over the range of 1.55 – 6.21 eV with a spectral width of 2 nm. A quartz window was used to position the powders. Reflectance spectra were obtained on sintered disks having theoretical densities of > 96% of Ca(Ti_{x},Zr_{1-x})O_{3}, where x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 and Ca(Ti_{0.795}Mn_{0.005}Zr_{0.2})O_{3}, which were crushed and ground into a powder with a mortar and pestle. Optical reflection curves were used to determine the reflectance (R_{\infty}) of the powdered samples by

$$\frac{\alpha}{s} = \frac{(1-R_{\infty})^2}{2R_{\infty}} = F(R_{\infty})$$

(Equation 2–6)

where \(\alpha\) is the absorption coefficient, \(s\) is the scattering coefficient, and \(F(R_{\infty})\) is the Kubelka–Munk function (Kubelka et al., 1931). To determine the band gap energies (\(E_g\)), Tauc plots of \(F(R_{\infty}h\nu)^n\) vs. photon energy (\(h\nu\)) were made according to the Tauc equation (Tauc et al., 1966),

$$[F(R_{\infty}h\nu)^n = B(E_g - h\nu)$$

(Equation 2–7)

where \(B\) is a constant. Band gaps were then calculated from the Tauc plots by fitting a line through the linear portion of the band edge region. A sample having a direct band gap shows a linear dependence where the Kubelka–Munk function first shows distinct increase if \(n = 2\), while one having an indirect gap will shows a linear dependence when \(n = 1/2\) (Tauc et al., 1966).

2.9.2 Spectroscopic Ellipsometry

There are several ambiguities associated with the data collection and analysis of reflectance data from UV–Vis, as outlined in detail in Chapter 3, which can be overcome by using spectroscopic ellipsometry. Sintered disks having theoretical densities of > 96% of Ca(Ti_{x},Zr_{1-x})O_{3}, where x = 0.0, 0.03, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.97, 1.0, Ca(Ti_{0.795}Mn_{0.005}Zr_{0.2})O_{3}, and Ca(Ti_{0.8},Hf_{0.2})O_{3} were ground down to 1 mm thickness, polished using 15 μm to 5 μm alumina powder with deionized water, then polished for 1 hr using 0.05 μm colloidal silica. All samples had a mirror polished finish.

Room temperature ellipsometric spectra (in \(\Delta, \psi\)) were collected ex situ at an angle of incidence of \(\Theta_i = 75^\circ\) from 0.74 – 6.52 eV using a variable angle, multichannel rotating compensator ellipsometer (Lee et al., 1998; Johs et al., 1998) (Model M–2000, J. A. Woollam
Co., Lincoln, NE). The optical properties in the form of the complex dielectric function spectra \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), or alternately the complex index of refraction \( N = n + ik \), and microstructural parameters (for example bulk layer thickness \( d_b \), surface roughness thickness \( d_s \), and relative void fraction in the surface roughness layer \( f_{\text{void}} \)) were extracted using a least squares regression analysis and an un–weighted error function \( \sigma \) (Cong et al., 1991), to iteratively fit a structural model to the measurement using WVASE Software (J. A. Woollam Co., Lincoln, NE). The relationships between the complex optical constants are shown in Table 2–1.

Table 2–1: Equations for complex optical constants, where \( n \) is the refractive index and \( k \) is the extinction coefficient (Pankove, 1971).

<table>
<thead>
<tr>
<th>Complex Optical Constant</th>
<th>Real Component</th>
<th>Imaginary Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon = \varepsilon_1 + i\varepsilon_2 )</td>
<td>( \varepsilon_1 = n^2 - k^2 )</td>
<td>( \varepsilon_2 = 2nk )</td>
</tr>
<tr>
<td>( N = n + ik )</td>
<td>( n = \sqrt{\left(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right)/2} )</td>
<td>( k = \sqrt{\left(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right)/2} )</td>
</tr>
<tr>
<td></td>
<td>( n = \varepsilon_2 / 2k )</td>
<td>( k = \varepsilon_2 / 2n )</td>
</tr>
</tbody>
</table>

The best fit was achieved using the Levenberg–Marquardt algorithm to minimize an error function defined by (Alterovitz et al., 1998):

\[
MSE = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left\{ \sum_{j=1}^{n} \left[ \beta_{ij}^{\text{mod}} - \beta_{ij}^{\text{exp}} \right]^2 \right\}} \tag{Equation 2–8}
\]

where \( N \) is the number of measured \( A \) and \( \psi \) pairs, \( M \) is the number of independent fit parameters, \( n \) is the number of separate \( \beta \) values, and the superscripts “mod” and “exp” designate values from the model and the experimental data respectively. For this research, \( n = 3 \) with \( \beta_{i1} = \cos(2\psi) \), \( \beta_{i2} = \sin(2\psi)\cos(2\psi) \), and \( \beta_{i3} = \sin(2\psi)\sin(A) \). The model structure consisted of a semi–infinite bulk material / surface roughness / air ambient structure where free parameters correspond to the surface roughness thicknesses, \( f_{\text{void}} \), present in the surface roughness region, and parameterizations of the bulk material optical properties in the form of \( \varepsilon \) or \( N \).
To model the surface roughness, a Bruggeman effective medium approximation (EMA) consisting of a varied amount of the volume to be identical to the bulk material and the other varying amount of the volume as void (Fujiwara et al., 2001; Aspnes, 1982). Since the bulk ceramics in this research are polycrystalline, modeling $\varepsilon$ at photon energies having non–zero absorption using the critical–point parabolic band approximation (CPPB) is valid. The CPPB approximation is defined by (Aspnes, 1980):

$$\varepsilon(E) = Ae^{i\theta} \left( \frac{\Gamma}{2E_n - 2E - i\Gamma} \right)^\mu$$  \hspace{1cm} (Equation 2–9)

where $A$ is the amplitude, $\theta$ is the phase projection factor, $E_n$ is the critical point resonance energy, $\Gamma$ is the broadening parameter, and the exponent $\mu$ relates to the dimensionality of the critical points. The CPPB approximation only applies to energies where the material is absorbing (above the band gap). As a result, a divided spectral range model was implemented in which the full spectral range was separated into a low photon energy range in which no significant absorption was present, and a high photon energy range where the material was highly absorbing and critical point features were present.

The low energy region was parameterized separately to avoid incorrect use of the CPPB approximation within the non–absorbing energy range. Depending on the composition, one to two Sellmeier oscillators were used to model the low photon energy range, which are defined by (Collins et al., 2005):

$$\varepsilon(E) = \frac{A}{E_0^2 - E^2}$$  \hspace{1cm} (Equation 2–10)

where $A$ is the amplitude and $E_0$ is the resonance energy. All fitted parameterizations and ranges over which low and high energy ranges were modeled are contained in Appendix B. While $\varepsilon$ was determined independently for each of the high and low photon energy ranges, a common surface roughness thickness, $d_s$, was simultaneously fit and applied to both photon energy ranges.

After the surface roughness was determined via the divided spectral range parameterization, its value was fixed and $\varepsilon$ was extracted through numerical inversion for the full spectral range. Examples of the divided spectral range parameterization of $A$, $\psi$, $\varepsilon_1$ and $\varepsilon_2$ for $x = 0.8$ CTZ are shown in Fig. 2–8.
Fig. 2–8 shows that the use of the divided spectral range technique show good fits to the inverted data. Using these thicknesses for numerical inversion then allowed for unambiguous and accurate generation of $\varepsilon$ for the entire spectral range. To calculate the band gap for each composition, the absorption coefficient, $\alpha$, was calculated from $\varepsilon$ (Collins et al., 2005):

$$\alpha = \frac{4\pi}{\lambda} \sqrt{\frac{\varepsilon_2 + \varepsilon_1^2 - \varepsilon_1}{2}}$$

(Equation 2–11)
where \( \lambda \) is the photon wavelength. The direct band gap energy was determined by taking the zero–intercept of the linear portion of the first onset of absorption in \( \alpha^2 \) vs. photon energy. The same method was used for the indirect band gap with \( \alpha^{0.5} \) vs. photon energy.

2.10 Current – Voltage and Conductivity Measurements

Current–voltage (I–V) measurements were performed on bulk, sputtered Pt–electroded samples using a pA meter/DC voltage source HP–4140B (HP, Santa Clara, CA) and a Kepco bipolar power supply/amplifier model BOP 1000M (Kepco, Flushing, NY) in a custom–built high temperature box furnace at 250 °C over the electric field range of 1 to 25 kV/cm, as shown in Fig. 2–9.

A schematic of a typical circuit layout for a I–V measurement as used in this research is shown in Fig. 2–10.
For all electrical measurements involving bulk samples, one side of the disk/square was entirely sputtered with Pt, whereas the other side was masked so that 2 – 6 individual electrodes could be sputtered, minimizing variations in density and sample preparation from measuring multiple individual samples. An example of an electroded sample is shown in Fig. 2–11.

![Diagram of circuit](image)

Figure 2–10: Schematic of the circuit used in I–V measurements. The S is the switch, R is resistor, $I_m$ is the current measured, V is voltage, and C is the capacitor.

For all electrical measurements involving bulk samples, one side of the disk/square was entirely sputtered with Pt, whereas the other side was masked so that 2 – 6 individual electrodes could be sputtered, minimizing variations in density and sample preparation from measuring multiple individual samples. An example of an electroded sample is shown in Fig. 2–11.

![Image of sample](image)

Figure 2–11: Example of bulk, Pt–electroded sample bottom (left) and masked top (right) for multiple electrical measurements on a single sample. Samples had electrode areas of 3.0 mm$^2$ and thicknesses of 0.2 to 0.5 mm.

The steady state leakage current was measured after the sample was held at a constant bias for 5 to 10 minutes. Samples had electrode areas of 3.0 mm$^2$ and thicknesses of 0.2 to 0.5 mm. Conductivity vs. temperature measurements were made using the same setup with an applied
field of 25 kV/cm from room temperature to 300 °C, allowing 5 minutes to equilibrate at each temperature.

2.11 Polarization – Field Hysteresis Loops

Polarization vs. field (P–E) hysteresis loops were measured using a Labview–designed P–E program with a modified Sawyer–Tower circuit using a Trek model 30/20 ± 30 kV (Medina, NY) voltage amplifier system in custom box furnaces at 25, 100, 200, and 300 °C as shown in Fig. 2–12.

Figure 2–12: Experimental setup for measuring high temperature polarization – field (P–E) hysteresis loops.

A schematic of the modified Sawyer – Tower circuit used in P–E measurements is shown in Fig. 2–13.
At least 10 samples at each temperature were subjected to sinesoidal wave fields with a frequency of 10 Hz starting from a bias of 100 V and increasing in 20 V increments until the capacitor failed. Characteristic breakdown strengths were obtained using Weibull statistics, in which the breakdown strengths are ranked in increasing order and the median rank (MR) of the data is calculated as

$$MR = \frac{j-0.3}{N+0.4}$$  

(Equation 2–12)

where $j$ is the rank and $N$ is the total number of samples. The characteristic breakdown strength is then determined from the zero–intercept of $\ln(E)$ vs. $\ln(\ln(1/(1-MR)))$. The Weibull modulus, which determines the degree of variation in the data set, is determined from the slope of the linear trend line.

The maximum capacitor energy density ($U_{vol}$) in the absence of dielectric loss can be related to the dielectric breakdown strength ($E_b$) by

$$U_{vol} = \frac{\varepsilon_0 \varepsilon_r E_b^2}{2} \text{ J/cm}^3,$$  

(Equation 2–13)

where $\varepsilon_r$ is the relative dielectric permittivity and $\varepsilon_0$ is the free–space permittivity ($8.85\times10^{-14}$ F/cm) (Love, 1990).
The overall maximum energy storage of a lossless linear capacitor is proportional to the dielectric constant and the square of the dielectric breakdown strength, while the energy storage is proportional to the dielectric constant and the square of the operating voltage \( V \) (Love, 1990). A schematic of how energy density is quantified from hysteresis loops in linear dielectrics is shown in Fig. 2–14.

The energy density was quantified as the area between the positive \( y \)-axis and the maximum polarization value on the discharge/decreasing field \( E \) portion of the unipolar curves where

\[
U_{vol} = \int EdP \ (J/cm^3),
\]  

(Equation 2–14)

with the dielectric displacement approximated using polarization, \( P \) (Burn, 1972). Dielectric loss was quantified according to (Uchino et al., 2001),

\[
\tan \delta = \left( \frac{1}{2\pi} \right) \left( \frac{w_e}{2U_e} \right)
\]

(Equation 2–15)

where \( w_e \) is the within the unipolar loop and \( U_e \) is the recoverable energy density. When a capacitor is being utilized, there are more variables involved that lead to volumetric loss through

Figure 2–14: Schematic of how energy density and dielectric loss are quantified for linear dielectrics.
heat dissipation and Watt loss. The Watt loss can be accounted for by calculating the power dissipation density \( P / V \) (Moulson, 2003),

\[
\bar{P} = \frac{1}{2} E_b^2 \omega \varepsilon_0 \varepsilon_r \tan \delta \text{ (W/cm}^3\text{),}
\]

where \( \bar{P} \) is the time average power dissipated, \( E_b \) is the breakdown strength (V / cm), and \( \omega \) is the frequency of the applied field (Hz)

Dielectric breakdown was quantified as the last field sustained before failure occurred. All values were obtained using a script written in Mathematica (Wolfram Research, Champaign, IL). Power dissipation densities were calculated using values required for Eq. 2–16 from P–E loops at the maximum field before breakdown occurred.

2.12 Impedance Spectroscopy

Impedance spectroscopy was used to measure the dielectric properties of capacitors for various compositions as a function of frequency. Since contributions to the electric dipole moment exist at specific frequencies, the various contributions to conductivity at elevated temperatures can be measured and modeled using equivalent circuits. For the measurement, a voltage \( U_0 \) having a fixed frequency of \( \omega / 2 \) is applied to a material. This voltage causes a current \( I_0 \) at the same frequency in the material, as shown in Fig. 2–15.
Generally, there is a phase shift between the current and voltage denoted as the phase angle ($\varphi$). The ratio of the phase angle to $U_0$ and $I_0$ is determined by the dielectric properties of the material being measured. Typically, complex notation is used to describe $U(t)$ and $I(t)$ where,

$$U(t) = U_0 \sin(\omega t) = Re\left(U^* e^{i\omega t}\right)$$

(Equation 2–17)

$$U(t) = I_0 \sin(\omega t + \varphi) = Re\left(I^* e^{i\omega t}\right)$$

(Equation 2–18)

where the following relations apply:

$$U^* = U' + U'' = U_0$$

(Equation 2–19)

$$I^* = I' + iI''$$

(Equation 2–20)

$$I_0 = \sqrt{I' + iI''}$$

(Equation 2–21)

$$\tan \varphi = \frac{i''}{I'}$$

(Equation 2–22)

Figure 2–15: Amplitude and phase relation between voltage ($U(t)$) and current ($I(t)$) of a dielectric material (After Alpha High Resolution Dielectric Analyzer User’s Manual).
When a material shows a linear dielectric response to the field, the measured impedance of the capacitor is

\[ Z^* = Z' - iZ'' = \frac{U^*}{I^*} \quad \text{(Equation 2–23)} \]

which relates to the complex dielectric function as

\[ \varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega) C_0} \quad \text{(Equation 2–24)} \]

where \( \omega \) is the frequency of the applied field and \( C_0 \) is the capacitance of the material.

### 2.12.1 Measurement and Equivalent Circuit Modeling

Impedance measurements were performed using a custom–built high temperature box furnace under an oscillation voltage of 100 mV using a Solartron S11287 (Hampshire, UK) electrochemical interface and a 1255B frequency response analyzer. Spectra were fitted using Z–View software (Scribner Associates). For the air–fired CTZ and CTH systems, with and without Mn, and quenched CTH + Mn, impedance spectra were collected at 600, 625, 650, 675, and 700 °C. For the quenched CTH + Mn system, impedance spectra were collected every hour for 13 hours as the sample re–oxidized in situ. at 700, 725, and 750 °C. For the un–doped CTZ and quenched CTH + Mn systems, the effect of applying a direct current (dc) bias in addition to the alternating current (ac) oscillation voltage on the spectra was observed by applying a bias of 0 to 1.0 V while measuring impedance.

The equivalent circuit used to model the un–doped CTZ and CTZ systems was based on previous research investigating mixed ionic – electronic conduction in Pb(Zr\(_{0.53}\)Ti\(_{0.47}\))O\(_3\) capacitors having ionically blocking and electronically reversible electrodes (Donnelly et al., 2010). When developing an equivalent circuit for modeling impedance data, it is more useful to start with a simple circuit and add elements sequentially until the entire spectrum is fit, rather than building a complete model and fitting the whole data set at once. By doing this, a better understanding of how each circuit element contributes to the fitting is achieved.

The impedance spectra for the un–doped CTZ and CTH compositions were fit using the same model. The first step in the modeling is shown in Fig. 2–16.
It can be seen from Fig. 2–16 that as expected, the parallel combination of the ionic and electronic resistances with the bulk capacitance generates a high frequency semicircle in the $Z^*$ plot. However, it does not fully fit the feature. Due to limitations of the measurement equipment, the data do not begin at 0. To compensate for this, an offset resistance ($R_{\text{offset}}$) can be assigned the value of $Z'$ at which the data begins collecting to aid in fitting. The stretching of the feature can be attributed to a grain boundary impedance, as suggested by Donnelly et al. (Donnelly et al., 2010), which can be incorporated into the equivalent circuit by the parallel combination of $R_{\text{G.B.}}$ ($R_{\text{G.B.}} = d/\sigma_{\text{G.B.}}A$) and constant phase element (CPE), where $Z_{\text{CPE}} = Z_0/(i\omega)^\rho$, in series in the ionic rail as shown in Fig. 2–17.
It can be seen from Fig. 2–17 that this addition to the circuit successfully fits the high frequency feature. Since partially blocking electrodes are being considered, the low frequency feature can be modeled using a Warburg element, \( Z_W = Z_W^0 (i\omega)^{-0.5} \), which represents diffusion–limited behavior, and a double layer capacitance represented by a CPE representing the capacitance due to ionic polarization of the ceramic–electrode interface. In un–doped CTH, it was found that the double layer capacitance dominated the low frequency behavior and therefore the Warburg was ignored. The result of the final fitting is shown in Fig. 2–18.
44

It can be seen in Fig. 2–18 that the impedance model shows a good fit to the entire impedance spectrum. Conductivities can be directly extracted from equivalent circuit modeling. If the conductivities show Arrhenius behavior, activation energies ($E_a$) for each circuit element can be determined according to

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}}$$

(Equation 2–25)

where $k$ is Boltzmann’s constant (8.617×10⁻⁵ eV/K), $T$ is the absolute temperature (Kelvin), $\sigma$ is conductivity (S/cm), and $\sigma_0$ is a pre–exponential constant. Additionally, transference numbers, which describe the motion of charge carriers relative to each other, can be calculated according to

$$I_{elec} = \sigma_{elec} / (\sigma_{elec} + \sigma_{ion})$$

and

$$I_{ion} = 1 - I_{elec}.$$

The doped systems, CTZ + Mn and CTH + Mn, were much less complicated and did not appear to exhibit the characteristics of mixed conduction. The response was well described by a simple parallel RC combination composed of the bulk capacitance, $C_{bulk}$, in parallel with a single resistance, which, due to the absence of any electrode polarization effect was apparently the
electronic resistance, $R_{\text{elec}}$. For fitting purposes, a CPE could be added in parallel to both of these elements to compensate for the slight dispersion.

The quenched CTH + Mn impedance spectra showed a distinctly different response compared to the doped and undoped systems. Rather than a high frequency bulk feature with included grain boundary impedance and low frequency double layer feature, three distinct features were observed. If quenching CTH + Mn freezes in the Mn$^{3+}$ valence state, it will act as an acceptor on the Ti$^{4+}$ site, yielding a corresponding amount of oxygen vacancies according to Eq. 2–4 and ionic conduction will dominate. As a result, it is likely that while CTH + Mn is still a mixed conductor, ionic conduction will dominate the impedance spectra until the sample re-oxidizes. For this reason, the quenched CTH + Mn was modeled assuming ionic conduction dominated in a diffusion–based grain–grain boundary (or in-grain chemical relaxation)–electrode double layer model with RC circuits in series (Jamnik et al., 1999; Yang et al., 2004; Guo et al., 2001; Jamnik et al., 2003).

The first step to modeling the quenched CTH + Mn system is shown in Fig. 2–19.

![Complex impedance and first step in the equivalent circuit model fitting for the high frequency feature of the quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) composition at 675 °C.](image)

**Figure 2–19:** Complex impedance and first step in the equivalent circuit model fitting for the high frequency feature of the quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) composition at 675 °C. $R = $ resistance and C.P.E = constant phase element.
From Fig. 2–19, it can be seen that the equivalent circuit fits the high frequency relaxation well. By substituting a CPE for a regular capacitor, the fit is close but not comparable to that of the CPE due to the natural dispersion that occurs in polycrystalline ceramics (Donnelly et al., 2010). The second feature was fit by adding a grain boundary or interfacial RC circuit in series with the bulk RC circuit as shown in Fig. 2–20.

![Complex impedance and second step in the equivalent circuit model fitting for the high frequency feature of the quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) composition at 675 °C. R = resistance, C.P.E = constant phase element, and G.B = grain boundary/interface.](image)

Lastly, similarly to the un–doped CTH and CTZ models, the third feature was fit assuming a parallel combination of a diffusional Warburg impedance and a double layer capacitance in the form of a CPE. The final fit is shown in Fig. 2–21.
From Fig 2–21, it can also be seen that the equivalent circuit fits well to the experimental data. The impedance spectra for the quenched system will be discussed in further detail in Chapter 5.

![Equation Diagram](image)

Figure 2–21: Complex impedance and final step in the equivalent circuit model fitting for the high frequency feature of the quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) composition at 675 °C. R = resistance, C.P.E = constant phase element, D.L. = double layer and G.B = grain boundary/interface.

2.13 Thermally Stimulated Depolarization Current

The thermally stimulated depolarization current (TSDC) measurement was originally developed by Bucci and Fieschi in 1964 (Bucci, 1964). For decades, TSDC has been used to characterize depolarization currents in polymer systems because they typically only possess a single relaxation mechanism, which can be measured at low temperatures. Eventually, interest in the TSDC method grew for analyzing inorganic systems as a method to study the transport behavior of charge carriers such as oxygen vacancies (Jeong et al., 2006; Szymczak et al., 2007; Jeong et al., 2006, Liu et al., 2008).

The technique consists of heating a sample to a specific temperature, $T_p$, and poling it under a constant electric field, $E_p$ for a time, $t_p$. During this poling time, the possible defects that
exist in the system, namely oxygen vacancies, respond to the field and form a dipole distribution. The sample is then quickly cooled to a lower temperature, $T_0$, freezing in the defects. The field is then removed and the sample is heated at a constant rate, $\beta$. The increase in temperature creates thermal energy to excite lattice vibrations, activating the polarized defects. These polarized states or charges then relax, which results in a small current in the external current known as the TSDC. This is outlined schematically in Fig. 2–22.

![Graphical depiction of the temperature and electric field profile for the thermally stimulated depolarization current (TSDC) measurement. $T_p$ = poling temperature and $E_p$ = poling field.](image)

The circuit used for I–V testing was also utilized for TSDC. The TSDC technique was used to qualitatively support claims made by impedance spectroscopy on contributions to conduction in the CTH, CTH + Mn, and quenched CTH + Mn systems. For all systems, bulk, Pt–electroded samples were heated to a $T_p$ of 250 °C, and poled for a $t_p$ of 1 min to avoid degradation using the same equipment as I–V and conductivity measurements. Longer poling times were tested and this $t_p$ was sufficient to obtain peaks in the TSDC spectra. Poling fields ($E_p$) of 5, 10, 15, 20, and 25 kV/cm were applied, and the samples were then cooled to a $T_0$ of 60 °C with the respective field still applied. The field was then removed, and the samples were heated at a $\beta$ of 5
°C/min to 500 °C to fully depolarize all frozen in defects. The samples were then cooled to $T_p$ and the experiment was repeated with the next incremental field.
3.1 Introduction

The main focus of this chapter is to identify an optimum composition of Ca(Ti\textsubscript{x},Mn\textsubscript{y}Zr\textsubscript{0.2})O\textsubscript{3} (CTZ + Mn) that minimizes both ionic and electronic conduction to yield high energy densities. Initially, characterization of Ca(Ti\textsubscript{x}Zr\textsubscript{1-x})O\textsubscript{3} (CTZ) across the entire solid solution will be presented to develop an initial understanding of the basic trends that exist in the system such as unit cell volume, microstructure, and dielectric permittivity. Focus will then be directed to characterization of compositions on the higher permittivity (CaTiO\textsubscript{3}) end of the binary mixture, with various amounts of Mn doping added to minimize ionic conductivity. Lastly, optical characterization will give insight into identifying compositions with attractive band gap energies for minimizing electronic conductivity in the system.

3.2 Background

C0G–type materials have recently been shown to be competitive with polymer film capacitors, and are commonly used in power inverters for power electronics systems (Randall et al., 2009; Lostetter et al., 2009). A typical C0G composition is Sr, Mn doped Ca(Ti\textsubscript{0.2}Zr\textsubscript{0.8})O\textsubscript{3}, which yields a relative permittivity of $\varepsilon_r \sim 34$–75, breakdown strengths of 0.65–1.75 MV/cm, thermal coefficient of capacitance (TCC) of 30 ppm/°C or ± 0.5 % from −50 to 125 °C, and energy densities of up to 5 J/cm\textsuperscript{3} (Randall et al., 2009). Ultimately, the breakdown strength and relative permittivity determine the maximum recoverable energy density, $U_{vol}$, by

$$U_{vol} = \frac{\varepsilon_0 \varepsilon_r E_b^2}{2} \text{ (J/cm}^3\text{)}$$

(Equation 3–1)

where $\varepsilon_r$ is the relative dielectric permittivity and $\varepsilon_0$ is the free–space permittivity (8.85x10\textsuperscript{-14} F/cm), and $E_b$ is the breakdown strength (kV/cm) (Love, 1990). While the breakdown strengths of zirconate–rich systems are high, the low permittivity associated with CaZrO\textsubscript{3} limits the recoverable energy density.
By using C0G compositions as a basis but focusing on the higher permittivity ends of the binaries such as CTZ where $x = 0.7, 0.8, 0.9$, a larger polarization can be achieved. The breakdown strength of CaTiO$_3$ is typically lower than that of CaZrO$_3$, which would limit the recoverable energy density. However, this can be attributed to a large amount of ionic polarization in the CaTiO$_3$ system relative to CaZrO$_3$. In an attempt to minimize the ionic conduction and obtain high breakdown strengths, acceptor doping with Mn can be utilized. Acceptor doping with Mn has been used in both CTZ and similar systems as a means to minimize high temperature and high field losses that are often absent in room temperature measurements to improve high temperature breakdown stability and reliability (Osawa et al., 1993; Pinceloup et al., 2006; Jeong et al., 2007).

Binary dielectric systems such as Pb(Zr$_x$Ti$_{1-x}$)O$_3$, Ba(Zr$_x$Ti$_{1-x}$)O$_3$, and (1–$x$)(BaTiO$_3$–Gd$_2$O$_3$–MgO–MnO)–xBaZrO$_3$ and those in this research are typically treated as mixed ionic–electronic conductors (Donnelly et al., 2010; Levi, 2006; Nakamura et al. 1999). While the dominant material parameter that governs the electronic conductivity of semiconductors and insulators is the electronic band gap, there are a number of factors that affect the ionic conductivity in orthorhombic perovskite systems, some of which are the average bond energy, thermal vibration of cations, jumping distance between adjacent anions, and polarizability. Ionic conductivity is largely dominated by the mobility of oxygen anions affecting diffusion through the crystal lattice, while the dominant material parameter that governs the electronic conductivity of semiconductors and insulators is the electronic band gap.

The average bond energy (ABE kJ/mol) determines the energy necessary to break metal–oxygen bonds from their respective coordination, which form vacancies and thus has a large effect on ionic conductivity (Kilner, 1981; Cook et al., 1991). The ABE for ABO$_3$ perovskites is calculated by,

$$\text{ABE} = \frac{1}{12} \left( \Delta H_{AO} - \Delta H_A - \frac{1}{2} D_{O2} \right) + \frac{1}{6} \left( \Delta H_{BO2} - \Delta H_B - \frac{1}{2} D_{O2} \right)$$  \hspace{1cm} \text{(Equation 3–2)}$$

where $\Delta H_{AO}$ and $\Delta H_{BO2}$ are the heat of formation of the oxides, $D_{O2}$ is the dissociation energy of oxygen, and $\Delta H_A$ and $\Delta H_B$ are the heat of vaporization of the metals. The calculated ABEs for CaTiO$_3$ and CaZrO$_3$ are 311.1 kJ/mol and 358.3 kJ/mol respectively, so it is expected that compositions with higher CaZrO$_3$ content will have less oxygen vacancies.
The thermal vibration of cations also affects the diffusion of oxygen vacancies across the crystal lattice, the amplitude of which is inversely proportional to the square root of the cation molecular weight (Mogensen et al., 2004). For Zr\(^{4+}\) and Ti\(^{4+}\), the proportional thermal vibration energies are \(1.2 \times 10^{-4} \text{ (g/mol)}^{-2}\) and \(4.3 \times 10^{-4} \text{ (g/mol)}^{-2}\) respectively. Since Zr is nearly twice as heavy as Ti, ionic conductivity is expected to be lower in Zr–rich compositions in the binary.

Since the migration of anions through the perovskite structure is expected to occur via vacancy exchange, the diffusion of oxygen anions is inversely proportional to the jumping distance between available sites within the oxygen octahedral (Kilner et al., 1982). The distance between adjacent oxygen sites for CaTiO\(_3\) and CaZrO\(_3\), calculated from lattice parameters obtained via X–ray diffraction (XRD), were 4.68 Å and 4.91 Å respectively. As a result, it is expected that the diffusion coefficient for oxygen anions should be smaller in compositions that contain more CaZrO\(_3\) than CaTiO\(_3\).

Lastly, the polarizability of the material can also contribute to ionic conductivity, since the activation energy of anion migration decreases as lattice polarizability increases (Mogensen et al., 2004; Sammells et al., 1992). The polarizability (\(\alpha\)), refractive index (\(n\)), dielectric constant (\(\varepsilon\)), electric polarization (\(P\)), and electric field (\(E\)) are related by the scalar relationships,

\[
\varepsilon E = E + 4\pi P = E + 4\pi N\alpha E \quad \text{(Equation 3–3)}
\]

\[
\varepsilon - 1 = n^2 - 1 = 4\pi N\alpha \quad \text{(Equation 3–4)}
\]

where \(N\) is the number of atoms/cm\(^3\). Since CaTiO\(_3\) has a larger relative permittivity (\(\varepsilon_r \sim 171\) compared to 30 for CaZrO\(_3\)), it is expected that CaTiO\(_3\) – rich compositions will have a higher polarizability, and thus exhibit more ionic conductivity relative to CaZrO\(_3\) – rich compositions (Kersch et al., 2009; Feteira et al., 2008). It has been found in BaTiO\(_3\) and BaZrO\(_3\) that there is not a significant difference in ionic polarizability at room temperature in the cubic phase, but the materials considered here are orthorhombic and will most likely vary more (Roberts, 1951).

The parameters of the end members give insight into how ionically and electronically conducting various binary compositions of the end members may be. However, the trends in material properties may not be linear across the entire composition range. As a result, it is crucial to obtain an understanding of the trends in material properties such as unit cell volume, microstructure, relative permittivity, and band gap energy as well as how doping with acceptors
such as Mn affects these properties. By measuring these trends, the best compositions for optimizing the ambient and high temperature recoverable energy density can be obtained by following the schematic in Fig. 3–1.

The reasons for why Mn doping improves electrical properties in similar systems, including BaTiO$_3$ and (Ca$_{0.7}$Sr$_{0.3}$)(Zr$_{0.97}$Ti$_{0.03}$)O$_3$, have been largely based on speculations such as Mn valence state, site occupation, and lattice/grain boundary incorporation leading to reduced concentrations and/or mobility of oxygen vacancies (Osawa et al., 1993; Pinceloup et al., 2006; Jeong et al., 2007). The valence of Mn has been known to change from Mn$^{2+}$ at low oxygen activities, to Mn$^{3+}$ or a mixture of Mn$^{3+}$ and Mn$^{4+}$ in increasing oxygen activities such as re–oxidation, and to Mn$^{3+}$ or Mn$^{4+}$ when fired in air. The latter are the assumed possible valence states for this work (Desu, 1981).

Figure 3–1: Schematic representation of objectives to establish routes towards high energy density linear dielectric materials.
Based on B–site incorporation in BaTiO$_3$, Mn is assumed to occupy the B site in CTZ. The assumption is also valid if one considers the similarities of ionic radii (Ba$^{2+} = 161$ pm (XII), Ti$^{4+} = 61$ pm (VI), Ca$^{2+} = 134$ pm (XII), Zr$^{4+} = 72$ pm (VI), Mn$^{4+} = 53$ pm (VI)) between BaTiO$_3$ and CTZ (Shannon, 1976). The solubility limit of Mn in CTZ and closely related systems has not been extensively studied. The solubility limit of Mn in Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ has been determined by energy dispersive X–ray spectroscopy (EDS) to be ~ 0.5 mol% (Hu et al., 2005).

### 3.3 Ca(Ti$_x$Zr$\_{1-x}$)O$_3$ (CTZ) and Ca(Ti$_x$Mn$_y$Zr$\_{0.2}$)O$_3$ (CTZ + Mn) Crystal Structure and Microstructure

The difficulties associated with avoiding mixed phases of binary end members in calcined powders of similar Ca–based perovskite systems have been experienced by previous researchers, who attempted to achieve a single perovskite phase through various solid state and chemical processing routes (Xu et al., 2000). For solid state processing, it was found that fluorite (ZrO$_2$) 2nd phases were common when samples were heated at less than 1200 °C, but were minimized when heated above 1200 °C. In this research, minimal fluorite content was observed upon sintering of dense bulk samples at 1250 °C to > 96% theoretical density, but was still present in some XRD patterns. However, the amount of ZrO$_2$ as indicated by the Rietveld analyses was typically less than 1.0 %. The indexed room–temperature XRD pattern for $x = 0.8 = \text{Ca(Ti}_x\text{Zr}_{1-x}\text{)O}_3$ (CTZ) and $x = 0.7$, 0.8, and 0.9, $y = 0.005 \text{Ca(Ti}_x\text{Mn}_y\text{Zr}_{0.2}\text{)O}_3$ (CTZ + Mn) are shown in Fig. 3–2.
The main Bragg reflections show slight splitting, indicating CTZ and CTZ + Mn have an orthorhombic structure. A small peak at ~ 30\(^\circ\) 2\(\theta\), denoted with a circle, was indexed as the fluorite phase \(\text{ZrO}_2\) and has been observed by previous authors for similar systems as either \(\text{ZrO}_2\) or \(\text{ZrTiO}_4\) (Lamrani et al., 2011).

Fig. 3–3 shows the corresponding unit cell volumes for the entire CTZ composition range for sintered and crushed bulk samples without Mn doping.
Indexing of the XRD pattern also results in an orthorhombic unit cell having symmetry described by the \( Pcmn \) space group for CTZ \( x = 0.0 \) to 0.6 and \( Pbnm \) for CTZ \( x = 0.7 \) to 1.0, shown schematically in Fig. 3–4.

Figure 3–3: Unit cell volumes across the entire undoped \( \text{Ca(Ti}_{x}\text{Zr}_{1-x}\text{)}\text{O}_3 \) (CTZ) composition range measured from sintered and crushed bulk samples. The error bars were ± 0.01 Å and could not be seen on the plot.

Figure 3–4: Schematic of an orthorhombic \( \text{ABO}_3 \) perovskite having the \( Pbnm \) space group. Red spheres represent the A cation, yellow spheres represent B cations, and gray shaded planes represent oxygen octahedra.
As seen in Fig. 3–3, the trend in unit cell volume across the composition range generally follows Vegard’s law (Vegard, 1921). Slight deviations occur at x = 0.3 and 0.7, which may indicate solubility gaps, but are more likely due to ZrO$_2$ 2nd phases. Numerous attempts at eliminating the ZrO$_2$ phase including reactive calcinations could not remove the ZrO$_2$ phase (Kim et al., 1991). Specific unit cell volumes for compositions of interest were 233.18 Å, 230.70 Å, and 227.03 Å for x = 0.7, 0.8, and 0.9 respectively. The theoretical X–ray densities were calculated to be 4.16 g/cm$^3$ for x = 0.8 CTZ and 4.23, 4.15, and 4.09 g/cm$^3$ for x = 0.7, 0.8, and 0.9, y = 0.005 CTZ + Mn with 0.5 mol% Mn doping respectively. These values are close to the theoretical density of the compositions calculated using the series mixing rule with the theoretical densities of CaTiO$_3$ (4.03 g/cm$^3$) and CaZrO$_3$ (4.63 g/cm$^3$) (Koopmans et al., 1983).

Sintered, laminated samples for both CTZ and CTZ + Mn were > 97% theoretical density. Scanning electron microscope (SEM) images of grain microstructures for several air fired compositions across the un–doped CTZ composition range are shown in Fig. 3–5. In general, no specific trend in the grain size value was observed across the CTZ composition range. However, as also observed in the Ba(Zr$_{x}$Ti$_{1-x}$)O$_3$ solid solution, the grain microstructure becomes more bimodal towards the CaZrO$_3$ – rich end of the binary as shown by an increase in small grains relative to the majority of grain sizes (Levi, 2006). This is most likely due to the refractory nature of CaZrO$_3$, which generally requires higher sintering temperatures relative to CaTiO$_3$. Since CaTiO$_3$ fully densifies at lower temperatures than CaZrO$_3$, there is more time for homogenous grain growth to occur in CaTiO$_3$. 
From Fig. 3–5, there are no clear differences in contrast in the $x = 0.3 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ composition that would indicate $\text{ZrO}_2$ 2nd phases. Previous researchers have reported improved densification and dielectric properties in $(\text{Ca}_{0.7}\text{Sr}_{0.3})(\text{Zr}_{0.97}\text{Ti}_{0.03})\text{O}_3$ with high levels of Mn doping (up to 4.4 mol\% sintered in air as well as reducing atmospheres (Pinceloup et al., 2006). This doping study was duplicated in the $\text{CaTiO}_3$ – rich CTZ system to determine the optimum dopant.

Figure 3–5: Scanning electron microscope (SEM) images of thermally etched grain microstructures for several un–doped, air–fired $\text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) compositions across the composition range.
concentration. First, trends in densification were investigated by dilatometry on bulk samples that did not contain any glass frits as a sintering aid, as shown in Fig. 3–6 for $x = 0.8$ CTZ, to determine what doping amount would sinter at the lowest temperature and yield the smallest grain size.

Figure 3–6: Dilatation (shrinkage) curves for un–doped $x = 0.8 \text{Ca(Ti}_{x}\text{Zr}_{1-x})\text{O}_3$ (CZT) and $x = 0.8$, $y = 0.005$, 0.02, 0.03, and 0.04 $\text{Ca(Ti}_{x-y}\text{Mn}_{y}\text{Zr}_{0.2})\text{O}_3$ (CTZ + Mn) in air and without glass frits as a sintering aid.

It can be seen from Fig. 3–6 that unlike the CaZrO$_3$ – rich compositions studied by Pinceloup et al., lower mol% Mn doping yielded earlier onsets of densification (Pinceloup et al., 2006). The temperatures at which densification began and theoretical densities (T.D.) after heating to 1400 °C without a sintering aid are listed in Table 3–1.
Contrary to doping on the CaZrO $\text{3}$ – rich end of the composition range as seen by previous researchers, the un–doped and 0.5 mol% Mn–doped CaTiO $\text{3}$ – rich CTZ samples showed the earliest onset of densification (Pinceloup et al., 2006). It is important to note that while the 0.5 mol% Mn–doped showed a low final % theoretical density relative to the compositions doped with higher mol% Mn, the 0.5 mol% Mn – doped composition reached % T. D. of > 96% when sintered with the glass frit sintering aid at 1200 °C, whereas samples with higher mol% Mn doping yielded lower values. The SEM images of corresponding thermally etched grain microstructures for CTZ with and without Mn doping sintered at 1300 °C are shown in Fig. 3–7.

Table 3–1: Densification onset temperature and % theoretical density in air for $x = 0.8$ Ca$\text{Ti}^{x}\text{Zr}^{1-x}\text{O}_3$ (CTZ) and $x = 0.8$, $y = 0.005, 0.02, 0.03, 0.04$ Ca$\text{Ti}^{x-y}\text{Mn}^{y}\text{Zr}_{0.2}\text{O}_3$ (CTZ + Mn).

<table>
<thead>
<tr>
<th>CTZ $x = 0.8$ Sample</th>
<th>Densification Onset T (°C)</th>
<th>% Theoretical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-Doped</td>
<td>850</td>
<td>96</td>
</tr>
<tr>
<td>0.5 mol% Mn</td>
<td>850</td>
<td>94</td>
</tr>
<tr>
<td>2 mol% Mn</td>
<td>950</td>
<td>94</td>
</tr>
<tr>
<td>3 mol% Mn</td>
<td>975</td>
<td>98</td>
</tr>
<tr>
<td>4 mol% Mn</td>
<td>925</td>
<td>96</td>
</tr>
</tbody>
</table>
The grain sizes measured for the CTZ + Mn system were 2.10, 2.41, 1.39, 1.09, and 1.13 μm for un-doped $x = 0.8 \text{ Ca(Ti}_x\text{Zr}_1\text{x)O}_3$ and $x = 0.8$, $y = 0.005$, 0.02, 0.03, and 0.04 $\text{Ca(Ti}_x\text{Mn}_y\text{Zr}_0\text{.2)O}_3}$ (CTZ + Mn) respectively. Contrary to the literature on but CaZrO$_3$ – based compositions, grain growth was promoted with low levels of Mn doping, and retarded with higher levels of Mn doping (Pinceloup et al., 2006). To assess whether a valence change from Mn$^{4+}$ to Mn$^{3+}$ and/or Mn$^{2+}$ had an effect on grain size, samples were sintered at 1300 °C at pO$_2 = 10^{-11}$ atm. The SEM images of the thermally etched, reduced CTZ and CTZ + Mn samples are shown in Fig. 3–8.

Figure 3–7: SEM images of thermally etched $x = 0.8$, $y = 0.005$, 0.02, 0.03, and 0.04 $\text{Ca(Ti}_x\text{Mn}_y\text{Zr}_0\text{.2)O}_3}$ (CTZ + Mn) samples fired in air at 1300 °C.
The measured grain sizes for the CTZ samples fired in low pO$_2$ conditions were 2.86 μm for $x = 0.8$ Ca(Ti$_{1-x}$Zr$_{1-x}$)O$_3$ (CTZ) and 1.30, 1.50, 1.53, and 1.71 μm for $x = 0.8$, $y = 0.005$, 0.02, 0.03, and 0.04 Ca(Ti$_{1-x}$Mn$_y$Zr$_{0.2}$)O$_3$ (CTZ + Mn) respectively. The grain sizes for the low pO$_2$ firing follow the trend observed by Pinceloup et al. more closely, but it is not possible to discern whether the trend is due to Mn being incorporated into the lattice or segregating to the grain boundaries from grain microstructures in this work and will be addressed in a later chapter (Pinceloup et al., 2006). In an attempt to determine how homogenous the distribution of atoms was and whether Mn was segregating at all, energy dispersive X–ray spectroscopy (EDS) was performed on air–fired $x = 0.8$ CTZ doped with 0.5 and 4 mol% Mn as shown in Fig. 3-9.

Figure 3-8: SEM images of thermally etched $x = 0.8$, $y = 0.005$, 0.02, 0.03, and 0.04 Ca(Ti$_{1-x}$Mn$_y$Zr$_{0.2}$)O$_3$ (CTZ + Mn) fired at 1300 °C at pO$_2 = 10^{-11}$ atm.
Figure 3–9: Energy dispersive X–ray spectroscopy (EDS) images of air–fired $x = 0.8$ Ca(Ti$_{x-y}$Mn$_y$Zr$_{0.2}$)O$_3$ with a) $y = 0.05$ (05 Mn CTZ) b) $y = 0.4$ (4 Mn CTZ).
From Fig. 3–9, it can be seen that all elements show a generally homogeneous distribution throughout the sample. While some Mn segregation can be seen on grain boundaries, it is inconclusive from EDS whether doping with low or high levels of Mn results in grain boundary segregation of the acceptor dopant. There was no evidence of the glass sintering aid segregating to grain boundaries in the EDS elemental analysis.

### 3.4 Electrical Characterization

The temperature coefficient of capacitance (TCC) for the air–fired CaTiO₃ — rich end of the CTZ binary and dielectric loss from –50 to 150 °C at 1 kHz is shown in Fig. 3–10.

![Graph showing TCC and dielectric loss](image)

**Figure 3–10:** Temperature coefficient of capacitance (TCC) and dielectric loss (tanδ) for $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) and $x = 0.7, 0.8, \text{and 0.9}$, $y = 0.005 \text{Ca(Ti}_{x-0.3}\text{Mn}_0.3\text{Zr}_{0.2})\text{O}_3$ (CTZ + Mn), from –50 to 150 °C at 1 kHz.

Doping with 0.5 mol% Mn showed a significant decrease in dielectric loss above 100 °C relative to the un–doped material and the lower losses compared to higher Mn doping concentrations. All samples doped with Mn showed dielectric loss values < 0.01 and showed minimal frequency dependence over the measured temperature range. Values for TCC were
similar between the systems, calculated as ±18.1% for Ca(Ti_{0.8}Zr_{0.2})O_3 and ±16.3%, ±17.4%, and ±17.2% for Ca(Ti_{x-y}Mn_yZr_{0.2})O_3 y = 0.005 and x = 0.7, 0.8, and 0.9, respectively. It is important to note that while low TCC values are important for C0G applications, deviations from room temperature are acceptable for this research providing the higher permittivities yield large energy densities at high temperatures. Regardless, Mn doping slightly decreased the TCC for all compositions measured.

The room temperature relative permittivities across the un–doped Ca(Ti,xZr_{1–x})O_3 solid solution are shown in Fig. 3–11a and relative permittivities for Ca(Ti_{x–y}Mn_yZr_{0.2})O_3 y = 0.005 and x = 0.7, 0.8, and 0.9 are shown in Fig. 3–11b.

Figure 3–11: Room temperature relative permittivities a) across the un–doped Ca(Ti,xZr_{1–x})O_3 composition range with linear fit to show Vegard’s Law behavior and b) room temperature relative permittivities for x = 0.7, 0.8, and 0.9, y = 0.005 Ca(Ti_{x–y}Mn_yZr_{0.2})O_3 and compared to the un–doped compositions.

As seen in Fig. 3–11a, the room temperature relative permittivities were 133 ± 7, 157 ± 5, and 185 ± 8 for x = 0.7, 0.8, and 0.9 Ca(Ti,xZr_{1–x})O_3 respectively. The measured relative permittivities were generally higher than that predicted from the fractions of the end members (ε_r = 129, 147, and 157 for x = 0.7, 0.8 and 0.9 Ca(Ti,xZr_{1–x})O_3 respectively). Doping with Mn showed little effect on relative permittivity within the reported error as shown in Fig. 3–11b.
From the results of the basic characterization, 0.5 mol% Mn was selected as the optimal doping concentration.

CaTiO$_3$ is commonly regarded as an incipient ferroelectric and typically shows increasing permittivities as the material approaches the ferroelectric phase transition at low temperatures. CaZrO$_3$, on the other hand, is a linear dielectric. As a result the latter exhibits constant permittivity, typically at lower values than incipient ferroelectrics. Overall, the dielectric and electrical properties of these perovskite materials are determined by the BO$_6$ octahedra, and more specifically the electronic distributions associated with the B – O bonds. The materials studied in this work have a higher percentage of CaTiO$_3$, so it is not surprising that the dielectric properties trend towards the properties of that end member. Using a solid solution of CaTiO$_3$ and CaZrO$_3$ results in materials with higher permittivities than CaZrO$_3$ at the expense of the low TCC value commonly associated with materials similar to CaZrO$_3$. The slightly higher $\varepsilon_r$ relative to that predicted by the fractions of the end members may be due to favorable lattice distortions/tilting as the larger Zr$^{4+}$ ion is substituted into the lattice. The TCC value for the CTZ ceramic is larger than that of similar C0G–type materials due to the contributions of polarization mechanisms at different temperatures.

Materials such as Ca(Zr$_{0.8}$,Ti$_{0.2}$)O$_3$ have low TCC values of $< 0.4\%$ from –55 to 125 °C, largely due to the dominance of temperature–independent ionic polarization of CaZrO$_3$. Overall, there was little difference between the basic dielectric properties of CTZ and CTZ + Mn since the small amount of Mn was either too small to distort the lattice if incorporated, or only present on the grain boundaries. However, as will be shown, the latter is unlikely since impedance measurements indicate clear effects of Mn on bulk transport, which would indicate some incorporation into the lattice.

### 3.5 Optical Characterization and Band Gap Energy Determination

Applications such as multilayer ceramics for power electronics applications, positive temperature variable resistors, solid oxide fuel cells, voltage variable resistors, and piezoelectric actuators rely heavily on minimization of leakage current (Yamaoka et al., 1983; Rossinelli et al., 1989; Nakono et al., 1990; Kutty et al., 1991; Heywang, 1971; Higuchi et al., 2004). For all of these applications, minimization of conduction and the time dependent properties of leakage current are of major concern. The band structure plays a key role in designing compositions that
meet the requirements for long–term leakage stability such as controlling the potential of the Schottky barrier at grain boundaries (Yang et al., 2004; Robertson et al., 1999; Robertson, 2000). It has been shown in binary solid solutions such as $\text{Ba}_x\text{Sr}_{1-x}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$ and $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ that while lattice volume follows a linear Vegard’s law symmetry, the band gap energy shows a strongly non–linear trend that cannot be fit with typical parabolic polynomials used in semiconductors such as Si – Ge, which show a “bowing effect” trend in the band gaps (Lee et al., 2010; Shi et al., 2008)

Currently, there is little literature concerning the solid solution band gap behavior of binary compositions including $\text{CaTiO}_3$ and $\text{CaZrO}_3$. There are several reports of the band gap of the end members themselves and single binary compositions obtained by a variety of techniques as shown in Table 3–2.

Table 3–2: Direct or indirect band gap data for various calcium zirconates and titanates obtained by several methods.

<table>
<thead>
<tr>
<th>Material</th>
<th>Band Gap (eV)</th>
<th>Direct/Indirect</th>
<th>Measurement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CaZrO}_3$</td>
<td>4.15</td>
<td>Indirect</td>
<td>UV-Vis</td>
<td>[Lee et al., 2010]</td>
</tr>
<tr>
<td>$\text{CaZrO}_3$ (Orthorhombic)</td>
<td>4.10</td>
<td>Direct</td>
<td>ab initio</td>
<td>[Stoch et al., 2012]</td>
</tr>
<tr>
<td>$\text{CaZrO}_3$ (Cubic)</td>
<td>3.30</td>
<td>Indirect</td>
<td>ab initio</td>
<td>[Stoch et al., 2012]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.38</td>
<td>Indirect</td>
<td>UV-Vis</td>
<td>[Lee et al., 2010]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.50</td>
<td>N/A, n-type</td>
<td>Photoemission</td>
<td>[Ueda et al., 1999]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.50</td>
<td>N/A, n-type</td>
<td>Bremsstrahlung</td>
<td>[Ueda et al., 1999]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.30</td>
<td>Indirect</td>
<td>UV-Vis</td>
<td>[Eng et al., 2003]</td>
</tr>
<tr>
<td>$\text{Ca}(\text{Ti}<em>{0.95}\text{Zr}</em>{0.05})\text{O}_3$</td>
<td>3.30</td>
<td>Optical</td>
<td>UV-Vis</td>
<td>[Cavalcante et al., 2008]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.46</td>
<td>Indirect</td>
<td>Photoluminescence</td>
<td>[Pontes et al., 2002]</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>3.48</td>
<td>Indirect</td>
<td>pO$_2$ vs. Conductivity</td>
<td>[Balachandran et al., 1982]</td>
</tr>
</tbody>
</table>
details of perovskite and oxide band structures associated with the nature of the band gap. Several researchers have attempted, through experimental and modeling techniques for SrTiO$_3$, to determine the nature of the band structure and have concluded that SrTiO$_3$ is an indirect band gap semiconductor (van Benthem et al., 2001; Cardona, 1965). From both UV–Vis diffuse reflectance and spectroscopic ellipsometry, it is likely that there is not enough sensitivity in the measurements to discern between indirect and direct band gaps. As a result, both direct and indirect interpretations of the band gaps will be presented for this research. Overall, the trends observed in the indirect band gaps from both spectroscopic techniques in comparison with existing literature suggest that the band gaps in the CTZ system are most likely indirect.

3.5.1 Ultraviolet–Visible Diffuse Reflectance Spectroscopy Results

Details of the data analysis for ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis) concerning the Kubelka–Munk equation and Tauc analysis are located in Chapter 2. Examples of the Tauc plots constructed to extract the indirect band gaps, $(F(R)hv)^{0.5}$, and direct band gaps, $(F(R)hv)^{2}$, from the zero–intercept of the linear portion of the curve at the first significant increase of absorption as well as the defect tail are shown in Fig. 3–12.

As seen in Fig. 3–12, an apparent Urbach or defect tail exists in the reflectance data, which has also been observed in similar systems (Lee et al., 2010). Tauc and Knief et al. suggested that transitions associated with localized defects such as excitons bound to acceptors could result in a “tail” at the absorption edge, which is at an energy lower than the band gap and could be proportional to the acceptor concentration (Tauc et al., 1966; Knief et al., 1999). As will be shown in the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ (CTZ) system with other characterization methods, it is likely that oxygen vacancies play a large role in controlling ionic conduction in the CTZ solid solution. The summary of the direct and indirect band gap energies extracted from the Tauc plots in Fig. 3–12 is shown in Fig. 3–13 across the CTZ solid solution.
Figure 3–12: Tauc plots constructed to extract the indirect band gaps, \((FR)hv^{0.5}\), and direct band gaps, \((FR)hv\), from the zero–intercept of the linear portion of the curve at energies above the defect/Urbach tail for \(x = 0.7, 0.8, \) and \(0.9 \text{ Ca}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3\).
It can be seen from Fig. 3–13 that both the indirect and direct band gaps extracted from the UV–Vis data show a non-linear relationship, with the larger band gaps weighted towards the CaZrO$_3$–rich end of the composition range. Table 3–3 contains the summary of band gaps with standard deviations as well as the range of $(F(R)h\nu)^n$ over which the band gaps were extracted for each composition. From Table 3–3, it can be seen that the indirect band gaps for CaTiO$_3$ and CaZrO$_3$ are in agreement with those obtained from UV–Vis in Table 3–2, and differ from the indirect gap measured by photoluminescence by over 0.1 eV. The values measured for the direct band gap of CaTiO$_3$ are in agreement those measured by photoemission, Bremsstrahlung isochromatic, and $p$O$_2$ vs. conductivity, but none of this literature reported whether the measured gap was direct or indirect. However, it is most important to note that the overall non-linear trend in the indirect band gap is consistent with similar alkaline earth perovskite solid solutions observed by previous researchers and will be elaborated upon shortly (Lee et al., 2010).

Figure 3–13: Direct and indirect band gap summary across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ (CTZ) composition range as extracted from Tauc plots constructed from UV–Vis measurements. Error bars for the direct band gap energy were included but were typically 0.01 eV and were smaller than the data points.
As mentioned previously, there are a number of factors that can yield erroneous results from obtaining band gaps for from UV–Vis, one being erroneous interpretation of the Kubelka–Munk equation for low–reflecting materials (Kubelka, 1931). This error becomes problematic when using UV–Vis to analyze the band gap of darkly–colored Mn–doped CTZ compositions as shown in Fig. 3–14.

Table 3–3: Indirect band gaps obtained from UV–Vis diffuse reflectance with range of $(F(R)*hν)^{0.5}$ that was used to obtain $E_g$ from the zero–intercept of $(F(R)*hν)^{0.5}$ vs. photon energy and direct band gaps obtained from UV–Vis diffuse reflectance with the range of $(F(R)*hν)^2$ that was used to obtain $E_g$ from the zero–intercept of $(F(R)*hν)^2$ vs. photon energy across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Indirect $E_g$ (eV)</th>
<th>$(F(R)*hν)^{0.5}$ Range (AU)</th>
<th>Direct $E_g$ (eV)</th>
<th>$(F(R)*hν)^2$ Range (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.11 ± 0.01</td>
<td>1.53 – 2.35</td>
<td>4.60 ± 0.02</td>
<td>13.8 – 57.6</td>
</tr>
<tr>
<td>0.10</td>
<td>3.85 ± 0.01</td>
<td>1.52 – 4.46</td>
<td>4.01 ± 0.01</td>
<td>103 – 680</td>
</tr>
<tr>
<td>0.20</td>
<td>3.75 ± 0.01</td>
<td>1.33 – 3.31</td>
<td>3.89 ± 0.01</td>
<td>37.2 – 157</td>
</tr>
<tr>
<td>0.30</td>
<td>3.67 ± 0.01</td>
<td>1.57 – 4.51</td>
<td>3.88 ± 0.01</td>
<td>75.1 – 510</td>
</tr>
<tr>
<td>0.40</td>
<td>3.63 ± 0.01</td>
<td>1.45 – 4.05</td>
<td>3.81 ± 0.01</td>
<td>14.5 – 80.0</td>
</tr>
<tr>
<td>0.50</td>
<td>3.57 ± 0.01</td>
<td>1.24 – 2.77</td>
<td>3.70 ± 0.01</td>
<td>23.7 – 83.2</td>
</tr>
<tr>
<td>0.60</td>
<td>3.59 ± 0.01</td>
<td>1.17 – 2.87</td>
<td>3.70 ± 0.01</td>
<td>23.4 – 83.5</td>
</tr>
<tr>
<td>0.70</td>
<td>3.56 ± 0.02</td>
<td>1.49 – 3.07</td>
<td>3.68 ± 0.01</td>
<td>29.4 – 146</td>
</tr>
<tr>
<td>0.80</td>
<td>3.55 ± 0.02</td>
<td>1.47 – 3.25</td>
<td>3.65 ± 0.01</td>
<td>41.5 – 147</td>
</tr>
<tr>
<td>0.90</td>
<td>3.50 ± 0.02</td>
<td>1.57 – 3.00</td>
<td>3.61 ± 0.01</td>
<td>35.4 – 139</td>
</tr>
<tr>
<td>1.00</td>
<td>3.35 ± 0.01</td>
<td>32.7 – 105</td>
<td>3.55 ± 0.01</td>
<td>32.2 – 163</td>
</tr>
</tbody>
</table>
From Fig. 3–14, it is apparent that the Mn–doped CTZ sample shows low reflectance over the photon range from which the band gap was extracted compared to the CTZ sample. As a result, extrapolation of the indirect band gap for CTZ + Mn is obscured and yields a value of 2.43 ± 0.02 eV from the Tauc plot, which is over 1.0 eV lower than that determined for the un–doped composition. It is important to note that the CTZ + Mn samples measured with UV–Vis were crushed, sintered pellets. It is possible that measuring a polished sintered disk could yield a sufficient amount of reflectance for a more accurate determination of the band gap. Since Mn doping has shown a minimization in dielectric loss and as will be shown with impedance data, a decrease in conductivity, this result is unrealistic and likely an artifact due to the low reflectance over the measured energy range.

Overall, while UV–Vis successfully yielded band gap trends and values supported by other researchers, it is limited in terms of the inability to measure Mn–doped compositions of CTZ and ambiguity in the data analysis due to the mutual dependence of the absorption and scattering coefficients. It should also be noted that different ranges were used in the extrapolation of each band gap, and there is no deconvolution between the scattering and absorption coefficients. Spectroscopic ellipsometry can overcome these limitations in addition to having the ability to measure dense, bulk samples, which gives a more “in–use” depiction and unambiguous
band gap determination as opposed to measuring calcined powders or sintered and pulverized disks. Additionally, optical constants such as the complex index of refraction and complex relative permittivity can be extracted directly from the data.

### 3.5.2 Spectroscopic Ellipsometry Results

A detailed explanation of the data collection and modeling of ellipsometric data is found in Chapter 2. Fig. 3–15 plots the absorption coefficient for several of the un–doped CTZ compositions, focusing on the defect tail near the onset of absorption, and a comparison of the absorption coefficient and defect tails for the full range of CTZ and the CaTiO$_3$ – rich end of the composition range.

![Figure 3–15: a) Absorption coefficient (α) vs. photon energy across the Ca(Ti,$\text{Zr}_{1-x}$)O$_3$ composition range with emphasis on the defect tail trend and b) absorption coefficient vs. photon energy for the CaTiO$_3$ – rich compositions of the CTZ solid solution, with emphasis on the defect tails.](image)

From Fig. 3–15a, it can be seen that the photon energy at the onset of band absorption shows a decreasing trend with increasing Ti content in CaZrO$_3$. Interestingly, the tails at the edge of absorption for end members show significantly higher absorption coefficients relative to the binary compositions. Currently, we do not fully understand the origin of the absorption of the
tails, and the topic is reserved for future work. Regardless, the tail in the absorption spectrum is interesting and worth elaborating upon, since the classification of the tail can vary between various material systems.

Urbach identified exponential (not Gaussian) tails at edges of excitonic and optical interband transitions more than 50 years ago (Urbach, 1953). The tails appear as exponentially decaying absorption features that can be seen at energies below the band gap, and are quantified through Urbach’s rule by (Urbach, 1953),

$$\alpha(v, T) = \alpha_0 e^{-\sigma_0(hv_0-hv)/kT}$$

(Equation 3–5)

where $T$ is temperature, $h\nu$ is the photon energy and $\sigma_0$, $v_0$, and $\alpha_0$ are constants specific to the crystal. At low temperatures, the Urbach rule can be simplified to,

$$\alpha = \alpha_0 e^{\gamma h\nu}$$

(Equation 3–6)

where $\gamma$ is a temperature dependent parameter. In order to match the theoretical line shape for an Urbach tail, the slope of the natural logarithm of the absorption coefficient tail should be approximately unity (Urbach, 1953). For the CTZ composition range, only CaZrO$_3$ meets this criterion. Even at $x = 0.03$, the slope begins to deviate from unity. For CaTiO$_3$, the slope is $> 3.0$. Also, it can be seen in all compositions that the transition from the absorption spectra show Gaussian distributions, not exponential. The binary compositions show the appearance of a more exponential tail in appearance compared to the Gaussian end members, which could indicate a different origin.

In photoluminescence studies of amorphous CaTiO$_3$, a similar absorption spectrum to that of Fig. 3–15 was observed, with the tails being attributed to defect states promoted by the disordered amorphous structure, suggesting a non–uniform band gap structure with a tail of localized states and mobile edges (Pontes et al., 2002). Overall, it was deduced that the edge was most likely due to a radiative recombination between trapped electrons and trapped holes in tail and gap states as shown in Fig. 3–16, and is dependent on the degree of structural and thermal disorder in the CaTiO$_3$ crystal lattice.
Tauc et al. investigated the optical properties and electronic structure of amorphous germanium and identified a Gaussian tail in the absorption spectrum as well. As a result, it was deduced that the tail was not indicative of a transition from or into the valence or conduction bands, since one would expect an exponential edge rather than a Gaussian onset (Tauc, 1953). It was suggested that the defect tail was due to excitons bound to acceptors, which are likely present in CTZ solid solutions as doubly ionized oxygen vacancies. The acceptors capture an electron by thermal excitation, and the photon excites the electron into a state where the acceptor binds an electron and a hole (Tauc, 1953). This process would be proportional to the product of the ionized acceptor concentration and concentration of holes. More importantly, this is a thermally activated process, and validation of this theory for the CTZ system would require measuring the high temperature dependence of the absorption coefficient, which is another interesting topic for future work.

Several authors have suggested that both defects and electron–phonon interactions within the crystal lattice can influence the tails, that certain perovskites involve energy levels within the forbidden energy gap that are associated with the presence of oxygen vacancies, and that both Urbach and Gaussian tail theories can be coupled to describe the origin of the tail in semiconducting systems (Keil, 1966; Mahr, 1963; Redfield, 1963; Berglund et al., 1967; Ikegami et al., 1961; Cronemeyer, 1959). In Ba(Ti,Zr)O₃, it has been observed that the presence of oxygen...
vacancies result in actual peaks in the absorption tails when little Zr is present in BaTiO$_3$, which are attributed to fewer defects resulting with an increase in Zr content (Levi, 2006). However, no peaks were observed in CaTiO$_3$–rich compositions in this research, even though it is expected that such compositions would have a high concentration of oxygen vacancies relative to CaZrO$_3$–rich compositions. Additionally, little effect was observed in the absorption spectrum of reduced and re-oxidized samples in this research.

By combining theories on Urbach and Gaussian absorption tails for alkali halide systems, several authors have deduced that observation of an appreciable exponential tail in the exciton band is coupled with the existence of certain modes around point defects, which are quadratically coupled to electronic transitions (Mahr, 1963; Keil, 1966). This coupling can become increasingly important when the lattice is distorted and translation invariance is destroyed. Overall, while the band gap values were the main objective for the optical investigation of the CTZ system, the definitive origin of the tails in the CTZ absorption spectrum is difficult to identify and is an important topic for future work.

As mentioned previously, UV–Vis was unable to accurately measure the reflectance and thus band gap for the Mn–doped samples due to a low % reflectance. This is not the case for ellipsometry, and the absorption coefficients for $x = 0.8$ CTZ and $x = 0.8$ CTZ + Mn are shown in Fig. 3–17.
As seen in the inset plot of Fig. 3–17, the Mn–doped sample showed a slightly more pronounced Gaussian shape and higher absorption at the tail. This may be due to the presence of Mn\(^{3+}\) ions, which act as additional acceptors when substituted for Ti\(^{4+}\). The summary of extinction coefficient \((k)\) and refractive index \((n)\) as well as fitting examples from divided spectral range modeling is shown in Fig. 3–18.
From the extinction coefficient, it can be seen that near the titanium rich side of the composition range, additional high-energy transitions develop above the band gap. From the refractive index, it can be seen that starting at $x = 0.5$, a sharp decrease in refractive index occurs at energies above 4.8 eV. It is useful to report the refractive index at the photon energy of a red laser (1.96 eV or 633 nm), as it is commonly used in single wavelength ellipsometry experiments. The low energy inverted refractive index vs. photon energy with model fits for select CTZ compositions and refractive indices at 1.96 eV across the entire composition range are shown in Fig. 3–19.

Figure 3–18: a) Modeled and inverted ellipsometry data for extinction coefficient $k$ (top) and refractive index $n$ (bottom) for $x = 0.8 \text{Ca(Ti},Zr_{1-x})\text{O}_3$ (CTZ) and b) extinction coefficient $k$ (top) and refractive index $n$ (bottom) vs. photon energy across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range.
From Fig. 3–19, it can be seen that the generated models show good fit to the experimental inverted data. The refractive indices for the CTZ composition range, shown in Fig. 3–19b, show a generally linear trend with some deviation from the trend near the Ti–rich end of the binary. In addition to the relationships in Eqs. 3–3 and 3–4, the Gladstone–Dale relation is an empirical method that is effective for describing and predicting refractive indices based upon information for the elements within the compound (Gladstone et al., 1864). The refractive index at 588 nm (helium arc) is a direct function of the density, $\rho$, which was obtained from XRD lattice parameters and is related by

$$n = 1 + \rho \sum_i p_i k_i$$  \hspace{1cm} (Equation 3–7)

where $p_i$ is the weight fraction of the $i^{th}$ component and $k_i$ is the $i^{th}$ refractive coefficient or specific refractive energy obtained from literature (Larsen et al., 1934). The results of the calculated and measured refractive indices are shown in Fig. 3–20.
It can be seen that the trend in the refractive index at 588 nm is similar to that for 633 nm. More importantly, all refractive indices were within 3.5% of the calculated value and the majority of the values were within < 2.0% of the calculated value. The agreement of the measured values with those calculated gives extra validity to the accuracy of the band gap measurements via spectroscopic ellipsometry.

Another useful comparison that can be obtained with ellipsometry is the differentiation between the electronic and ionic contributions to the relative permittivity. Because the ellipsometry setup measures the room temperature complex relative permittivity with no dc bias, only the electronic polarization contributes to the relative permittivity and the relationship \( n = \sqrt{\varepsilon} \) is valid. The relative permittivity associated with electronic polarization can be calculated from ellipsometry measurements and compared to the room temperature measurements made under dc bias as shown in Fig. 3–21.

Figure 3–20: Calculated refractive index from the Gladstone–Dale relation and measured refractive index at 588 nm (helium arc) across the Ca(Ti\(_x\)Zr\(_{1-x}\))O\(_3\) composition range. Error bars were typically ± < 0.001 and could not be visible on the plot in b).
It can be seen from Fig. 3–21 that the ionic polarization contributes approximately 97% of the total relative permittivity in the CTZ linear dielectric system. Overall, the permittivity decreases at energies greater than any absorption feature. Additionally, vibrational modes present with also cause a decrease in the relative permittivity. For ferroelectric and antiferroelectric systems, the 1 kHz value would be substantially larger due to the additional contributions of dipolar polarization.

The summary of $\alpha$ from which indirect ($\alpha^{0.5}$) and direct ($\alpha^2$) band gaps were extracted is shown in Fig. 3–21 alongside an example for band gap extrapolation. The same technique was used to extract band gaps from UV–Vis diffuse reflectance spectroscopy.
The summary of direct and indirect gaps, first direct transition as obtained from the critical–point parabolic–band (CPPB) fit, and indirect band gaps from UV–Vis is shown in Fig. 3–23.
From Fig. 3–23, it can be seen that the indirect band gaps follow a similar asymmetric trend as the indirect band gaps obtained by UV–Vis but with higher values and a more symmetrical trend between the end members. It is interesting that due to the more symmetrical trend in the indirect gaps extracted from ellipsometry, there is less of a difference between the indirect band gaps from ellipsometry and UV–Vis for compositions where $x \leq 0.2$ for $\text{Ca(Ti}_x\text{Zr}_{1-x}\text{)O}_3$. Additionally, the indirect band gap values track with the energy of the first direct transition. It is important to note that the band gaps for $\text{CaZrO}_3$, $5.54 \pm 0.02$ eV and $5.92 \pm 0.01$ eV for indirect and direct band gaps respectively, are considerably larger than values reported in literature. The minimum doping amount of Ti to initiate a first direct transition is unclear from this research and is an interesting topic for future work. The direct band gaps, similarly to UV–Vis, did not follow as strong of an asymmetric trend. The values of the band gap energies and energy of the first direct transition are shown in Table 3–4. There was little difference in the
absorption spectra between x = 0.8 and x = 0.8 CTZ + Mn, and the band gap values were the same within the reported error.

Table 3–4: Direct band gap (E_g) and range of absorption (α^2), where AU is absorbance units, that was used to obtain E_g from the the zero–intercept of α^2 vs. photon energy, indirect band gap (E_g) and range of absorption (α_0.5) that was used to obtain E_g from the zero–intercept of α_0.5 vs. photon energy, and energy of the first direct transition obtained from the first high energy CPPB oscillator for Ca(Ti_xZr_1-x)O_3 where Composition = x.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Indirect E_g (eV)</th>
<th>α_0.5 Range (cm^-0.5)</th>
<th>Direct E_g (eV)</th>
<th>α^2 Range (x10^10 cm^2)</th>
<th>First Direct Transition (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.54 ± 0.02</td>
<td>512 – 1023</td>
<td>5.92 ± 0.01</td>
<td>24.7 – 155</td>
<td>6.08 ± 0.01</td>
</tr>
<tr>
<td>0.03</td>
<td>3.95 ± 0.03</td>
<td>182 – 392</td>
<td>4.52 ± 0.01</td>
<td>0.433 – 2.92</td>
<td>4.97 ± 0.02</td>
</tr>
<tr>
<td>0.05</td>
<td>4.10 ± 0.03</td>
<td>123 – 415</td>
<td>4.61 ± 0.04</td>
<td>0.544 – 4.01</td>
<td>5.02 ± 0.02</td>
</tr>
<tr>
<td>0.10</td>
<td>4.05 ± 0.02</td>
<td>167 – 508</td>
<td>4.55 ± 0.01</td>
<td>1.47 – 10.8</td>
<td>4.54 ± 0.01</td>
</tr>
<tr>
<td>0.20</td>
<td>4.02 ± 0.01</td>
<td>184 – 624</td>
<td>4.51 ± 0.04</td>
<td>4.10 – 24.4</td>
<td>4.54 ± 0.01</td>
</tr>
<tr>
<td>0.30</td>
<td>3.82 ± 0.01</td>
<td>232 – 622</td>
<td>4.28 ± 0.01</td>
<td>4.89 – 35.9</td>
<td>4.64 ± 0.01</td>
</tr>
<tr>
<td>0.50</td>
<td>3.74 ± 0.02</td>
<td>280 – 697</td>
<td>4.17 ± 0.01</td>
<td>5.56 – 40.4</td>
<td>4.26 ± 0.01</td>
</tr>
<tr>
<td>0.70</td>
<td>3.73 ± 0.01</td>
<td>223 – 738</td>
<td>4.09 ± 0.02</td>
<td>7.78 – 47.4</td>
<td>4.19 ± 0.002</td>
</tr>
<tr>
<td>0.80</td>
<td>3.73 ± 0.01</td>
<td>235 – 832</td>
<td>4.04 ± 0.01</td>
<td>11.6 – 87.3</td>
<td>4.15 ± 0.002</td>
</tr>
<tr>
<td>0.90</td>
<td>3.65 ± 0.01</td>
<td>403 – 922</td>
<td>3.94 ± 0.01</td>
<td>10.7 – 106</td>
<td>4.08 ± 0.01</td>
</tr>
<tr>
<td>0.95</td>
<td>3.59 ± 0.01</td>
<td>323 – 845</td>
<td>3.96 ± 0.01</td>
<td>12.5 – 126</td>
<td>4.08 ± 0.01</td>
</tr>
<tr>
<td>0.97</td>
<td>3.61 ± 0.01</td>
<td>260 – 896</td>
<td>3.93 ± 0.01</td>
<td>12.0 – 117</td>
<td>4.06 ± 0.01</td>
</tr>
<tr>
<td>1.00</td>
<td>3.55 ± 0.01</td>
<td>261 – 672</td>
<td>3.91 ± 0.01</td>
<td>16.0 – 118</td>
<td>4.06 ± 0.003</td>
</tr>
</tbody>
</table>

The sharp increase in band gap near an end member of the binary has been linked to various material properties including bond energy, bond length, degree of ionicity, strain, point defects and formation enthalpy (Vijh, 1970; Lawaetz, 1971; Dingle et al.; 1974; Lang et al., 1999). It is possible that with increasing Zr content in CaTiO_3, the band gap increases with the above trend due to variations in these physical parameters, which are largely governed by the difference in ionic size between Zr^{4+} (72 pm) and Ti^{4+} (61 pm) (Shannon et al. 1976).
It has also been reported that defects such as oxygen vacancies can have a large influence on the band gap trend. Frye et al. reported that the presence of oxygen vacancies can decrease the band gap since they deplete the O 2p densities of states at the top of the upper valence band (Frye et al., 2003). However, it is unlikely that the concentration of oxygen vacancies is large enough to cause such an effect in these materials as evidenced by high resistivities at elevated temperatures. It has also been suggested by Eng et al. that octahedral tilt distortion can increase the band gap energy in perovskite–type oxides as a result of the distortion of the linear B–O–B bonds, which narrows the conduction band (Eng et al., 2003). A useful structure–property relationship that can relate trends in band gap energies such as those related to octahedral tilt is the Goldschmidt tolerance factor (Goldschmidt, 1926),

\[ t = \frac{r_A + r_O}{\sqrt{2}[x r_{B1} + (1-x) r_{B2} + r_O]} \]

(Equation 3–8)

where \( r_A \), \( r_{B1} \), \( r_{B2} \) and \( r_O \) represent ionic radii for A, B, and O in \( AB_1B_2O_3 \) compounds, respectively. As observed by Reaney et al., the onset of a room temperature tilted structure is estimated to be at a crossover tolerance factor \( t_c \) ~0.98, for which structures having tolerance factors below this point are tilted and those above it are not (Reaney et al., 1994). For the CTZ compositions in this study, all tolerance factors across the solid solution are below \( t_c \) and are likely tilted.

As stated previously, the non-linear behavior observed in the indirect band gaps of the CTZ solid solution has been observed in perovskite–type solid solutions such as \( xBaTiO_3 - (1-x)BaZrO_3 \) (Lee et al., 2010). It was found that the optical data could be fit using an asymmetric weighted function,

\[ E_g[Ca(Ti_x Zr_{1-x})O_3] = x E_g(CaTiO_3) + (1-x)E_g(CaZrO_3) + E_g(Excess) \]

(Equation 3–9)

where the excess band gap energy of mixing \( (E_g(Excess)) \) is similar to the bowing parameter commonly associated with semiconductors (Berrah et al., 2008). This, in turn, is related to the activity of each end member by a parabolic polynomial,

\[ E_g(Excess) = W_{CaTiO_3} x(1-x)^2 + W_{CaZrO_3} x^2(1-x) \]

(Equation 3–10)
where $W$ corresponds to the weighting parameter for the respective end member. The values for the weighting parameters for indirect gaps from UV–Vis were $-2.5$ and $0.25$ for CaZrO$_3$ and CaTiO$_3$, respectively, and $-1.35$ and $1.05$ respectively for CaZrO$_3$ and CaTiO$_3$, respectively, for ellipsometry indirect gaps. Figure 3–24 shows the indirect band gaps extracted from ellipsometry and UV–Vis with the asymmetric Vegard’s Law fit and tolerance factors across the composition range. In order to adjust the scaling so that the comparison in of the asymmetric Vegard’s law trend could clearly be seen, the CaZrO$_3$ band gap of 5.5 eV was omitted from Fig. 3–24.

Figure 3–24: Indirect band gaps obtained via UV–Vis diffuse reflectance spectroscopy and spectroscopic ellipsometry across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ solid solution with calculated asymmetric Vegard’s Law fits.

As seen in Fig. 3–24, the modified Vegard’s law equation shows good fit to the majority of the data for both UV–Vis and ellipsometry. It is worth noting that slight deviations from the fit close to the end members and on the Zr–rich side of BaZr$_x$Ti$_{1-x}$O$_3$ have also been observed in other systems (Levi, 2009). For UV–Vis, the compositions near the CaZrO$_3$ end of the binary deviate from the trend, most likely due to CaZrO$_3$ having a considerably higher band gap compared to the $x = 0.1$ composition, which offsets the weighting parameters in the polynomial.

Regardless, it can be seen that for the majority of the compositions, both ellipsometry and UV–Vis show similar trends, but with ellipsometry yielding higher band gaps for every
composition compared to UV–Vis. In order to obtain ideal breakdown strengths of > 1.0 MV/cm, it can be seen from Fig. 1–8 that band gaps between 3.5 and 4.0 eV are required. The band gaps measured from ellipsometry were between 3.5 and 3.7 eV from x = 0.7 to 1.0 CTZ, respectively. It should be noted that spectroscopic ellipsometry quantitatively determines the absorption coefficient, as opposed to the convolution of scattering and absorption coefficients in UV–Vis. Therefore it is not clear if the slightly lower values from UV–Vis are sensitive to lower values of the absorption coefficient or affected by a scattering artifact.

3.6 Conductivity Measurements

To investigate the influence of the band gap on resistivity in the CTZ system, low field (1 kV/cm) current–voltage (I–V) measurements were made at 250 °C for bulk x = 0.0, 0.03, 0.2, 0.8, 0.97, and 1.0 Ca(TiₓZr_{1-x})O₃ with sputtered Pt electrodes. The voltage was applied for 10 minutes to allow the leakage current to reach steady state. Since the x = 1.0 (CaTiO₃) composition began to degrade before reaching steady state current under the applied field, the 250 °C resistivity was not reported. The results are shown in Fig. 3–25. As discussed in the introduction, the polarizabilities can be calculated from the measured refractive index. The calculated trend in polarizabilities is shown in Fig. 3–26.
From Fig. 3–25, it can be seen that similar to the band gap results, the resistivity was higher for the CaZrO$_3$–rich compositions, yielding resistivities an order of magnitude larger than those of CaTiO$_3$–rich compositions under the testing conditions.

It can be seen from Figs. 3–25 and 3–26 that as predicted, CaTiO$_3$–rich compositions have a larger polarizability relative to CaZrO$_3$–rich compositions. This can be related to the high temperature ionic conductivity trend shown in Fig. 3–25. Materials expected to contain more oxygen vacancies show lower resistivities at elevated temperatures. The calculated polarizability for CaTiO$_3$ from the measured refractive index (1.59 Å$^3$) agrees with literature (1.61 Å$^3$) (Roberts, 1949).

Figure 3–25: Resistivity at 250 °C and 1 kV/cm for several compositions across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range measured on bulk samples.
As shown in Fig. 3–27, the resistivity also scales with the direct and indirect band gaps with larger band gaps corresponding to higher resistivities. Overall, while the resistivities of the CaTiO$_3$ – rich compositions lower than those on the CaZrO$_3$ – rich end of the composition range, the compositions on the CaTiO$_3$ – rich end possess permittivities five times higher than those of the CaZrO$_3$ – rich compositions.

Figure 3–26: Calculated room temperature polarizabilities across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range using Eqns. 3–3 and 3–4. Error bars were on the order of ± 10$^{-3}$ and were smaller than the size of the data point.
With the basic properties of the CTZ and CTZ + Mn systems established, an understanding of material behavior under higher fields and temperatures was obtained through current–voltage (I–V) testing. This characterization is valuable for eliminating compositions that may behave well under low fields, but show signs of early degradation under harsher conditions. The current density ($J$) vs. electric field at 250 °C and up to a maximum field of 25 kV/cm for $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) and $x = 0.7, 0.8, \text{and} 0.9, y = 0.005 \text{Ca(Ti}_{x-y}\text{Mn}_y\text{Zr}_{0.2})\text{O}_3$ (CTZ + Mn) is shown in Fig. 3–28.

Figure 3–27: Steady state resistivity at 250 °C and 1 kV/cm versus direct and indirect band gap energies for the $\text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ system measured on bulk samples.
It can be seen from Fig. 3–28 that Mn doping clearly reduces current density at elevated temperature and fields in the CTZ system. The slopes of the log–log I–V curves can give insight into the behavior of the current in the system, following the relation $I = kV^\alpha$, where $k$ and $\alpha$ are constants. For Ohmic behavior, $\alpha \approx 1$, as observed here in the CTZ + Mn compositions under the measurement conditions. Calculated resistivities were 54.5 kΩ.cm, 347 kΩ.cm, and 288 kΩ.cm for $x = 0.7$, 0.8, and 0.9 CTZ + Mn respectively. While $x = 0.8$ and 0.9 CTZ + Mn show similar responses, they yield lower current densities overall compared to the $x = 0.7$ composition. Overall, it is most important to note that doping the $x = 0.8$ CTZ system with 0.5 mol% Mn resulted in a decrease in current density by approximately 5 orders of magnitude.

### 3.7 Polarization – Field Loops and Energy Density Evaluation

As a result of these basic characterization techniques, single layer, 12 μm–thick Pt electrode $x = 0.8$ Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ (CTZ) and $x = 0.8$, $y = 0.005$ Ca(Ti$_{x-y}$Mn$_y$Zr$_{0.2}$)O$_3$ (CTZ + Mn) capacitors were prototyped for polarization – field (P–E) hysteresis measurements to further
minimize loss and maximize breakdown strength compared to bulk samples. Fig. 3–29 shows the temperature evolution of P–E hysteresis loops for a) un–doped CTZ at 1/4 of the breakdown strength ($E_b$) for un–doped $x = 0.8$ CTZ and b) $x = 0.8$ CTZ + Mn.

![Temperature evolution of P–E hysteresis loops for a) un–doped CTZ at 1/4 of the breakdown strength ($E_b$) for un–doped $x = 0.8$ CTZ and b) $x = 0.8$ CTZ + Mn.]

Figure 3–29: Temperature evolution of P–E hysteresis loops for a) $x = 0.8$ Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$ at 0.25$E_b$ and b) $x = 0.8$, $y = 0.005$ Ca(Ti$_{x-k}$Mn$_y$Zr$_{0.2}$)O$_3$ at 0.25$E_b$.

It can be seen from Fig. 3–29a that while dielectric loss, which is proportional to the area contained within the unipolar loop, was low at room temperature, the loss increases substantially at 100 °C for un–doped CTZ. At 150 °C, the sample is too lossy to measure any substantial recoverable energy density. In Fig. 3–29b, however, it can be seen that Mn doping results in low losses up to 300 °C. Fig. 3–30 shows the unipolar P–E loops obtained at room temperature and 300 °C for the $x = 0.8$ CTZ + Mn capacitors having the highest measured energy densities.
The maximum room temperature energy density obtained for CTZ + Mn was 7.00 J/cm$^3$ at a $E_b$ of 1.1 MV/cm and $P/V$ of 0.38 W/cm$^3$, and the maximum energy density at 300 °C was 5.36 J/cm$^3$ at $E_b = 1.0$ MV/cm and $P/V$ of 2.84 W/cm$^3$. At ~1/4$E_b$, the energy densities were 0.98, 0.86, and 0.68 J/cm$^3$ at 100, 200, and 300 °C respectively. Based on these results, doping CTZ with Mn allows for the breakdown strength to be maintained up to 300 °C. In addition, Mn doping minimized the decrease in energy density from dielectric loss and the temperature dependence of the relative permittivity. These results indicate that Mn doping has strong effects on minimizing conductivity in the CTZ system, but the underlying mechanisms that control this behavior are often speculative in similar systems in terms of Mn valence state, site occupation, and lattice/grain boundary incorporation leading to reduced concentrations and/or mobility of oxygen vacancies (Osawa et al., 1993; Pinceloup et al., 2006; Jeong et al., 2007).

The P–E loops for $x = 0.8$ CTZ + Mn capacitors prototyped with Ni electrodes, fired in an atmosphere of $pO_2 = 10^{-11}$ atm followed by 9 and 12 hr re–oxidations at 900 °C and $pO_2 = 10^{-9}$ atm are shown in Figs. 3–31a and 3–31b respectively.
The maximum energy densities for the capacitors tested under the room temperature conditions shown in Fig. 3–31 were 5.04 J/cm$^3$ for the 9 hr re–oxidation and 5.12 J/cm$^3$ for the 12 hr re–oxidation with breakdown strengths of 0.74 and 0.84 MV/cm respectively. It can be seen from the plots in Fig. 3–31 that the longer re–oxidation time reduced the high field dielectric loss and yielded a slightly higher energy density. However, it was found that dielectric loss dominated at higher temperatures and the recoverable energy density was greatly reduced. Additional attempts at re–oxidizing in higher pO$_2$ (10$^{-9}$ atm) atmospheres and longer holding times did not show significant improvement.

### 3.8 Impedance Spectroscopy

In an attempt to better understand how Mn controls conduction, high temperature impedance spectroscopy was performed on x = 0.8 CTZ and x = 0.8 CTZ + Mn capacitors. The impedance spectra of x = 0.8 CTZ and CTZ + Mn capacitors measured from 600 to 700 °C are shown in Fig. 3–32. Here, good fits using equivalent circuits described in Chapter 2 are observed.
for both materials over the measured temperature range.

Figure 3–32: High temperature impedance spectra for a) \( x = 0.8 \) \( \text{Ca(Ti}_{x-1}\text{Zr}_x\text{O}_3 \) (CTZ) and b) \( x = 0.8, y = 0.005 \) \( \text{Ca(Ti}_{x-y}\text{Mn}_y\text{Zr}_{0.2}\text{O}_3 \) (CTZ + Mn) measured from 600 to 700 \(^\circ\)C. Samples were buried Pt electrode, single layer, air–fired capacitors.

It has been shown that systems such as \( \text{Pb}_{1-x/2}[(\text{Zr}_{0.525}\text{Ti}_{0.475})_{1-x}\text{Nb}_x]\text{O}_3 \) (PZT + Nb) where \( x=0.0075 \), exhibit mixed ionic and electronic conduction at temperatures \( > 500 \) °C (Donnelly et al., 2010). Impedance spectroscopy of PZT + Nb has shown evidence of both electronic and ionic conductivity, which can be modeled using an equivalent circuit consisting of bulk ionic and electronic rails and a diffusional Warburg and double layer capacitance to incorporate low frequency ionic space charge conduction (Donnelly et al., 2010). While a grain boundary impedance was not observed in PZT + Nb, an ionic or electronic grain boundary RC circuit can be incorporated into the equivalent circuit when present (Donnelly et al., 2010).

Similarly to the work on PZT + Nb, the spectra for CTZ show two slightly overlapping semicircles indicative of mixed conduction with selectively blocking electrodes (Donnelly et al., 2010). The deviation from an ideal semicircle in the high frequency relaxation indicates the presence of a grain boundary feature, which was incorporated into the ionic rail of the equivalent used to fit the data. When doped with 0.5 mol% Mn, however, one distinct semicircle is observed representing electronic conduction only, indicating that Mn doping has a clear affect on bulk
transport in this material. By applying the impedance model introduced in Chapter 2, the conductivities associated with the ionic and electronic components were directly extracted and corrected for capacitor geometry. The conductivities extracted from the impedance modeling are shown in Fig. 3–33 for both \( x = 0.8 \) CTZ and \( x = 0.8 \) CTZ + Mn. It is clear from the plots in Fig. 3–33 that doping \( x = 0.8 \) CTZ with 0.5 mol% Mn not only minimized ionic conductivity but it further reduced the electronic conductivity of the material relative to the undoped sample.

By directly extracting conductivities from the impedance modeling, activation energies for the involved conduction mechanisms in each material can be calculated using the slopes of the curves in Fig. 3–33 if they show Arrhenius behavior. For CTZ, the bulk electronic activation energy was \( 1.73 \pm 0.02 \) eV, the bulk ionic activation energy was \( 0.70 \pm 0.01 \) eV, and the grain boundary activation energy was \( 1.18 \pm 0.01 \) eV, both of which are common values for oxygen transport in perovskite systems (Chroneos et al., 2010). The electronic activation energy was approximately half of the measured band gap.
For $x = 0.8$, $y = 0.005$ CTZ + Mn, the electronic activation energy was determined to be $1.72 \, \text{eV} \pm 0.01 \, \text{eV}$. The electronic activation energy show some indication that Mn doping drives the CTZ system more towards intrinsic behavior since the activation energy for CTZ + Mn is near half of the value for the indirect band gap (3.42 eV). The extracted transference numbers ($t$) for the un–doped sample are shown in Table 3–5. As is seen in the table, ionic carriers dominate conduction as expected at these temperatures.
When plotting impedance spectra, it is useful to overlap the plots of the imaginary parts of the complex impedance ($Z''$) and complex modulus ($M''$) vs. frequency. A peak in the $M''$ plot corresponds to the component in the impedance model with the lowest capacitance, whereas peaks in the $Z''$ plot correspond to components with the highest impedance (Costa et al., 2013). If the two graphs possess peaks that occur at different frequencies, the peaks can be attributed to different sources. The comparison of $M''$ and $Z''$ vs. frequency from 600 to 700 °C is shown in Fig. 3–34.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$t_{\text{electronic}}$</th>
<th>$t_{\text{ionic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td>625</td>
<td>0.09</td>
<td>0.91</td>
</tr>
<tr>
<td>650</td>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td>675</td>
<td>0.17</td>
<td>0.83</td>
</tr>
<tr>
<td>700</td>
<td>0.21</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 3–5: Transference numbers ($t$) for un–doped $x = 0.8 \text{Ca(Ti}_x\text{Zr}_{1-x})\text{O}_3$ extracted from conductivities modeled with impedance spectra.

Figure 3–34: Overlap of the imaginary part of the complex impedance ($Z''$) and complex modulus ($M''$) at 600, 625, 650, 675, and 700 °C for $\text{Ca(Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ (CTZ). The blue data represents the $Z''$ plot while orange data represents $M''$. 
From Fig. 3–34, it can be seen that the low frequency peak in the $Z'$ plot does not correspond to a peak in the $M'$ plot, which was attributed to an ionic double layer effect at the ceramic – electrode interface. The high frequency peak was attributed to the combination of the bulk ionic and grain boundary impedances as well as the bulk electronic impedance. From the plot of $M'$, it can be seen that a slight peak or edge is present at the same frequency as the high frequency $Z'$ peak. As stated previously, if peaks overlap in the $Z'$ and $M'$ spectra, they can be attributed to the same source (Costa et al., 2013). This is also supported by the fact that the start of the peak in the $M'$ plot shows a slight edge before increasing at approximately the same frequency as the high frequency peak in the $Z'$ data. Since peaks in the $M'$ plot correspond to the feature with the highest capacitance, which is the bulk contribution for these materials, the large increase in the $M'$ plot at high frequencies most likely corresponds to the electronic bulk contribution since an overlapping peak in the $Z'$ plot is not present. It can be seen that a slight peak/edge is present in the $M'$ data at a similar frequency to the largest peak in the $Z'$ data. It is likely that the edge corresponds to the ionic grain boundary component, since it shows the largest impedance of the observed features.

Previously, it was shown in Fig. 3–10 that the relative permittivity decreases in a weakly linear trend as temperature increases to 150 °C, and the dielectric loss for un–doped $x = 0.8$ CTZ remains low until it begins to increase at approximately 100 °C. Electronic conductivity remains high and there is minimal evidence of space charge conductivity due to ionic migration. At higher temperatures (600 °C to 700 °C), ionic mobility is significantly higher and space charge conduction most likely begins to dominate as shown in Fig. 3–35.
It can be seen from Fig. 3–35 that in the high temperature regime, the undoped \( x = 0.8 \) CTZ capacitors behave like barrier layer capacitors as a result of oxygen vacancies creating space charge layers at the grain boundaries and the dielectric–electrode interface. This is supported by the large permittivity and high dielectric losses observed. The large effective permittivity is the result of enhanced capacitance of a single element in the barrier layer structure according to,

\[
C_i = \frac{\varepsilon_r \varepsilon_0 t_g^2}{t_b}
\]  

(Equation 3–11)

where \( t_g \) is the grain size and \( t_b \) is the barrier layer thickness and \( \varepsilon_r \) is the room temperature relative permittivity of a composite dielectric (Moulson et al., 2003). When the capacitors are connected in series, as is the case when considering grains in a polycrystalline ceramic, the capacitance is represented by

\[
\frac{C_i}{\text{# of elements in column}} = \frac{\varepsilon_r \varepsilon_0 t_g^2}{t/t_g}
\]  

(Equation 3–12)

and the overall capacitance per unit area is
\[ C = \frac{\varepsilon_r \varepsilon_0 t_g}{tt_b} \]  
(Equation 3–13)

since \(1/t_g^2\) columns per unit area are present. Overall, the effective permittivity of the barrier layer capacitor can be calculated according to

\[ \varepsilon_e = \frac{\varepsilon_r t_g}{t_b} \]  
(Equation 3–14)

and the barrier layer thickness (depletion layer width, \(t_b\)) can be back calculated from the effective permittivity measured from high temperature impedance spectroscopy (Moulson et al., 2003).

The behavior shown in Fig. 3–35 is well supported by literature concerning barrier layer capacitors in ceramic ferrites, \(\text{Bi}_{2/3}\text{Cu}_{3/4}\text{Ti}_4\text{O}_{12}\), Barium Plumbate, \(\text{BaTiO}_3\), and \(\text{SrTiO}_3\) (Largeteau et al., 1991; Liu et al., 2004; Hiremath et al., 1992; Fujimoto et al., 1985; Costa et al., 2013). In \(\text{ZrO}_2\) and other mixed conducting titanates, highly resistive layers tend to form at electrode and grain boundary interfaces and are commonly interpreted as depletion space charge layers, similar to Schottky barriers at semiconductor interfaces (Waser et al., 1992; Stratton et al., 1983; Neumann et al., 1986). Typically, a similar relaxation feature is observed in tan\(\delta\), such as with barium plumbate, but at higher frequencies compared to this research due to the smaller size of \(\text{Ca}\) (Hiremath et al., 1992). The trends in the effective permittivity and tan\(\delta\) can be explained by Maxwell–Wagner–type contributions of depletion layers at the interface between the sample and electrode and at grain boundaries, and have been used to model relaxation features in similar systems showing a single relaxation (Lunkenheimer et al., 2002; Hiremath et al., 1992).

Other authors have observed similar Debye–like relaxations in the permittivity spectra of boundary layer capacitors, seen in Fig. 3–35 where the dielectric constant becomes relatively independent of frequency and temperature near the relaxation (Liu et al., 2004). In acceptor–doped \(\text{SrTiO}_3\), a depletion layer thickness of approximately 115 nm was observed, and the origin of the depletion layer was assumed to be due to the donor–type interface states (Waser et al., 1992). The depletion layer thicknesses calculated for the \(x = 0.8\) CTZ system for the grain boundary and double layer (electrode interface) are shown in Fig. 3–36.
It can be seen from Fig. 3–36 that the grain boundary depletion layer thicknesses are larger than those observed in acceptor–doped SrTiO$_3$, which can be attributed to a larger concentration of oxygen vacancies in the undoped Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ system. As the temperature increases, it can be seen that the depletion layer thickness decreases as the grain boundaries become increasingly conducting, and the double layer depletion layer increases as the double layer becomes slightly more resistive as more oxygen vacancies accumulate at the interface.

As a result of the symmetry of a grain boundary, the depletion layer can be defined as a back–to–back double Schottky barrier (Waser et al., 1996). Donor–type charges at the grain boundary result in a depletion of the positively charged mobile carriers, which are oxygen vacancies ($V'_O$) and holes ($h^+$) in the CTZ system. The immobile acceptors in the depletion layers form a negative space charge, and the width of the depletion layer is established such that the positive grain boundary charges are just compensated by the negative space charge (Waser et al., 1996). It can be concluded that the trends in the high temperature effective permittivity and tanδ are attributed to a barrier layer space charge effect caused by the accumulation of oxygen vacancies at grain boundaries and the electrode–dielectric interface. It is important to note that the tanδ values observed at these high temperatures are extremely large. As a result, these materials would not function as barrier layer capacitors due to the inability to sustain a substantial field.

Figure 3–36: Grain boundary and double layer (electrode interface) thicknesses vs. temperature for $x = 0.8$ Ca(Ti$_{x}$Zr$_{1-x}$)O$_3$. 
This can be proven further by applying a dc bias in addition to the ac amplitude to show the effects of voltage on the ionic conductivity at the grain boundaries and double layer, as will be shown.

From Fig. 3–10 it was shown that the relative permittivity decreases with increasing temperature as increasing thermal vibrations reduce the ionic polarization of the crystal lattice. While this effect still exists at high temperatures, ionic charge carriers become highly mobile and begin to accumulate at interfaces such as grain boundaries and the electrode–dielectric interface. This results in a space–charge layer, which acts as a boundary–layer capacitor with a deceptively large relative (effective) permittivity. When the applied bias increases, the space charge layer becomes conductive and results in degradation or breakdown of the capacitor. The application of a dc bias to a material undergoing impedance spectroscopy is also useful for proving or disproving impedance models.

One difficulty associated with impedance modeling is that it is often possible to obtain good fits with more than one impedance model. While activation energies obtained from fits may seem reasonable when compared to literature or band gaps, another method for supporting claims that impedance features are specifically ionic or electronic in character is to apply an increasing dc bias with the ac oscillation amplitude and observe how the features change. The effect of dc bias on the impedance spectrum of un–doped $x = 0.8$ CTZ at 700 °C is shown in Fig. 3–37.
From Fig. 3–37, it can be seen that with a bias of 0.2 V, there is little change in the impedance spectrum. At 0.4 V, the bulk portion of the high frequency peak becomes slightly more conducting, the grain boundary feature becomes clearly distinguishable from the main semicircle, and the low frequency ionic interface/electrode relaxation disappears as oxygen vacancies migrate to the electrode. At 0.6 V, the grain boundary feature becomes more resistive as a space charge layer forms at the grain boundaries due to the migration and pile up of oxygen vacancies, and the low frequency data begins to show the curvature of a full circle, which is likely due to degradation of the sample. With further increasing bias, all features become more conductive.

From Fig. 3–37a, it can be seen that with a bias of 0.2 V, there is little change in the impedance spectrum. At 0.4 V, the bulk portion of the high frequency peak becomes slightly more conducting, the grain boundary feature becomes clearly distinguishable from the main semicircle, and the low frequency ionic interface/electrode relaxation disappears as oxygen vacancies migrate to the electrode. At 0.6 V, the grain boundary feature becomes more resistive as a space charge layer forms at the grain boundaries due to the migration and pile up of oxygen vacancies, and the low frequency data begins to show the curvature of a full circle, which is likely due to degradation of the sample. With further increasing bias, all features become more conductive. In Fig. 3–37b, it can be seen that after the 1.0 V spectrum was collected, the sample was more conductive overall, indicating some degradation had occurred during the measurements. The effect of dc bias supports the claim that the high frequency circle contains an ionic grain boundary feature, which becomes distinguishable from the main relaxation at a bias of 0.4 eV and is more resistive than the bulk as would be expected for the development of a resistive Shottky barrier at the interface (Denk et al., 1997; Fleig et al., 2000).

Overall, electrical characterization of the CTZ and CTZ + Mn systems showed that doping with Mn results in clear effects on bulk transport compared to the undoped system.
proving that at least some of the Mn is incorporated into the bulk of the ceramic. However, without knowing definitively whether Mn exists exclusively in the bulk or both in the bulk and on grain boundaries, the exact mechanisms for the improvements cannot be deduced and are currently being investigated.

3.9 Summary

By understanding trends in structure–property relationships, band gaps, relative permittivity, conductivity, and effects of Mn doping across the composition range, an appropriate composition range was isolated that minimized both ionic and electronic conductivity. Overall, it has been demonstrated that the $x = 0.8 \text{Ca}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) composition doped with 0.5 mol% Mn satisfies the requirements shown in Fig. 3–1 in this chapter for identifying the optimum composition and doping concentration in the CTZ system for obtaining high energy densities and breakdown strengths.

Basic characterization of the $\text{Ca}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CTZ) solid solution revealed that phase purity was generally observed with the exception of slight ZrO$_2$ phases observed in $x = 0.3$ and $x = 0.7$ compositions. Overall, the grain sizes across the CTZ composition range showed no significant trend, but compositions closer to the CaZrO$_3$ – rich end of the composition range showed a slightly more bimodal distribution in grain sizes. Observations of densification and sintered microstructures in both air and low pO$_2$ atmospheres revealed that higher levels of Mn doping resulted in a decrease in grain size with increasing Mn content when fired in air, and an increase in grain size with increasing Mn content when fired in low pO$_2$ atmospheres. Studies by EDS of the distribution of atoms in the $x = 0.8, y = 0.005, 0.04 \text{Ca}(\text{Ti}_x\text{Mn}_y\text{Zr}_{1-x})\text{O}_3$ CTZ + Mn samples were inconclusive as to whether Mn resides in grain boundaries, grains, or both. Overall, it was concluded that the optimum Mn doping concentration was 0.5 mol% substituted for Ti$^{4+}$.

Basic electrical characterization of $x = 0.7, 0.8$, and 0.9, $y = 0.005 \text{Ca}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ showed weakly linear trends in TCC and relative permittivity as expected. Values for TCC were similar between the systems, calculated as ± 18.1% for $x = 0.8$ CTZ and ± 16.3%, ± 17.4%, and ± 17.2% for $x = 0.7, 0.8$, and 0.9 CTZ + Mn respectively. Doping with 0.5 mol% Mn showed significant reductions in dielectric loss relative to the undoped $x = 0.8$ sample up to 150 °C. Room temperature relative permittivities showed a generally linear trend with 133 ± 7, 157 ± 5, and 185
± 8 for x = 0.7, 0.8, and 0.9 respectively. Little variation in relative permittivity within the reported error was observed for the same compositions doped with 0.5 mol% Mn.

Optical characterization by UV–Vis diffuse reflectance spectroscopy revealed that the indirect band gaps followed an asymmetric Vegard’s law trend across the solid solution. However, it was found that due to the low % reflectance of Mn–doped CTZ, diffuse reflectance could not be used to accurately determine the band gaps of Mn doped compositions. Overall, several assumptions and ambiguities surrounding the analysis of UV–Vis data led to a more in–depth optical analysis of the CTZ composition range using spectroscopic ellipsometry. By modeling the data, trends in absorption coefficients, band gaps, and indices of refraction were unambiguously extracted from the optical data. Additionally, samples doped with Mn could be analyzed accurately. The refractive indices showed a linear trend across the solid solution and were within 3.5% of values calculated using the Gladstone–Dale relation, providing additionally validity to the measurement technique. Extrapolated indirect band gaps showed a similar asymmetric trend to that of UV–Vis, but the trend was more symmetrical between the end members. The first direct transition also correlated well with the trend in indirect band gaps. The direct band gaps showed a more linear trend across the solid solution. The indirect band gaps for both ellipsometry and UV–Vis showed good fits to the asymmetric Vegard’s trend observed in literature.

Conductivity measurements correlated with band gap measurements as predicted, with CaZrO$_3$ – rich compositions having resistivities an order of magnitude larger than CaTiO$_3$ – rich compositions. From I–V measurements at 250 °C, ohmic behavior was observed and Mn doping in x = 0.7, 0.8, and 0.9 CTZ yielded current densities up to 5 orders of magnitude lower than undoped x = 0.8 CTZ. Calculated resistivities were 54.5 kΩ.cm, 347 kΩ.cm, and 288 kΩ.cm for x = 0.7, 0.8, and 0.9 CTZ + Mn respectively.

High temperature P–E loops revealed that in un–doped x = 0.8 CTZ, low losses were observed at room temperature, but increasing the temperature to 150 °C resulted in a dominance of dielectric loss and minimization of recoverable energy density. When doped with 0.5 mol% Mn, low losses were observed up to 300 °C and the maximum room temperature energy density obtained was 6.14 J/cm$^3$ at a $E_b$ of 0.94 MV/cm and $P/V$ of 0.38 W/cm$^3$, and the maximum energy density at 300 °C was 5.36 J/cm$^3$ at $E_b = 1.04$ MV/cm and $P/V$ of 2.84 W/cm$^3$. At ~1/4$E_b$, the energy densities were 0.98, 0.86, and 0.68 J/cm$^3$ at 100, 200, and 300 °C respectively. When
base–metal capacitors fired in reducing atmospheres and re–oxidized were tested, it was found that at room temperature recoverable energy densities were 5.04 J/cm³ for the 9 hr re–oxidation and 5.12 J/cm³ for the 12 hr re–oxidation with breakdown strengths of 0.74 and 0.84 MV/cm respectively. However, similarly to un–doped air–fired CTZ, the presence of oxygen vacancies resulted in dielectric loss minimizing the recoverable energy density at elevated temperatures.

Impedance spectroscopy revealed that in un–doped x = 0.8 CTZ, two distinct relaxations were observed. The high frequency relaxation was attributed to the combination of bulk ionic/electronic conductivity and ionic grain boundary conductivity, while the low frequency relaxation was attributed to ionic polarization of the ceramic–electrode interface. When doped with 0.5 mol% Mn, only one relaxation was observed in the impedance spectra, which was attributed to electronic conductivity. Overall, doping x = 0.8 CTZ with 0.5 mol% Mn not only minimized ionic conductivity but it further reduced the electronic conductivity of the material relative to the un–doped sample. From conductivity plots of x =0.8 CTZ, the bulk electronic activation energy was 1.73 ± 0.02 eV, the bulk ionic activation energy was 0.70 ± 0.01 eV, and the grain boundary activation energy was 1.18 ± 0.01 eV, both of which are common values for oxygen transport in perovskite systems (Chroneos et al., 2010).

For CTZ + Mn, the electronic activation energy was determined to be 1.72 eV ± 0.01 eV, which is closer to the intrinsic activation energy of the material. Transference numbers showed that ionic charge carriers dominated the un–doped CTZ system. Additional support for the impedance model and separation of ionic and electric contributions to conductivity were provided through $M^\prime$ and $Z^\prime$ comparisons, high and low temperature relative permittivity trends, and dc voltage dependence of high temperature impedance features. Overall, while these results indicate that the CTZ + Mn system shows promise for high energy density, high temperature capacitor applications, it was speculated that where other perovskites such as CaHfO₃, which have been reported to have band gaps as high as 6.4 eV and relative permittivities as high as 38, could yield better high temperature performance (Kersch et al., 2009; Feteira et al., 2008). Therefore, substitution of Zr with Hf may lead to even further reductions in conductivity when paired with CaTiO₃, which will be explored in the next chapter (Kersch et al., 2009; Feteira et al., 2008).
4.1 Introduction

This chapter introduces the effects of the substitution of Hf for Zr on the properties of Ca(Ti<sub>0.8</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH) and Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Mn) systems in terms of the microstructure, optical properties, basic electrical properties, conductivity, and ultimately energy density at high temperatures. A systematic approach to evaluating the energy density at temperatures up to 300 °C and high electric fields is presented. Comparisons of the various characterization methods shown in Chapter 2 are made between compositions containing Zr and Hf.

4.2 Background

There is little literature concerning the use of CaHfO<sub>3</sub> in binary, ternary, or quaternary dielectric compositions. CaHfO<sub>3</sub> and CaZrO<sub>3</sub> thin films have been utilized as gate insulators for pentacene organic field–effect transistors (OFETs) due to their wide band gaps. The films are useful as gate insulator materials since low leakage currents and breakdown currents can be achieved (Shubuya et al., 2004; Kwon et al., 2003; Yu et al., 2004). In a comparison study of Al<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub>, CaHfO<sub>3</sub>, and CaZrO<sub>3</sub>, it was found that CaHfO<sub>3</sub> showed the largest breakdown strength, (10 MV/cm) compared to CaZrO<sub>3</sub> (2 MV/cm) and was found to be the superior gate insulator (Yaginuma et al., 2005).

In high temperature ionic and electronic conduction studies of CaZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaZrO<sub>3</sub>, CaHfO<sub>3</sub>, SrHfO<sub>3</sub>, and La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> compounds, it was found that the Hf compounds showed a remarkably lower partial electronic conductivity than the Zr compounds, with La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> and CaHfO<sub>3</sub> showing the lowest conductivities (Pandit et al., 1994). There is little literature on the optical properties or band gaps of CaHfO<sub>3</sub> compounds. Estimates based on published values for BaZrO<sub>3</sub>, ZrO<sub>2</sub>, and HfO<sub>2</sub> suggest the band gap should be above 5 eV for all three materials (Robertson, 2000). First principles calculations of orthorhombic CaHfO<sub>3</sub> have suggested the indirect band gap of CaHfO<sub>3</sub> could be as high as 6.4 eV compared to 4 – 5.5 eV for CaZrO<sub>3</sub>.
(Kersch et al., 2009). The low measured ionic conductivity and large band gap implies that substituting CaHfO$_3$ for CaZrO$_3$ should yield higher breakdown strengths and thereby energy densities at high temperatures.

As mentioned in Chapter 3, the average bond energy (ABE), thermal vibration of cations, jumping distance between adjacent oxygen sites, and polarizability of the perovskite oxides in the binary composition give insight into how conductive the material should be (Kilner, 1981; Cook et al., 1991). The ABE of CaHfO$_3$ was calculated to be 368.8 kJ/mol compared to 358.3 kJ/mol for CaZrO$_3$, suggesting that more energy would be required to break the metal – oxygen bonds to form oxygen vacancies in CaHfO$_3$.

The thermal vibration of cations also affects the diffusion of oxygen vacancies across the crystal lattice, the amplitude of which is inversely proportional to the square root of the cation molecular weight (Mogensen et al., 2004). For Zr$^{4+}$ and Ti$^{4+}$, the proportional thermal vibration energies are $1.2 \times 10^{-4} \text{ (g/mol)}^{-2}$ and $3.1 \times 10^{-5} \text{ (g/mol)}^{-2}$ respectively. Since Hf is nearly twice as heavy as Zr, ionic conductivity is expected to be lower in CaHfO$_3$.

Since the migration of anions through the perovskite structure is expected to occur via vacancy exchange, the diffusion of oxygen anions is inversely proportional to the jumping distance between available sites within the oxygen octahedral (Kilner et al., 1982). The distance between adjacent oxygen sites for CaTiO$_3$ and CaZrO$_3$, calculated from lattice parameters obtained via X-ray diffraction (XRD), were 4.68 Å and 4.91 Å respectively. As a result, it is expected that the diffusion coefficient for oxygen anions should be smaller in compositions that contain more CaZrO$_3$ than CaTiO$_3$. Since the ionic radii of Hf and Zr are similar, it is not expected that substitution of Hf for Zr will affect the diffusion coefficient.

Lastly, the polarizability of the material can also contribute to ionic conductivity, since the activation energy of anion migration decreases as lattice polarizability increases (Mogensen et al., 2004; Sammells et al., 1992). The polarizability ($\alpha$), refractive index ($n$), dielectric constant ($\varepsilon$), electric polarization ($P$), and electric field ($E$) are related by the scalar relationships,

$$\varepsilon E = E + 4\pi P = E + 4\pi N\alpha E$$  \hspace{1cm} (Equation 4–1)

$$\varepsilon - 1 = n^2 - 1 = 4\pi N\alpha$$  \hspace{1cm} (Equation 4–2)
where \( N \) is the number of atoms/cm\(^3\). Since CaTiO\(_3\) has a larger relative permittivity (\( \varepsilon_r \approx 171 \) compared to 30 for CaZrO\(_3\)), it is expected that CaTiO\(_3\) – rich compositions will have a higher polarizability, and thus exhibit more ionic conductivity relative to CaZrO\(_3\) – rich compositions (Kersch et al., 2009; Feteira et al., 2008). It has been found in BaTiO\(_3\) and BaZrO\(_3\) that there is not a significant difference in ionic polarizability at room temperature in the cubic phase (Roberts, 1951), but the materials considered here are orthorhombic and will most likely vary more. However, there is little difference between the relative permittivity of CaHfO\(_3\) and CaZrO\(_3\).

### 4.3 Structure – Property Characterization of Ca(Ti\(_{0.2}\)Hf\(_{0.8}\))O\(_3\) (CTH) and Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Hf\(_{0.2}\))O\(_3\) (CTH + Mn)

The reasons for Mn resulting in improved properties in similar systems, including BaTiO\(_3\), (Ca\(_{0.7}\)Sr\(_{0.3}\))(Zr\(_{0.97}\)Ti\(_{0.03}\))O\(_3\), and CaZrO\(_3\) have been largely based on speculation of aspects such as Mn valence state, site occupation, and lattice/grain boundary incorporation (Jeong et al., 2004; Morita et al., 2002; Rodel et al., 1984; Sumita et al., 1991; Osawa et al., 1993; Pinceloup et al., 2006; Cai et al., 2010; Jeong et al., 2004; Jeong et al., 2007; Yoneda et al., 1997; Jeong et al., 2006). The valence of Mn has been known to change from Mn\(^{2+}\) at low oxygen activities, Mn\(^{3+}\) in increasing oxygen activities such as reoxidation, and Mn\(^{4+}\) when fired in air, which is the assumed valence state for this work (Cai et al., 2010). Based on B–site incorporation in BaTiO\(_3\), Mn is assumed to occupy the B site in Ca(Ti\(_{0.8}\)Hf\(_{0.2}\))O\(_3\) CTH for this work as well as based on similarities in ionic radii (Ba\(^{2+}\) = 161 pm (12–coord.), Ti\(^{4+}\) = 61 pm (6–coord.), Ca\(^{2+}\) = 134 pm (12–coord.), Hf\(^{4+}\) = 85 pm (6–coord.), Mn\(^{4+}\) = 67 pm (6–coord.)) and valence state (Shannon et al., 1976). However, due to the intermediate size of the Mn\(^{4+}\) ion compared to the Ca\(^{2+}\), Hf\(^{4+}\), and Ti\(^{4+}\) ions, it may also be possible for Mn to occupy the A–site. The solubility limit of Mn in CTH and closely related systems has not been extensively studied. The solubility limit of Mn in Ba\(_{0.6}\)Sr\(_{0.4}\)TiO\(_3\) has been determined by energy dispersive X–ray spectroscopy (EDS) to be \(~ 0.5\) mol\% (Hu et al., 2005).

The difficulties associated with achieving phase purity in calcined powders of similar Ca–based perovskite systems have been observed by previous researchers, who also only observed full phase purity upon sintering of dense bulk samples (Xu et al., 2000). The room–temperature XRD patterns for sintered and crushed laminated tapes of CTH and Ca(Ti\(_{0.795}\)Mn\(_{0.005}\)Hf\(_{0.2}\))O\(_3\) (CTH + Mn) are shown in Fig. 4–1.
The main Bragg reflections show slight splitting, indicating CTH and CTH + Mn have an orthorhombic structure. A small peak at ~ 30° 2θ was indexed as the fluorite phase ZrO₂ and has been observed by previous authors for similar systems, noting that the dielectric properties were unaffected by small inclusions of a second phase (Xu et al., 2005; Lamrani et al., 2011). Similarly to the Ca(Ti₀.₈Zr₀.₂)O₃ system characterized in Chapter 3, indexing of the pattern also results in an orthorhombic unit cell having symmetry described by the Pcmₐ space group with \(a = 5.421(1), b = 7.712(1), \) and \(c = 5.499(1) \) Å for CTH and \(a = 5.421(1), b = 7.712(1), \) and \(c = 5.497(1) \) Å for CTH + Mn. The unit cell volumes were 229.982 Å³ for CTH and 229.845 Å³ for CTH + Mn. The theoretical X-ray densities were calculated to be 4.70 g/cm³ for CTH and 4.68 g/cm³ for CTH + Mn. These values are close to the theoretical density of 4.61 g/cm³ calculated using the series mixing rule with the theoretical densities of CaTiO₃ (4.03 g/cm³) and CaHfO₃ (6.95 g/cm³) (Koopmans et al., 1983; Feteira et al., 2008). Sintered, laminated samples for both CTH and CTH + Mn were > 97% theoretical density.

Figure 4–1: X-ray diffraction patterns for Ca(Ti₀.₈Hf₀.₂)O₃ (CTH) and Ca(Ti₀.₇₉₅Mn₀.₀₀₅Hf₀.₂)O₃ (CTH + Mn). Main diffraction peaks are indexed and the star denotes the location of the ZrO₂ 2nd phase peak. A more thorough indexing of all peaks can be found in reference to the Ca(Ti₀.₈Zr₀.₂)O₃ in Fig. 3–2.
The grain microstructures for CTH and CTH + Mn are shown in Fig. 4–2.

Figure 4–2: Grain microstructures from scanning electron microscopy for Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) (left) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) (right).

The grain sizes were determined to be approximately 2.42 μm and 2.41 μm for CTH and CTH + Mn respectively. Previous researchers have reported that in low oxygen partial pressure firing at fixed temperature for (Ca$_{0.7}$Sr$_{0.3}$)(Zr$_{0.97}$Ti$_{0.03}$)O$_3$–based systems, the grain size increases with increasing Mn content, but is still smaller than the un–doped material (Pinceloup et al., 2006). In this work, no grain size dependence on Mn addition was observed within the reported error.

As noted previously, it has been reported that the band gap of CaHfO$_3$ is larger than that of CaZrO$_3$. From spectroscopic ellipsometry, the comparison of the absorption coefficient vs. photon energy for CaZrO$_3$ and CaHfO$_3$ is shown in Fig. 4–3.
From Fig. 4–3, it can be seen that the onset of absorption at the band edge occurs at a higher photon energy for CaHfO$_3$ than CaZrO$_3$. For CaHfO$_3$, the energy of the first direct transition is beyond the spectrum of the ellipsometer utilized. It can be seen in the CaHfO$_3$ data that a slight peak occurs between 4.8 and 5.6 eV, which is not clearly present in the CaZrO$_3$ sample. It is difficult to discern whether this is an actual peak indicative of the first direct transition, since the magnitude of the absorption is lower than would be expected.

The trend in absorption coefficient for CTH + Mn compared to Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn) with focus on the absorption tails potentially due to defects is shown in Fig. 4–4.
From Fig. 4–4, it is observed that the absorption of the defect tail for CTH + Mn is larger than that of CTZ + Mn. It is possible that by replacing Hf with Zr, more defects are present in the CTH + Mn system, but the origin of said defects is unclear at this point. The comparison of $\alpha^{0.5}$ and $\alpha^2$ from which the indirect and direct band gaps were determined from for CTH, CTH + Mn, and a comparison between $\alpha^{0.5}$ and $\alpha^2$ for CTH + Mn and CTZ + Mn are shown in Fig. 4–5.

Figure 4–4: Defect tails in the absorption coefficient of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) and Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn) from spectroscopic ellipsometry.
The direct and indirect and band gaps for CTH and CTH + Mn were both determined to be 4.05 ± 0.01 eV and 3.71 ± 0.01 eV respectively. As shown in Chapter 3, the direct and indirect band gaps for CTZ + Mn were 4.07 ± 0.01 and 3.77 eV respectively. Regardless, the band gaps are still attractive for minimizing electronic conductivity in the CTH + Mn system.

The comparison of the extinction coefficient and refractive index between the CTH + Mn and CTZ + Mn compositions are shown in Fig. 4–6.

Figure 4–5: Comparison of $\alpha^{0.5}$ and $\alpha^2$ from which the indirect and direct band gaps were determined for CTH, CTH + Mn, and comparison between $\alpha^{0.5}$ and $\alpha^2$ for CTH + Mn and CTZ + Mn from spectroscopic ellipsometry.
The refractive index for CTH + Mn is slightly lower than that of CTZ + Mn, and deviates slightly from the refractive index calculated from the Gladstone - Dale relation. The origins of the difference are unclear.

**4.4 Electrical Characterization of Ca(Ti$_{0.2}$Hf$_{0.8}$)O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn)**

The temperature coefficient of capacitance (TCC) and dielectric loss from −50 to 150 °C for CTH and CTH + Mn are shown in Fig. 4–7.
Both materials yielded similar values for the TCC over the measured frequency range. The relative permittivities ($\varepsilon_r$) for CTH were 199, 171, and 143 at $-50$, 25, and $150$ °C respectively and were 197, 170, and 144 at the same temperatures for CTH + Mn. The room temperature permittivities are higher than would be predicted using the series mixing rule from the binary values ($\varepsilon_r = 142$), where CaTiO$_3$ $\varepsilon_r = 171$, and $\varepsilon_r = 27$ for CaHfO$_3$ (Koopmans et al., 1983; Feteira et al., 2008). The relative permittivity for $x = 0.8$ CTH + Mn was higher than that of $x = 0.8$ CTZ + Mn ($\varepsilon_r = 157$), which may be due to differences in how the replacement of Zr with Hf changes the amplitude of phonon scattering in the lattice. Losses for both samples were $< 10^{-3}$ over the entire temperature and frequency range, but the Mn doped sample showed a significant decrease in dielectric loss compared to CTH at elevated temperatures. For CTH, the TCC deviation from the room temperature value at $-50$ and $150$ °C was $\pm 16.4\%$ and was $\pm 15.8\%$ for CTH + Mn, or $-820$ and $-790$ ppm/°C respectively. As shown in Fig. 4–8, CTH + Mn showed little frequency dependence over the measured temperature range.
The impedance spectra of CTH and CTH + Mn capacitors measured from 600 to 700 °C are shown in Fig. 4–9, with good fits to the equivalent circuits described in Chapter 2 being obtained for both materials over the measured temperature range.

Figure 4–8: Frequency dependence of the temperature coefficient of capacitance for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) from –50 to 150 °C.

Figure 4–9: Impedance spectra from 600 to 700 °C for a) Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and b) Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn).
The impedance spectra for CTH show two slightly overlapping relaxations indicative of mixed conduction with selectively blocking electrodes as explained in Chapter 3 for the CTZ system (Donnelly et al., 2010). When doped with 0.5 mol% Mn, however, one distinct relaxation is observed representing electronic conduction only. The specific conductivities extracted from fitting the spectra are shown in Fig. 4–10 for the doped and un–doped samples.

![Impedance Spectra](image.png)

Figure 4–10: Specific conductivities extracted from fitting the impedance spectra for Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn).

It is clear from the plots in Fig. 4–10 that not only did 0.5 mol% Mn doping of CTH minimize ionic conductivity, it further reduced the electronic conductivity of the material relative to the un–doped sample similarly to CTZ. The extracted transference numbers for the un–doped sample are shown in Table 4–1 and show that ionic carriers dominate conduction, similarly to the CTZ.
system.

Table 4–1: Transference numbers for un–doped Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) calculated from impedance spectroscopy fitting.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$t_{\text{electronic}}$</th>
<th>$t_{\text{ionic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td>625</td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td>650</td>
<td>0.07</td>
<td>0.93</td>
</tr>
<tr>
<td>675</td>
<td>0.09</td>
<td>0.91</td>
</tr>
<tr>
<td>700</td>
<td>0.10</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Activation energies for the conduction mechanisms in each material were calculated using the slopes of the curves in Fig. 4–9 with error determined from a least squares regression fit. The extracted conductivities showed Arrhenius behavior allowing for activation energies to be calculated. For CTH, the bulk electronic activation energy was 1.90 ± 0.02 eV, and the bulk ionic activation energy was 1.00 ± 0.01 eV, which is a common value oxygen transport in many perovskite systems (Chroneos et al., 2010). For CTH + Mn, the electronic activation energy was determined to be 1.70 eV ± 0.01 eV.

As discussed in Chapter 3 for CTZ, the plot of $M''$ vs. frequency shows the component with the lowest capacitance, whereas the plot of $Z''$ vs. frequency shows the component with the highest impedance. In an overlapping plot of $Z'$ and $M''$ vs. frequency, if peaks occur at the same frequency for $Z''$ and $M''$, the peaks can be attributed to the same source. Non–overlapping peaks can be attributed to different sources. As shown in Fig. 4–11, there is a high frequency edge/peak in the $M''$ plot, which is at the same frequency as the most dominant peak in the $Z''$ data. From the impedance spectra in Fig. 4–9 and as discussed in Chapter 3 for the equivalent circuit modeling, it can be seen that the high frequency semicircle is composed of both the bulk ionic and electronic impedance as well as the grain boundary impedance. The grain boundary capacitance is higher than that of the bulk, so the peak in the $M''$ plot is most likely due to the bulk component, which is dominated by the electronic resistivity. The low frequency peak in the $Z''$ data, for which a peak in $M''$ is not present, is then due to the ionic polarization of the electrode as predicted.
The comparison of $Z''$ and $M''$ vs. frequency for CTH and CTZ at 625 °C is shown in Fig. 4–12.

Figure 4–11: $Z''$ and $M''$ vs. frequency for un–doped Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) from 600 to 700 °C.

Figure 4–12: Comparison of $Z'$ and $M'$ vs. frequency for un–doped Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) and Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) at 625 °C.
As seen in Fig. 4–12, the plot of $Z''$ shows that overall, the CTH sample shows a higher impedance compared to the CTZ sample, and the coinciding high frequency peak in the $M''$ data is more pronounced for the CTH sample, most likely due to the higher resistivity of the bulk. Both peaks in the CTH plot are shifted to lower frequencies compared to CTZ, and the impedance at 1 kHz is significantly higher compared to CTZ.

The effective permittivity and dielectric loss ($\tan\delta$) vs. frequency from impedance spectroscopy for un–doped CTH are shown in Fig. 4–13.

Figure 4–13: Effective permittivity and dielectric loss ($\tan\delta$) vs. frequency for Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) from 600 to 700 °C.

In the high temperature regime, the un–doped $x = 0.8$ CTH capacitors behave like barrier layer capacitors as a result of oxygen vacancies creating space charge layers at the grain boundaries and dielectric–electrode interface, similarly to the CTZ system. This is supported by the colossal permittivity and high dielectric losses. As calculated for CTZ in Chapter 3, the depletion layer thickness for the CTH system from 600 to 700 °C is shown in Fig. 4–14.
It can be seen from Fig. 4–14 that the depletion layer thickness decreases at the grain boundary with increasing temperature, whereas the depletion layer thickness at the double layer at the double layer (electrode interface) remains relatively the same with only a slight decrease with increasing temperature. At high temperatures, the depletion layer thicknesses for both the double layer and the grain boundary are thinner than that of the CTZ system, suggesting that less oxygen vacancies were present to accumulate at the interfaces, which is supported by the overall decrease in ionic conductivity relative to the CTZ composition.

The comparison of the effective permittivity and dielectric loss (tanδ) vs. frequency from impedance spectroscopy for un–doped CTH and CTZ at 650 °C is shown in Fig. 4–15.
It can be seen from Fig. 4–15 that while the values of losses are high overall, CTH showed lower losses at 1 kHz relative to the CTZ composition. The peak in the dielectric loss was also shifted to lower frequencies relative to CTZ. The effective permittivities for CTH and CTZ show similar trends and values, and are both indicative of a barrier layer capacitor effect.

The comparison of the conductivities extracted from impedance spectroscopy fitting between CTH and CTZ are shown in Fig. 4–16.
It can be seen from Fig. 4–16 that the CTH and CTH + Mn systems showed decreases in ionic and electronic conductivity at high temperatures compared to CTZ and CTZ + Mn.

Thermally stimulated depolarization current (TSDC) measurements were performed in order to correlate observations from impedance spectroscopy with a high field dc bias measurement. The results of TSDC measurements on CTH and CTH + Mn at 250 °C are shown in Fig. 4–17.
From Fig. 4–17, it can be seen that undoped CTH shows two distinct peaks at ~100 °C and ~250 °C, whereas CTH + Mn only shows one diffuse peak at temperatures above 300 °C. Several authors have investigated the TSDC behavior of solid dielectric systems such as Fe–doped SrTiO₃, Mn– and Ho–doped BaTiO₃, and Fe–doped (Ba,Sr)TiO₃ (Liu et al., 2008; Fukami et al., 1987; Jeong et al., 2007; Scymzak et al., 2007; Jeong et al., 2006). In the (Ba₀.₄Sr₀.₆)(Ti₀.₉₉Fe₀.₀₁)O₃ system, 2 peaks were observed at approximately 80 and 120 °C, and were overlapping. The higher temperature peak was attributed to oxygen vacancies migrating within the crystal grain. The lower temperature peak was speculated to be attributed to defect dipoles associated with the $[Fe^+_n\cdot\cdot\cdot]$ neutral defect complex, but no quantified proof was provided (Fukami et al., 1987). In the Fe–doped SrTiO₃ system, 3 peaks were observed with a voltage dependence and were attributed to polarized dipoles (similarly to Fukami et al.), traps, and oxygen vacancies (Liu et al., 2008; Fukami et al., 1987). Measurements of Bi–modified BaTiO₃ showed TSDC peaks, and were attributed to the influence of homocharges in stabilization of heterocharges associated with orientation of polar microregions (Scymczal et al., 2007). Investigations of Mn–doped BaTiO₃ showed TSDC peaks around transition temperatures, and the magnitude of the peaks was suppressed when doped with Mn (Jeong et al., 2006).

![Figure 4-17: Thermally stimulated depolarization current (TSDC) measurements at 250 °C for Ca(Ti₀.₈Hf₀.₂)O₃ (CTH) and Ca(Ti₀.₇₉₅Mn₀.₀₀₅Hf₀.₂)O₃ (CTH + Mn).](image)
For the CTH system, it is difficult to deduce the exact origin of the TSDC peaks. If the low temperature peak in the undoped system were of dipole origin, a low temperature dipole peak of smaller magnitude would still be observed in the Mn–doped system as well. No such peak was observed in CTH + Mn, even when measurements were taken starting from room temperature. By correlating the TSDC results with impedance spectroscopy, it is most likely that all peaks are associated with oxygen vacancies, either in the bulk or at interfaces. In the CTH + Mn TSDC spectra, the single high temperature peak is associated with space charge as well, and the Mn suppresses the oxygen vacancy concentration and accumulation of oxygen vacancies at interfaces.

The current–voltage (I–V) results at 250 °C for the CTH and CTH + Mn systems are shown in Fig. 4–18.

![Figure 4–18: 250 °C current–voltage (I–V) leakage current results for a) Ca(Ti₀.8Hf₀.2)O₃ (CTH) and b) Ca(Ti₀.795Mn₀.005Hf₀.2)O₃ (CTH + Mn).](attachment:figure.png)

From Fig. 4–18, it can be seen that in the undoped system, the current does not reach steady state within the measurement time. This can be attributed to a large concentration of oxygen vacancies migrating under bias. When doped with Mn, the leakage current is stable and shows a decrease in the overall leakage current.
The comparison of the 250 °C current density with increasing field for CTZ + Mn and CTH + Mn is shown in Fig. 4–19.

Figure 4–19: Current density with increasing electric field at 250 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) and Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn).

From Fig. 4–19, it is shown that the CTH + Mn decreases the current density by an order of magnitude relative to CTZ + Mn. Both materials showed ohmic behavior within the measured temperature range. Overall, the dielectric properties of CTH + Mn and CTZ + Mn were similar, but CTH + Mn showed significant decreases in conductivity. The overall comparison of properties of interest is shown in Table 4–2.

Table 4–2: Comparison of basic dielectric properties between Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) and Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn). TCC = temperature coefficient of capacitance.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Grain Size (µm)</th>
<th>$\varepsilon_r$</th>
<th>Band Gap (eV)</th>
<th>TCC (%)</th>
<th>250 °C Resistivity (GΩ.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTZ + Mn</td>
<td>2.41</td>
<td>157</td>
<td>3.77</td>
<td>$\pm$ 20</td>
<td>0.03</td>
</tr>
<tr>
<td>CTH + Mn</td>
<td>2.41</td>
<td>171</td>
<td>3.71</td>
<td>$\pm$ 16</td>
<td>0.46</td>
</tr>
</tbody>
</table>
It can be seen from Table 4–2 that the most significant differences in properties are in relative permittivity and resistivity, which are the two governing properties for determining energy density. The most significant difference in structure–property relationships was in thermal vibration energy between CTH + Mn and CTZ + Mn, which is most likely the main contribution to the minimization of conductivity in the CTH–based system.

4.5 Energy Density Evaluation of Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn)

The summary of the polarization–field (P–E) loops for capacitors having the highest energy density at each temperature is shown in Fig. 4–20.

![Figure 4–20: Summary of the polarization–field (P–E) loops for capacitors having the highest energy density at each temperature in a) Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) and b) Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn).]

The average energy densities, characteristic breakdown strengths, high field losses, and volumetric power dissipations for CTH and CTH + Mn are listed in Table 4–3.
The maximum room temperature energy density measured for CTH was 9.0 J/cm³ at 1.2 MV/cm, while that of CTH + Mn was 9.5 J/cm³ at 1.3 MV/cm. Both CTH and CTH + Mn continued to experience low losses and high fields at 100 °C with maximum energy densities of 7.7 J/cm³ at 1.2 MV/cm for CTH, and 8.9 J/cm³ at 1.3 MV/cm for CTH + Mn. At 200 and 300 °C, CTH + Mn maintained low high field losses, but losses in the CTH capacitors limited the breakdown strength and the energy density dropped considerably. However, while high field losses began to increase in CTH + Mn, they remained on the order of 10⁻³, thus allowing the high breakdown strengths to be maintained, with the recoverable energy density being limited only by the decrease in $\varepsilon_r$ associated with the elevated temperature. As a result, CTH + Mn showed maximum energy densities of 8.6 J/cm³ at 1.3 MV/cm for 200 °C and 6.5 J/cm³ at 1.3 MV/cm for 300°C.

In Fig. 4-21, the trend in energy density with increasing field for CTH and CTH + Mn with the highest energy density at the breakdown strength for various temperatures is compared.

Table 4-3: Summary of average values extracted from room and high temperature polarization vs. field loops for Ca(Ti₀.₈Hf₀.₂)O₃ (CTH) and Ca(Ti₀.₇₉₅Mn₀.₀₀₅Hf₀.₂)O₃ (CTH + Mn).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average $U_{vol}$ (J/cm³)</th>
<th>Max $U_{vol}$ (J/cm³)</th>
<th>Characteristic $E_b$ (MV/cm)</th>
<th>Max $E_b$ (MV/cm)</th>
<th>Average Loss (%)</th>
<th>Average P/V (W/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.6 ± 1.0</td>
<td>8.99</td>
<td>1.1 ± 0.14</td>
<td>1.20</td>
<td>0.77 ± 0.12</td>
<td>0.72 ± 0.17</td>
</tr>
<tr>
<td>100</td>
<td>6.2 ± 1.5</td>
<td>7.67</td>
<td>1.1 ± 0.13</td>
<td>1.16</td>
<td>2.85 ± 1.04</td>
<td>2.05 ± 0.47</td>
</tr>
<tr>
<td>200</td>
<td>0.77 ± 0.14</td>
<td>0.93</td>
<td>0.54 ± 0.06</td>
<td>0.57</td>
<td>32.5 ± 7.94</td>
<td>5.14 ± 0.50</td>
</tr>
<tr>
<td>300</td>
<td>0.18 ± 0.11</td>
<td>0.38</td>
<td>0.25 ± 0.12</td>
<td>0.42</td>
<td>72.0 ± 7.60</td>
<td>14.1 ± 11.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average $U_{vol}$ (J/cm³)</th>
<th>Max $U_{vol}$ (J/cm³)</th>
<th>Characteristic $E_b$ (MV/cm)</th>
<th>Max $E_b$ (MV/cm)</th>
<th>Average Loss (%)</th>
<th>Average P/V (W/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8.6 ± 0.68</td>
<td>9.52</td>
<td>1.2 ± 0.05</td>
<td>1.25</td>
<td>0.35 ± 0.08</td>
<td>0.34 ± 0.10</td>
</tr>
<tr>
<td>100</td>
<td>7.4 ± 0.91</td>
<td>8.86</td>
<td>1.2 ± 0.06</td>
<td>1.25</td>
<td>0.57 ± 0.07</td>
<td>0.51 ± 0.12</td>
</tr>
<tr>
<td>200</td>
<td>7.6 ± 1.1</td>
<td>8.57</td>
<td>1.2 ± 0.14</td>
<td>1.29</td>
<td>1.5 ± 0.12</td>
<td>1.3 ± 0.37</td>
</tr>
<tr>
<td>300</td>
<td>4.3 ± 0.99</td>
<td>6.49</td>
<td>1.1 ± 0.12</td>
<td>1.26</td>
<td>6.5 ± 0.72</td>
<td>3.7 ± 0.96</td>
</tr>
</tbody>
</table>
From Fig. 4–21, it can be seen that the energy densities scale with $E^2$, and decrease with increasing temperature due to the decrease in relative permittivity. For CTH + Mn, it can be seen that the dominant reduction in energy density is due to the decrease in permittivity with increasing temperature. For the CTH samples, the energy density behaves similarly up to 100 °C, but begins to decrease significantly at higher temperatures due to high dielectric losses reducing the breakdown strength and energy density.

The Weibull plots for the breakdown strengths at all temperatures are shown in Fig 4–22. Here the difference in temperature dependence between the two materials and the benefits associated with Mn doping in this system can clearly be seen. Characteristic breakdown strengths were obtained using Weibull statistics, in which the breakdown strengths are ranked in increasing order and the median rank (MR) of the data is calculated as

$$MR = \frac{j - 0.3}{N + 0.4}$$

(Equation 4–3)

where $j$ is the rank and $N$ is the total number of samples. The characteristic breakdown strength is
then determined from the zero–intercept of \( \ln(E) \) vs. \( \ln(\ln(1/(1-MR))) \). The Weibull modulus, which determines the degree of variation in the data set, is determined from the slope of the linear trend line.

Figure 4–22: Weibull breakdown plots for \( \text{Ca(Ti}_{0.8}\text{Hf}_{0.2})\text{O}_3 \) (CTH) and \( \text{Ca(Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3 \) (CTH + Mn) for a number of isothermal breakdown tests. Weibull parameters for CTH were 13.89, 8.15, 8.46, and 2.70 for 25, 100, 200, and 300 °C respectively. Weibull parameters for CTH + Mn were 24.49, 18.59, 17.02, and 17.87 for 25, 100, 200, and 300 °C respectively.

From this data, the difference in temperature dependence between the two materials and the benefits associated with Mn doping in this system can clearly be seen. Un–doped CTH shows
similar breakdown behavior for room temperature and 100 °C, but the breakdown strength decreases at higher temperatures as seen in Fig. 4–20a. When doped with Mn, however, the breakdown statistics are similar for all temperatures, with high Weibull moduli indicating good reproducibility of the breakdown strength. Weibull parameters for CTH were 13.89, 8.15, 8.46, and 2.70 for 25, 100, 200, and 300 °C respectively. Weibull parameters for CTH + Mn were 24.49, 18.59, 17.02, and 17.87 for 25, 100, 200, and 300 °C respectively. It is worth noting that while measuring the energy density at the breakdown voltage yields the maximum recoverable energy density, voltage de-rating for actual capacitor use typically reduces the operating voltage by 2–10x. However, since the capacitors in this work were fabricated by hand, it is likely that through automated industrial fabrication, submicron grain sizes, and ~1 µm dielectric layer thicknesses, significant increases in recoverable energy densities could be achieved compared to this work.

The comparison of P–E loops yielding the highest energy densities for CTH + Mn and CTZ + Mn at room temperature and 300 °C is shown in Fig. 4–23.

Figure 4–23: Comparison of P–E loops yielding the highest energy densities for Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Mn) and Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Zr<sub>0.2</sub>)O<sub>3</sub> (CTZ + Mn) at room temperature and 300 °C.
From Fig. 4–23, it is observed that both CTH + Mn and CTZ + Mn show low losses at room temperature, but the CTH + Mn sample shows a larger breakdown strength and polarization. At 300 °C, both CTZ and CTH + Mn show an increase in loss, but the breakdown strength does not deviate strongly from the room temperature value. Again, the CTH + Mn sample shows a larger polarization and breakdown strength. Table 4–4 shows the comparison of energy densities, breakdown strengths, and power dissipation energies for CTH + Mn and CTZ + Mn.

Table 4–4: Comparison of energy densities, breakdown strengths, and volumetric power dissipations for Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) and Ca(Ti0.795Mn0.005Zr0.2)O3 (CTZ + Mn).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CTH + Mn</th>
<th>CTZ + Mn</th>
<th>CTH + Mn</th>
<th>CTZ + Mn</th>
<th>CTH + Mn</th>
<th>CTZ + Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max. U\textsubscript{vol} (J/cm\textsuperscript{3})</td>
<td>Max. U\textsubscript{vol} (J/cm\textsuperscript{3})</td>
<td>Max. E\textsubscript{b} (MV/cm)</td>
<td>Max. E\textsubscript{b} (MV/cm)</td>
<td>Max. E\textsubscript{b} (MV/cm)</td>
<td>Max. E\textsubscript{b} (MV/cm)</td>
</tr>
<tr>
<td>25</td>
<td>9.52</td>
<td>6.14</td>
<td>1.25</td>
<td>1.10</td>
<td>0.34</td>
<td>0.38</td>
</tr>
<tr>
<td>300</td>
<td>6.49</td>
<td>5.36</td>
<td>1.26</td>
<td>1.00</td>
<td>3.70</td>
<td>3.80</td>
</tr>
</tbody>
</table>

From Table 4–4, it is seen that CTH + Mn proved superior to CTZ + Mn in breakdown strength and energy density. The volumetric power dissipations were similar at room temperature and 300 °C for CTH + Mn and CTZ + Mn.

4.6 Summary

Ca(Ti0.8Hf0.2)O3 (CTH) and Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) were characterized for basic structure–property relationships such as phase purity and microstructure. Optical properties including refractive index and band gap, dielectric properties including relative permittivity, TCC, conductivity, and energy density were also studied. Basic characterization of the CTH and CTH + Mn systems showed a similar orthorhombic structure from X–ray diffraction and minimal appearance of ZrO\textsubscript{2} phases. Air–fired microstructures showed homogenous grain sizes similarly to the Ca(ZrTi)O\textsubscript{3} (CTZ) system.

Originally, it was anticipated that the CTH system would have a higher band gap compared to CTZ since previous research predicted higher band gaps in CaHfO\textsubscript{3}. In this research, observations of the absorption spectra for CaHfO\textsubscript{3} and CaZrO\textsubscript{3} showed that the first direct transition occurred at a higher energy for CaHfO\textsubscript{3} than for CaZrO\textsubscript{3}. However, the band gap
extrapolation for CTH yielded a slightly lower band gap (3.71 eV) compared to CTZ (3.77 eV). The origin of the lower band gap in the CTH system is unclear.

Basic dielectric characterization of the CTH and CTH + Mn systems showed a similar TCC to the CTZ system, but with a higher relative permittivity, with $\varepsilon_r = 171$ for CTH compared to 157 for CTZ. This is likely due to the different chemistries resulting in changes in charge carrier scattering, which could change the amplitude of phonon scattering in the lattice. There was minimal frequency dependence of the TCC for CTH + Mn from 100 Hz to 1 MHz. Impedance spectroscopy of CTH and CTH + Mn showed similar features to the CTZ system, but with an overall reduction of both ionic and electronic conductivity. Similarly to the CTZ system, transference numbers showed that ionic carriers dominate the conduction in the un–doped CTH system at high temperatures. Plotting $M''$ and $Z''$ vs. frequency showed that in the CTH system, there is a more defined overlap of the $M''$ and $Z''$ peaks at high frequencies, suggesting that the high frequency peak is dominated by bulk resistivity. Comparing the $M''$ and $Z''$ vs. frequency plots of CTZ and CTH, it was found that CTH showed a higher impedance overall, and both features were shifted to lower frequencies. Comparing the effecting permittivity and tan$\delta$ of CTH and CTZ from impedance spectroscopy, it was found that CTH showed lower dielectric losses at 1 kHz relative to CTZ.

By measuring the TSDC of the CTH and CTH + Mn systems, it was found that two distinct peaks were observed at ~100 °C and ~260 °C for CTH, and only one diffuse peak was observed above 300 °C for CTH + Mn. Since no low temperature peak was observed in the CTH + Mn system, it is difficult to confirm whether the low temperature peak in the CTH spectrum is due to defect dipoles. It is most likely that all peaks are associated with either the migration of oxygen vacancies or the accumulation of oxygen vacancies at interfaces. The high temperature peak in the CTH + Mn spectrum is most likely due to space charge due to accumulation of oxygen vacancies at an interface. Current–voltage measurements showed that the CTH system did not reach steady state leakage current during the measurement time and began to degrade at 20 kV/cm, which is indicative of a large amount of ionic mobility due to oxygen vacancies. In the CTH + Mn system, low steady state leakage currents were observed, indicating that Mn has a clear effect on minimizing ionic conductivity and mobility in the CTH system. The comparison of current density vs. field for CTH + Mn and CTZ + Mn showed that the CTH + Mn system decreased the overall current density by an order of magnitude relative to CTZ + Mn.
Un–doped CTH single layer capacitors exhibited room temperature energy densities as large as 9.0 J/cm$^3$ at 1.2 kV/cm, but showed a drastic decrease in energy density as temperature was increased due to a large onset of loss and subsequent decrease in breakdown strength. When doped with 0.5 mol% Mn, however, the temperature dependence of the breakdown strength was minimized, resulting in room temperature energy densities as high as 9.6 J/cm$^3$ at 1.3 kV/cm. Energy densities similar to room temperature values were observed up to 200 °C, and a 300 °C maximum value of 6.5 J/cm$^3$ at 1.3 kV/cm was measured. When compared to the CTZ + Mn system, CTH + Mn showed higher breakdown strengths at all temperatures, resulting in higher energy densities. Dielectric losses in the P–E loops were similar between CTH + Mn and CTZ + Mn. Weibull breakdown statistics for the CTH and CTH + Mn systems clearly showed the temperature dependence of the breakdown strength in the CTH system, and independence of temperature in the CTH + Mn sample with good reproducibility.

Overall, the CTH + Mn system showed the highest breakdown strength and lowest dielectric losses of the compositions studied thus far. It is clear that doping CTH with Mn results in a decrease in ionic conductivity, and a subsequent decrease in electronic conduction as well. Up to this point, it has been unclear as to whether Mn is suppressing the conductivity due to its valence state when fired in air, whether the dopant resides on grain boundaries in order to minimize oxygen vacancy migration, or if Mn doping suppresses the mobility of oxygen vacancies or their initial concentration. It is important to obtain an understanding of how Mn doping controls the high temperature conductivity in the CTH system. It has been speculated that partial Schottky defects control the conductivity in the un–doped CTH system, which would be supported by the reduction in both ionic and electronic conductivity in the CTH + Mn system if Mn$^{4+}$ dominates when fired in air and cooled slowly. However, if the valence state of Mn is 3+, it is likely that compensating oxygen vacancies would be present, and an increase in ionic conductivity would be occur. It is likely that Mn exists in the 3+ state at high temperatures and compensating oxygen vacancies are present, but as the ceramic cools in air Mn$^{3+}$ changes to Mn$^{4+}$ and the oxygen vacancy concentration is suppressed. It is also possible that Mn doping minimizes the mobility of oxygen vacancies or their initial concentration in the CTH + Mn system. These ideas can be investigated by quenching in the Mn$^{3+}$ state from high temperatures, and observing the effects on impedance spectroscopy as the sample re–oxidizes over time.
5.1 Introduction

This chapter will discuss the role of Mn in multiple valence states and ionic compensation that impacts the control of ionic conductivity in Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) dielectrics when either quenched from 1250 °C or slowly cooled by convection. The CTH + Mn formula assumes that Mn$^{4+}$ is the dominant valence state, substituting for Ti$^{4+}$ isovalently. The influence of firing in low pO$_2$ atmospheres with re–oxidation on the high temperature conductivity will be addressed. It was shown in Chapter 4 that doping CTH with Mn resulted in a decrease in ionic conductivity and a subsequent decrease in electronic conductivity relative to the un–doped system.

Based on earlier work in Fe–doped SrTiO$_3$, it is likely that this trend is due to partial Schottky defects dominating ionic conduction in the un–doped system (Moos et al., 1997). In CTH + Mn, oxygen vacancies are likely present at the sintering temperature since Mn is most likely in the Mn$^{3+}$ or Mn$^{2+}$ valence state at high temperatures. As CTH + Mn slowly cools, Mn most likely changes to the Mn$^{4+}$ state, reducing the total oxygen vacancy concentration compared to the high temperature state of the system. It is hypothesized that if quenched from the sintering temperature, Mn should be frozen in the Mn$^{3+}$ or Mn$^{2+}$ valence states and will show multiple features in impedance spectroscopy as opposed to a single bulk electronic feature when slowly cooled. When the quenched capacitors are annealed in air at the sintering temperature and slowly cooled, only one dominant feature indicative of a bulk electronic resistivity should be observed. Transmission electron microscopy (TEM) will also be used to identify whether Mn is located in grains, segregated to grain boundaries, or both, for quenched and slow cooled CTH + Mn.

5.2 Background

The overriding goal for minimizing ionic and electronic conductivity in multilayer ceramic capacitors (MLCCs) is to minimize degradation and breakdown under electrical field stress to maximize the performance of the capacitor. When an electric field is applied to an
MLCC, both $p$– and $n$–type conduction increases in the dielectric material near the electrodes, being the anode and cathode respectively (Waser et al., 1990; Buessem et al., 1976). An ongoing challenge for maximizing the energy density, volumetric efficiency, and overall performance of such devices is maintaining adequate insulation resistance and dielectric breakdown strength at high temperatures and electric fields, which depends strongly on the temperature and oxygen activity during processing. If a significant amount of oxygen activity exists, degradation can occur during direct current (dc) bias due to electromigration of charged defects such as oxygen vacancies.

It has been shown that doping for high temperature, high energy dielectrics such as Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) with multivalent Mn there is a decrease in ionic conductivity and a subsequent decrease in electronic conductivity at high temperatures (Shay et al., 2012). However, the role of Mn in controlling conduction in such dielectrics is not thoroughly understood. As a result, an understanding of the thermochemical defect chemistries in bulk, grain boundaries and electrode interfaces is crucial for controlling the macroscopic dielectric behavior and degradation kinetics. For power electronics applications where high temperatures and electric fields are involved, it is especially important to understand the relationships between electrical properties, defect chemistry, and microstructure.

The overall reliability of the MLCC is important for maintaining high electrostatic energy densities and electrical performance at high fields and temperatures, and is associated with time–dependent degradation in insulation resistance of the capacitors. This is characterized by a slow increase in the leakage current under applied dc field stress, as typically seen in BaTiO$_3$ dielectrics (Yang et al., 2004). The net insulation resistance contains contributions from metal–dielectric internal electrode interfaces, dielectric grain boundaries, and the dielectric layers themselves. As a result, the decrease in total insulation resistance of the MLCC can be controlled by the degradation of one or all three microstructural components (Chazono et al., 2001). In general, the long–term time–dependent failure of MLCCs is dominated by electromigration of oxygen vacancies across the grain boundaries in the dielectric layers, so it is important that the grain boundaries act as barriers to oxygen transport (Chazono et al., 2001; Morita et al., 2002, Randall et al., 2013). Several researchers have investigated degradation in systems similar to CTH such as air–fired, $p$–type SrTiO$_3$ and concluded that degradation is initiated by the oxygen vacancy electromigration towards the cathode with respect to time, electric field, and temperature (Chazono et al., 2001; Waser, 1989; Waser et al., 1990; Yang et al., 2004).
It is possible for dopants and defects to segregate to grain boundaries during the sintering process, resulting in the formation of space charge layers at the grain boundaries (Yang et al., 2004). The grain boundaries act as electrical barriers against oxygen vacancy electromigration and electronic transport, thus slowing the degradation process and electronic transport (Chazono et al., 2001; Waser et al., 1990; Kishi et al., 2003). When the dielectric layer thickness is decreased within the capacitor, the role of each grain boundary must be optimized since there are fewer grain boundaries between the anode and cathode to limit ionic and electronic transport. The insulation resistance of the electrode–dielectric interface is also important since it can control electron injection at the cathode (Cann et al., 1996). Insulation resistance at the electrode interface results from the Schottky contact between the internal electrodes and dielectric. It has been suggested that oxygen vacancies can be blocked by such electrode interfaces (Chazono et al., 2001). The oxygen vacancies move towards the cathode under a dc electric field, leading to a high concentration of oxygen vacancies near the cathode and a double layer space charge effect results. Both the contributions to conductivity by the grain boundaries and electrode interfaces, as well as the bulk, can be observed and measured by impedance spectroscopy as shown in this chapter.

There is minimal literature on the mechanisms controlling ionic conduction in systems such as CTH and CTH acceptor–doped with 0.5 mol % Mn (CTH + Mn). Electrical degradation in acceptor–doped titanates is common, since a large concentration of doubly ionized oxygen vacancies, \( [V_0^{**}] \), are typically present (Waser, 1989). Such oxygen vacancies are compensated by the acceptor concentration as well as quenched in metal vacancy concentrations associated with the Schottky disorder reaction at high temperatures (Opitz et al., 2003). In dielectrics such as BaTiO\(_3\), SrTiO\(_3\), and CaTiO\(_3\), Schottky reactions can consist of \( V_{Ca}'' + V_{O}^{**} \) (CaO partial Schottky) and \( V_{Ca}'' + V_{Ti}' + 3V_{O}^{**} \) (CaTiO\(_3\) full Schottky), with the defect notation being that of Kröger and Vink (Kröger et al., 1956; Lee et al., 2009). In orthorhombic CaTiO\(_3\), it has been found that among the neutral vacancy species, the CaO partial Schottky is the most preferable defect reaction when fired in air (oxidizing conditions) (Lee et al., 2009).

In previous work on CTH and CTH + Mn, it was found that when fired in air and slow cooled by convection, undoped CTH exhibited a significant amount of ionic conductivity as well as electronic conductivity at high temperatures (Shay et al., 2012). When doped with 0.5 mol% Mn, the ionic conductivity was minimized, and a subsequent decrease in electronic conductivity was observed. There is little literature focusing on why Mn controls the ionic conduction in
binary mixed ionic conducting systems. Thus, it is of great interest to gain an understanding of how such multivalent dopants control the conductivity in these systems. It is speculated that in the un–doped, slow–cooled case, the CaO partial Schottky reaction dominates at high temperatures, creating a significant amount of oxygen vacancies. As the dielectric is cooled, these oxygen vacancies are frozen in at room temperature and dominate the high temperature conductivity.

As observed in Fe–doped SrTiO₃, when CTH is doped with Mn, it is possible that at the sintering temperature of 1250 °C in air, Mn³⁺ is the dominant valence state and a corresponding concentration of oxygen vacancies exists for electroneutrality (Merkle et al., 2003). As the dielectric is slowly cooled, the Mn⁴⁺/Mn³⁺ changes valence state to mostly Mn⁴⁺, thus eliminating the compensating oxygen vacancies and minimizing ionic conductivity (Cai et al., 2010; Jeong et al., 2007). If this is the case, there should be significantly more ionic conductivity present in a Mn–doped CTH dielectric that has been quenched from the sintering temperature compared to the slow–cooled dielectric. Relative to the un–doped case, the reduction in ionic conductivity may be due to the valence change of Mn and other contributions such as a reduction in the mobility of oxygen vacancies or reduction in initial concentration of ionic charge carriers. For this research, impedance spectroscopy can be used to observe the change in impedance from a single electronic relaxation to multiple impedance features, and those features should change as a function of time as the material re–oxidizes at high temperatures. This is an important consideration for understanding the cooling of high resistivity dielectrics and understanding their re–oxidation kinetics in situ. Additionally, attempts to estimate diffusion coefficients are useful for estimating different sized multilayer devices and determining re–oxidation thermal schedules.

**5.3 Effect of Oxygen Vacancies on Conductivity in Ca(Ti₀.8Hf₀.2)O₃ (CTH) and Ca(Ti₀.795Mn₀.005Hf₀.2)O₃ (CTH + Mn)**

Typically, base metal electrodes (BME) such as Ni are preferred over Pt electrodes for commercial MLCC production for significantly minimizing cost. As a result, the capacitors must be sintered in a reducing atmosphere such as N₂/H₂ or CO/CO₂ to prevent oxidization of the Ni electrodes at temperatures between 1200 and 1300 °C (Burn et al., 1975). Sintering in a reducing atmosphere produces a large concentration of oxygen vacancies, so a gentle re–oxidation treatment is often used in which the MLCCs are treated in a slightly oxidizing atmosphere such as N₂ containing 1–50 ppm O₂ or H₂O vapor at temperatures from 800 to 1000 °C (Hagemann et al., 1982). This re–oxidation treatment creates a metastable state where metal vacancies are
immobile, but the anion sublattice is amended in order to minimize the concentration of oxygen vacancies. In the CTH + Mn dielectric, samples prepared with Ni electrodes were sintered at 1250 °C with \( pO_2 = 10^{-11} \) atm for 3 hours, followed by a re–oxidation treatment at a \( pO_2 = 10^{-9} \) atm for 6 hours. The resulting impedance spectra and thermally stimulated depolarization current (TSDC) spectra for the capacitors are shown in Fig. 5–1.

![Impedance and TSDC spectra](image)

**Figure 5–1:** a) Temperature dependence of impedance spectroscopy for Ca(Ti_{0.795}Mn_{0.005}Hf_{0.2})O_3 (CTH + Mn) sintered at 1250 °C and \( pO_2 = 10^{-11} \) atm followed by 6 hr reoxidation at 900 °C and \( pO_2 = 10^{-9} \) atm and b) thermally stimulated depolarization current (TSDC) spectra at 250 °C for CTH + Mn fired under similar conditions.

From Fig. 5–1a, it can be seen that the resulting impedance spectra for CTH + Mn shows features similar to that of un–doped CTH, but with an increase in conductivity by 2 orders of magnitude. The familiar features of bulk, grain boundary/interface, and electrode/double layer impedance are present. Since it is well known that low \( pO_2 \) firing increases the oxygen vacancy concentration, the resulting impedance spectra show support that ionic conductivity dominates the conduction in un–doped, air–fired CTH. Since the samples were considerably conducting at the temperatures measured, the main high frequency impedance feature was not fully resolved at high temperatures and could not be adequately modeled for activation energy calculations. Overall, however, it is expected that since the reduction/re–oxidation process increases the oxygen vacancy concentration relative to the air–fired case, the features are most likely due to ionic
conductivity from oxygen vacancies in the bulk and at interfaces, similarly to the un–doped CTH system.

Additional support is gained by observing the TSDC spectra for reduced/re–oxidized CTH + Mn shown in Fig 5–1b. Shown in Chapter 4, the TSDC for un–doped CTH showed 2 distinct peaks at ~100 and ~250 °C and a slight high temperature peak at T > 300 °C, all of which were attributed to oxygen vacancies. The TSDC for reduced/re–oxidized CTH + Mn in Fig. 5–1b shows distinct peaks at ~120 °C (A), ~180 °C (B), and T > 300 °C (C), with higher depolarization currents overall. The temperature and field dependence of peak C is consistent with a space charge relaxation. It was shown by Grossweiner that the activation energy of TSDC peaks could be estimated by using the temperature at the maximum of a TSDC peak (T_m) and the temperature at which the peak is at half its maximum (T_1) shown schematically in Fig. 5–2 (Grossweiner, 1957).

\[ E_a \approx \frac{1.51 k_B T_m T_1}{T_m - T_1} \]  

(Equation 5–1)

Figure 5–2: Schematic of the procedure used to estimate TSDC peak activation energies, \( E_a \) (after Levi, 2003).
where \( k_B \) is Boltzmann’s constant. The activation energy for peak C was 0.84 ± 0.04 eV, which can most likely be attributed to in–grain oxygen vacancies piling up at grain boundaries or the electrode interface as seen in Fe–doped SrTiO\(_3\) previously (Liu et al., 2008). The exact origins of peaks A and B could not be identified without further experimentation, but some possibilities include relaxation of oxygen vacancies across grain boundaries or defect dipoles. Overall, however, the peaks are most likely the result of oxygen vacancies as supported by the increase in conductivity in the impedance spectra and the appearance of relaxation features similar to that of the un–doped system when reduced/re–oxidized.

It is most likely that oxygen vacancies dominate the reduced/re–oxidized CTH + Mn dielectric as well, but temperatures may be shifted slightly since Mn, most likely in the Mn\(^{2+}\) state, may be playing a minor role in the control of ionic conduction. Overall, it was found that even with long re–oxidation treatments in more oxidizing conditions (\( pO_2 = 10^{-7} \) atm), the large amount of oxygen vacancies present resulted in a significant amount of ionic conduction in reduced/re–oxidized CTH + Mn.

Alkaline earth titanate–based ceramics show behavior in which a suitable high–temperature process converts an electrically highly conducting sample into a well–insulating one (Moos et al., 1997). In addition to the chemical composition, high temperature processes including temperature, gas atmosphere, high temperature holding time, and cooling rate dictate the electrical behavior of the dielectric at the working temperature. These processes can be described by defect–chemical reactions using mass–action laws and mass–action constants. As a result, the defect chemistry can be used to determine the concentration of various types of atomistic point defects at different temperatures, and has been done so extensively for donor–doped and un–doped SrTiO\(_3\) as well as Fe–doped SrTiO\(_3\), and can be applied directly to dielectrics such as CaTiO\(_3\) and CTH (Moos et al., 1997; Merkle et al., 2003).

For un–doped alkaline earth titanates under oxidizing firing conditions, a stoichiometric excess of oxygen is compensated by extrinsic \( V_0^{**} \), resulting in the oxygen incorporation reaction,

\[
V_0^{**} + \frac{1}{2} O_2 \leftrightarrow O_0^{\times} + 2h^* \tag{Equation 5–2}
\]

where \( h \) is the concentration of holes. The corresponding mass action law is:
\[ K_{ox}(T) = \frac{p^2}{v \cdot pO_2^{1/2}} = K_{ox}^0 \exp \left( -\frac{E_{ox}}{kT} \right) \]  

(Equation 5–3)

where \( pO_2 \) is the partial pressure of oxygen (atm), \( v \) is the oxygen vacancy concentration, \( p \) is the hole concentration, \( E \) is the activation energy, \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. Since \( v \) is fixed by the impurity/acceptor content \( (m) \), according to the electroneutrality condition \( 2v \approx m \),

\[ p = \left( \frac{K_{ox}(T) \cdot m}{2} \right)^{1/2} \cdot pO_2^{1/4} \]  

(Equation 5–4)

is determined. Overall, the electroneutrality condition for doped alkaline earth, titanate–based ceramics must be satisfied according to,

\[ n + [A'] + 2[V_M'] \approx 2[V_O^{**}] + [D^+] + p \]  

(Equation 5–5)

where \( n \) denotes electron concentration, \( A' \) is a singly ionized acceptor, \( M \) is the metal site, \( D^+ \) is a singly ionized donor, and \( p \) is the hole concentration.

Since the occupation of oxygen on interstitial sites can be neglected in SrTiO\(_3\) and CaTiO\(_3\), intrinsic acceptors only occur in the form of oxygen vacancies (Moos et al., 1997). In SrTiO\(_3\), Sr vacancies have been found to be predominant (Tien et al., 1967; Eror et al., 1981; Moos et al., 1997). While not necessarily a predominant defect consideration in this research due to the dependence on the solubility of Ca\(_{1-x}\)Ti\(_{1+y}\)O\(_3\), Ca vacancies are still an important consideration for the un–doped case. As mentioned previously, the dominant disorder reaction in un–doped SrTiO\(_3\) and CaTiO\(_3\) is that of the partial Schottky reaction (Moos et al., 1997),

\[ \text{Ca}_{\text{Ca}}^X + O_O^X \leftrightarrow V''_{\text{Ca}} + V_0^{**} + \text{CaO} \]  

(Equation 5–6)

The partial Schottky reaction results in a simplified mass action law, where the CaO concentration, \([\text{CaO}]\), is assumed to be constant:

\[ K_s(T) = [V''_{\text{Ca}}][V_0^{**}] = K_s^0(T) \exp \left( -\frac{E_s}{kT} \right) \]  

(Equation 5–7)
where $E_s$ is referred to as the Schottky energy and $K_s$ is the Schottky constant. At the sintering temperature in oxidizing conditions, the electroneutrality condition for the partial Schottky reaction in the case of CaTiO$_3$ is,

$$2[V''_{Ca}] = 2[V''_O] + p \quad \text{(Equation 5-8)}$$

as un–doped CTH is cooled from the sintering temperature, there are no species present to neutralize the oxygen vacancies and a large amount of oxygen vacancies are frozen in at room temperature to contribute to ionic conductivity.

Another important intrinsic defect reaction to consider is the generation of electrons and holes by thermal excitation across the band gap, known as band–band transfer,

$$\text{nil} \leftrightarrow e' + h^* \quad \text{(Equation 5-9)}$$

for which the corresponding mass action equation is,

$$K_B = n \cdot p = K_B^0 \exp \left( -\frac{E_B - \beta_B T}{kT} \right) \quad \text{(Equation 5-10)}$$

where $n$ and $p$ are the electron and hole concentrations respectively, $E_B$ is the band gap energy, and $\beta_B$ is the temperature coefficient of the band gap.

The most important defect reactions to consider for the CTH and CTH + Mn systems are those involving the effect of Mn doping on the temperature dependence of electronic and ionic conductivity. When a trivalent acceptor such as Mn$^{3+}$ is incorporated on the Ti site at high temperatures, the resultant formation of oxygen vacancies in CaTiO$_3$ can be described by (Moos et al., 1997),

$$A_2O_3 + 2Ti_T^X + O_O^X \leftrightarrow 2Mn_T^X + V''_O + 2TiO_2 \quad \text{(Equation 5-11)}$$

This results in a corresponding amount of oxygen vacancies and holes being created at the sintering temperature, described by,

$$2[Mn_T^X] = [V''_O] + p \quad \text{(Equation 5-12)}$$

for which the simplified electroneutrality condition is,
\[ 2v + p = m + n \]  
(Equation 5–13)

where \( m = [Mn_T^+] \) and \( v \) is the oxygen vacancy concentration.

While there are a considerable amount of oxygen vacancies expected to be present at high temperatures due to \( Mn^{3+} \), the valence state is expected to change to \( Mn^{4+} \) upon cooling in oxidizing atmospheres according to,

\[ Mn_T^x \leftrightarrow Mn_T^+ + h^* \]  
(Equation 5–14)

for which the mass action equation is,

\[ K_{Mn} = \frac{[Mn_T^+]^p}{[Mn_T^x]} = K_{Mn}^0 exp \left( -\frac{E_{Mn} - \beta_{Mn} T}{kT} \right) \]  
(Equation 5–15)

Upon cooling to room temperature, since the majority of the Mn is expected to be \( Mn^{4+} \) if fired in oxidizing conditions, the concentration of compensating oxygen vacancies that resulted from \( Mn^{3+} \) at high temperatures will be minimized, thus reducing the ionic conductivity in CTH + Mn according to,

\[ O_T^x + 2Mn_T^x \leftrightarrow 2Mn^{3+} + V_O^{2+} + \frac{1}{2}O_2 \]  
(Equation 5–16)

Together, these mass action laws make it possible to determine the temperature dependence of concentrations of oxygen vacancies, Mn, and holes to describe the expected contributions to conductivity similar to Fe–doped SrTiO\(_3\) as shown in Fig. 5–3.
It is important to note that Fig. 5–3 was prepared for acceptor–doped SrTiO$_3$, so the exact temperatures may not be identical for the CTH + Mn system and should be interpreted qualitatively. Regardless, it is likely that the Mn–doped CTH system behaves similarly, just with slightly different temperature dependencies.

Overall, Fig. 5–3 supports the hypothesis used to explain the impedance spectra of CTH + Mn. When fired in air and slowly cooled, the ionic conductivity is minimized as Mn$^{4+}$ minimizes the oxygen vacancy concentration. The overall concentration of holes is reduced as well, resulting in the subsequent reduction in electronic conductivity observed. The reduced/re–oxidized CTH + Mn system showed an increase in ionic conductivity and an inability of Mn to minimize the conductivity. This is most likely due to the presence of Mn$^{2+}$ or Mn$^{3+}$ as opposed to Mn$^{4+}$ when fired in air, which would normally minimize the ionic conductivity. It should be the case that if quenched from the sintering temperature of 1250 °C, Mn$^{3+}$ should be the dominant valence state and a corresponding concentration of oxygen vacancies should be present. This should result in a change in the impedance spectra from a single bulk electronic feature to several ionic and/or electronic relaxations. Upon annealing the quenched samples in air and slowly cooling, only one dominant bulk impedance relaxation should be present.
5.4 Effects of High Temperature Quenching on High Temperature Conductivity in Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn)

Single layer capacitors of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) for the high temperature quenching study were first sintered in air at 1250 °C and slowly cooled by convection. When slow–cooled, the above formula for CTH applies since Mn$^{4+}$ is the assumed valence state according to Fig. 5–3 and is expected to substitute for Ti$^{4+}$. The capacitors were then heated in air to 1250 °C in a quenching furnace and held for 3 hours before being quenched to room temperature, ideally quenching in the Mn$^{3+}$ state for which the CTH + Mn stoichiometry may be modified due to the change in valence state. The temperature dependence of the impedance spectroscopy for a quenched sample is shown in Fig. 5–4.

![Figure 5–4: a) Impedance spectroscopy for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C and b) equivalent circuit modeling used to fit the data in a) at 675°C °C. R = resistivity, C.P.E. = constant phase element, G.B. = grain boundary/interface, D.L. = double layer.](image)

From Fig. 5–4a, it can be seen that there are three distinct relaxations observed in the quenched CTH + Mn impedance spectra. As shown in Chapter 4, the slowly cooled CTH + Mn only showed one distinct semicircle, which was fit using a simple RC circuit assuming a bulk electronic resistance and capacitance. To fit the quenched CTH + Mn, the equivalent circuit shown in Fig. 5–4b was used. The equivalent circuit used for the quenched sample differs from that of slow–cooled, un–doped CTH since the highest frequency relaxation does not show any
evidence of a grain boundary contribution. Therefore the impedance spectra were modeled assuming a high frequency bulk impedance and a grain boundary/interface impedance with electrode double layer impedance to model the two lower frequency relaxations. The equivalent circuit showed good fit to the impedance spectra at all temperatures measured.

It can be seen from Fig. 5–4a that in addition to the high frequency bulk impedance, there are two additional impedance relaxations at lower frequencies, which were attributed to interfacial effects. It has been observed previously that high resistivity regions exist at grain boundaries and electrode interfaces, showing a blocking effect to electronic and oxygen transport across the interfaces (Neumann et al., 1986; Waser et al., 1992; Stumpe et al., 1983). While it is difficult to determine the exact origins of the low frequency relaxations, the quenched–in grain boundary/interface feature can be described in terms of symmetrical (back–to–back) Schottky barriers as evaluated extensively in SrTiO$_3$ with the development of a specific grain boundary model (Denk et al., 1997; Waser et al., 1992; Waser, 1992; Vollmann et al., 1994, Waser, 1995). Quenching of CTH + Mn from 1250 °C results in the presence of Mn$^{3+}$, yielding a corresponding concentration of oxygen vacancies and holes according to Fig. 5–3 and Eqn. 5–12. The oxygen vacancies form a space charge layer at the grain boundaries, enhanced by grain boundary segregation of Mn$^{3+}$, resulting in a distribution of positively charged donor states within the grain boundary plane. The distribution is electrically compensated by a symmetrical space charge region, which shows an enrichment of electrons and acceptors. As a result, a depletion of oxygen vacancies and holes form the positive potential of the space charge layer as seen in Fe–doped SrTiO$_3$ (Denk et al., 1997). The depletion layers yield an overall decrease in the electronic ($h^-$) and ionic ($V_o^{\alpha^+}$) carriers at the grain boundary, referred to as a depletion space charge layer with a non–equilibrium space charge density as shown in Fig. 5–5.
The lowest frequency impedance relaxation is most likely indicative of an additional depletion layer due to the electrode–bulk interface, which has been observed in Fe–doped SrTiO\textsubscript{3}, specifically when platinum or chromium/gold electrodes are used (Denk et al.; 1997). Diffusional processes are generally observed at lower frequencies, which indicates a significant hindering of electronic transport rather than implications towards oxygen exchange processes (Denk et al., 1997). Overall, it is likely that both of the low frequency relaxations are controlled by back–to–back Schottky barriers (depletion space charge layers). As a result of Coulombic repulsion, bulk regions adjacent to grain boundaries are depleted of mobile holes and oxygen vacancies. The negatively charged acceptor ions that remain form a Schottky–type space charge layer that compensates the grain boundary donor charge for electroneutrality. As a result of the depleted mobile charge carriers, electronic conductivity within the space charge layer is largely reduced with respect to the bulk, as evidenced in the low frequency impedance features in Fig. 5–4a.

When plotting impedance spectra, it is useful to overlap the plots of the imaginary parts of the complex impedance ($Z''$) and complex modulus ($M''$) vs. frequency. Plotting the impedance spectra as $M''$ and $Z''$ as a function of frequency gives different weightings to the data and highlights different features of the sample. Spectroscopic plots of $M''$ are an excellent method to probe grain responses in electrically heterogeneous ceramics. For a homogeneous ceramic, a single $M''$ Debye peak should exist, from which the relative permittivity and grain resistivity of the bulk can be determined from the peak height and relaxation frequency. The height of the $M''$

Figure 5–5: Schottky depletion model for the description of grain boundary interfaces in $p$–type SrTiO\textsubscript{3} (after Denk et al., 1997).
peak is inversely proportional to the relative permittivity where $M'' = 1/(2\varepsilon_r)$, and $M'/\varepsilon_0 = 1/(2\varepsilon_0\varepsilon_r) = 1/2C$, where $\varepsilon_0$ is the free space permittivity and $C$ is the capacitance (Costa et al., 2013). Typically, if present, multiple peaks in the $M''$ plot can be separated into comparatively resistive and semiconducting bulk components and can minimize ambiguity in equivalent circuit modeling. For this research, a single peak in the $M''$ plot corresponds to the component in the impedance model with the lowest capacitance, typically the in–grain or bulk component, whereas peaks in the $Z''$ plot correspond to components with the highest capacitance. If the two plots possess peaks that occur at different frequencies, the peaks can be attributed to different sources. The impedance plots isolate the most resistive elements in the sample, since the impedance peak height, $Z_{max}''$ is equal to $R/2$ for that specific element. Peaks that overlap in $M''$ and $Z''$ correspond to contributions to conductivity of a similar type. The temperature dependence of $M''$ and $Z''$ versus frequency is shown in Fig. 5–6.

![Graph](image)

**Figure 5–6:** Temperature dependence of $Z''$ and $M''$ vs. frequency from 600 to 700 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C.

From Fig. 5–6, it can be seen that the only peak in $M''$ occurs at high frequencies and overlaps the high frequency $Z''$ feature, corresponding to the bulk, whereas the two lower frequency peaks do not overlap with a peak in $M''$. An additional peak in the $M''$ plot begins to
form at the highest frequencies, which may be due to an internal barrier layer effect, but the exact origins have not been determined. The bulk capacitance is expected to have a lower capacitance relative to a grain boundary or electrode double layer feature, so Fig. 5–6 supports the choice of equivalent circuit modeling. From equivalent circuit modeling, the capacitance of the bulk feature was typically $\sim 10^{-9}$ F whereas that of the grain boundary feature was $\sim 10^{-6}$ F. The summary of conductivities from impedance modeling using the equivalent circuit shown in Fig. 5–3b for the temperatures of interest is shown in Fig. 5–7.

![conductivity summary graph]

**Figure 5–7**: Conductivity summary obtained from fits to data in Fig. 3 for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C.

From Fig. 5–7, it can be seen that as expected, the bulk is more conductive than the grain boundary overall. The bulk and grain boundary conductivities show Arrhenius behavior from which activation energies were calculated. The calculated activation energies were $1.07 \pm 0.01$ eV and $1.90 \pm 0.02$ eV for the bulk and grain boundary conductivities respectively. The activation energy for the bulk contribution is a common value for oxygen transport in many perovskite systems (Chroneos et al., 2010), while the grain boundary activation energy is equal to approximately half the band gap (3.71 eV). The grain boundary/interface activation energy
suggests that the conduction is electronic in nature as suggested by a depletion layer. It is important to note that the activation energies in the quenched state are difficult to interpret and calculate unambiguously, especially for the interfacial features, since the sample is re–oxidizing \textit{in situ} and Mn is changing valence state in addition to oxygen vacancies being filled, so the impedance features may become more or less conductive during the measurement. The difference in activation energies also supports the equivalent circuit model and difference in overlapping peaks in Fig. 5–4 with the non–overlapping peak in $Z'$ corresponding to an electronic contribution while the bulk feature corresponds to ionic conductivity.

Transference numbers, which describe the ratio of the motion of charge carriers relative to each other under electroneutrality, can be calculated according to $t_{\text{elec}} = \sigma_{\text{elec}} / (\sigma_{\text{elec}} + \sigma_{\text{ion}})$ and $t_{\text{ion}} = 1 - t_{\text{elec}}$. The transference numbers calculated from the conductivities in Fig. 5–7 are shown in Table 5–1 and show that ionic carriers are dominant in quenched CTH + Mn, and that electronic carriers are more prevalent compared to un–doped CTH, which showed predominantly ionic conduction (Table 4–1).

Table 5–1: Transference numbers for Ca(Ti_{0.795}Mn_{0.005}Hf_{0.2})O_{3} (CTH + Mn) quenched from 1250 °C calculated from conductivities obtained from fits to impedance spectra.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$t_{\text{electronic}}$</th>
<th>$t_{\text{ionic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.21</td>
<td>0.79</td>
</tr>
<tr>
<td>625</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>650</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>675</td>
<td>0.37</td>
<td>0.63</td>
</tr>
<tr>
<td>700</td>
<td>0.46</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Previous studies on microcontact impedance measurements of individual highly resistive grain boundaries with selectively blocking electrodes in acceptor–doped SrTiO$_3$ revealed similar impedance spectra, in which the low frequency arc was attributed to either residual electrode effects (poorly resolved, resistive semicircle), short diffusion distances between neighboring grain boundaries (considerably more resistive arc relative to the bulk feature), as in this research, or longer diffusion distances between grain boundaries (considerably less resistive arc relative to the bulk feature) (Fleig et al., 2000). It is possible that due to the increase in electronic conductivity with an increase in hole concentration, the results can be interpreted in terms of a space charge
layer adjacent to the grain boundary core (double Schottky barrier), in which the relevant charge carriers (holes) are depleted.

In conclusion, quenching of CTH + Mn from the sintering temperature showed a clear difference in the temperature dependence of the impedance spectroscopy relative to the un–doped system. Compared to air–fired, slow–cooled CTH + Mn, which showed a single impedance relaxation attributed to electronic resistivity with minimal ionic conductivity, the quenched CTH + Mn showed three distinct relaxations dominated by ionic conductivity. When modeled, the high frequency peak yielded an activation energy of 1.07 ± 0.01 eV, which could be attributed to a bulk ionic response dominated by oxygen vacancy transport. The two lower frequency relaxations are more difficult to interpret due to the in situ re–oxidation of the dielectric. It is possible that the low frequency relaxations are of electronic, interfacial origins such as double back–to–back Schottky barriers (depletion layers) at interfaces such as grain boundaries and/or electrode interfaces as observed in Fe–SrTiO$_3$. The lowest frequency relaxation was attributed to an electrode double layer effect. The mid–frequency relaxation was modeled as an interfacial feature, possibly related to grain boundaries, and the relaxation energy was determined to be 1.90 ± 0.02 eV. The grain boundary/interfacial activation energy is approximately half the band gap, providing support for modeling the relaxation as being electronic in origin. In the next section, a further investigation into the role of thermal histories and multivalent states of Mn on controlling conductivity in the CTH + Mn system will be explored by combining multiple high temperature impedance measurements with TSDC measurements.

5.5 Effects of Re–Oxidation on Impedance Spectra of Quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn)

Manganese is a multivalent ion depending on oxygen partial pressure and temperature, with Mn$^{3+}$ and Mn$^{4+}$ being the expected valence states for this research (Jeong et al., 2007), with the exception of heavily reduced CTH + Mn in which the valence state may also be Mn$^{2+}$. The defect reactions for Mn$^{3+}$ and Mn$^{4+}$ are, respectively,

$$2Mn''_{Ti} + 2V_{O}^{**} + \frac{1}{2}O_2 \rightarrow 2Mn'_{Ti} + V_{O}^{**} + O_O$$ (Equation 5–17)

$$2Mn'_{Ti} + V_{O}^{**} + \frac{1}{2}O_2 \rightarrow 2Mn_{Ti}^{x} + O_O$$ (Equation 5–18)
Similarly to Fe-doped SrTiO$_3$, it is expected that at high temperatures and slightly reducing atmospheres Mn$^{3+}$ is dominant, acting as an acceptor on the Ti site to create a corresponding amount of oxygen vacancies according to:

$$[Mn'_{Ti}] = 2[V_{O^{**}}] + p$$  \hspace{1cm} (Equation 5–19)

However, as the sample is cooled, Mn$^{4+}$ becomes the dominant valence state and the concentration of compensating oxygen vacancies is decreased, minimizing ionic conductivity.

When CTH + Mn is quenched from high temperatures, it is expected that Mn$^{3+}$ is the quenched–in dominant valence state, resulting in a corresponding concentration of compensating oxygen vacancies and an increased concentration of holes relative to the slow–cooled state as seen in Fig. 5–3. When held at temperatures $\geq 700$ °C, where impedance measurements are taken, it is expected that several contributions will lead to an overall decrease in both electronic and ionic conductivity. As re–oxidation occurs, oxygen vacancies will be filled, decreasing the ionic conductivity overall. Additionally, it is expected that Mn$^{3+}$ will gradually transition to Mn$^{4+}$, further minimizing the compensating concentration of oxygen vacancies that resulted from the high temperature quenched in Mn$^{3+}$ acceptor concentration. To maintain electroneutrality, it is expected that a subsequent decrease in the concentration of holes will result, further reducing the conductivity as the concentration of compensating oxygen vacancies shown in Eqn. 5–14 is minimized. As a result, it is expected that the high frequency impedance feature will become more resistive, while the grain boundary/interface and electrode double layer relaxations will become more conductive as the impedance spectra approaches that of a slow–cooled capacitor with a single relaxation. Overall, the change in impedance spectra should reflect the change in concentrations with temperature as shown in Fig. 5–3. The results of the re–oxidation study are shown in Fig. 5–8.
From Fig. 5–8, it can be see that as expected, the high frequency arc becomes more resistive over time while the grain boundary/interface and electrode double layer features become more conductive. It can be seen in Fig. 5–8a that after 12 hours at 700 °C, the grain boundary/interface relaxation is still present whereas both the grain boundary/interface and electrode double layer features are minimized as the bulk conductivity becomes saturated at 725 and 750 °C. It can also be seen that with increasing temperature, the rate at which the conductivity becomes saturated increases. Most likely, the change in impedance features are due to a combination of filling oxygen vacancies, which leads to the bulk impedance transitioning.
from mostly ionically dominated at 0 hours to mostly electronically dominated at 12 hours, and the change of the Mn valence state from Mn$^{3+}$ to Mn$^{4+}$, which minimizes the concentration of compensating oxygen vacancies. Additionally, the concentration of oxygen vacancies at the depletion layer is minimized, reducing the depletion layer thickness and reducing the grain boundary resistivity. If the Mn$^{3+}$ is mostly located on grain boundaries rather than the Ti$^{4+}$ site, it could be possible that the grain boundary/interface arc is suppressed over time due to the Mn valence change from Mn$^{3+}$ to Mn$^{4+}$ as well. The evolution of $Z''$ and $M''$ as a function of frequency for impedance collected over 12 hours at 725 °C is shown in Fig. 5–9.

Figure 5–9: Evolution of $Z''$ and $M''$ vs. frequency at 725 °C over 12 hours during re–oxidation for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C.
It can be seen from Fig. 5–9 that similarly to the temperature dependence of $Z''$ and $M''$ vs. temperature, only the bulk features overlap. As the capacitor re-oxidizes, it is clear that the two low frequency peaks, due to grain boundary/interface and electrode double layer impedances, become minimized until only the bulk feature is dominant in the spectra. The conductivities extracted from the impedance modeling over time are shown in Fig. 5–10.

![Figure 5-10: Bulk and grain boundary conductivity extracted from fitting the impedance model in Fig. 5-4b at a) all temperatures and b) 700 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C.](image)

From Fig. 5–10, it is seen that for all temperatures, the bulk conductivity decreases exponentially and begins to reach a saturation or steady state conductivity, while the grain boundary conductivity increases even after the bulk conductivity has saturated. During the re-oxidation process in air, the capacitor re-equilibrates with the environment through the surface exchange reaction,

$$\frac{1}{2} O_2 + V^\circ \leftrightarrow O^\circ + 2h^\circ$$

(Equation 5–20)

for which the diffusion of oxygen into the internal microstructure from the surface is typically the rate-limiting process at high temperatures (Kaneda et al., 2011). By measuring the impedance relaxation in situ at high temperatures, it is possible to calculate an effective chemical diffusion...
coefficient or diffusivity of the diffusing species in polycrystalline media (Song et al., 1999; Song et al., 2000; Metselaar et al., 1976). Since the local pO$_2$ within the capacitor is inhomogeneous during re–oxidation, the local diffusion coefficient can vary and is thus termed the “effective” diffusion coefficient.

The transient conductivity can be modeled by treating the active dielectric region as a slab with sides of length $L$ and thickness $d$ contained between two Pt electrodes. It is assumed that the Pt electrodes are selectively blocking to oxygen transport but not electronic, the diffusion distance from the external surface is small relative to $L$, and the sides of the slab are significantly greater than the slab thickness ($L >> d$). With these assumptions, the system is reduced to a two–dimensional phenomenological model. The long–time impedance change can then be expressed through the normalized, mean conductivity, $\sigma^*(t)$ (Donnelly et al., 2010; Song et al., 1999; Kingery et al., 1976; Kaneda et al., 2011),

$$\sigma^*(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \left(\frac{8}{\pi^2}\right)^2 \exp\left[-\frac{2\pi^2}{L^2} \tilde{D}_{\text{eff}}(t - t_0)\right]$$

(Equation 5–21)

where $\sigma(0)$ is the initial conductivity in the slab, $\sigma(\infty)$ is the final steady–state conductivity, and $t_0$ is the total time of the exchange.

The plot of $\sigma^*(t)$ is shown in Fig. 5–11a along with the extracted effective diffusivities for quenched CTH + Mn.
From Fig. 5–11 it can be seen that the normalized conductivity shows good fit to the exponential dependence in Eq. 5–21. The effective diffusivities for CTH + Mn are several orders of magnitude lower than similar systems such as Fe–doped SrTiO$_3$ ($10^{-4} - 10^{-6}$ cm$^2$/s) and acceptor/donor–doped BaTiO$_3$ ($10^{-4} - 10^{-7}$ cm$^2$/s) at similar temperatures (Donnelly et al., 2010; Kaneda et al., 2011). This is most likely due to the CTH + Mn system having a higher resistivity at these temperatures. However, even lower effective diffusion coefficients have been observed in bulk X7R dielectrics through $^{18}$O tracer diffusion experiments for re–oxidation anneals (Opitz et al., 2003). Since the effective diffusivities show Arrhenius behavior, the activation energy for oxygen diffusion can be calculated yielding an activation energy of 0.92 ± 0.01 eV, which as previously stated is common for bulk oxygen transport in perovskite oxides (Chroneos et al., 2010).

After the quenched samples were measured at 700, 725, and 750 °C for 12 hours, the samples were heated to 1250 °C, held for 3 hours, and slow cooled to room temperature in order to fully re–oxidize the samples. The impedance spectra after the high temperature annealing are shown in Fig. 5–12 and compared to the corresponding impedance spectra after quenching.
From Fig. 5–12, it can be seen that for each temperature, the slowly cooled sample shows one distinct relaxation with only a slight low frequency tail, possibly due to the electrode double layer. Overall, the total real part of the impedance is approximately the same at each temperature, but the grain boundary and electrode double layer contributions are minimized and the remaining resistivity can be interpreted as being dominated by the bulk. The annealed, slow–cooled samples were modeled using a parallel combination of a bulk electronic resistivity and capacitance, yielding Arrhenius behavior with an activation energy of 1.70 ± 0.01 eV, which is approximately the same as the electronic activation energy determined from the slow–cooled CTH + Mn impedance vs. temperature study discussed in the previous chapter. Overall, it can be deduced that the annealing process resulted in a transition of the quenched CTH + Mn conductivity from being predominately ionically controlled when quenched, to predominantly electronically controlled as oxygen vacancies are filled during annealing and the transition of Mn$^{3+}$ to Mn$^{4+}$ results in the minimization of the remaining concentration of compensating oxygen vacancies. In Fig. 5–12b, it can be seen that when comparing the bulk relaxation of quenched CTH + Mn and un–doped CTH, the quenched sample shows more conduction, most likely indicating that more
oxygen vacancies are present in the quenched sample as would be expected, but the sample is more resistive overall due to the depletion layer created by the highly resistive interfaces.

As shown in Fig. 5–13, the comparison of $M''$ and $Z''$ vs. frequency shows that there is only one significant peak in both $Z''$ and $M''$, which overlaps to indicate a dominant bulk contribution.

Figure 5–13: Temperature dependence of $Z''$ and $M''$ vs. frequency for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) originally quenched from 1250 °C, then heated to 1250 °C in air and slowly cooled to room temperature.

In Chapter 3, it was shown that when a dc bias was applied to CTZ during impedance measurements, the assumed grain boundary feature became more resistive, indicating space charge behavior before showing signs of degradation. In the un–doped CTH capacitors, the grain boundary feature was modeled as an ionic contribution. In the quenched CTH + Mn capacitors, the activation energy of the grain boundary feature (~1.90 eV) suggested electronic conduction dominated. When a dc bias is applied to the quenched CTH + Mn features, the grain boundary feature becomes more conductive as shown in Fig. 5–14a.
Similarly to the re-oxidation study, the bulk feature becomes more resistive as oxygen vacancies are moved out of the grains and towards interfaces by the bias. The double layer electrode feature becomes more conductive as oxygen vacancies pile up at the electrode interface and a space charge layer forms. Unlike the undoped CTH capacitors, however, the capacitor does not degrade during the measurement. The most likely scenario for the evolution of impedance relaxations with increasing dc bias is as follows: the positive charge carriers increasingly drift into the depletion layer and across the grain boundary interface to an extent (Höbling et al., 2002). As a result, an increase in concentration of both oxygen vacancies and holes occurs in the depletion layer. The increase in hole concentration in the depletion layer increases the conductivity of the grain boundary, as shown in Fig. 5–14a with increasing voltage. When the bias is removed, a redistribution of oxygen vacancies occurs and the depletion layer returns to a near-equilibrium state as shown in Fig. 5–14b. It can be seen in Fig. 5–14a that even at 1.0 V, a low frequency impedance feature remains, which is most likely due to the space charge layer formed by oxygen vacancies at the selectively blocking electrodes under bias. However, without additional measurements it is difficult to specifically identify the exact source of the lowest frequency interface feature.

Figure 5–14: a) Voltage dependence of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C and b) comparison of 0.0 bias impedance spectra before collecting data with applied dc bias and after all voltages had been applied.
Previous researchers have investigated the effect of dc bias during impedance measurements across single grains in Fe–doped SrTiO$_3$ polycrystals and observed a similar voltage dependence of the grain boundary feature (Rodewald et al., 2001; Denk et al., 1997). As observed in Fe–doped SrTiO$_3$, the grain boundary conductivity, and thus current–voltage behavior shows a non–linear trend as shown in Fig. 5–15. In Fe–doped SrTiO$_3$, the temperature dependence of conductivity from impedance modeling also indicated oxygen transport, whereas electronic carriers are likely responsible for the arc in quenched CTH + Mn. The voltage dependence of Fe–doped SrTiO$_3$ showed that the grain boundary also became more conducting with increasing voltage, but the bulk component showed little voltage dependence.

![Figure 5–15: a) Voltage dependence of conductivity from impedance modeling of dc bias impedance spectroscopy for grain boundary and bulk and b) voltage dependence of bulk capacitance with capacitances extracted from impedance modeling of dc bias impedance spectroscopy of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn).](image)

Similarly to the trend in bulk and grain boundary/interface resistivities from the temperature and time impedance studies, the bulk conductivity decreases, approaching steady state conditions, while the grain boundary conductivity increases. The trend in grain boundary conductivity with increasing voltage corresponds well with $p$–type SrTiO$_3$ (Denk et al., 1997). At low bias, the grain boundary displays nearly ohmic behavior as evidenced by a decreasing slope from 0.2 to 0.0 V. With increasing bias, the conductivity increases within the varistor regime and
approaches a third change in slope towards saturation at 1.0V, and would be expected to saturate at higher voltages until dielectric breakdown occurs. Initially, the total current consists of both electronic (holes) and ionic (oxygen vacancy) contributions. Once Debye, or space–charge relaxation occurs, the ionic contribution to the current vanishes. As a result, before degradation the current would be predominantly electronic in nature (hole–type). The oxygen vacancies no longer contribute to the dc conductivity, and the long–term total conductivity would be determined by the spatial profile of the hole concentration in the space–charge depletion layer at the grain boundaries (Denk et al; 1997). It is important to note, however, that additional complexities arise when evaluating the quenched CTH + Mn system since the capacitor is re–oxidizing in situ, resulting in additional changes in oxygen vacancy concentration and Mn valence state.

Additional support for the back–to–back Schottky barrier analysis can be gained from Eqn. 5–22. From the impedance modeling, a capacitance–voltage (C–V) method can be used to evaluate the Schottky barrier behavior. For a uniformly doped system,

\[
\left( \frac{1}{C} \right)^2 = \frac{2}{q \varepsilon_r N_a N_d} \left( \phi_i - V_{gb} \right)
\]

(Equation 5–22)

where \( C \) is the capacitance, \( q \) is charge, \( \varepsilon_r \) is relative permittivity, \( N_a \) and \( N_d \) are acceptor and donor concentrations respectively, \( \phi_i \) is the bulk potential, and \( V_{gb} \) is the voltage across the grain boundary (Singh et al., 1994). From Eqn. 5–22, plotting \((1/C)^2\) vs. \( V_{gb} \) should yield a linear relationship, as shown in Fig. 5–13b, specifically for voltages above 0.2 V.

Similarly to the temperature and time dependence of quenched CTH + Mn impedance spectra, the comparison of \( M' \) and \( Z' \) vs. frequency shows that only the bulk feature overlaps as shown in Fig. 5–16, confirming that the grain boundary/interface and electrode peaks are due to different, most likely electronic sources compared to the ionically dominated bulk.
Thermally stimulated depolarization current (TSDC) measurements were used to further investigate the effects of quenching on conductivity in CTH + Mn. The TSDC spectra for quenched CTH + Mn along with the current–voltage (I–V) behavior during the poling step of TSDC are shown in Fig 5–17.

Figure 5–16: Voltage dependence at 0, 0.2, 0.4, 0.6, 0.8, and 1.0V of $Z''$ and $M''$ vs. frequency for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C measured by dc bias impedance spectroscopy at 700 °C.

Thermally stimulated depolarization current (TSDC) measurements were used to further investigate the effects of quenching on conductivity in CTH + Mn. The TSDC spectra for quenched CTH + Mn along with the current–voltage (I–V) behavior during the poling step of TSDC are shown in Fig 5–17.

Figure 5–17: a) TSDC of Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C measured at 250 °C and b) current density during the poling time for the TSDC measurement.
From Fig. 5–17a, it can be seen that there is a slight peak at ~140 °C (A) and a significant peak at ~300 °C (B). Similarly to reduced/re-oxidized CTH + Mn, the activation energy of peak B was determined to be 0.87 ± 0.02 eV. Due to the temperature at which it is observed, the peak is most likely due to space charge caused by oxygen vacancies accumulating at interfaces. The activation energy of the low temperature peak could not be determined using Eqn. 5–1, and the exact origin of the peak is unclear at this time. Most importantly, there is very good evidence for a significant amount of ionic conduction in the TSDC spectra. This is supported by the I–V curves for the quenched and slow-cooled CTH + Mn capacitors during the poling step of TSDC shown in Fig. 5–17b. The quenched capacitor does not reach a steady state leakage current during the poling time. This is similar to the I–V behavior of undoped CTH and is indicative of a large amount of ionic conductivity in the system. The same sample after a high temperature anneal and slow cooling shows a steady state leakage current, indicating that the ionic conductivity has been minimized. Additionally, the current density vs. time obeys the well-known Curie–von Schenidler law for transient leakage current, $J = \beta t^n$, where $J$ is the leakage current, $\beta$ is a pre-exponential factor, $t$ is time, and $n$ is the slope of the log–log plot of $J$ vs. $t$, where $0 \leq n \leq 1$ if it obeys the law (Jonscher, 1983). The average slope of quenched CTH + Mn was 0.25 and the average slope for slow-cooled CTH + Mn was 0.01, clearly indicating that different conduction mechanisms are present due to the different thermal histories. The comparison of the TSDC spectra for the quenched CTH + Mn capacitor and the same capacitor annealed and slow cooled from 1250 °C is shown in Fig. 5–18.
From Fig. 5–18, it can be seen that the slow–cooled sample shows peaks at similar temperatures as the quenched CTH + Mn capacitor, but the current density decreased by approximately 2 orders of magnitude. Additionally, there is an additional peak contained within the low temperature peak, which could be due to an additional relaxation mechanism. It is possible that going from low to high temperature, the peaks correspond to a distributed defect dipole, in grain relaxation, and interfacial space charge relaxation respectively, but the exact origin of each peak is unclear without further experimentation. It is interesting to note that the TSDC spectra for the annealed and slow–cooled (previously quenched) CTH + Mn sample shows a peak at ~120 °C whereas the TSDC spectra for the slow–cooled CTH + Mn sample with no previous quenching treatment, discussed in Chapter 4, did not exhibit any peaks other than the space charge peak at temperatures > 300 °C. This is most likely due to either incomplete reoxidation of the capacitor, which is supported by the slight low frequency feature in the slow–cooled samples in Fig. 5–15, or incomplete valence change of Mn$^{3+}$ to Mn$^{4+}$, which may segregate to the grain boundaries rather than incorporate into the lattice if in the Mn$^{3+}$ state. In the annealed and slow–cooled sample, the activation energy of the low–temperature peak was determined to be 0.63 ± 0.03 eV and the high temperature peak was 1.08 ± 0.10 eV. The low temperature peak

![Figure 5–18: Comparison of 250 °C TSDC spectra for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C (green) and the same samples heated to 1250 °C and slow cooled in air (blue). Poling fields were 5, 10, and 15 kV/cm.](image)
activation energies are different between undoped CTH (0.76 ± 0.04 eV) and quenched/annealed CTH + Mn, indicating different conduction mechanisms as proposed by equivalent circuit modeling. The high temperature space charge peaks showed similar activation energies (0.98 ± 0.07 eV), both of which are common for oxygen transport in perovskite materials, indicating that ionic space charge is present in both materials as expected.

To assess the effects of quenching on the high temperature, high electric field properties of quenched CTH + Mn capacitors, polarization – field (P–E) loops were measured at increasing temperatures as shown in Fig. 5–19.

![Figure 5–19: Polarization – Field (P–E) loops at various temperatures for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) quenched from 1250 °C. Loops shown were measured at the last field sustained before breakdown.](image)

From Fig. 5–19, it can be seen that the evolution in P–E loops is similar to that of the undoped CTH system. At room temperature, the dielectric loss is minimal, the breakdown strength is over 1.0 MV/cm, and the energy density approaches 10 J/cm$^3$. As temperature is increased, the breakdown strength is reduced and the energy density is ultimately degraded by the onset of dielectric loss. Similarly to the undoped CTH system, the dielectric loss is most likely due to quenched-in oxygen vacancies and the increased concentration of compensating oxygen vacancies from quenching in Mn$^{3+}$. 
The use of Mn doping in the linear dielectric Ca(Ti\textsubscript{x}Hf\textsubscript{1-x})O\textsubscript{3} system has been investigated in terms of the thermal histories and the multiple ionization states of Mn. Through a combination of impedance spectroscopy and thermally stimulated depolarization current methods, the role of ionic conduction in Mn\textsuperscript{3+}–compensated cases has been demonstrated. The kinetics of the re–oxidation process were also considered, and the calculation of effective diffusion coefficients could be useful in designing base metal CTH + Mn dielectrics with Ni inner electrodes. While it is difficult to determine the exact origins of the impedance relaxations induced by high temperature quenching, the combination of re–oxidation and dc bias impedance measurements gives strong indication of quench–induced double back–to–back Schottky barriers (depletion layers) resulting in large interfacial resistivities, presumably at the grain boundaries and electrode–ceramic interface. The quenched in oxygen vacancies and compensating oxygen vacancies due to Mn\textsuperscript{3+} are responsible for the formation of the depletion layers, which is supported by consistent space charge features in thermally stimulated depolarization measurements. During re–oxidation and dc bias application, the electronic impedance relaxations become more conducting due to the gradual suppression and minimization of the ionic space charge layers. Overall, it has been clearly demonstrated that mixed ionic conduction has to be controlled in high temperature, high voltage dielectrics that are of interest to power electronics applications.

5.6 Microstructural Analysis of Quenched and Slow–Cooled Ca(Ti\textsubscript{0.795}Mn\textsubscript{0.005}Hf\textsubscript{0.2})O\textsubscript{3} (CTH + Mn)

As mentioned previously, when CTH + Mn is sintered and slowly cooled in air, Mn\textsuperscript{4+} is most likely the dominant valence state, which would most likely substitute for Ti\textsuperscript{4+} in the lattice. When reduced/re–oxidized or quenched, Mn\textsuperscript{2+} and Mn\textsuperscript{3+} exist, which may not fully substitute for Ti\textsuperscript{4+}, resulting in possible grain boundary segregation as observed in Mn–doped BaTiO\textsubscript{3} (Chiang et al., 1990). It is possible that segregation of Mn\textsuperscript{3+} to grain boundaries in quenched CTH + Mn contributes to the back–to–back Schottky barrier formation observed in impedance spectroscopy. Transmission electron microscopy (TEM) was used with energy dispersive X–ray spectroscopy (EDS) to determine whether any segregation of Mn was present in quenched CTH + Mn or slow–cooled CTH + Mn. The bright field TEM image of quenched CTH + Mn is shown in Fig. 5–20.
It can be seen from Fig. 5–20 that an apparent inclusion or possible “pseudo core–shell” region exists, circled in red. However, it is difficult to determine the origin of the feature since only one grain was analyzed for the TEM analysis. It can also be seen that there exists induced ferroelastic domain walls showing fringes inclined towards the electron beam, resulting in a spontaneous strain. The EDS results for the “core” and “shell” of the inclusion are shown in Fig. 5–21.

Figure 5–20: Transmission electron microscope (TEM) image of a single grain of Ca(Ti_{0.795}Mn_{0.005}Hf_{0.2})O_3 (CTH + Mn) quenched from 1250 °C. The red circle denotes an inclusion or pseudo core–shell feature. Image courtesy of collaboration with Dr. Weiguuo Quo, Penn State (2013).
From Fig. 5–21, it can be seen that the inclusion is Hf deficient relative to the shell area (grain), and Ti–rich with minimal difference in the remaining constituents. However, it is difficult to determine whether the inclusion is representative of the entire sample. It is important to note that EDS data taken on Mn–doped Ca(Ti, Zr)O$_3$ via scanning electron microscopy (SEM) in Chapter 3 did not show any evidence of Zr or Ti segregation within grains. The EDS results from the TEM analysis of the quenched CTH + Mn sample is shown in Fig. 5–22 for the grain, grain boundary (GB), and triple junction (3J).

Figure 5–21: Energy dispersive X–ray spectroscopy (EDS) of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) for the inclusion (core) and shell (main grain).
Overall, the full analysis of the EDS spectra does not show a strong detection of Mn in the grain, grain boundary, or triple junction, which is expected due to the low mol % doping (0.5 mol%). There is no clear difference in counts between the three locations for the remainder of the constituents. When the EDS spectrum is zoomed in on the Mn peak, a slight peak in intensity is observed as shown in Fig. 5–23.

Figure 5–22: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn).

Figure 5–23: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of quenched Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), zoomed in to emphasize the Mn peak.
While a slight peak in intensity is observed in Fig. 5–23, it cannot be deduced as to whether any Mn segregation preferentially occurs at the grain boundary or triple junction since there is minimal variation in peak intensity between the three locations. It is possible that Mn is located in all three locations, which would support the interpretation of impedance measurements. The TEM bright field image of slow–cooled CTH + Mn is shown in Fig. 5–24.

Figure 5–24: TEM image of Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) slowly cooled from 1250 °C. The red circles denote A) in grain and B) an inclusion or pseudo core–shell feature. Image courtesy of collaboration with Dr. Weiguo Quo, Penn State (2013).

Similarly to the quenched CTH + Mn sample, an inclusion is observed within the sampled grain. Ferroelastic domains are observed here as well, but there are not so many fringes and the walls are closer to edge–on towards the electron beam. The EDS analysis of the inclusion and bulk of the grain is shown in Fig. 5–25.
Unlike the quenched CTH + Mn sample, there does not appear to be any difference in peak intensity for any of the constituents between the inclusion and shell areas. The EDS analysis of the grain, grain boundary (GB), and triple junction (3J) is shown in Fig. 5–26.

Figure 5–25: EDS analysis of slow-cooled Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Mn) for the inclusion (area A) and shell (area B).

Figure 5–26: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of slow-cooled Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Mn), zoomed in to emphasize the Mn peak.
Similarly to quenched CTH + Mn, the overall analysis of the grain, grain boundary, and triple junction does not show any significant presence of Mn due to the low doping content. Additionally, there do not appear to be any discrepancies in the main constituents between the three locations. It is unclear why there is a slight Mg peak in the EDS spectrum, since only Mn doping was utilized in this study. The zoomed in Mn peak for the slow–cooled CTH + Mn spectra is shown in Fig. 5–27. Overall, the microstructural study shows that the Mn is distributed in the bulk, grain boundaries, and triple junctions with no apparent preferential segregation. The presence of Mn in the bulk supports the effect of doping on bulk ionic conductivity observed by impedance spectroscopy. The presence of Mn in the grain boundaries and triple junctions as well supports the possibility of additional blocking behavior at the grain boundaries.

![Figure 5-27: EDS analysis of grain, grain boundary (GB) and triple junction (3J) from TEM of slow–cooled Ca(Ti\textsubscript{0.795}Mn\textsubscript{0.005}Hf\textsubscript{0.2})O\textsubscript{3} (CTH + Mn), zoomed in to emphasize the Mn peak.](image)

More so than the quenched sample, the Mn peak can be resolved in the three locations with the best–resolved peak occurring in the triple junction. Since Mn is located in the bulk, grain boundaries, and triple junctions, it is likely that the presence of the dopant in all three locations contributes to the minimization of oxygen transport in CTH + Mn. Since both quenched and slow–cooled CTH + Mn show Mn at all three locations, it is unlikely that the differences in impedance spectra are due to preferential segregation of Mn. It is more likely due to the reduction
in oxygen vacancy concentration with the valence of Mn\(^{3+}\) to Mn\(^{4+}\) and reduction in ionic mobility overall.

### 5.7 Summary

Impedance spectroscopy was used to determine the effects of high temperature quenching vs. slow cooling CTH + Mn capacitors in terms of thermal histories and multiple ionization states of Mn on the role of ionic conduction in CTH + Mn. Capacitors originally sintered and slowly cooled from 1250 °C were quenched from 1250 °C in order to determine if oxygen vacancies as well as Mn\(^{3+}\) and its compensating concentration of oxygen vacancies and holes existed at high temperatures. Concentrations of charge carriers were minimized when slowly cooled due to the re-oxidation of the ceramic as well as minimization of compensating oxygen vacancies through the Mn valence transition to Mn\(^{4+}\).

Impedance spectroscopy of quenched CTH + Mn revealed the presence of two low frequency relaxations in addition to the high frequency bulk feature, compared to only one bulk electronic feature being observed in slow-cooled CTH + Mn. The two low frequency impedance features were attributed to interfacial effects due to the presence of symmetrical (back-to-back) Schottky barriers at the grain boundaries and/or electrode interfaces according to the following: the oxygen vacancies form a space charge layer at the grain boundaries, resulting in a distribution of positively charged donor states within the grain boundary plane. The distribution is electrically compensated by a symmetrical space charge region, which shows an enrichment of electrons and acceptors. As a result, a depletion of oxygen vacancies and holes form the positive potential of the space charge layer. The depletion layers yield an overall decrease in the electronic (\(h^+\)) and ionic (\(V_{O''}^{0}\)) at the grain boundary, referred to as a depletion space charge layer with a non-equilibrium space charge density. Impedance modeling of the quenched CTH + Mn data showed good fits with calculated activation energies of 1.07 ± 0.01 eV and 1.90 ± 0.02 eV for the bulk and grain boundary/interface conductivities respectively, suggesting that the bulk is ionically controlled and the interfaces are electronically controlled. Because the samples are possibly re-oxidizing during the measurements, unambiguous interpretation of the activation energies is difficult and would require additional experimentation to confirm. Transference numbers showed that ionic charge carriers are dominant in the quenched CTH + Mn system but with an increase in electronic carriers relative to the slow-cooled, un-doped case described in Chapter 4.
To understand the kinetics of the re-oxidation of quenched CTH + Mn and its influence on determining overall conduction in the CTH + Mn system, a re-oxidation study was performed in which impedance spectra was collected every hour over 12 hours at 700, 725, and 750 °C. The resulting impedance spectra showed a gradual decrease in ionic conductivity and an increase in the grain boundary/interface and electrode conductivity as oxygen vacancies were filled and the compensating concentration of oxygen vacancies from Mn$^{3+}$ were minimized by the valence change to Mn$^{4+}$. Over time, the decrease in bulk conductivity reached a level of saturation, as did the increase in interfacial conductivity. Calculated effective diffusivities showed a decrease with increasing temperature as expected, with lower values compared to BaTiO$_3$, SrTiO$_3$, and PbZrTiO$_3$ as expected due to the overall higher resistivity of the CTH + Mn system. When the same samples were heated to 1250 °C and slowly cooled, impedance spectroscopy showed one main relaxation, which when modeled using a simple RC circuit yielded an activation energy of approximately half the band gap, indicating that re-oxidation resulted in a transition from the bulk being primarily ionically controlled to electronically controlled. It is possible that the re-oxidation study can give insight into effective re-oxidation of multilayer ceramic capacitors (MLCC) as well as determining ideal re-oxidation processes for MLCCs having various dimensions.

The effects of applying a dc bias during impedance spectroscopy showed a similar effect compared to the re-oxidation study with the bulk conductivity decreasing with increasing bias, and the low frequency interfacial features showing increasing conductivity. Most likely, the positive charge carriers increasingly drifted into the depletion layer and across the grain boundary interface to an extent with an applied voltage. As a result, an increase in concentration of both oxygen vacancies and holes occurred in the depletion layer. The increase in hole concentration in the depletion layer increased the conductivity of the grain boundary with increasing voltage. When the bias was removed, a redistribution of oxygen vacancies occurred and the depletion layer returned to a near-equilibrium state. Through impedance modeling, the increase in grain boundary conductivity with increasing field showed transitions through a near ohmic regime, varistor regime, and an approach towards saturation before degradation. By plotting $(1/C)^2$ vs. voltage, it was shown that a generally linear trend existed, further supporting the back–to–back Schottky barrier theory for the CTH + Mn system.

Current–voltage and TSDC measurements showed no indication of steady–state leakage current in the quenched CTH + Mn system during the poling time, indicating a large
concentration of mobile oxygen vacancies as expected. When slow–cooled, low current, and steady state leakage current was observed. The I–V responses for both quenched and slow–cooled CTH + Mn showed Curie– von Schweidler behavior but with different slopes, indicating a difference in conduction mechanisms. For TSDC, a significant amount of space charge depolarization was observed in the quenched CTH + Mn sample, and subsequent high temperature annealing and slow–cooling showed a reduction in depolarization current by ~2 orders of magnitude with three TSDC peaks, which could be correlated to the three relaxations in the impedance spectra. Further analysis would be necessary for a direct relation. Polarization–field loops showed similar behavior compared to the un–doped CTH system with high breakdown strengths and energy densities observed up to 100 °C, but a large onset of loss and low breakdown strengths at higher temperatures due to a large amount of ionic conduction.

Microscopy analysis via TEM of quenched and slow–cooled CTH + Mn showed the presence of an inclusion in both heat treatments, resulting in the presence of ferroelastic domains. It is unclear whether the inclusions are representative of the entire sample since only one grain was analyzed for each heat treatment. An EDS analysis of the grain, grain boundary, and triple junction of each sample showed slight Mn peaks, but there was not enough qualitative data and difference between the intensity of Mn peaks in quenched vs. slow–cooled CTH + Mn to determine if Mn location of Mn can be used to explain the electrical properties of quenched vs. slow–cooled CTH + Mn. Overall, the EDS analysis revealed that Mn is distributed in the bulk of the grains as deduced by impedance spectroscopy, and Mn was also found in the grain boundary and triple junction regions.

So far, only Mn has been used to modify the conductivity in Ca(Ti,Zr)O₃ and Ca(Ti,Hf)O₃ and an understanding of how the valence state of Mn controls the conductivity at different temperatures and cooling rates has been achieved. The incorporation of dopants such as Dy³⁺, Gd³⁺, and Sm³⁺ modifies both the lattice (substitution of large ions onto the A–site) and microstructure (increase or decrease in grain size) (Paunovis et al., 2010). Additionally, when co–doped with Mn, it has been speculated that the formation of donor–acceptor complexes such as 2[DyCa⁺]–[MnTi³⁺] may prevent Mn²⁺ from converting to Mn³⁺. This could further reduce the dielectric loss, especially when fired in reducing atmospheres (Albertson et al., 1998). In the next chapter, a final attempt to improve the breakdown strength, minimize conductivity, and maximize energy density will be made by co–doping Ca(Ti₀.₈Hf₀.₂)O₃ with rare earth dopants and either Mn, Mg, or both.
6.1 Introduction

This chapter will outline doping strategies used to further optimize high temperature insulation resistance and minimize ionic conductivity in Ca(Ti\textsubscript{0.795}Mn\textsubscript{0.005}Hf\textsubscript{0.2})O\textsubscript{3} (CTH + Mn) through co–doping with rare earths (Dy, Gd, or Sm) and Mn, Mg, or Mn + Mg. First, the CTH + Mn system will be doped with 1 mol% Dy, Gd, or Sm to determine which rare earth has the most desirable effects on microstructure, optical properties, basic dielectric properties, and current density. Once the ideal rare earth dopant is identified, additional variations in acceptor doping will be investigated. Thus far, only Mn has been used as an acceptor dopant in the Ca(Ti\textsubscript{0.8}Hf\textsubscript{0.2})O\textsubscript{3} (CTH) and Ca(Ti\textsubscript{0.8}Zr\textsubscript{0.2})O\textsubscript{3} (CTZ) systems. Isovalent Mg as well as Mg + Mn will be investigated to determine if 0.5 mol% Mn is the ideal acceptor dopant for minimizing ionic conductivity in the CTH system. In addition to microstructure, optical properties, and basic dielectric characterization, polarization vs. field (P–E), high temperature impedance spectroscopy, and thermally stimulated depolarization current (TSDC) measurements will be utilized to determine the optimal co–doping strategy and understand how the developed stoichiometry affects ionic conductivity in the co–doped CTH system.

6.2 Background

Rare earth dopants are commonly used in dielectrics such as BaTiO\textsubscript{3} in order to produce low conductivity, low dielectric loss, and avoid electrical degradation at elevated temperatures (Paunović et al., 2010; Kishi et al., 2001; Kishi et al., 1999; Park et al., 2009; Qi et al., 2009). Dopants such as Dy, Gd, and Sm are trivalent and modify the microstructural and dielectric properties of doped BaTiO\textsubscript{3}. In BaTiO\textsubscript{3}, rare–earth dopants can either dissolve on the A–site (donors), B–site (acceptors), or show amphoteric behavior depending on the ionic radius relative to that of the A–site cation. To determine whether a rare–earth dopant will occupy the A–site, B–site, or both, the GoldSchmidt tolerance factor \((t)\) can be used:
\[ t = \frac{(1-x)r_{A1}+xr_{A2}+r_O}{\sqrt{2[(1-y)r_{B1}+y_A+r_O]}} \]  
(Equation 6–1)

where \( r_A, r_B \) and \( r_O \) denote ionic radii for A, B, and O in A\(_{1-x}\)A\(_x\)B\(_1\)B\(_{1-x}\)-O\(_3\) compounds for rare earth ion occupation of the A–site versus B–site from smallest to largest ionic radii. It has been observed in BaTiO\(_3\) that with decreasing ionic radii from 0.9 Å, the expected site occupation switched from the A–site, to amphoteric, to B–site occupation based on the value of the tolerance factor (Tsur et al., 2001). If the incorporation into the A–site yields a tolerance factor closer to unity than its incorporation into the B–site, then incorporation into the A–site would be preferred (Tsur et al., 2001). Systems based on CaTiO\(_3\) possess considerably smaller unit cells compared to Ba–based dielectrics, and as shown in Fig. 6–1 it is not expected that any rare earth dopants would show B–site or amphoteric incorporation in the CTH system.

![Figure 6–1: Goldschmidt tolerance factor calculations for A or B site occupation of rare earths in Ca(Ti\(_{0.8}\)Hf\(_{0.2}\))O\(_3\).](image)

As seen in Fig. 6–1, there is no crossover in A– to B–site incorporation due to the smaller size of Ca, and thus it is expected that any rare earth dopant selected will act as a donor on the A–site. When substituted for Ca\(^{2+}\), the formation of negatively charged defects occurs. The three compensation mechanisms possible are Ca vacancies (\( V''_{Ca}\)), titanium vacancies (\( V''''_{Ti}\)) and electrons (\( e'\)). When fired in air as with this research, the dielectrics are insulators and the
principle doping mechanism is through ionic compensation. For high pO\textsubscript{2} (up to 10\textsuperscript{5} Pa) conditions, as with this research, Ca vacancies act as intrinsic acceptors to compensate the donors (Ca vacancy compensation) similarly to SrTiO\textsubscript{3} and yield the electroneutrality condition (Moos et al., 1997)

\[ 2[V'\text{Sr}'] \approx [D^+] \quad \text{(Equation 6-2)} \]

It is difficult to determine whether the exact dominant ionic mechanism is through the creation of Ca or Ti vacancies, although literature on SrTiO\textsubscript{3} suggests the former is more likely in these types of systems (Paunović et al., 2010; Moos et al., 1997).

It has been observed that when doping with low concentrations (up to 0.5 mol\%) of rare earths on the A–site, a bimodal microstructure was formed and anomalous grain growth (7–10 μm) occurred, leading to more semiconducting than insulating properties in the dielectric (Paunović et al., 2010; Morrison et al., 2001). When doped up to 1 mol\%, a small–grained microstructure (0.3–3.0 μm) was observed with high insulation resistance and good reliability. Minimal grain growth with a high density (>95% theoretical density) is ideal for this research since high breakdown strengths can be achieved in thin dielectric layers if there are a substantial number of grain boundaries present to block ionic and electronic charge carriers from reaching the cathode.

Several researchers have reported improvements in insulation resistance and high field reliability of BaTiO\textsubscript{3} doped with rare earths, with the observed improvements believed to be due to oxygen vacancy trapping by the dopants (Sakabe et al., 2002; Saito et al., 1991; Kishi et al., 1999; Sakabe et al., 2002). Typically, the improvement of dielectric properties due to rare earth substitution on the A–site is understood in terms of the extra oxygen of Re\textsubscript{2}O\textsubscript{3} filling oxygen vacancies accompanied by acceptor impurities (Jeong et al., 2007). Theoretical studies on interactions between oxygen vacancies and rare earth (RE) dopants in BaTiO\textsubscript{3} have shown that the efficiency of oxygen vacancy trapping increases in the order of Sm, Gd, Dy, and Er (Honda et al., 2011). The mechanism of oxygen vacancy trapping has been proposed by Honda et al. as follows: the rare earth ions substituting for Ca (RE\textsubscript{Ca}) have the same coordination, but smaller ionic radii (Shannon, 1976). As a result, the average bond length of RE\textsubscript{Ca} – O is longer than would be preferred. In the absence of oxygen vacancies, RE\textsubscript{Ca} stays at the Ca site center due to centrosymmetric restriction (Honda et al., 2011). The bond length of RE\textsubscript{Ca} – O is kept longer, and
the total energy of the system increases. The presence of oxygen vacancies at the first nearest O site to RE$_{Ca}$ breaks the centrosymmetry, allowing RE$_{Ca}$ to shift towards the oxygen atom at the opposite side of the oxygen vacancy, referred to as vacancy expansion (Honda et al., 2011). The resultant shift decreases the total energy of the system and stabilizes the oxygen vacancies since the bond length of RE$_{Ca}$ – O approaches the preferred length.

Co–doping of BaTiO$_3$ with rare earths and acceptor dopants such as Mn, Mg, and Mn + Mg have also shown improvements in insulation resistance and dielectric degradation resistance (Cha et al., 2006; Kishi et al., 1999; Paunović et al., 2010; Kishi et al., 2001; Lee et al., 2004; Jeong et al., 2007). It was observed by Cha et al. that doping BaTiO$_3$ with combinations of Mn and Mg showed significant reductions in dielectric loss relative to the undoped case (Cha et al., 2006). Doping BaTiO$_3$ with Mn and rare earths has also been shown to reduce the dissipation factor due to the formation of donor–acceptor complexes such as 2[RE$^{3+}_{Ba}$] – [Mn$^{3+}_{Ti}$], which can prevent the valence change from Mn$^{2+}$ to Mn$^{3+}$ (Paunović et al., 2010). However, since the assumed valence state is Mn$^{4+}$ when fired in air as with this work, it is unclear whether such complexes would exist or what effect Mn would have on dielectric properties in addition to those reported in previous chapters, such as Mn$^{4+}$ minimizing the overall concentration of oxygen vacancies.

Theoretical and experimental studies on BaTiO$_3$ co–doped with Re$^{3+}$ and isovalent Mg$^{2+}$ showed a similar vacancy trapping effect compared to rare earth doping, but with a synergistic effect when co–doped with Mg (Honda et al., 2011). Similarly to RE$_{Ca}$, oxygen vacancies are trapped by RE$_{Ca}$ at the first nearest oxygen site. Vacancy expansion results when oxygen vacancies occupy this site since the centrosymmetry of RE$_{Ca}$ is broken and RE$_{Ca}$ shifts to result in the RE–O length becoming close to that of RE$_2$O$_3$, thus reducing the total energy of the system and stabilizing the oxygen vacancy. When Mg$^{2+}$ substitutes for Ti$^{4+}$, it was found that Mg$^{2+}_{Ti}$ traps the oxygen vacancy at the first nearest oxygen site, but the second nearest oxygen site is a secondary stable position (Honda et al., 2011). When an oxygen vacancy occupies this position, the oxygen atom next to both Mg$_{Ti}$ and the oxygen vacancy shifts towards the oxygen vacancy, known as vacancy compression. The relaxation of the Mg$^{2+}_{Ti}$ – O$^{2–}$ bond length makes the system more stable, thus trapping the oxygen vacancy. Overall, the vacancy compression and vacancy expansion correspondingly result in stabilizing the system by effectively relaxing bond lengths. The oxygen vacancies are thus trapped strongly by the two dopants through a synergistic
effect, as illustrated in Fig. 6–2 compared to only Gd or Mg doping in BaTiO$_3$ (Honda et al., 2011).

![Diagram of atomic structures around dopants and VO in BaTiO$_3$.](image)

Figure 6–2: Local atomic structures around dopants and VO in BaTiO$_3$. (a) GdBa–MgTi–VO, (b) GdBa–VO and (c) MgTi–VO. Arrows denote the shifts of GdBa ($u1$) and O neighboring to both MgTi and VO ($u2$) (after Honda et al., 2011).

In order to investigate the effects of co–doping on air–fired Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), the system was stoichiometrically doped with 1 mol % Dy, Gd, or Sm substituted for Ca as (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$. Once the rare earth–doped composition with the ideal combination of properties was identified, the acceptor dopant was varied in terms of 0.5 mol % Mn, Mg, or 0.5 mol% Mn + 0.5 mol% Mg. The systems were then structurally and dielectrically characterized and compared to results in previous chapters. The composition with the best dielectric properties was then used to prototype single layer capacitors and a systematic energy density evaluation was performed. Impedance spectroscopy was also used to understand how co–doping affects the dielectric properties.

### 6.3 Structure–Property Characterization of \((\text{Ca}_{0.99}\text{RE}_{0.01})(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + X + RE)

Stoichiometric compositions of \((\text{Ca}_{0.99}\text{RE}_{0.01})(\text{Ti}_{0.795}\text{X}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + X + RE) where RE = Dy, Gd, or Sm and X = Mn, Mg, or Mn$_{0.005}$ + Mg$_{0.005}$ were prepared by mixed oxide processing as described in Chapter 2. Bulk samples were sintered at 1300 °C for 3 hours to obtain
> 96% theoretical density for X-ray diffraction (XRD), scanning electron microscopy (SEM), optical characterization, and basic dielectric characterization. Single layer, air–fired, Pt electrode capacitors of \((\text{Ca}_{0.99}\text{RE}_{0.01})(\text{Ti}_{0.795}\text{Mg}_{0.005}\text{Hf}_{0.2})\text{O}_3\) were prototyped as described in Chapter 2 for polarization vs. field (P–E) loops and impedance spectroscopy. The XRD patterns for CTH + Mn + RE are shown in Fig. 6–3.

![X-ray diffraction (XRD) patterns](image)

**Figure 6–3:** X–ray diffraction (XRD) patterns for \((\text{Ca}_{0.99}\text{RE}_{0.01})(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + Mn + RE) where RE = Dy, Gd, or Sm compared to \(\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + Mn).

From Fig. 6–3, it can be seen that there are no clear 2nd phases and a similar orthorhombic phase to un–doped CTH is observed. Since the radii of the rare earths substituting for Ca are at maximum ~20 pm smaller and the doping concentration is low, little difference was observed in the unit cell volume between CTH + Mn and CTH + Mn + RE. While the unit cell dimensions were essentially unaffected by rare earth doping, the calculated theoretical densities increased relative to CTH + Mn due to the significant increase in molecular weight as shown in Fig. 6–4.
Figure 6–4: Calculated theoretical densities for \((\text{Ca}_{0.99}\text{RE}_{0.01})(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + Mn + RE) where \(\text{RE} = \text{Dy, Gd, or Sm}\) compared to \(\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3\) (CTH + Mn).

A seen in Fig. 6–4, rare earth doping results in an increased theoretical density as expected, which could lead to a decrease in thermal vibration of atoms at elevated temperatures, leading to an increase in high temperature resistivity. As mentioned previously, rare earth doping has been shown to result in either a reduction in grain size or promotion of anomalous grain growth depending on the doping concentration. The grain microstructures obtained from SEM for sintered, polished, and thermally etched CTH + Mn + RE are shown in Fig. 6–5.
Figure 6–5: Scanning electron microscope (SEM) images of the grain microstructures of CTH + Mn + RE. Average grain sizes were measured to be 8.9, 8.7, and 7.7 μm for RE = Dy, Gd, and Sm respectively.
As reported in Chapter 4, the grain size for CTH + Mn was approximately 2.7 μm. The grain sizes determined from the line intercept method for CTH + Mn + RE were 8.9, 8.7, and 7.7 μm for RE = Dy, Gd, and Sm respectively. The increase in grain size is opposite to that observed in BaTiO$_3$, where lower doping concentrations of rare earths yielded grain size reduction (< 0.5 mol% RE) and higher doping concentrations resulted in anomalous grain growth (Paunović et al., 2010). It is important to note that only one concentration of rare earth doping was utilized in this research, and that a more in–depth compositional study of rare earth doping concentrations could determine a doping concentration that yields improved dielectric properties with a coinciding grain size reduction to improve the breakdown strength.

The absorption coefficient spectra for CTH + Mn compared to CTH + Mn + RE obtained from spectroscopic ellipsometry are shown in Fig. 6–6.

![Absorption spectra](image)

Figure 6–6: Absorption ($\alpha$) spectra for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm obtained from spectroscopic ellipsometry.
As seen from Fig. 6–6, there is little variation in the absorption spectra between the materials. The tail at the onset of the band edge can give insight into the types and amount of defects that are present in the material (Tauc et al., 1966). It is observed that only CTH + Mn + Sm shows a slightly suppressed defect tail in comparison to the other materials. The origins of the tail suppression are unclear at this time, but most importantly it can be seen that co–doping has little effect on the general optical properties compared to doping with Mn only. To determine the band gap for each composition, the absorption coefficient, $\alpha$, was calculated from $\varepsilon$ as described in Chapter 2 (Collins et al., 2005):

$$
\alpha = \frac{4\pi}{\lambda} \sqrt{\frac{\varepsilon_2^2 + \varepsilon_2^2 - \varepsilon_1}{2}}
$$

(Equation 6–3)

where $\lambda$ is the photon wavelength. The indirect band gap energy was determined by taking the zero–intercept of the linear portion of the first onset of absorption in $\alpha^{0.5}$ vs. photon energy. The indirect band gaps for CTH + Mn doped with Dy, Gd, and Sm were 3.74 ± 0.01 eV, 3.72 ± 0.02 eV, and 3.81 ± 0.01 eV respectively. It is unclear why CTH + Mn + Sm yielded a slightly larger band gap relative to Dy and Gd doping. It is also noted that there is a suppression of the defect tail with Sm doping as shown in Fig. 6–6.

6.4 Electrical Characterization of (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE)

Basic electrical characterization was performed on dense, sintered disks electrode with sputtered Pt. The temperature coefficient of capacitance (TCC) is of concern in NP0–type capacitors since they are designed to have minimal variation in capacitance from –55 °C to approximately 125–150 °C. While there is less concern over the TCC for the applications of concern in this research, it is useful to determine whether co–doping can improve the temperature independence of the capacitance relative to the singly doped case. The TCCs up to 150 °C for CTH + Mn and CTH + Mn + RE with the corresponding temperature dependence of dielectric loss ($\tan\delta$) are shown in Fig. 6–7.
For CTH + Mn, the TCC values were ± 15–18% at −50 and 150 °C respectively. For all CTH + Mn + RE samples, the TCC values were ± 14–17% at −50 and 150 °C respectively. While co–doping showed minimal effect on the TCC values, it can be seen from Fig. 6–7 that co–doping resulted in a reduction in dielectric loss for all rare earth–doped samples relative to CTH + Mn, with CTH + Mn + Dy and CTH + Mn + Gd showing a slightly lower dielectric loss relative to CTH + Mn + Sm. Overall, all dielectric losses were low over the temperature range of interest. The variation in relative permittivity ($\varepsilon_r$) for CTH + Mn compared to CTH + Mn + RE from −50 to 200 °C is shown in Fig. 6–8.

Figure 6–7: Temperature coefficient of capacitance (TCC) and dielectric loss ($\tan\delta$) from −50 to 150 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.9}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm.
The relative permittivities for CTH + Mn at –50, 25, and 200°C were 190, 170, and 140 respectively. For CTH + Mn + RE, the relative permittivities at the same temperatures showed minimal variation between rare earth dopants and were approximately 180, 157, and 130 respectively.

Current–voltage (I–V) measurements were taken at 250 °C and the steady state current was recorded after 10 minutes of field application to determine the field dependence of the current density as shown in Fig. 6–9.
From Fig. 6–9, it can be seen that compared to CTH + Mn, only CTH + Mn + Dy showed a decrease in current density at high temperatures and electric fields. It is difficult to determine the reasons for why only Dy doping showed a decrease in current density since grain sizes and low field dielectric losses were similar for the three materials. It is possible that the higher molecular weight of Dy may add additional thermal stability to the lattice at high temperatures compared to Gd and Sm as shown in Fig. 6–3.

Overall, it was found that co–doping CTH + Mn with 1 mol% of various rare earths resulted in anomalous grain growth relative to the CTH + Mn sample, reduction in dielectric constant and TCC, and overall decrease in dielectric loss. At high temperatures and fields, however, only CTH + Mn + Dy showed a decrease in overall current density. It is difficult to determine whether the rare–earth dopant and Mn have a synergistic effect in trapping oxygen vacancies as discussed previously since Mn$^{4+}$ is most likely present. In order to determine if isovalent Mg$^{2+}$ has a synergistic effect in minimizing oxygen vacancy transport, Mg and Mg + Mn co–doping with Dy was investigated.

Figure 6–9: Electric field dependence of current density obtained from current–voltage measurements (I–V) at 250 °C for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$RE$_{0.01}$)(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn + RE) where RE = Dy, Gd, or Sm . All currents were measured at steady state after 10 minutes of applied electric field.
6.5 Modification of Acceptor Dopants and Effects on Dielectric Properties in 
(Cao.99Dy0.01)(Ti0.8−xXxHf0.2)O3 (CTH + X + Dy)

Previous researchers have reported from first principles calculations that co–doping 
BaTiO₃ with rare earths and isovalent acceptors such as Mg²⁺ could result in a synergistic effect 
on the crystal lattice in which coinciding oxygen octahedral contraction and expansion could 
stabilize the oxygen vacancies and overall energy of the system, minimizing their transport 
(Honda et al., 2011). It has been shown in this research that co–doping CTH + Mn with Dy 
resulted in a further decrease in current density at 250 °C compared to CTH + Mn when measured 
in bulk (~0.2 mm) samples. However, only Mn has been utilized as an acceptor dopant thus far. 
In order to determine whether Mg²⁺ or (Mn⁴⁺ + Mg²⁺) have an additional effect on minimizing 
high temperature, high field conductivity, (Ca₀.₉₀₉Dy₀.₀₁)(Ti₀.₈−ₓXₓHf₀.₂)O₃, (CTH + X + Dy) where 
Xₓ = Mg₀.₀₀₅, Mn₀.₀₀₅, or (Mn₀.₀₀₅ + Mg₀.₀₀₅) compositions were investigated and characterized in 
terms of phase purity, optical properties, and basic dielectric properties and compared to 
Ca(Ti₀.₇₉₅Mn₀.₀₀₅Hf₀.₂)O₃ (CTH + Mn). The composition showing the lowest current density at 
high temperatures and fields was then selected for single layer, air–fired, Pt–electrode capacitors 
for an energy density evaluation and impedance spectroscopy analysis.

The XRD patterns for (Ca₀.₉₀₉Dy₀.₀₁)(Ti₀.₈−ₓXₓHf₀.₂)O₃, (CTH + X + Dy) where Xₓ = 
Mg₀.₀₀₅, Mn₀.₀₀₅, or (Mn₀.₀₀₅ + Mg₀.₀₀₅), and CTH + Mn are shown in Fig. 6–10.
Figure 6–10: XRD patterns for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$Dy$_{0.01}$)(Ti$_{0.8-x}$X$_x$Hf$_{0.2}$)O$_3$, (CTH + X + Dy) where $X_x = $ Mg$_{0.005}$, Mn$_{0.005}$, or (Mn$_{0.005}$ + Mg$_{0.005}$) with major reflections indexed. A complete indexing can be found in Fig. 6–3.

Figure 6–11: Comparison of refractive index for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$Dy$_{0.01}$)(Ti$_{0.8-x}$X$_x$Hf$_{0.2}$)O$_3$, (CTH + X + Dy) where $X_x = $ Mg$_{0.005}$, Mn$_{0.005}$, or (Mn$_{0.005}$ + Mg$_{0.005}$) from spectroscopic ellipsometry.
From Fig. 6–10, it can be seen that co–doping with CTH + Mn with Dy and either Mn, Mg, or Mn + Mg does not introduce any observable secondary phases into the pattern. The comparison of the refractive index obtained from spectroscopic ellipsometry for the co–doped systems are shown in Fig. 6–11.

The refractive indices at 633 nm (HeNe laser) were approximately 2.26 for all materials measured. The higher energy (> 3.5 eV) refractive indices are larger for the co–doped systems in comparison to CTH + Mn, but the origin of the increase is unclear at this time. The reasons for such trends are rarely well documented. It is possible that the co–doping minimizes the concentration of lattice defects in the system, which affects the optical properties in the higher energy (absorbing) region. The absorption spectra for the same materials are shown in Fig. 6–12.

![Absorption spectra](image)

**Figure 6–12:** Absorption spectra obtained from spectroscopic ellipsometry for Ca(Ti0.795Mn0.005Hf0.2)O3 (CTH + Mn) compared to (Ca0.99Dy0.01)(Ti0.8–xX0.2)O3, (CTH + X + Dy) where Xx = Mg0.005, Mn0.005, or (Mn0.005 + Mg0.005).

From Fig. 6–12, it is observed that the apparent defect tail before the onset of absorption is suppressed in all co–doped compositions relative to the CTH + Mn composition. It is possible that the previously mentioned oxygen vacancy stabilization from co–doping plays a role in minimizing the concentration of defects in the system, but it is difficult to determine without further experimentation. The indirect band gaps determined from the zero–intercept of the plot of...
\( \alpha^{0.5} \) vs. photon energy yielded similar band gaps for the co–doped compositions with an average of 3.78 ± 0.01 eV, which is slightly higher compared to CTH + Mn (indirect \( E_g = 3.71 \) eV).

The temperature dependence of the relative permittivity and dielectric loss (tan\( \delta \)) from 0 to 150 °C for CTH + Mn compared to CTH + Dy co–doped with Mn, Mg, or Mn + Mg is shown in Fig. 6–13.

![Figure 6–13: Temperature dependence of the relative permittivity and dielectric loss (tan\( \delta \)) from 0 to 150 °C for CTH + Mn compared to CTH + X co–doped with Mn, Mg, or Mn + Mg.](image)

The relative permittivity of CTH + Dy co–doped with Mg and Mg + Mn showed a slight decrease in relative permittivity by about 1.5 compared to CTH + Dy + Mn, which is more likely due to extrinsic rather than intrinsic properties of the material. All co–doped materials showed a decrease in relative permittivity over the measured temperature range, which could be due to a difference in how Dy scatters electronic carriers and changes the amplitude of phonons. All co–doped systems showed a decrease in dielectric loss relative to CTH + Mn and low losses overall. The comparison of the field dependence of the current density at 250 °C for CTH + Mn and co–doped CTH + Dy + Mn, Mg, or Mn + Mg measured on bulk, air–fired, Pt–sputtered electrode samples is shown in Fig. 6–14.
From Fig. 6–14, it is observed that CTH + Dy + Mg showed the lowest current densities at the measured electric fields, with CTH + Dy + Mg + Mn showing the next lowest current densities. The CTH + Dy + Mg system yielded the highest resistivities at 250 °C for any material studied in this work at 1.76 GΩ.cm. Resistivities for the other systems calculated from the slopes of the curves in Fig. 6–14 were 0.72 GΩ.cm for Dy + Mn, and 1.46 GΩ.cm for Dy + Mn + Mg. These results indicate that the synergistic effect of Dy and Mg reducing the total energy of the system to trap oxygen vacancies through a vacancy compression/contraction effect may be possible. Since Mn$^{4+}$ is most likely the dominant valence state for CTH + Dy + Mn, it is likely that the mechanisms for controlling ionic conduction are different for that system. Gaining a more thorough understanding of how the variations in co–doping strategies affect ionic conduction in these materials requires further experimentation and is an interesting topic for future work.

The temperature dependence of conductivity at 25 kV/cm for CTH + Mn compared to CTH + Dy co–doped with Mn, Mg, or Mn + Mg is shown in Fig. 6–15. The steady–state current was recorded after the field was applied for 5 minutes.
The temperature dependence of the conductivity showed Arrhenius behavior for CTH + Mn and CTH + Dy + Mg, but not for CTH + Dy co-doped with Mn or Mn + Mg. As previously mentioned, it is likely that there are multiple contributions to the control of ionic conduction in samples co-doped with Mn and Dy, rather than a single dominant contribution such as the synergistic oxygen vacancy stabilization effect that is possible in CTH + Dy + Mg. The activation energies for CTH + Mn and CTH + Mn + Mg at 250 °C and 25 kV/cm were 0.416 eV and 1.16 eV, indicating that nearly three times the amount of energy is required to mobilize charge carriers in the CTH + Dy + Mg system compared to CTH + Mn. Based on these results, single layer Pt-electrode capacitors of CTH + Dy + Mg were prototyped to evaluate the high temperature energy density capabilities and impedance spectroscopy. The SEM image of a prototyped single layer 15 μm dielectric layer thickness CTH + Dy + Mg capacitor is shown in Fig. 6–16.

Figure 6–15: Log conductivity vs. 1000/T for Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn) compared to (Ca$_{0.99}$Dy$_{0.01}$)(Ti$_{0.8-x}$X$_x$Hf$_{0.2}$)O$_3$, (CTH + X + Dy) where X$_x$ = Mg$_{0.005}$, Mn$_{0.005}$, or (Mn$_{0.005}$ + Mg$_{0.005}$) at 25 kV/cm for bulk samples.
From Fig. 6–16, it can be seen that a bimodal grain microstructure is present with a mixture of 1–3 μm grains and 7–9 μm grains. The P–E loops for capacitors having the highest energy density at 25, 100, 150, and 200 °C are shown in Fig. 6–17.

Figure 6–16: SEM image of single layer, Pt-electrode, air–fired, polished, and thermally etched (Ca$_{0.99}$Dy$_{0.01}$)(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$, (CTH + Mg + Dy) single layer capacitor. Dielectric layer thicknesses ranged from 10–15 μm.

Figure 6–17: Polarization vs. field loops for Ca$_{0.99}$Dy$_{0.1}$($\text{Ti}_{0.795}\text{Mg}_{0.005}\text{Hf}_{0.2}$)O$_3$ (CTH + Mg + Dy) single layer capacitors with increasing temperatures. Loops shown are for capacitors yielding the highest energy density at each temperature.
The P–E loops shown in Fig. 6–17 for the samples having the highest energy density at each temperature show that losses were minimal at room temperature, but began to increase at 150 °C. By 200 °C, dielectric loss became substantial and began to significantly limit the recoverable energy density. The onset of loss and temperature dependence of the breakdown strength is most likely due to the bimodal grain microstructure containing large grain sizes. The CTH + Dy + Mg system showed good dielectric properties in bulk samples, but the large grains of the bimodal grain microstructure limit the number of insulating grain boundaries per dielectric layer when the dielectric layer thickness is reduced to 10–15 μm. For future work, it is important to identify the optimal balance of stoichiometry between Dy and Mg that results in high insulation resistance at elevated temperatures and shows small grain sizes with a homogenous size distribution.

The energy density was quantified as the area between the positive y–axis and the maximum polarization value on the discharge/decreasing field (E) portion of the unipolar curves where

\[ U_{vol} = \int E dP \ (J/cm^3) , \]  

(Equation 6–4)

with the dielectric displacement approximated using polarization, \( P \) (Burn, 1972). Dielectric loss was quantified according to (Uchino et al., 2001),

\[ \tan \delta = \left( \frac{1}{2\pi} \right) \left( \frac{w_e}{2U_e} \right) \]  

(Equation 6–5)

where \( w_e \) is the area within the unipolar loop and \( U_e \) is the recoverable energy density. When a capacitor is being utilized, there are more variables involved that lead to volumetric loss through heat dissipation and watt loss. The watt loss can be accounted for by calculating the power dissipation density (\( P / V \)) (Moulson, 2003),

\[ \bar{P} / V = \frac{1}{2} E_0^2 \omega \varepsilon_0 \varepsilon_r \tan \delta \ (W/cm^3), \]  

(Equation 6–6)

where \( \bar{P} \) is the time average power dissipated, \( E_0 \) is the breakdown strength (V / cm), and \( \omega \) is the frequency of the applied field (Hz).

Dielectric breakdown was quantified as the last field sustained before failure occurred. Characteristic breakdown strengths were obtained using Weibull statistics, in which the
breakdown strengths are ranked in increasing order and the median rank (MR) of the data is calculated as

$$MR = \frac{j - 0.3}{N + 0.4}$$

(Equation 6–7)

where $j$ is the rank and $N$ is the total number of samples. The characteristic breakdown strength is then determined from the zero–intercept of $\ln(E)$ vs. $\ln(\ln(1/(1-MR)))$. The Weibull modulus, which determines the degree of variation in the data set, was determined from the slope of the linear trend line. The Weibull statistics for CTH + Dy + Mg capacitors are shown in Fig. 6–18.

Figure 6–18: Weibull breakdown statistics for the $\text{Ca}_{0.99}\text{Dy}_{0.1}(\text{Ti}_{0.795}\text{Mg}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CTH + Mg + Dy) system for a number of isothermal breakdown tests. Weibull parameters ranged from 6.32 to 6.79.

In addition to the wide distributions of breakdown strengths seen in Fig. 6–18, the Weibull parameters were low (6.32 to 6.79), indicating a significant amount of variation in the breakdown strengths. Again, this is most likely due to the bimodal grain size distribution affecting the breakdown strength as the dielectric layer thickness approaches the size of the larger grain sizes. The summary of properties obtained from P–E loops is shown in Table 6–1.
Of the energy densities obtained in this research, the CTH + Dy + Mg system yielded the highest maximum room temperature energy density. The breakdown strengths are also some of the highest measured thus far despite the bimodal grain size. It is possible that the reduction in energy density at elevated temperatures is due to a significant contribution of ionic space charge as evidenced by the opening of the P–E loops seen in Fig. 6–17. Impedance spectroscopy was performed on CTH + Dy + Mg single layer capacitors to gain insight to the contributions to high temperature conductivity in the system. The temperature dependence of impedance spectroscopy is shown in Fig. 6–19.

Table 6–1: Summary of properties obtained from P–E loops for CTH + Dy + Mg from room temperature to 200 °C. Energy density = U_{vol}, E_b = breakdown strength, and P/V = power dissipation energy.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average U_{vol} (J/cm³)</th>
<th>Average E_b (kV/cm)</th>
<th>Max. U_{vol} (J/cm³)</th>
<th>Max. E_b (kV/cm)</th>
<th>Average Loss (%)</th>
<th>Average P/V (W/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.2 ± 1.6</td>
<td>1.1 ± 0.1</td>
<td>10.3</td>
<td>1.3</td>
<td>0.2 ± 0.1</td>
<td>0.15 ± 0.1</td>
</tr>
<tr>
<td>100</td>
<td>6.7 ± 1.7</td>
<td>1.0 ± 0.1</td>
<td>8.3</td>
<td>1.2</td>
<td>0.7 ± 0.2</td>
<td>0.50 ± 0.2</td>
</tr>
<tr>
<td>150</td>
<td>6.2 ± 1.4</td>
<td>1.0 ± 0.2</td>
<td>8.5</td>
<td>1.3</td>
<td>2.1 ± 1.4</td>
<td>1.3 ± 0.8</td>
</tr>
<tr>
<td>200</td>
<td>4.9 ± 1.1</td>
<td>1.0 ± 0.1</td>
<td>6.1</td>
<td>1.2</td>
<td>12.3 ± 8.6</td>
<td>8.2 ± 6.1</td>
</tr>
</tbody>
</table>
From Fig. 6–19, it can be seen that the impedance spectra show two distinct relaxations that are similar in appearance to capacitors showing grain–grain boundary conduction (Yang et al., 2004). It has been shown previously in CTH + Mn and Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ that there is also an electrode or double layer contribution to conductivity in these buried electrode capacitors, which can be seen in the deviation from Debye–like relaxation in the low frequency feature. Good fits to the impedance spectra were obtained using the equivalent circuit shown in Fig. 6–20.

![Equivalent circuit model](image)

**Figure 6–19:** Temperature dependence of impedance spectroscopy for single layer, air–fired, Pt–electrode capacitor of Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy).

**Figure 6–20:** Equivalent circuit model used to fit high temperature impedance spectra for Ca$_{0.99}$Dy$_{0.1}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mg + Dy). An offset resistivity was utilized when the data collection began at a non–zero value. G.B. = grain boundary/interface.

The conductivities obtained from equivalent circuit modeling are shown in Fig. 6–21.
The trends in conductivity for bulk, grain boundary/interface, and electrode double layer showed Arrhenius behavior from which activation energies were calculated. The activation energies were calculated to be 1.29, 1.51, and 1.27 eV for bulk, grain boundary/interface, and electrode double layer relaxations respectively. The activation energy for the bulk relaxation is higher than the value previously reported for Ca(Ti\textsubscript{0.8}Hf\textsubscript{0.2})O\textsubscript{3} (~1.0 eV), which is a common value for oxygen transport as observed in similar systems (Chroneos et al., 2010). The activation energies for the bulk and electrode contributions are approximately the same, indicating similar contributions to conductivity. Conductivity at the electrode interface is commonly attributed to space charge due to the accumulation of oxygen vacancies, but the higher activation energy than would be expected do to oxygen vacancy transport alone could indicate the presence of back–to–back Schottky barriers (depletion layers) as discussed in Chapter 5 for quenched CTH + Mn. The higher activation energy and resistivity of the grain boundary/interface feature would also imply the depletion layer effect is present.

In order to further investigate the contributions to conductivity in CTH + Dy + Mg at elevated temperatures, thermally stimulated depolarization current (TSDC) measurements were
taken at 250 °C. To determine whether space charge or depletion layers were prevalent, 5 and 10 minute poling times were used to observe the evolution of TSDC peaks. The TSDC results using 5 and 10 minute poling times along with a comparison of TSDC for CTH + Dy + Mn compared to CTH + Mn and undoped CTH are shown in Fig. 6–22. Poling was performed at 250 °C and a heating rate of 3 °C/min was used to measure the depolarization current.

The TSDC spectra in Fig. 6–22 shows that the depolarization current increases significantly by increasing the poling time from 5 minutes to 10 minutes, which is evidence for space charge conduction in the system. The 5 minute poling spectrum shows two overlapping peaks from ~150 to 300 °C and a smaller peak at ~375 °C. When the poling time was increased to 10 minutes, one main feature with a low and high temperature shoulder was present, indicating 3 distinct features as supported by the relaxations observed in impedance spectroscopy. It was not possible to estimate activation energies from the TSDC peaks for CTH + Dy + Mg since overlapping features were present. It is difficult to determine whether the features are due to a depletion layer effect as a result of space charge, oxygen transport, or interfacial space charge.
polarization without further experimentation, but it can be deduced that there is a significant amount of ionic space charge conductivity present in CTH + Dy + Mg.

In Fig. 6–22b, it can be seen that different features are present in each of the CTH, CTH + Mn, and CTH + Dy + Mn spectra, which supports the use of different equivalent circuit models to understand conduction using impedance spectroscopy for each of the systems. The CTH + Mn sample was poled for 5 minutes and is compared to CTH + Dy + Mg in Fig. 6–22b. It can be seen that the peaks occur at similar temperatures, but there is lower depolarization current in CTH + Dy + Mg, supporting the decrease in 250 °C current density measured previously. Overall, it can be concluded that mitigating the ionic conductivity is crucial for optimizing the high temperature energy density in these systems. As evidenced by a combination of dielectric measurements, it is clear in all systems studied that ionic space charge is prevalent whether it be the accumulation of oxygen vacancies at interfaces as space charge layers or the formation of back–to–back Shottky barriers (depletion layers) at interfaces. There is evidence that co–doping CTH + Dy with Mg results in the stabilization of oxygen vacancies due to a synergistic effect, with support from high resistivities and low dielectric losses in bulk. However, the bimodal grain size limits the recoverable energy density when the dielectric layer thickness is reduced for capacitor prototyping. For the CTH + Dy + Mg system, there is potential for considerably higher energy densities if the grain size can be minimized, which requires the investigation of additional stoichiometries and is an important topic for future work.

6.6 Summary

Initial co–doping of CTH + Mn with Dy, Gd, and Sm revealed a slight decrease in relative permittivity and temperature coefficient of capacitance relative to CTH + Mn, and an overall decrease in low field dielectric loss. However, the grain size increased from 2.7 μm for CTH + Mn to 7.7–8.9 μm when stoichiometrically co–doped with 1 mol% rare earth. Spectroscopic ellipsometry showed that co–doping had little effect on the refractive index and indirect band gap relative to CTH + Mn. At high temperatures and fields, only CTH + Dy + Mn showed a decrease in overall current density relative to CTH + Mn. As a result, CTH + Dy was chosen for further analysis involving co–doping with Mn, Mg, or Mn + Mg based on the results of previous researchers in which co–doping BaTiO3 with rare earths and Mg showed a synergistic
effect between rare earths and Mg, resulting in the trapping of oxygen vacancies (Honda et al., 2011).

Characterization of CTH + Dy doped with 0.5 mol% Mn, 0.5 mol% Mg, and 0.5 mol% Mn + 0.5 mol% Mg revealed, similarly to the initial study, that all compositions showed a decrease in relative permittivity compared to CTH + Mn and an overall decrease in low field dielectric loss at elevated temperatures. Optical properties showed minimal change in refractive index and indirect band gap. As expected, the CTH + Dy + Mg and CTH + Mg + Mn compositions showed the lowest current densities at 250 °C and up to 25 kV/cm when measured in bulk samples, with CTH + Dy + Mg showing the lowest current densities of any composition studied in this work. These results support the synergistic effect of co–doping CTH with Mg and Dy on trapping oxygen vacancies. The CTH + Dy + Mn composition showed a lower current density compared to CTH + Mn. It is unclear at this time why co–doping CTH with Mn and Dy does not yield a lower current density compared to Mg, but it is likely that doping with Mn⁴⁺ does not have the same lattice stabilization effect as Mg co–doping if that is the mechanism which mitigates the high temperature ionic conductivity in these systems.

Single layer, Pt buried electrode, air–fired capacitors of CTH + Dy + Mg were prototyped for systematic energy density characterization and impedance spectroscopy with dielectric layer thicknesses ranging from 10 – 15 μm. It was found that a bimodal grain size distribution existed with grain sizes ranging between 2 – 9 μm. Polarization – field loops showed that dielectric loss remained low up to 100 °C, but increased significantly up to 200 °C when the recoverable energy density began to be overcome by dielectric loss. A maximum room temperature energy density of 10.3 J/cm³ was measured, with a maximum energy density of 6.13 J/cm³ measured at 200 °C. Breakdown strengths as high as 1.34 MV/cm were measured, which is surprising considering the large grain sizes. Weibull statistics showed a significant variation in breakdown strengths, which is most likely due to the bimodal grain size distribution and limited number of grains per dielectric layer to maintain adequate insulation resistance at high temperatures and electric fields.

Impedance spectroscopy showed different relaxation features compared to previously studied compositions, with more traditional grain – grain boundary – electrode behavior being observed. Equivalent circuit modeling using 3 RC circuits in series for grain, grain boundary, and electrode contributions showed good fits to the data. Conductivities extracted from the equivalent circuit modeling yielded Arrhenius behavior when plotted against temperature, and the activation
energies for bulk and electrode double layer contributions were ~ 1.3 eV while the grain boundary/interface activation energy was ~1.5 eV. The calculated activation energies were intermediate between typical values for oxygen transport (~1.0 eV) and intrinsic/electronic transport ($0.5E_g$). It is difficult to definitively determine the origins of conduction in CTH + Dy + Mn from impedance spectroscopy, but it is possible that double back–to–back Schottky barriers (depletion layers) are present, or the previously mentioned synergistic effect between Dy and Mg on stabilizing oxygen vacancies may play a significant role in the impedance spectroscopy relaxations.

Thermally stimulated depolarization current measurements on CTH + Dy + Mg showed the presence of multiple overlapping peaks, which increased in intensity for longer poling times, possibly indicating a space charge effect due to oxygen vacancies. When compared to CTH + Mn and CTZ, all three materials showed different peaks in the TSDC spectra. Further understanding the role of Dy and Mg in controlling high temperature conductivity under high electric fields is an interesting topic for future work. Overall, the CTH + Dy + Mg system shows strong potential for a high temperature, high energy density linear dielectric, provided the appropriate stoichiometry is identified in which the grain size is homogeneous and minimized.
CHAPTER 7
FUTURE WORK AND SUMMARY OF DISSERTATION

7.1 Introduction

First, this chapter will provide a summary of the results obtained in this dissertation. This chapter will also provide suggestions for the continuation of this research to further optimize the energy density of existing compositions as well as developing new antiferroelectric or ferroelectric compositions having base metal compatibility. Next, strategies for producing high purity, submicron particle size powders via chemical processing routes will be addressed. The chemical processing routes considered are oxalate/hybrid oxalate–mixed oxide, sol–gel, and polymerized complex processing. Characterization of the powders includes X–ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Additionally, antiferroelectric or ferroelectric/antiferroelectric compositions based on \((\text{Na}_0.5\text{K}_0.5)\text{NbO}_3\) and \(\text{xBaTiO}_3 – (1–\text{x})\text{NaNbO}_3\) will be discussed as options for base–metal compatible capacitor materials for achieving high energy densities at elevated temperatures. Lastly, some final suggestions for further optimizing the compositions studied in this dissertation will be provided.

7.2 Chemical Powder Synthesis

Dielectric breakdown studies in \(\text{BaTiO}_3\), \(\text{SrTiO}_3\), and \(\text{TiO}_2\) have shown that grain boundaries play a crucial role in minimizing the transport of charge carriers across a capacitor dielectric (Yang et al., 2004; Neumann et al., 1986; Ye et al., 2003). It has been observed that Maxwell–Wagner relaxation and breakdown at the grain boundaries strongly influence the overall degradation strength of the dielectric, and that by minimizing the grain size to maximize the number of grain boundaries per dielectric layer, significant improvements in breakdown strength can be achieved (Yang et al., 2004; Neumann et al., 1986; Ye et al., 2003). It has been shown previously that a combination of rapid–rate sintering, rate–controlled sintering, and two–step sintering under controlled atmospheres can be utilized to suppress grain growth and obtain dense ceramics (Polotai et al., 2005). However, it is also possible to minimize the final grain size of dense fired ceramics by utilizing highly active starting powders having submicron particle sizes, since the final grain size is a strong function of starting particle diameter (McNeal et al., 1998).
For this work, starting particle sizes of ~1.0 μm have been used to produce ceramics with grain sizes of ~2.0 μm to yield capacitors having energy densities of ~10 J/cm³ at room temperature. It was proposed that by chemically processing Ca(Ti₀.₈Zr₀.₂)O₃ (CTZ), a reduction in particle size could be achieved, yielding an increase in breakdown strength and energy density as shown in Fig. 7–1.

![Figure 7–1: Schematic of hypothetical increase in energy density achieved by producing capacitors having submicron grain sizes using starting particle sizes of ~0.1 μm compared to ~1.0 μm. The recoverable energy density of > 30 J/cm³ is estimated and has not been experimentally verified.](image)

Chemically synthesized ceramic powders are advantageous compared to solid state synthesis due to their increased phase purity, reduced particle size, and improved sintering properties. Minimal literature exists on the chemical synthesis of binary compositions such as CTZ. Oxalate or hybrid oxalate – mixed oxide processing has been used to produce high purity BaTiO₃ and CaTiO₃ powders having particle sizes of 20–40 nm with mixed success (Bera et al., 2003; Manmood et al., 2011; Yamamura et al., 1985, Patil et al., 2007). Common difficulties associated with the oxalate route have been identified as irregular particle sizes and loss of Ti⁴⁺ due to the reaction of the TiCl₄ precursor with air (Manmood et al., 2011; Bera et al., 2003). The sol–gel method, commonly used for the preparation of perovskite thin films, has also been
utilized for producing CaTiO$_3$ and BaTiO$_3$ nanopowders (Pfaff et al., 1992; Pfaff, 1994). More closely related to this research, a modified Pachini process, or citrate process, has been shown to successfully produce highly reactive particles of Ca(Ti$_{1-x}$Zr$_x$)O$_3$, where $x = 0.0$–$0.15$ (Sun et al., 2007). These chemical processing routes have been utilized to an extent in this research, the preliminary results of which will be outlined in this chapter. However, there is a considerable amount of future work needed to perfect these processing routes to produce phase pure, highly active, un-agglomerated starting powders. Additionally, it would be interesting to produce these materials in sputtered thin film form to evaluate their breakdown strengths and the influence of decreasing grain size on electrical properties.

7.1.1 Oxalate and Hybrid Oxalate Processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$

Oxalate powder processing involves mixing cation chlorides stoichiometrically in an oxalic acid solution to yield a precipitation reaction of the desired perovskite from solution. Initial oxalate processing of Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ (CTZ) was performed using a completely solution–based route utilized by previous authors, which required TiCl$_4$ as a precursor (Manmood et al., 2011; Yamamura et al., 1985, Patil et al., 2007). However, such processing requires an environment containing minimal humidity, since TiCl$_4$ easily hydrolyzes. Since such an environment was difficult to obtain, compositions originally prepared by this route showed a significant loss of Ti in the final powders. As a result, a hybrid oxalate–mixed oxide processing route was utilized as outlined in Fig. 7–2 (Bera et al., 2003).
The measured thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for CTZ prepared by the hybrid oxalate processing route is shown in Fig. 7–3 alongside the XRD spectrum for a pulverized disk sintered for 3 hours at 1300 °C. Calcination of the powder at 850 °C did not yield a fully phase pure powder.
From Fig. 7–3a, it can be seen that there are multiple decomposition steps leading to 800 °C, and a significant increase in heat flow at T > 800 °C. Temperatures were held for 1 hr at each decomposition temperature, and the powder was calcined at 850 °C for up to 12 hours. However, a single phase was not obtained upon calcination. When sintered into a dense disk (>96% theoretical density), it was found that significant 2nd phases of ZrO$_2$ were present as shown in Fig. 7–3b, indicating that the processing route was not yielding a homogenous distribution of elements. This is supported by scanning electron microscopy (SEM) and the elemental distribution analysis from energy dispersive X–ray spectroscopy (EDS) as shown in Fig. 7–4.

Figure 7–3: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for hybrid oxalate–mixed oxide prepared Ca(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ and b) indexed XRD spectrum for a pulverized disk of the same powder sintered at 1300 °C for 3 hours.
From Fig. 7–4, it can be seen that unlike the mixed oxide–produced CTZ microstructures shown in Chapter 3, which showed slight ZrO₂ phases in XRD but no clear segregation in SEM, there is a clear segregation of Zr in the chemically derived powder. Additionally, there is a bimodal grain size distribution and the larger grains are on the order of those observed in the mixed oxide processed ceramics. The transmission electron microscopy image of the hybrid oxalate–mixed oxide processed powder is shown in Fig. 7–5.

Figure 7–4: a) Scanning electron microscopy (SEM) microstructure of sintered disk of hybrid oxalate–mixed oxide processed Ca(Ti₀.₈Z₀.₂)O₃ (CTZ) and b) elemental distribution analysis from energy dispersive X–ray spectroscopy (EDS).

Figure 7–5: Transmission electron microscopy (TEM) image of hybrid oxalate–mixed oxide processed Ca(Ti₀.₈Z₀.₂)O₃ (CTZ).
The TEM image shown in Fig. 7–5 shows minimal presence of aggregation. The particle size was determined using light scattering with a Malvern Instruments Mastersizer (Malvern, Worcestershire, UK) and the Brunauer–Emmett–Teller (BET) surface area was measured using a Micrometrics Gemini BET surface area analyzer (Micrometrics, Norcross, GA). The particle size analysis yielded a measured particle size of 0.38 μm compared to 1.08 μm for mixed oxide processing. The measured BET was 10.68 m²/g compared to 7.08 m²/g for mixed oxide, indicating a higher reactivity for the chemically–derived powder. However, due to the segregation of Zr, further work is needed to optimize the oxalate processing route. It has been shown that the oxalate method poses certain difficulties in terms of control of the speciation of solution complexes, stability of solution speciation to pH, and control of microstoichiometry as observed here (Potdar et al., 1993). As a result, more work is needed for controlling the oxalate processing of CTZ. Previous researchers have shown that calcium titanyl oxalate hexahydrate (CTO) can be used to produce CaTiO₃ using the oxalate route, which could be an option for future oxalate processing of CTZ (Patil et al., 2007). Additionally, if a low enough humidity for preventing the hydrolysis of TiCl₄ can be accessed, the fully chemical oxalate route could be used to process highly reactive CTZ nanoparticles.

7.1.2 Sol–Gel Processing of Ca(Ti₉Zr₀₂)O₃

Processing of fine ceramic powders by the sol–gel method involves the conversion of monomers into a colloid solution, or a sol, which acts as the precursor for an integrated network, or gel, of discrete particles. Sol–gel processing of CTZ was also attempted in this work based on previous success in CaTiO₃ and BaTiO₃ (Pfaff et al., 1992; Pfaff, 1994). The flow chart for the sol–gel processing route is shown in Fig. 7–6.
The thermal analysis and XRD for powders derived from the sol–gel processing route are shown in Fig. 7–7. Similarly to the oxalate–derived powders, phase purity was not obtained upon calcination and a sintered, pulverized disk was used to obtain XRD data.
The thermal analysis shows several stages of decomposition as well as a significant spike in heat flow between 300 °C and 600 °C. Unlike the oxalate–derived powders, the XRD spectrum for the sol–gel–derived CTZ powder shows phase purity when sintered into a dense ceramic. However, the microstructure shows the presence of grains having a different morphology than typically observed in the CTZ system as shown in Fig. 7–8.

Figure 7–7: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for sol–gel–prepared Ca(Ti_{0.8}Zr_{0.2})O_{3} and b) indexed XRD spectrum for a pulverized disk of the same powder sintered at 1300 °C for 3 hours.

The thermal analysis shows several stages of decomposition as well as a significant spike in heat flow between 300 °C and 600 °C. Unlike the oxalate–derived powders, the XRD spectrum for the sol–gel–derived CTZ powder shows phase purity when sintered into a dense ceramic. However, the microstructure shows the presence of grains having a different morphology than typically observed in the CTZ system as shown in Fig. 7–8.

Figure 7–8: Microstructure of sintered, thermally etched disk of sol–gel–derived Ca(Ti_{0.8}Zr_{0.2})O_{3} (CTZ) from scanning electron microscopy.
Interestingly, the TEM investigation of the sol–gel–derived CTZ powders shows the presence of a rod–like morphology rather than particles as shown in Fig. 7–9.

![TEM images](image_url)

**Figure 7–9**: a) TEM image of rod–like morphology in Ca(Ti_{0.8}Zr_{0.2})O_3 (CTZ) obtained from sol–gel processing and b) TEM image of a large rod observed in sol–gel–derived CTZ.

It is possible that the calcination profile for sol–gel–derived CTZ may play a role in the formation of the rod–like morphology observed in Fig. 7–9, since hour–long holds were utilized at each decomposition temperature shown in Fig. 7–7. It has been shown that amorphous TiO_2 crystallizes as anatase at lower temperatures, and rutile at higher temperatures (Matthews, 1976). Due to the observed morphology, it was suspected that anatase (TiO_2) may form at lower temperatures as the CTZ primary phase is formed, but finally crystallizes as rutile TiO_2 as it approaches the sintering temperature, resulting in a final rod–like morphology. To determine whether anatase and rutile are formed during the sintering process, disks were removed from the sintering furnace at 200 °C intervals and pulverized for XRD. The presence of anatase was confirmed as shown in Fig. 7–10, which shows the formation of anatase between 400 °C and 800 °C, and a change to rutile at 1000 °C.
Anatase forms between 400 °C and 800 °C and is no longer a dominant phase at 1000 °C when the rutile phase begins to form. Neither anatase nor rutile phases are present as 2nd phases in the XRD pattern after final sintering at 1250 °C. It is unclear as to why the final sintered XRD pattern shows no 2nd phases but a rod–like morphology, but it could be possible that the rods are of the CTZ phase, but have formed in such a way due to the crystallization of rutile TiO₂ before final sintering to the CTZ phase. Overall, it is possible that CTZ could be synthesized using the sol–gel route presented here, but a more tailored calcination or sintering profile may be necessary to minimize the formation of the rod–like morphology. Additionally, there are numerous precursor types and sol–gel–based processing routes, and only one route was investigated here. It would be important for future work to further investigate sol–gel processing to obtain CTZ nanoparticles.
7.1.3 Polymerized Complex Processing of Ca(Ti_{0.8}Zr_{0.2})O_3

Previous authors have shown that the polymerized complex method, based on the Pechini method, is successful in preparing high purity, highly reactive particles of Ca(Ti_{1-x}Zr_x)O_3 where x = 0.0 – 0.15 (Sun et al., 2007). The polymerized complex method involves the chelation of metal cations though a hydroxycarboxylic acid such as citric acid. Citric acid forms poly(basic acid) chelates with the metal cations, and the chelates undergo polysterification when heated with a poly(hydroxy alcohol) such as ethylene glycol to form a polymeric precursor resin. The cations are expected to be dispersed uniformly throughout the resin, and heating of the resin in air leads to the removal of organics and the formation of a char with controlled cation stoichiometry and little cation segregation. The char can then be heated to higher temperatures and oxidized to form the oxide ceramic (Pechini, 1967). One of the advantages of the polymerized complex method is that phase–pure compounds can be obtained at significantly lower temperatures compared to the mixed oxide processing route (Sun et al., 2007). The flow chart for the polymerized complex method is shown in Fig. 7–12.
The thermal analysis and XRD pattern for powders derived from the polymerized complex processing route are shown in Fig. 7–12. Unlike the oxalate and sol–gel processing routes, full CTZ phase purity was observed upon calcining for 3 hours at 900 °C with the polymerized complex processing route.
Figure 7–12: a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for polymerized complex–prepared Ca(Ti0.8Zr0.2)O3 and b) indexed XRD pattern for a pulverized disk of the same powder sintered at 1300 °C for 3 hours.

As seen in Fig. 7–12a, there are significantly less decomposition steps compared to the oxalate and sol–gel processing routes, with only one significant increase in heat flow observed between 400 °C and 600 °C, with reactions completed by approximately 600 °C. After calcining for 3 hours at 900 °C, the XRD pattern in Fig. 7–12b shows phase pure orthorhombic CTZ with no clear 2nd phases as were observed in the hybrid oxalate–mixed oxide powders. While only 900 °C was investigated as a calcining temperature, it is possible based on Fig 7–12a that even lower calcination temperatures could yield phase pure CTZ and smaller particle sizes.

When the particle size of the polymerized complex–derived powders was measured, an average size of 13.4 μm was measured, indicating a significant amount of aggregation. The BET surface area was measured to be 13.4 m²/g as well, indicating a high particle reactivity and small primary particle size. The TEM analysis of the powders confirmed aggregation as shown in Fig. 7–13.
Overall, the polymerized complex method provides the best route for future processing of highly reactive, fine particles of CTZ or CTH provided the powders can successfully be de–agglomerated. One difficulty associated with de–aggregation of the powders is that a large amount of processing time and precursor solutions are required for a small powder yield, making processes such as attrition milling difficult. Additionally, since a minimum of 50 g of powder is typically required to prototype a sufficient amount of capacitors, the processing route is time and material intensive. However, the low calcination temperature for achieving phase purity and small primary particle sizes make the polymerized complex route a very interesting process for future work.

7.3 Development of Non–Reducible, Non–Linear Dielectrics

Development and characterization of materials in this work has focused on CaTiO$_3$–rich, linear/weakly linear dielectric compositions thus far. While attempts at firing in reducing atmospheres have been made and show comparable electrical performance at room temperature, duplicating the high temperature results obtained with air firing have not been successful, likely due to the increase in concentration of highly mobile oxygen vacancies. In addition to further
understanding chemical processing of CTZ for obtaining highly reactive nanoparticles, the majority of the future work for this project will focus on optimizing and understanding the low pO$_2$–fired electrical performance of ferroelectric/antiferroelectric alkali–niobate based systems. Additionally, optimization of these types of systems in terms of minimizing conductivity through donor doping, for example, has been given little attention and needs to be addressed.

Recently, Kobayashi et al. have made progress in optimizing the sinterability and low pO$_2$–fired electrical properties of alkali–niobate systems such as (Na$_{0.5}$K$_{0.5}$)NbO$_3$ (NKN) systems through doping with LiF as a sintering aid (Kobayashi et al., 2012). Typically, low pO$_2$ firing of perovskites increases the concentration of oxygen vacancies, which contribute to an increase in electronic and ionic conductivity. Even when fired in air, the alkali metals can easily volatilize at ~ 800 °C, complicating the control of stoichiometry. When 100 mol% LiF was added as a sintering aid, it was found that when fired in pO$_2$ = 10$^{-10}$ atm, the theoretical density increased from 91% to 95% relative to air firing. Electrical properties, such as resistivity, significantly increased compared to air fired samples, implying a decrease in point defect concentrations when reduced. A summary of the characteristic properties of the air–fired compared to low pO$_2$–fired NKN–LiF samples are shown in Table 7–1.

Table 7–1: Characteristic properties of (Na$_{0.5}$K$_{0.5}$)NbO$_3$–LiF ceramics fired in reduced and air atmospheres (Kobayashi et al., 2012).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dielectric constant</th>
<th>Dielectric loss [%]</th>
<th>$d_v$ [pC/N]</th>
<th>$k_p$ [%]</th>
<th>$\varepsilon_{in}$</th>
<th>Resistivity [Ω·m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced fired</td>
<td>415.6</td>
<td>3.3</td>
<td>138</td>
<td>36</td>
<td>65.9</td>
<td>2.70 × 10$^{9}$</td>
</tr>
<tr>
<td>Air fired</td>
<td>479.4</td>
<td>2.5</td>
<td>152</td>
<td>38</td>
<td>75.8</td>
<td>5.49 × 10$^{8}$</td>
</tr>
</tbody>
</table>

Interestingly, it was found that the thermal difference $\Delta T = (T_o - T_c)$ differed between the firing conditions, owing to the presence of a low permittivity grain boundary phase. This grain boundary phase plays an important role in controlling conduction mechanisms in the NKN–LiF system, but the underlying reason is currently not understood. As shown in this work, impedance spectroscopy can give insight into how differences in doping, and in this case firing, directly affect conduction mechanisms. Additionally, little work has been done on optimizing the resistivity in the NKN system through acceptor or donor doping. A major focus for future work will be to utilize dopants such as Sn$^{2+}$, Sb$^{3+}$, Ca$^{2+}$, Zr$^{4+}$, La$^{3+}$ etc. to maximize resistivity and further enhance
the candidacy of these materials for high energy density, high temperature ceramics with base metal compatibility, and to understand how they affect properties with characterization techniques used in this proposal.

Another focus for future work is to move away from Ti–rich compositions and investigate higher permittivity antiferroelectric/ferroelectric binaries such as $x\text{BaTiO}_3 - (1-x)\text{NaNbO}_3$, (NNBT) where $x=0.05, 0.1, 0.15, 0.2$, and $0.25$, or even smaller concentrations of BaTiO$_3$ as candidates for reduced–fired, high energy density dielectrics. Currently, there is minimal literature focusing on solid solutions of NNBT outside of basic characterization (Zeng et al., 2006; Khemakhem et al., 2000). Since BaTiO$_3$–rich NNBT compositions are relaxors, the majority of the attention has been on that end of the binary mixture. When doped with small amounts of BaTiO$_3$, NaNbO$_3$–rich compositions, fired in air, have been shown to convert antiferroelectric NaNbO$_3$ to ferroelectric, yielding a large remnant polarization and dielectric constant, as shown in Fig. 7–14, and good piezoelectric properties ($x = 0.1$ NNBT $d_{33} = 147$ pC/N) (Zeng et al., 2006).

![Figure 7–14: a) Temperature dependence of the dielectric constant at 1 kHz and b) P–E hysteresis loops of the Na$_{1-x}$Ba$_x$Nb$_{1-x}$Ti$_x$O$_3$ ceramics at room temperature (right) (Zeng et al., 2006).](image)

For future work with this system, by combining the knowledge obtained through Kobayashi et al.’s work with the KNN–LiF system and an understanding of donor and acceptor doping to minimize dielectric loss, it is projected that this system could be a strong candidate for highly resistive, high temperature, lead–free piezoelectrics for base metal compatible, high energy density applications.
7.4 Further Optimization of Existing Compositions

Throughout this work, significant improvements in minimization of current density and dielectric loss leading to improvements in energy densities have been observed through acceptor doping with Mn, substitution of Zr with Hf, and co–doping with rare earth cations and Mg/Mn. However, there is significant room for further investigation with additional acceptor/donor dopant concentrations and possibly the introduction of ternary systems involving higher permittivity dielectrics such as SrTiO$_3$ or SrZrO$_3$. It would be interesting to investigate concentrations involving various amounts of SrTiO$_3$, having a relative permittivity that generally exceeds > 300. This combination could yield weakly linear dielectrics having higher overall relative permittivities with low dielectric losses, but high breakdowns strengths when coupled with CaHfO$_3$ and acceptor/donor doping. Additionally, co–doping of Ca(Ti$_{0.8}$Hf$_{0.2}$)O$_3$ (CTH) with Dy and Mg showed the highest resistivities and lowest dielectric losses at 250 °C in this work, but showed significant grain growth that limited the recoverable energy when prototyped into thin single layer capacitors. However, it is important to note that only one rare earth doping concentration was investigated, and further investigation into smaller or larger doping concentrations could yield a microstructure with even smaller grain sizes than previously observed in Mn–doped CTH, but with improved electrical performance.

Regarding the optical properties of the materials studied in this dissertation, multiple opportunities for future work were suggested in Chapter 3. An asymmetric trend in the CTZ solid solution was shown and compared to systems such as Ba(Zr,Ti)O$_3$ in which a similar trend was observed. While there are numerous and varying explanations in literature for this type of behavior, a more systematic study focusing on explaining the trend would be useful. Interesting trends in the absorption tails from ellipsometry were also observed, for which there is considerable disagreement on their origin within literature. Studying the defect states that may be responsible for the tail may require some measurements sensitive to lower values of the absorption coefficient, and the temperature dependence of the absorption tails and band gap values may also yield some information regarding their origin. Lastly, Fourier transform infrared (FTIR) ellipsometry could be used to help identify vibrational modes that may differ for any contaminant species or pick up differences in the bonding at grain boundaries. FTIR can be used to identify vibrational modes caused by bonding configuration in compositional elements. It may be possible to deduce variations in structure based on their relative strengths and location shifts. The technique could also possibly yield a relationship between the real part of the complex
dielectric constant near 0.04 eV with electrical measurements typically made from room temperature capacitance measurements. The resulting trend would make spectroscopic ellipsometry a non–contacting and non–destructive probe for measuring the real part of the dielectric constant at low frequencies.

7.5 Summary of Dissertation

With each new linear dielectric system investigated in this research, improvements have been made in overall dielectric properties, leading to increases in resistivity, minimization of ionic conductivity, and high energy densities at elevated temperatures. Starting with the base binary composition of Ca(Ti_{x}Zr_{1-x})O_{3}, a solid solution study was utilized to identify an optimum combination that balanced a relatively high band gap with a moderate permittivity, having an emphasis on higher permittivity CaTiO_{3}– based compositions rather than lower permittivity CaZrO_{3}– based dielectrics. The solid solution characterization isolated the Ca(Ti_{0.8}Zr_{0.2})O_{3} (CTZ) composition to display an ideal combination of these properties.

When doped with 0.5 mol% Mn, it was found that at high temperatures and electric fields, ionic conductivity was minimized and energy densities as high as 7.0 J/cm^{3} at 1.1 MV/cm were measured at room temperature with low dielectric losses and power dissipation. Energy densities as high as 5.4 J/cm^{3} at 1.0 MV/cm were measured at 300 °C. Impedance spectroscopy revealed that doping CTZ with Mn resulted in a minimization of ionic conductivity and a subsequent decrease in electronic conductivity. From the CTZ + Mn composition, it was hypothesized that by replacing Zr with Hf, the higher band gap of HfO_{2} could further minimize electronic conductivity, and the heavier Hf atom could minimize thermal vibration of atoms at high temperatures, further reducing ionic conductivity.

While it was found that the band gap did not increase by replacing CaZrO_{3} with CaHfO_{3}, Ca(Ti_{0.795}Mn_{0.005}Hf_{0.2})O_{3} showed a reduction in current density at 250 °C by over an order of magnitude. A systematic evaluation of the energy densities of single layer, air–fired capacitors showed that when doped with Mn, the CTH system showed nearly temperature independent breakdown strengths up to 300 °C compared to the un–doped system, which showed a drastic onset of dielectric loss at 200 °C that limited the recoverable energy density. Similarly to the CTZ system, impedance spectroscopy revealed that doping with Mn resulted in a decrease in both ionic and electronic conductivity, suggesting that partial Schottky defects control the high
temperature conductivity in undoped CTH. When doped with Mn and slowly cooled in air, Mn$^{4+}$ is present at room temperature and minimizes the concentration of compensating oxygen vacancies and holes that exist at high temperatures when Mn$^{3+}$ is dominant, similarly to Fe–doped SrTiO$_3$. A high temperature quenching study with various impedance spectroscopy techniques was then utilized to verify the hypothesis that for CTH + Mn at high temperatures, Mn$^{3+}$ is dominant and a corresponding concentration of compensating oxygen vacancies exists. When re-oxidized or annealed in air, Mn$^{4+}$ should become the dominant valence state, minimizing the concentration of compensating oxygen vacancies. The impedance analysis of quenched CTH + Mn showed multiple relaxations compared to a single electronic relaxation in slow–cooled CTH + Mn. Re–oxidation and dc bias impedance spectroscopy of the quenched samples showed evidence for double back–to–back Schottky barriers (depletion layers) at grain boundary and/or electrode interfaces, which became more conductive during re–oxidation and upon application of a dc bias while the bulk relaxation became more resistive.

In a final attempt to further increase the insulation resistance and energy density of the CTH + Mn system at high temperatures, co–doping strategies were investigated involving CTH + Mn co–doped with Dy, Gd, or Sm and CTH + Dy co–doped with Mn, Mg, or Mn + Mg. For the initial study, it was found that CTH + Mn + Dy showed the lowest current density at 250 °C and all co–doped systems showed an overall decrease in high temperature dielectric loss relative to CTH + Mn. When different acceptor dopants such as Mg were investigated, the highest resistivities of any composition studied were observed at 1.75 GΩ.cm at 250 °C and up to 25 kV/cm. However, all co–doping compositions showed a significant increase in grain growth, with grain sizes approaching 9.0 μm compared to ~2.5 μm for CTH + Mn. As a result, when 10 – 15 μm single layer capacitors were prototyped and evaluated for high temperature energy densities, a large onset of loss occurred as temperature increased, most likely due to the limited number of grain boundaries per dielectric layer. High room temperature energy densities of > 10 J/cm$^3$ were observed, but at 200 °C the recoverable energy density became limited due to the onset of dielectric loss. Impedance spectroscopy and thermally stimulated depolarization current measurements suggested classic grain–grain boundary–electrode contributions to conductivity, with a significant amount of ionic space charge at interfaces present. It is possible that with further investigation of CTH + Dy + Mg stiochiometries, an ideal composition can be identified that maintains the high resistivities observed in this work, but minimizes the occurrence of anomalous grain grown.
The overall comparison of the 250 °C current density with increasing electric field for materials prototyped into single layer capacitors for energy density evaluations are shown in Fig. 7–15.

Figure 7–15: Comparison of 250 °C bulk current density up to 25 kV/cm for Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn), Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), and Ca$_{0.99}$Dy$_{0.01}$(Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Dy + Mg) that were eventually prototyped into single layer capacitors for energy density evaluations.

From Fig. 7–15, it is seen that with each new material system investigated, an improvement in high temperature insulation resistance was observed. In Fig. 7–16, the temperature evolution of maximum energy densities and average power dissipation factors are compared between the same compositions shown in Fig. 7–15.
Overall, the CTH + Mn system showed the most temperature–independent breakdown strengths and energy densities in this work. The CTH + Dy + Mg system showed high energy densities at low temperatures, but the large–grained, bimodal microstructure limited the recoverable energy density at high temperatures. Table 7–2 shows the overall property summary for compositions optimized for single layer capacitor prototyping in this work.

Figure 7–16: Comparison of the temperature evolution of maximum energy density and average power dissipation factor for Ca(Ti$_{0.795}$Mn$_{0.005}$Zr$_{0.2}$)O$_3$ (CTZ + Mn), Ca(Ti$_{0.795}$Mn$_{0.005}$Hf$_{0.2}$)O$_3$ (CTH + Mn), and Ca$_{0.99}$Dy$_{0.01}$Ti$_{0.795}$Mg$_{0.005}$Hf$_{0.2}$O$_3$ (CTH + Dy + Mg) prototyped into single layer, Pt–electrode, air–fired capacitors.
Impedance spectroscopy of each material system gave insight into the types of conductivity controlling each system at high temperatures, as deduced by calculating activation energies of bulk ionic, bulk electronic, and/or grain boundary (G.B.)/interface relaxations. The summary of activation energies determined from fitting impedance spectra to the appropriate equivalent circuit is shown in Table 7–3.

Table 7–2: Property summary for Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Zr<sub>0.2</sub>)O<sub>3</sub> (CTZ + Mn), Ca(Ti<sub>0.795</sub>Mn<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Mn), and Ca<sub>0.99</sub>Dy<sub>0.01</sub>(Ti<sub>0.795</sub>Mg<sub>0.005</sub>Hf<sub>0.2</sub>)O<sub>3</sub> (CTH + Dy + Mg) prototyped into single layer, Pt–electrode, air–fired capacitors for energy density evaluations.

<table>
<thead>
<tr>
<th>Property</th>
<th>CTZ + Mn</th>
<th>CTH + Mn</th>
<th>CTH + Dy + Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>157</td>
<td>171</td>
<td>157</td>
</tr>
<tr>
<td>250 °C Resistivity(GΩ.cm)</td>
<td>0.03</td>
<td>0.46</td>
<td>1.76</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>3.77</td>
<td>3.71</td>
<td>3.78</td>
</tr>
<tr>
<td>Grain Size (µm)</td>
<td>2.41</td>
<td>2.41</td>
<td>8.99</td>
</tr>
<tr>
<td>TCC (%)</td>
<td>± 20</td>
<td>± 16</td>
<td>± 14</td>
</tr>
<tr>
<td>Max. U&lt;sub&gt;vol&lt;/sub&gt; 25 °C (J/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>7.00</td>
<td>9.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Max. U&lt;sub&gt;vol&lt;/sub&gt; 100 °C (J/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>--</td>
<td>8.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Max. U&lt;sub&gt;vol&lt;/sub&gt; 200 °C (J/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>--</td>
<td>8.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Max. U&lt;sub&gt;vol&lt;/sub&gt; 300 °C (J/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>5.4</td>
<td>6.5</td>
<td>--</td>
</tr>
<tr>
<td>Max. E&lt;sub&gt;b&lt;/sub&gt; 25 °C (kV/cm)</td>
<td>1.1</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Max. E&lt;sub&gt;b&lt;/sub&gt; 100 °C (kV/cm)</td>
<td>--</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Max. E&lt;sub&gt;b&lt;/sub&gt; 200 °C (kV/cm)</td>
<td>--</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Max. E&lt;sub&gt;b&lt;/sub&gt; 300 °C (kV/cm)</td>
<td>1.0</td>
<td>1.3</td>
<td>--</td>
</tr>
<tr>
<td>Avg. P / V 25 °C (W/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>0.38</td>
<td>0.34 ± 0.10</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>Avg. P / V 100 °C (W/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>--</td>
<td>0.51 ± 0.12</td>
<td>0.50 ± 0.21</td>
</tr>
<tr>
<td>Avg. P / V 200 °C (W/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>--</td>
<td>1.3 ± 0.37</td>
<td>8.20 ± 6.08</td>
</tr>
<tr>
<td>Avg. P / V 300 °C (W/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>2.8</td>
<td>3.7 ± 0.96</td>
<td>--</td>
</tr>
<tr>
<td>Refractive Index (n)</td>
<td>2.25</td>
<td>2.26</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Table 7–3: Activation energies extracted from Arrhenius behavior of conductivity determined from modeling of impedance spectra with the appropriate equivalent circuit for $x = 0.8$ 

<table>
<thead>
<tr>
<th>Composition</th>
<th>Bulk Ionic (eV)</th>
<th>Bulk Electronic (eV)</th>
<th>G.B. / Interface (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTZ</td>
<td>0.70 ± 0.01</td>
<td>1.73 ± 0.02</td>
<td>1.18 ± 0.01</td>
</tr>
<tr>
<td>CTZ + Mn</td>
<td>--</td>
<td>1.72 ± 0.01</td>
<td>--</td>
</tr>
<tr>
<td>CTH</td>
<td>1.00 ± 0.01</td>
<td>1.90 ± 0.02</td>
<td>--</td>
</tr>
<tr>
<td>CTH + Mn</td>
<td>--</td>
<td>1.70 ± 0.01</td>
<td>--</td>
</tr>
<tr>
<td>Quenched CTH + Mn</td>
<td>1.07 ± 0.01</td>
<td>--</td>
<td>1.90 ± 0.02</td>
</tr>
<tr>
<td>CTH + Mg + Dy</td>
<td>1.29 ± 0.01</td>
<td>--</td>
<td>1.51 ± 0.01</td>
</tr>
</tbody>
</table>

As discussed in Chapter 1, it has been observed that by selecting materials having larger electronic band gaps, band conduction can be reduced and high dielectric breakdown strengths can be achieved. The trend of increasing breakdown strength with increasing band gap with data obtained from this dissertation is shown in Fig. 7–17. It is important to note that the materials compared to in the figure are nanostructured and likely have higher breakdown strengths compared to the types of bulk compositions observed in this work.
Overall, it can be seen that acceptor and donor doping plays a crucial role in optimizing the high temperature energy density of medium permittivity, linear dielectrics for power electronics applications. It is of the most importance to identify doping strategies that mitigate ionic conductivity present at high temperatures in these types of materials, and understand how such doping strategies control the conduction through coupling various dielectric characterization techniques. This work has identified several compositions that show potential for high temperature, high energy density capacitor applications, and significantly higher energy densities can be achieved through the minimization of grain size and identification of additional stoichiometries that minimize ionic conductivity and maximize breakdown strength at high temperatures. Additionally, it is of interest for future work to identify linear or antiferroelectric compositions that can be fired in low pO$_2$ atmospheres for base metal electrode compatibility to minimize production costs. Overall, the strategies that were outlined and tested in the study of this Ph.D. have future merit across many ceramic–based dielectric materials.

Figure 7–17: Trend in breakdown strength with increasing band gap energy for various covalent, ionic–covalent, and polymer dielectric materials (Tan et al., 2007). The star designates the breakdown strengths and band gaps achieved in this work. It is important to note that the materials compared to are nanostructured.
"Good science is done by being curious in general, by asking questions all around, by acknowledging the likelihood of being wrong and taking this in good humor for granted, by having a deep fondness for nature, and by being made jumpy and nervous by ignorance."

– Lewis Thomas, MD
REFERENCES


Kishi, H., Kohzu, N., Sugino, J., Ohsato, H., Iguchi, Y., and Okuda, T., “The Effect of Rare–Earth (La, Sm, Dy, Ho and Er) and Mg on the Microstructure in BaTiO3,” Journal of the European Ceramic Society, 19, 1043–1046 (1999).


Appendix A

OPTICAL PROPERTIES BACKGROUND

The study of electromagnetic energy (light) as it is reflected, scattered, or emitted from a sample, which includes non–visible wavelengths, is known as spectroscopy (Springsteen, 1998). Light can be quantified in terms of frequency and wavelength according to

\[ \lambda \nu = c \]  

(Equation A–1)

where \( \lambda \) is wavelength (m), \( \nu \) is frequency (Hz, s\(^{-1}\)) and \( c \) is the speed of light (2.998\( \times \)10\(^8\) m/s).

Photons, or quanta of light, carry a specific amount of energy related to the frequency or wavelength as

\[ E = h \nu \]  

(Equation A–2)

where \( E \) is energy (J) and \( h \) is Planck’s constant (6.626\( \times \)10\(^{-34}\) J s). As a result, higher frequencies yield higher energy, and lower wavelengths yield lower energy (Umland et al., 1996). This can be qualitatively seen in the electromagnetic spectrum shown in Fig. A–1.

![Diagram of the electromagnetic spectrum.](image)

Figure A–1: Diagram of the electromagnetic spectrum.

Solid – state materials can scatter, transmit, reflect, diffract, and absorb light, all of which can be quantified and qualified through spectroscopic techniques. The most direct method for probing band structures, specifically the band gap of insulating and semiconducting materials, is to measure the absorption spectrum. Absorption is generally expressed in terms of a coefficient
\( \alpha(hv) \), defined as the relative rate of the decrease in light intensity \( L(hv) \) along its propagation path (Pankove, 1971),

\[
\alpha = \frac{1}{L(hv)} \frac{d[L(hv)]}{dx} \quad \text{(Equation A–3)}
\]

During the absorption process, a photon of known energy excites an electron from a lower– to higher–energy state (Pankove, 1971). By analyzing how bulk and powder samples interact with electromagnetic radiation via techniques such as ultraviolet–to–visible diffuse reflectance spectroscopy (UV–Vis) and spectroscopic ellipsometry (SE), we can observe the transitions an electron can make and obtain quantitative information regarding the band gaps of semiconducting and insulating materials.

**UV–Vis Diffuse Reflectance Spectroscopy**

When the dimensions of particles are small relative to the incident beam cross section, but large relative to the wavelength of the incident light, diffraction phenomena result since rays striking the crystal and passing by it yield interferences among elementary waves (Torrent et al., 2008). For powdered, randomly oriented materials of this size, some of the incident light reflects at all angles into the region of the light’s origin. The sum of the reflection, refraction, and diffraction by particles oriented in all directions is referred to as diffuse reflection as opposed to regular or specular reflection from a plane phase boundary (Torrent et al., 2008).

In UV–Vis experiments, a spectrophotometer is equipped with a diffuse reflectance accessory known as an integrating sphere, which collects the reflected flux as shown in Fig. A–2.
The integrating sphere is a hollow sphere coated internally with a white material having a diffuse reflectance close to 1. The sphere contains apertures that a beam of radiant energy can penetrate through, in addition to multiple ports for placing the detector, standards, and samples. Baffles prevent directly reflected light from superimposing on the sample or the area of the surface being viewed (Torrent et al., 2008).

Data analysis for obtaining the band gap from diffuse reflectance measurements is based upon Kubelka – Munk theory (Kubelka et al., 1931), which assumes that a plane–parallel layer having a thickness $X$, is capable of both scattering and absorbing radiation in the $-x$ direction with a diffuse monochromatic radiation flux $I$ as shown in Fig. A–3.
Assuming this plane – parallel layer is extensive relative to $X$, it can be split into an infinite number of layers having a thickness $dx$. The diffuse radiation flux can be separated into positive and negative directions, designated as $J$ and $I$ respectively. If the downward flux $I$ decreases by an amount $\alpha Idx$ by absorption and increases by $sIdx$ by scattering when passing through $dx$, we can use similar reasoning for the upward flux $J$ to yield

$$\frac{-dl}{dx} = -(\alpha + s)I + SJ$$  \hspace{1cm} (Equation A–4)

$$\frac{dj}{dx} = -(\alpha + s)J + sI$$  \hspace{1cm} (Equation A–5)

where $s$ and $\alpha$ are the scattering and absorption coefficients of the sample, respectively.

Explicit hyperbolic solutions to these equations were obtained by Kubelka (Kubelka, 1948) and are outlined in detail by Wyszecki and Stiles (Wyszecki et al., 1982), the most general solution to which is

$$R = \frac{1-R_g(a-b \coth bsX)}{a-R_g+b \coth bsX}$$  \hspace{1cm} (Equation A–6)
where $R$ is the reflectance of the layer over a background of reflectance $R_g$, $\coth(bsX)$ is the hyperbolic cotangent of $bsX$, $X$ is the layer thickness, $a = 1 + \alpha / s$, and $b = (a^2 - 1)^{0.5}$. However, measurements are typically made on layers that are thick enough so that a further increase in thickness will not change the overall reflectance. As a result, the reflectance ($R_\infty$) is

$$\frac{\alpha}{s} = \frac{(1-R_\infty)^2}{2R_\infty} = F(R_\infty)$$

(Equation A–7)

where $F(R_\alpha)$ is the Kubelka–Munk function (Kubelka et al., 1948). It is important to note that plots utilizing $F(R_\alpha)$ vs. photon energy only reflect the true absorption spectrum if the scattering coefficient is independent of wavelength and known, which is only true when the average grain size is large relative to the wavelength. If not, the scattering coefficient decreases with increasing wavelength (Torrent et al., 2008). If the behavior of the scattering coefficient as a function of wavelength is known, the correct value of the absorption coefficient can be determined.

There are several important notes to be made about the Kubelka–Munk function. First, the reflectance at any specific wavelength is a function of the $\alpha / s$ ratio, not absolute values of $\alpha$ or $s$, in addition to there being controversy over the poor definition of the $s$ parameter (Torrent et al., 2008). As a result, neither of these values can be directly obtained from Eq. A–7. Second, significant deviations from Kubelka–Munk theory can occur at $R_\alpha < 0.6$ (Torrent et al., 2008). This becomes a problem when comparing a typically white or tan sample such as CaTiO$_3$ that has been slightly doped with an acceptor dopant such as Mn, which will turn the sample dark brown / black. Third, there has been concern over the lack of physical meaning of the reflectance since it can be measured in multiple ways (Hapke, 1981; Hapke, 1993). Lastly, Tauc plots of some materials may show multiple changes in slope across the measured energy range, and there is no convention concerning which slope is appropriate to extrapolate the band gap. Another technique that can be used to probe the optical properties and band gap of various materials is spectroscopic ellipsometry, which possesses several advantages over UV–Vis.

**Spectroscopic Ellipsometry**

In spectroscopic ellipsometry (SE), a beam of polarized light is incident on a reflective sample, and both the change in amplitude and polarization state of the incident light beam induced by the interaction with the sample is determined. For ellipsometric measurements, the electric field of the light incident on the sample must be known. The polarized electric field
vector components are chosen as perpendicular \((s)\) and parallel \((p)\) to the plane of incidence as shown in Fig. A–4.

Figure A–4: (Left): Schematic of the plane of incidence along with propagation wave vectors \(k'\) and \(k'\) where \(i\) and \(r\) refer to the incident and reflected beams respectively and (right): cross-sectional amplitudes and phase angles of \(s\) and \(p\) polarized light in the \(xy\) plane (Ferreira, (2004); Ferlauto, (2001).

Complex amplitude reflection coefficients represent the optical response of a specularly reflecting surface, a disk polished on one side in this research, and are represented by

\[
\rho_p(s) = \left| r_p(s) \right| e^{i\phi_p(s)} = \frac{E_p}{E_p(s)} \tag{Equation A–8}
\]

where \(E_p(s)\) is the electric field amplitude, \(\phi_p(s)\) is the phase shift after reflection, and \(i\) and \(r\) refer to the incident and reflected beams respectively. From these expressions, the complex amplitude reflection ratio is defined:

\[
\rho_r = \frac{r_p}{r_s} = \left| \frac{r_p}{r_s} \right| e^{i(\phi_p - \phi_s)} \tag{Equation A–9}
\]

in terms of the ellipsometric angles \((\psi, \Delta)\), equivalent to the relative amplitude \((\tan\psi)\) and phase shift \((\Delta)\) between the \(p\) and \(s\) waves, can also be used to describe \(\rho_r\) by \(\rho_r = (\tan\psi)\exp(i\Delta)\), where
\[
\tan \phi = \frac{|r_p|}{|r_s|} \quad \text{and} \quad \Delta = \phi_p - \phi_s.
\]
The ellipsometer measures the ellipsometric angles, and modeling is used to obtain information about the optical properties of the material.
Appendix B

ELLIPSOMETRY MODELING PARAMETERS

Table B–1: Sellmeier oscillator energies and magnitudes for the low energy (transparent region) across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition (comp.) range. Surface roughness layer thickness as represented by a Bruggeman effective medium approximation (EMA) is also listed. The low energy range was 0.732 – 3.00 eV for all samples. The 0.80 Mn composition was doped with 0.5 mol% Mn. EMA: Effective Medium Approximation

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Sellmeier #1 (eV)</th>
<th>Amplitude (eV$^2$)</th>
<th>Sellmeier #2 (eV)</th>
<th>Amplitude (eV$^2$)</th>
<th>% Void</th>
<th>EMA Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.10 ± 0.145</td>
<td>191 ± 7.03</td>
<td>0.001</td>
<td>0.057 ± 0.006</td>
<td>15.1 ± 2.31</td>
<td>101 ± 14.6</td>
</tr>
<tr>
<td>0.03</td>
<td>8.69 ± 0.215</td>
<td>221 ± 11.0</td>
<td>0.001</td>
<td>0.032 ± 0.003</td>
<td>97.5 ± 2.13</td>
<td>200 ± 165</td>
</tr>
<tr>
<td>0.05</td>
<td>8.89 ± 0.075</td>
<td>223 ± 4.02</td>
<td>0.001</td>
<td>0.022 ± 0.002</td>
<td>99.3 ± 0.047</td>
<td>677 ± 48.4</td>
</tr>
<tr>
<td>0.10</td>
<td>8.55 ± 0.078</td>
<td>218 ± 4.05</td>
<td>0.001</td>
<td>0.007 ± 0.002</td>
<td>98.5 ± 0.170</td>
<td>412 ± 48.8</td>
</tr>
<tr>
<td>0.20</td>
<td>7.07 ± 0.040</td>
<td>155 ± 1.74</td>
<td>0.001</td>
<td>0.009 ± 0.002</td>
<td>11.3 ± 0.580</td>
<td>124 ± 6.37</td>
</tr>
<tr>
<td>0.30</td>
<td>7.41 ± 0.082</td>
<td>177 ± 3.93</td>
<td>0.001</td>
<td>0.011 ± 0.002</td>
<td>69.6 ± 40.4</td>
<td>36.4 ± 22.1</td>
</tr>
<tr>
<td>0.50</td>
<td>6.83 ± 0.064</td>
<td>158 ± 2.94</td>
<td>--</td>
<td>--</td>
<td>86.7 ± 9.48</td>
<td>80.3 ± 47.7</td>
</tr>
<tr>
<td>0.70</td>
<td>6.51 ± 0.106</td>
<td>153 ± 2.02</td>
<td>0.001</td>
<td>0.003 ± 0.002</td>
<td>75.4 ± 17.3</td>
<td>49.6 ± 21.2</td>
</tr>
<tr>
<td>0.80</td>
<td>6.02 ± 0.059</td>
<td>135 ± 2.65</td>
<td>--</td>
<td>--</td>
<td>75.7 ± 33.9</td>
<td>47.1 ± 40.4</td>
</tr>
<tr>
<td>0.80Mn</td>
<td>6.08 ± 0.038</td>
<td>138 ± 1.74</td>
<td>--</td>
<td>--</td>
<td>75.9 ± 9.00</td>
<td>71.4 ± 16.6</td>
</tr>
<tr>
<td>0.90</td>
<td>5.80 ± 0.070</td>
<td>130 ± 3.13</td>
<td>--</td>
<td>--</td>
<td>93.1 ± 0.201</td>
<td>48.1 ± 43.5</td>
</tr>
<tr>
<td>0.95</td>
<td>6.03 ± 0.111</td>
<td>143 ± 5.27</td>
<td>--</td>
<td>--</td>
<td>85.4 ± 3.65</td>
<td>67.2 ± 43.9</td>
</tr>
<tr>
<td>0.97</td>
<td>5.76 ± 0.106</td>
<td>131 ± 5.85</td>
<td>--</td>
<td>--</td>
<td>73.6 ± 50.6</td>
<td>56.8 ± 52.9</td>
</tr>
<tr>
<td>1.00</td>
<td>5.94 ± 0.058</td>
<td>140 ± 2.73</td>
<td>--</td>
<td>--</td>
<td>87.3 ± 3.61</td>
<td>149 ± 36.2</td>
</tr>
</tbody>
</table>
Table B–2: Sellmeier oscillator energies and magnitudes for the high energy (absorbing region) oscillators across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sellmeier #1 (eV)</th>
<th>Amplitude (eV$^2$)</th>
<th>e1 Offset (eV)</th>
<th>Energy Range (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5.52 – 6.49</td>
</tr>
<tr>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.72 – 6.49</td>
</tr>
<tr>
<td>0.05</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.75 – 6.49</td>
</tr>
<tr>
<td>0.10</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.72 – 6.49</td>
</tr>
<tr>
<td>0.20</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.30 – 6.49</td>
</tr>
<tr>
<td>0.30</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.21 – 6.49</td>
</tr>
<tr>
<td>0.50</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.02 – 6.49</td>
</tr>
<tr>
<td>0.70</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.71 – 6.49</td>
</tr>
<tr>
<td>0.80</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.80 – 6.49</td>
</tr>
<tr>
<td>0.80Mn</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.80 – 6.49</td>
</tr>
<tr>
<td>0.90</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.86 – 6.49</td>
</tr>
<tr>
<td>0.95</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.86 – 6.49</td>
</tr>
<tr>
<td>0.97</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.80 – 6.49</td>
</tr>
<tr>
<td>1.00</td>
<td>--</td>
<td>--</td>
<td>-7.00 ± 2.61</td>
<td>3.76 – 6.49</td>
</tr>
</tbody>
</table>
Table B–3: First high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti\(_{x}\)Zr\(_{1-x}\))O\(_3\) composition range.

<table>
<thead>
<tr>
<th>1st Oscillator Composition</th>
<th>Amplitude (eV)</th>
<th>Energy (eV)</th>
<th>Broadening (eV)</th>
<th>Phase (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>9.39 ± 0.070</td>
<td>6.03 ± 0.018</td>
<td>0.578 ± 0.016</td>
<td>-8.01 ± 1.07</td>
</tr>
<tr>
<td>0.03</td>
<td>3.33 ± 0.281</td>
<td>5.25 ± 0.098</td>
<td>1.86 ± 0.081</td>
<td>26.4 ± 6.49</td>
</tr>
<tr>
<td>0.05</td>
<td>2.78 ± 0.049</td>
<td>5.05 ± 0.015</td>
<td>1.18 ± 0.019</td>
<td>24.5 ± 1.53</td>
</tr>
<tr>
<td>0.10</td>
<td>3.30 ± 0.043</td>
<td>4.99 ± 0.014</td>
<td>1.04 ± 0.017</td>
<td>23.1 ± 1.65</td>
</tr>
<tr>
<td>0.20</td>
<td>6.67 ± 0.089</td>
<td>4.73 ± 0.009</td>
<td>1.08 ± 0.016</td>
<td>-2.67 ± 0.606</td>
</tr>
<tr>
<td>0.30</td>
<td>7.15 ± 0.156</td>
<td>4.64 ± 0.015</td>
<td>1.65 ± 0.041</td>
<td>-7.01 ± 0.931</td>
</tr>
<tr>
<td>0.50</td>
<td>5.75 ± 0.219</td>
<td>4.16 ± 0.027</td>
<td>0.677 ± 0.061</td>
<td>-51.0 ± 5.27</td>
</tr>
<tr>
<td>0.70</td>
<td>5.39 ± 0.137</td>
<td>4.20 ± 0.002</td>
<td>0.492 ± 0.004</td>
<td>-34.1 ± 0.706</td>
</tr>
<tr>
<td>0.80</td>
<td>8.53 ± 0.397</td>
<td>4.15 ± 0.006</td>
<td>0.372 ± 0.015</td>
<td>-27.9 ± 0.755</td>
</tr>
<tr>
<td>0.80Mn</td>
<td>8.45 ± 0.229</td>
<td>4.17 ± 0.002</td>
<td>0.430 ± 0.006</td>
<td>-25.5 ± 0.587</td>
</tr>
<tr>
<td>0.90</td>
<td>9.94 ± 0.631</td>
<td>4.09 ± 0.005</td>
<td>0.415 ± 0.018</td>
<td>-24.3 ± 0.570</td>
</tr>
<tr>
<td>0.95</td>
<td>8.21 ± 0.761</td>
<td>4.09 ± 0.006</td>
<td>0.469 ± 0.019</td>
<td>-27.0 ± 0.941</td>
</tr>
<tr>
<td>0.97</td>
<td>10.2 ± 1.01</td>
<td>4.04 ± 0.007</td>
<td>0.421 ± 0.024</td>
<td>-26.6 ± 0.896</td>
</tr>
<tr>
<td>1.00</td>
<td>9.49 ± 0.279</td>
<td>4.00 ± 0.005</td>
<td>0.411 ± 0.007</td>
<td>-23.6 ± 1.77</td>
</tr>
</tbody>
</table>
Table B-4: Second high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amplitude</th>
<th>Energy (eV)</th>
<th>Broadening (eV)</th>
<th>Phase (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.03</td>
<td>8.24 ± 0.596</td>
<td>6.05 ± 0.005</td>
<td>0.473 ± 0.015</td>
<td>-40.8 ± 2.53</td>
</tr>
<tr>
<td>0.05</td>
<td>7.78 ± 0.116</td>
<td>6.10 ± 0.003</td>
<td>0.533 ± 0.006</td>
<td>-31.3 ± 0.763</td>
</tr>
<tr>
<td>0.10</td>
<td>7.53 ± 0.167</td>
<td>6.16 ± 0.004</td>
<td>0.583 ± 0.006</td>
<td>-32.2 ± 0.530</td>
</tr>
<tr>
<td>0.20</td>
<td>8.47 ± 0.107</td>
<td>6.17 ± 0.004</td>
<td>0.596 ± 0.006</td>
<td>-36.8 ± 0.738</td>
</tr>
<tr>
<td>0.30</td>
<td>6.65 ± 0.101</td>
<td>6.35 ± 0.008</td>
<td>0.814 ± 0.034</td>
<td>-50.8 ± 2.10</td>
</tr>
<tr>
<td>0.50</td>
<td>4.50 ± 0.441</td>
<td>5.37 ± 0.036</td>
<td>1.48 ± 0.072</td>
<td>60.9 ± 5.33</td>
</tr>
<tr>
<td>0.70</td>
<td>4.43 ± 0.052</td>
<td>5.46 ± 0.008</td>
<td>1.12 ± 0.030</td>
<td>52.1 ± 1.96</td>
</tr>
<tr>
<td>0.80</td>
<td>4.88 ± 0.080</td>
<td>5.44 ± 0.016</td>
<td>0.994 ± 0.032</td>
<td>55.6 ± 3.58</td>
</tr>
<tr>
<td>0.80Mn</td>
<td>4.83 ± 0.062</td>
<td>5.40 ± 0.008</td>
<td>0.934 ± 0.027</td>
<td>52.2 ± 2.90</td>
</tr>
<tr>
<td>0.90</td>
<td>4.86 ± 0.171</td>
<td>5.46 ± 0.022</td>
<td>0.898 ± 0.041</td>
<td>61.4 ± 5.15</td>
</tr>
<tr>
<td>0.95</td>
<td>6.28 ± 0.579</td>
<td>5.46 ± 0.054</td>
<td>1.22 ± 0.119</td>
<td>44.4 ± 6.91</td>
</tr>
<tr>
<td>0.97</td>
<td>6.21 ± 0.554</td>
<td>5.53 ± 0.053</td>
<td>0.992 ± 0.051</td>
<td>70.5 ± 5.23</td>
</tr>
<tr>
<td>1.00</td>
<td>9.85 ± 1.07</td>
<td>5.71 ± 0.031</td>
<td>1.13 ± 0.079</td>
<td>99.4 ± 5.74</td>
</tr>
</tbody>
</table>
Table B–5: Third high energy critical–point parabolic–band (CPPB) oscillator parameters across the Ca(Ti$_x$Zr$_{1-x}$)O$_3$ composition range.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amplitude</th>
<th>Energy (eV)</th>
<th>Broadening (eV)</th>
<th>Phase (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.05</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.20</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.50</td>
<td>5.67 ± 0.400</td>
<td>6.39 ± 0.013</td>
<td>0.645 ± 0.017</td>
<td>-42.2 ± 3.11</td>
</tr>
<tr>
<td>0.70</td>
<td>3.48 ± 0.050</td>
<td>6.46 ± 0.009</td>
<td>0.610 ± 0.025</td>
<td>-49.2 ± 3.50</td>
</tr>
<tr>
<td>0.80</td>
<td>3.47 ± 0.065</td>
<td>6.38 ± 0.009</td>
<td>0.549 ± 0.026</td>
<td>-67.1 ± 4.74</td>
</tr>
<tr>
<td>0.80Mn</td>
<td>3.23 ± 0.054</td>
<td>6.33 ± 0.009</td>
<td>0.552 ± 0.020</td>
<td>-79.0 ± 3.53</td>
</tr>
<tr>
<td>0.90</td>
<td>3.06 ± 0.193</td>
<td>6.36 ± 0.014</td>
<td>0.604 ± 0.047</td>
<td>-83.0 ± 5.40</td>
</tr>
<tr>
<td>0.95</td>
<td>3.92 ± 0.645</td>
<td>6.35 ± 0.038</td>
<td>0.965 ± 0.098</td>
<td>-105 ± 9.84</td>
</tr>
<tr>
<td>0.97</td>
<td>3.94 ± 0.576</td>
<td>6.45 ± 0.030</td>
<td>0.902 ± 0.129</td>
<td>-80.6 ± 5.92</td>
</tr>
<tr>
<td>1.00</td>
<td>66.6 ± 53.8</td>
<td>7.97 ± 0.280</td>
<td>0.947 ± 0.320</td>
<td>61.7 ± 13.1</td>
</tr>
</tbody>
</table>
VITA

Dennis Patrick Shay was born November 27, 1984 in Lowell, Massachusetts, the son of Charles and Diane Shay. Dennis graduated from Tyngsborough High School in 2003, where he filled his plate by playing three sports, working 2 jobs, playing drums in an alternative rock band, and being the yearbook editor. He chose to pursue Materials Science and Engineering at The Pennsylvania State University rather than journalism (with the hope of a slightly more successful career) and culture-shock himself by switching from a class of 113 to 8,000. Within the first week of classes at Penn State, Dennis asked his freshman seminar professor, Prof. Digby MacDonald, a question about nuclear reactors, and included in his answer was an unexpected job offer to work in his lab group.

Once introduced to the world of academic research, Dennis continued to get his hands dirty by receiving an undergraduate research fellowship working for Profs. Elizabeth Dickey, Clive Randall, and Dr. Anton Polotai on developing MLCC sintering profiles for minimizing grain growth and maximizing electrode continuity. His research resulted in co-authorship of several well-cited papers. His junior year, Dennis was the “guinea pig” for the International Internship, traveling to the University of Sheffield in the UK to work with Prof. Ian Reaney to perform his senior dissertation research, “Investigation of a High T_C Piezoelectric System for Sensor/Actuator Applications: (x)BiFeO3 – (x)Bi(Mg0.5Ti0.5)O3 – (1-x)PbTiO3.” Dennis graduated from the Schreyer Honors College at Penn State in December 2007.

While applying to graduate schools, Prof. Clive Randall approached Dennis with an offer he couldn’t refuse. With the opportunity to develop new materials and travel the world to present his results, he gladly accepted. During his graduate years at Penn State, Dennis worked to develop new linear dielectric ceramic compositions for high temperature, high energy density power electronics applications, producing capacitors having the highest energy densities at 300 °C observed in literature to date. He has had the opportunity to present his research in Japan twice, Scotland, Portugal, and Vancouver, and suffered from exhaustion on several occasions by intentionally visiting too many countries in too little time. He received the National Defense Science and Engineering Graduate Fellowship (NDSEG) in 2010, and published several papers, one of which received the Edward C. Henry Paper of the Year Award from the Journal of the American Ceramics Society. His research resulted in a Ph.D. dissertation in May 2014.