Optimal Sintering Temperature of Ceria-doped Scandia Stabilized Zirconia for Use in Solid Oxide Fuel Cells

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OPTIMAL SINTERING TEMPERATURE OF CERIA-DOPED SCANDIA STABILIZED ZIRCONIA FOR USE IN SOLID OXIDE FUEL CELLS

by

AMANDA KAY ASSUNÇÃO

A thesis submitted in partial fulfillment of the requirements for the Honors in Major Program in Aerospace Engineering in the College of Engineering and Computer Science and in the Burnett Honors College at the University of Central Florida
Orlando, Florida

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Thesis Chair: Nina Orlovskaya, Ph.D.
ABSTRACT

Carbon emissions are known to cause decay of the Ozone layer in addition to creating pollutant, poisonous air. This has become a growing concern among scientists and engineers across the globe; if this issue is not addressed, it is likely that the Earth will suffer catastrophic consequences. One of the main culprits of these harmful carbon emissions is fuel combustion. Between vehicles, power plants, airplanes, and ships, the world consumes an extraordinary amount of oil and fuel which all contributes to the emissions problem. Therefore, it is crucial to develop alternative energy sources that minimize the impact on the environment. One such technology that is currently being researched, is the Solid Oxide Fuel Cell (SOFC). This is a relatively simple device that converts chemical energy into electrical energy with no harmful emissions. For these devices to work properly, they require an electrolyte material that has high ionic conductivity with good phase stability at a variety of temperatures. The research presented in this study will concentrate intensively on just one of the many candidates for SOFC electrolytes. 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$ manufactured by Treibacher Industries was analyzed to better understand its sintering properties, phase stability, and molecular structure. Sintering was performed at temperatures ranging from 900°C to 1600°C and the shrinkage, density and porosity were examined for each temperature. Raman Spectroscopy and X-Ray Powder Diffraction were also conducted for comparison with other known compositions to see if the powder undergoes any phase transitions or instability.
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1 INTRODUCTION AND BACKGROUND

1.1 Overview of Problem

Over the past couple of decades, a major shift has occurred in the engineering industry. Since the start of the Industrial Revolution in the mid-1800s, engineers have focused most of their time and resources on producing the most powerful forms of machinery and equipment with little thought given to the effects of operation [1]. The cumulative amount of CO₂ emissions was on the range of 6,100 megatons by 1949 [2]. In the past few decades, however, this mentality has dramatically shifted. With the rise of CO₂ emissions, global surface and ocean temperatures have risen at a worrisome rate with most scientists estimating a global temperature increase of nearly 2°C above pre-industrial levels [3]. This has caused the scientific and engineering communities to shift their focus onto clean and renewable energy sources with the hopes of combatting the rise of greenhouse gases [4].

1.2 Background of Solid Oxide Fuel Cells

1.2.1 Efficiency Comparison

One of the most promising forms of renewable energy is the solid oxide fuel cell (SOFC). The basic idea of an SOFC is relatively simple but the manufacturing process can be quite complex and involves some very specific materials. The main reason SOFCs have gained so much attention in recent years, is due to their high efficiency levels of 45-60% [5] with some reaching up to 70-90% if heat is recovered [4]. The typical coal-fired power plant has an average efficiency of only 33-40% [6]. The difference in efficiency levels can be attributed to the ability of SOFCs to convert
chemical energy directly to electrical energy [7]. Coal-fired and natural gas power plants rely more heavily on a series of conversion processes which can result in significant energy loss [8].

1.2.2 How a Fuel Cell Operates

Solid oxide fuel cells produce energy through the conversion of chemical energy into an electric current [9]. The basic components of an SOFC include: the electrodes (anode and cathode) and electrolyte. Figure 1 below shows the complete setup of a traditional solid oxide fuel cell.

![Diagram of the solid oxide fuel cell cycle](image)

**Figure 1: Diagram of the solid oxide fuel cell cycle [4], [9]**

Both the anode and cathode consist of a mixed conductor, typically a ceramic material such as yttria stabilized zirconia (YSZ) or strontium doped lanthanum manganite (LSM) [9], [10], [11]. They must possess both an ionic and electronic conductivity, have a porosity of about 30-40% to
allow the diffusion of gas particles, and must also be very robust to endure the high operating temperatures [10]. The electrolyte (ionic conductor) differs from the electrodes in that it must have a high ionic conductivity but a low electronic conductivity. It must also be very dense with minimal porosity to ensure only oxygen ions are transported through [10]. These necessary qualities are most evident in zirconia-based ceramics [10], [11].

The difference in electrical charge between the anode and cathode is essential in the energy conversion process. This helps to drive the oxygen ions through the electrolyte material while also serving as the positive and negative terminals for the electrical circuit [9]. The energy conversion process begins with the introduction of oxygen at the cathode side [4], [9]. The oxygen molecules gain electrons from the electrical circuit and become negative ions [4], [9]. These diffuse through the electrolyte material until effectively reaching the anode [4], [9]. Meanwhile, a fuel source, typically hydrogen, enters the anode [4], [9]. As the hydrogen diffuses into the anode, it combines with the oxygen ions to produce water [4], [9]. During this chemical reaction, electrons are released and begin to travel through the electrical circuit and back to the cathode where the process continues [4], [9]. The chemical reaction for this process is shown below. So long as there is available fuel (hydrogen and air), this cycle will continue with an average lifetime spanning from about 20,000-40,000 hours [12]. Although similar to the operation of a battery, SOFCs do not require charging [4].

\[
\begin{align*}
    H_2 + O^{2-} & \Rightarrow H_2O + 2e^- & \text{Eq (1)} \\
    \frac{1}{2}O_2 + 2e^- & \Rightarrow O^{2-}
\end{align*}
\]
1.3 Pros and Cons of Solid Oxide Fuel Cells

Solid oxide fuel cells have many benefits that make them promising candidates as future renewable energy sources. SOFCs have an efficiency level between about 60-80% and can be improved further through the harnessing of heat during the chemical reaction [4], [11]. This harnessed heat can be utilized in combined cycles with turbines, making the SOFC highly applicable for large power plants [13]. In addition to high efficiency, these devices release no harmful emissions: the only byproduct is water and heat [4]. Based a report presented by the U.S. Energy Information Administration, Carbon Dioxide emissions in 2016 were recorded to be 1,928,401 thousand metric tons with coal and natural gas accounting for 64% of the total net energy generation [14], [15]. Renewable energy sources, including hydroelectric, accounted for only 15% of the total net generation [14] based on a 2016 annual energy report produced by the U.S. Energy Administration. Table 1 below shows a breakdown of energy generation sources based on a 2016 annual energy report produced by the U.S. Energy Information Administration [16].

Table 1: Generation from Various Power Plants [16]

<table>
<thead>
<tr>
<th>Total net generation</th>
<th>4,079,079 thousand megawatt hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric utility net generation</td>
<td>2,304,081 thousand megawatt hours</td>
</tr>
</tbody>
</table>

*Share of total net generation by energy source*

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>34%</td>
</tr>
<tr>
<td>Coal</td>
<td>30%</td>
</tr>
<tr>
<td>Nuclear</td>
<td>20%</td>
</tr>
<tr>
<td>Hydroelectric</td>
<td>7%</td>
</tr>
<tr>
<td>Nonhydro renewables</td>
<td>8%</td>
</tr>
<tr>
<td>Petroleum and other</td>
<td>1%</td>
</tr>
</tbody>
</table>
Based on these statistics, if power plants and vehicle fuel systems can be converted to solid oxide fuel cells, the amount of carbon emissions will significantly decrease. Other long-term benefits include: lower operating costs, less dependence on foreign oil supply, and a greater selection of natural fuel choices [4], [17].

Solid oxide fuel cells may sound great in theory, but they do have some limitations. Currently, SOFCs require a high operating temperature, typically in the range of 1000°C [7]. This greatly limits the choice of materials for the electrolyte and electrodes, effectively increasing the cost [17]. The other implications of a high operating temperature include the need for thermal shielding to protect workers and other system components from the extreme heat [4]. In order to create safer and more economical fuel cells, scientists and engineers have been working together to create materials that can operate in the low-intermediate temperature range [18]. This study will focus on one promising electrolyte material, scandia doped zirconia, which shows a high ionic conductivity and stability in the lower temperature range.

1.4 Research Objective

Before a cost effective and efficient fuel cell can be made, a great deal of research must be conducted on the materials that constitute the cell. Our investigations will focus on the sintering behavior, densification, and phase stability of scandia stabilized zirconia for its potential application as an oxygen ion electrolyte. This composition consists of 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$ (SCSZ). Being a ceramic, this powder must be sintered to be utilized as an effective electrolyte. Sintering is the solid-state process by which interfacial free energy is reduced so that densification can take place [19], [20]. The gas-solid interfaces are decreased on the particle, thereby reducing the surface free energy and allowing mass to be transported into the
porous space between individual particles [19], [21]. The stages of this process are illustrated in Figure 2 below [22].

![Figure 2: Sintering process from initial contact to the final stage with pore size effectively decreasing [22]](image)

There are different sintering techniques but for our investigation only dry air, pressure-less sintering will be addressed. This process takes place at atmospheric pressure inside a heated furnace at temperatures roughly 2/3 of the material’s melting temperature [21], [20]. For diffusion to occur, the samples must be left to dwell at these elevated temperatures for several hours [21]. The question we would like to investigate is: what is the optimal sintering temperature for maximum ionic conductivity and suitable mechanical properties? This research hopes to answer the question at hand while also providing a basic understanding of the suitability of scandia doped zirconia as electrolytes in solid oxide fuel cells.
2 LITERATURE REVIEW

Before conducting research on the sintering behavior of ceramic electrolytes, a review of current literature is necessary. Most research on solid oxide fuel cells has centered around yttria stabilized zirconia [23], [24], [25], [26]. The major benefit to using yttria as a dopant is its stabilizing effect and cheaper cost compared to other compositions [27]. The major downside is the high temperature operating range of about 1000°C [27], [28]. Zirconia doped with scandia and ceria is a promising alternative with lower operating temperatures ranging from 500°C-750°C [27]. Lowering the temperature is very significant in the advancement of fuel cells, because it lowers the operating costs, increases durability, and results in safer operations [27], [29], [30], [31], [32]. Therefore, this work will focus on the sintering behavior of scandia and ceria doped zirconia at various temperatures. Theoretical density will also be discussed for its role in calculating the porosity of ceramic samples, as well as the importance of Raman Spectroscopy and powder diffraction in identifying phase structure and stability.

2.1 Fundamentals of Raman Spectroscopy

Raman Spectroscopy is a necessary tool in helping to identify the structure and phase stability of compositions. This tool in combination with x-ray diffraction can identify possible phase transitions at varying temperatures as well as identify the presence of impurities. Before discussing the meaning of the Raman spectrum, it is important to understand the fundamental process of Raman Spectroscopy.

This scientific tool operates on the principle of energy transfer. When an electromagnetic field interacts with a molecule, energy is transferred to the molecule which excites it into a higher energy state [33]. In Raman spectroscopy, this process is achieved with laser beams that typically
have wavelengths in the visible (532 nm) or near infrared (785 nm) region of the electromagnetic spectrum. When the laser beam is focused onto a sample, most of the light will be scattered perpendicular to the incident beam via either Rayleigh or Raman scattering [33]. Rayleigh scattered light will have the same frequency as the incident beam while Raman scattered light is much weaker and contains the incident frequency plus or minus the vibrational frequency of the molecule [33]. If the incident beam transfers energy to the molecule, causing it to vibrate, the energy level of the molecule will increase slightly. This necessarily means the scattered light will have a frequency equal to the incident frequency minus the vibrational frequency of the molecule. This type of scattering is called Stokes [33], [34]. If the opposite occurs and the incident beam gains energy from the molecule, the scattering is called anti-Stokes [33], [34]. Figure 3 shows the difference between Stokes, anti-Stokes, and Rayleigh scattering [34]. The Raman spectra captures this shift in frequency of the scattered light [33].

Figure 3: Raman and Rayleigh scattering energy diagram; S₀ is the ground state and S₁, S₂, and S₃ are excited electronic energy levels. The horizontal black lines represent vibrational levels [34].
2.1.1 Raman Spectroscopy Process

The actual process of Raman Spectroscopy is quite complex. High energy photons are projected onto a material which causes the molecules within that material to vibrate and scatter radiation [35]. Since every molecular composition will vibrate in a unique way, the shift in the photon frequency will be specific to that composition [35]. Therefore, Raman is a special tool that can be used on known molecular compounds and materials to create a database of spectra data which can be compared to unknown samples. The basic components of the Raman Spectroscopy process are shown below in Figure 4.

Many different types of Raman spectroscopy exist, but the one most pertinent to this study is Confocal Raman microscopy [35]. In this type of spectroscopy, a laser is focused on the sample through a microscope. A small pinhole refocuses the backscattered Raman photons and collects the data on a charge coupled device camera [35]. This produces a visual spectrum which can be further analyzed to see the Raman shifts and their associated intensities [35]. With this useful qualitative data, all types of compositions can be evaluated for phase stability, impurities present, and molecular structure if they are Raman active.

![Figure 4: Basic components of the Raman Spectroscopy system [35]](image-url)
2.2 Fundamentals of X-ray Powder Diffraction

Another very useful scientific tool which works well in conjunction with Raman spectroscopy is X-ray Powder Diffraction (XRD). The main purpose of this tool is to determine the phase structure of a material and the lattice parameters [36]. X-rays are projected onto the surface of a material and will travel through the lattice structure until encountering an atom. This interaction causes the x-ray to scatter at the same angle as the incident beam, as seen in Figure 5 [37].

![Figure 5: Scattering of x-ray beams as they strike atoms (black dots); d is the spacing between layers of atoms and \( \theta \) is the angle of incidence [37]](image)

The relationship between the incident angle (\( \theta \)), lattice spacing (d), and wavelength (\( \lambda \)) of the x-ray is expressed in Bragg’s Law where n is an integer [36], [37]. This is shown equation 2 below.

\[
n\lambda = 2dsin(\theta)
\]

Eq (1)
A detector will read the intensity of the diffracted x-rays as shown in Figure 6 [37]. A variety of incident angles will be used to create a complete profile for the crystalline material. An XRD plot will compare the diffracted 2θ angle with its associated intensity, creating peaks where the diffraction is strongest. Based on the 2θ angle of these peaks, lattice parameters can be calculated for the material [37]. This is essential in determining the phase structure of a given composition, which will further help to relate the peaks in a Raman spectrum to different phases.

![Figure 6: Basic set up for x-ray diffraction where θ is the incident angle [37]](image)

2.3 Density After Sintering of Scandia Stabilized Zirconia

Before the above tools of Raman spectroscopy and X-ray Powder Diffraction can be utilized, density must be discussed. Density is an important characteristic because it directly impacts the ionic conductivity of an electrolyte material. As density of a material increases, the porosity decreases which allows for better ionic conductivity [18]. For electrolytes in solid oxide fuel cells, this increased density means the oxygen ions will have an easier time transporting through the lattice structure [9], [10]. One of the most widely studied electrolyte compositions is
scandia stabilized zirconia (SCSZ). The main component of SCSZ powder is zirconium dioxide (zirconia). This compound has been intensively studied for its oxygen conductivity properties. Pure zirconia, however, is not particularly stable when heated [38]. Other components must be added to zirconia in order to increase the phase stability. The most common example of this is yttria stabilized zirconia [38]. It has a very good ionic conductivity at high temperatures (1000°C), but at lower temperatures, the conductivity decreases [32].

A more suitable companion for zirconium dioxide is the ceria doped scandia. In two separate research studies [32], [39] scandia stabilized zirconia powder was tested from two different manufacturers, Daiichi Kigenso Kagaku Kogyo (DKKK) and Praxair. The manufacturer listed the composition for both powders as 10 mol % Sc₂O₃ – 1 mol % CeO₂ – ZrO₂ (SCSZ). Even though the powders were of near identical compositions, the Praxair had more impurities and was manufactured using a spray pyrolysis as opposed the DKKK which used wet coprecipitation [32]. Inductively coupled plasma mass spectroscopy also revealed that the Praxair powder contained 15 mol% Sc₂O₃ compared to the 10.07 mol% in the DKKK powder [39].

To test the sintering behavior, samples were uniaxially pressed at 20 MPa and sintered in air at temperatures ranging from 1100°C to 1600°C in 100°C increments [32], [39]. The density was calculated for all samples utilizing the Archimedean immersion method and later compared with the theoretical density [32], [39]. The resulting measurements showed that the DKKK powder reached 93-95% of the theoretical density at 1300°C, while the Praxair only reached this level at 1500°C [32], [39]. The DKKK was much more active, which makes it a better candidate for the testing of SCSZ electrolytes. The shrinkage and porosity data are shown below in Figure 7 [39].
Another good indicator of the density after sintering is the shrinkage rate of the sample. In another study published in the International Journal of Applied Ceramic Technology [40], thin, flat sheets of scandia stabilized zirconia (SCSZ) were tape casted and sintered at various temperatures. Similar to the uniaxially pressed samples, the thin sheets reached very near theoretical density at temperatures between 1300°C and 1500°C [40]. The porosity in this range was measured to be between 0.1% and 0.35% [40]. At a sintering temperature just below this range, 1200°C, the porosity was significantly higher with values between 0.8% and 6.5% [40]. Through the use of hot stage microscopy, the shrinkage rates were plotted as a function of sintering temperature. From 900°C to about 1350°C, the shrinkage rate reached a maximum [40]. Then, after 1350°C, the rate became relatively constant [40]. This is a very important finding, because it implies that a sintering temperature of 1350°C is sufficient to create a highly dense electrolyte.
Collectively, these studies point to an optimal sintering range of 1300°C to 1600°C. It is also evident that the DKKK powder is much more active in the sintering process than its Praxair counterpart. As such, the DKKK powder may be a better choice for the testing of SCSZ electrolytes.

2.4 Lattice Structure and Phase Stability

Another crucial aspect of electrolytes is their phase stability during the heating and cooling processes. The molecular phase structure can greatly impact the ionic conductivity. In the examination of the DKKK and Praxair powders, x-ray diffraction was used to assess the phase structure. The diffraction patterns of the DKKK and Praxair powders sintered at various temperatures are shown below [39].

![Diffraction patterns](image)

**Figure 8: Diffraction patterns for Praxair and DKKK powders sintered at different temperatures (A: Praxair, B: DKKK) [39]**

Both powders showed a combination of cubic and rhombohedral phases before sintering [32]. The DKKK samples sintered at 1100°C and 1200°C retained a combination of these two
phases. The Praxair powder showed pure cubic structure for sintering temperatures between 1100°C and 1600°C while DKKK was cubic only at 1300°C and above [32], [39].

The DKKK powder showed some interesting characteristics during the heating process. At about 300°C, the powder structure began to change from a cubic structure to almost completely rhombohedral by around 400°C [32]. At 500°C, the structure changed back to nearly entirely cubic [32]. This process also seemed to be reversible during the cooling process [32]. The Praxair composition did not appear to duplicate this same pattern. Even though this may not be a desirable quality for the DKKK powder, it does not appear that it would cause too much of an issue, because the operating temperatures for fuel cells are 700-900°C. At these higher temperatures, the structure is a fully stable cubic [32].

In a similar study, Ramon spectroscopy was conducted on 10 mol% Sc₂O₃ – 1 mol% CeO₂ – 89 mol% ZrO₂ powder utilizing both the 532 nm and 785 nm laser to excite the sample [41]. The full spectra of the rhombohedral (β) phase and cubic phase are shown below in Figure 9 [41]. Both phases have possible impurities present which are visible in the 532 nm spectrum from 4000 cm⁻¹ to 6410 cm⁻¹ and in the 785 nm spectrum from 1000 cm⁻¹ to 2000 cm⁻¹. The characteristic rhombohedral and cubic peaks are seen between 50 cm⁻¹ and 1000 cm⁻¹ [41]. A magnified plot of these peaks is shown in Figure 10 [41].
Figure 9: Full spectral range of 10 mol% Sc$_2$O$_3$ – 1 mol% CeO$_2$ – 89 mol% ZrO$_2$ (A: 532 nm laser, B: 785 nm laser) [41]
Another important consideration that was investigated in this study [41] is the effects of temperature on the Raman spectra of the ceria and scandia doped zirconia powder. The powder was heated from room temperature to 1000°C in increments of 100°C with a dwell time of 5 minutes before collecting the spectrum. As can be seen below in Figure 11, the spectrum underwent some significant changes as the powder was heated [41]. The 480 cm$^{-1}$ peak at room temperature completely disappeared after 500°C, while the 315 cm$^{-1}$ and 378 cm$^{-1}$ peaks merged into one broad peak at 800°C [41]. The specific cause of these shifts in the Raman spectra were not conclusively identified, however it is suggested that the changes are due to possible phase transitions upon heating [41].
Figure 11: The effects of increasing temperature on the Raman spectra of scandia and ceria doped zirconia powder; temperature was raised from room temperature to 1000°C in increments of 100°C with a dwell time of 5 minutes [41].
In a separate study conducted on the mechanical properties of ceria and scandia doped zirconia, powders were created through the hydro/solve-thermal method [42]. Sc$_2$O$_3$ and CeO$_2$ were dissolved in nitric acid and mixed with solid ZrOCl$_2$$\cdot$H$_2$O at a molar concentration of 1 mol% Ce – 10 mol% Sc – 89 mol% Zr [42]. The compound was then separated and stirred in a solvent and dried. After drying, the compound was ground up into a powder using agate mortar [42]. This powder was pressed into small pellets and sintered at various temperatures ranging from 600°C to 1500°C [42]. X-ray diffraction showed results very similar to the results from the studies listed above. For the pellets sintered below 1100°C and above 1300°C, only the cubic phase was present [42]. Between these temperatures, there was a mixture of cubic and rhombohedral phases [42].

In a study published in 2009, nanocrystal particles consisting of Scandia stabilized Zirconia were calcinated at various temperatures to test the effect of crystal size on the phases present [43]. This research looked at 10, 12, and 14 mol% Sc$_2$O$_3$ – ZrO$_2$ and found that as calcination temperature was raised, the diameter of the nanocrystals increased, and the percentage of rhombohedral phase also increased [43]. X-ray diffraction and Raman spectroscopy were used to assess the phases present at room temperature for the nanocrystal particles. At very small diameters (10 and 25 nm), the particles were single-phase [43]. The 10 mol% Sc$_2$O$_3$ show strictly tetragonal phase while the 12 and 14 mol% Sc$_2$O$_3$ showed cubic phase. At diameters larger than this, the rhombohedral phases became more prominent [43]. The Raman spectroscopy results of their study are shown below in Figure 12 [43]. This study concluded that nanoparticles of 25 nm or less are more favorable as electrolytes because of the single phase tetragonal or cubic structure [43]. This form allows for better ionic conductivity compared with the rhombohedral phases.
Figure 12: Raman spectra of Sc$_2$O$_3$-ZrO$_2$ with Sc$_2$O$_3$ doping levels of 10mol%, 12mol%, and 14mol% at various calcination temperatures (A: 10mol%, B: 12mol%, C: 14mol%). Stars represent tetragonal structure, filled circles represent rhombohedral β phase, and open squares represent rhombohedral γ phase. [43]

Comparing the results of these studies, it appears that the cubic phase is most desirable for maintaining high ionic conductivity. The studies conducted on DKKK and Praxair powders demonstrated that sintering can be used to create a single-phase structure. A sintering temperature
greater than 1300°C is necessary to ensure a purely cubic phase structure [42]. This is very important for an electrolyte, because the cubic structure is more open than the rhombohedral, which allows for oxygen ions to diffuse through the lattice more easily. Another important consideration is the possibility of phase transitions during the heating and cooling of the electrolyte material [41]. Depending on the operating temperature of the solid oxide fuel cell, these phase transitions could prove detrimental to the proper functioning of the fuel cell.

2.5 Grain Properties

In addition to phase structure and density, grain boundaries are also affected by sintering. Sintering temperatures in the range of 600°C to about 1100°C, produced little to no grain growth, but at 1200°C, the grain size begins to increase substantially in an exponential fashion [42]. Sintering at 1500°C produced grain sizes roughly two times the size of the 1200°C sintered samples [42].

Related to grain size, is the fracture mode. Scanning Electron Microscopy was used to compare the fracture mode of the DKKK and Praxair manufactured powders [32]. The DKKK samples displayed a transgranular fracture mode that followed the edges of the lattices, ignoring the grain boundaries [32]. Praxair displayed these same fractures in addition to intergranular fracture modes [32]. An intergranular fracture occurs when the fracture follows the lines of the grain boundaries [32]. These differences are most likely related to the different manufacturing processes employed by each company in producing these powders.

Mechanical properties of electrolyte materials are very important when designing solid oxide fuel cells. In order to create an electrolyte with a very high ionic conductivity, the material must be very thin. The one drawback to this, is the fragility of thin ceramics.
The Young’s modulus was determined for both DKKK and Praxair powders through the natural frequency method [44]. At room temperature, the DKKK powder sintered at 1500°C had a Young’s modulus of 217.67 ± 0.61 GPa, while the Praxair powder sintered at 1600°C had a value of 188.23 ± 2.81 GPa [44]. When the tests were conducted at increasing temperatures, a decline in Young’s modulus was observed until 500°C [44]. Above this temperature, the modulus began increasing again. This can be attributed to the phase transformation from cubic to rhombohedral during the lower temperatures and back to cubic structure above 500°C [44].

Another important mechanical property the electrolyte is its flexural strength. This was measured using the four-point test method [44]. The DKKK samples showed strength values between 200 and 230 MPa at room temperature [44]. Upon heating, these values decreased slightly until reaching a value of about 170 MPa at 1000°C [44]. The Praxair samples performed significantly worse with a maximum strength of only about 78 MPa at room temperature. These differences can be attributed to the higher porosity and inhomogeneous grain structure in the Praxair samples [44].

These properties can be effectively improved by sandwiching thin sheets of SCSZ between Yttria stabilized zirconia (YSZ) [44], [45], [46]. This is due to the difference in thermal expansion coefficients for both materials. The thermal expansion coefficient is lower for SCSZ from 20-600°C but becomes slightly higher than that of YSZ between 600 and 1000°C [45]. Although the difference is small, it is still important in producing residual stress. Upon sintering, the outer layers of YSZ contain compressive stresses while the inner core of SCSZ contains tensile stresses [45]. This is very important because the outer compressive stresses increase the fracture toughness and strength of the electrolyte while the inner tensile stresses improve the ionic conductivity [44], [45].
In assessing the biaxial strength, ring on ring technique can be utilized. The combination of SCSZ and YSZ has a biaxial strength of around 200 MPa at room temperature and 150 MPa at 800°C [45]. This aligns with very well with the above results of the DKKK samples.

Overall, it appears the electrolytes are strongest at room temperature, and as the temperature rises, strength decreases. It is also evident that the DKKK manufactured composition has much better mechanical properties. The processing technique of Praxair introduces a significant amount of impurities within the powder which contributes to the decrease in mechanical performance.

2.6 Theoretical Density Calculations

One of the most important steps in determining the porosity of an electrolyte material is calculating the theoretical density [47]. This process begins by determining the chemical formula and molecular structure. Sc$_2$O$_3$-CeO$_2$-ZrO$_2$ (SCSZ), has a fluorite structure which follows the chemical form of AO$_2$ [47]. Since Sc$_2$O$_3$ does not fit within this form, the entire chemical formula must be normalized so that the chemical formula matches the form of AO$_2$. After this, the unit cell mass can be calculated, and x-ray diffraction can be used to obtain the lattice parameters [47]. These lattice parameters are used to find the volume. After obtaining these values, the theoretical density is found by taking the unit cell mass and dividing it by the unit cell volume [47].

Although seemingly simple, great care must be taken to ensure the theoretical density is calculated correctly for each electrolyte composition. If there is any discrepancy in this value, the porosity of the material cannot be correctly determined.
2.7 Literature Review Summary

Solid oxide fuel cells are a revolutionary alternative to traditional fuel sources. With lower long-term operating costs, high efficiency ratings, and clean emissions, SOFCs are superior to most other forms of energy. In order to produce effective fuel cells, an electrolyte with a high ionic conductivity at lower operating temperatures is necessary. The current research suggests that Ceria-doped Scandia-stabilized Zirconia may be an excellent choice for this electrolyte material. It has a stable cubic phase structure, high conductivity, and high strength. Further research is needed to confirm these propositions, but the outlook is promising. This paper will seek to validate the current research as well as fill in the gaps regarding the optimal sintering temperature for SCSZ ceramics.
3 METHODOLOGY

3.1 Sintering Temperature and its Effect on Shrinkage, Density, and Porosity

Based on the literature review presented in Chapter 0 (p. 15) density is crucial factor in determining candidate materials for solid oxide fuel cells. Scandia and Ceria stabilized Zirconia has shown some of the highest conductivity levels and is more stable than other Zirconia based compositions [18]. In an effort to further improve the density and likewise reduce porosity, ceramic powders should be sintered at high temperatures, normally in the range of 1100°C to 1600°C [20], [21], [18].

For this research, 10 mol% Sc2O3 - 1 mol% CeO2 – ZrO2 (SCSZ) was chosen due to its improved phase stability at lower operating temperatures. The addition of Scandia and Ceria have shown to improve phase stability in the intermediate temperature range of 700-900°C [40]. For the purposes of this study, only one commercial powder of SCSZ was tested (Treibacher Industries).

3.1.1 Procedure for Calculating Shrinkage, Density, and Porosity

A standard mass balance was used to separate out 3.7g of the Treibacher SCSZ powder. This was poured into a cylindrical die and uniaxially pressed at 20 MPa as shown in Figure 13. A total of 80 samples were formed and separated into batches of 10. Prior to sintering, the dimensions of the cylinders were measured using a standard digital caliper. The average diameter and length of the cylinders were measured to be 10.15 mm and 18.28 mm respectively. A portion of the pre-sintered samples can be seen in Figure 14.
Figure 13: Uniaxial press of SCSZ powder in a cylindrical steel die

Figure 14: SCSZ samples prior to sintering
Next, the samples were sintered in batches of 10 at temperatures ranging from 900°C to 1600°C in 100°C increments. For the purpose of these experiments, pressureless dry air sintering was used. This is a method in which ceramic samples are exposed to standard atmospheric air pressure and heated to an appropriate temperature to allow solid state sintering to take place. As stated in the introduction (p. 13), sintering is a process in which the surface free energy is reduced, and mass is transported into the gaps between particles. This allows densification to occur and pores to be minimized [19], [20], [21]. To accomplish this, an open-air furnace (Micropyretics Heaters International, MHI) was used and the temperature was carefully controlled. Each batch of 10 samples was placed in a ceramic container and covered completely with additional SCSZ powder. The batch was then placed inside the furnace to begin the sintering process. The heating and cooling rate were kept constant at 5°C/min. Once the furnace reached the desired sintering temperature, a dwell time of 4 hours was used to hold the furnace at that temperature. The samples were then cooled back down to room temperature at a rate of 5°C/min. This process was repeated for each batch at temperatures ranging from 900°C to 1600°C. After all the batches were sintered, the diameter and length of each sample were measured again using the same digital caliper to check for shrinkage.

Density was calculated by utilizing the Archimedean emersion method [19]. This method is based on Archimedes principle which states that the buoyancy force acting on a submerged solid is equal to the weight of the displaced fluid [48]. The apparent weight of the solid in water is equal to the weight in air minus the buoyancy force. Through algebraic manipulation, the unknown density of the solid can be determined as seen in equation 3. $M$ is the mass in air of the solid, $\rho_w$
is the density of water (1 g/cm$^3$), $M_w$ is the mass in water of the solid, and $\rho$ is the density of the solid [48].

$$\rho = \frac{M \rho_w}{M - M_w}$$  \hspace{1cm} \text{Eq (2)}

The density of each batch of SCSZ cylinders was calculated using equation 3. The mass in water was measured using a density kit as pictured in Figure 15 below.

![Density setup with wire frame and water-filled beaker](image)

**Figure 15: Density setup with the wire frame and water-filled beaker placed inside an enclosed scale [49]**

A wire frame with an upper dish and lower basket was attached to the plate on the base of the scale. A stand was carefully placed around and over this plate so that the water-filled beaker could be situated onto the stand without its mass being registered by the scale. Each sample was first placed into the upper dish and its mass in air was measured. Then, tweezers were used to
lower the sample into the submerged basket and the mass in water was measured. After obtaining these measurements, the density of the sample was calculated.

To understand how this relates to porosity, the next step was to calculate the theoretical density. This is essentially a mathematical determination of the maximum density a chemical compound can obtain given its unique molecular structure [47]. An extensive guide to calculating theoretical density was provided by Rachel Rosten and others in an article published in the Journal of Undergraduate Materials Research at Virginia Tech [47]. The procedure set forth in this study was used to obtain the theoretical density of the Treibacher SCSZ powder. For the study of SCSZ, it was assumed that there are some minor impurities in the powder in the form of hafnium dioxide (HfO₂) and titanium dioxide (TiO₂). These were accounted for in the theoretical density calculations. The density percentage was found by taking a ratio of the experimentally found density to the theoretical density (equation 4). The porosity is simply the remaining percentage (equation 5). This data is useful in determining the optimal sintering temperature for maximum density.

\[
\%Density = \frac{\text{Density}_{\text{experimental}}}{\text{Density}_{\text{theoretical}}} \times 100\% \quad \text{Eq (3)}
\]

\[
\%Porosity = (1 - \frac{\text{Density}_{\text{theoretical}}}{\text{Density}_{\text{experimental}}}) \times 100\% \quad \text{Eq (4)}
\]

3.2 Raman Spectroscopy

Raman Spectroscopy is another important tool that helps identify phase stability and lattice structure of a given compound. Since intermediate temperature solid oxide fuel cells are still in the beginning stages of research, there is a lack of information pertaining to certain electrolyte
compositions, namely 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$. There have been, however, many studies published on Scandia doped Zirconia as discussed in the literature review (p. 22). This known data serves as a reference point to better understand the novel composition containing Ceria. The overall structure of both the 10 mol% Sc$_2$O$_3$ – 90 mol% ZrO$_2$ and 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$ is of the fluorite, AO$_2$ form. This implies that the Raman shifts for both compositions should have some similarities. The experiments conducted on the Scandia and Ceria doped Zirconia aim to uncover the lattice structure and associated phases of this composition.

3.2.1 Procedure for Obtaining Raman Spectra

For the Raman Spectroscopy tests, a Renishaw InVia Raman microscope was used as pictured in Figure 16.

![Figure 16: Renishaw InVia Raman Microscope](image-url)
Before samples were tested, a system health check was performed through InVia’s Wire software to ensure all internal motors are properly aligned. A small sample of silicon was used to calibrate the microscope. The 50x magnifying lens was used to bring the silicon surface into focus and a Raman spectrum was collected. Silicon is a great material to use for the Raman calibration because it has a known Raman shift at 520 cm\(^{-1}\). The collected spectrum of the silicon must match this shift of 520 cm\(^{-1}\) with an error of no more than 1 cm\(^{-1}\). If the spectrum does not clearly show this shift, then the Raman Microscope must be calibrated before testing can begin. This process was repeated each time the microscope was turned on and before tests were run on the SCSZ powder to ensure the collected spectrums were free from errors.

Several Raman spectra were collected on the Ceria and Scandia doped Zirconia powder to determine if the lattice structure is temperature dependent and whether there is any appreciable phase transition. To establish a baseline spectrum for the SCSZ powder, Raman was collected at room temperature (20°C) utilizing both the 532nm and 785nm laser to obtain the complete spectral range. For the varying temperature experiments, two heating stages were used, Linkam THMS600 and Linkam TS1500 as seen in Figure 17 and Figure 18, with a heating/cooling rate of 20°C min\(^{-1}\). Cooling lines were attached to the stages and a water pump to ensure the stages did not overheat during testing.
After the baseline spectra were collected at room temperature, additional Raman spectra were collected at various temperatures and dwell times using the 532nm laser. For the first experiment, the powder was placed inside the THMS600 stage and the temperature of the heating stage was increased from 23°C to 583°C in increments of 50°C at a rate of 20°C min⁻¹. Spectral
measurements were taken at 23°C and each increment thereafter with no appreciable dwell time. Before and after images were taken of the powder utilizing the optical microscope to ensure the Raman spectrum was being collected at the same location on the powder’s surface for each Raman scan (images can be found in the results section, p.51).

The next Raman scans were taken with the 532 nm laser using the TS1500 stage at temperatures ranging from 20°C to 1150°C in increments of 50°C with no dwell. The heating rate was kept constant at 20°C min⁻¹. The 50x long working distance lens was used to refocus the laser before each scan.

To determine whether dwell time influences molecular structure and phase transition, additional Raman spectra were taken at 300°C with increasing dwell times. The TS1500 stage was heated to 300°C and scans were taken with the 532 nm laser starting at no dwell and increasing in increments of 10 minutes to a dwell time of 4 hours. The laser was refocused before each scan using the 50x long working distance lens.

3.3 Powder Diffraction

To test phase structure and lattice parameters, the samples were sent to Argonne National Laboratory in Lemont, Illinois for high resolution x-ray diffraction testing. To prepare the samples for testing, one sample from each sintering temperature was ground up using a mortar and pestle (Figure 20). The ground powder was then placed into eight Kapton capillary tubes with each tube containing powder from a different sintering temperature (900°C, 1000°C, 1100°C, 1200°C, 1300 °C, 1400 °C, 1500 °C, and 1600 °C). These tubes were placed into mounting bases and covered with a magnetic cap. The basic set up of the capillary tubes and associated equipment is shown in Figure 19 and Figure 20.
Once the samples arrived at Argonne National Laboratory, they were placed into the Beamline 11-BM powder diffraction instrument and diffraction tests were run at a temperature of 295K.
4 RESULTS AND DISCUSSION

4.1 Shrinkage

Before sintering, the cylindrical samples had an average diameter of 10.15 mm and an average length of 18.28 mm. At sintering temperatures of 900°C and 1000°C, there was minimal shrinkage. The 900°C batch saw the least amount of shrinkage of all the samples with a decrease in diameter and length of 0.88% and 3.56% respectively. At 1000°C, the shrinkage was slightly higher but still less than 8%. The 1100°C batch was the first to show a significant change with shrinkage of about 18% for both the diameter and length. For sintering temperatures above 1100°C, the shrinkage began to level off with values ranging from 21.69% to 26.61%. Figure 22 shows the average shrinkage in the diameter and length for each sintering temperature. As can be seen in Figure 22, higher sintering temperatures produce greater shrinkage, but only up until a temperature of about 1200°C. Above 1200°C, the shrinkage was relatively constant at about 24%. This aligns very well with the results obtained in former studies as seen in Figure 7 from the literature review [39]. This study used the same composition of 1 mol% CeO₂ – 10 mol% Sc₂O₃ – 89 mol% ZrO₂ but from a different manufacturing company (Daiichi Kigenso Kagaku Kogyo Co.). They found a constant shrinkage percentage of about 22% beginning at around 1200°C [32].
Visually, the decrease in size was seen most clearly at about 1200°C. Figure 23, Figure 24, Figure 25, Figure 26, and Figure 27 show the samples after sintering. These images are a good visual representation of the shrinkage with respect to sintering temperature. The batches sintered at 1200°C, 1300°C, 1400°C, 1500°C, and 1600°C all appear to be very close in size.
Figure 23: Diagonal view of sintered SCSZ samples

Figure 24: Side view of sintered SCSZ samples
Figure 25: Top view of sintered SCSZ samples
Figure 26: Top view of 900°C, 1200°C, and 1600°C showing that at 1200°C, the shrinkage becomes relatively constant

Figure 27: Side view of 900°C, 1200°C, and 1600°C showing that at 1200°C, the shrinkage becomes relatively constant
4.2 Density and Porosity

Since the shrinkage in volume and density are inversely related, it was expected that the density should increase with increasing sintering temperature. This was indeed the case for the SCSZ samples. The density of the 900°C samples was the lowest at 3.0809 g/cm³. The density began to increase until reaching a sintering temperature of 1300°C. At 1300°C and above, the density remained relatively constant at about 5.6 g/cm³. The densities at each temperature are shown in Figure 28. Again, this data is consistent with known sintering behavior of Scandia stabilized zirconia [32], [39], [40].

![Density vs Sintering Temperature](image)

**Figure 28: Density vs sintering temperature for SCSZ ceramic**

To determine the porosity, it was necessary to first determine the theoretical density. This was calculated by normalizing the SCSZ chemical formula into the AO₂ form. A sample of these calculations can be seen Appendix A: Sample Theoretical Density Calculation (p.64).
theoretical density was calculated twice to account for any impurities that may be present. In the first calculation, it was assumed the powder had small impurities of HfO$_2$ and TiO$_2$ which resulted in a theoretical density of 5.736 g/cm$^3$. The second calculation assumed there were only HfO$_2$ impurities, which resulted in a theoretical density of 5.765 g/cm$^3$. Therefore, the presence of TiO$_2$ impurities is shown to only slightly decrease the density of the powder. The ratio of the experimentally determined densities and the theoretical density was calculated as a percentage. The porosity is found by taking the remainder of this percentage as presented in Eq (4. Smaller porosity is desired to improve the ionic conductivity of the ceramic. At 900°C and 1000°C, the porosity was the highest at about 39% and 46%. At 1100°C, the porosity dropped significantly to about 17%. It continued to drop until reaching 1300°C, at which point, the porosity became nearly constant at about 2%. In Figure 29 the porosity for each sintering temperature is plotted using both theoretical density calculations, with and without TiO$_2$ impurities. This data closely resembles the porosity of DKKK manufactured SCSZ powder found in past studies [39]. Their porosity results are shown in Figure 7 in the literature review.

The density and porosity of Ceria-doped, Scandia-stabilized Zirconia is greatly affected by sintering temperature. Density and porosity are inversely related, so as the density increases with sintering temperature, the porosity decreases. The lowest porosity that was obtained using the open-air, pressureless sintering method was about 2%. Sintering above 1300°C did not significantly improve this lower limit of porosity. Based on this information, it appears that sintering should be kept at temperatures of 1300°C and above in order to maintain a high level of ionic conductivity.
Figure 29: Porosity percentage vs sintering temperature for SCSZ powder assuming impurities present

4.3 Raman Spectra

In order to have consistent data, before and after images were taken of the Ceria-doped, Scandia-stabilized Zirconia powder (SCSZ) to help locate the position on the sample at which Raman tests were conducted. The microscope lens and laser were also refocused before each measurement. This is a crucial step because the particles will shift throughout the heating process due to thermal energy and expansion. Before and after images of the powder at 23, 350, and 583°C are shown in Figure 30.
Figure 30: Before and after microscopic images of SCSZ powder using 50X long working distance magnification lens. Images show the powder at 23°C, 350°C, and 583°C.

The full Raman spectrum of the SCSZ powder was taken at room temperature (20°C) with and without a dwell period. Figure 31, graph A, shows the full spectrum associated with the 532 nm laser for no dwell as well as a 4-hour dwell. Graphs B-E are magnifications of the two Raman spectra. When looking at the Raman shift from 0-1200 cm⁻¹, graphs B (4-hour dwell) and D (no dwell) show a very similar peak pattern. In the case of no dwell, the peaks are more pronounced and closer together with Raman shift values of 146, 260, 315, 371, 438, 604, and 966 cm⁻¹. After a dwell time of 4 hours, the peaks become broader and lower in intensity with key values of 146, 255, 322, 387, 448, 593, 972 cm⁻¹. These values align very closely with a similar study conducted.
on 10mol% Sc$_2$O$_3$-1mol% CeO$_2$-89mol% ZrO$_2$ but are not identical [41]. In this study, the powder was manufactured by DKKK in Japan and was known to consist of a cubic lattice structure based on previous x-ray diffraction analysis [32]. The study recorded peaks at 315, 378, 480, 620, and 971 cm$^{-1}$ [41]. Considering the strong similarities and peak behavior of the Raman tests conducted in this work and past studies, the Treibacher SCSZ powder is reasoned to be cubic in nature as well.

Another very significant component of the Raman spectra occurs between 5000 and 8000 cm$^{-1}$. In this region, there is a strong excitation response to the 532nm laser that is beyond the expected frequency range of the cubic SCSZ powder. These peaks are nearly identical to past studies and were found to be the result of small impurities within the powder [41]. The exact type of impurity is difficult to tell based solely on the Raman results.
Figure 31: Full range Raman spectra of SCSZ powder at 20°C with a 4-hour dwell and without a dwell, 532 nm laser, TS1500 stage. (A: Full range comparison, B, C, D, E: Magnified segments of the spectra showing Raman shifts peaks)
When a 785nm excitation laser is used at 20°C with no dwell, the Raman spectrum changes quite significantly as seen in Figure 32. The characteristic cubic peaks are no longer evident, and the peaks associated with impurities shift in frequency. In the range of 1000-2000 cm\(^{-1}\), the peaks are of the same structure as the impurity peaks in Figure 31. There are also two peaks beyond 2000 cm\(^{-1}\) that appear in former studies and may also be attributed to impurities [41].

Between 0 and 1000 cm\(^{-1}\), there are strong peaks at 402 and 593 cm\(^{-1}\) and two broader, smaller peaks at 178 and 265 cm\(^{-1}\). This is very different from other studies which place the peaks at 239, 398, 478, 620, and 707 cm\(^{-1}\) [41]. One possible reason for this is the difference in manufacturing process between the DKKK powder used in past research and the Treibacher powder studied in this work. It is possible that the impurities in the Treibacher powder react more strongly to the 785nm laser than the fluorite SCSZ structures.
Figure 32: A: Full range Raman spectra of SCSZ at 20°C without dwell, 785 nm laser, TS1500 stage. B: Magnified segment of Raman spectra.
After establishing a baseline Raman spectrum for the powder, temperature was increased to determine whether there would be any appreciable impact on the spectrum. In the initial stages of heating, the peaks of the Raman spectra did not appear to change significantly. There were consistent peaks measuring at 147, 253, 321, 378, 445, 614, and 964 cm\(^{-1}\) for both the TS1500 and THMS600 stages, Figure 33 and Figure 34. After 400\(^{\circ}\)C, the majority of peaks in the range of 250 and 600 cm\(^{-1}\) become less intense and eventually flatten out. The peaks at 147 and 614 cm\(^{-1}\) were clearly visible for each increasing temperature and are very similar to previous studies conducted on Scandia doped Zirconia [43] [41]. The peak at 964 cm\(^{-1}\) is very prominent at room temperature, but very quickly flattens out once the temperature reaches 300\(^{\circ}\)C. Once the temperature was raised to 1100\(^{\circ}\)C and above, Raman fluorescence can be seen in the sudden increase in slope of the spectra trendline. In both Figure 33 and Figure 34, it is evident that most of the changes in the spectrum occur between 300\(^{\circ}\)C and 600\(^{\circ}\)C.
Figure 33: Raman spectra of SCSZ powder with increasing temperature and no dwell, 532 nm laser, TS1500 stage
Figure 34: Raman spectra of SCSZ powder with increasing temperature and no dwell, 532 nm laser, THMS600 stage
When considering the effects of dwell time on the Raman spectrum and associated phase transitions of Ceria and Scandia doped Zirconia, a constant temperature of 300°C was used with the 532nm excitation laser. The temperature of 300°C was chosen based on Figure 33 and Figure 34, which showed a transition in the Raman spectra beginning at about 300°C. This temperature was also chosen based on past x-ray diffraction experiments which showed a transition from cubic to beta phase for the SCSZ powder at about 300°C [32].

As can be seen in Figure 35, the Raman spectra collected on the Treibacher powder showed little to no change at 300°C with varying dwell time. Peaks can be seen at 144, 246, 322, 387, 448, and 597 cm\(^{-1}\). This indicates that at 300°C, this powder does not experience a phase transition from cubic to rhombohedral as witnessed in other studies [32]. The peaks are, however, broader and less intense when compared to the spectra taken at room temperature (20°C).
Figure 35: Raman spectra of SCSZ powder at 300°C with increasing dwell time, 532 nm laser, TS1500 stage
4.4 X-Ray Powder Diffraction

The results from the 11-BM X-Ray powder diffraction experiments showed consistent diffraction peaks for each sample, which suggests that the Treibacher powder phase structure is stable at room temperature regardless of the sintering temperature used. This data, however, varied greatly from previous studies conducted on scandia and ceria doped zirconia. As shown in Figure 36 below, there are visible diffraction peaks at 2θ angles of 8, 9, 13 15. This data contradicts previous findings that reported peaks at 30, 35, 50, and 60 (2θ angle in degrees) [39]. These differences in diffraction patterns may be attributed to a different lattice structure for the sintered Treibacher powder, but further experiments and testing are necessary to determine if this is indeed the case.
Figure 36: 11-BM Beamline X-Ray Powder Diffraction for SCSZ powder sintered at different temperatures
CONCLUSION AND FUTURE WORK

Further research must be conducted to determine the phase stability of the Treibacher SCSZ powder at various temperatures. For the highest ionic conductivity to be achieved, the phase structure must be preferably cubic in nature [43]. This type of lattice structure leaves greater room for the transportation of oxygen ions compared with the rhombohedral phase. This work investigated the shrinkage, density, and porosity of 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$ produced by Treibacher Industries. Raman spectroscopy and X-Ray Powder Diffraction was utilized to determine phase stability at various temperatures. The Raman spectrum of the powder shifted with increasing temperature with some peaks disappearing altogether. Most of the change happened between 300$^\circ$C and 600$^\circ$C. This is a possible indication of phase transition. When a constant temperature of 300$^\circ$C was chosen and the powder was subjected to increasing dwell times, the Raman spectrum remained constant, which suggests that there was no phase transition at this temperature. The X-Ray Powder Diffraction results showed consistency among the different samples, however the data varied greatly from past studies on SCSZ powder. Before an optimal sintering temperature can be determined for scandia and ceria doped zirconia, additional powder diffraction and Raman spectroscopy experiments should be completed. The phase structure’s dependence on dwell time can be further investigated by dwelling at temperatures ranging from 350$^\circ$C to 650$^\circ$C in increments of 50$^\circ$C. With this additional data, a more accurate conclusion can be drawn regarding the optimal sintering temperature for the Treibacher 1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$ composition.
APPENDIX A: SAMPLE THEORETICAL DENSITY CALCULATION
Theoretical Density Sc2O3-CeO2-ZrO2 including TiO2

Mole Percentages

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc_{2}O_{3}</td>
<td>0.1</td>
</tr>
<tr>
<td>CeO_{2}</td>
<td>0.01</td>
</tr>
<tr>
<td>HfO_{2}</td>
<td>0.008</td>
</tr>
<tr>
<td>ZrO_{2}</td>
<td>0.868</td>
</tr>
<tr>
<td>TiO_{2}</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Ions

- O_{1} = 3 \cdot Sc_{2}O_{3} = 0.3
- O_{2} = 2 \cdot CeO_{2} = 0.02
- O_{3} = 2 \cdot HfO_{2} = 0.016
- O_{4} = 2ZrO_{2} = 1.736
- O_{5} = 2TiO_{2} = 0.028

Solution Formula

\[ Ce_{0.01}Hf_{0.008}Ti_{0.014}Sc_{0.2}Zr_{0.868}O_{2.1} \]

\[ \text{O}_{\text{tot}} = O_{1} + O_{2} + O_{3} + O_{4} + O_{5}, \quad \text{O}_{\text{tot}} = 2.1 \]

Normalize to AO_{2}

\[ \sum_{A} := Sc + Ce + Hf + Ti + Zr = 1.1 \]

Normalized Charges

- \( Ce_{\text{norm}} := \frac{Ce}{\sum_{A}} = 9.091 \times 10^{-3} \)
- \( Ti_{\text{norm}} := \frac{Ti}{\sum_{A}} = 0.013 \)
- \( Hf_{\text{norm}} := \frac{Hf}{\sum_{A}} = 7.273 \times 10^{-3} \)
- \( Zr_{\text{norm}} := \frac{Zr}{\sum_{A}} = 0.789 \)
- \( Sc_{\text{norm}} := \frac{Sc}{\sum_{A}} = 0.182 \)
- \( O_{\text{norm}} := \frac{O_{\text{tot}}}{\sum_{A}} = 1.909 \)

Normalized Formula

\[ Ce_{0.000391}Hf_{0.007273}Ti_{0.013}Sc_{0.182}Zr_{0.789}O_{1.909} \]

* 1 amu = 1.6605 \times 10^{-24} \text{ g} *

Mass of Chemical Formula

- \( Ce_{\text{mass}} = 140.12 \text{ amu} \)
- \( Hf_{\text{mass}} = 178.49 \text{ amu} \)
- \( Sc_{\text{mass}} = 44.956 \text{ amu} \)
- \( Ti_{\text{mass}} = 47.867 \text{ amu} \)
- \( Zr_{\text{mass}} = 91.224 \text{ amu} \)
- \( O_{\text{mass}} = 15.999 \text{ amu} \)
Mass in one formula unit

\[ \text{FormUnit}_{\text{mass}} = \text{Ce}_{\text{mass}} \times 0.009091 + \text{H}_{\text{mass}} \times 0.007273 + \text{Sc}_{\text{mass}} \times 0.182 + \text{Ti}_{\text{mass}} \times 0.013 + \text{Zr}_{\text{mass}} \times 0.789 + \text{O}_{\text{mass}} \times 1.909 \]

\[ \text{FormUnit}_{\text{mass}} = 113.894 \quad \text{amu} \]

*There are four AO_2 formula units per unit cell*

Mass in one unit cell

\[ \text{UnitCell}_{\text{mass}} = \text{FormUnit}_{\text{mass}} \times 4 = 455.576 \quad \text{amu} \]

\[ \text{UnitCell}_{\text{Total}} = \text{UnitCell}_{\text{mass}} \times 1.6605 \times 10^{-24} \]

Lattice Parameter

\[ \text{Lattice} = 5.09 \times 10^{-8} \quad \text{cm} \quad \text{Unit Volume} = \text{Lattice}^3 \]

Theoretical Density

\[ \text{Density}_{\text{theory}} = \frac{\text{UnitCell}_{\text{Total}}}{\text{Unit Volume}} \]

\[ \text{Density}_{\text{theory}} = 5.736 \quad \text{g/cm}^3 \]
LIST OF REFERENCES


https://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html.
[Accessed 27 October 2018].


