Fabrication and Electrical Characterization of Uranyl-based Semiconductors

Seth Lawson

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I am submitting herewith a dissertation written by Seth Lawson entitled "Fabrication and Electrical Characterization of Uranyl-based Semiconductors." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

Thomas T. Meek, Major Professor

We have read this dissertation and recommend its acceptance:

Claudia Rawn, Roberto Benson, Howard Hall

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
FABRICATION AND ELECTRICAL CHARACTERIZATION OF URANYL-BASED SEMICONDUCTORS

A Dissertation Presented for the Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Seth Douglas F. Lawson
August 2019
ACKNOWLEDGEMENTS

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ABSTRACT

Highly dense pellets of U₃O₈ [uranyl uranate] and UO₃ [uranyl oxide] were fabricated to evaluate their possible use as solid state, direct conversion, semiconductor neutron detectors. By utilizing uranium oxide semiconductors, devices would not require a neutron moderating layer to first interact with neutrons, reducing the probability of reaction products failing to produce a signal in the semiconductor. In addition, fissile isotopes of uranium, such as ²³⁵U [uranium-235] have a high probability of undergoing fission when absorbing thermal neutrons, with resulting reaction products from neutron induced fission producing quantities of electron-hole pairs orders of magnitude more than produced by lighter high neutron cross-section isotopes such as ¹⁰B [boron-10] or ⁶Li [lithium-6].

This dissertation investigates the modification of electrical properties, such as electrical resistivity, by changing conditions of fabrication to include uniaxial pressing and heating to increase sintering as well as changes to composition by varying available oxygen. By use uniaxial hot pressing, electrical resistivity of uranyl oxide pellets was measured in the 10⁹-10¹¹ Ω-cm [ohm centimeter] range, orders-of-magnitude higher than the largest previously reported values.
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CHAPTER ONE
INTRODUCTION AND LITERATURE REVIEW

1.1 Neutron Detection Materials

Neutron detection, with greater resolution and increased efficiency is vital for advances in many areas of scientific research as well as medicine and homeland security concerns. Limits on $^3$He-based detectors has driven development toward alternative, solid-state materials with large neutron interaction cross sections paired conventional semiconductor devices to collect signal from neutron interaction products using sophisticated geometries and processing methods. Alternatively, high neutron cross section semiconductors have the potential to achieve higher total efficiency with simplified devices. Uranium has a large neutron interaction cross section as well as semiconductor properties when formed as an oxide [1]–[3], with available quantities of uranium in the tens of thousands of metric tons. In addition to these properties $^{235}$U can undergo neutron-induced fission, resulting in reaction products of 165MeV, providing increased detector efficiency as well as improved gamma ray rejection sensitivity.

The primary focus for this research has been on the radioactive candidate materials such as U$_3$O$_8$ and UO$_3$ as the hardware components of solid-state neutron detection, acting both as the semiconductor and the high-cross-section neutron interaction layer. While software and electronics do play important roles on effective neutron detection, their role in this dissertation will largely be to place reasonable constraints on proposed device properties based on preexisting technologies used in current neutron detectors. Unlike charged particles, neutrons do not have Coulombic interactions, thus detectors
must utilize neutron absorption events within the detector material to generate a signal. Such materials must then have both a high cross section for neutron interaction, measured in barns, as well as the ability to produce high energy reaction products when a neutron is absorbed. Thermal neutron absorbing include helium-3, lithium-6, boron-10, and uranium-235, which allow for detection of the reaction products instead of the neutron itself by producing ionized, high energy particles such as alpha particles or other light ions, protons or additional neutrons, gamma rays, or even heavy ions when considering actinides such as uranium. These particles must be discriminated from external high energy particles such as gamma rays depending on the type of detector and the gamma sensitivity of the isotope being used. For uranium, resulting energies from neutron induced fission are typically far in excess of other possible sources requiring signal discrimination, even with natural isotopic compositions (<0.1% $^{235}$U).

## 1.2 Detector Types

Lighter elements such as $^3$He, $^6$Li and $^{10}$B are used in gas proportional detectors, scintillation detectors, or even semiconductor detectors. The probability of neutron absorption occurring within any of these detector types depends on the energy of the incident neutron, the cross-section of the isotope at that energy level, and the atomic density of the interactive isotope. This can best be visualized by imagining the difference between catching a small object with a large mesh net versus a tightly woven material. As a neutron is smaller than repulsive forces on the nuclei would allow, many layers would need to be in place to increase the chance a catching it. Furthering this example, detecting additional neutrons would require additional layers be present to overcome any damage previous interactions may have caused.
The first method for neutron capture uses gas proportional counters, or GPCs, using $^3$He as a neutron reactive gas. They can be very useful for neutron detection in both science and security applications as the isotope is less sensitive to gamma rays and very large cross-section of 5337 barns to thermal neutrons, making it an ideal candidate for high efficiency neutron detection. As the interaction area is gaseous, the atomic density is lower, and the physical dimensions of the detector are large. However, $^3$He production is tied to tritium decay, generally part of production and maintenance of nuclear weapons. Due to the end of such production, the limited supply has shrunk rapidly with the heightened demand for portal monitors capable of detecting nuclear materials at high value targets or within shipping containers following the 9/11 attacks. The resulting rationing of $^3$He usage outlined the need for accelerated development for newer, innovative ways of neutron detection using materials available in abundance. Alternatively, $^{10}$B enriched BF$_3$ can also be used in a GPC but is highly toxic. Boron-based GPCs are also typically limited for thermal neutron detection, so high energy neutrons would require moderating layers resulting in a narrowed detection spectrum. For the area
of nuclear security, various neutron energy levels can be of simultaneous interest. Larger single detectors with uniform moderating thicknesses to thermalize incident neutrons would be less practical for detecting varying energy neutrons. Multiple smaller detectors, potentially with varying thermalization thicknesses or even just physical distances separating them would have increased value for retaining as much mission critical information for threat determination.

Scintillators using $^6$Li glass fibers and later LiCaAlF$_6$ crystals provide high $^6$Li densities to aid in neutron interactions but suffer from higher gamma ray sensitivity. The glass fiber detectors are robust, scalable to mission parameters and, despite a neutron interaction cross section about 20% of $^3$He, have an order of magnitude increase in capture efficiency due to the atom density within the fiber. The LiCaAlF$_6$ crystal require scintillating dopants, typically rare earth elements, whose selection must balance needs for increased photon generation, and better pulse height discrimination, with the need for shorter decay times in high radiation environments.

Semiconductor detectors present new possibilities as well as challenges for neutron detection. Like the previous detector types, these devices pair neutron reactive materials with the ability to measure the resultant signal energy. Conventional semiconductor materials such as silicon and germanium have low interaction probabilities with neutrons. For example, the thermal neutron cross section for silicon is approximately 2 barns, compared to over 5000 barns for $^3$He. This would require detector thickness of several inches, negating the portability advantages possible with solid-state silicon detectors. The more obvious mechanism for increasing neutron interaction probability is pairing the semiconductor with a layer of neutron sensitive material within the device structure, such
that reaction products would pass into the semiconductor, producing large quantities of electron-hole pairs beyond neutron absorption layer. These conversion layer devices can utilize typical Si or GaAs semiconductors as Schottky diodes or p-n junctions to separate these electron-hole pairs with a thin layer or $^{10}$B or $^6$LiF deposited on the semiconductor surface. Reaction energies from the primary nuclear reaction typically measure 0.5 – 1.5 MeV and capable of generating additional reactions through exciting and ionizing atoms along their path. Energies from the primary products as well as those generated through cascade interactions can contribute to the signal for determining neutron interaction. Electron-hole pairs are typically within the diffusion length with the space charge region when operating in reverse bias, allowing collection at the contact surfaces. A p-i-n device can also be utilized to enhance response times and charge carrier collection efficiencies. Schematics for a planar configuration p-n type device is shown in Figure 2.
A planar conversion device relies on enough thickness of the neutron absorption material to capture a high probability of incident neutrons, with probability increasing with thickness. For example, $^{10}$B requires approximately 50 μm to absorb 90% of thermal neutron flux. However, the average range of travel, or mean free path, are less than 4μm, resulting in detection efficiencies less than 5% [4]. Compared to $^{3}$He GPC efficiencies above 70%, the planar configuration is not a viable alternative. Figure 3 [4] illustrates the results of neutron capture used in indirect conversion semiconductor detection. Further, reaction products deposit energy while migrating through the conversion layer, resulting in fewer e-h pairs for detection to occur. Additionally, as the two charged particles travel in opposite directions relative to each other, only half of reaction products generally contribute to generation of electron-hole pairs. Three-dimensional geometries using ion etching, lithographies, and material deposition methods have provided additional efficiency improvements above 20% and calculations for stacked thin planar devices exceeding 25% [5]. Figure 4 shows neutron absorption products reaching semiconductor layers filled in around neutron reactive pillars through the device thickness. Three dimensional illustrations of some of the more complex device heterostructures are shown in Figure 5, including the pillar design (e,f) [5].

With these unique geometries, proper thicknesses for neutron conversion layers could generate increased charge carrier densities, improving detection efficiencies rivaling that of $^{3}$He according to modelling. However, fabrication of these devices is challenging. Fabricating such geometries would likely make the detectors less robust, especially when exposed to damage from neutron interaction cascades.
Figure 3. Neutron reactions for thermal neutron detection [4].

Figure 4. Cross sectional schematic for pillar structured neutron detector.
Figure 5. Complex indirect-conversion heterostructures [5]. Orange and green regions represent neutron reactive material.
1.3 Radioactive Detector Materials

Actinides present unique qualities when considered for use as neutron interaction materials when compared to those currently being explored as indirect conversion solid-state detectors. In addition to comparable, or in some cases larger, neutron interaction cross-sections, certain isotopes will release substantial energy (>165 MeV) as products from neutron-induced fission [6]. The energy deposition of these daughter fragments into an actinide semiconductor material would result in electron-hole-pair production by as much as four orders of magnitude. Uranium oxides (specifically UO$_2$, U$_3$O$_8$, and UO$_3$), have been documented as semiconductors [7]–[10]. This increase in carrier concentration offsets material limitations such as increased leakage current, lower carrier mobility, and higher recombination sites associated with direct conversion neutron detectors. Further, the lower level discriminator may be set well above the energy levels of any background decay or photon.

![Figure 6. Schematic of direct conversion neutron detector.](image)
Structural properties within the $\text{U}_3\text{O}_8$–$\text{UO}_3$ system play an important role in the semiconductor properties of these compounds, both of which are of importance to their capabilities for use as direct conversion neutron detection devices. The processing methods for the uranium-oxygen compounds have been systematically characterized based on stoichiometry for nearly a century and contains many intermediate compounds that coexist in solid solution and in a variety of nonstoichiometric compositions. Physical properties of these compounds in their established polymorphic variations are included in Table 1. However, as the oxygen composition increases toward the trioxide ratio, other compounds begin to form even in ambient conditions. Therefore, the uranyl oxide-hydroxide-peroxide system should be considered. This system has remained difficult to fully characterize in part due to the process history playing a role in formation of various polymorphic phases and the hydrolysis of $\text{UO}_3$ even in ambient conditions [11]–[15]. Physical properties for these hydrated phases are shown in Table 2. As noted, only the $\text{U}_3\text{O}_8$ hydroxide compound was reported with diffraction calculated density values.

Of major interest early on was the use of $\text{U}_3\text{O}_8$ as a neutron detector material. $\text{U}_3\text{O}_8$ is naturally occurring as a further oxidized component of the mineral form of $\text{UO}_2$, uraninite, also referred to as pitchblende. As expected by the increased percentage of oxygen, $\text{U}_3\text{O}_8$ is less dense than $\text{UO}_2$, at 8.3 vs 10.97 g/cm$^3$. Additionally, $\text{U}_3\text{O}_8$ is chemically stable in ambient conditions and is one of the preferred forms for the disposal of post-enrichment waste after conversion from uranium hexafluoride ($\text{UF}_6$) and can also be easily produced by heating uranyl oxide ($\text{UO}_3$) [16], [17] generated during mining and refinement or uranium ores [18]–[20].
Table 1. Physical properties of stoichiometric uranium oxides [21].

<table>
<thead>
<tr>
<th>Formula</th>
<th>Color</th>
<th>nt.p (K)</th>
<th>Symmetry</th>
<th>Lattice parameters</th>
<th>Density (g·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>UO₂</td>
<td>brown to black</td>
<td>3138</td>
<td>fcc</td>
<td>5.4704</td>
<td></td>
</tr>
<tr>
<td>U₄O₉</td>
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<td></td>
<td>bcc</td>
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<tr>
<td>U₁₆O₃₇(*)</td>
<td>black</td>
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<td>tetragonal</td>
<td>5.407</td>
<td>5.497</td>
</tr>
<tr>
<td>U₈O₁₅(*)</td>
<td>black</td>
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<td>monoclinic</td>
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<td>5.559</td>
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<tr>
<td>α-U₃O₇</td>
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<td>tetragonal</td>
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<td>5.400</td>
</tr>
<tr>
<td>β-U₃O₇</td>
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<td>tetragonal</td>
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<td>5.547</td>
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<tr>
<td>γ-U₃O₇</td>
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<td>tetragonal</td>
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<td>β-U₂O₅</td>
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<td>hexagonal</td>
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<td>5.481</td>
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<td>U₈O₂₁</td>
<td>orthorhombic</td>
<td></td>
<td>6.796</td>
<td>3.958x8</td>
<td>4.145x2</td>
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<td>U₁₁O₂₉</td>
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<td>6.765</td>
<td>3.956x11</td>
<td>4.140x2</td>
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<tr>
<td>α-U₃O₈</td>
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<td>orthorhombic</td>
<td>6.716</td>
<td>11.960</td>
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<tr>
<td>β-U₃O₈</td>
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<td></td>
<td>orthorhombic</td>
<td>7.069</td>
<td>11.445</td>
</tr>
<tr>
<td>U₁₂O₃₅(*)</td>
<td>black olive</td>
<td></td>
<td>orthorhombic</td>
<td>6.910</td>
<td>3.920</td>
</tr>
<tr>
<td>A-UO₃</td>
<td>orange</td>
<td>723(d)</td>
<td>amorphous</td>
<td></td>
<td>6.80</td>
</tr>
<tr>
<td>α-UO₃</td>
<td>beige</td>
<td>723(d)</td>
<td>orthorhombic</td>
<td>6.840</td>
<td>43.450</td>
</tr>
<tr>
<td>β-UO₃</td>
<td>orange</td>
<td>803(d)</td>
<td>monoclinic</td>
<td>10.340</td>
<td>14.330</td>
</tr>
<tr>
<td>γ-UO₃</td>
<td>yellow</td>
<td>923(d)</td>
<td>orthorhombic</td>
<td>9.813</td>
<td>19.930</td>
</tr>
<tr>
<td>δ-UO₃</td>
<td>deep</td>
<td>673(d)</td>
<td>cubic</td>
<td>4.160</td>
<td></td>
</tr>
<tr>
<td>ε-UO₃</td>
<td>brick red</td>
<td>673(d)</td>
<td>triclinic</td>
<td>4.002</td>
<td>3.841</td>
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<td>ζ-UO₃</td>
<td>brown</td>
<td></td>
<td>orthorhombic</td>
<td>7.511</td>
<td>5.466</td>
</tr>
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</table>

(d): decomposes
(*): Parameters refer to pseudo-cell
Table 2. Physical properties of UO$_3$ and UO$_4$ hydrates [21].

<table>
<thead>
<tr>
<th>Formula</th>
<th>Color</th>
<th>Symmetry</th>
<th>Lattice parameters</th>
<th>Density (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
</tr>
<tr>
<td>α-UO$_3$•0.8H$_2$O</td>
<td></td>
<td>orthorhombic</td>
<td>4.27-4.30</td>
<td>10.19-10.24</td>
</tr>
<tr>
<td>α-UO$_2$(OH)$_2$ (=UO$_3$•H$_2$O)</td>
<td>greenish yellow</td>
<td>orthorhombic</td>
<td>4.242</td>
<td>10.302</td>
</tr>
<tr>
<td>β-UO$_2$(OH)$_2$ (=UO$_3$•H$_2$O)</td>
<td>yellow-green</td>
<td>orthorhombic</td>
<td>5.6438</td>
<td>6.2867</td>
</tr>
<tr>
<td>γ-UO$_2$(OH)$_2$ (=UO$_3$•H$_2$O)</td>
<td>gray-chamois</td>
<td>monoclinic</td>
<td>6.419</td>
<td>5.518</td>
</tr>
<tr>
<td>UO$_2$(OH)$_2$•H$_2$O (=UO$_3$•H$_2$O) (schoepite)</td>
<td>bright yellow</td>
<td>orthorhombic</td>
<td>13.977</td>
<td>16.969</td>
</tr>
<tr>
<td>U$_3$O$_8$(OH)$_2$</td>
<td>violet</td>
<td>triclinic</td>
<td>6.802</td>
<td>7.417</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_4$•4H$_2$O</td>
<td>pale yellow</td>
<td>monoclinic</td>
<td>11.85</td>
<td>6.78</td>
</tr>
<tr>
<td>UO$_4$•2H$_2$O</td>
<td>pale yellow</td>
<td>orthorhombic</td>
<td>6.502</td>
<td>4.216</td>
</tr>
</tbody>
</table>

(*): Density from X-ray.

Full decomposition of UO$_3$ to U$_3$O$_8$ can occur at 650 °C after 90 minutes, resulting in a black to dark olive color solid [22]. Above 800 °C, oxygen loss occurs, but is reversible with slow cooling rates generally result in stoichiometric composition of U$_3$O$_8$ as determined by thermogravimetric analysis [23]. The quantification of uranium is often determined by using redox titration [24]–[28], with the recognized standard established by Davies and Gray in 1964 [29]. For this work, a similar methodology to the Davies and Grey method, a redox titration method utilizing reduction of cerium and oxidation of iron known as cerimetry, was used as the primary method of measuring the stoichiometry of U$_3$O$_8$ and later UO$_3$. The electrical resistivity measurements in early work with U$_3$O$_8$ were
in the range of \(10^2\text{-}10^3\ \Omega\cdot\text{cm}\) as summarized by Katz and Rabinowitch in 1951 [7], though one source reported a value exceeding \(10^6\ \Omega\cdot\text{cm}\). The lower range has repeatedly been reported in agreement with more recent values in the Gmelin Handbook [30]. Given the ease of sintering \(\text{U}_3\text{O}_8\), it can be reasonably assumed that these values are for specimen with near theoretical densities.

While \(\text{U}_3\text{O}_8\) provides moderate resistivities along with ease of production and sintering, its electrical resistivity does not approach that of \(\text{UO}_3\). While most of the previous work looking into uranium oxides has focused on the dioxide form for its use in nuclear fuels, the trioxide form is an important intermediate compound in mining, processing and purifying of uranium containing ores. \(\text{UO}_3\), like \(\text{UO}_2\) and \(\text{U}_3\text{O}_8\), exhibits semiconductor properties and remains stable over a range of nonstoichiometric compositions without complete changes in phase. An optical band gap of 2.38 eV was reported by Khilla et al. [31] for \(\gamma\)-\(\text{UO}_3\) powder with the definition of band gap as equivalent to photon energy at the middle point of the absorption edge. Using density function theory (DFT) and local density approximation (LDA+U) [2] He et al. reported a band gap a value of 2.35 eV, but did not specify as direct or indirect. However, the electrical properties are strongly influenced by the uranyl group, \(\text{UO}_2^{2+}\), presents as a linear \([\text{O}=\text{U}=\text{O}]^{2+}\) configuration for all but a single polymorph of uranyl oxide, the nomenclature for \(\text{UO}_3\) found more commonly in publications relating to inorganic chemistry or mineralogy. Unlike the small polaron mechanisms related to the 5f orbital found to the primary influence in carrier transport for the p-type \(\text{UO}_2\) semiconductors [32], [33], uranyl oxides appear to be generally n-type [34] with the ionic uranyl group becoming the driving force for carrier transport and recombination. The intrinsic resistivity for the gamma polymorph of uranyl
oxide reaches as high as $10^8 \Omega \cdot \text{cm}$ at room temperature for values reported by Hanafi [35]. Hanafi’s electrical conductivity of UO$_3$ polymorphs were described as calcinated uranium oxides cold uniaxially pressed into compacts with densities reaching approximately 60% of theoretical density for each polymorph. While reports of any higher densifications for compacted uranyl oxide powders from Hanafi or any other author could not be found, this resistivity meets the proposed threshold for discrimination of noise generated by internal alpha decay within a uranium-based semiconductor device.

Additional interest in the properties of UO$_3$ has increased in recent years, but electronic properties, when reported, vary greatly. Predominately discussed are thin films [2], though other reports lack specifics on fabrication and stoichiometry. These inconsistencies could be due to the difficulty in producing a high purity single phase within this complex system.

This work involves the characterizing the electrical resistivity of U$_3$O$_8$ and UO$_3$. Most commonly, linear four-point probe measurements were performed at the University of Tennessee at Knoxville (UTK) to avoid coating contact material to sample surfaces, though van der Pauw measurements and painted contacts were applied on early samples. Specifics are detailed in Chapter 2. These samples were then provided to support research of Shailesh Dhungana at the University of Missouri at Kansas City (UMKC) into additional electronic characterization such as the optical band gap, carrier mobilities and lifetime, as well as determining the most suitable contact materials. These measurements related directly to changes in fabrication and experimental design for this dissertation.
In order to evaluate the capability of $\text{U}_3\text{O}_8 \pm x$ and $\text{UO}_3 \pm x$ materials to capitalize on the high energy fission products and simplified geometries described in Chapter 1, sample fabrication requirements included bulk thicknesses greater than those needed for absorption of neutron-induced fission products. In addition, the ability to uniformly modify and measure stoichiometry, microstructure, and density aided in efforts at University of Missouri at Kansas City (UMKC) in determining electronic transport properties [6]. Uniaxial pressing of natural uranium powders was determined to be the most practical method for producing varying characteristics while allowing for nominally repeatable physical size for sintered pellets based on starting weight.

### 2.1 Fabrication of $\text{U}_3\text{O}_8$ Samples

Pellets of $\text{U}_3\text{O}_8$ were prepared by uniaxial pressing and furnace sintering, with an emphasis on consistency. Batches of two to six pellets were fabricated under varying temperatures and times to allow for destructive testing of duplicate samples. A subset of these samples was characterized to determine grain size, stoichiometry, physical structure from powder x-ray diffraction, and electrical resistivity.

#### 2.1.1 Powder Preparation of $\alpha$-$\text{U}_3\text{O}_8$

Powder preparation began with uranyl acetate dihydrate slowly heated to 650 °C in the Barnstead Thermolyne F21100 tube furnace shown in Figure 7 and held at temperature for 90 minutes. From 250 to 450 °C, acetate anions and moisture begin to
decompose or evaporate, resulting in a bright orange, nominally UO$_3$ powder. At 650 °C, the UO$_3$ will fully reduce in air to U$_3$O$_8$ after 90 minutes, resulting in a black to dark olive color solid [22]. The identity of this solid was confirmed by powder x-ray diffraction (PXRD).

2.1.2 Pressing of U$_3$O$_8$ Pellets

Prior to pressing, U$_3$O$_8$ powder was ground in a zirconia crucible to break apart any large agglomerates and produce roughly uniform particle size. To avoid escape of uranium oxide dust, powder was wetted with isopropanol which evaporated before subsequent steps. Approximately 0.6 g of powder was weighed out to produce pellets with an approximate thickness of 1 mm after sintering. This powder was then pressed using a Carver uniaxial press shown in Figure 8.

Initially, a graphite lubricated, round, half inch diameter stainless-steel die was pressed at 5 – 8 ksi for approximately one minute until a closely packed green pellet was produced. Green pellet densities were on the order of 45 – 50% of theoretical density for α-U$_3$O$_8$. In order to reduce possible surface carbon contamination, the lubrication was changed to mineral oil with a low evaporation temperature and polished steel plates were used with the SPEX® SamplePrep 13 mm die shown in Figure 8. Data tables presented for stoichiometric U$_3$O$_8$ samples in the subsequent chapter denotes the die used for each sample fabricated. The pellet geometry was approximately 13 mm in diameter and 1 – 2 mm in thickness for green density compacts. Furnace sintered pellets were approximately 1 mm with a 9.5 – 11 mm diameter.
Figure 7. Barnstead Thermolyne F21100 tube furnace used for powder conversion.

Figure 8. Die (left) and uniaxial press (right) used for U3O8 pellet pressing.
2.1.3 U₃O₈ Pellet Sintering

Stoichiometric U₃O₈ pellets were then sintered on an alumina plate in a Carbolite HTF 1800 furnace shown in Figure 9 at 1350 °C for the times up to 10 hours using 13 mm polished die samples. This temperature was selected because sintering at 1350 °C and slowly cooling the pellets down to room temperature ensures that stoichiometric compositions of U₃O₈ will result. Specifically, a heating rate of 1.5 °C/min is used to slowly heat the samples up to the target temperature. The samples are then allowed to slowly cool to room temperature at a cooling rate of 3.0 °C/min.

2.1.4 U₃O₈±ₓ Sample Preparation

Nonstoichiometric sample preparation is performed with the addition of conditioning gases flowing through the furnace to alter the available oxygen. Gas mixtures are generated using a Witt Gas Flex 10-2 gas mixer shown in Figure 10. This mixer allows for highly repeatable mixes of 5 – 92% oxygen/argon. This is within ±10% of the nominal value of gas percentage, but without run to run variability. The quartz tube in the furnace is sealed with a fitted flange and pressure gauge system on the exhaust stream which allows for leak and overpressure checks before and during high temperature operation. The closed gas flow system was later connected to a series of two cold traps filled with an EDTA complexing agent and an inline HEPA filter allowing for limited heating of actinides in a standard fume hood. The initial hypostoichiometric and hyperstoichiometric samples were made with mixtures of 12% and 30% O₂, respectively. Identical gas mixtures were used for both powder conversion and pellet sintering with alumina boats fabricated for secure placement of pellets within the tube.
Figure 9. Carbolite HTF 1800 and furnace and MTI OTF-1200-S-NT-25-110 tube furnace used for $\text{U}_3\text{O}_8$ pellet sintering.

Figure 10. Witt KM10-2 Flex Gas Mixer (5-92% oxygen/argon).
2.2 U₃O₈ Characterization

Grain size modifications were the first method investigated for optimizing the balance between electrical resistivity and charge carrier mobility for neutron reaction product transduction in stoichiometric U₃O₈. Electrical measurements from UMKC indicated mobility values on the order of 0.1–10 cm²/Vs, carrier concentration on the order of 10¹⁴–10¹⁵ cm⁻³ and a work function for two samples at 3.7 and 4.1 eV. Detection efficiency calculations at UMKC indicate that intrinsic detection efficiencies for neutrons of a few percent will be possible without enrichment of fissile isotopes if high enough charge collection efficiency and low enough leakage current can be achieved. These efficiencies are lower than lighter (¹⁰B, ⁶Li, ³He) isotope-based detectors due to the high abundance of ²³⁸U but is offset by the large interaction cross-sections and high energy (>165 MeV) fission products produced by thermal neutron capture by ²³³U and ²³⁵U as described in Chapter 1. To achieve successful neutron detection, charge transport targets include mobilities of 10–100 cm²/V·s, μτ values on the order of 10⁻³ cm²/V, and leakage current on the order of or less than the alpha particle decay background.

2.2.1 Density

Density was measured by using the Archimedes' Method using a XS64 Mettler Toledo Balance equipped with a density kit shown in Figure 11. The following equation was used to calculate the density:

\[ \rho = \frac{A}{A - B} (\rho_0 - \rho_L) + \rho_L \]
where ρ is the density, A is the weight of the sample in air, B is the weight of the sample in an auxiliary liquid, ρ₀ is the density of the auxiliary liquid, and ρₐ is the density of air (taken to be 0.0012 g/cm³). The measured density is then compared to the theoretical density of stoichiometric U₃O₈ which is 8.3 g/cm³.

2.2.2 X-ray Photoemission Spectroscopy

X-ray photoemission spectroscopy (XPS) serves as an additional check on material composition. XPS was used to confirm the identity of the dominant oxide phase. While not as sensitive to changes in stoichiometry as other techniques, the elemental composition determined during phase determination can provide an estimate. Survey scans were performed after sputter-cleaning the samples using argon ion etching, with oxygen uranium ratio of 2.7 ± 0.1, which corresponds to a general stoichiometry of U₃O₈.

Figure 11. XS64 Mettler Toledo Balance with density kit.
2.2.3 Powder X-ray Diffraction

Powder x-ray diffraction (PXRD) is another tool for confirming the dominant oxide phase of the material, as well as identifying other minor phases potentially present in the material. Facility restrictions required encapsulation of radioactive samples using Kapton film, resulted in masking of low 2θ values. However, the peaks used for matching U₃O₈ spectra are generally larger than the Kapton masked angles as shown in Figure 12. This pattern indicates powder after conversion from uranyl acetate dihydrate is α-U₃O₈ with no secondary phases present and belonging to space group C2mm (38) with a, b, and c lattice parameters being 6.726 Å, 11.961 Å, and 4.149 Å respectively.

Figure 12. X-ray diffraction spectra for a U₃O₈ sample sintered for 12 hours at 1350 °C with inset α-U₃O₈ unit cell.
2.2.4 $U_3O_8$ Stoichiometry

Stoichiometry measurements were carried out using a redox titration method adapted from the Davies and Grey method mentioned in Chapter 1. Thermogravimetric analysis, or TGA, was also considered as it would provide potentially nondestructive stoichiometry values for $U_3O_8$ but would require decomposition of $UO_3$. In addition, facility restrictions for actinide heating combined with the high costs for TGA systems capable of matching or exceeding a better than 0.1% resolution offered by redox titration made it a less viable technique for this work. Titration data suggested this initial $U_3O_8$ produced was close to stoichiometric $U_3O_8$ with a O/U ratio of $2.668 \pm 0.001$.

2.2.5 Cerimetric Titration

A known amount of Ce(IV) in solution is added to a dissolving uranium oxide specimen in excess of that needed oxidize all uranium to U(VI). By titrating a standardized Fe(II) solution, the amount of excess cerium is measured, allowing the starting oxidation state of uranium to be calculated based on specimen weight. The redox reaction can be written as:

$$e^- + Ce^{+4} \rightarrow Ce^{+3}$$

$$Fe^{+2} \rightarrow Fe^{+3} + e^-$$

The overall redox reaction can be summarized as:

$$Ce^{+4} + Fe^{+2} \rightarrow Ce^{+3} + Fe^{+3}$$
If U(IV) or U(V) are present within an acidic solution, they will oxidize prior to a cerium iron redox reaction. This changes the reaction to the following:

\[ U^{+4} \rightarrow U^{+6} + e^- \]
\[ 2e^- + 2Ce^{+4} \rightarrow 2Ce^{+3} \]
\[ U^{+4} + 2Ce^{+4} \rightarrow U^{+6} + 2Ce^{+3} \]

By using these simple reactions, it is possible to determine the U(IV) and U(VI) content within an U₃O₈₋ₓ sample expressed as a molar ratio. This ratio can then be related to the oxygen content. This process has been documented to give a \( x \pm 0.002 \) accuracy to the stoichiometry of a hypostoichiometric uranium oxide [25], [27].

Initial U₃O₈±ₓ stoichiometry was evaluated using a redox titration method known as cerimetry by using visual measurement of the endpoint by use of color change using a ferroin indicator with results found to be accurate to within 5 μL of titrant. This method has been recognized as an effective technique of determining the relative amount of oxygen to uranium, or the O/U ratio, since its use in precise measurement of the uranium content by Davies and Gray in 1964 [29].

Potentiometric titration using software determining the equivalence point based on the inflection point of plotted mV/mL values measured during titration allowed an accuracy within 1 μL of titrant, calibrated using a NIST certified U₃O₈ standard. Overall accuracy was further increased by increasing the sample weight from 20 – 30 mg to 200 – 300 mg, decreasing the significance of the 0.1 mg weight accuracy by an order of magnitude. Cerimetry can be used at this level of accuracy for UO₂+x to UO₃-x. Stoichiometric variations were U₃O₇.9919± 0.0004 using 12% O₂ and U₃O₈.0091± 0.0010 using 30% O₂.
2.2.6 Polishing of $\text{U}_3\text{O}_8$ Samples

Portions of pellets used for destructive testing were mounted for polishing using a Buehler Minimet semiautomatic polisher shown in Figure 13. Segregated containers were used to avoid cross contamination of differing abrasive particle sizes and samples were rinsed and either swabbed with cotton or air dried between steps depending on the abrasive size of the step. Grinding of mounted samples used SiC paper at standard grit increments from 320 to 800 using water lubricant. Samples were then polished using diamond suspensions from 9 to 3 µm using TexMet C nonwoven cloth with a final polish using 1 µm diamond suspension on napped MicroCloth™ pad. Average grain size was determined using the Heyn Lineal Intercept Procedure on multiple fields of view for digital micrographs of the sample surfaces.

Figure 13. Buehler Minimet Polisher 69-1000 used for semiautomatic polishing of uranium oxide samples.
2.3 Resistivity Measurement Techniques

The electrical resistivity of the uranium oxide pellets was measured using multiple techniques as mentioned in Chapter 1. In addition to their other characterization work, UMKC provided additional resistivity measurements as well as assistance in evaluating the varying techniques used. While only electrical resistivity was characterized with these methods at the University of Tennessee, fabrication efforts facilitated more advanced electronic characterization at UMKC. This approach allowed for reproducibility of results and as well as determine the optimal measurement techniques for use with \( \text{U}_3\text{O}_{8\pm x} \) samples, allowing for feedback to fabrication conditions immediately following sintering.

2.3.1 Four Point Probe – van der Pauw

The first electrical resistivity measurement technique used for the thin disc shaped pellets described in Section Pressing of U3O8 Pellets, was the van der Pauw method. This method uses four small contacts at the edges of the sample and is suitable for measuring the electrical resistivity as well as the Hall coefficient of a thin sample of arbitrary shape [36]. For this reason, generally a probe system in which the tip of the probe is extremely small (e.g., tens of micrometer in diameter) is used. Measurements performed at UMKC used a custom-built probe system shown in Figure 14 using gold/tungsten probes connected to a Keithley 2400 sourcemeter and measured voltage using a Keithley 2000 multimeter.
In the van der Pauw configuration, resistances are determined by dividing the voltage between 2 neighboring points by a sourced current applied to the other 2 points. For example, $R_{1234}$ is defined as voltage between points 3 and 4, $V_{34}$, divided by the sourced current between points 1 and 2, $I_{12}$.

\[ R_{1234} = \frac{V_{34}}{I_{12}} \]

Following this approach with other arrangements such as $R_{3412}$ with equivalent source current $I_{34}$,

\[ R_{3412} = \frac{V_{12}}{I_{34}} \]
Reciprocity indicates equivalent theoretical resistances,

\[ R_{1234} = R_{3412} \]

Experimentally, \( R_{1234}, R_{3412}, R_{2341}, \) and \( R_{4123} \) vary slightly, requiring averages denoted as \( R_1 \) and \( R_2 \),

\[ R_1 = \frac{1}{2} (R_{1234} + R_{3412}) \quad R_2 = \frac{1}{2} (R_{2341} + R_{4123}) \]

The resistivity, \( \rho \), is determined using the equation,

\[ \exp \left( -\frac{\pi t R_1}{\rho} \right) + \exp \left( -\frac{\pi t R_2}{\rho} \right) = 1 \]

where \( t \) is the sample thickness.

2.3.2 Four Point Probe – Linear

Differing from the van der Pauw method, which maximized the contact point separation, a four-point probe system places four contacts of equal size at equidistant and collinear intervals along the sample surface as shown in the schematic in Figure 15 [37]. The outer probes are used to source current through the sample, while the potential drop across the inner probes is measured. In order to apply the method, the following assumptions must hold: (1) the material has a uniform resistivity; (2) the contact surface between the probes and the sample is hemispherical and the contact radii are small relative to the probe spacing; (3) the sample surface is flat and the recombination rate is so high that any charge injected from the probes recombines close to the probes [38].
The resistivity is given as [39]:

\[ \rho = 2\pi s \frac{V}{I} F \]

where, \( s \) is the probe spacing and \( F \) is a correction factor. There are various factors which affect the value of \( F \) [39]. The correction factors for finite thickness and finite diameter were applied in these experiments. If the thickness \((t)\) of the sample is on the order of the probe spacing \((s)\) or less, the correction factor is given as:

\[
F_1 = \frac{\left(\frac{t}{s}\right)}{2 \ln \left[ \frac{\sinh \left(\frac{t}{s}\right)}{\sinh \left(\frac{t}{2s}\right)} \right]}
\]

If \( t \leq s/2 \), the above equation reduces to:

\[
F_1 = \frac{t}{s} \frac{1}{2 \ln(2)}
\]

For samples of finite diameter, the correction factor is given as:

\[
F_2 = \frac{\ln(2)}{\ln(2) + \ln \left[ \frac{\left(\frac{D}{s}\right)^2 + 3}{\left(\frac{D}{s}\right)^2 - 3} \right]}
\]
The initial apparatus used at UMKC used four silver-painted contacts, about 1 mm in diameter, with center-to-center spacing of 2 mm, connected by gold wires to source current and measure voltage as shown in Figure 16. Steps of 2 μA up to 200 μA were sourced through outer contacts with a Keithley 2400 sourcemeter, measuring the voltage across the inner probes using a Keithley 2000 multimeter. At UTK, a probe station connected to a Keithley 2400 sourcemeter was used with and without silver paint contacts. Current was measured for a 0 – 5 mV sweep using four probes spaced 1.016 mm apart in a straight line along the sample surface. The resulting data for all U₃O₈ samples measured resulted in a linear relation in which the slope indicates resistance. Resistivity is then calculated using:

$$\rho = 2\pi s \frac{V}{I} F_1 F_2$$

with correction factors, $F_1$ and $F_2$, related to sample dimensions relative to probe spacing.
2.3.3 Metal-Insulator-Metal

Metal–insulator–metal (MIM) geometry, shown in Figure 17 was investigated in preparation for any sample compositions or geometries less suitable for the four point methods previously described. In this method, contacts are coated on the opposite faces of the sample. A potential difference is applied across the electrodes, and the resulting current in the circuit is measured. The slope of the current–voltage \((I–V)\) graph gives the resistance \((R)\) of the sample, which is used to determine its resistivity \((\rho)\).

\[
\rho = \frac{RA}{d}
\]

where \(A\) and \(d\) stand for the contact area and thickness of the sample.
For the U$_3$O$_8$ pellets measured at UMKC, circular silver paint contacts were applied using Vernier calipers to measure silver contact diameter and connected to a circuit board with gold wire. Voltage was sourced with a Keithley 2400 sourcemeter, and current was measured using a Keithley 6485 picoammeter. UTK measurements were performed with a Keithley 2400 to provide estimated values without a separate ammeter.

After evaluation of various techniques, resistivity of subsequent U$_3$O$_8$ samples was gathered using a four-point collinear probe station at UTK for the previously mentioned adjustments in fabrication conditions. These measurements, while not as accurate using the source meter to also provide measurements, provided immediate feedback on changes to fabrication conditions.

Figure 17. Resistivity measurement of U$_3$O$_8$ in MIM geometry.
2.4 Fabrication of UO$_3$ Samples

2.4.1 Decomposition of Uranyl Nitrate

As described in Chapter 1, the greatest thermal stability and electrical resistivity for uranyl oxide is found in the gamma polymorph, making it the principle phase of interest. Based on literature [16], [17], [20], $\gamma$-UO$_3$ could be produced by decomposition of uranyl nitrate heated in air at 400 °C for 60 hours. The conversion process is described by the following decomposition reactions [40]:

$$UO_2(NO_3)_2 \cdot 6H_2O \rightarrow UO_2(NO_3)_2 \cdot H_2O + 5H_2O$$

$$UO_2(NO_3)_2 \cdot H_2O + 5H_2O \rightarrow UO_3 \cdot H_2O + 2NO_2 + \frac{1}{2}O_2$$
Uranyl nitrate hexahydrate heated in this manner produced a rich orange powder was then finely ground in a zirconia mortar and pestle. Powder immediately following cooling was evaluated by PXRD analysis using a PANalytical Empyrean, refined using GSAS-II, and compared with a γ-UO$_3$ reference pattern, as shown in Figure 19. The powder stoichiometry was determined by potentiometric redox titration to be UO$_{2.9863 \pm 0.0005}$ and UO$_{2.9955 \pm 0.0005}$. Initially, unused U$_3$O$_8$ samples were also dissolved in nitric acid, dried, and converted in this manner to be repurposed toward UO$_3$ samples. However, samples generated from uranyl nitrate were inconsistent, indicating a lack of complete denitrification that would not be evident in diffraction scans.

Figure 19. Powder XRD pattern of powder relative to reference γ-UO$_3$ pattern [41].
2.4.2 UO$_{3+x}$ Powder Preparation

UO$_3$ powder purchased from IBI Labs and shown in Figure 20, appeared consistent with a partially hydrated structure. To produce nonstoichiometric UO$_3$, powder was conditioned by heating to 200 – 480 °C in a tube furnace with gas mixtures generated using a Witt Gas Flex 10-2 gas mixer. Gas mixtures varied from 5% to 92% O$_2$. Powder was conditioned up to 60 hours to evaluate the effect of conditioning time on material properties. Conditioned powder was placed in an argon filled glove box following cooling to room temperature if not immediately pressed. The resulting powder generally became orange in appearance at temperatures below 400 °C, consistent with prior work and literature. When heated to 480 °C, a brown colored powder was observed, likely indicating a change in the UO$_3$ phase or phases present. Samples 423 and 424 were pressed from this darker starting powder and were identified as α-UO$_3$ using X-ray diffraction.

![UO$_3$ – UO$_2$(OH)$_2$ and α-UO$_3$](image)

Figure 20. UO$_3$ Powder from vendor (left) and after 480 °C heating (right).
2.4.3 Uniaxial Hot Pressing of UO$_3$ Samples

A 13 mm diameter ID 250 °C heated die from Across International, shown inside the Carver uniaxial press in Figure 21, allowed for internal temperature monitoring and uniform heating of the die and sample. Die lubrication was changed from mineral oil to Krytox™ PTFE high temperature grease due to the increased temperature within the die. Pressure was applied during the heating ramp, and sintering time was defined as the dwell at set point for both temperature and pressure, with pressure released after cooling below 75% of set temperature in 5 – 10 minutes. The die would then cool to room temperature in approximately 2 hours before removing the pellet. Powder and pellets were stored in an argon-filled glove box to prevent hydration.

Due to pellet fragmentation with conditioned powder, the specific parameters for pressing were modified starting with sample 421 to avoid specific endothermic transition peaks for any hydrated phases still present. Uniaxial pressure was applied to the pellet during the heating process after the die reached 150 °C to avoid internal stresses associated with formation of amorphous-UO$_3$ from specific monohydrates [13]. The set temperature was also reduced to 180 °C after observing a decrease in heating rate near 190 – 195 °C while at increased pressures. While a reason for this observation has not been verified, the large uniaxial pressure applied could decrease the reaction temperature for transitions such as an anisotropic thermal expansion of β-UO$_2$(OH)$_2$ [13] by what is commonly referred to as the Hedvall effect [42].
2.4.4 Long-term heating of UO$_3$ Pellets

In order to modify grain sizes of hot pressed UO$_3$ pellets, heating for extended periods was evaluated. Increased hot press sintering time resulted in damaged pellets, so a tube furnace was used without pressure on previously pressed pellets. To reduce risks to effluent release, the tube furnace had additional safeguards in place. Gas was mixed at 92% O$_2$/Ar gas and flowed through the furnace. The exhaust gas then bubbled through a series of 2 cold traps filled with an EDTA solution buffered to a pH of 8 to capture any uranium ions reaching the trap. The gas flow then exited the system through an in-line HEPA filter into the fume hood. A schematic of the furnace with added features is shown in Figure 22.
2.5 UO$_3$ Characterization

2.5.1 Stoichiometry – Cerimetric Titration of Uranyl Compounds

Cerimetric titration for evaluating stoichiometries of U$_3$O$_8$ used addition of iron to a cerium saturated solution, allowing for determination of reduced Ce$^{4+}$ ions and calculating the number of uranium ions below the U$^{6+}$ state based on the initial weight of the solid. As this method measures the cerium oxidation change to determine changes with uranium oxidation, initial concerns related to capabilities of measuring UO$_{3+x}$ in which all uranium should occupy the U$^{6+}$ state. However, it was found that hydrated compositions would also impact the ability of titration to measure UO$_{3-x}$ due to valance changes between hydrates even if the amount of hydrate could be quantified. Table 3 lists selected man-made uranium trioxide hydrates and corresponding mineral structures. The “schoepite family” contains more than 20 variations of uranyl-oxide hydroxyl-hydrate mineral structures to date. These compounds often form thin layers of uranyl oxide hydroxide, linked by hydrogen bonds of interlaying water molecules as shown with schoepite in Figure 23. The symmetry of this structure is water-sensitive, with schoepite
spontaneously altering to meta- or para-schoepite. Due to the complex nature of this system, including the possible changes to bond valance during dissolution as well as the polyvalent nature of uranyl hydroxide, it was thought that measurement of stoichiometry by change to uranium oxidation state might not yield reliable results. Available radioactive material approved equipment allowed for the alternative measurements to several samples to combine a direct quantification of uranium using inductively coupled plasma mass spectrometry (ICP-MS) and quantification of hydrate content through X-ray diffraction. These same samples in solution were also characterized with cerimetry.

<table>
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<th>Mineral Name</th>
<th>Empirical Formula</th>
<th>Chemical Formula</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ianthinite (1)</td>
<td>UO₂(OH)₂</td>
<td>(UO₂)·5(UO₃)·10(H₂O)</td>
<td>94.07% UO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.93% H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>88.81% UO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.19% H₂O</td>
</tr>
<tr>
<td>Schoepite</td>
<td>(UO₂)₈O₂(OH)₁₂</td>
<td>(UO₂)₈O₂(OH)₁₂·12(H₂O)</td>
<td>82.69% UO₂</td>
</tr>
<tr>
<td></td>
<td>·12(H₂O)</td>
<td>or U₂O₅(OH)₂·3(H₂O) (2)</td>
<td>12.41% H₂O</td>
</tr>
<tr>
<td>Metaschoepite</td>
<td>UO₃·1.5(H₂O)</td>
<td>(UO₂)₄O(OH)₆·5(H₂O)</td>
<td>91.37% UO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.63% H₂O</td>
</tr>
<tr>
<td>Paraschoepite</td>
<td>UO₃·1.9(H₂O)</td>
<td></td>
<td>88.81% UO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.19% H₂O</td>
</tr>
</tbody>
</table>

(1): Composition varying due to polyvalent uranyl hydroxide
(2): Chemical formula of β-dihydrate determined by Porte et al. using Proton Magnetic Resonance [43]
Figure 23: Structural model of schoepite (a), metaschoepite (b), and ianthenite (c).
2.5.2 Stoichiometry – Inductively Coupled Plasma Mass Spectrometry

To determine uranium content, small pieces of pressed UO$_3$ pellets were dissolved and diluted in stages to concentrations in the parts per billion range in a 2% nitric acid solution for analysis in ICP-MS. A calibration curve was generated using serial dilutions of a 1000 µg/ml uranium standard manufactured by SPEX CertiPrep to encompass the entire range of possible uranium concentrations from dissolved samples. Using the known values from the calibrated standards, $^{238}$U intensities were then used to determine the starting uranium mass fraction for each sample. Hydrate contribution to mass was estimated from X-ray diffraction data in the same manner used for titration measurements, allowing for stoichiometry to be calculated.

2.5.3 X-ray Diffraction

Determining the phases of UO$_3$ and knowing the approximate composition of any hydrate is an important factor in determining the stoichiometric oxygen-to-uranium ratios of each sample. Ideally, the method of doing this is powder x-ray diffraction (PXRD); however, this was not possible due to restrictions placed on radioactive powder use with available equipment. As a result, grazing incidence x-ray diffraction (GIXRD) available at UMKC was used on the pellet surfaces to determine phase composition. The samples were placed into an aluminum sample holder and scanned from 10 – 70 °2θ with a scan rate of 1 °2θ / min in a Rikagu Miniflex+ benchtop diffractometer using a cobalt x-ray source (CoK$\alpha_1$ = 1.78897 Å, CoK$\alpha_2$ = 1.79285 Å).

Unlike powders, bulk samples diffract x-rays as a function of the orientation of the individual grains within the sample. The x-ray source is fixed at a specific angle, $\omega$, relative
to the sample. The x-ray detector is then rotated about the sample at a controlled 2θ angle, as shown in Figure 24. Since it cannot be assumed that each grain is randomly orientated in the bulk sample, counting statistics can be greatly reduced based upon the preferred orientation (or texture) of the grains, which is related to processing methods. This can lead to a loss of information as certain planes of diffraction may be absent in the resultant spectra. Analysis of diffraction patterns was performed using automated Rietveld refinement tools and powder diffraction file matching databases included in the Malvern Panalytical HighScore Plus software.

Figure 24: Diagram of GIXRD method.
2.5.4 Density

Density was measured by using the Archimedes’ Method and XS64 Mettler Toledo Balance described in Section 2.2.1. Petroleum ether, with a density of approximately 0.77 at room temperature, was used as the liquid medium to prevent formation of a hydrate phase. Increasing sintering time from a minimum of 10 minutes showed minimal changes in pellet density. X-ray diffraction of pellets indicated lattice parameters most closely matching reported values of γ-UO$_3$ with a theoretical density of 7.80 g/cm$^3$ and hydrated phase density of 5.24 g/cm$^3$.

2.5.5 Microstructure

UO$_3$ polishing was accomplished using a similar technique to that outlined for U$_3$O$_8$ in Section 2.2.6. To avoid prolonged exposure to water, alcohol-based lubricant was used. Unpolished sample surfaces were also imaged and it was determined that while unmounted samples had reduced clarity, polished steel plates used during hot pressing eliminated sufficient surface roughness for grain size determination nondestructively.

2.5.6 UO$_3$ Electrical Characterization

Electrical resistivity of UO$_3$ pellets was determined metal–insulator–metal (MIM) geometry described previously with U$_3$O$_8$ samples. The current–voltage behavior is shown for two representative samples, 204 and 410, in Figure 25. Additional high-voltage data for sample 410 is shown with a possible space-charge region above 1000 V. At sufficiently high electric field, the current through a semiconductor is independent of its resistivity; instead it depends on the charge carrier mobility ($\mu$) [44]. suggesting a charge carrier mobility is lower than $8 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$.
Figure 25. $I$–$V$ characteristics of samples 204 and 410 with additional high-voltage measurements for sample 410.
CHAPTER THREE
RESULTS AND DISCUSSION

Phase determination for UO$_3$ pellets fabricated at UTK was provided by UMKC using grazing incidence x-ray diffraction (GIXRD) with a cobalt source (CoK$_\alpha_1$ = 1.78897 Å, CoK$_\alpha_2$ = 1.79285 Å) as described in Section 2.5.3. These findings, as well as supplemental micrographs not presented in Chapter Three can be found in Appendix A.

3.1 Stoichiometric U$_3$O$_8$ Samples

As described in previous chapters, U$_3$O$_8$ sintered easily with conventional heating and typically recovered oxygen losses, resulting in stoichiometric compositions with cooling rates of 3 °C/min used. Increased cooling rates could have been used as either an alternative to, or in conjunction with, gas mixing, to adjust hypostoichiometric composition. However, these changes were not explored due to the goal of maximizing electrical resistivity. As mentioned in Section 2.1.2, U$_3$O$_8$ pellets were prepared initially with a ½” steel die using graphite spray lubricant. The physical properties and sintering times at 1350 °C for these samples are shown in Table 4. Samples prepared using the polished steel plates and mineral oil in the SPEX® SamplePrep 13mm die are shown in Table 5. Initial test samples were used to determine required sizes for sample holders used for resistivity measurements at UTK or mobility and photoconductivity experiments by UMKC and were not measured using a density kit.
Table 4. Sample details for U$_3$O$_8$ pellets sintered at 1350 °C using die A.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Thickness (mm)</th>
<th>Diameter (mm)</th>
<th>Density (g/cm$^3$)</th>
<th>Theoretical Density (%)</th>
</tr>
</thead>
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<td>A0101</td>
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<td>1.86</td>
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<tr>
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<td>-</td>
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<td>10.08</td>
<td>7.8</td>
<td>94.0</td>
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</tr>
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Table 5. Sample details for U₃O₈ pellets sintered at 1350 °C using die B.

<table>
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<th>Sample</th>
<th>Time (hrs)</th>
<th>Weight (g)</th>
<th>Thickness (mm)</th>
<th>Diameter (mm)</th>
<th>Density (g/cm³)</th>
<th>Theoretical Density (%)</th>
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<td>8.06</td>
<td>97.1</td>
</tr>
</tbody>
</table>
3.1.1 Density of Stoichiometric U₃O₈ Samples

Percent theoretical density shown for all U₃O₈ samples is compared to the theoretical density of the α-U₃O₈ phase, or 8.38 g·cm⁻³. As shown in Figure 27, U₃O₈ rapidly sinters to 95% of theoretical density when heated at 1350 °C for times in hours. It should be noted that these results are presented as sintering time at 1350 °C. The furnace temperature was increased and decreased slowly as described in Section 2.1.3, providing additional hours at lower sintering temperatures.

3.1.2 Microstructure of Stoichiometric U₃O₈ Samples

As charge carriers can be impeded by boundaries, the grain sizes present within samples can have a significant influence on electrical resistivity and mobility in a polycrystalline semiconductor.

Figure 26 shows selected fields of view, illustrating an apparent bimodal distribution of grain sizes caused by the onset secondary grain growth. It is possible that, with sufficiently long sintering times, a large, equiaxed microstructure could form, though it is also possible that such times would result in sufficient oxygen losses to result in decomposition to UO₂⁺ₓ structures before cooling. Figure 28 shows the correlation between increasing U₃O₈ sintering times at 1350 °C and an increasing average grain size from 23 μm at 1 hours to 35 μm at 10 hours.
Figure 26. Sintered U$_3$O$_8$ photomicrographs for (a) 2 hours, (b) 4 hours, (c) 9 hours and (d) 10 hours.
Figure 27. Density as a function of sintering time at 1350 °C for U₃O₈ pellets.

Figure 28. Average grain size as a function of sintering time for U₃O₈ pellets.
3.1.3 Powder X-ray Diffraction of $\text{U}_3\text{O}_8$

Figure 29 shows the indexing performed on the test sample of $\text{U}_3\text{O}_8$ previously shown in Figure 12 with peaks matched to the corresponding reference pattern for $\alpha$-$\text{U}_3\text{O}_8$.

3.2 Nonstoichiometric $\text{U}_3\text{O}_{8\pm x}$ Samples

To produce nonstoichiometric variations of $\text{U}_3\text{O}_8$, available oxygen in the furnace was controlled with gas flow through a tube furnace as outlined in Chapter 2. While the change in furnace type required sintering temperatures lower than 1200 °C, a lower sintering temperature was already planned based on the stoichiometric $\text{U}_3\text{O}_8$ results in the previous sections. Conditions and measurements for $\text{U}_3\text{O}_{8\pm x}$ samples are compiled in Table 6.

Figure 29. X-ray diffraction spectra for $\text{U}_3\text{O}_8$ sintered pellet at 1350 °C for 12 hours indexed to reference pattern for $\alpha$-$\text{U}_3\text{O}_8$ [45].
Table 6: Processing conditions and measured properties of U$_3$O$_{8\pm x}$ samples

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hrs)</th>
<th>% O$_2$</th>
<th>Composition (U$<em>3$O$</em>{8\pm x}$)$_x$</th>
<th>Density (g·cm$^{-3}$)</th>
<th>Grain Size (µm)</th>
<th>Theoretical Density (%)</th>
<th>Resistivity (Ω·cm)</th>
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</thead>
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<tr>
<td>900</td>
<td>40</td>
<td>Air</td>
<td>&lt;±0.001</td>
<td>7.72</td>
<td>2.8</td>
<td>93.0</td>
<td>1.64·10$^3$</td>
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<tr>
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<td>Air</td>
<td>&lt;±0.001</td>
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<td>4.2</td>
<td>85.9</td>
<td>9.83·10$^2$</td>
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<tr>
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<td>8</td>
<td>Air</td>
<td>&lt;±0.001</td>
<td>6.89</td>
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<td>83.0</td>
<td>1.04·10$^3$</td>
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<td>1000</td>
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<td>&lt;±0.001</td>
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<td>92.5</td>
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<td>6.73·10$^2$</td>
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<td>3.4</td>
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<td>8.5</td>
<td>95.9</td>
<td>7.00·10$^2$</td>
</tr>
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<tr>
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<td>8.00</td>
<td>9.0</td>
<td>96.3</td>
<td>4.58·10$^2$</td>
</tr>
</tbody>
</table>

* denotes a stoichiometric green pellet sintered in 12% O$_2$.

3.2.1 Density of U$_3$O$_{8\pm x}$ Samples

Density measurements were performed identically to those of stoichiometric U$_3$O$_8$ samples, using to 8.3 g/cm$^3$ as the theoretical density of U$_3$O$_8$. A sample prepared without gas flow conditioned powder showed lower density, indicating that stoichiometric changes delayed sintering kinetics. Figure 30 illustrates that flowing gas in general results in greater density increases. As seen in Figure 31, conditioning gas flow has resulted in increased densification compared to in-air sintering at lower sintering times, though this difference appears to diminish at longer sintering times. Due to the generally low electrical resistivity of all U$_3$O$_8$ samples, this was not explored further.
Figure 30. Photograph displaying relative size of U₃O₈ pellets sintered at 1000 °C in air (left) and with air flow (right).

Figure 31. Density of U₃O₈ at 1000 °C as a function of sintering time.
3.2.2 Microstructure of U$_3$O$_{8\pm x}$ Samples

Unlike samples sintered at 1350 °C which displayed visible grain boundaries due to thermal etching, samples sintered at or below 1000 °C were prepared using the polishing steps outlined in Section 2.2.6. Figure 32 shows sample microstructures after sintering in air at 900 °C with sintering times from 4 to 40 hours.

Figure 33 and Figure 34 showing the microstructures for sintering at 1000 °C with varying sintering times and gas flow. Grain size increased with sintering time, with apparent normalization of grain growth between air and gas flow by 20 hours with average grain sizes for each condition between 8.5 and 9.4 µm. Shorter sintering times showed reduced grain growth with gas flow as compared to air sintering for the same duration.

Figure 32. Microstructure of U$_3$O$_8$ sintered at 900°C for 4 (a), 8 (b), 20 (c), and 40 hours
Figure 33. Microstructure for U$_3$O$_8$ samples sintered at 1000°C for 4 hours in air (a), 8 hours in air (b), and 8 hours with 12% O$_2$ flow (c, d) for powder conversion in air (c) and in 12% O$_2$ (d)

Figure 34. Microstructure for U$_3$O$_8$ samples sintered at 1000°C for 20 hours in air (a) and in 12% O$_2$ (b)
3.2.3 Stoichiometry of $U_3O_{8±x}$ Samples

$U_3O_{8±x}$ stoichiometry used potentiometric titration using the increased sample mass outlined in Section 2.2.5. Stoichiometric results found in Table 6 were found by dissolving portions of sintered pellets produced simultaneously in identical conditions to those listed. Pellets sintered using 12% $O_2$ produced composition of $U_3O_x$ with $x = 7.9919 ± 0.0004$ and 30% $O_2$ produced $x = 8.0091 ± 0.0010$.

3.2.4 Resistivity of $U_3O_{8±x}$ Samples

Resistivity of $U_3O_{8±x}$ samples used the four-point collinear probe station at UTK. Figure 35 shows that resistivity for $U_3O_{8±x}$ samples does not appear to exhibit significant increase with grain sizes approaching 1µm as seen with UO$_2$ [46].

![Figure 35. Resistivity of $U_3O_{8±x}$ compositions as a function of grain size.](image)
3.3 UO$_3$ Samples

Samples originating from uranyl nitrate contained an unknown level of nitrogen remaining after heat treatment, resulting in inconsistent fabrication. With lower density measurements but no visible porosity after breaking, those samples were not considered valid results for the uranyl oxide/hydroxide system being investigated. All samples discussed were already washed of nitrogen ions resulting in UO$_3$-UO$_2$(OH)$_2$ composition from the vendor. Lattice parameters measured by UMKC indicated the UO$_2$(OH)$_2$ phase similar to lanthinite, with a density of 5.24 g·cm$^{-3}$. While the sample phase composition varied, the hydroxide phase was measured between 5 – 15 %. Table 7 includes a majority of these hot pressed UO$_3$ samples. Densities are compared to theoretical density of both an anhydrous γ-UO$_3$ phase as well as a composite phase calculated for an “average” hydrated composition, 10% UO$_2$(OH)$_2$ and 90% γ-UO$_3$. Samples 423 and 424, as noted, are α-UO$_3$–UO$_2$(OH)$_2$, resulting in higher displayed percentages when compared to the γ-UO$_3$ phases. The resistivity for powder conditioned samples shows electrical resistivity of the γ-UO$_3$ phase higher than α-UO$_3$, in agreement with Hanafi [35]. However, these values are orders of magnitude higher than previously published values. Early test pellets, designated 201 and 204, exhibited even higher resistivities when hot pressed at or near the maximum operating temperature for the die (250 °C) without powder conditioning and using mineral oil lubricant. At these temperatures, mineral oil completely evaporated, causing sample surfaces to darken, crack or delaminate resulting in the change to a the PFTE-based grease. Later 200 and 300 series samples show a decrease in density, reflecting a seasonal increase in humidity, resulting in storage of all UO$_3$ materials in an argon filled glove box mentioned in Section 2.4.3.
Table 7. Processing conditions and measured properties of UO₃ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Powder Conditioning</th>
<th>O₂ (%)</th>
<th>Temp (°C)</th>
<th>Time (hrs)</th>
<th>Hot Press Temp (°C)</th>
<th>Time (min)</th>
<th>Density g/cm³</th>
<th>Theoretical % (O:U)</th>
<th>Grain Size (µm)</th>
<th>UO₃ (O:U)</th>
<th>ρ (Ω·cm)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>No Powder Conditioning</td>
<td>421</td>
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<td>10</td>
<td>7.400</td>
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¹ Density of γ-UO₃ is 7.80 g/cm³. Composite density of 7.544 g/cm³ is calculated with an estimated 10% hydrated phase UO₂(OH)₂ and 90% γ-UO₃.

² Samples 423 and 424 were α-UO₃=UO₂(OH)₂, resulting in larger percentages when compared to γ-UO₃ density.

* Measurements performed at University of Missouri Kansas City

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### 3.3.1 Hot Pressed UO$_{3+x}$ Samples

Starting with gas flow conditioned powder in 400-series samples, samples exhibited visible damage such as cracks through the entire thickness or delamination of at least one surface. Examples are shown from samples 411 and 419 in Figure 36. This type of damage changed the nominal geometry of a uniform thin disc, placing restrictions on the configuration of contacts and the correction factors used with four-point resistivity methods. This resulted in resistivity measurements for UO$_3$ samples utilizing the MIM configuration for consistency. Samples 420 and 421 were pressed on the same day using the same batch of conditioned powder. The band gap provided by UMKC for both samples were equal, indicating a high likelihood of the same phase composition. With a decrease in density and slight increase in average grain size, electrical resistivity is also similar. The only variable change was a 20 °C decrease in pressing temperature, resulting in the first pellet exhibiting no visible damage as seen in Figure 37. Figure 38 shows additional delamination and fragmenting found in α-UO$_3$ samples. Additional samples were fabricated with powder conditioned for increased times at 200 °C. These increased times did result in any noticeable changes to pellet density, in agreement with literature on “dehydrated schoepite” [19], [47]. If interlayer H$_2$O is present but removed during hot pressing, this would explain the delamination issues commonly seen as hydroxides like schoepite or metaschoepite would experience a collapse of stacked layers when dehydrating to an α-UO$_2$(OH)$_2$. Additionally, this would explain why increases to hot press sintering time only sometimes resulted in sample fracture.
Figure 36. Pellet Delamination (top, middle) for Sample 411 and cracking (bottom) in Sample 419.
Figure 37. Sample 421 exhibiting no visible damage with reduced pressing temperature.

Figure 38. Delamination and fracture of $\alpha$-UO$_3$ samples 423 (left) and 424 (right).
3.3.2 Density of $\text{UO}_3^{\pm x}$ Samples

Pellets after uniaxial hot pressing exhibit no visible porosity, with densities measured generally above 80-85% of the theoretical density for $\gamma$-$\text{UO}_3$. Figure 39 shows higher density $\text{UO}_3$ pellets, with resistivities orders of magnitude higher than $10^6$ and $10^8$ Ω-cm reported by Hanafi for these phases [35]. Literature review found no indication of previous bulk densification for $\gamma$-$\text{UO}_3$ samples or resistivities higher than those reported by Hanafi. In addition, discrepancies were also found, such as the theoretical densities for $\alpha$-$\text{UO}_3$ in Table 1 [21] not in agreement with other work from the same authors cited [17]. These $\alpha$-$\text{UO}_3$ samples also exhibit a darker color than described. Lighter, yellow colors common to natural uranyl hydroxides and those described in Table 2, could explain these differences. However, the $\text{UO}_3$–$\text{H}_2\text{O}$ system was more commonly investigated than anhydrous $\text{UO}_3$ work. A more likely explanation is the presence of lighter elements from precursor materials, such as carbon or nitrogen, that are difficult to fully remove without heat treatments above decomposition temperatures for the desired uranyl compound and often transparent to the X-ray diffraction methods used in characterizing the various polymorphs. The earlier attempts at UTK to make $\gamma$-$\text{UO}_3$ pellets from uranyl nitrate produced powder matching $\text{UO}_3$ patterns as shown by Figure 19 in Section 2.4.1. However, pellets made from the converted powder turned from orange to a yellow color like the powder shown in Figure 20 after storage in ambient conditions. While later samples made from purchased $\text{UO}_3$ powder did show decreased density with similar storage conditions, they did not exhibit any color changes. This is further evidence that previous work likely did not achieve full conversion to $\text{UO}_3$ from the precursor materials.
3.3.3 Microstructure of $\text{UO}_3^{x}$ Samples

In order maximize the electrical resistivity, $\text{UO}_3$ samples were fabricated with the goal of smaller grain sizes. When it became evident that resistivities achieved exceeded the original proposed goal of $10^8$ $\Omega\cdot$cm, hot pressing times were increased from 10 up to 45 minutes. Figure 40 shows sample 519 (left), with a slightly larger average grain size than sample 521 (right) that was sintered for a longer time. Similar electrical resistivities were observed for all grain sizes produced, as plotted in Figure 41.
Figure 40. UO$_3$ microstructures of samples 519 (left) and 521 (right).
Due to the low decomposition temperatures of UO$_3$ at atmospheric pressures, pressed pellets were placed in the tube furnace with a 92% O$_2$ gas flow. According to Cordfunke [48], γ-UO$_3$ could be produced at 500 °C in air from uranyl nitrate and verified with X-ray diffraction and ignition to U$_3$O$_8$, so this temperature was used for the first experiment. Samples were heated at 1 °C/min and held at 500 °C for two weeks. The UO$_3$ samples changed color to that of α-UO$_3$, exhibiting similar discrepancies described earlier with previous work that attempted to convert from uranyl precursors with only heat treatment. The grain size of these samples remained approximately the same to those immediately after hot pressing, as shown in Figure 42. Additional pellets were heated with the same procedure, but the temperature was lowered to 400 °C. Figure 43 shows these samples before and after furnace heating. Samples on the left were hot
pressed without powder conditioning with samples on the right were prepared at 200 °C like samples in the 500 series in Table 7. These unconditioned samples appeared less uniform, with the lighter color indicating higher hydroxide phase presence. After the first 14-day heat treatment, the unconditioned pellets were fractured and darker than expected for $\gamma$-UO$_3$. A second, identical heat treatment was then performed on the same pellets, with additional micrographs taken after a total of 28 days at 400 °C. Based on Figure 44, it appears that visibility of grain boundaries is increased by these heat treatments similar to the thermal etching seen in U$_3$O$_8$. There is an increased number of larger grains visible, with a slight increase in average grain size.

Figure 42. $\alpha$-UO$_3$ sample after heating at 500 °C for 14 days.
Figure 43. Pellets heated at 400 °C for 28 days without (left) and with (right) powder conditioning.
Figure 44. Microstructures for UO$_3$ pellets with unconditioned powder (top), after pressing (left) and after 28 days at 400 °C (right).
3.3.4 Stiochiometry of UO$_{3\pm x}$ Samples

The stoichiometry of several UO$_3$ samples were determined with ICP-MS due to concerns over hydroxide contributions reducing the accuracy of potentiometric titration methods adapted from earlier U$_3$O$_8$ work. As seen in Figure 45, sample composition determined by both methods, denoted by arrows, shows only a slight deviation in the oxygen uranium ratio.

![Figure 45. Resistivity of UO$_3$ samples based on stoichiometry.](image_url)
CHAPTER FOUR
CONCLUSIONS

Uniaxially pressed uranyl uranate (U$_3$O$_8$) and uranyl oxide (UO$_3$) compounds were fabricated through various methods, resulting in increased pellet density and changes to grain morphology and stoichiometry. U$_3$O$_8$ did not increase resistivity by changes to microstructure or stoichiometry, differing from the relatively large changes to resistivity seen in UO$_2$ [49]. Larger average grain sizes produced in U$_3$O$_8$ samples were the result of secondary grain growth, therefore the effects on resistivity for larger equiaxed sizes were not characterized. The structure of $\alpha$-U$_3$O$_{8-2x}$ is made up of a similar layered UO$_7$ pentagonal bipyramid polyhedral that comprise $\gamma$-UO$_3$, but with at least one vacant edge with shared oxygen between layers to form the U$_3$O$_8$ composition [50]. With such a high oxygen coordination, it is therefore unsurprising that small changes to composition did not result in large changes to resistivity. The $\beta$-U$_3$O$_8$ unit cell is more closely matched to an ideal UO$_3$ lattice [51], future work could investigate this polymorph with changes in composition.

Pellets of UO$_3$ were compounds of uranyl oxide and hydroxide due to the purification processes from the manufacturer. As observed with early efforts in this work as well as recognized by inconsistencies in literature, uranyl nitrate precursors do not fully convert to uranyl oxide in air. This does not seem to be apparent using powder x-ray diffraction (PXRD). With oxygen pressures greater than 10 atmospheres [48], it is possible that conversion could complete prior to decomposition, but this was not investigated. Like U$_3$O$_8$, stoichiometric changes did affect a first order change in electrical resistivity. In addition to the likely reasons noted for U$_3$O$_8$, the hydroxide phase likely impedes structural
changes through oxygen addition or removal. Due to the low temperatures of decomposition, UO$_3$ pellets were uniaxially hot pressed. This process produced nearly fully dense pellets, ranging from 80 – 95% of theoretical density for γ-UO$_3$. By using grazing incidence x-ray diffraction (GIXRD), pellet phase composition could be estimated. Using the average hydroxide composition, samples were as high as 99% of theoretical composite density. The electrical resistivity for these high-density pellets ranged from $10^9 – 10^{11}$ Ω·cm, the largest values ever reported. This is an increase of 1-4 orders of magnitude compared to cold uniaxially pressed compacts reported by Hanafi [35]. In order to aid further investigations into charge carrier mobility-lifetime, sintered pellets were heated for periods of 2 – 4 weeks in order to hopefully increase grain growth. At 400 °C, no noticeable grain growth was observed. Additional investigations for UO$_3$ as a candidate for neutron detection, should therefore consider the addition of dopant materials to promote grain growth or otherwise enhance carrier mobility lifetimes.
LIST OF REFERENCES


Figure 46: X-ray diffraction pattern with Rietveld refinement overlay for sample 423. Best matched with $\alpha$-UO$_3$ at 91.2% and UO$_2$(OH)$_2$ with 8.8% phase composition.
Figure 47. GI XRD of UO$_3$ without (left) and with (right) aluminum peaks from sample holder.
Figure 48. Unconditioned UO$_2$ pellet (top) cracking after 28 day furnace heating. Conditioned pellet (bottom) reveals surface roughness produced by steel plates in hot press.
VITA

Seth Lawson moved to Knoxville at the age of two. After graduating from the University of Tennessee in 2006 with a Bachelor of Science in Materials Science and Engineering, he served as Space and Missile officer in the United States Air Force. After four years of service, he returned to the University of Tennessee, earning a Master of Science degree working with iridium alloys used to shield radioisotope thermoelectric generators powering NASA probes such as Cassini and New Horizons. After graduation, Seth hopes to continue to contribute to new discoveries and scientific advancements.