

Spring 5-1-2017

# The Optimization of the Microwave Synthesis and Subsequent Characterization of Sodium Tungsten Bronze ( $\text{Na}_x\text{WO}_3$ ) Materials

Jessica Murdzek

University of Connecticut - Storrs, [jessica.murdzek@uconn.edu](mailto:jessica.murdzek@uconn.edu)

Follow this and additional works at: [https://opencommons.uconn.edu/srhonors\\_theses](https://opencommons.uconn.edu/srhonors_theses)

---

## Recommended Citation

Murdzek, Jessica, "The Optimization of the Microwave Synthesis and Subsequent Characterization of Sodium Tungsten Bronze ( $\text{Na}_x\text{WO}_3$ ) Materials" (2017). *Honors Scholar Theses*. 532.  
[https://opencommons.uconn.edu/srhonors\\_theses/532](https://opencommons.uconn.edu/srhonors_theses/532)

The Optimization of the Microwave Synthesis and Subsequent Characterization of Sodium

Tungsten Bronze ( $\text{Na}_x\text{WO}_3$ ) Materials

By: Jessica Murdzek

Department of Chemistry, University of Connecticut, Storrs, CT 06269

May 2017

In partial fulfillment of an Honors Senior Thesis project under the supervision of Dr. Steven Suib

## **Acknowledgements**

I would like to thank my wonderful PI, Dr. Steven L. Suib. Whenever I stepped into his office I knew I was going to learn something, or receive meaningful advice. He helped me see my own potential and helped guide me through the graduate school application and decision process. I'm grateful I was able to find his lab to work in my freshman year at UConn. My honors advisor, Dr. Thomas Seery, has always been there for me when I had questions about chemistry classes or about life after graduation. He encouraged me to take advantage of the opportunities available to me during my undergraduate career. Osker Dahabsu was the first person in the chemistry department that reached out to me when I declared my major, and I appreciate that he got me involved in research almost immediately.

I worked with many graduate students during the time of this project. First, David Kriz helped me start on this project, showed me how to use the microwave, and was available to discuss the results and further directions when I wanted to. He gathered much of the data for my samples with SEM, EDAX, and Raman. Other graduate students who were a big help during my project include Dr. Curtis Guild, Dr. Lakshitha Pahalagedara, Niluka Wasalathanthri, Yang Wu, Wenqiao Song and Mahbubur Shakil.

I would like to thank my parents, my family, and my friends for always being available for emotional and mental support. Even when you were busy, you all made time for me, which I will always be thankful for. A special thanks for my mom and dad for raising me and cultivating my curious mind.

This study would not have been possible without the Office of Undergraduate Research (OUR), the Honors Program, and the Summer Undergraduate Research Fellowship, specifically funded by the Dr. John Tanaka Academic Enhancement Fund for Honors.

## Table of Contents

1. Abstract.....	4
2. Introduction.....	5
A. General Overview.....	5
B. Effects of Different Ratios of Sodium to Tungsten.....	5
C. Methods Used To Synthesize Sodium Tungsten Bronze.....	6
D. Doping Sodium Tungsten Bronze.....	9
E. Goals.....	10
3. Experimental Design.....	11
A. Details of the Microwave Synthesis.....	11
B. Steps Taken to Optimize the Synthesis.....	12
C. Different Reagents Used To Synthesize Sodium Tungsten Bronze.....	13
D. Characterization.....	15
4. Results.....	18
A. Initial Results.....	18
B. Substrate Effects.....	23
C. Effects of Different Reagents and Reagent Combinations.....	24
D. Effect of Microwaves on Pre-Made Samples.....	33
5. Discussion.....	34
6. Conclusions and Future Work.....	38
7. References.....	40

## 1. Abstract

The microwave synthesis of heavily doped sodium tungsten bronze materials has been investigated. This solid state synthesis is more environmentally friendly than other syntheses typically used. The typical synthesis procedure involves heating the reagents to high temperatures for a long period of time, which requires a lot of energy. The microwave synthesis takes only 5-10 minutes, and needs 800-900 W of power, which uses much less energy. Even though there are clear benefits, the microwave synthesis has not previously been optimized and investigated in depth. The materials synthesized in this study were characterized with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDAX), Transmission Electron Microscopy (TEM), Raman Spectroscopy, and multiple conductivity tests. The gathered data showed which methods resulted in the materials with the cleanest XRD patterns, or highest conductivities. SEM and EDAX helped confirm that the sodium was incorporated into the bronze structure. The ideal reagent combination included sodium tungstate, tungsten trioxide, and tungsten metal powder. The materials with the highest sodium to tungsten ratio (0.80-0.95) were most conductive, and most often had a clean XRD pattern. The properties of the sodium tungsten bronze materials varied between samples, even when the same microwave procedure was carried out, which indicated that the microwave synthesis was not very predictable.

## 2. Introduction

### *A. General Overview*

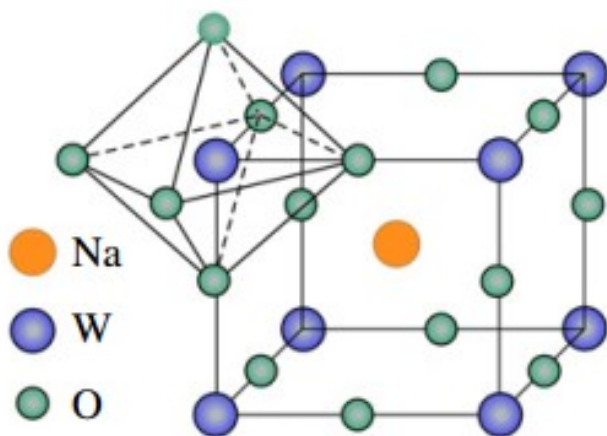
Tungsten trioxide ( $\text{WO}_3$ ) has been doped with various alkali metals, usually lithium, potassium, or sodium, and the resulting materials have been shown to have varying electrical properties.<sup>1</sup> The materials were named “bronzes” because of their shiny surfaces and bronze-like appearance. These doped materials contain tungsten in two different oxidation states, 5+ and 6+. In order to change some tungsten atoms in tungsten trioxide from 6+ to 5+, usually a reducing agent is used in the reactions. The added alkali metal with a 1+ oxidation state balances out the reduced tungsten atoms, and keeps the material overall neutral. One of the most promising classes of doped bronzes is the sodium tungsten bronzes ( $\text{Na}_x\text{WO}_3$ ). They have been synthesized with varying, nonstoichiometric, sodium to tungsten ratios. The materials can be used in various applications, including sensors, heterogeneous catalysis, solid fuel cells, and secondary batteries.<sup>2</sup> Recently, an interest has been taken in thin films. The Suib group at UConn has been investigating conductive sodium tungsten bronze thin films on a copper substrate for applications in circuit breakers. One of the challenges faced was synthesizing an electrically homogenous, conductive material using a cheap, quick, environmentally friendly methodology.

### *B. Effects of Different Ratios of Sodium to Tungsten*

The materials with different ratios of sodium to tungsten demonstrate a range of properties. For example, the color of the material changes from blue to red to yellow as the ratio of sodium to tungsten is increased.<sup>3</sup> The resistivity decreases as the ratio increases, which has been shown with resistivity measurements on electrically homogenous materials at various ratios and temperatures.<sup>4</sup> At room temperature, the resistivity of materials with high sodium to tungsten ratios is around  $20 \mu\text{ohm}\cdot\text{cm}$ .<sup>4</sup> Studies have shown that superconductivity is possible below 90 K

in sodium tungsten bronzes.<sup>5</sup> At a ratio of 0.25, there is a non-metal (insulating) to metal (conducting) transition.<sup>6</sup> The reason this transition takes place is due to Anderson delocalization within the material.<sup>6</sup>

Sodium tungsten bronzes have a crystal structure that changes as the sodium to tungsten ratio changes. At a low ratio, the structure is monoclinic or tetragonal.<sup>3, 6a, 7</sup> When the sodium to tungsten ratio is larger than 0.25, the material forms a warped perovskite structure with the sodium ion in the center of the cube, and the  $\text{WO}_6$  octahedra on the corners, so this material has a cubic structure (Figure 1).<sup>3, 6a, 7</sup>



**Figure 1.** A cartoon rendition of the structure of cubic sodium tungsten bronze when the sodium to tungsten ratio is larger than 0.25.<sup>7c, 7d</sup>

### *C. Methods Used To Synthesize Sodium Tungsten Bronze*

In the past, the methods for synthesizing these materials have been time consuming, expensive, and not environmentally friendly. One of the more common approaches to the synthesis of sodium tungsten bronzes is a solid state synthesis at high temperatures. The powdered reagents (sodium tungstate, tungsten (VI) oxide, and tungsten metal) are mixed together and then heated in a furnace for a long period of time.<sup>1, 7a, 8</sup> Very high temperatures, a large amount of energy, and very long periods of time are needed to complete this synthesis

method. The necessary temperature and time range conditions are 200-500 °C for 50-400 hours.<sup>1,</sup>  
<sup>7a, 8</sup> A similar synthesis process involves melting the reactants, and then combining them.<sup>6b, 9</sup> This molten process also requires very high temperatures in order to melt the compounds.

A few different electrolytic methods have been used to prepare bronze crystals as well. One study in 1961 prepared the samples via electrolysis (at 700 °C) of sodium tungstate and tungsten trioxide.<sup>4, 10</sup> A graphite anode and a nichrome cathode were used, with the crystals grown on the cathode. The largest and most pure single crystals were grown when the cathode was seeded.<sup>4</sup> Another similar technique involves growing crystals on seeded gold wire from a mixture of sodium tungstate and tungsten trioxide.<sup>11</sup> Again, a very high temperature is needed to complete the reaction.

Aqueous reactions have also been shown to produce tungsten bronzes. These reactions are done in an oven, often with the reactants enclosed in an autoclave.<sup>12</sup> Various solvents can be used, including ethanol or acetic acid,<sup>12a</sup> water, or ethylenediamine.<sup>12c</sup> A variety of reducing agents can be used; citric acid<sup>11b</sup> and ethylenediamine<sup>11c</sup> are just two of the possibilities. The Paul group has taken a different approach to the aqueous synthesis. Crystals of sodium tungsten bronze are synthesized by creating a very high temperature solution of a mixture of sodium oxide and tungsten trioxide, and then slowly cooling the mixture.<sup>7c, 7d</sup>

In another method, tungsten trioxide and sodium are evaporated onto a silica substrate.<sup>13</sup> This method requires gaseous reactants, and subsequently very high temperatures. This procedure allows for a very exact methodology that can be used to create precise, uniform films with one ratio of sodium to tungsten.<sup>13</sup> The measured properties can more clearly be associated with different dopant ratios when homogenous films are analyzed. Another way to create thin films is to use pulsed laser deposition on a sapphire base.<sup>3</sup> A mixture of the reagents (sodium



tungstate and tungsten trioxide) is ground, made into a pellet, and sintered in air at 630 °C for 3 days.<sup>3</sup> Then the films are grown at a substrate temperature of 550 °C.<sup>3</sup> This method is also time consuming and requires high temperature.

In order to avoid these labor-intensive methods, a microwave synthesis has been investigated. One attempt utilized a hydrothermal method, in which the reagents were placed in an autoclave with a solvent, and then microwaved.<sup>14</sup> The resulting precipitate was dried for 12 hours, and then heat treated for 2 hours at 300 °C.<sup>14</sup> This progression was still time consuming, and still required a high temperature. A different microwave process was inspired by solid state synthesis. The reagents (sodium tungstate, tungsten trioxide, and tungsten metal) were ground together and pressed into a pellet.<sup>2</sup> The pellet was placed in a small crucible, and that crucible was placed inside a large crucible with copper oxide powder between the two, to help absorb the heat from the microwaves.<sup>2</sup> The set-up in the microwave can be seen in Figure 2.<sup>2</sup> The crucibles with the pellet inside were microwaved at 800 W for 13-15 minutes, which was much less time than with the previous methods.<sup>2</sup> Despite this major advantage, very few studies on this microwave synthesis of sodium tungsten bronze are reported in the literature. This may be because this method can be less dependable and tends yield sporadic results, possibly because the microwave usually heats unevenly. The other methods to create thin films previously mentioned are very accurate and precise; however, they are expensive, and time and energy consuming. The microwave synthesis takes little energy, is fast, and has no by-products. This work further explores the solid state microwave synthesis and the different variables involved in producing sodium tungsten bronze product.

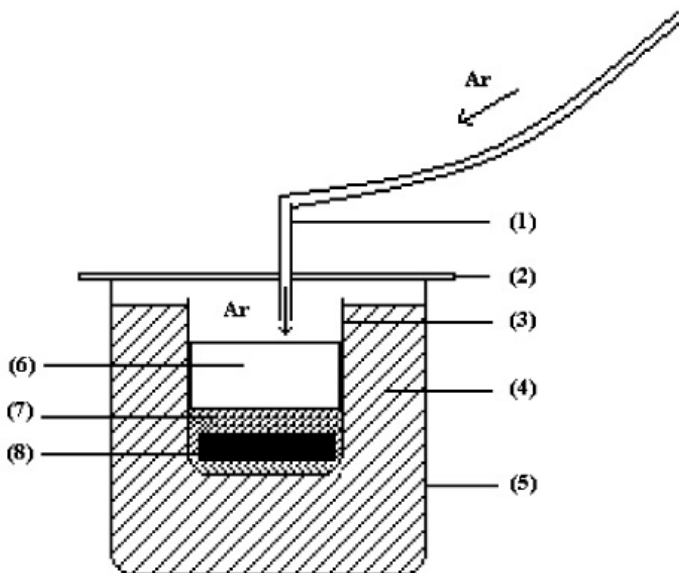


Fig. 1. Schematic illustration of microwave heating setup: (1)  $\text{Al}_2\text{O}_3$  tube, (2)  $\text{Al}_2\text{O}_3$  pellet, (3) small crucible, (4)  $\text{CuO}$  powder, (5) large crucible, (6) thermal insulation material, (7) reactants powder, and (8) reactants pellet.

**Figure 2.** The reaction set up for Guo's experiment done in a microwave.<sup>2</sup>

#### *D. Doping Sodium Tungsten Bronze*

The sodium tungsten bronze family has been doped with other metals. One study investigated adding small amounts of a noble metal (gold, palladium, platinum, or iridium) to sodium tungsten bronze.<sup>9</sup> When gold, palladium, or platinum were added, the tungsten bronze was activated towards oxygen reduction.<sup>9</sup> Another study looked exclusively at platinum doping of sodium tungsten bronze electrodes, with the sodium to tungsten ratio 0.7.<sup>11a</sup> The materials doped with platinum activated the bronze towards oxygen reduction.<sup>11a</sup> Niobium and tantalum doping of sodium tungsten bronzes was investigated in materials with a sodium to tungsten ratio of 0.8.<sup>11b</sup> The metal dopant was determined to decrease the conductivity of the bronzes.<sup>11b</sup> Vanadium doping of potassium tungsten bronzes was also investigated. A small amount of vanadium can be substituted into the bronze lattice before the material decomposes into non-

bronze phases.<sup>7a</sup> Light doping resulted in success, so light vanadium doping was incorporated into this work.

### *E. Goals*

One goal of this work is to synthesize cubic sodium tungsten bronze using a microwave because that method is faster, cheaper, and more environmentally friendly. The ideal samples will have an X-Ray pattern that shows pure cubic bronze with few to no impurities, a homogenous surface and composition, and a high conductivity. The materials with higher sodium to tungsten ratios will be focused on because according to the literature, materials with a cubic structure are more conductive, and the actual sodium to tungsten ratio is close to the original ratio of reagents put into the sample. One challenge that will be investigated is how to replicate samples with the same characteristics. The microwave heats unevenly, which can lead to problems such as having a wide range of characteristics over a group of samples where the same conditions are used. Another question that will be investigated is if doping the sodium tungsten bronze with transition metals yields any improved characteristics. Various combinations of reagents and reducing agents will be investigated as well, and the effect of the microwave synthesis will be recorded.

### 3. Experimental Details

#### *A. Details of the Microwave Synthesis*

Sodium tungsten bronze thin films were synthesized using the microwave solid state synthesis method. The basic solid state microwave procedure was detailed in the above section, and a very similar procedure was used in this work. In order to determine the ratios of reagents, the following equation was used:



The first ratio used was 3:2:2 molar ratios of  $Na_2WO_4 \cdot 2H_2O$ : $WO_3$ :W. The sodium tungstate and tungsten trioxide were bought from Sigma Aldrich, and the tungsten powder was from Strem Chemicals, Inc. All other reagents used in this work were from Sigma Aldrich, unless otherwise specified. The correct amounts of each reagent were weighed out, and thoroughly ground together with a mortar and pestle. Half a gram of this reagent material was pressed into a pellet (with diameter 13 mm) with five tons for five minutes. Other pellet weights were investigated, including 0.2, 0.3, 0.4, and 0.6 g of reagent powder, but the 0.5 g pellet was ideal because the pellet was sturdy enough not to break. Then the pellet was placed in a porcelain 10 mL crucible, and then that crucible was placed in a porcelain 25 mL crucible, with copper (II) oxide in between the two crucibles. A lid was placed on the crucibles, with a hole in the top for the argon purge. The microwave used was a CEM MARS microwave, and the wattage and time can be controlled. A variety of wattages, from 600-1200 W were used, and enough time was given for the reagents to react and form the sodium tungsten bronze. The resulting pellet was rinsed with distilled water after the material cooled down in order to eliminate unreacted sodium tungstate, which is water soluble. This rinsing technique was proven to work by X-Ray Diffraction (XRD) patterns taken before and after rinsing the sample.

### *B. Steps Taken to Optimize the Synthesis*

After microwaving the crucibles, the two crucibles often stuck together, with the copper (II) oxide in the middle. This study investigated if these sets of crucibles could be reused in subsequent experiments. The experiments showed they could be reused, but this procedure works best if additional copper (II) oxide is added in between the crucibles. This step was included whenever a synthesis was carried out with reused crucibles.

Different types of substrates were placed underneath the reagent pellets before the reaction in order to test if the pellet could adhere to the different surfaces. The substrates investigated were aluminum foil, copper foil, and steel blocks. The copper foil showed the most success, so the copper foil was most often used moving forward in further experiments. The impact of the shape of the copper foil (a square or a circle the same size of the pellet) was also investigated. The circular shape was more beneficial for the adherence and uniform melting of the pellet, so this shape was more utilized moving forward.

Another factor that was investigated was if adding copper (II) oxide to the pellet itself would help the reagents more evenly heat up and react. A variety of amounts were investigated: 1%, 2.6%, 4.5%, and 9% mass percent of copper (II) oxide was added into the pellets. This technique was not determined to be helpful, so this procedure was not used in subsequent syntheses.

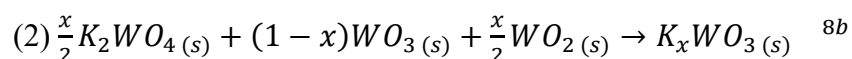
Different treatments of the copper foil substrate were executed in order to improve the adherence of the sodium tungsten bronze film. For one treatment, the copper foil was briefly dipped in nitric acid, and then rinsed in distilled water and dried. Another treatment involved using sandpaper or a file to mechanically roughen the surface of the copper foil. Since this treatment resulted in improved adhesion, this method was continued for the remainder of the

samples so they could all have superior adhesion. The nitric acid treatment did not change the level of adhesion, and in some cases actually reduced the amount of adhesion. This treatment was not continued after these results were clear.

Different ratios of sodium to tungsten were investigated in order to find out how the properties would be any different from materials synthesized using other methods. Equation 1 was used to calculate the different x values, which were the sodium to tungsten ratios. The ratios investigated were 0.5, 0.75, 0.85, and 0.95. Two samples of each ratio were synthesized, one with a copper foil substrate and one without a substrate, in order to find out if the copper foil significantly interfered with the various samples.

### *C. Different Reagents Used To Synthesize Sodium Tungsten Bronze*

A different synthesis method, utilizing a different combination of reagents was attempted, which was inspired by the Haldolaarachchige group. In Haldolaarachchige's paper dealing with potassium tungsten bronze, different reagents were used for the solid state synthesis.<sup>8b</sup> The reaction is as follows:



This chemical equation uses tungsten (IV) oxide as a reducing agent instead of the tungsten metal that was used in the previous equation. For these experiments, sodium replaced potassium in the equation, so sodium tungstate instead of potassium tungstate was used. The following values of x were investigated: 0.85, 0.9, and 1.0.

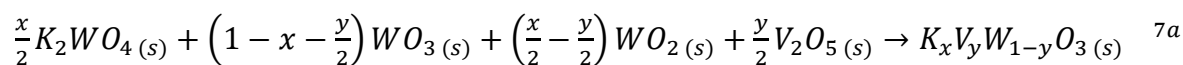
Another different synthesis method was investigated, using ethylenediamine (EDA) as a reducing agent. There was one study that used EDA as a reducing agent in an aqueous synthesis reaction.<sup>12c</sup> The amount of EDA added to the reaction was calculated from the amount of tungsten metal in the original reaction. The number of moles of EDA and tungsten metal were

the same, since they would be serving the same purpose as a reducing agent. Since EDA is a liquid, an aqueous approach, instead of a solid state synthesis, was taken. 0.330 g sodium tungstate was dissolved in 5 mL of distilled water in a 10 mL crucible. Then 0.600 mL of EDA was added, and the solution was stirred. The small crucible was placed inside the 25 mL crucible, with copper (II) oxide between them. The crucibles were microwaved at 600 W for 15 minutes.

A technique using only sodium tungstate and tungsten trioxide was investigated. A previous study used Pulsed Laser Deposition (PLD) to deposit these two reactants onto a substrate, so a synthesis method using these same reactants in a microwave oven was investigated.<sup>3</sup> Ratios of 0.85 and 0.95 of sodium to tungsten were attempted. Since there was no reducing agent used here, the copper foil acted as a reducing agent. Two trials were done: one with copper foil and one without copper foil.

Vanadium doping was carried out, based on a paper that doped potassium tungsten bronzes with vanadium.<sup>7a</sup> The following equation was given in the paper, and was used in this work as well:

(3)



For this work with sodium tungsten bronzes, sodium replaced potassium in the equation. Various x and y values were investigated, according to Table 1.

trial	x-value	y-value
1	0.85	0.05
2	0.85	0.10
3	0.85	0.20
4	0.95	0.10
5	0.90	0.20

**Table 1.** A summary of the different trials attempted when vanadium (V) oxide is used to dope sodium tungsten bronzes. The x and y values were used to determine the mole ratios of reagents according to Equation 3.

Sodium tungsten bronze was doped with vanadium in another way. Vanadium (III) oxide was utilized as a comparison to vanadium (V) oxide. The sample pellets had varying amounts of vanadium (III) oxide added to them. 0.001 g, 0.002 g, 0.005 g, and 0.01 g of vanadium (III) oxide were added to individual pellets. The reagent powder was ground with a mortar and pestle prior to pressing the pellet to ensure the reagents were well mixed in the pellet. Two trials of each mass of vanadium (III) oxide were synthesized.

An aqueous synthesis procedure was tried, in a different microwave, a Biotage Initiator Classic. The first precursor material mixture was used, with the reagent ratio of 3:2:2. Half a gram of this powder was dissolved in water and the reaction vessel was sealed. Then the microwave was used to heat the sample. Various temperatures and lengths of time were investigated.

Previously synthesized sodium tungsten bronze samples from other methods were microwaved in order to find out how the microwaves might change the sample's characteristics. Samples synthesized via the microwave were also re-microwaved and the characteristics were monitored as a comparison.

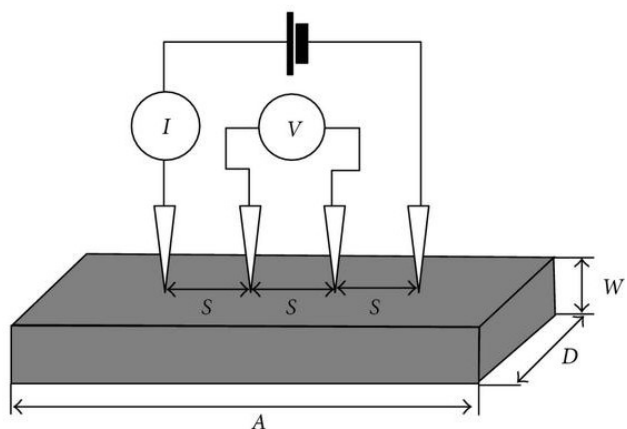
#### *D. Characterization*

In order to characterize all of these materials, a set of methods and instruments were used. X-Ray Diffraction (XRD) helped determine the purity of the samples, which crystalline



form the bronze was, and helped identify peaks coming from impurities. Scanning Electron Microscopy (SEM) was utilized to get pictures of the surfaces of the samples, and to determine the morphologies of the samples. Energy-Dispersive X-ray Spectroscopy (EDAX) helped determine what elements were present on the surface, helped find the sodium:tungsten ratio on the surface, and the mapping tool could show if the elements were spread evenly over the material's surface, or if the elements were clumped into sections. Transmission Electron Microscopy (TEM) was carried out for one sample to determine if the internal composition was similar to the surface seen in SEM/EDAX.

Conductivity tests were carried out using two different methods. A four probe set up, as seen in Figure 3, was used to measure the conductivity along the surface of the samples. Four probes are placed equidistance apart in a straight line. Then, a current is run between the outer two probes, and the voltage is measured between the two inner probes. From these data, along with the thickness of the sample, the resistivity can be calculated for each sample.



**Figure 3.** A drawing of how the four-probe conductivity measurements are taken along the surface of the samples.<sup>15</sup>

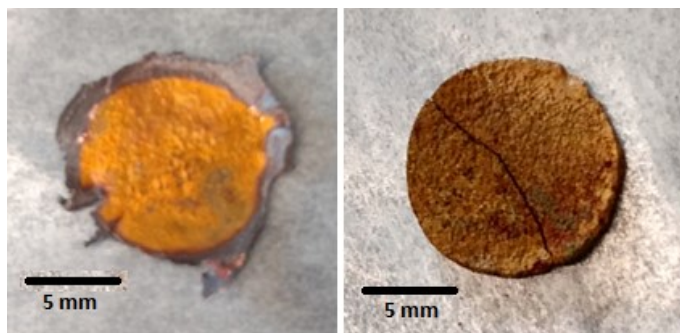
Another way that conductivity was measured was with Electrochemical Impedance Spectroscopy (EIS). This technique measured the current through the sample instead of along the surface, which is what the previous technique did. In addition, EIS can help determine if the

conductivity seen in a sample is due to electronic movement or ionic movement. Raman Spectroscopy was the last technique used to determine what impurities were in the samples, and what synthesis techniques reduced the amount of impurities.

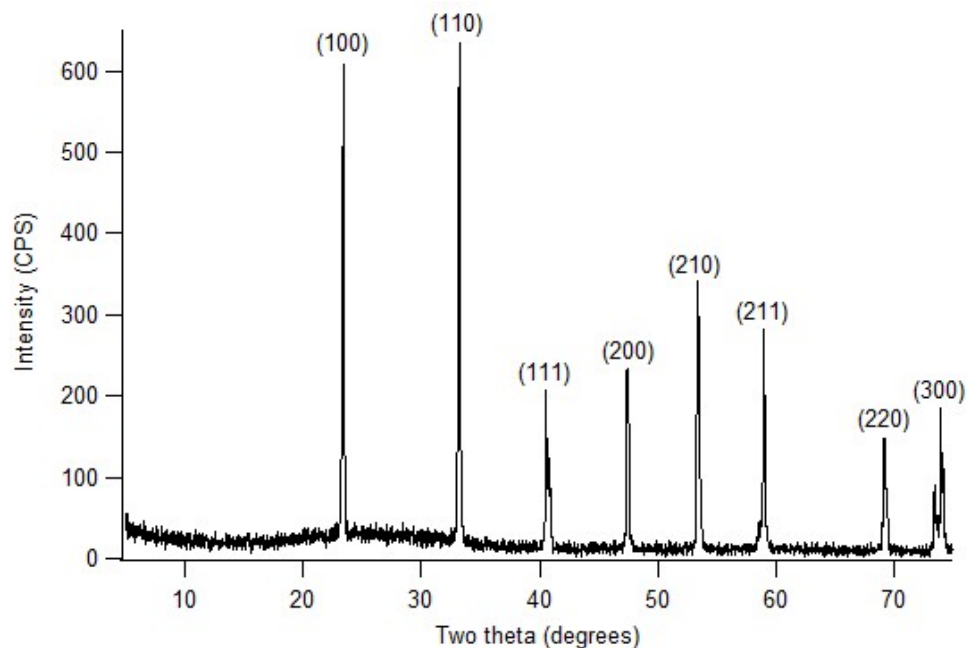
## 4. Results

### *A. Initial Results*

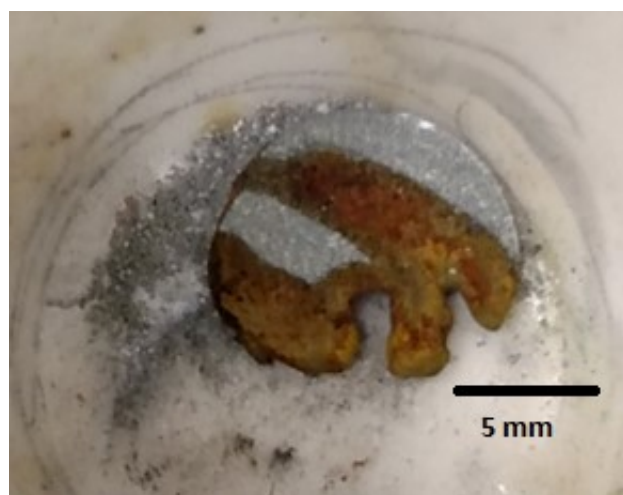
When the gray-green precursor material reacted to form the sodium tungsten bronze, the color changed to brown or gold (Figure 4). X-Ray Diffraction (XRD) was the first definitive way to determine if the synthesized bronze was pure. An XRD pattern of pure cubic sodium tungsten bronze is included (Figure 5). The samples that were synthesized with a microwave power of 700-900 W for 5-10 minutes yielded clean XRD patterns like Figure 5. The samples microwaved for less time were not pure bronze. For these samples, there were peaks from the precursor materials, which show that the reagents did not have enough time to fully react and form the bronze. The materials synthesized at lower powers did not react at all, or only part of the sample reacted (Figure 6). This indicated that the material did not heat to the needed temperature to react. The lower powers were not sufficient to finish the reaction. The XRD pattern also showed that rinsing the sample with distilled water would eliminate excess, unreacted sodium tungstate. According to Figure 7, all of the sodium tungstate peaks were removed after the sample was rinsed with distilled water. This is the reason why all samples were rinsed with distilled water after they cooled.



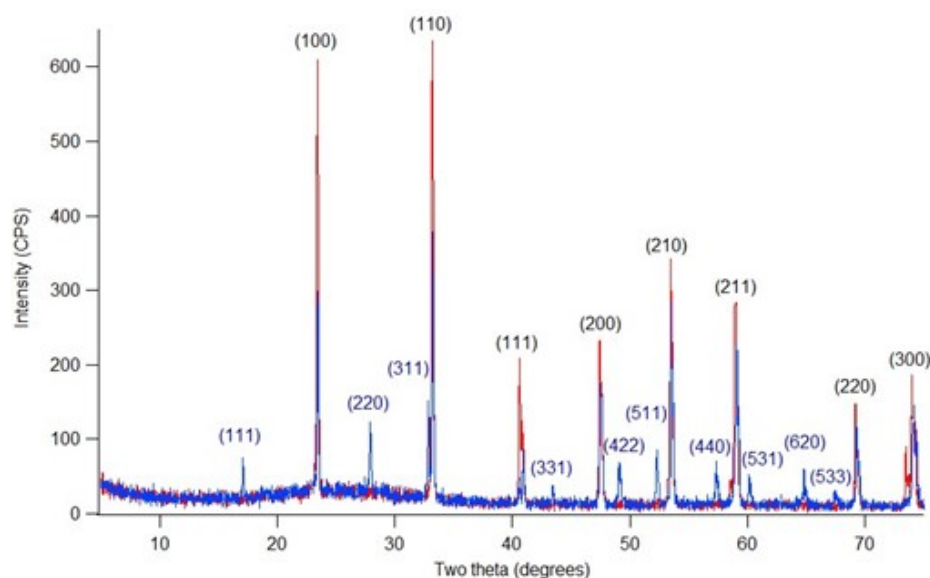
**Figure 4.** Two examples of the sodium tungsten bronze. The sample on the left was synthesized in the microwave for 4 minutes at 900 W. The sample on the right was synthesized for 6 minutes at 900 W.



**Figure 5.** The expected X-Ray pattern for pure cubic sodium tungsten bronze.



**Figure 6.** A sample that has not finished reacting. The conditions for this sample were 2.5 minutes at 800 W, then 5 minutes at 600 W. The given time and power were not enough for the crucible to sufficiently heat up.



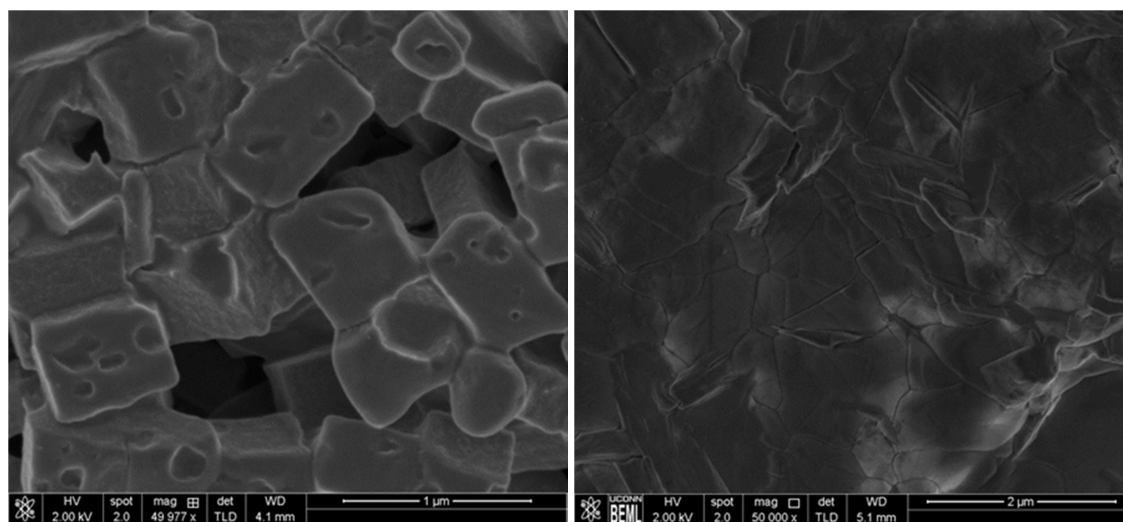
**Figure 7.** The blue pattern is for a sample with sodium tungstate impurities. The blue labels show where the sodium tungstate peaks are, and the black labels show where the cubic sodium tungsten bronze peaks are. The red pattern is for the same sample that has been rinsed with distilled water. No sodium tungstate peaks are seen.

The conductivity tests using the four probe set-up showed which samples were conductive. Table 2 gives a summary of the measured resistivities for a group of representative samples. The resistivity can vary a huge amount between samples. Samples that received the same treatment in the microwave had a large range of conductivity measurements. For example, the first two samples in the table received the same treatment, but the conductivities of the two were different by an order of magnitude. These results showed that there are other variables besides synthesis time and microwave power that affect the conductivity of a sample. Two clear trends were that samples subjected to a lower power or not enough time reacted unevenly, and were not conductive.

Time in Microwave (min)	Power of Microwave (W)	Resistivity ( $\Omega\cdot\text{m}$ )
5	800	$1.01 \times 10^{-7}$
5	800	$9.80 \times 10^{-6}$
5	900	$2.87 \times 10^{-7}$
9	900	675
5	900	14.10

**Table 2.** A summary of how a representative group of samples were synthesized and the resistivity measurements from the four probe set-up.

In order to observe the surface morphologies of the samples, SEM was used. The two main morphologies seen were cubes or long, flat structures. Samples were also likely to show some combination of these two. Figure 8 shows examples of these two shapes. The most conductive samples had a combination of these two morphologies. Often, the two shapes were mixed together well, so the surface was approximately homogeneous. A few samples were observed to have large surface areas with one morphology, and other areas of the sample with the other morphology. The samples with the best-defined cubes had few, if any, impurities in the XRD pattern.

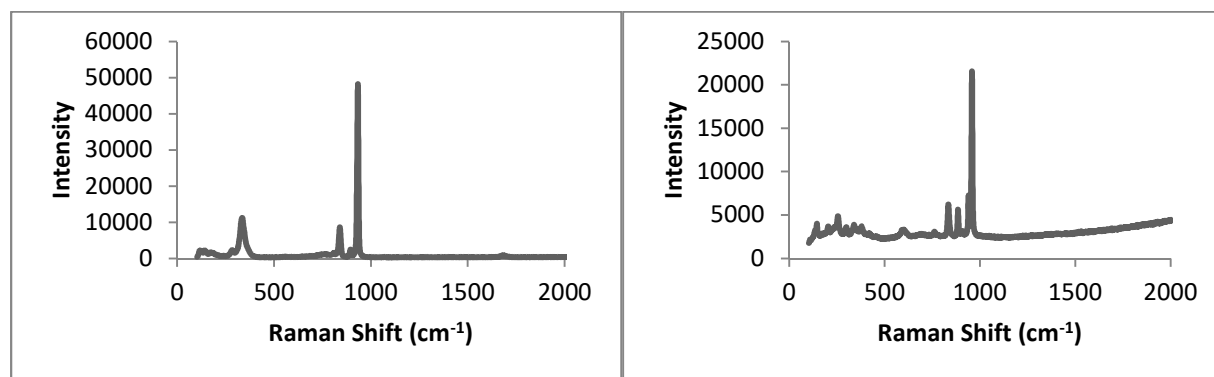


**Figure 8.** The left panel shows the typical cubic structure. The right panel shows the long, flat plane morphology.

EDAX was used to determine if the ratio of sodium to tungsten was the same as the ratio put in the sample. For all of the samples, the ratio of sodium to tungsten varied throughout the

sample. A few different spots were measured with EDAX and the average sodium to tungsten ratio was determined. The ratios of sodium to tungsten tended to be sporadic. Sometimes the actual ratio in the material was the same as the intended ratio, but other times the two ratios were very different. The source of this large variation was difficult to determine. One reason for the variation could be that the sodium tungstate sometimes did not react with the other precursors completely. In these cases, a large amount of sodium tungstate was rinsed out of the sample. The mapping tool showed that the sodium, tungsten, and oxygen were all homogenously dispersed over each sample.

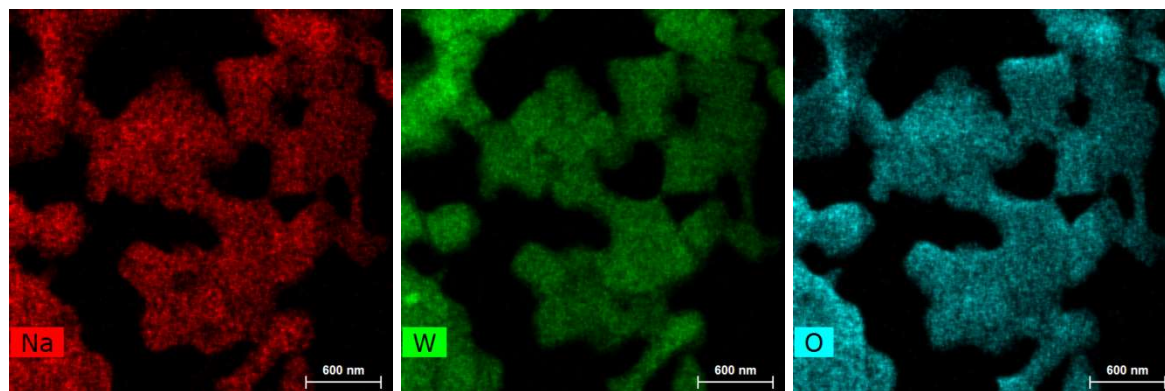
Raman was used as a tool to determine what impurities were in the samples, and helped show if the samples were homogenous or heterogeneous. The samples that had sodium tungstate impurities in the XRD showed the same impurities in Raman (Figure 9). Many samples were determined to be heterogeneous. Different spots of the material showed differing levels of impurities.



**Figure 9.** The Raman spectra on the left is for pure sodium tungstate. The Raman spectra on the right is for one of the samples of sodium tungsten bronze. There are sodium tungstate impurities in the sample.

TEM data showed that the sodium, tungsten, and oxygen are evenly dispersed in the material, which is similar to the results found on the surface with EDAX (Figure 10). A cubic

structure can be seen in the sample, which is similar to the cubic structures seen on the surface with SEM.



**Figure 10.** TEM mapping data from one conductive sample of sodium tungsten bronze.

EIS was attempted, although there were some problems that called into question the results. The set-up included immersing the sample in an aqueous solution, but when the samples were immersed for too long, the material started to come off the copper substrates and dissolve into the solution. Towards the end of the measurement, the conductivity of the copper substrate was being measured, not the sample, since so much of the sample had dissolved off. The data were discarded because the technique could not produce accurate results.

### *B. Substrate Effects*

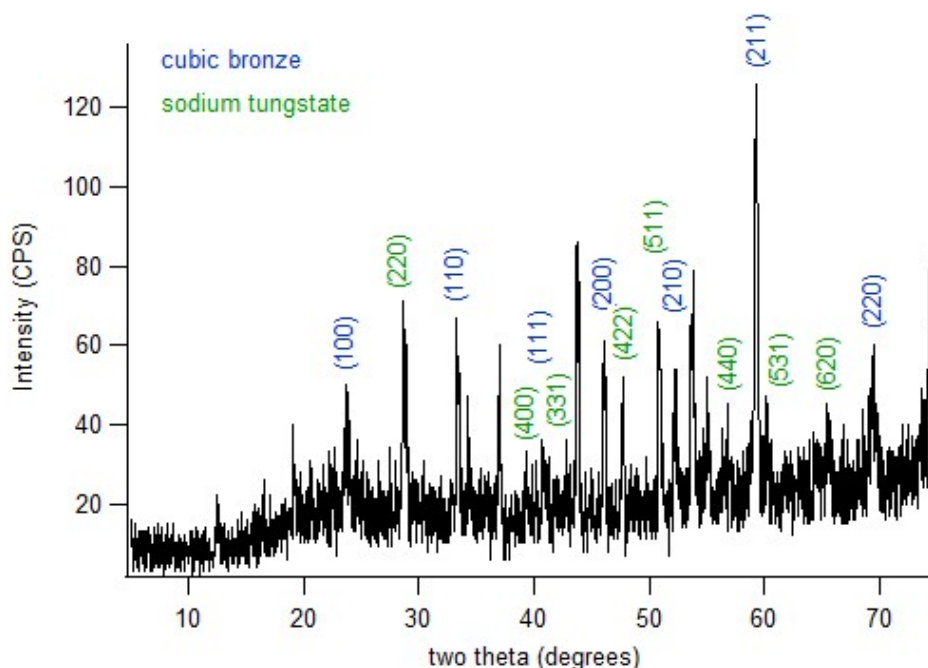
When the samples were synthesized on a steel substrate, the SEM images showed that the surface appeared more cracked than the other samples. The samples were still conductive, although they were less conductive than the samples on copper foil. The aluminum foil as a substrate was not strong enough to support the bronze. When the sample did stick to the aluminum foil, the foil would peel off or break very easily. This is why copper foil was determined to be the best. The copper foil was strong enough to support the sample and the resulting material was conductive.



The materials that were synthesized on copper sometimes stuck to the copper foil, and sometimes did not. To try and stop this unpredictable behavior, and make the sample adhere to the surface every time, the copper foil was subjected to different treatments. The nitric acid treatment did not help improve adhesion. This treatment actually diminished adhesion. Mechanical roughening of the surface was attempted, and this technique was found to help adhesion. The mechanical roughening helped the sample adhere to the substrate more often, but this technique did not work every time. The samples that did not stick to the copper were less conductive than those that did. The copper foil played an important role in improving the conductivity, so synthesizing samples that adhered to the copper foil substrate became a goal for this work as a result of these observations.

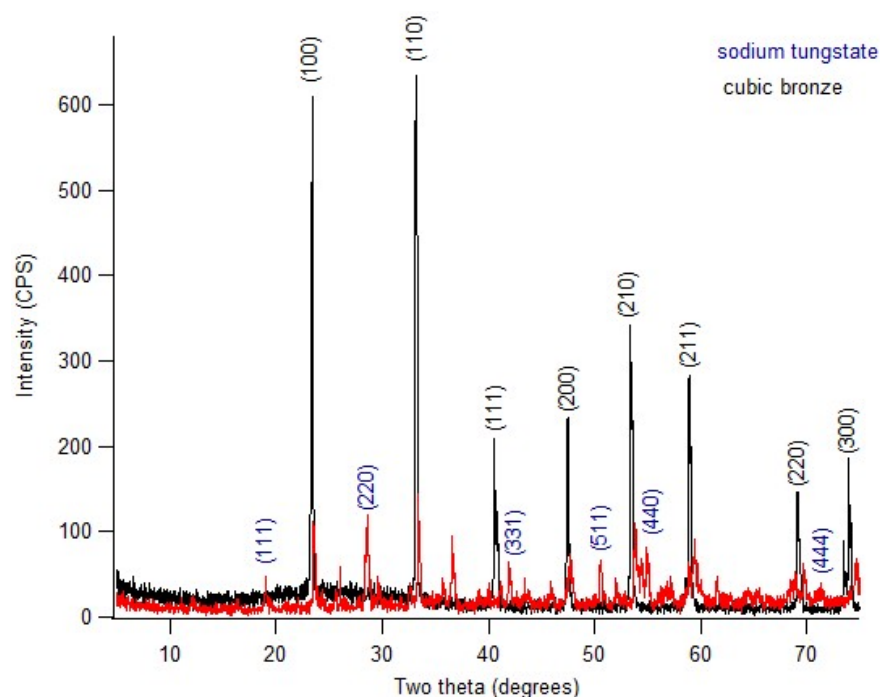
### *C. Effects of Different Reagents and Reagent Combinations*

Copper (II) oxide in various mass percentages was added to the pellet itself to see if the addition would help the pellet heat more evenly, since copper (II) oxide is a heat sink. The resulting XRD patterns showed that the resulting material had more amorphous character and shorter peaks for the cubic bronze at each doping value. Even after rinsing with distilled water, the sodium tungstate peaks persisted in the X-Ray pattern (Figure 11). Adding copper (II) oxide did not make the material melt any more evenly. Instead, the copper (II) oxide contaminated the sample with more impurities and did not help the product form a crystal. The copper (II) oxide may have interacted with the sodium tungstate to make the sodium tungstate less soluble and less likely to come out of the sample after rinsing, which is a problem when the goal is to create pure cubic sodium tungsten bronze.

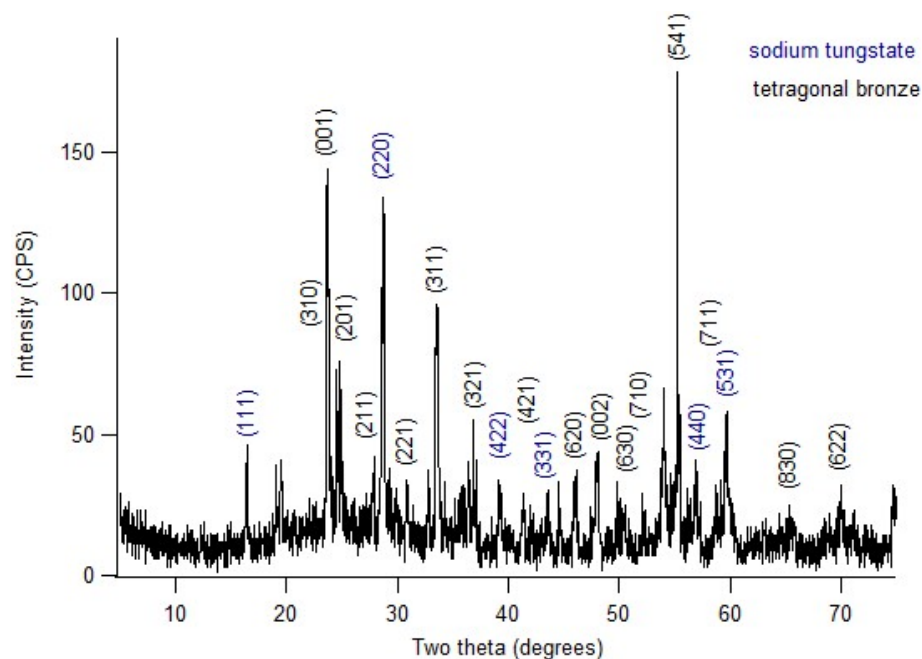


**Figure 11.** The XRD pattern for one of the samples to which copper (II) oxide was added before microwave treatment. This sample was rinsed before taking this X-Ray pattern. The blue-labeled peaks indicate cubic bronze, and green-labeled peaks indicate sodium tungstate impurities.

The samples with different ratios of sodium to tungsten reacted to the microwave synthesis differently. The materials with ratios of 0.75 and below did not show pure cubic bronze XRD patterns (Figure 12). Often the materials contained sodium tungstate, tungsten trioxide, or other unknown impurities. Tetragonal bronze peaks were seen at a lower ratio of 0.5 (Figure 13). SEM showed a wide variety of surface structures. These low ratio samples were not conductive. The microwave synthesis did not work well to synthesize sodium tungsten bronze with lower sodium to tungsten ratios. Higher ratios of 0.85 or 0.95 showed cleaner XRD patterns, and SEM showed they were more homogeneous than the other ratios. The samples were less resistive, in the range of 64.9-172.1  $\Omega \cdot \text{m}$ . These samples were not among the most conductive, but they were relatively more conductive than the lower ratio samples. From these data, the 0.85 or 0.95 ratios were utilized most often when further optimizing the synthesis procedure.

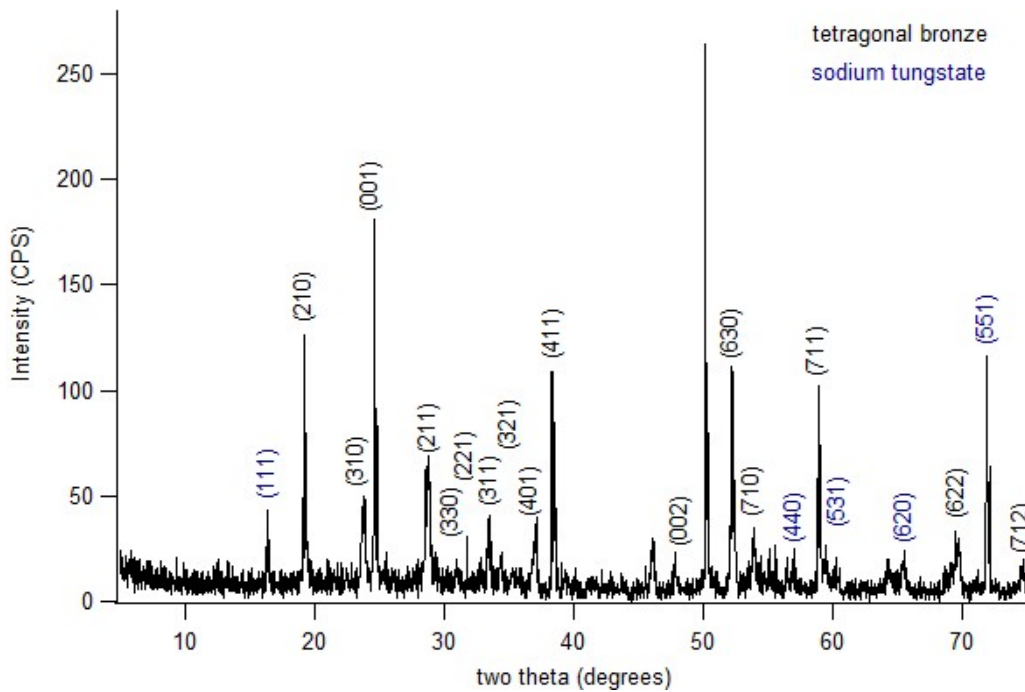


**Figure 12.** The XRD of a sample synthesized with the 0.75 ratio (in red) compared to the pure sodium tungsten bronze pattern (in black). There were many impurities in the 0.75 sodium to tungsten ratio sample, some of which could not be identified. The blue labeled peaks correspond to sodium tungstate and the black labeled peaks correspond to cubic sodium tungsten bronze.

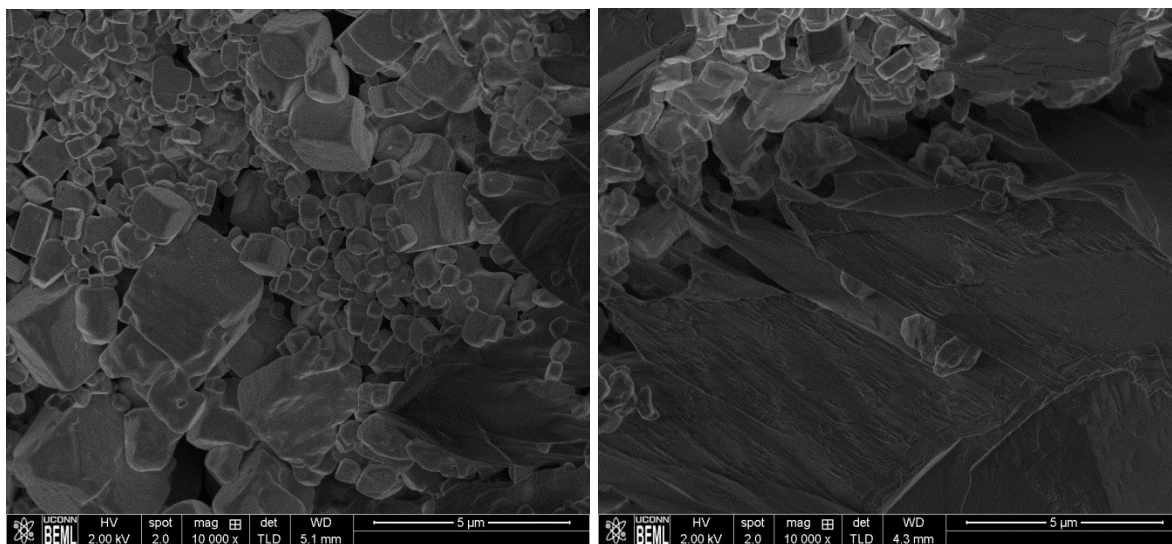


**Figure 13.** The XRD pattern from a sample made with a sodium to tungsten ratio of 0.5. The black peaks are from tetragonal sodium tungsten bronze, and the blue peaks are from sodium tungstate.

The synthesis method that used tungsten (IV) oxide instead of powdered tungsten metal as a reducing agent did not help meet the goals of this work. Despite the fact that only high ratios (above 0.85) of sodium to tungsten were synthesized, often tetragonal bronze was created instead of cubic bronze, which can be seen from the XRD pattern (Figure 14). The sodium tungstate impurities also seemed to persist even after rinsing. The SEM images revealed that these samples were not homogeneous. There was a variety of morphologies on the surface (Figure 15). EDAX showed that the sodium to tungsten ratio on the sample surface is heterogeneous. Different points were measured, and the sodium to tungsten ratio varied between 0.3 and 0.7. Finally, the conductivity tests showed the samples were not conductive. The measured resistivity for the best conductor was  $5.99 \times 10^4 \Omega \cdot \text{m}$ .



**Figure 14.** An XRD pattern from a typical sample synthesized using tungsten (IV) oxide as a reducing agent. The black-labeled peaks are from the tetragonal bronze structure and the blue-labeled peaks are from sodium tungstate impurities.

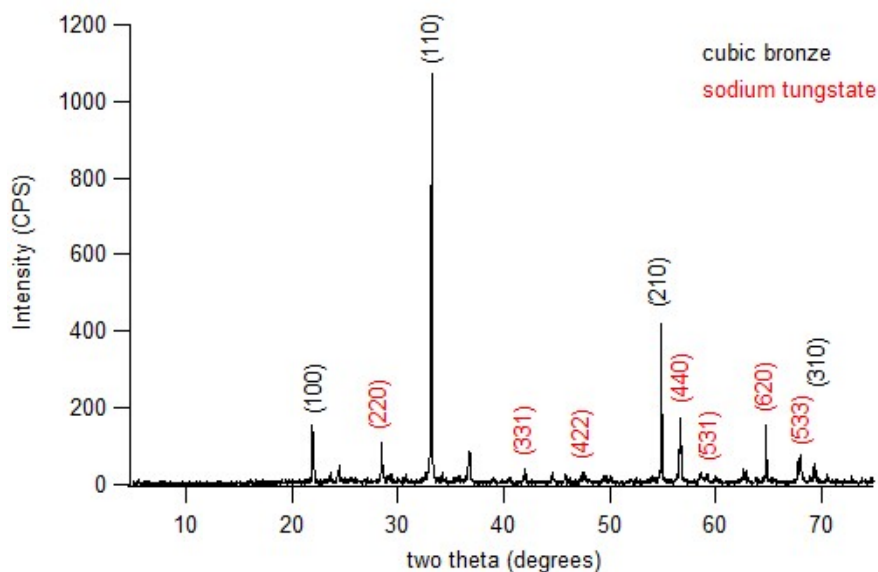


**Figure 15.** SEM images from one of the samples synthesized using tungsten (IV) oxide as a reducing agent. The surface shows a variety of structures depending on the location of the surface examined.

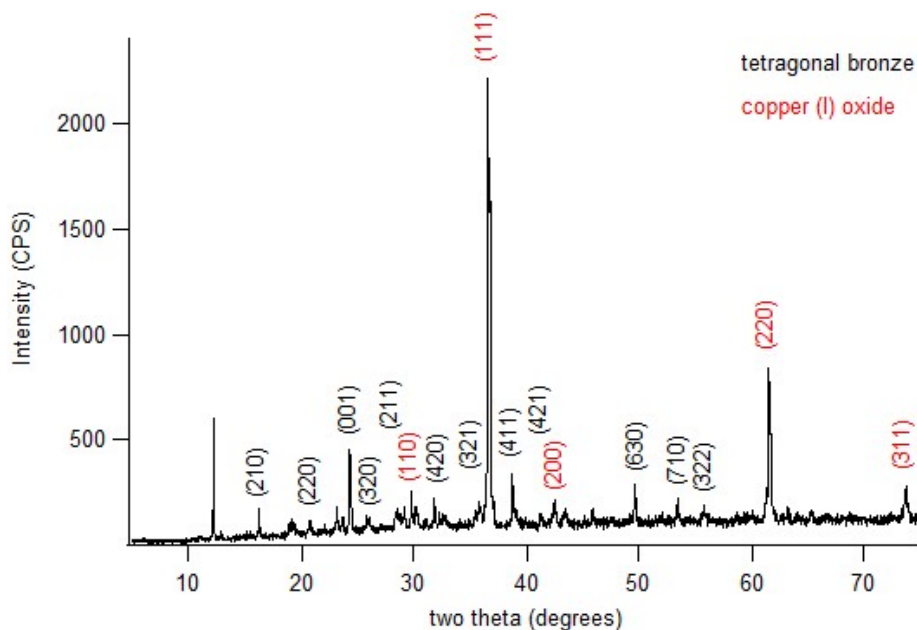
The next method utilized ethylenediamine (EDA) as a reducing agent. This aqueous synthesis was not successful at creating sodium tungsten bronze. The EDA evaporated before reaction with sodium tungstate could take place. Only solid sodium tungstate was left after the crucibles were microwaved, which was verified with XRD.

The synthesis method using only sodium tungstate and tungsten trioxide as reagents was investigated. This method produced heterogeneous samples. A variety of products were obtained. When copper foil was not used as a substrate, cubic sodium tungsten bronze, sodium tungstate, or  $\text{Na}_2\text{W}_2\text{O}_7$  peaks were seen in XRD patterns (Figure 16). When copper foil was used as the substrate, the copper foil acted as a reducing agent. XRD showed peaks from copper (I) oxide and tetragonal bronze (Figure 17). The SEM images showed long flat plane structures. These long flat planes could have been due to tetragonal bronze in the samples. EDAX maps showed very clearly that the sample surfaces were heterogeneous (Figure 18). The copper (I) oxide and sodium tungsten bronze were separated in the sample. The image showed that two reactions took

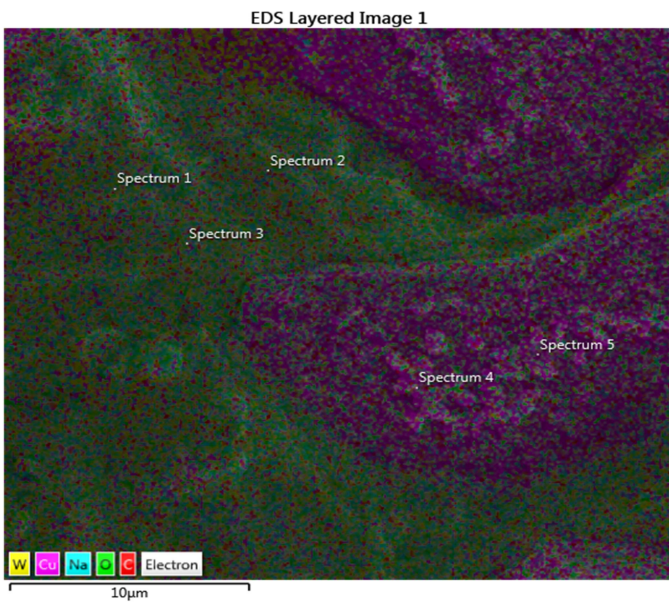
place while the sample was heated in the microwave: copper was oxidized to copper (I) oxide, and the sodium tungsten bronze was formed from tungsten trioxide and sodium tungstate.



**Figure 16.** The XRD pattern for one of the samples synthesized with sodium tungstate and tungsten trioxide without a copper foil substrate. The black-labeled peaks correspond to cubic bronze peaks, and the red-labeled peaks correspond to sodium tungstate impurity.



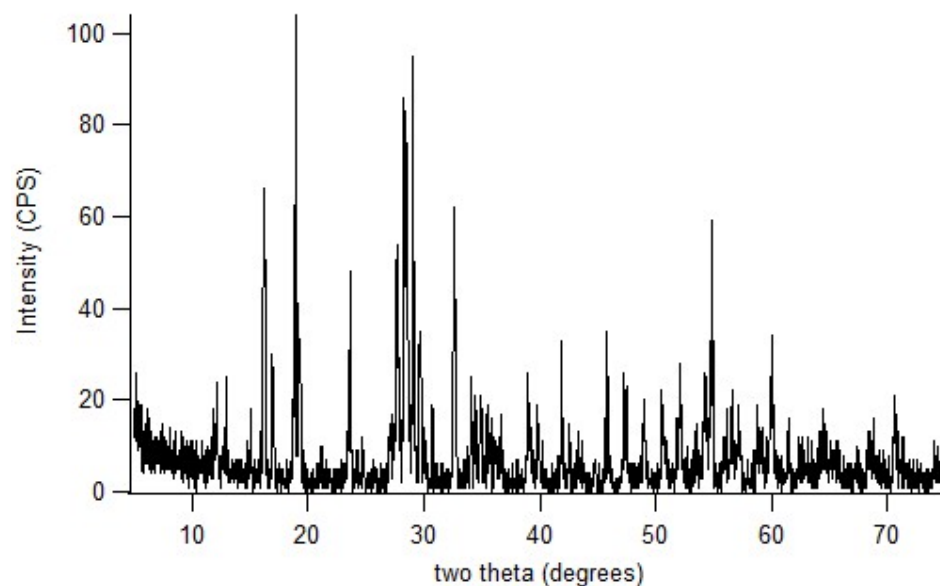
**Figure 17.** The XRD patterns for one of the samples synthesized with sodium tungstate and tungsten trioxide with a copper foil substrate. The black-labeled peaks are for tetragonal bronze, and the red-labeled peaks are for copper (I) oxide.



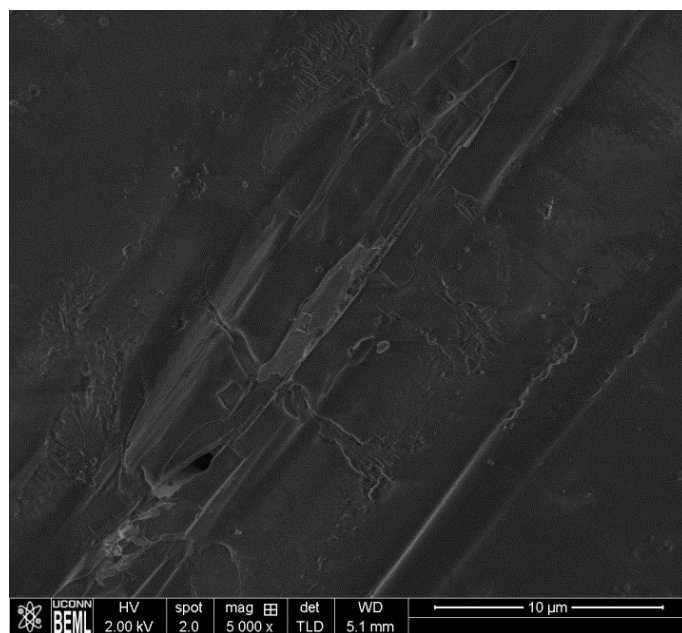
**Figure 18.** An image of an EDAX map for a sample synthesized with sodium tungstate and tungsten trioxide with copper foil. The produced copper (I) oxide (purple) and tetragonal sodium tungsten bronze (green) separated.

Studies were also done on vanadium doping of the sodium tungsten bronze. For the studies using vanadium (V) oxide, many by-products were seen in the X-Ray patterns, including  $\text{NaV}_6\text{O}_{11}$ ,  $\text{VO}_2$ ,  $\text{Na}_2\text{W}_2\text{O}_7$ ,  $\text{V}_3\text{O}_7$ ,  $\text{Na}_{12}\text{V}_6\text{O}_{19}$ , and  $\text{NaVO}_3$ , as well as peaks from the precursor materials. Some XRD patterns had so many peaks that assigning peaks to the impurities or the bronze was difficult (Figure 19). The SEM images showed that the surfaces of all of the samples were similar: they had the long flat morphology (Figure 20). The samples that were lightly doped with vanadium had decent resistivity, between  $49.8\text{--}400\ \Omega\cdot\text{m}$ . The samples heavily doped with vanadium were not conductive: they had an average resistivity of  $2.0 \times 10^4\ \Omega\cdot\text{m}$ .





**Figure 19.** The X-Ray pattern for a vanadium (V) oxide doped sample of sodium tungsten bronze. This sample was synthesized with  $x=0.9$ ,  $y=0.2$  (see equation 3). Assigning peaks to the impurities was difficult because there were so many peaks. These impurities include  $\text{Na}_2\text{W}_2\text{O}_7$ .

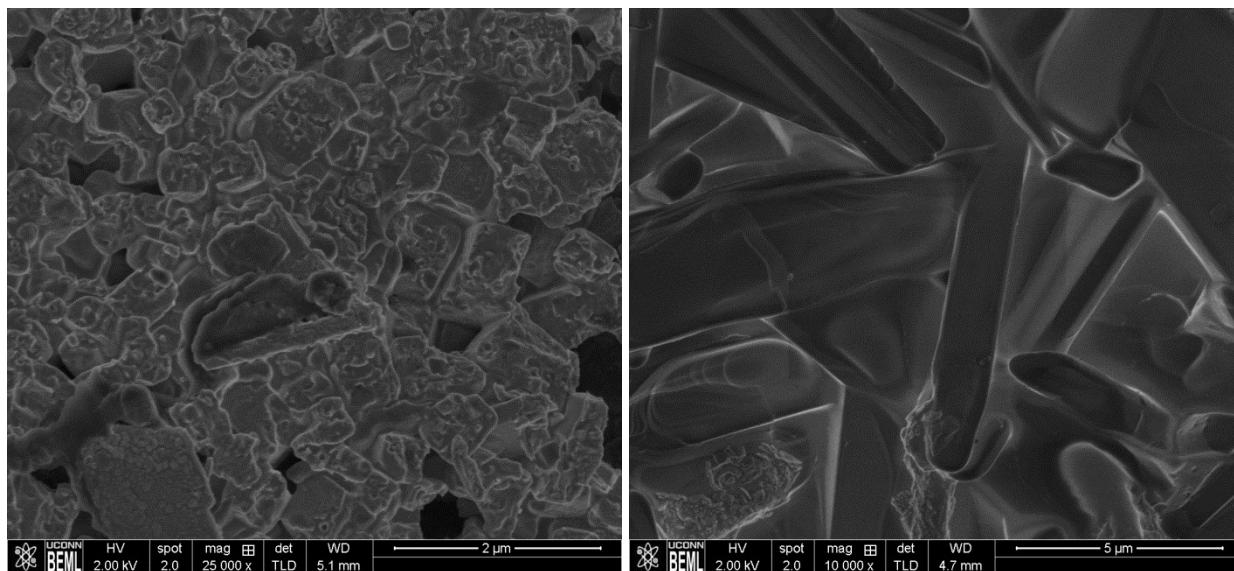


**Figure 20.** A typical SEM image of one of the sodium tungsten bronze samples doped with  $\text{V}_2\text{O}_5$ . All of the samples had this similar flat morphology.

The materials synthesized using vanadium (III) oxide had a large variety of resulting products. The vanadium was never incorporated into the bronze lattice structure. The vanadium



(III) oxide reacted with the reagents and formed side products, and peaks were observed from  $\text{VO}_2$ ,  $\text{Na}_2\text{W}_2\text{O}_7$ , vanadium, as well as from the precursor reagents. A few different surface structures were observed in this set of doped materials (Figure 21). One structure looked like cubes, which was similar to the morphologies seen previously in other sodium tungsten bronze samples. The other structure was more needle-like in structure, also including some long flat planes. This morphology, again, was similar to the structures seen before. According to EDAX, only some of these samples contained vanadium in their final structures. The other samples were either too lightly doped (0.001 g  $\text{V}_2\text{O}_5$  added) or the vanadium may have been washed out when the samples were rinsed with water. Either way, the vanadium didn't make a large impact on the characteristics of these materials.



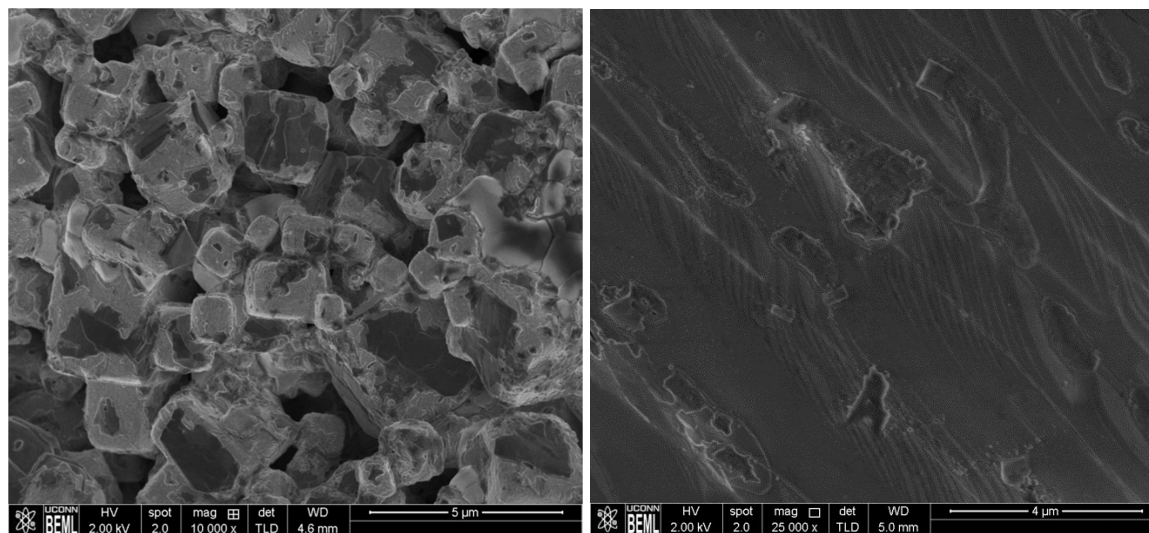
**Figure 21.** Two surface structures observed in sodium tungsten bronze samples doped with vanadium (III) oxide.

The aqueous microwave synthesis did not produce sodium tungsten bronze. The environment was not hot enough for the reagents to react and form the material. The highest temperature the reaction vessel achieved was 106 °C. If the temperature was increased much

more, then the pressure would be too much for the reaction vessel to sustain, so a higher temperature was not attempted.

#### *D. Effect of Microwaves on Pre-Made Samples*

Pre-made samples were microwaved in order to find out if and how the microwaves would affect the samples. One sample made in the microwave and one sample made by solid state synthesis in the oven, were microwaved. The sample that was originally synthesized in the microwave changed a small amount. The X-ray pattern showed a new impurity,  $\text{Na}_2\text{W}_3\text{O}_{10}$ , after microwaving again. The sample did not become conductive after re-microwaving. The surface morphology was the same before and after re-microwaving. The sample originally synthesized in the oven did change. The surface consisted of cubes when the sample was originally synthesized, but after microwaving, the surface had long flat planes (Figure 22). The XRD pattern did not change after being microwaved.



**Figure 22.** The left is an SEM image of a sample synthesized in the oven. The right is an SEM image of the same sample after the sample was subject to microwaves.

## 5. Discussion

The variety of results shows that the microwave synthesis needs specific conditions to work properly. Only a select range of sodium to tungsten ratios reacted and produced materials with pure X-Ray patterns. The higher ratios, between 0.80 and 0.95 are the most conductive, and most pure bronze. A microwave power of 700-900 W for a time of 5-10 minutes are the optimal conditions to allow the sample to completely react and form the bronze. The optimal reagent mixture contains sodium tungstate, tungsten trioxide, and tungsten metal. Tungsten metal was shown to be the most effective reducing agent. Few, or even no other by-products were formed, in direct contrast to when tungsten (IV) oxide was used as a reducing agent, or the copper foil acted as a reducing agent.

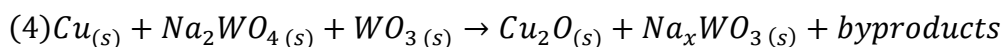
This study showed that the microwave synthesis process can be unpredictable at times, and there are a few phenomenon that can't quite be explained by trends in the data. The first is that sometimes the pellet sticks to the substrate, whether that be the bottom of the crucible, or the copper foil, depending on if foil was used for the synthesis or not. Even samples synthesized the same way sometimes adhered to the substrate differently. The mechanical roughening of the copper foil did help the sample adhere more often to the foil, but this technique did not work every time. The adherence continued to be unpredictable, which is a major problem if this synthesis procedure was to be scaled up to an industrial level. The number of times the pellet would not stick to the substrate as expected would be too numerous to be a reliable process.

For the four-probe conductivity measurements, there were also a few problems that could prevent getting reliable sample conductivity measurements. This method required that the sample be flat so that all four probes could touch the surface. Often times, the samples were not perfectly flat. The sample might have been thicker on one side, or the surface could have been covered

with small holes or cracks. Both of these issues would interfere with getting precise measurements. One of the four probes might not be able to touch the sample, which prevents any data from being measured accurately. Sometimes one probe would get moved over a little bit by a hole in the surface of the sample, changing the distance between probes. This also creates problems, since the distance between probes needs to be a known quantity in order to calculate the conductivity. The thickness of the sample also must be a known quantity in the calculations. If the sample had different thicknesses, an average thickness was used in the calculations; however, this reduces the accuracy of the measurement. The data reported were determined to be the most reliable conductivity data. These data came from the samples that were most homogenous, the flattest, and of most uniform thickness.

The conductivity or resistivity of the samples can be compared to copper. The bulk resistivity of copper is  $1.68 \times 10^{-8} \Omega \cdot \text{m}$ . The most conductive sample synthesized had a resistivity of  $1.01 \times 10^{-7} \Omega \cdot \text{m}$ , almost a full order of magnitude more than copper. This level of conductivity is on par with platinum or tin, which have resistivities of  $1.06 \times 10^{-7}$  and  $1.09 \times 10^{-7} \Omega \cdot \text{m}$ , respectively. In the literature, heavily doped sodium tungsten bronzes have a resistivity around  $500 \Omega \cdot \text{m}$ <sup>4</sup>. When compared to this number, many of the sodium tungsten bronze samples synthesized with the microwave had higher conductivities. It's possible the microwave synthesis is a better method for creating conductive sodium tungsten bronze samples.

The synthesis method using only sodium tungstate and tungsten trioxide as reagents resulted in forcing the copper foil to become a reducing agent when the copper foil was used as a substrate. The following is the main reaction that takes place when this method with copper foil is attempted:



A variety of by-products are seen with this reaction, made from any leftover atoms. They can vary based on what the sodium to tungsten ratio is. Some of the copper foil is oxidized to copper (I) and some of the tungsten is oxidized from tungsten (V) to tungsten (VI) to give the tungsten in the sodium tungsten bronze product mixed valency. Since the copper is only found on the foil, the reaction can only take place at the interface between the foil and the precursor pellet. This results in some leftover precursor material that was not close enough to the copper foil, and could not react.

The samples that were the most conductive had a high ratio of sodium to tungsten (0.85-0.95) and most often had the long, flat surface structures. Those samples had the sodium, tungsten, and oxygen evenly dispersed over the entire sample, meaning the entire sample was bronze with a uniform sodium to tungsten ratio. Samples with a small variation of the ratio were also conductive. Some of these samples had a few impurities, and a few did not have any impurities. This shows that as long as the sample is mostly sodium tungsten bronze, a small amount of impurities will not change the conductivity.

The bronzes were doped with vanadium (V) oxide and vanadium (III) oxide. Both of these methods yielded samples with many impurities. The vanadium compounds reacted with the reagents to make products other than cubic bronze. Usually the samples doped with less vanadium yielded fewer impurities. These impurities also reduced the conductivity of the materials. For  $V_2O_3$  doping, The surface structures were similar to the structures usually observed in sodium tungsten bronzes. For  $V_2O_5$  doping, the surface morphology was flat and not very similar to the other sodium tungsten bronze samples.

The sample that was re-microwaved showed that too much microwaving can produce new impurities. The  $Na_2W_3O_{10}$  was created during the second microwaving. For the sample that

was synthesized in the oven, the microwave treatment changed the surface morphology to the flat structures from the cubes. The microwaves favor the long flat planes, although the reason why is unknown.

The methods that used an aqueous state instead of a solid state synthesis did not produce sodium tungsten bronze product. The two methods explored in this work were when EDA was used as a reducing agent, and then when the aqueous synthesis using sodium tungstate, tungsten trioxide, and tungsten metal was attempted. The EDA evaporated before this reducing agent even had a chance to react with the sodium tungstate. This happened even at low microwave powers. Sodium tungstate was dissolved in water for this experiment, but the water also evaporated before any reaction could take place. The aqueous synthesis with sodium tungstate, tungsten trioxide, and tungsten metal could not heat up enough to allow the precursors to react and form bronze product. The water would all vaporize in the sealed reaction vessel, and then the pressure would increase too much for the microwave to sustain. The reaction to form sodium tungsten bronze requires a temperature that cannot be reached when in an aqueous environment.

Overall, exposure to microwaves for a short period of time will not allow the reagents enough time to react, but too much time exposed to microwaves can create new impurities. Each sample must be exposed to the correct amount of microwaves to react and create sodium tungsten bronze.

## 6. Conclusions and Future Work

Sodium tungsten bronze with varying ratios of sodium to tungsten were successfully synthesized in a microwave. The materials with sodium to tungsten ratios between 0.8 and 0.95 were the most conductive, and always had a cubic structure. The lower ratios could be cubic or tetragonal, depending on how the material reacted and what the resulting sodium to tungsten ratio was. The microwave synthesis is an unreliable process, and the synthesized materials had sporadic properties, such as differing surface morphologies and conductivities even when the samples were synthesized the same way. As long as producing samples with a variety of properties is acceptable, the microwave synthesis can produce sodium tungsten bronze.

This study could be continued by looking at a larger diversity of substrates for the sodium tungsten bronze. Many other metal blocks or foils could be used as a substrate. The effects of these substrates on the properties of the materials should be measured to find the optimal substrate. The optimal substrate might not actually be copper foil, which was extensively used in this study. Various correlations between properties of the substrate, properties of the materials, and microwave conditions could be determined.

Another experiment that may be beneficial to do with these materials is a temperature dependence conductivity test. The materials might have very different conductivity levels at different temperatures, which could be useful to determine. The sodium tungsten bronze material could be used in high temperature applications, and knowing how the samples behave at high temperature would be necessary. There was a study that looked at the X-Ray patterns at different temperatures, and the data showed that the  $\text{WO}_6$  octahedra get distorted at 300 K <sup>7d</sup>. If the structure changes at this temperature, other properties could change as well.

The microwave synthesis of potassium or lithium tungsten bronzes could be useful. This study focused on the sodium tungsten bronzes, but it is not known if the lithium and potassium tungsten bronzes would act the same way. Varying ratios of alkali metal to tungsten could be carried out, with different substrates as well.



## 7. References

1. Brown, B. W., Banks, E., The Sodium Tungsten Bronzes. *Journal of the American Chemical Society* **1954**, 76 (4), 963-966.
2. Juan Guo, C. D., Lihong Yang, Guangcai Fu, A green route for microwave synthesis of sodium tungsten bronzes  $\text{Na}_x\text{WO}_3$ . *Journal of Solid State Chemistry* **2004**, 178 (1), 58-63.
3. Lekshmi, I. C., Gayen, Arup, Prasad, V., Subramanyam, S. V., Hegde, M. S., Structure and electrical properties of sodium tungsten bronzes thin films. *Materials Research Bulletin* **2002**, 37 (11), 1815-1823.
4. Ellerbeck, L. D., Shanks, H. R., Sidles, P. H., Danielson, G. C., Electrical Resistivity of Cubic Sodium Tungsten Bronze. *The Journal of Chemical Physics* **1961**, 35 (1), 298-302.
5. (a) Reich, S., Tsabba, Y., Possible nucleation of a 2D superconducting phase on WO single crystals surface doped with Na. *Eur. Phys. J. B* **1999**, 9 (1), 1-4; (b) Shengelaya, A., Reich, S., Tsabba, Y., Müller, K. A., Electron spin resonance and magnetic susceptibility suggest superconductivity in Na doped  $\text{WO}_3$  samples. *Eur. Phys. J. B* **1999**, 12 (1), 13-15.
6. (a) Paul, S., Raj, Satyabrata, Understanding metal-insulator transition in sodium tungsten bronze. *Pramana - J Phys* **2015**, 84 (6), 957-966; (b) S. Raj, D. H., H. Matsui, S. Souma, T. Sato, T. Takahashi, D. D. Sarma, Priya Mahadevan, and S. Oishi Angle-Resolved Photoemission Spectroscopy of the Insulating  $\text{Na}_x\text{WO}_3$ : Anderson Localization, Polaron Formation, and Remnant Fermi Surface. *Physical Review Letters* **2006**, 96; (c) Sanhita Paul, A. G., and Satyabrata Raj, Metal-Insulator Transition in  $\text{Na}_x\text{WO}_3$  : Photoemission Spectromicroscopy Study. *Solid State Physics* **2014**.
7. (a) A. M. Abdullah, T. D., C. H. Rüschler, and A. Hussain, Synthesis and Characterization of Vanadium Substituted Potassium Tungsten Bronzes,  $\text{K}_x\text{V}_y\text{W}_{1-y}\text{O}_3$ . *Journal of Scientific Research* **2012**, 4 (2), 507-514; (b) Mackintosh, A. R., Model for the Electronic Structure of Metal Tungsten Bronzes. *The Journal of Chemical Physics* **1963**, 38 (8); (c) Sanhita Paul, A. G., Anirban Chakraborty, Luca Petaccia, D. Topwal, D.D. Sarma, S. Oishi, Satyabrata Raj, Temperature dependent photoemission spectroscopy on lightly-doped sodium tungsten bronze. *Solid State Communications* **2012**, 152, 493-496; (d) Sanhita Paul, G. D. M., Anirudha Ghosh, S. Oishi, and Satyabrata Raj, Temperature dependent x-ray diffraction study of lightly doped sodium tungsten bronze. *Applied Physics Letters* **2011**, 98.
8. (a) Kyunghwan Moon, J.-J. C., Ye-Bin Lee, Pil J. Yoo, Chung Wung Bark, and Juhyun Park, Near Infrared Shielding Properties of Quaternary Tungsten Bronze Nanoparticle  $\text{Na}_{0.11}\text{Cs}_{0.22}\text{WO}_3$ . *Bulletin of the Korean Chemical Society* **2012**, 34 (3), 731-734; (b) Neel Haldolaarachchige, Q. G., Jason Krizan, and R. J. Cava, Superconducting properties of the  $\text{K}_x\text{WO}_3$  tetragonal tungsten bronze and the superconducting phase diagram of the tungsten bronze family. *Physical review B* **2014**, 89.
9. J. H. Fishman, J. F. H., S. Tessore, Activation of Sodium Tungsten Bronzes with Noble Metals. *Electrochimica Acta* **1969**, 14 (12), 1314-1317.
10. F.H. Jones , K. R., R.A. Dixon, T.W. Fishlock, R.G. Egdel The surface structure of the metallic sodium tungsten bronze  $\text{Na}_{0.667}\text{WO}_3(001)$ . *Surface Science* **2000**, 460, 277-291.
11. (a) A. J. Appleby, C. V. D., Behavior of Pure and Platinum-Doped Sodium Tungsten Bronze Electrodes in Oxygen-Saturated Phosphoric Acid. *Electrochemical Science and Technology* **1976**, 123 (2), 200-203; (b) Paul F. Weller, B. E. T., Impurity effects in sodium tungsten bronzes: Niobium and tantalum doping. *Journal of Solid State Chemistry* **1970**, 2 (1), 9-15.
12. (a) Tingyu Wang, Y. X., Ruixing Li, Hongnian Cai, Dependence of infrared absorption properties on the Mo doping contents in  $\text{M}_x\text{WO}_3$  with various alkali metals. *The Royal Society of Chemistry* **2016**; (b) Jiayu Luo, J. L., Fei Shi, Qiang Xu, Yanyan Jiang, Guishan Liu and Zhiqiang Hu, Synthesis of Sodium Tungsten Bronze via Hydrothermal Method Assisted by Citric Acid. *Advanced Materials Research* **2013**, 712-715; (c) Gaoxiang Liu, S. W., Yuting Nie, Xuhui Sun, Yahong Zhanga and Yi Tang, Electrostatic-induced synthesis of tungsten bronze nanostructures with excellent photo-to-thermal conversion behavior. *Journal of Materials Chemistry A* **2013**, 1 (35).
13. (a) Mino Green, A. T., Sodium-Tungsten Bronze Thin Films II. Electrical properties of dilute bronzes. *Philosophical magazine B. Physics of condensed matter. Electronic, optical, and magnetic*

- properties* **1984**, 51 (5), 521-532; (b) Mino Green, A. T., SODIUM-TUNGSTEN BRONZE THIN FILMS - PART I. OPTICAL PROPERTIES OF DILUTE BRONZES. *Philosophical magazine B* **1985**, 51 (5), 501-520; (c) Kang, M. G. a. K., Sodium tungsten bronze thin films: Variation of chemical potential with sodium concentration. *Solid State Ionics* **1983**, 8 (4), 281-289.
14. Tiago A. Martins, T. R. M., Mateus M. Ferrer, Sonia M. Zanetti, Elson Longo, Facile microwave-assisted hydrothermal synthesis of hexagonal sodium tungsten bronze and its high response to NO<sub>2</sub>. *Materials Letters* **2016**, 185, 197-200.
  15. S. Ummartyotin, J. J., C. Wu, M. Sain, and H. Manuspiya, Deposition of PEDOT: PSS Nanoparticles as a Conductive Microlayer Anode in OLEDs Device by Desktop Inkjet Printer. *Journal of Nanomaterials* **2011**.