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ABSTRACT

The focus of this thesis is the investigation of ternary and quaternary reduced metal oxide compounds termed “bronzes.” The name bronze originally arose from the metallic-like luster of these compounds. Examples of these compounds range from sodium tungsten oxides to the more complex potassium cesium molybdenum oxides. These compounds are crystalline solids at room temperature.

The “bronzes” are compounds that have been studied since their initial synthesis by Wohler in 1824. These compounds belong to a class of compounds that are known as “nonstoichiometric” compounds. The general formula for reduced ternary transition metal oxides is $A_xM_yO_z$. In this general formula, the value of x is less than one, but greater than 0. The compounds vary in crystal structures due to the radius of the electropositive element, M. The compounds also vary in physical properties because of their crystal structures and energy level occupations. The compounds can range in color from purple to yellow and range in electrical conductivity from metallic behavior to semiconducting behavior.

The history of these compounds, including a classification of known bronze phases, will be reviewed with a focus on complex molybdate phases. Experimental methods, including experimental searches for new phases using ceramic synthesis techniques and electrolytic growth, and analysis of resulting products by powder x-ray diffraction and SEM studies will be discussed in this thesis. Single x-ray diffraction was utilized as well.

The thesis will document the results of the synthetic work aimed at producing new quaternary molybdenum bronze phases. Finally, new quaternary alkali bronze phases containing lithium and potassium, and sodium and potassium will be presented.

MONTCLAIR STATE UNIVERSITY

A STUDY AND SYNTHESIS:

BRONZE COMPOUNDS

By

Patricia Rose Olsen

A Master's Thesis Submitted to the Faculty of

Montclair State University

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

May 2020

College of Science and Mathematics

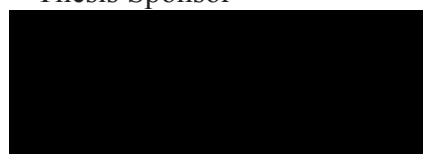
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A STUDY AND SYNTHESIS:
BRONZE COMPOUNDS

A THESIS

Submitted in partial fulfillment of the requirements
For the degree of Master of Science

By
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May 2020

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Introduction

The focus of this thesis is the investigation of ternary, quaternary and other complex reduced metal oxide compounds termed “bronzes.” If an alkali metal can be interstitially inserted in the crystal of a ternary molybdenum bronze compound, then a quaternary molybdenum bronze compound will be formed. Also studied will be the effect of the size of the atomic radii of the alkali metals on the structure.

The term “bronze” originally arose from the metallic-like luster of these compounds. They have been studied since their initial synthesis in 1824. These compounds belong to a class of compounds that are known as “nonstoichiometric” compounds. The general formula for reduced ternary transition metal oxides is $A_xM_yO_z$. In the general formula, the value of x is less than one, but greater than zero. The compounds vary in crystal structures due to the radius of the electropositive element, M . The compounds also vary in physical properties because of their crystal structures and electronic composition. The compounds are crystalline solids at room temperature and can range in color from purple to yellow and range in electrical conductivity from metallic behavior to semiconducting behavior. The history of these compounds, including a classification of known bronze phases, will be reviewed with a focus on the complex molybdate phases.

A known set of ternary purple molybdenum oxide bronzes exists for the alkali metals, Li, Na and K. This set of purple bronzes have similar but not exact structures. The alkali metals occupy sites between molybdenum oxide sheets. In the three purple bronzes the alkali metals occupy different sites; therefore, the structures are different for each crystal. Experiments were conducted to explore the possibility of combining more than one alkali metal into one structure to form a new quaternary molybdenum bronze.

Samples were prepared to explore the Li-K-Mo-O, Li-Na-Mo-O and the Na-K-Mo-O systems. A key aspect of the solid-state synthesis was the temperature ramping to produce a product that was not susceptible to a reaction involving the silica ampoule – or “tube attack.” The stoichiometry was adjusted in experiments to synthesize larger crystals for analysis.

Experimental methods, including experimental searches for new phases using ceramic solid-state synthesis techniques and analysis of resulting products by powder x-ray diffraction and SEM studies will be discussed. This thesis will document the results of the synthetic work aimed at producing new quaternary molybdenum bronze phases. Finally, new quaternary alkali bronze phases containing lithium and potassium, and sodium and lithium will be presented.

Background

Ternary bronze compounds have been successfully synthesized and studied for their properties. To show the extent of the many bronzes, some examples of known reduced ternary molybdenum oxides have been compiled in Table 1: Reduced Ternary Molybdenum Oxides (Bronzes), page 25. Noteworthy is the fact that most of these examples are non-stoichiometric compounds.

The general formula for reduced ternary transition metal oxides is $A_xM_yO_z$. “A” represents generally any cation from the alkali metals, alkaline earth metals or rare earth metals families. The “M” represents elements such as titanium, vanadium, manganese, niobium, molybdenum, tantalum, tungsten, and rhenium.¹ The intriguing part is that the “x” can be less than one, therefore “x” can be a fraction. The “x” can also be zero. Generally, the “x” is a ratio of small integers that denotes the compound formula of the constituent elements, known as a stoichiometric compound. When “x” is a fraction, this is termed a nonstoichiometric compound.

The tungsten bronzes are examples of nonstoichiometric compounds. The tungsten bronzes have a general formula of M_xWO_3 . “M” is generally an electropositive element where “x” would be greater than zero but less than one; therefore it can exist as a fraction. These compounds will crystallize in a number of different phases.² Nonstoichiometric compounds are solids in which the stoichiometry will vary over a small range of composition without affecting the basic crystal structure. This is common in transition metal oxides where transition metals can readily change to maintain a neutral charge. Two common ways in which variable stoichiometry occurs are from interstitial atoms, which are atoms inserted into the void spaces in a crystal structure or from vacancies of atoms in the crystal structure.³

The change in stoichiometry will have an effect on the compound’s properties, such as color or electrical properties, such as superconductivity. An example of this would be the two potassium molybdenum bronzes. $K_{0.28}MoO_3$ is blue and metallic at room temperature, while $K_{0.33}MoO_3$ is red and a superconductor at the same conditions. These compounds as well as being intensely colored, have a metallic luster in the crystalline form, and are chemically inert. The changes of the solid phases occur with the variation of x, the alkali metal; exhibiting definite and at times wide ranges of being homogeneous.⁴ Another class of bronzes are quaternary compounds, where two different metal cations are introduced into the structure are also classified as bronzes.¹ A general formula for a quaternary tungsten bronze is $A'_x A''_y WO_3$, where A’ and A’’ are two different metal cations. Subscripts x and y can be greater than zero and less than one.

“Bronze” compounds have a long history. The term “bronze” arose from the luster associated with these crystalline solid compounds. In 1824 Friederich Wohler passed dry hydrogen gas over heated sodium tungstate, Na_2WO_4 and tungsten trioxide, WO_3 . The product was golden yellow crystals that appeared to be metallic. The product was sodium tungsten oxide, termed “tungsten bronze” due to the metallic luster of the

compound.⁴ According to a review by M. Greenblatt, the tungsten bronzes have been continuously investigated since the 1940's.¹ Initially thought to be unique, other analogous compounds were later synthesized with other elements. Analogous compounds were synthesized with molybdenum by A. Wold, et al., vanadium by R.P. Ozerov, niobium by D. Ridgley and R. Ward, and titanium by M. Kestigian and R. Ward. These compounds were found to have similar properties to the tungsten bronzes. At this point the term "bronze" was extended to ternary metal oxides.⁴

The earliest reported molybdenum bronzes were in 1895 by A. Stavenhagen and E. Engels. They synthesized sodium molybdenum bronze, $\text{Na}_2\text{Mo}_5\text{O}_7$, by electrolytic reduction of fused sodium molybdate. They reported that their product appeared as indigo-blue needles with a metallic sheen.⁵ In 1930 C. Cannery reported to prepare lithium, sodium and potassium molybdenum bronzes by electrolytic reduction. The following year, W.G. Burger and J.A.M. van Liempt showed the "bronzes" synthesized by Cannery were mixtures of molybdenum (IV) oxide and molybdenum blue. A. Magneli reported in 1939, that similar experiments by G. Hagg in 1935, only led to molybdenum oxides.⁶

In the 1960's, A. Wold, W. Kunnmann, R.J. Arnott and A. Ferretti successfully synthesized alkali metal molybdenum bronzes by electrolytic reduction of $\text{A}_2\text{MoO}_4\text{-MoO}_3$ melts (A= electropositive element).⁷ The conditions that were favorable to synthesize these compounds were both the reduction temperature and the molar ratio of alkali metal molybdate to molybdenum (VI) oxide, MoO_3 . Sodium and potassium molybdenum bronze single crystals were formed as well as molybdenum (IV) oxide (MoO_2) single crystals. The range of temperatures that produced successful product was between 675°C and 550°C. To form sodium molybdenum bronze the molar ratio of molybdenum (VI) oxide to sodium molybdenum oxide (Na_2MoO_4) is 3:1 at 550°C. To form potassium molybdenum oxide the molar ratio of molybdenum (VI) oxide to potassium molybdenum oxide, K_2MoO_4 is 3.35:1 at 550°C and 3:1 at 560°C. Thus, the reduced temperatures of 550-560 °C produced the bronzes, which were identified by X-ray methods.⁸

In the 1980's the transitional metal oxides were studied with the discovery of the charge-density wave phenomena in the blue bronze, $\text{K}_{0.3}\text{MoO}_3$.⁹ Charge wave density occurs in certain metals where the normally uniform electron density shifts or modulates to lower the overall Coulombic energy.¹⁰

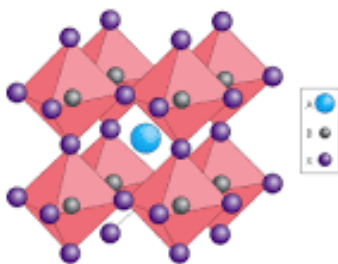
Vanadium is another metal that will form a ternary vanadium bronze phase. A new material, $\delta\text{-K}_{0.5}\text{V}_2\text{O}_5$ is being researched for its metal to insulator transitions. A practical application being researched by Texas A&M University is a "smart" window coating designed to improve energy efficiency of buildings.¹¹ Vanadium bronzes can occur naturally and have been the topic of geological reviews.¹²

Quaternary bronzes are being studied for their use as current-conducting corrosion-proof coatings; hemichrome and ion-selective electrode materials; in fuel cells and electronics. They are also used as catalysts in organic synthesis and nuclear power.¹³

In 2012, Russian scientists, T.I. Drobasheva, et al have reported synthesizing two potassium cesium molybdenum oxide bronzes. The scientists are investigating this type of compound to be used in the process of electrophoretic deposition for the anticorrosion protection of metals. Two quaternary bronzes were revealed for the first time: $K_{0.17}Cs_{0.16}MoO_3$ and $K_{0.27}Cs_{0.03}MoO_3$. These compounds were synthesized electrochemically by ionic melts of potassium and cerium molybdates. These scientists were also studying the electrical conductance of corrosion-proof bronzes in solutions of strong electrolytes, as well as the application of a 2D protective coating to metals.¹³ More recently, in June of 2016, an abstract was released about the formation of sodium-cesium molybdenum-oxide bronzes by the same Russian team.¹⁴

Crystal Structures

The bronze family of compounds can exhibit many different crystal structures. There are three general features of the tungsten bronze crystal structures. With the general formula, M_xWO_3 , as the value of x in M_xWO_3 decreases, the structure becomes less symmetric. The structure is also dependent on the size of the ionic radius of the ternary metal, M , which is the central atom pictured in Figure 1. The crystal structures of the tungsten bronzes are based on corner sharing of WO_6 octahedra as seen in Figure 1.

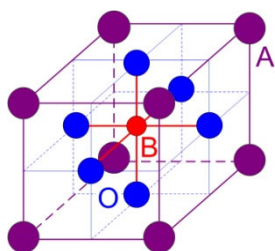


²³Figure 1 – Corner sharing of the WO_6 octahedra

The structure of sodium tungsten bronze, $NaWO_3$, where $x = 1$ is called a perovskite structure. The unit cell has the tungsten atom in the center of a cube surrounded by six oxygen atoms in an octahedral shape at the face centers. The cube corners are the interstitial sites that contain the sodium cations.

Perovskite structures received their name from the Russian mineralogist L.A. Perovski. The actual compound perovskite, calcium titanium oxide, was discovered in the Ural Mountains of Russia in 1839 by Gustav Rose. A material with the same crystal structure as perovskite is called a perovskite structure. The general stoichiometry is ABX_3 . “A” and “B” are cations where “A” has a larger ionic size than “B” and “X” is

oxygen. The perovskite structure may distort from the cubic to the orthorhombic shape depending upon the cations in the structure.¹⁵



Cubic Perovskite Structure

A= monovalent cation (sodium)

B= pentavalent cation (tungsten)

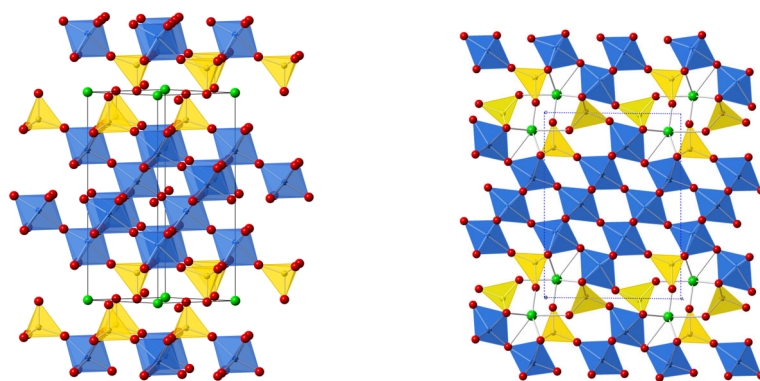
O= oxygen

²⁴Figure 2- Cubic Perovskite Structure

As the sodium content decreases the high cubic symmetry moves through two tetragonal phases. At very low sodium content (x is less than or equal to 0.05) an orthorhombic structure is formed. Alkali metals such as potassium, rubidium and cesium form a hexagonal crystal structure when x is approximately 0.3. The size of the ionic crystal will alter the crystal structure. Where M is 0.96\AA a cubic crystal shape is apparent, 0.96 and 1.29\AA is the tetragonal I and 1.63\AA would be the hexagonal crystal shape. Smaller cations such as lithium, 0.60\AA and sodium, 0.95\AA will take on the cubic structure. Potassium, 1.33\AA , rubidium, 1.48\AA and cesium, 1.69\AA , all form the hexagonal crystal shape.⁴

Bronzes other than tungsten will form more complex structures. Potassium molybdenum bronzes are made up of MoO_6 units that form infinite sheets that are held together by potassium ions.⁴ The structure of the blue bronzes, $\text{K}_{0.3}\text{MoO}_3$, $\text{Rb}_{0.3}\text{MoO}_3$ and $\text{Tl}_{0.3}\text{MoO}_3$ have the same monoclinic symmetry. The general formula being $\text{A}_{0.3}\text{MoO}_3$. The crystal is made of infinite sheets of distorted MoO_6 octahedra held together with the “A” cations.¹

Two purple molybdenum bronzes with similar stoichiometry have different crystal structures that are attributed to the different sizes of the potassium and lithium ions. A comparison of potassium molybdenum bronze, $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ and lithium molybdenum bronze, $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, respectively are illustrated below. The potassium molybdenum bronze is characterized as trigonal with a space group of $P3$. The structure is made up of slabs of molybdenum and oxygen corner sharing polyhedral. Each slab has four layers, which end with a layer of MoO_4 that share corners with the adjacent MoO_6 octahedra. The potassium ions are in a KO_{12} icosaheral.⁸ Whereas the lithium molybdenum bronze is characterized as monoclinic with a space group of $P21/m$. The crystal is a stack of slabs each consisting of 3 layers of distorted MoO_6 octahedra that are sharing corners. The lithium ions are inserted in the large vacant sites between the slabs.¹⁶



²⁵Figure 3: Crystal Structures of $K_{0.9}Mo_6O_{17}$ and $Li_{0.9}Mo_6O_{17}$, respectively

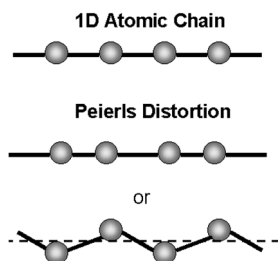
One of the most obvious properties of a material will be its color. The bronzes exhibit an array of colors. In the tungsten bronzes, the color will be dependent on the sodium content in the crystal. As the x increases in Na_xWO_3 , the color changes from grey to blue, purple, red, orange and finally golden yellow when x equals approximately one. The sodium content of $x = 0.2$ is dark blue, 0.4 is royal blue, 0.6 is purple, 0.8 is orange and $NaWO_3$ is yellow.⁴ Lithium tungsten bronze also exhibits color change as the amount of lithium in the crystal is varied. When $x = 0.1$ in Li_xWO_3 , the crystal is light blue, at $x = 0.2$ and 0.3, blue; at $x = 0.4$ and 0.5, dark blue; and $x = 0.6 - 0.7$, gold to brown.¹⁷ Other examples of bronzes and their respective colors are listed in Table 1: Reduced Ternary Molybdenum Oxides (Bronzes). As the color varies the crystal shape will vary as well, as noted in the table.

Other Properties

The electrical properties of the bronzes have been well documented. The bronzes will range from being conductors to semiconductors. Temperature is a factor in these transitions. Alkali metal tungsten bronzes, where M_xWO_3 is the general formula, show metallic conductivity when $x > 0.25$. The specific resistance is noted as very low and increases with temperature. Studies have shown that when $x = 0.25$ and below, there is a different method of conduction. Sodium tungsten bronze $Na_{0.025}WO_3$ and lithium tungsten bronze, $Li_{0.097}WO_3$ both exhibit semiconductor like behavior. The blue potassium molybdenum bronze, $K_{0.28}MoO_3$ is metallic at room temperature and will transition to a semiconductor at lower temperatures. The red potassium molybdenum bronze, $K_{0.33}MoO_3$ is a semiconductor at room temperature.⁴

The blue potassium molybdenum bronze, $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$ have been studied by many scientists, including Dr. Lynn Schneemeyer, exploring their unique electronic properties. These bronzes exhibit sliding charge-wave density (CDW) conductivity. The charge-density wave is the result of a Peierls distortion or transition, which is a metal to insulator transition, and is temperature dependent. The temperature of

importance is known as the Peierls temperature, T_p . This transition occurs in a one-dimensional metal, which refers to the chain of atoms that form in one direction which are responsible for the electronic conductivity. These bronzes are also described as anisotropic which describes the fact that there are unequal physical properties along different axes of the crystal. Above the T_p , the atoms are equally spaced, but below the T_p a distortion occurs to lower the energy of the system.¹⁸ The atoms position in the chain will move or oscillate breaking the perfect order of the one-dimensional crystal, as shown in the diagram below.



²⁶Figure 3: Peierls Distortion

In the above figure, the 1D atomic chain is showing ions uniformly spaced with uniform electron density. The Peierls Distortion is showing ions that have developed a static periodic distortion. This new array slightly lowers the kinetic energy of the highest energy electrons. This modulated electron density is known as charge wave density, CDW. This phenomenon occurs when the temperature is decreased below a critical transition temperature, T_p , and the electron gas and the ion lattice spontaneously develop the periodic modulation to lower the total free energy of the sample. When an electrical field is applied, the CDW will slide and emit an electrical note in which the pitch (frequency) is proportional to its velocity.¹⁰

Tungsten bronzes exhibit the behavior of weak temperature independent paramagnetic compounds. Paramagnetic compounds are weakly attracted to magnets due to one or more unpaired electrons (unpaired spin).⁴

The bronze compounds are generally insoluble. The property of solubility may vary, depending on the metal in the formula. Tungsten, niobium and titanium bronzes are insoluble in water and acids. Vanadium bronzes are soluble in inorganic acids, such as hydrochloric, nitric and sulfuric. The molybdenum bronzes are dissolvable in the very corrosive, aqua regia.⁴ Aqua regia, whose latin name is royal water is composed of three parts of hydrochloric acid and one-part nitric acid.¹⁹

The unique properties of this class of compounds have many facets of interest, which has driven the fascination for the extended research of these compounds.

Experimental Methods

In order to synthesize bronze compounds equipment had to be fashioned for each type of experimental method. To test that the equipment and methods used would be successful, known bronze compounds were first synthesized as trial runs. The products were viewed using an optical microscope, analyzed with a powder X-Ray Diffractometer and some with the SEM, scanning electron microscope. Once that was accomplished a series of experiments were performed to attempt to synthesize new bronze compounds.

Solid State Reaction

A vacuum pumping system was constructed out of copper pipes with fittings and a valve to regulate the vacuum pressure. Copper pieces were cut to desired lengths and solder was applied to the joints to hold the manifold together. Tubing was used to attach a vacuum pump, a pressure gauge and meter to the manifold. Tubing was also used to attach ampoules to the manifold. Silica rods were cut and fashioned into ampoules with the use of a propane torch.

Experimental trial samples were prepared by first determining the stoichiometry of the reaction for the desired product. Two grams of product was sought in each experiment for analysis. The reactants were measured and placed in a mortar and pestle to combine by grinding them together. The reactants were carefully transferred to an ampoule through the use of a long-stemmed glass funnel. The reactants needed to be at the bottom of the ampoule without any reactant on the sides of the silica ampoule. This was necessary to reduce the possible reaction of the reactants with the sides of the ampoule, referred to as 'tube attack'. Also, the reactants needed to be in the bottom of the ampoule as to not be sucked up by the vacuum in the evacuation process.

The ampoule containing the reactants was attached to the vacuum pumping system to be evacuated of air. This process took about 30 minutes with a pressure meter reading of 320 mTorr. Once this was completed while the ampoule was still attached to the vacuum pumping system, the ampoule was sealed off by means of torching the glass to form a closed container. The sealed ampoules were placed in a high-temperature oven that was programmed for ramping time, temperature and duration of the heating cycle. A firebrick was sculpted with ridges to hold the ampoules securely while in the oven. The rate of heat applied over time for the reactants to produce products was critical. A temperature that was too high or a rate of heating that was too fast caused the silica from the ampoule to react with the reactants.

The contents in the ampoules were visually inspected to be sure that a reaction had occurred. The cooled samples were viewed with an optical microscope. The optical microscope aided in distinguishing the presence of crystalline looking product as well as the color. Promising samples were further analyzed with a scanning electron microscope, SEM and/or Powder x-ray diffraction. Lastly, Single-crystal x-ray diffraction was used to

determine whether the parameters of two samples synthesized were unique and actually new compounds.

A scanning electron microscope uses an electron beam focused on a sample to create an image. Information about the surface topography and composition of a sample can be obtained. The sample must be conductive or its surface is sputter-coated with a thin film of gold or another conductive material. The prepared sample is placed in a chamber and then a vacuum pump removes the air, to avoid the scattering of electrons by the air. The heating of a filament, generally tungsten, produces the electrons that are produced and accelerated towards the sample. The beam passes through lenses and apertures to produce the focused beam that scans the surface of the sample. As the electron beam scans the surface, electrons are ejected from the atoms at the surface of the analyzed material. The image is displayed on a screen as a map of the surface. Backscattered fast electrons, also emitted by the sample, identify the actual types of elements present on the surface.²⁰

The limitation with this method is that elements with an atomic number less than 3 have a very low characteristic radiation and cannot be identified. Since lithium was present in some of the early experiments it was undetectable in the scan. This method also identifies the elements only at the surface of the sample and no information about the actual shape of the crystal.

Another method employed to analyze products of the experiments was powder X-ray diffraction. Crystalline substances are composed of layers of atoms or molecules arranged in a three-dimensional lattice. Planes drawn through the three-dimensional crystal lattice will show the spacing between adjacent atoms or molecules. In this technique the sample is ground into a fine powder so that the crystal planes are in a random arrangement. A monochromatic x-ray incident beam is directed onto the sample and the beam is reflected, or diffracted from all the layers of planes. The x-ray beam analyzes all possible planes of the crystal.²⁰ The x-rays directed at the sample are diffracted into a scintillating type detector. A signal spike at certain detector angles signifies that a particular crystal's orientation satisfies Bragg's law due to constructive wave interference.²¹

The results of powder x-ray diffraction are a series of peaks on a graph. The y-axis is the intensity, which is the peak height and the x-axis is the peak position or d spacing of the angle of the detector (2θ). Each crystalline material has its own unique x-ray diffraction pattern, which is referred to as its "fingerprint." Known x-ray diffraction patterns are cataloged so that sample results can be compared to known patterns of crystals for identification. This method validates a known compound that was synthesized in the lab, however it will not identify a new compound synthesized.

Single-crystal x-ray diffraction is similar to powder x-ray diffraction because x-rays are aimed at a sample and the diffracted rays are analyzed. However, in this technique a single-crystal, 50-250 microns in size, is mounted to sample holder. This is in

turn is mounted on a device that can adjust the crystal to be aligned into the different diffracting positions relative to the collimated incident beam of monochromatic x-rays. Diffracted rays are detected using an electronic detector and then a computer program analyzes the data. Data retrieved includes the location of the atoms as well as bond length and bond angles.²⁰

The limitation with this method is the size of the crystals synthesized. Crystals that are not large enough can't be analyzed.

Electrolysis

Electrolysis is a method to create a chemical change by passing an electric current through liquefied reactants. A thermal furnace was employed to melt the reactants before the electrolysis could be performed. A piece of firebrick was shaped to hold a thermal furnace. Another piece was shaped to form a platform for the crucible holding the reactants.

Ground reactants were placed in a 20 mL crucible. The crucible was placed into the firebrick platform. This assembly was placed inside a glass beaker, which was then placed inside the thermal furnace. The furnace was placed into the shaped firebrick to hold it steady. The furnace was attached to a ring stand with a chain type clamp. A glass lid with small open holes was placed on top of the beaker and furnace. A thermocouple was placed near the crucible to monitor the temperature. The furnace was attached to a temperature control source to supply the heat needed for the reaction.

Once the reactants were melted, the electrolysis was set to begin. A platinum wire electrode was placed in the melt to act as the working electrode and a piece of platinum was attached to a platinum wire to act as the counter electrode. After a period of time with no apparent results, this method did not yield any desired results. The power supply was deemed to not be working properly.

Results

Inquiry Set of Experiments

The initial set of experiments was carried out to determine the conditions appropriate for the synthesis of several known bronze compounds. A number of experiments were performed to optimize the process that was ultimately utilized. To gauge the progress and the results of the experiments, analysis was performed on experiments that yielded promising products. Products were deemed promising after observing the contents of the ampoules with an optical microscope. Shiny, colored crystals were the desired outcome, since luster is a property of bronze compounds.

At least 22 samples were prepared throughout the experimental period. The numbers of the samples presented here are not in consecutive order due to a variety of reasons. The ampoule might not have been sealed properly, there was no apparent reaction after a visual inspection or there was a reaction between the silica glass ampoule and the reactants. Only the experiments of relevance have been introduced in this thesis.

Listed below are the chemical reactions of selected initial experiments:

Sample 4	$0.33 \text{ K}_2\text{WO}_4 + 0.10 \text{ Li}_2\text{WO}_4 + 1.9\text{W} + 0.187\text{WO}_3 \rightarrow \text{Li}_{0.10}\text{K}_{0.33}\text{WO}_3$
Sample 5	$0.45 \text{ Li}_2 \text{ MoO}_4 + 0.483 \text{ Mo} + 5.07 \text{ MoO}_3 \rightarrow \text{Li}_{0.9} \text{ Mo}_6 \text{ O}_{17}$
Sample 6	$0.15 \text{ K}_2\text{MoO}_4 + 0.15 \text{ Li}_2\text{MoO}_4 + 0.10 \text{ Mo} + 1.6 \text{ MoO}_3 \rightarrow 0.02 \text{ Li}_{0.15}\text{K}_{0.15}\text{MoO}_3$
Sample 7	$0.15 \text{ Li}_2\text{MoO}_4 + 0.15 \text{ Nd}_2\text{O}_3 + 0.2 \text{ Mo} + 1.65 \text{ MoO}_3 \rightarrow 0.02 \text{ Li}_{0.15}\text{Nd}_{0.15} \text{ MoO}_3$

To have enough product to analyze, the stoichiometry was calculated to prepare 2.00 g of product. Sample 4 was prepared by combining 0.4386 g potassium tungstate, a white crystalline powder, 0.1068 g lithium tungstate, a white powder, 0.1075 g tungsten, a grey powder and 1.3472 g tungsten (VI) oxide, a green-yellow powder. The sample was placed in the oven and set for a ramping rate of 100 degrees Celsius per hour until the sample reached 750 degrees Celsius. The sample dwelled at this temperature for 82 hours. Observed by visual inspection was shiny material with a blue-purple color. The optical microscope observation showed needle-like crystals that appeared metallic with a blue-purple hue.

Dr. Laying Wu of Montclair State University performed analysis with Scanning Electron Microscopy and Electron Dispersive X-ray Spectroscopy, SEM/EDS on the initial experiments. Dr. Wu demonstrated how to prepare the samples for the SEM, demonstrated how to utilize the instrument and performed the actual analysis. She

reported that the crystals appeared to have a hollow column lengthwise; hopper growth, where the edges of the crystal are fully formed, and the crystals appeared to be non-uniform. Tungsten, potassium and oxygen were identified. Lithium was present in these samples but was undetectable because elements with an atomic number less than 3 have a very low characteristic radiation and cannot be identified.

Samples 5-7 were prepared in the same manner as sample 4. Sample 5 when viewed with the optical microscope appeared to have purple, needle like crystals. Sample 6 had crystalline red nuggets and appeared to have reacted with the ampoule. Sample 7 appeared to have black molten material with areas of purple and yellow-green crystals. Dr Wu reported that sample 6, lithium potassium molybdenum oxide, appeared to have needle-like crystals and the potassium, molybdenum and oxygen were identified. In this sample there was fiber apparent which is most likely silicon dioxide from the silica ampoules. The other two samples, 5 and 7, had no noticeable attributes and were noted as inconclusive.

A 2005 Phillips X-Pert X-Ray Diffractometer with Cu K α radiation and the associated software was utilized to analyze the crystal structure of samples. Instruction on how to prepare samples and operate the diffractometer was under the direction of Dr. Matthew Goring, Montclair State University. The sample patterns were analyzed with the Phillips' X-Pert High Score program. This program contains an ICDD (International Centre for Diffraction Data) database for known crystal substances and their parameters. Comparisons were made with the data of known compounds to identify the crystal samples that were produced in the lab. The reference numbers are from the ICDD database. A Geiger counter was in use during the instrument's utilization to ensure the safety of the users. A film badge ring was also worn during working with the instrument.

Analysis of lithium potassium tungsten oxide, $\text{Li}_{0.10}\text{K}_{0.33}\text{WO}_3$, also known as sample 4 with the Powder X-Ray Diffractometer with the X-Pert High Score computer program showed peaks that matched the compound, rubidium tungsten oxide, $\text{Rb}_{0.28}\text{WO}_3$ (Reference Code: 70-0803). The crystal shape for the known compound, $\text{Rb}_{0.28}\text{WO}_3$, is hexagonal. Most of the observed lines in the diffraction pattern matched the known phase with the exception of 2 lines at 20-22 degrees 2θ . The material that was synthesized also closely matched another related phase, ammonium tungsten oxide, $(\text{NH}_4)_{0.25}\text{WO}_3$ (Reference Code: 73-1084). The reason surmised that they were matches is because rubidium and ammonium both have a valence of 1+ which is the same as potassium and lithium. The material that was prepared was also compared with a known compound lithium potassium tungsten oxide, $\text{Li}_{0.9}\text{K}_{0.23}\text{WO}$ (Reference Code: 79-0769). In this case, however, very few lines matched and thus deemed an unrelated compound.

Culminating Set of Experiments

The next set of experiments to synthesize a pseudo-quaternary compound involved sodium and neodymium and a re-make of sample 7, now sample 14 with new heating conditions. Listed below are the chemical reactions for these experimental trials:

Sample10	$0.03 \text{ Na}_2\text{MoO}_4 + 0.03 \text{ Nd}_2\text{O}_3 + 0.04 \text{ Mo} + 5.93 \text{ MoO}_3 \rightarrow .06 \text{ Nd}_{0.10}\text{Na}_{0.10}\text{MoO}_3$
Sample11	$0.10 \text{ Na}_2\text{MoO}_4 + 0.05 \text{ Nd}_2\text{O}_3 + 0.083 \text{ Mo} + 0.817 \text{ MoO}_3 \rightarrow \text{Nd}_{0.10}\text{Na}_{0.20}\text{MoO}_3$
Sample12	$0.15 \text{ Na}_2\text{MoO}_4 + 0.15 \text{ Nd}_2\text{O}_3 + 0.233 \text{ Mo} + 1.62 \text{ MoO}_3 \rightarrow .02 \text{ Nd}_{0.15}\text{Na}_{0.15}\text{MoO}_3$
Sample14	$0.15 \text{ Li}_2\text{MoO}_4 + 0.15 \text{ Nd}_2\text{O}_3 + 0.2 \text{ Mo} + 1.65 \text{ MoO}_3 \rightarrow .02 \text{ Nd}_{0.15}\text{Li}_{0.15}\text{MoO}_3$

The reactants in these experiments were placed in the oven for a ramping rate of heating of 100 degrees Celsius per hour to 475 degrees Celsius for 12 hours. This was tried as to reduce the possibility of ‘tube attack’ and formation of undesired silica products. There was no apparent reaction at the end of this time period, so the heat was increased to 500 degrees Celsius and after a time period of eight days there was no apparent reaction. The heat was then increased to 530 degrees Celsius for 72 hours.

Observation with the optical microscope revealed that samples 10 & 12 had platelet shaped crystals and appeared black with a purple hue. The analysis with the Powder X-Ray Diffractometer had similar results. Peaks showed the sample matched the compound, molybdenite, MoO_3 (reference 76-1003) very closely. The crystal type is orthorhombic. Comparing with a known compound, sodium neodymium molybdenum oxide, $\text{Na}_{0.5}\text{Nd}_{0.5}\text{MoO}_4$ (reference 25-0852) showed mostly unmatched lines. In this case the molybdenum is a 7+ valence and the compound being synthesized has a variable valence of 5.1+ and 5.4+ for samples 10 & 12, respectively. The known compound has a tetragonal shape and does not match the orthorhombic shape of the molybdenite. From this observation I concluded that the desired reaction did not occur since molybdenite was a reactant that was 8 times greater than the sodium or neodymium component.

Samples 12 & 14 both had a grey powdery substance with shiny, dark crystals throughout when viewed with optical microscope. Note that sample 14 is a re-make of sample 7. Powder X-Ray Diffractometer results for sample 12, $\text{Nd}_{0.15}\text{Na}_{0.15}\text{MoO}_3$, matched it to $\text{Nd}_{0.5}\text{Na}_{0.5}\text{MoO}_4$ (reference 25-0852). The results were similar to samples 10 & 11. Analysis of sample 14 is best described as a combination of three different compounds to match the peaks. Neodymium molybdenum oxide, $\text{Nd}_2\text{Mo}_3\text{O}_9$ (reference 33-0936) matched a majority, 62%, of the peaks and was the closest match to the sample. Lithium molybdenum oxide, $\text{Li}_{0.42}\text{MoO}_3$ (reference 38-0045) matched 42% of the peaks, the data therefore suggest that this is possibly a side product. Additionally, gadolinium molybdenum oxide, $\text{GdMo}_{16}\text{O}_{44}$ (reference 87-1536) matched 40% of the observed

peaks. The possible reason for this choice is the fact that gadolinium is a member of the lanthanide series like neodymium.

The uncertainty of measurements of the X-ray Diffractometer is $\pm 0.01 2\theta$. This is a possible explanation for why compounds produced were not 100% matched to those in the ICDD database.

Finally, a series of experiments were carried out aimed at the synthesis of a compound in the Li-K-Mo-O, Li-Na-Mo-O and Na-K-Mo-O systems to produce a quaternary bronze compound. Listed below is a sampling of the chemical reactions for the experimental trials:

Sample 19	$.135\text{Li}_2\text{MoO}_4 + .135\text{Na}_2\text{MoO}_4 + .29\text{Mo} + 30.4\text{MoO}_3 \rightarrow .06 \text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$
Sample 20	$9\text{Li}_2\text{MoO}_4 + 9\text{Na}_2\text{MoO}_4 + 2 \text{Mo} + 70 \text{MoO}_3 \rightarrow 6\text{Li}_3\text{K}_3\text{Mo}_{15}\text{O}_{47}$
Sample 22	$.135\text{Na}_2\text{MoO}_4 + .135\text{K}_2\text{MoO}_4 + .29\text{Mo} + 30.4\text{MoO}_3 \rightarrow .06\text{Na}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$

The hypothesis explored was the possibility of combining more than one alkali metal into one structure to form a new quaternary molybdenum bronze. Some experiments were repeated to try to increase the crystal size of the product material for better analysis. One such experiment was the search for the product, lithium potassium molybdenum oxide, $\text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$. Samples 15-19 were prepared in the same manner but the soak temperature, the maximum temperature used in the synthesis, was adjusted in each trial to try to improve the crystal size. To prepare 2.00 g of product 0.0901g lithium molybdate, 0.1235 g potassium molybdate, 0.1069 g molybdenum, and 1.6797 g molybdenum trioxide were combined. Sample 19 yielded shiny, purple nuggets of product.

Upon analysis with the X-Ray Diffractometer no known compounds in the data base matched the product in Sample 19, $\text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$. Charts were created in Excel to document this observation with Intensity (Height) vs. the Position (2 theta) data. Chart 1, page 27, compares the product lithium potassium molybdenum oxide, $\text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$ with a possible product that can be synthesized with the same reactants used in this experiment, potassium molybdenum oxide, $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (Reference Code: 76-1265). Chart 2, page 27, compares the sample 19 product with another possible product, lithium molybdenum oxide, $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (Reference Code: 84-1235). Chart 3, page 28 compares $\text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$ with a possible product, potassium molybdenum oxide, $\text{K}_{0.85}\text{Mo}_6\text{O}_{17}$ (Reference Code: 24-0879). In all three cases the pattern for lithium potassium molybdenum oxide, $\text{Li}_{0.4}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$, does not resemble the possible product, $\text{K}_{0.85}\text{Mo}_6\text{O}_{17}$.

Sample 20, lithium sodium molybdenum oxide, $\text{Li}_3\text{Na}_3\text{Mo}_{15}\text{O}_{47}$ also yielded a few crystals and a large amount of powdery matter in the ampoule under the same conditions as Sample 19. Additional experiments were then carried out substituting sodium for potassium in samples 21 & 22. Sodium potassium molybdenum oxide, $\text{Na}_{0.45}\text{K}_{0.45}$

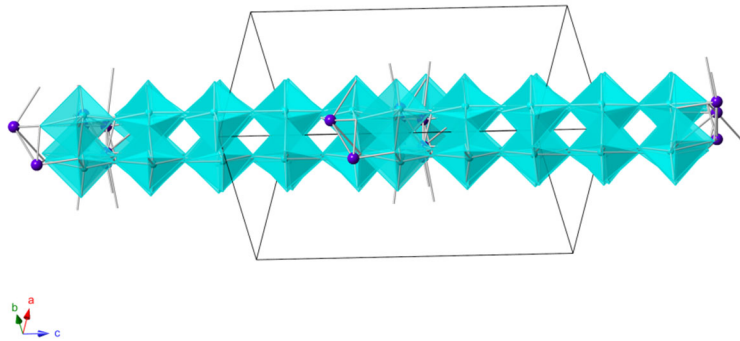
Mo₆O₁₇, a compound analogous to Sample 19 was prepared. When the conditions used yielded only powdery matter in the ampoule, the reaction temperature was raised in Sample 22. To prepare 3.00 g of product 0.1588 g sodium molybdate, 0.836 g potassium molybdate, 0.1589 g molybdenum, and 2.4984 g molybdenum trioxide were combined. Purple, crystalline, shiny platelets were produced in this experiment. Again, analysis with X-Ray Diffractometer showed no known materials with x-ray patterns that matched the compound obtained with this stoichiometry.

Single-Crystal X-Ray Diffraction was employed on two of the products produced from the experimentation process. This analysis was performed under the direction of Dr. Theo Siegrist, Professor, Department of Biomedical and Chemical Engineering at Florida State University. This technique measures the unit cell dimensions and the atom's position within the crystal lattice. The purpose in this instance was to determine if a new crystalline compound was formed.

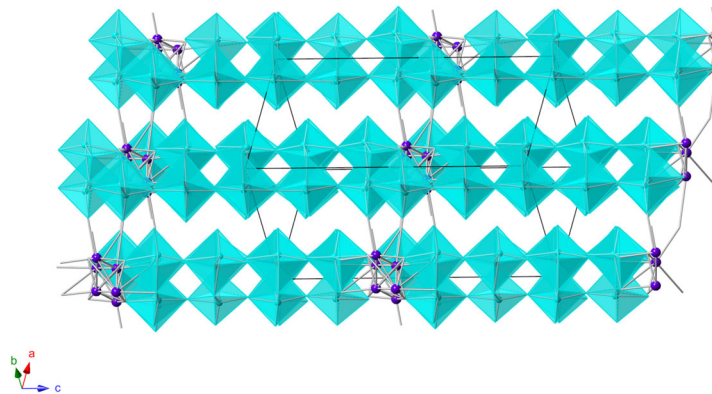
Portions of samples 19 and 22 were sent to Dr. Theo Siegrist for single crystal x-ray diffraction analysis using an array detector-based diffractometer. Dr. Theo Siegrist, reported that sample 19, Li_{0.45}K_{0.45}Mo₆O₁₇ represents a new molybdate phase. He reported the initial structure of this new phase as having a previously unknown triclinic unit cell with the lattice parameters: $a = 8.1594(5) \text{ \AA}$, $b = 10.4197(4) \text{ \AA}$, $c = 20.1477(9) \text{ \AA}$, $\alpha = 80.680(3)^\circ$, $\beta = 89.912(4)^\circ$, and $\gamma = 78.419(4)^\circ$. The space group was determined to be *P-1* with the positions of the Mo, K and O atoms observed, although not the Li atoms. There are two possibilities for the inability to find the Li atoms; first, poor crystal quality, and second, the fact that Li has only 3 electrons. The structure is formed of 2D sheets of condensed MoO₆ octahedra. The Li atoms are probably located between the layers. The oxidation state for Mo in this compound is 5.5+. Larger crystals with higher crystal quality would need to be synthesized to determine the exact locations of the Li atoms.

The other sample with no known match with the Powder X-Ray analysis was Sample 22, Na_{0.45}K_{0.45}Mo₆O₁₇. At this point, no crystals have been synthesized that were large enough or of sufficient quality to investigate the structure by use of single crystal X-ray diffraction.

The following schematic diagrams were sent from Dr. Siegrist after his analysis of sample 19. The diagrams show the arrangement of the MoO₆ octahedra and the probable positions of the potassium atoms, while it is surmised that the Li atoms are between the layers.



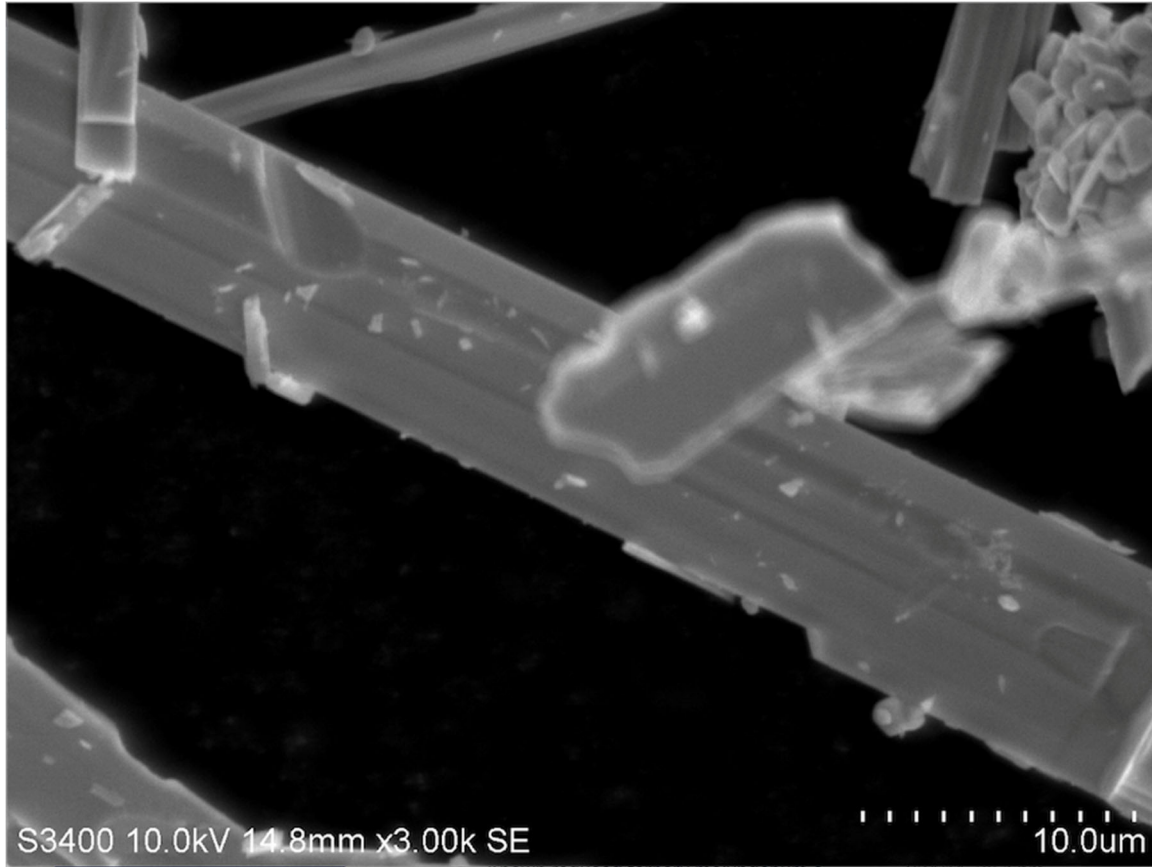
²⁷Figure 4: $\text{K}_{0.45}\text{Li}_{0.45}\text{Mo}_6\text{O}_{17}$ – Image 1



²⁸Figure 5: $\text{K}_{0.45}\text{Li}_{0.45}\text{Mo}_6\text{O}_{17}$ – Image 2

Figure 4 illustrates the 2D sheets of the condensed MoO_6 octahedra, while Figure 5 illustrates the orientation of multiple 2D sheets. The potassium ions are arranged at intervals between the MoO_6 octahedra.

This is the actual SEM image of the $\text{Li}_{0.4}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$ crystal that was synthesized



²⁹Figure 6: $\text{Li}_{0.45}\text{K}_{0.45}\text{Mo}_6\text{O}_{17}$ SEM image

Conclusion

The experimental period of this research was over a span of two years. If time permitted a re-make of some samples to get better results when analyzed with the X-ray diffractometer would be desired. Many of the products of the already established compounds, had similar diffraction patterns but were not exact when comparing to their actual reported patterns. The stoichiometry of the samples were calculated and then verified with a computer stoichiometry program. To compliment results, investigations using the method of electrolysis would be beneficial. Many journal articles point to this method of synthesizing bronze compounds.

The hypothesis explored was the possibility of combining more than one alkali metal into one structure to form a new quaternary molybdenum bronze. Bronze compounds of this class have reportedly been synthesized through the research incurred by this thesis. A compound of this type has not been reported in the scientific literature with the Li-K-Mo-O, Li-Na-Mo-O or Na-K-Mo-O system as the time of this experimentation period. The alkali metals used would have to have an ionic radius small enough to fit between the layers of the MoO₆ octahedra. In this case, lithium and potassium were inserted in the structure to form Li_{0.45}K_{0.45}Mo₆O₁₇.

The product of sample 19, Li_{0.45}K_{0.45}Mo₆O₁₇, yielded shiny, purple metallic looking crystals. To rule out that already known compounds were not being formed in this synthesis, powder x-ray analysis data was compared to the new substance formed. As discussed in the previous section, analysis of known compounds as possible products, with the substance actually synthesized did not match. The crystallographic data of Li_{0.45}K_{0.45}Mo₆O₁₇ was compared to a known product, K_{0.9}Mo₆O₁₇. It was also compared to another known product, Li_{0.9}Mo₆O₁₇ and also K_{0.85}Mo₆O₁₇. Refer to Charts 1-3 for this analysis. The single-crystal analysis by Dr. Siegrist documented that Li_{0.45}K_{0.45}Mo₆O₁₇ was a new molybdate phase.

Future research would include repeated experiments of the known compounds to have reproducible results with the X-Ray Diffractometer. Also, more trials to produce larger crystals for single X-ray diffraction would be beneficial. The method of electrolysis could also be utilized to synthesize the compounds.

Bronze compounds have made their mark in chemistry history. Innovative bronze compounds appear to be part of the future. The substitution of metal cations into crystalline shapes to form new compounds will continue to capture the imagination of many scientists.

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Figure References

- ²³Figure 1 – Corner sharing of the WO₆ octahedra (<http://www.solarchoice.net.au/blog/news/perovskites-the-next-solar-pv-revolution-240714>)
- ²⁴Figure 2- Cubic Perovskite Structure (<http://research.ncku.edu.tw/re/articles/e/20080411/1.html>)
- ²⁵Figure 3: Crystal Structures of K_{0.9}Mo₆O₁₇ and Li_{0.9}Mo₆O₁₇ Windows Photo Gallery
- ²⁶Figure 3: Peierls Distortion (<http://nanowiz.tripod.com/lowdim/peierls.gif>)
- ²⁷Figure 4: K_{0.45}Li_{0.45}Mo₆O₁₇ – Image 1 (<https://www.eng.fsu.edu/cbe/people/siegrist.html>)
- ²⁸Figure 5: K_{0.45}Li_{0.45}Mo₆O₁₇ – Image 2 (<https://www.eng.fsu.edu/cbe/people/siegrist.html>)
- ²⁹Figure 6: Li_{0.45}K_{0.45}Mo₆O₁₇ SEM image; Dr. Laying Wu –Montclair State University

Table 1: Reduced Ternary Molybdenum Oxides (Bronzes)

Color/Structure	Compound	Properties
Blue; monoclinic symmetry, space group C2/m with 20 molecules per unit cell ^a	$K_{0.28}MoO_3$	Metallic ^b
	$K_{0.28}Mo_{1.02}O_3$	Blue-black, transition from semiconductor to metallic behavior above -100 °C ^c
	$K_{0.30}MoO_3$	Blue, quasi 1-D ^d ; semiconductor to metal transition at 180K, quasi 1-D in metallic phase ^e
	$Rb_{0.30}MoO_3$ ^d	
	$Tl_{.3}MoO_3$ ^a	
Red; analogous to K compounds ^a	$K_{0.26}Mo_{1.01}O_3$	semiconductor behavior ^c
	$K_{0.33}MoO_3$	semiconductor ^b
	$Cs_{0.33}MoO_3$	diamagnetic, semiconductor ^f
Purple; monoclinic; C2 symmetry; pseudo-hexagonal ^a	$Li_{0.9}Mo_6O_{17}$	quasi 2-D metal ^g
	$Na_{0.9}Mo_6O_{17}$	quasi 1-D or bi-dimensional ^h ; distorted perovskite ^b ; metal to semiconductor transition at 87K and 30K ⁱ
	$K_{0.9}Mo_6O_{17}$	2-D metal, hexagonal ^e
Hexagonal; space groups $R\bar{3}$ or $R\bar{3}$	$GdMo_{16}O_{44}$	Yellow, semiconductor ^j
	$Nd_{0.25}Mo_4O_{11}$	Green, quasi 1-D ^k

Table I References

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Chart 1: $K_{.45}Li_{.45}Mo_6O_{17}$ vs. $K_9Mo_6O_{17}$

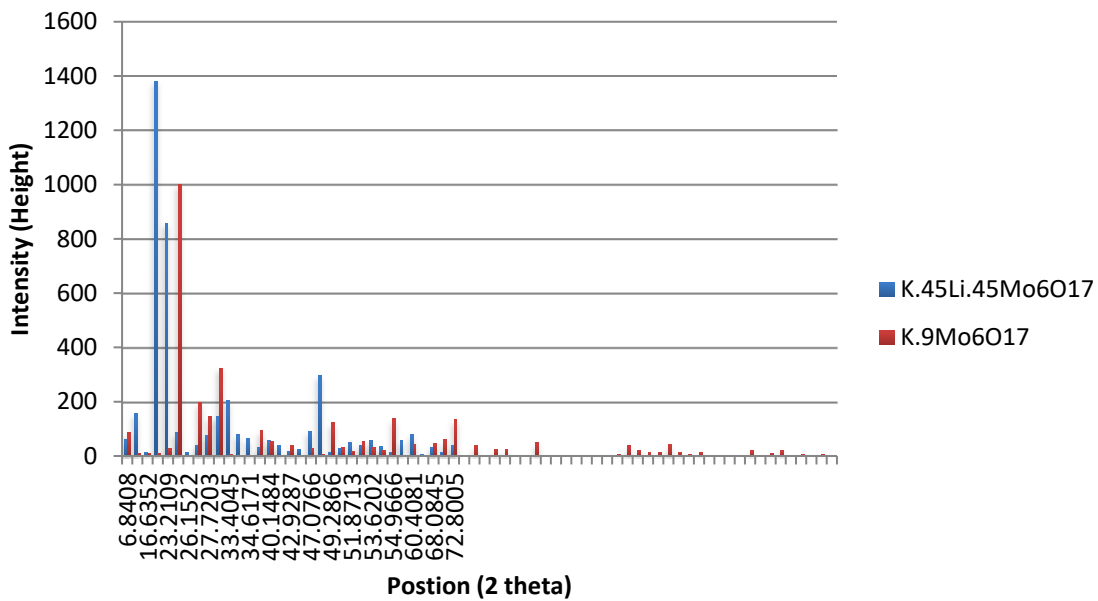


Chart 2: $K_{.45}Li_{.45}Mo_6O_{17}$ vs. $Li_9Mo_6O_{17}$

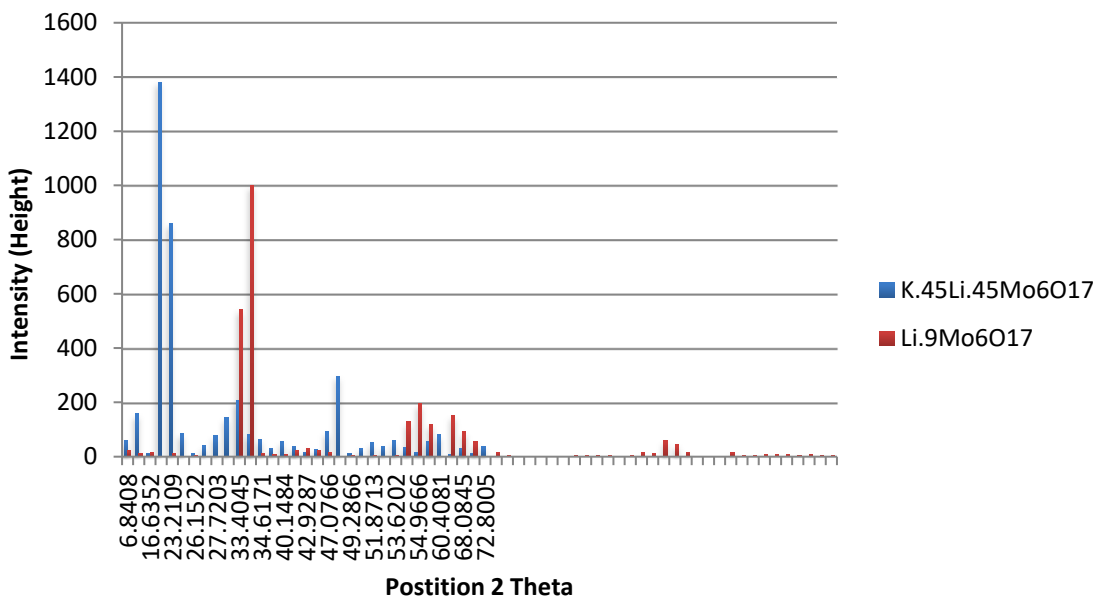


Chart 3: $K_{.45}Li_{.45}Mo_6O_{17}$ vs. $K_{.85}Mo_6O_{17}$

