

Final Report

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1 Motivation

The goal of this research project was to create a thin film of Sr₂RhO₄ using Pulsed Laser Deposition. Sr₂RhO₄ was briefly investigated for superconductivity in the mid-90s but was found to exhibit no interesting phenomena at the time. Recently, it has been discovered that electrons in Sr₂RhO₄ have an extraordinarily long mean free path meaning they travel for a long distance before interacting with something which would make them change direction. This means it is easier to observe the De Haas-Van Alphen effect (DHVA) [5]. The DHVA effect is quantum mechanical in nature and is when the magnetic susceptibility of a crystalline metal oscillates as a function of the magnetic field. Investigating the DHVA effect is outside the scope of this project, my goal was to just make the thin film of Sr₂RhO₄.

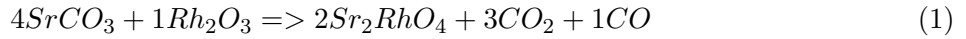
2 Getting Started

I arrived at UK a week after the program started so I planned on working overtime in order to get caught up. However, when I arrived I learned that the main objective for our research group currently was to move from the basement to the newly renovated third floor. This meant I didn't really start my research until the third week of the program.

Moving the lab took patience and perseverance. A lot of the specialized equipment in Seo's lab is very delicate, like the vacuum chambers and the laser. With the help of the campus moving group and the other three REU students, MacKenzie, Alkhatab, and Tina, we got the lab moved and we were able to begin research.

3 Preliminary Research

I began studying and preliminary research for this program in May before my University left for summer break. I was told I would be researching SrCoO_{2.5} so I began looking into finding its balanced stoichiometric equation from the two reactants SrCO₃ and Co₃O₄. However, when I presented my work to Professor Seo's graduate student Sujana, I learned that my compound was switched for another, Sr₂RhO₄ so I again found the balanced stoichiometric equation with the two reactants SrCO₃ and Rh₂O₃. The balanced equation is as follows:



I found the molar mass of each of the atoms in the compounds and used them to determine how many grams of the reactants would be required for one gram of the finished product. The results are in tables 1 and 2.

Table 1: Molar Masses of Elements in Reaction

Element	molar mass (gram/mol)
Sr	87.62
C	12.011
O	15.999
Rh	102.9055

Table 2: Required Grams of Reactants

Compound	Required Amount (grams)
SrCO ₃	0.863
Rh ₂ O ₃	0.3709

Getting the necessary amounts of each reactant is important, but we also needed a recipe for making Sr₂RhO₄. Just putting the reactants next to each other does not induce a chemical reaction. After looking through many papers, the preferred way of forming Sr₂RhO₄ was established using Shimura's technique without oxygen gas flow [6]. We would grind the two reactants together in a mortar and pestle, then press the combined mixture into a small pellet, see figure 1. Because the mixed powder was pressed into a pellet the molecules of the powder were tightly bound with one another which helped the chemical reaction occur when placed in the furnace. The furnace is what actually induced the solid state reaction between the reactants and allowed them to change into the product.



Figure 1: Mixed Powder of $\text{SrCO}_3 + \text{Rh}_2\text{O}_3$

4 Experimental

Typically, the longer the powders are ground together, the better the resulting reaction will be in the furnace. Professor Seo recommended a grinding time of three hours, but I only had time to grind for 30 minutes the first time. This may explain why my resulting product wasn't as pure as hoped. After grinding, the pellet was placed into a dry hydraulic press for one hour at 19 tons of pressure. After the hour was up the press read only 17 tons of pressure. The press gradually lowering in pressure was not a big issue as that magnitude of pressure was still sufficient for the powder to get pressed. See figure 2 for a picture of the pellet press and figure 3 of the completed pellet.

Now that the pressed pellet was completed, we needed to remove any extra carbon and any other impurities that may have found their way onto the sample. This can be achieved by calcination, the process of heating up a substance to remove carbon and other impurities. The pellet was placed into an aluminum crucible and then into a furnace at room temperature, around $\sim 20^\circ\text{C}$ and the furnace rose in temperature at a rate of 1 degree Celsius per minute until at 900 degrees Celsius. Then the pellet stayed in the furnace at constant temperature for 24 hours before the furnace dropped to room temperature again at a rate of 1 degree per minute. At higher temperatures the oven can decrease temperature at 1 degree per minute, but at a certain temperature the oven retains too much heat and the oven cools much slower. This meant the pellet was heated by the furnace for a total of 54 hours plus any additional time it took the oven to cool down. The crucible allowed for the pellet to not be placed on the 'floor' of the oven which kept the sample pure.

In order to check if the furnace induced the correct solid state reaction and created the proper product it was necessary to learn about X-Ray diffraction. X-Ray diffraction (XRD) is a technique which allows us to identify compounds by their crystal lattice. This means that after we take our mixture out of the furnace, we can use the XRD machine to accurately tell if what we have created is the desired product or if it is something else. Because we typically shoot these X-rays at a powder of the



Figure 2: Pellet Press

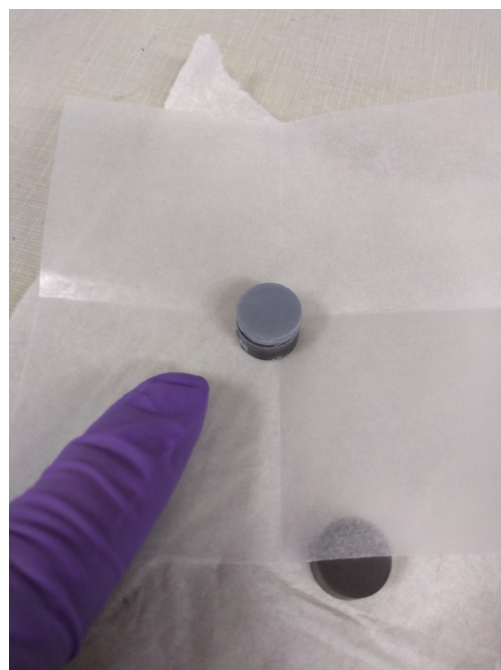


Figure 3: Pellet

crystalline substance, the X-rays will diffract in every direction, but will constructively interfere when they travel through a distance that is an integer multiple of the wavelength. When the waves constructively interfere we get peaks, and because we typically know the crystal structure of what we are studying, or we can predict it, we can tell which Miller index is responsible for each peak. This allows us to label each peak helping us differentiate compounds from one another. See figure 4 courtesy of Anton Paar.com for a pictograph representation. This means that because every compound with a crystalline structure has a unique crystal structure, we can identify the compound based on the resulting graph of refracted X-ray intensities. The reason X-rays are used is because the wavelength of X-rays is extremely small; it is so small it is comparable to the spacing in a crystal lattice. This allows for the previously mentioned constructive interference effect.

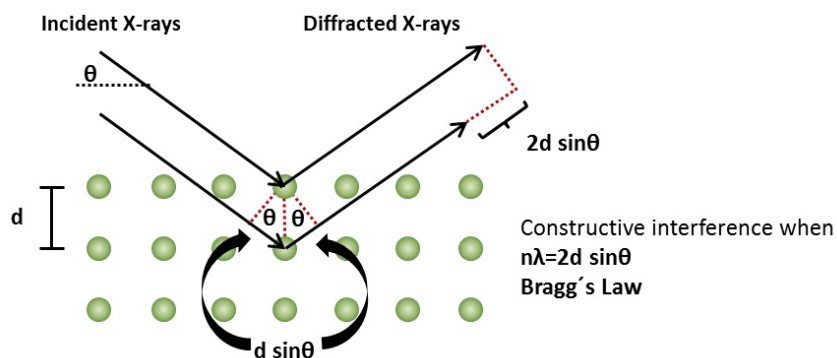


Figure 4: XRD Schematic

At this point our group's XRD machine was still in need of repairs so we were using the Material Science's XRD machine. After putting the calcined powder through the XRD machine I obtained a diffraction profile. I compared my diffraction profile, figure 5 to a diffraction profile downloaded from The Materials Project, figure 6. It is clear that my data does not precisely match the data as reported by the Materials Project. However, when I told Professor Seo and Sujan about this I learned that I should use only published sources in academic journals. They also noted that the huge peak I had at around the 15 degree point on the x-axis appeared to be noise as opposed to data. We tried to remove this noise but after several attempts we decided it would be simpler to wait for our XRD machine to be fixed as we are more familiar with that one. Possible reasons for the discrepancies of my calcined powder and the data from the Materials Project include: my powder didn't react completely and some the reactants are still present in the mixture, the Materials Project may have used different parameters when generating their diffraction pattern, and the XRD machine we used may be misaligned.

In order to try to remove all impurities and force the mixture into the 2 - 1 - 4 phase that we desire, I chopped and ground my pellet back into a powder then proceeded to grind it in a mortar and pestle for about two hours. I then placed it back into the furnace, this time for 36 hours at 1250 degrees Celsius. We set it to heat and cool at 1 degree per minute meaning it would be in the furnace for around 77 hours with additional time for cooling. We then used our recently fixed XRD machine to analyze the XRD pattern of the pellet, the data can be seen as one of the data sets in figure 7. Note how the data has quieted down and is much less noisy. I found an XRD pattern found by Itoh et al. from 1995 that I used to compare my results to. Itoh's XRD graph can be seen in figure 8 [3]. Because my data had numerous 'split' or double peaks where Itoh only had one and because I had a major peak in between the highest peaks at 30° and 33° which wasn't supposed to be there, I decided to sinter the pellet again. This meant breaking my pellet back into a powder with a razor blade as it was now quite firm, and then grinding the remains into a powder, re-pressing under the same conditions, and sintering in the oven at the same temperatures. After placing this newly minted pellet through the XRD our results were slightly better. The resulting data is graphed in figure 7 Peaks that seemed to split where they weren't supposed to now resolved into single sturdy peaks. However we still had the large peak in between 30° and 33° that wasn't supposed to show up. At this stage I believed the main contaminant in the sample was a different phase of Strontium Rhodate, perhaps SrRhO₃ instead of Sr₂RhO₃. An XRD graph of SrRhO₃ created by Li et al. supported this hypothesis as it has a peak in 30° and 33° [4].

Later, with Sujan's help, we were able to manually adjust the height of the XRD stage which removed the background noise peak at 30 degrees. By comparing to papers online I labeled as many Miller Indices corresponding to peaks as I could find. These Miller indices are a measure of the crystalline faces that arise from the crystal structure the compounds form. Figure 9 contains data on the pellet after its second sintering like figure 7 but now has reduced background noise and has labeled Miller indices. This final graph looks similar to a graph made by Varela et al shown in figure 10. Varela's group was studying the ability of Strontium Rhodate to have reversible reactions from the 2-1-4 phase to the 4-1-6 phase and back again [8]. This may mean based on their research that the main contaminant in the pellet is Sr₄RhO₆. As we ran out of time this is the target we used for PLD even though it was not purely Sr₂RhO₄.

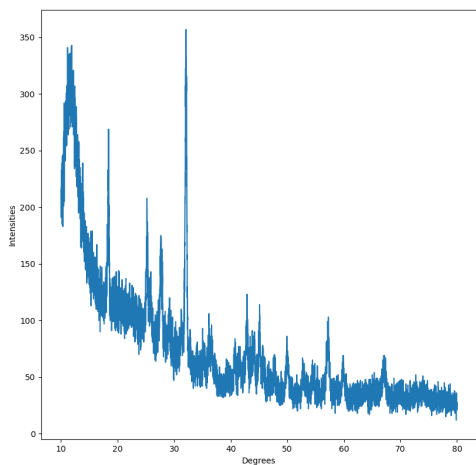


Figure 5: Calcinated XRD Profile

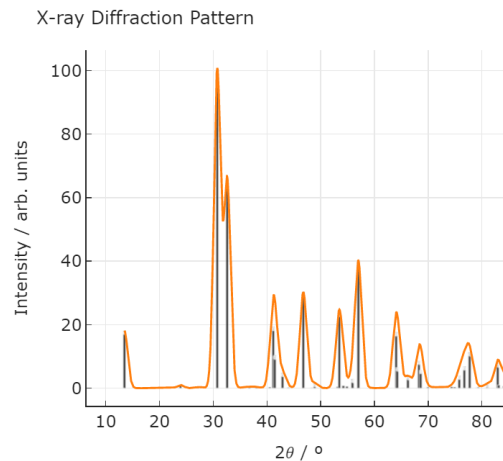


Figure 6: Materials Project XRD for Sr_2RhO_4

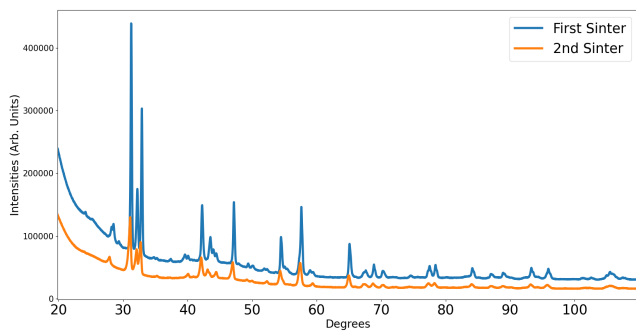


Figure 7: Sintered XRD Profiles

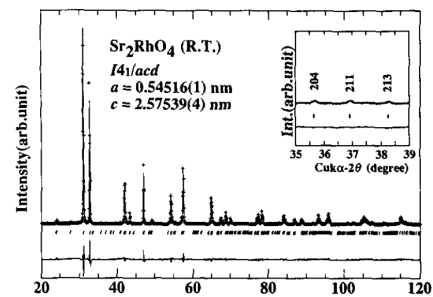


Figure 8: Itoh et. al XRD for Sr_2RhO_4

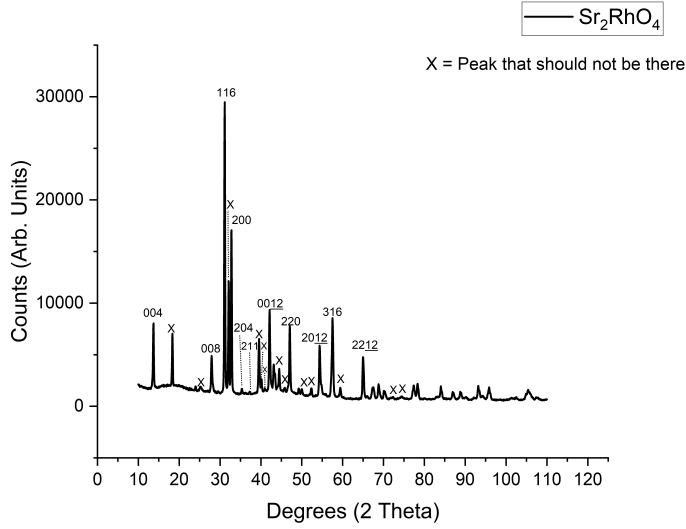


Figure 9: Second Sintered with no Background Noise and Labeled Miller Indices

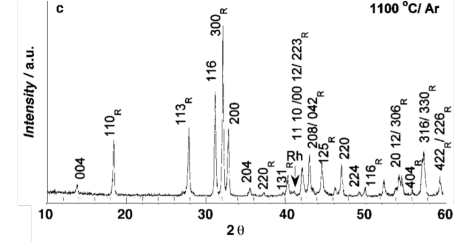


Figure 10: Varela et al. XRD for Sr₂RhO₄ annealed at 1100°C in Ar atmosphere

5 Next Steps

The main goal of my time here is to synthesize this compound, Sr₂RhO₄, and create a thin film of it using pulsed laser deposition. This pulsed laser deposition (PLD) technique involves shooting a laser of varying intensities at a target of Sr₂RhO₄. The laser will take the solid pellet of Sr₂RhO₄ and turn it into a hot plasma which will deposit onto a pre-selected substrate material.

We began working on selecting the substrate material around week 7. The substrate selection is important because not all substrates work for all targets. Our target Sr₂RhO₄ has a tetragonal lattice structure meaning two of its lengths are equal and all lengths are perpendicular to each other. The lengths of the lattice along particular axes are called its lattice constants. Sr₂RhO₄ has two lattice constants as one axis is equal length to another. The constants are $a = 5.4979$ Angstroms and $c = 25.798$ Angstroms [7]. We needed to pick a substrate with a lattice constant as close as possible to lattice constant a of Sr₂RhO₄ when a is divided by the square root of two. This division by square root of two allows us to change the tetragonal lattice constants of Sr₂RhO₄ into a pseudo-cubic format that substrates typically use. Now following equation 2 we derive that lattice mismatches for both SrTiO₃ and LSAT. The full results can be seen in table 3. Because LSAT involves a lower lattice mismatch we used this substrate.

$$strain = \frac{a_{substrate} - a_{bulk}}{a_{substrate}} \quad (2)$$

Table 3: Lattice Constants and Strain

Substrate	Lattice Constant	Strain
LSAT	3.87	0.413%
SrTiO ₃	3.905	1.3%

PLD is a process in which a target, in my case Sr₂RhO₄, is struck by a laser multiple times in a vacuum chamber. The laser will cause a small amount of the hit surface to go from the solid state to the plasma state. The plasma will then deposit onto a prepared substrate which is suspended above the target on a heater as heating the substrate is required for good thin film growth. The main goal of this research experience was to grow a thin film of Sr₂RhO₄ by PLD for further study. See figure 11 for an overview of how PLD works provided by Ted Sanders.

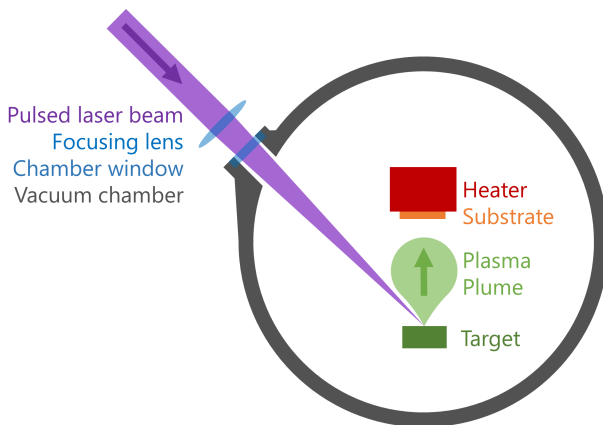


Figure 11: PLD Overview

Before we can utilize the laser for PLD we needed to properly prepare the substrate so that Sr₂RhO₄ will grow in the way we want it to on the surface of the LSAT substrate. LSAT is a commonly used abbreviation for the compound with the chemical makeup: La_{0.18}Sr_{0.82}Al_{0.59}Ta_{0.41}O₃. It has a cubic perovskite structure meaning it follows the formula ABX₃ where in this case X is Oxygen. While LSAT is made up of many elements the surface of it will be clumps of AO and BO₂. We do not require the surface of the substrate to be atomically smooth, rather we require all parts of the substrate's surface to end either with AO or BO₂ but not both. This type of surface is called 'singly terminated'. Typically approaches to achieving this singly terminated surface involve creating step-terraces in the surface of the substrate. See figure 12 created by Bachelet et al [1]. to see how this looks at the atomic level. In a paper by Connell et al. it was reported that by using de-ionized water it was possible to create singly terminated SrTiO₃ because the water would break down the ionic bonds of SrO which is water soluble [2]. Because we were using LSAT instead of SrTi₃ it was unclear whether or not this method would work for LSAT. Multiple academic papers reported on mixed results for trying water leaching and LSAT but since other methods of achieving singly terminated surfaces involve dangerous acids we tried wa-

ter leeching. We chose to prepare five separate wafers of LSAT in order to maximize our chances of creating a useable substrate. Water leeching was performed by mixing each substrate in a small amount of deionized water for thirty seconds, then blowing dry with air. After drying the substrates were annealed in the oven for two hours at 1150° degrees Celsius. After the first water leeching cycle the resulting substrate surfaces were very promising.

In order to tell if the surfaces were singly terminated we used an atomic force microscope to scan the topography of the substrates surface. The AFM uses a tiny needle to trace over the surface of the substance. We used a tapping mode which meant the needle was not in continuous contact with the surface of the sample. This was done because the AFM and its needle are extremely delicate instruments and we wanted to reduce wear and tear on the instrument. After cleaning the scans we were pleased to see that terraces had formed on the surface of each of the substrates, see figure 13. Looking at figure 13 it is impossible to tell whether or not the terraces are singly or doubly terminated. In order to check whether or not the terraces were singly terminated we selected a single line from the substrate's AFM scan near the midpoint and graphed its height as a function of position. At each of the steep drops the color has been changed in figure 15 to make it clearer where the terrace edges are. When measured each of the terrace drops corresponds to a height of approximately 5.4 Angstroms meaning the terraces were all of the same type meaning we had achieved our goal.

Because the paper by Connell et al. concerning SrTiO_3 recommended water leaching and annealing a second time we did so. After checking the substrates with AFM again we learned that huge clumps had formed on top of the terraces, see figure 14. We are not sure what they are, but they were completely absent on all five substrate samples before the second water leach and anneal cycle and now cover the surface of every substrate post second cycle. We would have tried to put them through another cycle to see if that would fix it, or create more substrate samples that went through only one cycle but unfortunately we ran out of time so we had to choose the best LSAT substrate from our prepared five and hope for the best.

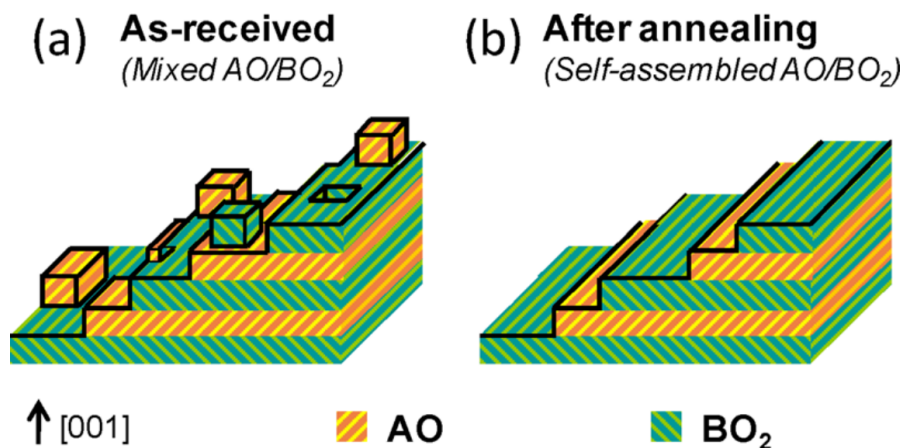


Figure 12: Doubly Terminated vs Singly Terminated

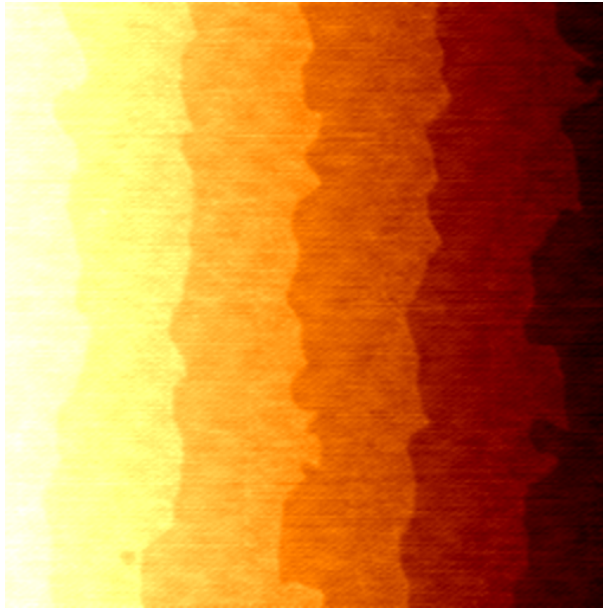


Figure 13: AFM Data for Water Leached and Annealed LSAT

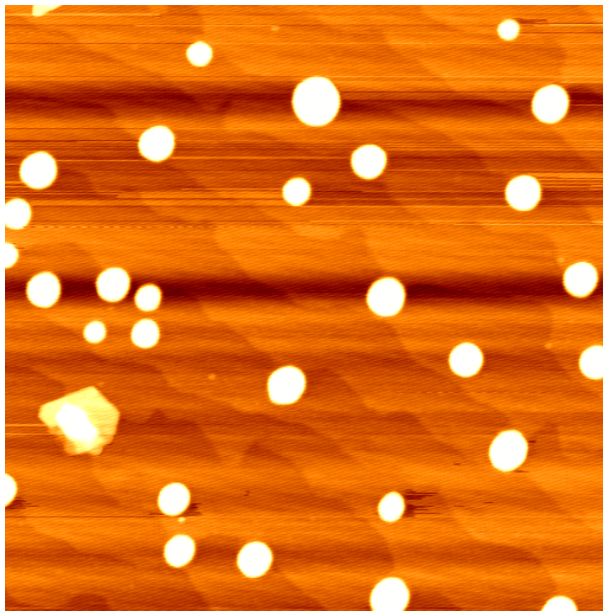


Figure 14: AFM Data for 2nd Water Leach Cycle

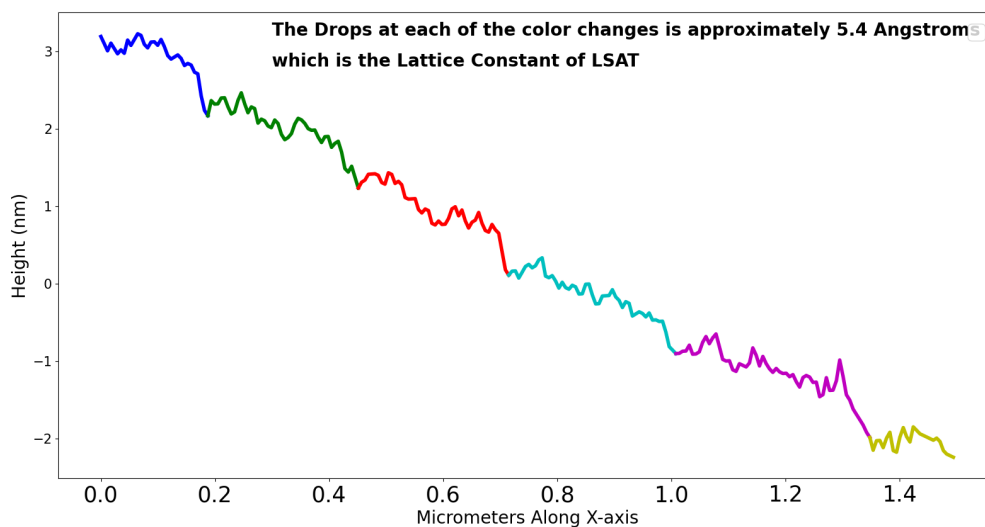


Figure 15: AFM Data for Single Line of Water Leached and Annealed LSAT

We attached the chosen substrate onto the heater of vacuum chamber three. We had to make sure the substrate was aligned perfectly over the top of the target pellet, otherwise the plume would not evenly deposit. This was the first time the heater would be used for an experiment so there was some measure of uncertainty as to how it would perform. The substrate was attached to the heater with a silver paste. The target Sr_2RhO_4 was placed in the vacuum chamber the night before so that any trapped moisture or gasses inside the sample would get sucked out of it by the vacuum pumps. The substrate was raised to a temperature of 700° Celsius although the internal thermometer of the heater only reached a temperature of 690°C . The laser parameters used are recorded in table 4.

Table 4: Laser Parameters

Pressure	10 mTorr
Aperture	3
Repetition Rate	10 Hz
Substrate Temperature	700°C
Voltage	28 KV

We meant to use aperture 1 instead of 3 but we forgot to change the set aperture. Aperture 1 is smaller than 3 and may have helped with the deposition.

References

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