Lab 4: Characterization of Perovskite La0.8Sr0.2MnO3 (LSM82) & Electrical Measurement of Semiconductors

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for
MSE 60: Advanced Laboratory in Synthesis and Characterization of Materials

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ABSTRACT *(Thaily Serrano-Alamo)*

This lab was conducted to characterize Perovskite La0.8Sr0.2MnO3 (LSM82) and determine its properties. La2O3, SrCO3, and MnCO3 powders were used to synthesize LSM82. They were all mixed together with a solvent and went through a roll milling machine. After the solvent was evaporated and the sample was compressed. The samples were then calculated at 1200C for 12 hours. They were grind and compressed again. Lastly they were put under heat again for 12 hours. Three samples that were at different temperatures, 900C, 1200C and 1500C for 8 hours went under X-Ray Diffraction (XRD) to analyze its crystal structure. Through the Archimedes density the relative density was calculated. Using 5 samples the electrical measurements were found. XRD showed that LaSO3 was found in low temperature but not high temperature. The density measurements showed that sintering increased the density and porosity. LSM82 was found to have a similar conductivity value to LSCF.

INTRODUCTION *(Kelsey Lawson)*

A new area of research is on some forms of ceramics behaving similarly to metals, semiconductors or insulators based on their electrical ability. It is commonly known that metals are materials that can allow the flow of electricity whereas insulators are the opposite and prevent this flow due to no free electrons. Moreover, semiconductors are the middle-ground materials that have a conductivity between that of an insulator and most metals either from the addition of impurities or due to temperature effects. Studying ceramic samples to create temperature stabilizing (TS0 coatings based on temperature-dependent emissivity, ε, compounds has been the main topic for spacecraft development (1). These TS coatings would be able to maintain a predetermined temperature for spacecraft flight applications and can even change the emissivity and flows of radiated energy regarding external conditions, referred to as smart

coatings (1). Within the lab conducted, Strontium substituted lanthanum manganite perovskite powder was synthesized in order to analyze the electronic and density properties alongside characterization through X-ray diffraction, XRD.

OBJECTIVE *(Keven Colchado)*

The purpose of this lab is to be able to synthesize the solid state of Strontium substituted lanthanum manganite perovskite and determine the emissive properties of the solids as well as other physical properties. Through density analysis the particle size distribution will be determined. And through electrical measurements tests, the resistance change of the powder will be examined in order to determine how effective the ceramic compound is at absorbing high temperature.

MATERIALS AND EXPERIMENTAL METHODS *(Keven Colchado)*

Materials

Electric Scale	La2O3	SrO3	MnCO3	Spatula	Funnel
Milling Jar (1L)	Gamry Instrument 1000	Roll Milling Machine	100mL Beakers	Alumoina milling balls	Weighted Paper
Mortar and Pestle	Cold Isostatic Pressing Jar	Compression Machine	Rubber Stopper	Painted Aluminum Electrode	Graphite Cylinder
Rubber spoon	Die Set	Latex Seal	Tweezers	Hydraulic Oil	Crucible
Acetone	Faraday Cage	Hot Plate	Electrodes	Tube Furnace	Metal Rod

Solid-State Synthesis of Strontium Substituted Lanthanum Manganite Perovskite La0.8Sr0.2MnO3 (LSM82)

First begin by measuring the raw powders of La2O3, SrCO3, and MnCO3 on an electric scale using weighted paper and a spatula. Then the powders will undergo ball milling. First prepare some alumoina milling balls into a one liter milling jar and add some acetone solvent. Add the powders into the jar and seal them. Leave jar on roll milling machine. Turn on the machine and leave the jar for 12 hours. After milling, pour liquid into a 100 mL beaker.

Evaporate the solvent on a hot plate at 50C for twelve hours. Pour the leftover solids into a mortal for grinding with a pestle. Begin cleaning the die set with a clean napkin then set up the die set. Using a spoon, pour in the raw powder into the opening of the die set. Make sure to clean off any residue left on top of the ring. Once clean, insert the plunger to compress the powder down. Pull out the plunger and insert a spacer in before reinserting the plunger. Lower the piston of the compression machine to match the level of the die set. Open the base of the die set and place a release ring on the opening. Compress the set for 100MPa. Clean the alumina crucible before pouring the leftover powder in. Then place the compressed solution on top of the powder. Place the closed alumina crucible into the tube furnace by using a metal rod. The crucible should be in the center of the crucible. Then insert the insulating rods to cover. Turn on the tube furnace and set it up for 1200C for 8 hours. Place the pellets to a clean mortar and grind them down with a pestle. Once they're in powder form, pour the mixture into a mixing jar and add acetone into the mixture. Seal the jar and place on the rolling machine for 12 hours. Pour the liquids into some beakers and place them onto the hot plate. Heat up the solution until it evaporates. Begin setting up the die set again by cleaning each piece. Repeat steps from the earlier compression. Once compressed for 100 MPa, insert the pellet into the latex seal, remove as much air from the seal and tie a knot to seal shut. Open the cold isostatic press jar and insert the sample with the latex seal. Add hydraulic oil into the opening and close the jar. Then compress the jar under the compression machine for 200 MPa. After compression, open the jar and remove the sample with the latex seal. Cut open the seal and pleace the pellet into an alumina crucible. Make sure to not have the pellet be in contact with the hydraulic oil. Return into the tube furnace and place the crucible by using a metal rod and seal the openings with an insulating tube. Turn on the machine

and set the furnace to 1200C for 12 hr. Remove the crucible once it has been cooled down naturally. The final product should be La0.8Sr0.2MnO3.

Characterization of Perovskite La0.8Sr0.2MnO3

For this lab, Perovskite will undergo characterization by X-Ray Diffraction and calculating the relative density by applying Archimedes density principle. The equation of Archimedes density is the relative density equaling the mass of the object in air times the density of water (1g/cm3) all over the mass of the object in air minus the mass of the object in water. For this experiment, the mass of the object in air was 9.5915g and in water 8.0471g. It also needed to calculate the theoretical density of the object in order to determine how dense the pellet became. If the density percentage equaled to over 90 percent then the object was dense.

Property Test

Electrical Measurements will be conducted using a 2 point and 4 point electrode. To set up the experiment, a painted aluminum working electrode will be placed on top of a cell unit inside a Faraday cage. The cell will be placed on top of the aluminum electrode and sealed with a rubber stopper. A graphite cylinder will go through the rubber stopper and touch the base of the cell. The graphite cylinder will serve as the counter. A mounted reference electrode will also go through the rubber stopper. For the 2 point electrode only the working and counter/reference electrode will be used. For a 4 point electrode, a working, working sense, reference, and counter electrode will be used. Once all connected, turn on the Gamry interface 1000 and measure the resistance change with temperature.

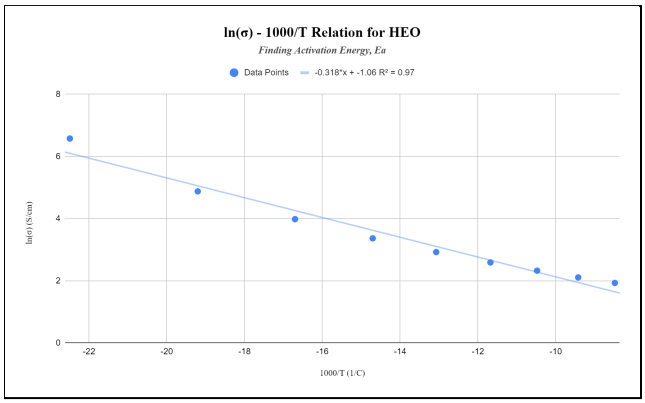
RESULTS

ELECTRICAL PROPERTY MEASUREMENT *(Kelsey Lawson)*

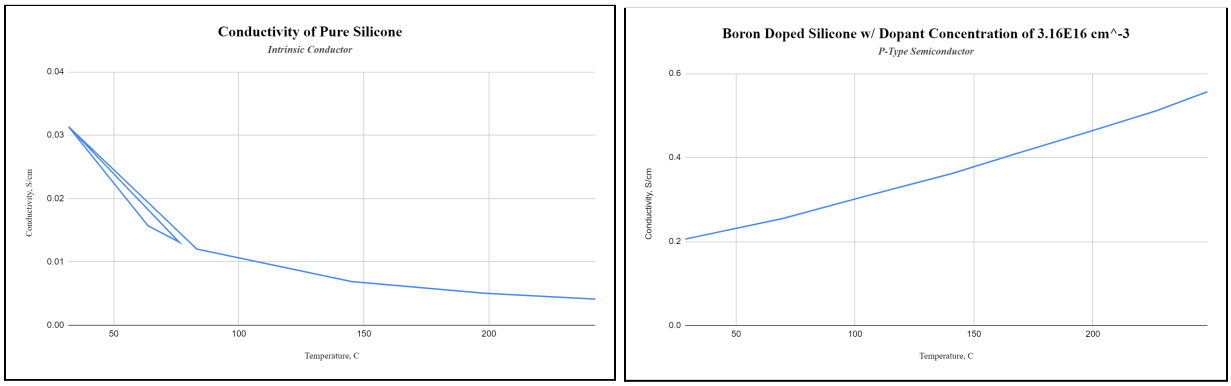
Equations used for calculating the electrical property measurements of (see Appendix for the data tables & derived calculations)

(1) Conductivity: $\sigma = \frac{d}{R(Area)}$

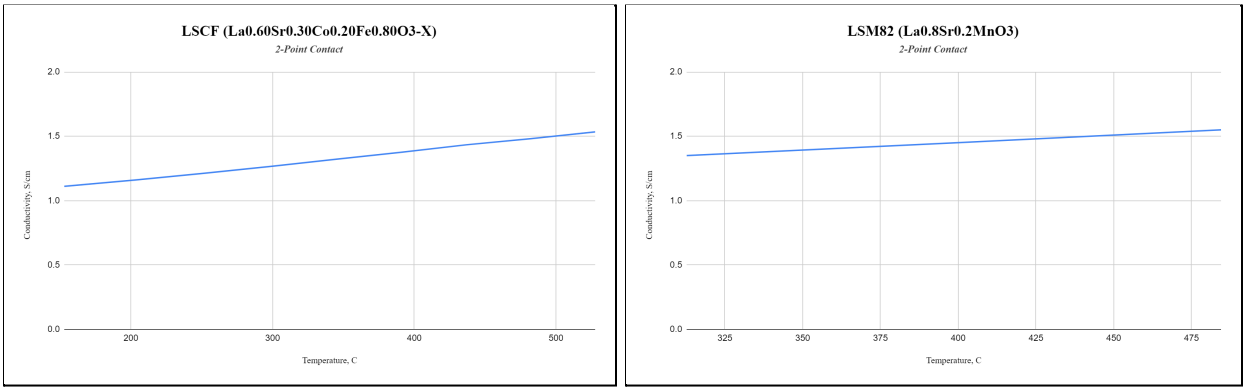
(2) Arrhenius Relation: $\sigma = Ae^{-\frac{E_a}{k_b T}}$



Graph 1. The graph is for the HEO Arrhenius relation to find the activation energy, E_a from the conductivity data. Using the slope found from the plotted data, E_a was calculated to be 2.74E-02.



Graph 2-3. The left graph is the conductivity of pure silicon plotted against temperature. It can be seen that there was a repeated value that made the line spring back then continue to higher temperatures still having a negative trend. The right graph is the conductivity of boron doped with silicone with a positive trendline.



Graph 4-5. The graph on the left is the conductivity of the LSCF sample with a positive trendline. The graph on the right is the conductivity of the LSM82 sample with a positive

trendline. Both graphs appear to have similar trends however, the LSM82 sample only had 3 recorded data points whereas the LSCF sample had upwards of 9.

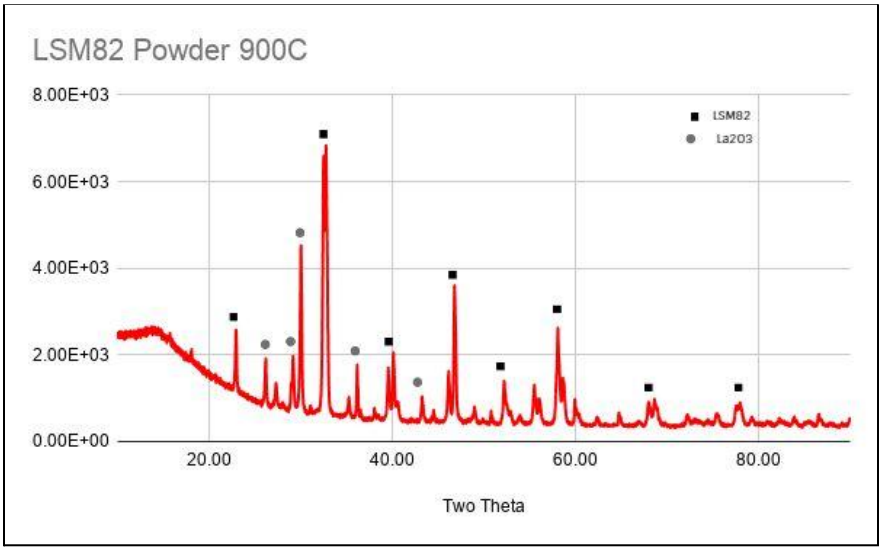
DENSITY MEASUREMENT *(Kelsey Lawson)*

Equations used for calculating the density percentage, ρ%, of the LSM82 pellet at 1200℃. (see Appendix for the data tables & derived calculations)

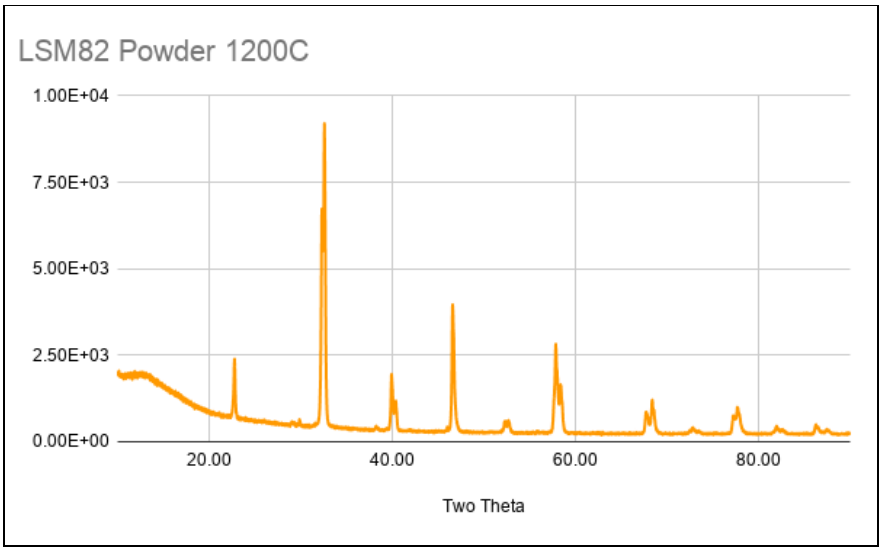
(3) Archimedes Density Measure: $\rho_{Real} = \frac{m_{Dry}}{m_{Dry} - m_{Wet}} \cdot \rho_{Water} = 6.210502461$

(4) Relative Density: $\rho\% = \frac{\rho_{Real}}{\rho_{Theoretical}} \cdot 100\% = 94.53\%$

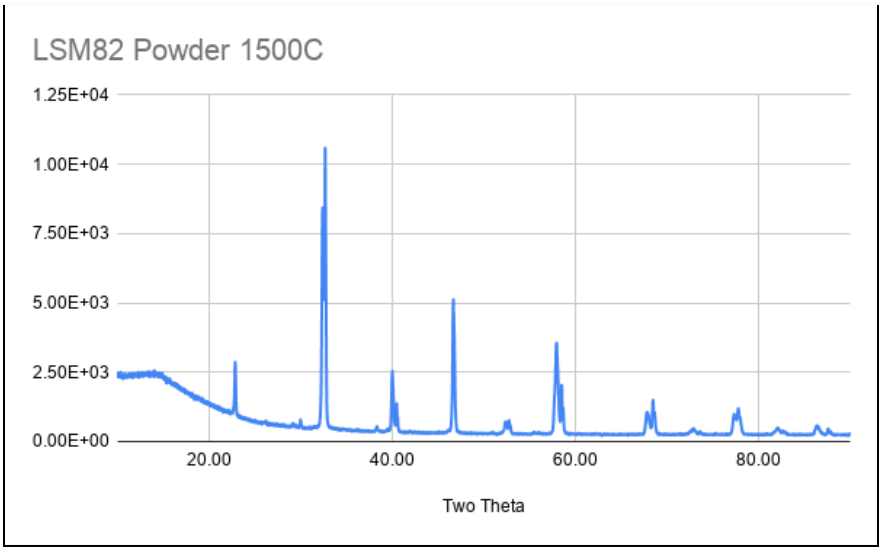
XRD (*Thaily Serrano-Alamo)*



Graph 6. This graph shows XRD of LSM82 powder that was heated to 900C for 8 hours. The square represents LSM82 and the circle represents La2O3.



Graph 7. This is the XRD graph of LSM82 powder that was heated to 1200C for 8 hours.This graph mostly shows the structure of LSM82. It does not seem there is another structure compared to the graph above.



Graph 8. This is the XRD graph of LSM82 powder that was heated to 1500C for 8 hour.The graph is very similar to the one above. There is not a significant difference between 1500℃ and 1200℃.

DISCUSSION

ELECTRICAL PROPERTY MEASUREMENT *(Kelsey Lawson)*

The electrical properties were measured for 5 samples with ranging data sets for: 7M-HEO (Hf0.284Ce0.284Zr0.284)(Y0.074Gd0.074)O1.926, Pure Silicone, Boron-Doped Silicone w/ Dopant Concentration 3.3E16 cm^{-3}, LSCF (La0.60Sr0.30Co0.20Fe0.80O3-X), and

LSM82 (La0.8Sr0.2MnO3). Each sample's conductivity, excluding HEO, was plotted using the provided data points. Comparing these samples, only pure silicone had a negative trend for conductivity which means at higher temperatures the ability to conduct electricity decreases. Both LSCF and LSM have similar conductivity values but compared to Boron-Doped Silicone, their average electricity over the temperature range is quite small. The Boron-Doped Silicone sample had the largest quantity of conductivity increasing over the temperature range and can be assumed to be the best material to conduct large amounts of electrical currents. For HEO, a different formula was used to find conductivity to then apply it to the Arrhenius Relation to find the activation energy.

DENSITY MEASUREMENT *(Kelsey Lawson)*

For this section of the lab, only the LSM82 pellet sample will be analyzed at 1200℃ that was sintered twice to find the density measurements of: the real density, ρ_{Real}, and the relative density, ρ%. All of the required densities to calculate the real density were provided as: m_{Dry} = 9.5915 g, m_{Wet} = 8.0471 g, ρ_{Water} = 1 g/cm3 at room temperature, and $\rho_{Theoretical}$ = 6.57 g/cm3. From these values plugged into Eq. 1, the real density was found to be ρ_{Real} = 6.210502461. This density was then plugged into Eq. 2 in order to determine the relative density percentage. This value was calculated to be 94.53% which is over the 90% threshold for considering the pellet to be well dense. This means when LSM82 is sintered it decreases any porosity in the sample and can be assumed that higher the amount of sintering, the pellet will continue to increase its density since the sample was sintered twice.

XRD (*Thaily Serrano-Alamo)*

LSM82 was heated at different temperatures for 8 hours. The crystal structures were analyzed through XRD. Their intensities were graphed above. Temperatures 1500℃ and 1200℃ seem to have similar peaks. There is no noticeable difference in height and wide of the peak.

This means that the crystal structure does not seem to change between 1200℃ and 1500℃. The peak height is a bit higher for 1500℃ than 1200℃ but not greatly. This could be from some machine/human error or a change in grain size. The difference is not great enough to make a conclusion. There is a noticeable change in peaks between 900℃ and 1200℃. It seems that 900℃ has peaks for LaSO3 and the rest of the graphs do not. This can conclude that 1200C and 1500℃ have peaks for LSM82 but not LasSO3. Also temperature does change the crystal structure of LSM82 powder as seen in the XRD graphs. As temperature increases, the formation of LaSO3 decreases.

CONCLUSION *(Thaily Serrano-Alamo)*

This lab synthesized the solid state of LSM8S and determined the emissive properties of the solid. Using the three powders, LaSO3, SrCO3, and MnCO3, LSM83 was created. The electrical properties were measured for 5 samples: 7M-HEO, Pure Silicone, Boron-Doped, Silicon w/ Dopant concentration, LSCF and LSM82. It was concluded that Boron-Doped Silicon was the best material to conduct large amounts of electrical current. The density was also measured. It was determined that sintering LSM82 decreased porosity and the density was increased. Through XRD, the crystal structure was analysed with different temperatures, 900C, 1200C and 1500C. It was found that as temperature increases, the formation of LaSO3 decreases. The LaSO3 structure was found in 900C but not in 1200C and 1500C.

References

(1) Mikhailov, M. M., et al. Solid state synthesis of $LaSrMnO_3$ powders for smart coatings. *Materials Research Bulletin* **89**, (154-160) 2017. http://dx.doi.org/10.1016/j.materresbull.2017.01.038

Appendix

Electrical Property Measurements & Density Measurement

All of the graphs and tables of the data provided are located in a Google Sheets file: https://docs.google.com/spreadsheets/d/1qHqxsnERIaIwByY8HDPXgkg6dnEcWSa_XPKkAbaPU9s/edit?usp=sharing