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Synthesizing and Characterizing Sr_2FeMoO_6 Bulk and Thin Films

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Abstract

A Sr_2FeMoO_6 (SFMO) pellet was synthesized to use as a target in the Pulsed Laser Deposition (PLD) chamber. The method chosen was a solid state reaction of $SrCO_3$, Fe_2O_3 and MoO_3. All three materials were combined stoichiometrically, ground in a ball mixer, and annealed for 36 hours at 1000°C. A pellet press was custom designed and used to press the annealed powders into a pellet. The magnetic and structural properties of the powder were studied using a Quantum Design MPMS SQUID magnetometer and powder X-Ray diffractometer, respectively. Previous studies of bulk SFMO suggest it to be ferrimagnetic or ferromagnetic, with a magnetic ordering near 400K. The magnetization data completely agrees with the reported data. The 1" diameter pellet was used as a target in the PLD chamber to grow a 200 nm thin film on a $SrTiO_3$ (001) substrate at 800°C and 10^{-6} torr. X-Ray diffraction was performed on the film to ensure it was epitaxially oriented. From this data, calculations were performed which found the thin film to have been grown epitaxially.

I. Background

A perovskite is a material which has the chemical formula $AA'O_3$, where A and A' are both cations, one larger than the other. These compounds have the same structure, called a perovskite structure. A variation on the perovskite formula is the double perovskite, generally $A_2BB'O_6$, where A is Ca, Ba or Sr, B is a 3d transition metal (e.g. Fe), and B' is a 4d transition metal (e.g. Mo). The double perovskite may be thought of as the single perovskites ABO_3 and $AB'O_3$ alternating in a 3-D manner. In this research, the compound Sr_2FeMoO_6 (SFMO) was studied. This material contains the two perovskites $SrFeO_3$ and $SrMoO_3$. Ideally, each Fe perovskite would be surrounded by 6 Mo perovskites and vice versa, which is best shown in Fig. 1. This does not occur, however, as some Mo perovskites can be vacant (that is, they lack only the Mo atom). The Fe perovskites tend not to be found in a vacant state[3]. Also, the Fe and Mo perovskites have a tendency to swap positions, becoming disordered, even to the point of having completely random positions[3,4].

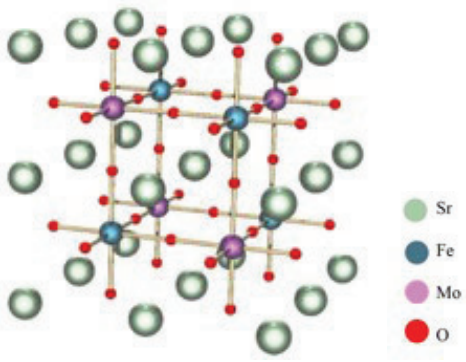

Fig. 1: The double perovskite structure of Sr_2FeMoO_6. Note that only 8 of the Sr atoms shown have the attached perovskite pictured. The remaining Sr atoms are shown for reference. Most important is the manner in which the Fe and Mo perovskites alternate.

In terms of conductivity, SFMO is a poor metallic conductor. A one inch diameter disc of the material, for example, has a resistance on the order of $10^6\,\Omega$, whereas a good conductor would be at least 6 orders of magnitude lower.

There is some debate as to which magnetic ordering SFMO actually possesses. The more popular theory is ferrimagnetic ordering, which is when the Fe and Mo atoms have a magnetic moment pointed in opposite directions, but of unequal magnitude[2,5,6]. Specifically, it is theorized that Fe has a +5 μ_B moment while Mo has a -1 μ_B moment, resulting in a net +4μ_B magnetic moment. However, another theory suggests that SFMO has a ferromagnetic ordering, which is when the Fe and Mo atoms have aligned moments[4,8]. With this assumption, Fe is theorized to have a +4 μ_B moment while Mo has no moment. The result is equal to the ferromagnetic ordering, that is, a +4 μ_B magnetic moment. There is considerable difficulty in determining with experimental certainty which ordering is present, but the leading result is ferrimagnetic ordering.

The process of synthesis is detailed in section II. Experiments are in section III, which includes X-Ray Diffraction, SQUID, and the growth of a SFMO thin film. A discussion of our data is in section IV and we conclude our work in section V.

II. Synthesis

Since we had no samples of Sr_2FeMoO_6 readily available, we had to synthesize the material. After determining the most feasible manner to synthesize SFMO, we decided to use a solid state reaction of $SrCO_3$ (99.99%), Fe_2O_3 (99.99%), and MoO_3 (99.998%)[2]. Using the chemical equation $4SrCO_3 + Fe_2O_3 + 2MoO_3 + H_2$ ' $2Sr_2FeMoO_6 + 4CO_2 + H_2O$ and accounting for the different purity levels, we determined that 8.3773g $SrCO_3$, 2.2577 g Fe_2O_3, and 4.0681 g MoO_3 would be used to give 12.0000 g of SFMO.

These starting materials were ground in a Spex ball mill until well combined. The solid state reaction chosen required a tube furnace to heat these powders to 1000°C for 24 hours, with ramping temperature rates of 1°C/min in both directions.

The result of the initial annealing showed a distinct change in volume and color of the material. The powders were re-ground at this point as part of the solid state reaction and various experiments were performed with this powder.

Due to the decrease in volume, we decided to produce a second batch of SFMO. The process with the ball mill and tube furnace was repeated. For unknown reasons, a distinct iron oxide appearance was present after annealing in this batch, which was not present in the first batch. Re-annealing at 1000°C for 12 hours removed the iron oxide appearance. Unfortunately, the programming unit on the furnace did not ramp down for the second batch, resulting in a second annealing of 48 hours instead of 12 hours.

Our goal to create a thin film of SFMO required the use of a Pulsed Laser Deposition (PLD) Chamber. The PLD uses a 1 inch diameter pellet of SFMO in order to produce a thin film of SFMO. As the laboratory did not have a 1 inch pellet die kit, we designed a pellet die kit, with assistance from the physics department machine shop at the University of Connecticut. The die kit consists of three basic parts: a base, a body and a plunger. The body was made from a 3" diameter cylinder of 4340 carbon steel with a 1" diameter hole in the center, the base was made from a 2.5 inch diameter cylinder of 1215 low carbon steel with a 1" diameter raised insert made of O1 tool steel, for strength. The plunger was made from 1215 low carbon steel as a handle with an inserted 3" long, 1" diameter O1 tool steel to act as the plunger. Once the body is placed on the base, powder is poured into the body and the plunger is inserted. This entire unit is then placed in a pneumatic pellet press to press the powders into a pellet. We estimated the die kit to be usable at 80,000 lbs force, with the weakest element being the 4340 carbon steel body.

When we pressed the powders at 24,000lbs, they formed a single solid pellet. At lower forces, the pellets were easily broken. This pellet was then transferred onto a fire brick which we pre-shaped to slide into the furnace's ceramic tube. The furnace was programmed to ramp at 1°C/min to 1200°C, hold for one hour, then ramp down to room temperature. Once completed, we removed the pellet and found the exposed side to be peeling; the side in contact with the firebrick was free of defects.

Shortly thereafter, a SFMO pellet from Dr. B. Dabrowski at Northern Illinois University (NIU) was received. Since this sample was not peeling, it was the sample we ultimately used to make a thin film in the PLD chamber.

III. Experiments

We performed two experiments on the powders, the first being X-Ray Diffraction (XRD) to ensure the correct structure was being formed. The second experiment we performed with a SQUID to investigate the magnetic ordering temperature. The data from the SQUID was also used to determine if the sample was ordered or disordered. We used the pellet in the PLD to grow a thin film, which we then used in a XRD experiment to ensure epitaxial growth.

A. Powder X-Ray Experiments

We performed X-Ray Diffraction on the powders after the initial annealing. As the objective was to determine the structures present in the powders it is necessary to use photons that have a wavelength smaller than the d-spacing (atomic plane separation). This spacing is approximately 79 nm from previously reported data [7], and the X-Rays produced in the diffractometer have a wavelength of 0.154 nm, which makes XRD a very useful atomic-level tool. The choice of photons is ideal since they do not have a charge and are extremely stable and easy to produce. The XRD experiments are entirely based on Bragg's Law, which describes the diffraction of a photon with a crystal lattice structure.

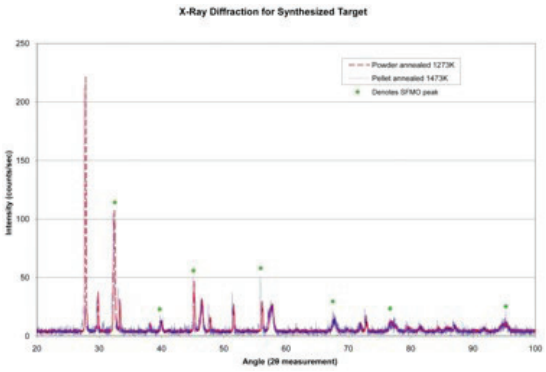

Fig. 2: X-Ray diffraction comparing the powders after a 24 hour and annealing at 1000°C with the pressed powder pellet after the 1200°C annealing. The green dots indicate a proper stricter, as found in [6].

The XRD revealed that all the peaks for SFMO were present, indicating the presence of a SFMO concentration in the powder. However, the additional lines indicate the presence of at least one impurity; $SrMoO_4$ is reportedly the most likely impurity [2,9].

We also performed XRD on the pellet received from NIU before it was used as the target in the PLD chamber. The result of this experiment is given in Fig. 3, which indicates that only SFMO peaks are present. This indicates a high purity sample, suitable for use as a target to grow thin films.

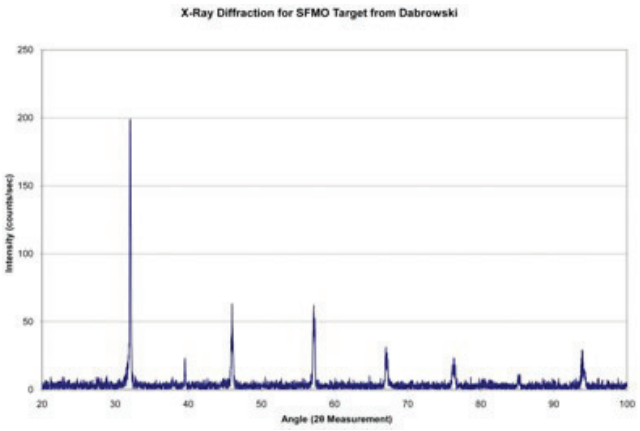

Fig. 3: X-Ray Diffraction experiment performed on the received target from Dr. Dabrowski at Northern Illinois University. Comparing with the green dots in Fig. 2, we see a perfect match. Since there are no extra peaks, we may conclude this sample is a high purity SFMO pellet.

B. Superconducting Quantum Interference Device (SQUID) Experiments

We used a Quantum Design MPMS Superconducting Quantum Interference Device (SQUID) Magnetometer to measure the magnetic moment of the produced powder. Magnetization was measured as a function of temperature over 5 to 350 K. The powder was measured after the second annealing at 1000°C. A highly ordered (> 90%) sample of SFMO should display an abrupt drop in magnetization [2,3]. The data from the SQUID experiment is presented in Fig. 4, which indicates that the sample is relatively disordered, but does not indicate how disordered it is.

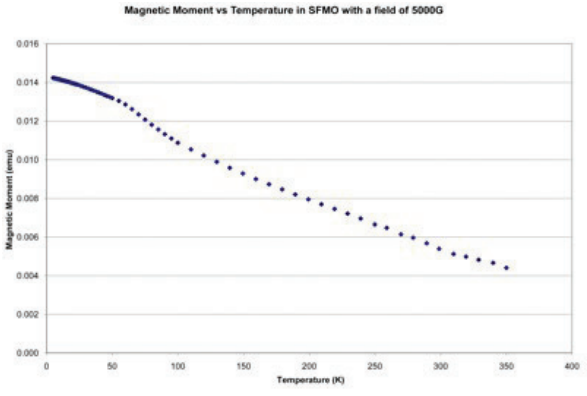

Fig. 4: Magnetic moment measurements taken as a function of temperature under an applied field of 5000G for SFMO powder after a 24 hour and subsequent 12 hour annealing at 1000°C. The relationship between magnetization and temperature is commonly seen in a disordered sample.

The impurity revealed in the XRD experiment could also be affecting the magnetization measurements. It is difficult to determine whether the ordering is ferrimagnetic or ferromagnetic using a SQUID magnetometer. Nevertheless it does measure how strong of a magnetic moment it has.

C. Pulsed Laser Deposition (PLD) Chamber A PLD, shown in Fig. 5, relies on a high-intensity laser to ablate the surface of a solid, causing a plasma plume to form. Inside the plume is the stoichiometric ratio of strontium, iron, molybdenum and oxygen. A mounting plate inside the PLD holds a substrate which the plume deposits onto, forming the thin film. In our case, the substrate was a 1 cm x 1 cm piece of $SrTiO_3$ oriented in the (001) direction, commonly referred to as STO (001). It was used because it has a close match to the lattice parameters of SFMO. This match is required for SFMO to grow properly on top of the substrate [5]. Deposition will occur only in a low pressure environment, so the entire metal chamber is held under vacuum during growth.

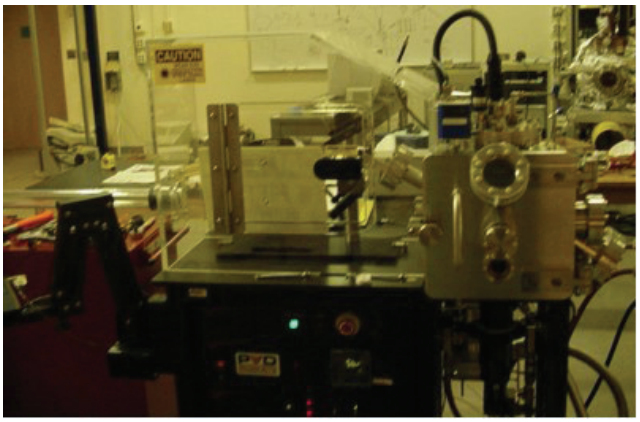

Fig. 5: The Pulsed Laser Deposition (PLD) Chamber. Optical devices are contained inside the chamber, which re-focus the beam into the metal chamber. The beam then hits the target, ablating the surface, and creating the plasma plume which will deposit onto the substrate.

The PLD has several important variables for growth. In the experiment performed, we used the following growth conditions: a substrate temperature of 800°C, a chamber pressure of 10^{-6} torr (1.3×10^{-9} atm), laser energy of 0.252 J with a frequency of 4 Hz and a growth time of 16 minutes. The exposure time varies depending on the required thickness of the film. The entire process takes several hours, as the chamber needs to be brought down to pressure and the substrate needs to heat up.

D.Thin Film X-Ray Experiment

Once we grew the film, we removed the thin film from the mounting plate and checked to see if it was grown properly. This was done with a XRD experiment, but with a different purpose than when performed for the powder. We used XRD on the thin film to determine if it grew with proper orientation. In Fig. 6, our thin film XRD experiment data is presented, in a logarithmic scale for the intensity values. Since the SFMO thin film is approximately 200 nm thick, and the substrate is a ~2 mm thick, it is not surprising that the substrate has a much higher intensity value. As a result, if we presented the data in linear rather than logarithmic, the SFMO peaks would be indistinguishable from background noise. As the peaks present have (002), (005) and (006) Miller Indices, we concluded that this thin film was grown properly.

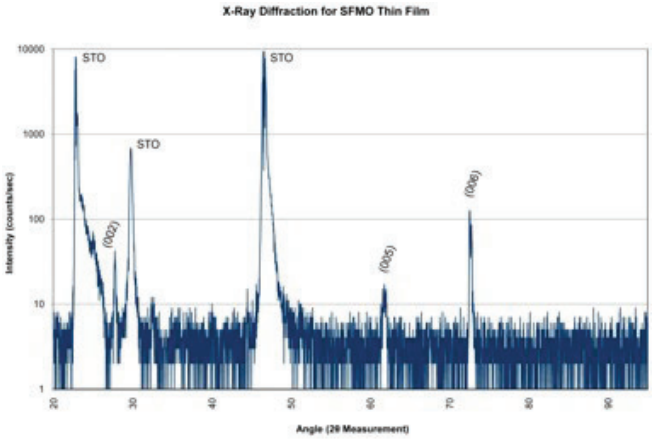

Fig. 6: X-Ray Diffraction performed on the thin film as grown. Note the intensity is in logarithmic scale. Due to the relative thickness of the substrate, we can observe that the largest SFMO peak is approximately 10% of the smallest substrate (STO) peak.

IV. Discussion

Since we did not have data which related a set of 2θ values to Miller Indices for SFMO, we had to compute this data. As we used STO (001) for a substrate, this forced the requirement that any peaks on the XRD experiments be in an (00l) plane, for an epitaxially grown thin film. We started with Bragg's Law, as it applies to X-Ray Diffraction:

$$n\lambda = 2d\sin\theta \quad (1)$$

Also, using the relationship between the lattice parameters a, b, and c (note that in SFMO, $b = a$ [7]) and the Miller Index (hkl)[1] we know that:

$$d = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} \quad (2)$$

Since STO (001) was used for a substrate, the only allowed planes are (00l) planes, thus $h = k = 0$.

$$d = \frac{1}{\sqrt{\left(\frac{0}{a}\right)^2 + \left(\frac{0}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} = \frac{1}{\sqrt{\left(\frac{l}{c}\right)^2}} = \frac{c}{l} \quad (3)$$

We replaced d from (3) into (1) and set $n = 1$, as is commonly done, to yield:

$$\lambda = \frac{2c\sin\theta}{l} \quad (4)$$

At this point the variable λ, wavelength of the incident photon, is a known value that is specific to the X-Ray Diffractometer, in our case 15.41 nm. Also, c is a known value from previously reported data and measured as 78.949 nm [7]. To determine if a specific angle measurement is a (00l) peak, we solved for the angle. Observing that the X-Ray Diffractometer actually measures 2θ:

$$\frac{\lambda l}{2c} = \sin\left(\frac{2\theta}{2}\right)$$

$$2\sin^{-1}\left(\frac{\lambda l}{2c}\right) = 2\theta = \frac{360}{\pi}\sin^{-1}\left(\frac{\lambda l}{2c}\right) \quad (5)$$

The final step in equation (5) is to convert from radians to degrees. With equation (5), it is easy to see if a peak is a (00l) peak or not. Since l is an integer, we evaluated for each l value starting at 1 until the inverse sine function was no longer defined. From this, we obtained a complete set of data relating 2θ to (00l) Miller Indices.

Any peaks that occur which do not appear on the list are a sign of a poorly grown thin film. If, however, every peak that occurs is the result of a (00l) peak, then we have shown epitaxial growth. This indicates that the thin film is of high quality, and has proper orientation. As the thin film produced yielded (002), (005) and (006) peaks, it was found to have been properly grown.

V. Conclusion

The Sr_2FeMoO_6 material was somewhat successfully synthesized. An impurity was found to exist in the powders, which remained through to the produced pellet. In addition, the pellet exhibited a peeling surface. As such, a sample from NIU was received with time to perform X-Ray Diffraction, which revealed high purity, and was in good physical condition. The thin film that was produced was found to have been successfully grown, as confirmed by the X-Ray Diffraction experiment.

At this point, the end of the research project was reached. The biggest goal that remained unfinished was performing the Spin-Resolved Photoelectron Emission Microscopy (Spin-Resolved PEEM) and resistance experiments. These experiments would show direct proof of whether or not the SFMO thin film had a half-metallic nature, which would indicate that it has some rare properties – such as Colossal Magnetoresistance. With confirmation of a half-metallic nature SFMO could be used in quantum devices, spintronics or advanced data storage devices.

Acknowledgements

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