

# STEM Imaging and Composition Mapping of Multiferroic Oxides

**Mr. Anthony Coleman, 2018 PARADIM REU Intern**

**Physics Engineering, Chicago State University**

*REU Program: 2018 Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials  
Research Experience for Undergraduates (PARADIM REU) Program*

*PARADIM REU Principal Investigator: Professor Darrell Schlom, PARADIM, Cornell University*

*PARADIM REU Mentor: Dr. Megan Holtz, PARADIM, Cornell University*

*Primary Source of PARADIM REU Funding: Support for PARADIM is provided under NSF Grant # DMR-1539918  
as part of the Materials Innovation Platform Program*

*Contact: [schlom@cornell.edu](mailto:schlom@cornell.edu), [meh282@cornell.edu](mailto:meh282@cornell.edu)*

*Websites: <http://paradim.cornell.edu/education>, [http://www.cnf.cornell.edu/cnf\\_2018reu.html](http://www.cnf.cornell.edu/cnf_2018reu.html)*

## Abstract:

Multiferroic materials are fast becoming materials that are being observed as thought-provoking materials with the potentials for the next generation of data storage technologies. Although there are a few ferroic orders, we will be specifically experimenting with the coupling of the electric and magnetic order. The realization of these multiferroic materials to be operative in room temperature are few, and even more are limited with robust, coupled magnetization and polarization. Molecular beam epitaxy with oxides (MBE), is an auspicious methodology to grow, and or produce, these materials. This procedure is very promising in the production of new innovative growth recipes of properties coupled in materials, through heterostructures and interface stages. In this investigation, ferroelectric  $\text{LuFeO}_3$  with the ferrimagnetic  $\text{CoFe}_2\text{O}_4$  was combined, creating superlattice layers. The purpose was to advance a material with polarization and magnetization, impulsive in nature, that contains the functioning, desired properties above room temperatures. The obtaining of the characteristics of the superlattice layers on the atomic scale, is vital in this research. After the Growth of the multiferroic oxide, scanning transmission electron microscopy (STEM), was used alone with the composition mapping, using x-ray energy dispersive spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). The STEM scanning and composition mapping of the material commenced. The investigation of interdiffusion between materials was the investigations purpose. We proceeded with the mapping of the elemental profiles through the film and across the bottom electrode. The inspection for the interdiffusion and growth conditions was completed and provided critical advice for the molecular beam epitaxy growth procedure following this research.

## Summary of Research:

The purpose of this research was to obtain new materials with the new coupled properties, magnetization and electrical polarization at room temperature. These new properties specifically would have very useful applications for next-generation memory devices in computer and sensors. For example, a new memory element that has four bits instead of two, using both the magnetic and electronic degrees of freedom, would be groundbreaking. Additionally, the control of magnetic memory by applying a voltage would make data storage more energy efficient. To develop this material, the electric field must govern the magnetism. Although multiferroic materials have been observed previously, the polarization or magnetism were only observed in well below room temperatures conditions, or properties of the magnetism were weak.

To generate such useful new properties, the heterostructures or interfaces must be grown. These materials required a STEM scanning and a composition mapping examination of the materials, on the atomic scale. The multiferroic oxide we intend to create is ferroelectric lutetium ferrite ( $\text{LuFeO}_3$ ), and ferromagnetic cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ). Ferroic materials have a long-range ordering of a macroscopic property due to the lattice structure. This long-range ordering, or the crystal atomic position, is also known as translational periodicity. When the

location of an atom and its neighbors are identified by STEM, the polarization of each atom is known exactly throughout the crystal structure.

The design of this new material began with using molecular beam epitaxy (MBE). The growth of this superlattice was done on a substrate of yttria-stabilized zirconia (YSZ), with the electrode layer made from the element iridium. The superlattice elements of 20 layers of  $\text{LuFeO}_3$  and 10 layers of  $\text{CoFe}_2\text{O}_4$  were repeated to form the superlattice (see Figure 1). The superlattice was grown in this alternating pattern, combining ferroelectric  $\text{LuFeO}_3$  and ferromagnetic  $\text{CoFe}_2\text{O}_4$  to achieve the material to exhibit simultaneous orders in the ground state of each electric and magnetic properties.

The substrate YSZ is very insulating and a direct current across the thin film is desired, however, the YSZ (substrate) prohibits traditional ferroelectric testing. The iridium electrode should allow the ferroelectric testing needed, due to it being a conductive material (see Figure 1). We used elemental mapping to determine if there is interdiffusion between the superlattice layers or in the iridium electrode (See Figures 2 and 3). This composition mapping will help in the growth methods using MBE, by means of the data collected from the investigation of interdiffusion between layers.

We used focused ion beam (FIB) lift out to remove a portion of the material for atomic resolution imaging with STEM. The FIB was used to lift out the sample by using a 30kV gallium ion beam to cut out a sample. It was then attached to a TEM grid and thinned with a 5kV and 2kV milling steps to reduce surface damage down to the desired size of 20-50 nm. We then loaded the sample into the TEM. Electrons were then accelerated through the sample measuring the elastic scattered high angles produced to be measured on the Annular dark field detector, for Z contrast images (see Figure 2). For the composition mapping, we used EDS (x-ray energy dispersive spectroscopy). The power of this mapping was to identify each element binding energy, providing elemental identification due to each elements being bound at different strengths. This would provide a fingerprint of each element producing images to locate any interdiffusion.

More composition mapping was done using EELS (electron energy loss spectroscopy). This detector of the TEM, measured the scattered electron that lost energy giving us chemical information on each element, producing more images to detect if interdiffusion was present. (see Figure 3).

### Results and Conclusions:

No interdiffusion in between the  $\text{LuFeO}_3$  and the  $\text{CoFe}_2\text{O}_4$  appeared to be present in the EDS images. EDS is not good for light elements but good for heavy detection. The absence of interdiffusion of the  $\text{LuFeO}_3$  and the  $\text{CoFe}_2\text{O}_4$  was due to the lower growth temperature of the  $\text{CoFe}_2\text{O}_4$  (~400°C, compared to 900°C for previous growths).

A background signal in iridium that was noticed was concluded as an artifact of multiple scattering in the heavy, dense, iridium electrode layer, which was confirmed in EELS. We found that cobalt does not diffuse into  $\text{LuFeO}_3$  when the  $\text{CoFe}_2\text{O}_4$  is grown at low temperature.

No interdiffusion in between the superlattice layers, or into the iridium electrode was present in the EELS mapping. Also, the EELS showed no Fe, Co or O diffusing into the iridium layer.

### Future Work:

Future growth on iridium electrodes should not try to compensate for interdiffusion into the electrode. From the STEM scanning and composition mapping performed by EDS and EELS on the multiferroic materials lutetium ferrite and cobalt ferrite, we obtained information to assist in developing better growth methods using oxide MBE. Further research and other characterizations shall be performed. The material looks promising.

### Acknowledgments:

I would like to thank my PI, Professor Darrell Schlom, and the PARADIM group, my mentor Dr. Megan Holtz for her expertise, time, and dedication she gave to the research. I would also like to thank John Grazul and David Muller at the microscopy facilities at CCMR, Dr. Julia Nucci and REU staff, Cornell University, my lab partner Iryna Glushchenko, and the NSF for funding under grant DMR-1539918 as part of the Materials Innovation Platform Program.

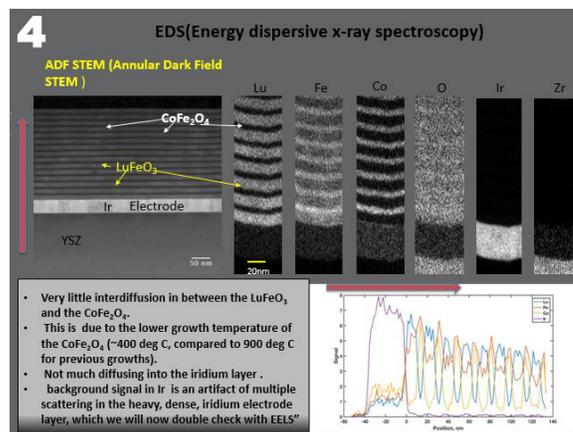
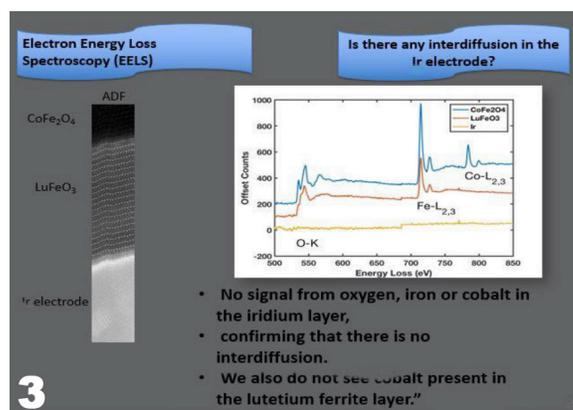
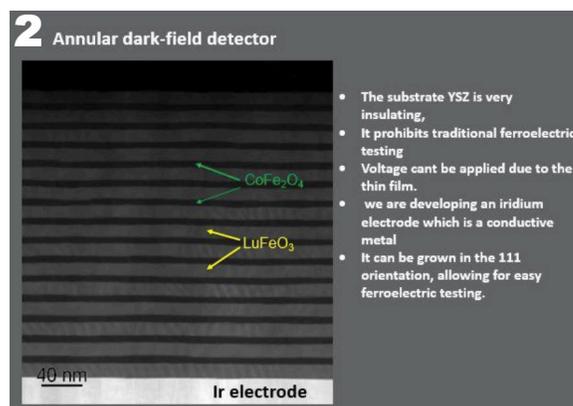
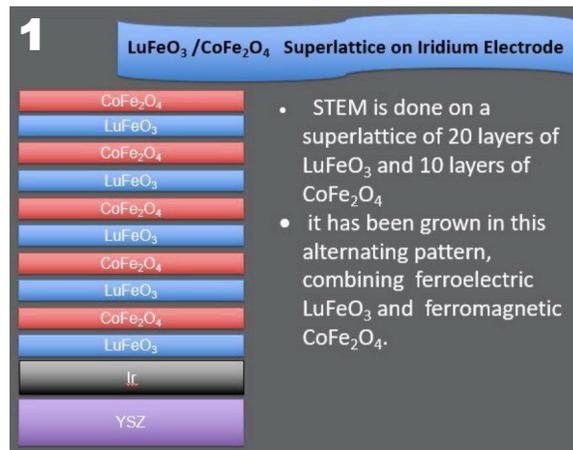


Figure 1, top: Superlattice growth. Figure 2, upper middle: STEM image. Figure 3, lower middle: EELS image. Figure 4, bottom: EDS image.