

## Structural and Electrical Characterization of Oxide Thin Films Grown by Molecular Beam Epitaxy

PARADIM REU FINAL Report

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**Abstract:** *Multiferroic (ferromagnetic and ferroelectric) oxide thin films may provide the foundation for the next generation of non-volatile memory which would use the magnetoelectric effect to overcome the issues and limitations of current devices. Using symmetry arguments and the appropriate ionic radii, a methodology for the calculation of approximate lattice parameter values and atomic positions for two different hexagonal crystal structures of the experimentally known Lutetium Ferrite ( $\text{LuFeO}_3$  and  $\text{LuFe}_2\text{O}_4$ ) and the theoretical Scandium Ferrite ( $\text{ScFeO}_3$  and  $\text{ScFe}_2\text{O}_4$ ). Models are then generated using CrystalMaker for the visualization of their crystal structures and their corresponding  $2\theta$  x-ray diffraction peaks are simulated using CrystalDiffract. Additionally, continued molecular beam epitaxy growth of Lutetium Ferrite was performed and structural characterization of the samples obtained using the Rigaku SmartLab X-Ray Diffractometer.*

### Introduction:

Multiferroic oxide thin films are a promising area of research for the creation of the next generation of non-volatile memory. These metastable compounds have the unique properties of being both ferromagnetic and ferroelectric and exhibit coupling between the two parameters via the magnetoelectric effect. This in turn allows the magnetic polarization of the material to be reversed by simply applying an electric field produced by a voltage<sup>[1]</sup>. As a result, these materials could potentially allow for electrically written and magnetically read devices that have a substantially lower power consumption and heat production.

Due to research performed by previous Schlom lab group members (Julia A. Mundy, Charles M. Brooks, John Heron, et. al.) regarding multiferroic oxide thin films of Lutetium Ferrite, the project adopted two different sides: the determination of the lattice parameters and atomic positions of never before grown Scandium Ferrite with the same symmetries as the known Lutetium Ferrite as well as the structural characterization of Lutetium Ferrite and Scandium Ferrite samples grown by Schlom lab group member Jessica Burton.

**Experimental Information:**

Two different types of hexagonal symmetries, each with a different composition, were examined. The  $\text{AFeO}_3$  system has a  $P6_3cm$  space group with a  $C_{6v}$  point group and the  $\text{AFe}_2\text{O}_4$  system has a  $R-3 2/m$  space group and a  $D_{3d}$  point group<sup>[2][3]</sup>. Additionally, the Wyckoff positions of the “foundational” atoms also contributed to the determination of the atoms’ locations within the unit cell. Furthermore, since the bonds between the atoms in these compounds are ionic, the oxidation states and coordination numbers of the atoms govern the ionic radii for each species and hence (in combination with the bond configurations of the atoms) control the distance between different neighboring species<sup>[4]</sup>. Through the combining of these different elements, approximate calculations for the lattice parameters and atomic positions for the Lutetium Ferrite and Scandium Ferrite compounds can be found. Following these calculations, the compounds’ structures were modeled using the software program CrystalMaker to create visual depictions of the structures and their  $2\theta$  XRD peaks were simulated using the software program CrystalDiffract.

In addition to these calculation, using PARADIM’s molecular beam epitaxy system, we produced multiple  $\text{LuFe}_2\text{O}_4 / \text{LuFeO}_3$  thin films grown on Yttrium Stabilized Zirconium (111) and Silicon Carbide (0001) substrates. These films were first grown by shuttering the different sources, and later through a co-deposition method. Following their growth, the Rigaku SmartLab X-Ray Diffractometer was utilized to perform  $2\theta$  x-ray diffraction measurements on the samples. The resulting XRD data was then used to characterize the different compositions and structures present in the films.

**Results & Discussion:**

In order to calculate the lattice parameters and atomic positions for the crystal systems, the O4 Oxygen atom in the  $\text{AFeO}_3$  system (which has a 2a Wyckoff position) was fixed halfway along the c-axis above the origin of the unit cell and the Lu1 Lutetium atom and Sc1 Scandium atom respectively in the

$\text{AFe}_2\text{O}_4$  system (which have 3a Wyckoff positions) were fixed at the origin of the unit cell<sup>[3]</sup>. Figures 1 and 2 show the calculated and experimental values for the known Lutetium Ferrite compounds and this “foundational” atom location fixing.

| LuFeO <sub>3</sub> Calculated |         |         |           | LuFeO <sub>3</sub> Experimental |           |         |            |
|-------------------------------|---------|---------|-----------|---------------------------------|-----------|---------|------------|
| a=                            | 5.94 Å  | c=      | 11.6795 Å | a=                              | 5.96522 Å | c=      | 11.70219 Å |
|                               | X       | Y       | Z         |                                 | X         | Y       | Z          |
| Lu1 (2a)                      | 0.00000 | 0.00000 | 0.29648   | Lu1 (2a)                        | 0.00000   | 0.00000 | 0.27207    |
| Lu2 (4b)                      | 0.33330 | 0.66670 | 0.22022   | Lu2 (4b)                        | 0.33330   | 0.66670 | 0.23320    |
| Fe1 (6c)                      | 0.33330 | 0.00000 | 0.00000   | Fe1 (6c)                        | 0.33300   | 0.00000 | 0.00000    |
| O1 (6c)                       | 0.33330 | 0.00000 | 0.16953   | O1 (6c)                         | 0.30300   | 0.00000 | 0.15420    |
| O2 (6c)                       | 0.61936 | 0.00000 | 0.33047   | O2 (6c)                         | 0.64900   | 0.00000 | 0.33200    |
| O3 (4b)                       | 0.33330 | 0.66670 | 0.00000   | O4 (4b)                         | 0.33330   | 0.66670 | 0.01700    |
| O4 (2a)                       | 0.00000 | 0.00000 | 0.50000   | O3 (2a)                         | 0.00000   | 0.00000 | 0.47200    |

Figure 1 A table of the calculated and experimental values of the lattice parameters and atomic positions for LuFeO<sub>3</sub><sup>[5]</sup>.

| LuFe <sub>2</sub> O <sub>4</sub> Calculated |          |         |          | LuFe <sub>2</sub> O <sub>4</sub> Experimental |          |         |         |
|---|----------|---------|----------|---|----------|---------|---------|
| a=  | 3.3915 Å | c=      | 24.603 Å | a=  | 3.4404 Å | c=      | 25.28 Å |
|   | X        | Y       | Z        |   | X        | Y       | Z       |
| Lu1 (3a)                                    | 0.00000  | 0.00000 | 0.00000  | Lu1 (3a)                                      | 0.00000  | 0.00000 | 0.00000 |
| Fe1 (6c)                                    | 0.00000  | 0.00000 | 0.20691  | Fe1 (6c)                                      | 0.00000  | 0.00000 | 0.21522 |
| O1 (6c)                                     | 0.00000  | 0.00000 | 0.12643  | O1 (6c)                                       | 0.00000  | 0.00000 | 0.12910 |
| O2 (6c)                                     | 0.00000  | 0.00000 | 0.28738  | O2 (6c)                                       | 0.00000  | 0.00000 | 0.29298 |

Figure 2 A table of the calculated and experimental values of the lattice parameters and atomic positions for LuFe<sub>2</sub>O<sub>4</sub><sup>[6]</sup>.

The Lutetium Ferrite systems exhibit differences between the lattice parameters of the calculated and experimental values of 0.423% and 0.194% for LuFeO<sub>3</sub> and 1.42% and 2.68% for LuFe<sub>2</sub>O<sub>4</sub> for a and c respectively. These slightly smaller lattice parameters result in simulated 2 $\theta$  XRD peaks that uniformly were shifted to higher degrees by approximately 1-2°<sup>[2]</sup>. Additionally, the intensities of the simulated 2 $\theta$  XRD peaks in the LuFe<sub>2</sub>O<sub>4</sub> system, exhibit slight decreases that were most likely due to the mixed iron 2+ and 3+ oxidation states in the structure introducing differences in the ionic radii between the atoms<sup>[6]</sup>. These therefore introduce minor differences in the locations of the iron atoms from the experimental values that could not be accounted for in the calculations.

Using the same methodology employed to calculate the lattice parameter values and atomic positions for the Lutetium Ferrite systems, values were obtained for the Scandium Ferrite systems. These results are presented in figures 3 and 4. Since, Scandium is a smaller atom than that of Lutetium, the lattice parameter values obtained are also appropriately smaller.

| ScFeO <sub>3</sub> Calculated |          |         |           |
|-------------------------------|----------|---------|-----------|
| a =                           | 5.9291 Å | c =     | 11.6569 Å |
|                               | X        | Y       | Z         |
| Sc1 (2a)                      | 0.00000  | 0.00000 | 0.30527   |
| Sc2 (4b)                      | 0.33330  | 0.66670 | 0.21421   |
| Fe1 (6c)                      | 0.33330  | 0.00000 | 0.00000   |
| O1 (6c)                       | 0.33395  | 0.00000 | 0.16986   |
| O2 (6c)                       | 0.63823  | 0.00000 | 0.33014   |
| O3 (4b)                       | 0.33330  | 0.66670 | 0.00000   |
| O4 (2a)                       | 0.00000  | 0.00000 | 0.50000   |

Figure 3 A table of the calculated values of the lattice parameters and atomic positions for ScFeO<sub>3</sub>.

| ScFe <sub>2</sub> O <sub>4</sub> Calculated |          |         |          |
|---|----------|---------|----------|
| a =   | 3.2175 Å | c =     | 24.255 Å |
|   | X        | Y       | Z        |
| Sc1 (3a)                                    | 0.00000  | 0.00000 | 0.00000  |
| Fe1 (6c)                                    | 0.00000  | 0.00000 | 0.207483 |
| O1 (6c)                                     | 0.00000  | 0.00000 | 0.12585  |
| O2 (6c)                                     | 0.00000  | 0.00000 | 0.289116 |

Figure 4 A table of the calculated values of the lattice parameters and atomic positions for ScFe<sub>2</sub>O<sub>4</sub>.

In figure 5, the 2θ XRD data for sample "JB215" shows that both LuFe<sub>2</sub>O<sub>4</sub>, LuFeO<sub>3</sub>, and the SiC (0001) substrate are present in the film. This is demonstrated by the XRD peaks approximately at 30°, 31°, and 31.5°, at 14°, 22.5°, 30°, and 31°, and at 12°, 23.5°, and 36° which correspond to some of the XRD peaks for LuFe<sub>2</sub>O<sub>4</sub>, LuFeO<sub>3</sub>, and the SiC (0001) substrate respectively. Thus, since this sample was grown by the co-deposition method, the 2θ XRD data shows preliminary evidence that co-deposition is possible.

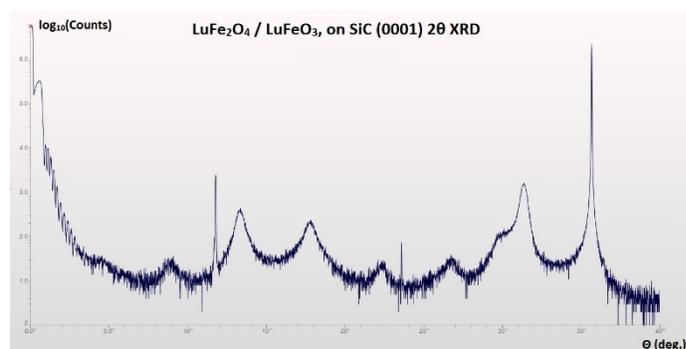


Figure 5 2θ x-ray diffraction data for sample "JB215" grown on SiC (0001).

### Conclusion:

Although a uniform error and a slight non-uniform error are present in the calculated values, we were able to successfully produce approximate values for LuFeO<sub>3</sub> and LuFe<sub>2</sub>O<sub>4</sub> that were within 0.5% and 3.0% respectively, of the experimentally known lattice parameters. Additionally, the simulated 2θ

XRD peaks for the calculated values matched well with those of the experimental values (when the uniform errors were considered). As a result, there is fairly high confidence in the approximate lattice parameter values and atomic positions for the theoretical structures of  $\text{ScFeO}_3$  and  $\text{ScFe}_2\text{O}_4$ . However, Density Functional Theory calculations remain to be done for these Scandium Ferrite structures to better determine what their lattice parameter values and atomic positions will be as well as continued MBE trials to determine if in fact they can be grown at all.

The MBE trials we performed have demonstrated the possibility for the co-deposition growth of  $\text{LuFeO}_3$  and  $\text{LuFe}_2\text{O}_4$ . Preliminary measurements performed by our collaborators at the University of California: Berkeley have also shown that the samples grown through this method may exhibit the desired multiferroic behavior without having the extremely ordered super lattice structures demonstrated in previous research.

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#### **References:**

- [1] Johnson, Dexter, "Multiferroic Memory Promises Low-Power, Instant-on Computing", *IEEE Spectrum*, 22 December 2014.
- [2] Cullity, B. D., and Stock, S. R. "Elements of X-Ray Diffraction", *Pearson Education, Ltd.* United Kingdom, 2014.
- [3] Bilbao Crystallographic Server, <<http://www.cryst.ehu.es>>.
- [4] Shannon, R. D. "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides" (1976).
- [5] Japanese Journal of Applied Physics (2010)

49, p09ME06-1-p09ME06-4  
[6] Physical Review Letters (2012) 108, p187601  
p187601-5