# Investigating the Structure of Multiferroic Oxides with STEM Imaging and Diffraction Mapping

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## Abstract:

**Multiferroics are a type of material that exhibit both ferroelectric and ferromagnetic properties. Their unique coupling of electric and magnetic ordering means these materials create exciting possibilities for data storage technologies. However, few multiferroics exist at room temperature, and those that do typically have weak magnetic moments or electrical polarization. Combining the ferroelectric $LuFeO_3$ with the ferrimagnetic $CoFe_2O_4$ into a superlattice by molecular beam epitaxy (MBE) promises to overcome this problem, creating a material with spontaneous polarization and magnetization at room temperature. Scanning transmission electron microscopy (STEM) is used to investigate how these materials are layered together at the atomic scale and gain feedback on our MBE growth. Through means of a pixel array detector developed at Cornell, we use scanning diffraction combined with new data processing techniques to study the crystal structure of our material.**

## Summary of Research:

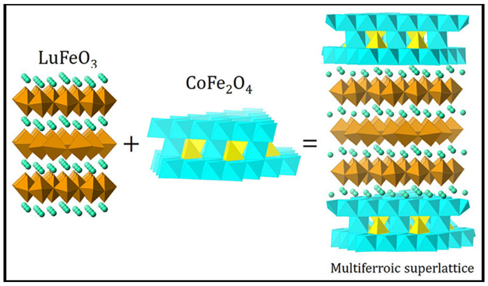

*Figure 1: A representation of the crystal structure of the $LuFeO_3$ and $CoFe_2O_4$ multiferroic film.*

To create a multiferroic material, we combined the ferroelectric $LuFeO_3$ with the insulating ferrimagnetic $CoFe_2O_4$ into a superlattice (Figure 1). The $CoFe_2O_4$ is particularly promising for future use in data storage technologies because it is not only structurally compatible with $LuFeO_3$, it also exhibits ferrimagnetic properties at a much higher temperature than the previous ferromagnetic material used in this multiferroic, $LuFe_2O_4$. Furthermore, the material must be insulating so as to not shield the polarization of the ferroelectric layers. The hexagonal $LuFeO_3$ is stabilized on the cubic yttrium stabilized zirconium (YSZ) <111> substrate, with a metal electrode in between to facilitate future ferroelectric testing.

Since our multiferroic had already been grown by MBE, we immediately began investigating its structure. To prepare a sample of our material for STEM analysis, we used a focused ion beam (FIB). Through STEM, we obtained information on the crystal structure of the multiferroic film on the atomic scale. We were specifically interested in the interfaces between the electrode, $LuFeO_3$, and $CoFe_2O_4$, and in examining the picometer-scale displacements driving ferroelectricity.

Afterwards, we mapped the crystal structure with a new pixel array detector developed at Cornell to produce convergent beam electron diffraction (CBED) patterns. While this is a promising method to identify different structures, CBED patterns have their drawbacks. They are easily influenced by tilts and thickness effects in the sample, which change the relative intensity of diffraction spots, making dark-field imaging of particular domains unreliable. Also, the resulting disks in diffraction space from a convergent beam are large, complicating the matter of precisely localizing diffraction spacings. To overcome these challenges, we used the Fourier Transform FT[log(CBED)]. The logarithm suppresses the effect of tilt variations, and the transform concentrates the diffraction disk signals into well-defined spots corresponding to atomic spacings. These can be separated by dark-field imaging, which can then be used to make real-space maps of the crystallographic zones inside our material.

## Results and Conclusions:

From atomic imaging, we discovered that although the film has good structure overall, it exhibits some uneven layering — there are several partial layers at the interfaces of the $LuFeO_3$ and $CoFe_2O_4$, so to further improve superlattice growths, we must perfect the shutter time calibration and the temperature during growth. Also, the electrode layer displays two crystal orientations with the <111> out-of-plane orientation, the $[01\bar{1}]$ and $[11\bar{2}]$, potentially because it nucleated with different grain orientations at the beginning of the MBE growth. Growing the electrode on a better lattice-matched substrate may improve the epitaxy. Excitingly, the $LuFeO_3$ layers exhibit ferroelectric distortion, and we observe domain walls where the polarization of the lutetium atoms changes throughout the layer (Figure 2). Finally, the interface between the $LuFeO_3$ and $CoFe_2O_4$ in our sample seems to prefer a 2/3 ratio of lutetium — while usually the lutetium is found in groups of three, at the interface it is in pairs. This suggests that there may not be enough lutetium added during growth.

Figures 3 displays the CBED data transformations, and as we can see, the logarithm drastically improves the amount of visible data. The Fourier Transformed data can be used to isolate the different crystal zone regions within our sample in real space (Figure 4). Even though we were already aware of our film structure, the purpose of this process is to develop this data processing technique — if applied to materials we know the structure of, we can construct a method and database that will be useful when we encounter more complex systems.

## Future Work:

Further research on this multiferroic can take several directions. This sample alone still holds a wealth of information — for instance, methods such as electron energy-loss spectroscopy (EELS) and x-ray energy dispersive spectroscopy (EDS) can determine the relation between interdiffusion and growth conditions. Long-term wise, the next step is to conduct ferroelectric testing on this material, such as determining how much electric field is needed for the ferroelectric layer to switch, or observing the polarization at different amounts of charge. Ultimately, the goal is to test whether the ferroelectric switching can be coupled to that of the magnetization.

## Acknowledgements:

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## References:

[1] Mundy, J., Brooks, C., Holtz, M., et al. "Atomically engineered ferroic layers yield a room temperature magnetoelectric multiferroic." Nature, Vol 537, 523-541, 22 September 2016.

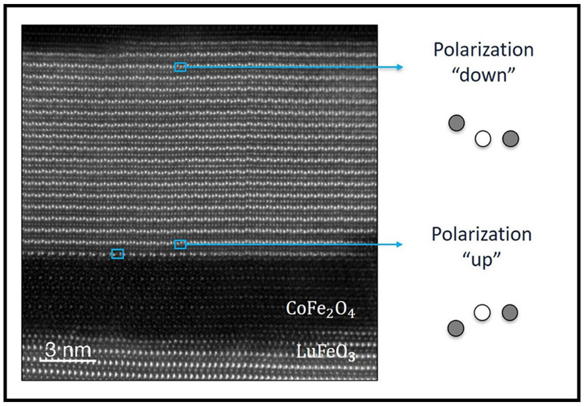

*Figure 2: A layer of $LuFeO_3$ displaying ferroelectric distortion and a 2/3 ratio of lutetium at the interface between the $LuFeO_3$ and $CoFe_2O_4$ layer.*

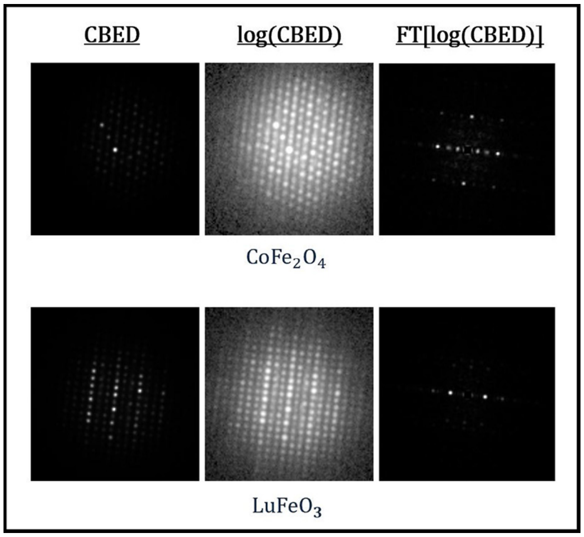

*Figure 3: CBED to FT[log(CBED)] data transformations for $LuFeO_3$ and $CoFe_2O_4$.*

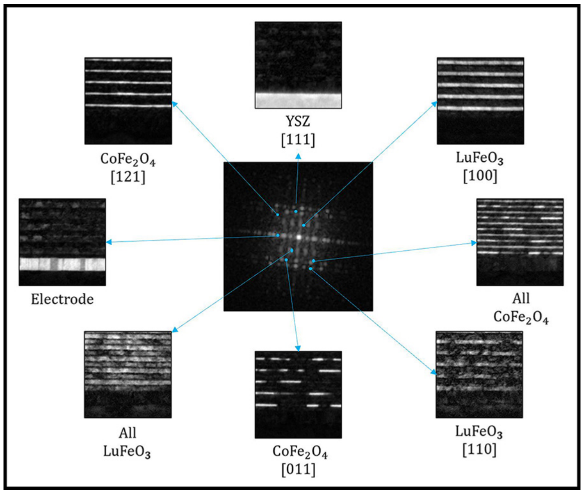

*Figure 4: The real-space crystallographic zones of the multiferroic film can be isolated using dark-field imaging from the diffraction patterns obtained after the Fourier Transform.*