Modeling $LaFeO_3$ Octahedral Tilting and Strain

Myles Klapkowski
Center for Emergent Materials – Ohio State University

ABSTRACT

The phenomenon of octahedral tilting caused by epitaxial strain in novel interfaces is currently poorly understood. With a greater wealth of knowledge on the tilting of the BX_6 octahedral, we may be able to finely tune the electronic and magnetic properties of perovskite materials. This study seeks to test the usefulness of digital crystal modeling when studying novel perovskite interfaces. This was accomplished through the use of the python packages PyTilting[2] and ASE[6] in order to strain and tilt a previously generated crystal model. These models can then be run through simulated x-ray diffraction and transmission electron microscopy in order to validate the accuracy of the models and simulation tools. Results show that this type of modeling provides an accurate and detailed look into the structure of novel perovskite interfaces.

I. Background and Introduction

Perovskites are crystals with an ABX_3, face-centered cubic. In this case, 'A' and 'B' are cations and 'X' is an anion that bonds to both. In most cases, this anion takes the form of oxygen.[1] These crystals have found many uses in recent years due to their remarkable properties including dielectric, ferroelectric, magnetic, and optical properties.[2]

One such perovskite is $LaFeO_3$ (LFO), which has been found in recent years to have a high thermal resistance. In order to observe the properties of this perovskite, a strained epitaxial film is grown. Under these conditions, the stable structure of the crystal can be expanded or compressed, and octahedral tilting can occur. This process occurs when the space between 'A' cations and the anion, 'B' pair is not filled. The BX_6 octahedral will rotate in order to properly fill the space. When this occurs, the lattice parameters and diffraction pattern of the crystal will be altered.[3]

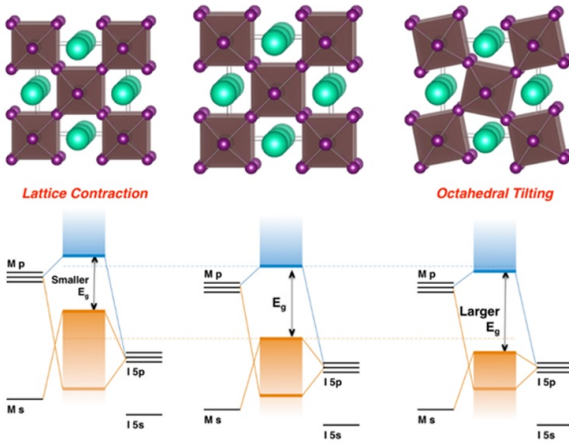

Figure 1. This figure shows the lattice pattern of a perovskite as octahedral tilting is increased. Below each diagram is a diagram of the different energy levels and how the band gap is affected by this tilting. Diagram and caption from source 8.

This process of octahedral tilting through strain potentially serves to tune the electronic and magnetic properties of the perovskite when a novel interface is created. This occurs when the compression of strain tilts the octahedral, opening or closing the valence band and band gap of the material as shown in figure 1. In the case of our models, a semiconducting substrate of $SrTiO_3$ (STO) was assumed while the LFO serves as the insulator and is the material octahedrally tilted.

In order to study the films produced, several common nondestructive methods of probing the material are used. To study the crystal structure and size x-ray diffraction (XRD) is generally performed while transmission electron microscopy (TEM) is generally performed to find surface roughness and material composition.

The goal of this project was thusly to precisely characterize and understand the type and degree of octahedral tilting present at the LFO-STO interface through its effect on simulated TEM and XRD data.

By modeling the octahedral tilting and strain of the LFO, we would ultimately be able to test our results against that of lab-made thin films. This allows us to create a precise model of our films that we could study in a non-destructive and accurate way.

II. Methods

The goal of this experiment is to classify the octahedral tilt of LFO from experimental results using digital models of the crystal structure. In order to accomplish this, we begin with a crystal basis from the Crystallography Open Database as shown in Figure 2. We then use the python package PyTiling[2] to create octahedral tilt and strain within the basis of the LFO crystal model, as shown in Figure 3. Next, XRD is simulated on our using the SingleCrystal software. Once an XRD pattern is simulated, we can measure the simulated results against our experimental data and determine the angle of octahedral tilt in our sample.

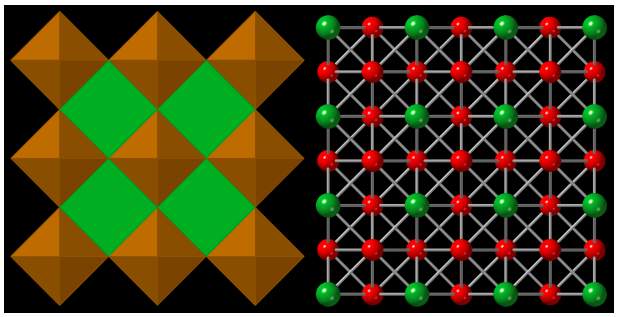

Figure 2. This figure shows the digital model of LaFeO3 in CrystalMaker before octahedral tilt. The left image is the model in polyhedral form while the right image is in ball and stick form.

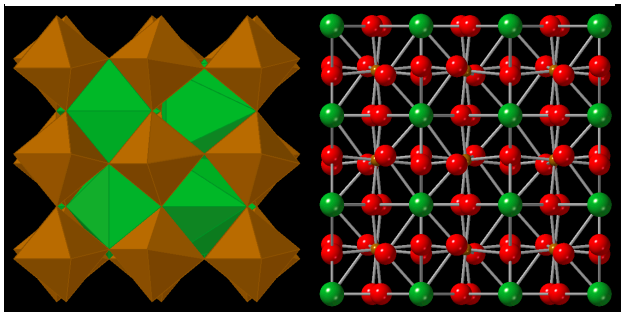

Figure 3. This figure shows the digital model of LaFeO3 in CrystalMaker after octahedral tilt and strain. The left image is the model in polyhedral form while the right image is in ball and stick form.

The characterization of the strain of our novel interface can be calculated rather simply given the XRD data from the lab thin film and the simulated XRD of a non-tilted, non-strained LFO model. This is done by

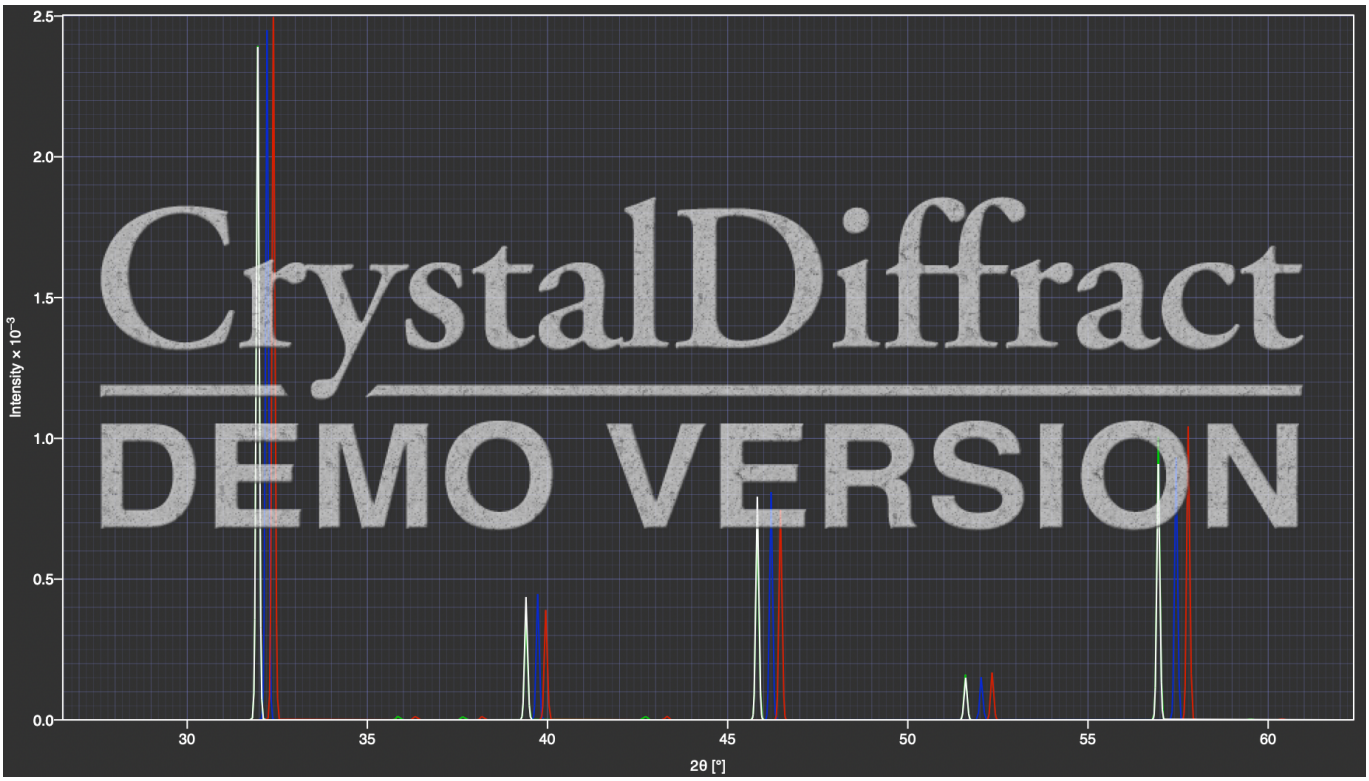

Figure 4. This figure shows the results from the simulated x-ray diffraction for each $LaFeO_3$ model. In red is the tilted, non-strained model. In white is the non-tilted, strained model. In green is the tilted, strained model. In white is the non-tilted, non-strained model.

measuring the shift that the peaks undergo after straining as follows:

$$\varepsilon = \frac{d_{strained} - d_{non-strained}}{d_{non-strained}} \quad [1]$$

This strain is a result of a mismatch in lattice parameters between the perovskite LFO and the epitaxial substrate STO.[5] Using this data and the python package ASE[6] we can create the necessary strain in our model. We estimate the strain to be approximately 1.013 given our XRD data and using equation 1.

After applying the strain to the model octahedral tilt is considered. It has been experimentally shown the LFO takes on an octahedral tilt magnitude of $a^-a^-c^+$ in Glazer notation.[7] This characterization means that the oxygen octahedral rotation pattern has two rotations of the same magnitude about the in-plane axes and one rotation about the c axis.

This accounts for the magnitude of tilt along each axis of potential rotation but does not give a precise estimate of the angle of rotation along each axis. In order to determine this rotational angle along each axis, we must match our model's simulated TEM and XRD results to that of our lab data.

Before we put the model through the range of possible angles of octahedral tilt, it is important to confirm that the effects of the model's octahedral tilting and strain provide

reasonable results in order to validate their effectiveness.

III. Results and Discussion

Simulated XRD Results

Results from the simulated XRD are shown in figure 4. This figure shows a clear separation of the tilted and strained peaks when compared to the peaks of the non-strained and non-tilted model. We see on average a difference of 0.55° between the non-strained and non-tilted models while the tilted models have an average difference of just 0.38°.

This difference demonstrates the effect that strain has on the XRD output of the simulated LFO models. Compared to the effect of the octahedral tilt, we see that the strain greatly affects the 2θ values of the crystal.

This outcome is expected as the expansion of the 'A' cations out-of-plane with the interface should cause a shift in the 2θ values of our XRD data. This result helps to confirm the accuracy of the strain in our model.

There are also characteristic peaks at ~36°, 38°, and 43° that are only seen in the models that contain octahedral tilt.

This is the expected result of LFO octahedral tilting and serves to confirm the accuracy of our model when it comes to tilting.

Simulated TEM Results

In figure 5, we see the simulated TEM results of our model. This data shows the difference between the non-tilt, non-strain model and each of the three test cases when

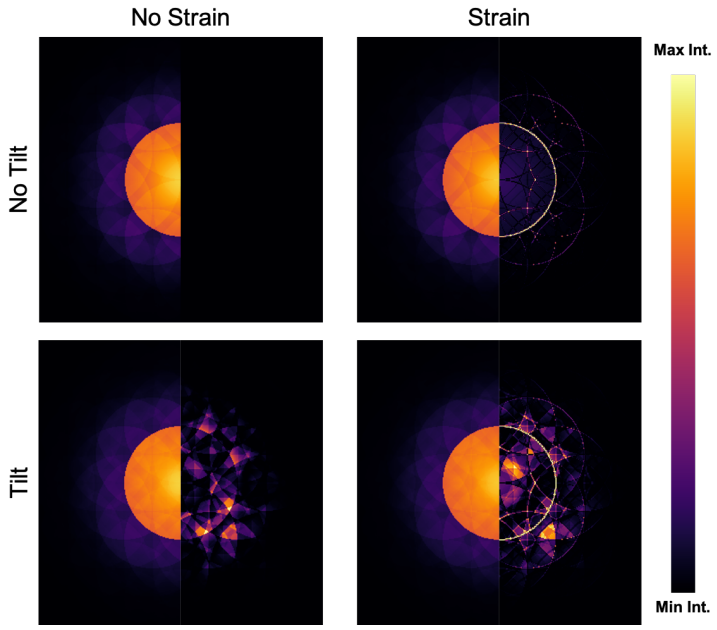

Figure 5. This figure shows the simulated TEM results of our $LaFeO_3$ models sampled at 10nm. On the left-hand side of each output is the raw TEM data. On the right-hand side of each output is the difference between the output and the no strain, no tilt model's output squared.

passed through TEM. We can see from the patterns of pixel intensity that strain creates a more even and controlled difference in intensity, while the octahedral tilt has a larger effect on the TEM, but is less controlled and more scattered.

This is the expected outcome of the TEM. We find that the strain creates a more predictable difference in the intensity of the TEM output because it changes the elongates or shorters the distances between 'A' cations. The octahedral tilt on the other hand causes distortions that are less well defined and more prone to uneven change across the crystal basis.

Based on the results of XRD and TEM on our models, we can see clearly that creating models with octahedral tilt and epitaxial strain is an accurate way to study the

perovskite crystals that create a novel interface.

Unfortunately, due to time constraints, we were unable to test the range of possible angles of the lab films on our models to find a match. However, we are able to confirm the usefulness of perovskite models going forward.

IV. Conclusions

We have found sufficient evidence that digital models of perovskite novel interfaces offer a nondestructive and precisely accurate way to study such structures. We see that both our XRD and TEM data match expected results. This result promises to improve our understanding of octahedral tilting in novel interfaces. Future work should attempt to the match lab results by testing the full range of possible angles of tilt within the LFO perovskite model.

V. Acknowledgments

Special thanks to Dr. Jinwoo Hwang and Dr. Fengyuan Yang for their mentorship throughout the REU program. I would also like to thank the graduate students Menglin Zhu, Jose Flores, and Joseph Lanier for their guidance along the way.

This REU program is part of an NSF Materials Research Science and Engineering Center (MRSEC) supported under NSF Award Number DMR-2011876.

VI. Footnotes, Endnotes and References

[1] A. M. Glazer, The Classification of Tilted Octahedra in Perovskites. *ACTA Crystallographica*, **28** (1972).

[2] N. Xie, J. Zhang, N. Zhang, X. Chen, and D. Wang. Generation of low-symmetry perovskite structures for ab initio computation. *J. Phys.: Condens. Matter* **32** 315901 (2020).

[3] P. M. Woodward. Octahedral Tilting in Perovskites. II. Structure Stabilizing Forces. *ACTA Crystallographica*, **53 (**1997).

[4] L. Sangaletti, L.E. Depero, B. Allieri, P. Nunziante, E. Traversa. An X-ray Study of Lax Sm1-x Fe O3 orthoferrites. *Journal of the European Ceramic Society,* **21** (2001).

[5] J. Wu, S. C. Liu, Z. Li, S. Wang, D. J. Xue, Y. Lin, J. S. Hu, Strain in perovskite solar cells: origins, impacts and regulation. *National Science Review*, (2021).

[6] A. H. Larsen, J. J. Mortensen, et al. The Atomic Simulation Environment—A Python library for working with atoms. *J. Phys.: Condens. Matter,* **29** (2017).

[7] M. Nord, A. Ross, et al. Three-dimensional subnanoscale imaging of unit cell doubling due to octahedral tilting and cation modulation in strained perovskite thin films. *Phys. Rev. Materials,* **3** (2019).

[8] R. Prasanna, A. Gold-Parker, T. Leijtens, B. Conings, A. Babayigit, H.-G. Boyen, M. F. Toney and M. D. McGehee, Band Gap Tuning via Lattice Contraction and Octahedral Tilting in Perovskite Materials for Photovoltaics, *J. Am. Chem. Soc.,* **139** (2017)