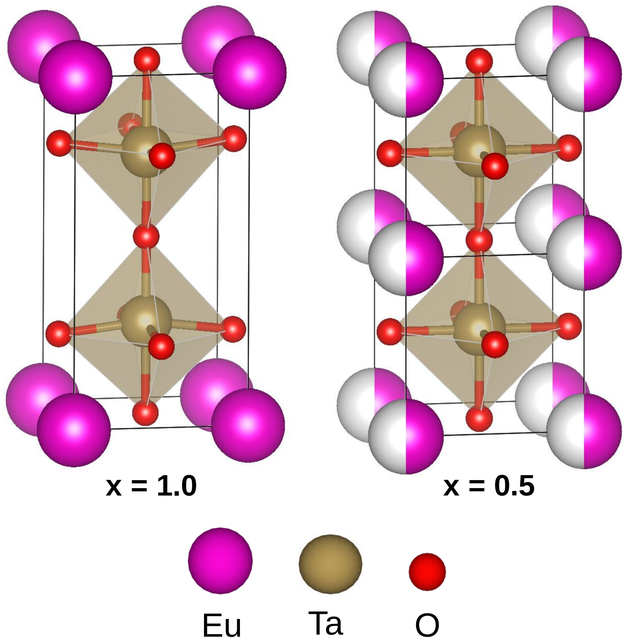
Quantifying Order in Fractional Double Perovskites Grown by Suboxide Molecular Beam Epitaxy

Sonia Hasko[1], Tobias Schwaigert[2,3], Darrell G. Schlom[2,3]

[1]Chemical and Biological Engineering, Princeton University [2]Materials Science and Engineering, Cornell University [3]PARADIM, Cornell University

Introduction

- Fractional double perovskites are a **novel** class of materials
- Degree of structural order correlates to physical properties
- Order parameter x in $Eu_xTa_{2x}O_{6x}$: When x = 0.5, ETO is disordered, and when x = 1.0, ETO is **fully ordered**.



The ordered unit cell is composed of two formula units, alternating between **unoccupied** and **fully occupied** A-sites.

- Miller indices for unit cell can be classified as **fundamental** or **R-type** reflections.
- R-type reflections can arise from octahedral-site cation ordering or out-of-phase octahedral tilting.
- Reflection intensities can be quantified to determine the **order** of A-site atoms in oxides.

Methods for Quantifying Order

Intensity ratios from experimental data were compared to theoretical curves, constructed using Python, to quantify the occupancy of Eu in ETO thin films.

- Occupancy-dependent displacements were considered in all calculations.

To determine theoretical intensity ratios, we calculated the atomic form factors using scattering vector-dependent fitting parameters:

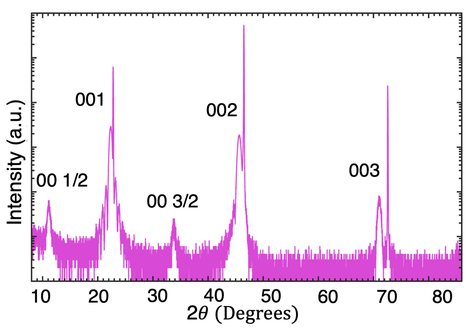
$$f\left(\left|\vec{G}\right|\right) = \sum_{i=1}^{4} a_i \exp\left(-b_i\left(\frac{G}{4\pi}\right)^2\right) + c$$

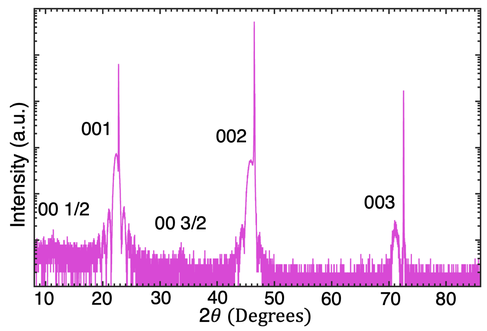
Structure factors and intensities were computed as follows:

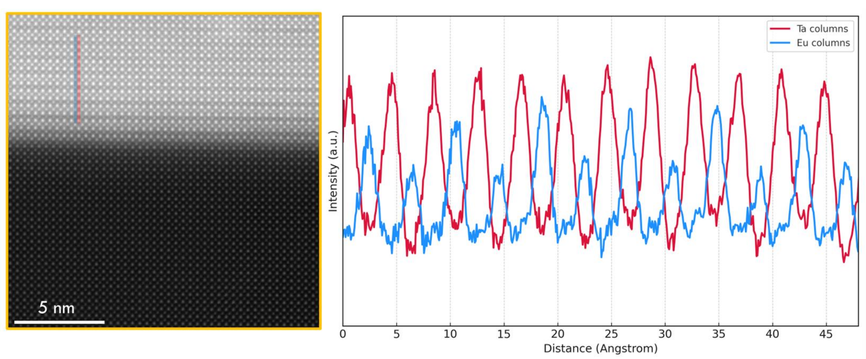
$$S_{hkl} = \sum_{j=1}^{J} f_j e^{-i2\pi(hx_j+ky_j+lz_j)} \qquad I_{hkl} = |S_{hkl}|^2 \cdot \frac{1+\cos^4(2\theta_M)\cos^2(2\theta)}{\sin(\theta)\cos(\theta)}$$

Results: $EuTa_2O_6$ on Nb:STO (001)

The XRD peaks shown include **typical perovskite** peaks (002, 004, and 006) and **half-order** peaks (001, 003). The half-order peaks indicate order.

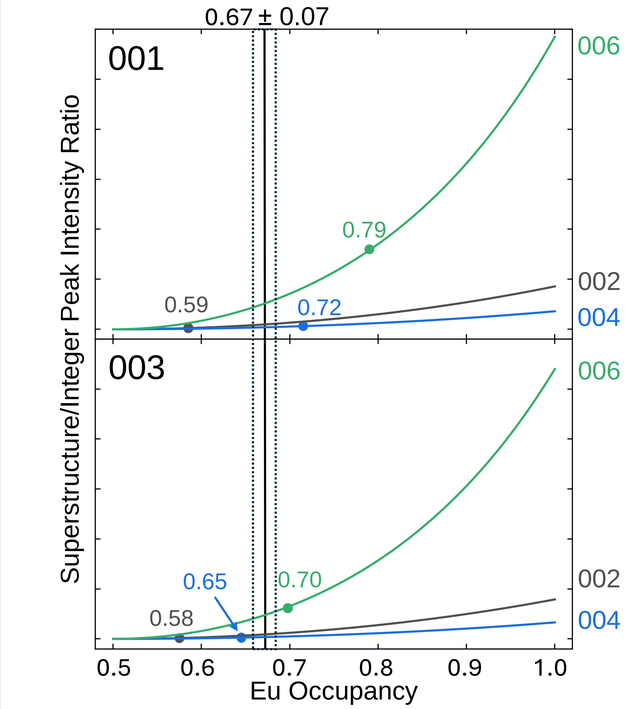






TEM results suggest Eu occupancy of 66% for the second sample.

Results



- Black points represent **interpolated occupancy values** based on the XRD intensity ratios obtained from measured samples.
- Eu occupancy is estimated as 67.2% ± 7.4% based on interpolation on the curves.

Conclusions

- Successfully quantified occupancies in **ETO thin films**
- Validated Python results with other methods, including TEM
- Used Python script on another novel fractional perovskites ($SrTa_2O_6$, $BaTa_2O_6$)
- Developed a **GUI** for our Python tool

Future goal: create a generalized Python software (**POMMES**) for quantifying order