

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

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## Abstract

Fractional double perovskites are a novel playing ground to explore changes to electronic and magnetic properties through atomic and orbital ordering. Quantifying the degree of structural order is an integral part of studying property-structure relationships.  $\text{EuTa}_2\text{O}_6$  and  $\text{SrTa}_2\text{O}_6$  are grown by suboxide molecular beam epitaxy, and subsequently structurally characterized by X-ray diffraction. In  $\text{EuTa}_2\text{O}_6$ , A-site order is represented by occupancy of europium atoms in two distinct crystallographic planes and can be successfully calculated and measured by X-ray diffraction. We developed a theoretical framework to assess A-site order in fractional double perovskites to guide the MBE experimenter with an accessible tool and quick feedback.

## Introduction

Physical properties of solids are sensitive to changes in the crystal structure and are studied as structure-property-relationships[1]. Specifically, A-site ordered perovskites like  $\text{SmBaMnO}_6$  and  $\text{LaBaMnO}_6$  see significant changes to their  $T_c$  and magnetoresistance controlling the periodic arrangement of La and Ba atoms [2] [3]. The crystal structure of  $\text{EuTa}_2\text{O}_6$  is similar to that of a perovskite[4] with the unit cell composed of two formula units along the crystalline c-axis, alternating between an unoccupied A-site and a fully occupied A-site. If the peaks in the diffraction pattern are indexed using a double-edge primitive unit cell, the Miller indices can be classified into one of two categories:

- (i) Sublattice reflections (or fundamental perovskite reflections) where h, k and l are all even numbers.
- (ii) R-type reflections where h, k and l are all odd numbers. These reflections can arise from either octahedral-site cation ordering or out-of-phase octahedral tilting.

If we limit the discussion to oxides and fluorides, which account for the majority of perovskites, it is possible to make some quantitative statements about the intensities of the superlattice reflections [5].

## Methods

Intensity ratios obtained from experimental data were compared to the theoretical intensity ratio curves to quantify the occupancy of europium in ETO thin films. We define the order parameter  $x$  in  $\text{Eu}_x\text{Ta}_{2x}\text{O}_{6x}$  (ETO), where  $0.5 \leq x \leq 1.0$ . In its most disordered form  $\text{Eu}_{0.5}\text{TaO}_3$  crystallizes in the  $Pm\bar{3}m$  space group with a lattice parameter of 3.925 Å. Conversely, when  $x = 1.0$ , ETO exists in its most ordered form:  $\text{EuTa}_2\text{O}_6$ .

The most ordered form of ETO,  $\text{EuTa}_2\text{O}_6$ , crystallizes as a tetragonal structure in the  $P4/mmm$  space group. This crystal has been refined by structural relaxation in DFT

calculations, resulting in lattice constants of  $a = b = 3.92574$  Å,  $c = 7.92937$  Å. The following atomic position basis is based on the DFT calculations:<sup>4</sup>

$$\begin{aligned}\text{Eu1} &= [0.0, 0.0, 0.0] \\ \text{Eu2} &= [0.0, 0.0, 0.50000] \\ \text{Ta1} &= [0.50000, 0.50000, z_{\text{Ta}}] \\ \text{Ta2} &= [0.50000, 0.50000, 1-z_{\text{Ta}}] \\ \text{O1} &= [0.50000, 1.0000, z_{\text{O1}}] \\ \text{O2} &= [0.50000, 0.0, 1-z_{\text{O1}}] \\ \text{O3} &= [0.0, 0.50000, z_{\text{O3}}] \\ \text{O4} &= [1.0000, 0.50000, 1-z_{\text{O3}}] \\ \text{O5} &= [0.50000, 0.50000, 1.0000] \\ \text{O6} &= [0.50000, 0.50000, 0.50000]\end{aligned}$$

Three additional atomic positions – Ta2, O2, and O4 – were added to account for the stoichiometry of the unit cell.

The values of  $z_{\text{Ta}}$ ,  $z_{\text{O1}}$ , and  $z_{\text{O3}}$  are occupancy-dependent: as the occupancy  $x$  of the Eu1 layer increases in the fractional perovskite  $\text{Eu}_x\text{Ta}_{2x}\text{O}_{6x}$ , the tantalum and oxygen atoms are displaced along the c-axis of the doubled unit cell. The displacements allow for the atoms to occupy optimal positions for charge transfer. In the most ordered state ( $x = 1.0$ ), the z-positions are equal to those reported in the DFT calculations. These calculations account for  $\text{Ta}^{5+}$  polarization and the resultant Ta and O displacements:

$$\begin{aligned}z_{\text{Ta}} &= 0.25966 \\ z_{\text{O1}} &= 0.22992 \\ z_{\text{O3}} &= 0.22999\end{aligned}$$

The ordered  $\text{EuTa}_2\text{O}_6$  structure is distinct from the disordered  $\text{Eu}_{0.5}\text{TaO}_3$  structure. In the disordered unit cell, the equal distribution of europium atoms in each plane is signified by a 50% occupancy of each Eu atom. As a result,  $\text{Ta}^{5+}$  ions are no longer displaced towards the vacancy layer, lowering the SOJT distortion of the polyhedral. When accounting for the lack of

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displacements, the occupancy-dependent  $z$ -positions become equivalent:

$$z_{Ta} = z_{O1} = z_{O3} = 0.25$$

To calculate theoretical XRD intensity ratios, atomic form factors for each distinct atom or ion in the crystal must be computed. The atomic form factors were computed for each ion or atom using the formula:

$$f(|\vec{G}|) = c_0 + \sum_{i=1}^4 a_i \exp\left(-b_i \left(\frac{G}{4\pi}\right)^2\right)$$

where  $G = |\vec{G}|$  is the reciprocal lattice vector, and  $a_i$ ,  $b_i$ , and  $c_0$  are angle-dependent empirical fitting parameters that are tabulated[6].

Structure factors were subsequently calculated as follows:

$$S_{hkl}(x) = xF_{Eu1} + (1-x)F_{Eu2} + F_{Ta} + F_O$$

$$F = f_j(|\vec{G}|) \sum_{j=1}^n \exp(2\pi i(hx_j + ky_j + lz_j))$$

where  $x$  is the occupancy of Eu1, and  $n$  corresponds to the number of atoms of the same element in the atomic position basis that share an occupancy value. XRD intensities for given Miller indices were computed using the following formula:

$$I_{hkl} = |S_{hkl}|^2 \cdot \frac{1 + \cos^4(2\theta_M) \cos^2(2\theta)}{\sin(\theta) \cos(\theta)}$$

Here,  $\theta_M$  is the Bragg reflection angle[7]. Intensity ratios were determined for various Miller index peaks.

## Results

Basis for the investigation of ordering are  $\text{EuTa}_2\text{O}_6$  thin films grown by Molecular beam intensity.  $\theta$ - $2\theta$  scans of a 16 nm thick, thin film of  $\text{EuTa}_2\text{O}_6$  show only  $00l$  peaks, indicating that the film is single-phase and oriented with its  $c$ -axis perpendicular to the plane of the substrate. Intensity ratio plotting and interpolation was done for the following ratios obtained from XRD scans: 001:002, 001:004, 001:006, 003:002, 003:004, and 003:006. These peak ratios represent the typical perovskite peaks and the half-order peaks present in our films (Fig. 1).

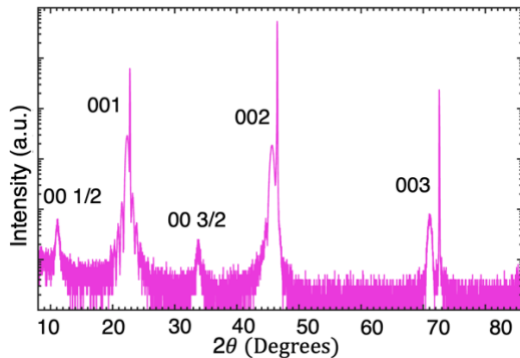


Figure 1. The XRD intensity plot is shown for one of the ETO samples grown on Nb:STO (001). The typical perovskite peaks (002, 004, and 006) are visible. In addition, half-order peaks (001 and 003) are visible for this sample.

The occupancy of europium in the sample is estimated to be  $67.2\% \pm 7.4\%$  based on interpolation of experimentally obtained XRD intensity ratios on each of the six curves. Those results have been experimentally verified by STEM, directly visualizing the occupational order of  $\text{EuTa}_2\text{O}_6$ .

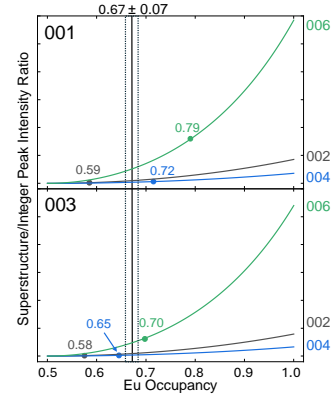


Figure 2. Intensity ratios for  $\text{EuTa}_2\text{O}_6$  for changes to its Eu occupancy. Top and bottom panel compare two R-type reflections to fundamental reflections. Black points represent interpolated occupancy values based on the XRD intensity ratios obtained from measured samples.

## Conclusions

The results of structure factor and intensity ratio calculations done using our Python script matched occupancy values quantified with TEM. In addition to successfully quantifying occupancies in ETO thin films, we used the script on our strontium tantalate samples. We ultimately developed a GUI with the goal of creating a generalized Python tool (POMMES) for quantifying order.

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