LA-UR-19-27917
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Title: Mapping Cation Disorder in Irradiated Gd2Ti2O7 Pyrochlore by 4D-STEM

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Intended for: Microscopy & Microanalysis 2019, 2019-08-04/2019-08-08 (Portland, Oregon, United States)

Issued: 2019-08-06

Mapping Cation Disorder in Irradiated $Gd_2Ti_2O_7$ Pyrochlore by 4D-STEM

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August 7, 2019

Los Alamos NATIONAL LABORATORY EST. 1943

NNSA National Nuclear Security Administration

LA-UR-19-#####

Overview

1. Background
   a) Pyrochlores
   b) 4D-STEM
2. Experimental
3. Results
4. Future Directions

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Pyrochlores: waste forms and ionic conductors

- Fast ion conductors
  - Use radiation "damage" as a tool to achieve metastable states and tune properties

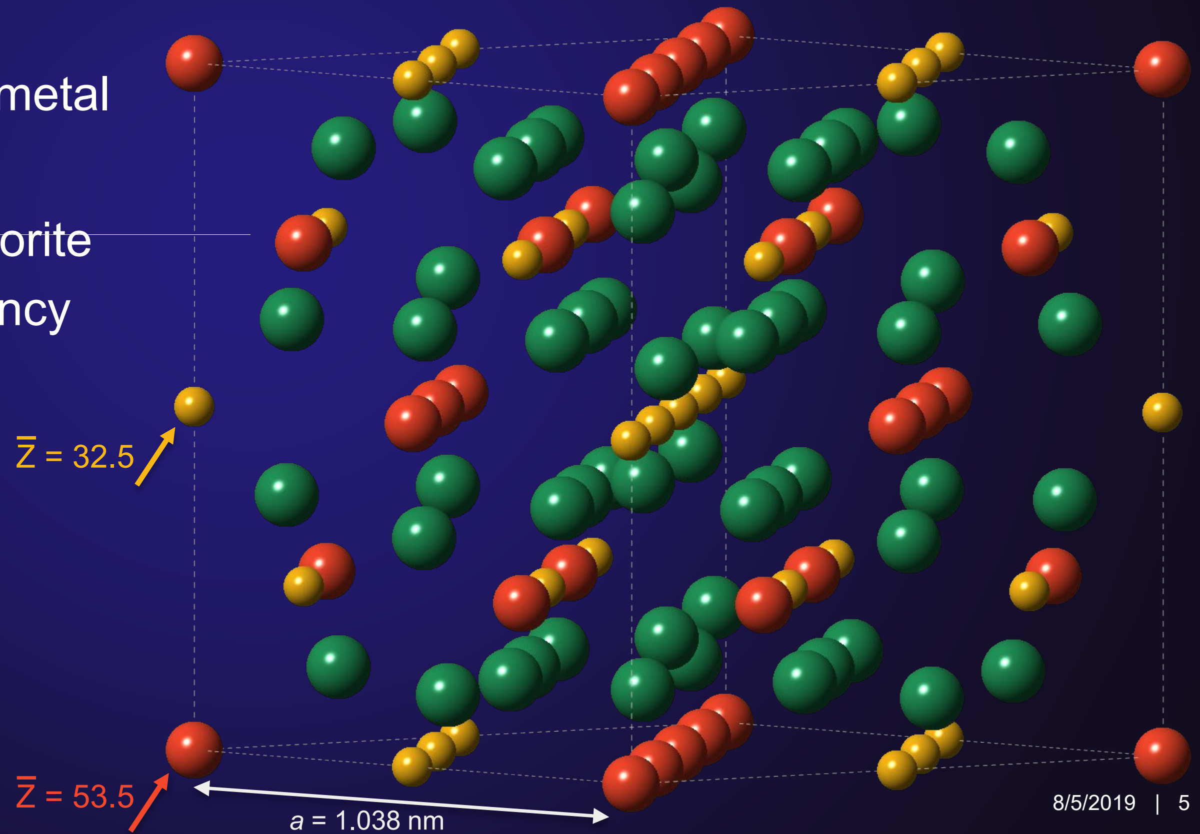
  Kreller et al., J Mater Chem A **7** (2019) p. 3917

- Nuclear waste forms
  - Pyrochlores are related to two of the main components of SYNROC
    - Zirconoloite ($CaZrTi_2O_7$) – chemistry
    - Perovskite ($CaTiO_3$) – cubic structure

  Holesinger et al., Acta Materialia **164** (2019) p. 250

Pyrochlores: structure and chemistry

- $(Na, Ca)_2Nb_2O_6(OH, F)$ – the mineral pyrochlore
- General name for chemicals with the formula $A_2B_2O_7$
  - A: Trivalent rare earth
  - B: Tetravalent transition metal
- Space group $Fd\bar{3}m$
  - Structure is related to fluorite
  - Systematic oxygen vacancy



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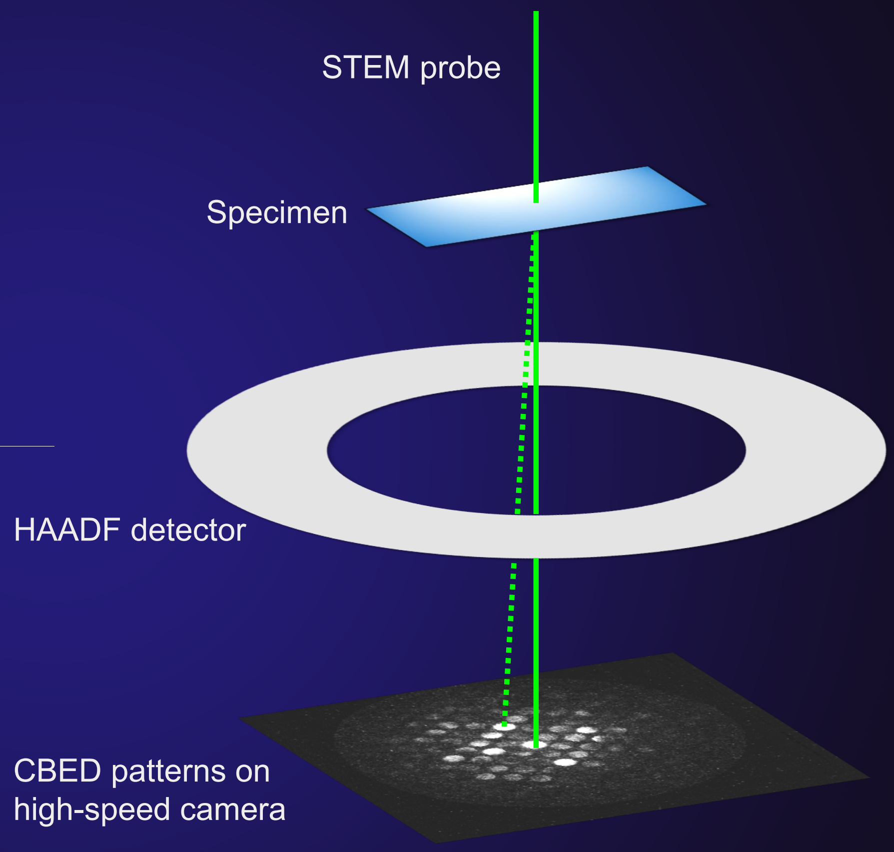
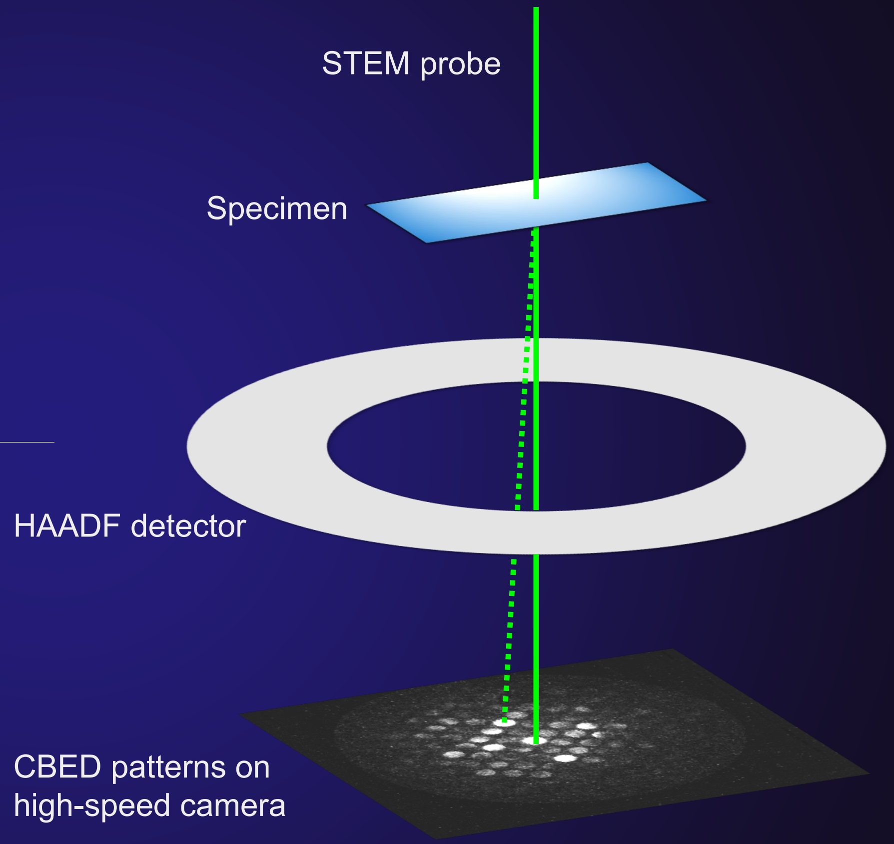
4D-STEM

- Collect a full convergent-beam pattern at every pixel
- Dataset is four-dimensional
  - 2 real-space dimensions
  - 2 reciprocal-space dimensions
- Information extracted from CBED patterns can be mapped in real space



4D-STEM

- Analysis based on finding the diffracted disks requires good separation
- Convergence angle of the probe must be reduced until disks don't overlap
- Resolving power inversely related to convergence angle
- Spatial resolution of a 4D-STEM scan is *fixed by the specimen crystallography*

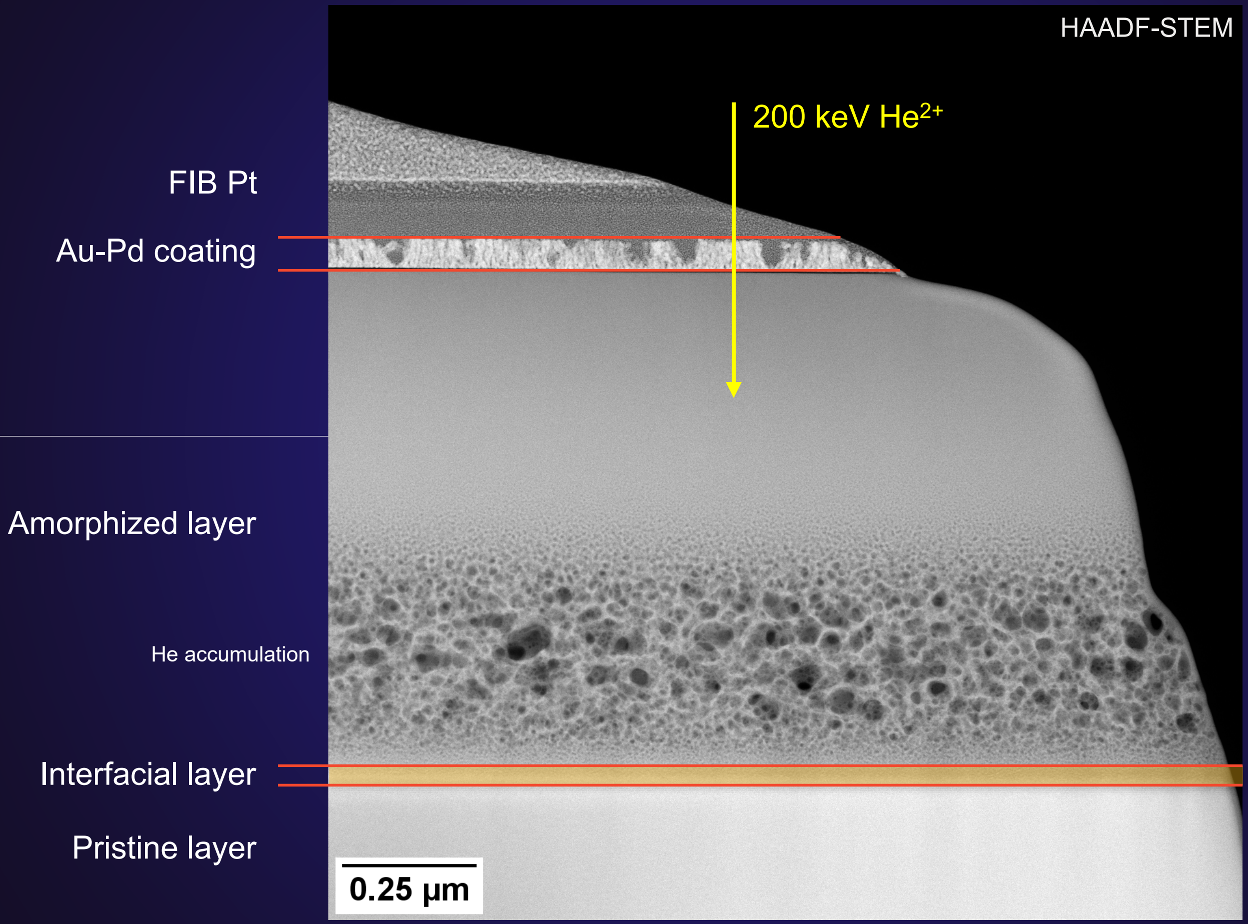


Overview

Experimental: sample history

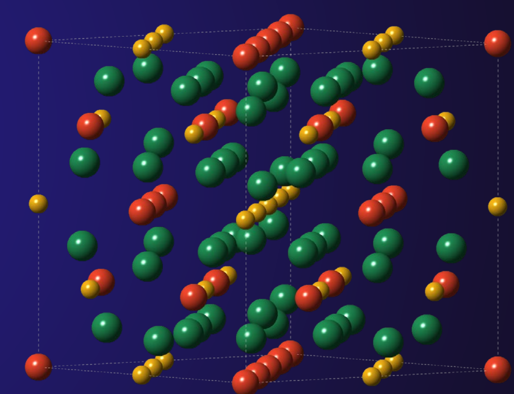
- Float-zone growth of single-crystal $Gd_2Ti_2O_7$
- Laue X-ray diffractometry for crystal orientation
- Polished to < 1nm surface roughness (verified by AFM)
- Irradiated with 200 keV He ions to $1x10^{17}$ ions/cm^2
- Structural changes confirmed with GIXRD
- TEM foils lifted out in a dual-beam FIB/SEM

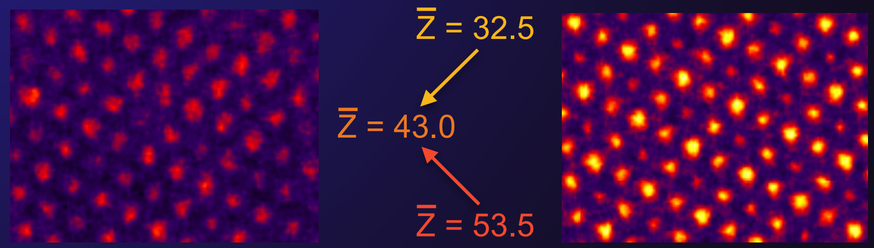
Experimental: sample overview



Experimental: concept and hypothesis

- As disorder on the cation sublattice increases, the {111} superlattice reflections become less intense since the structure factor difference between alternating planes tends toward zero
- Use {111} : {222} intensity ratio as a measure of cation disorder
- Two sets of virtual detectors
  - One for summing {111} reflection intensity
  - One for the {222} reflections
- Hypothesis: expect to see the lowest intensity at the top of the interfacial layer, the highest intensity in the pristine layer, with a gradient between the two
- Compare to library for quantitative measurement of cation disorder





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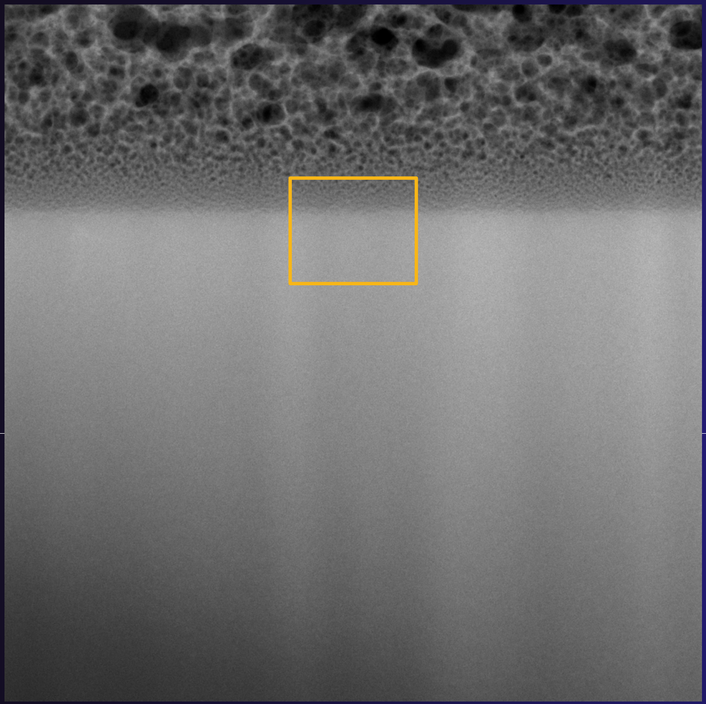
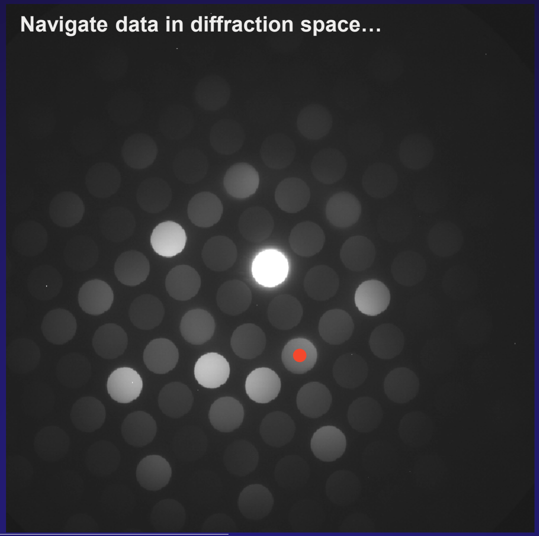
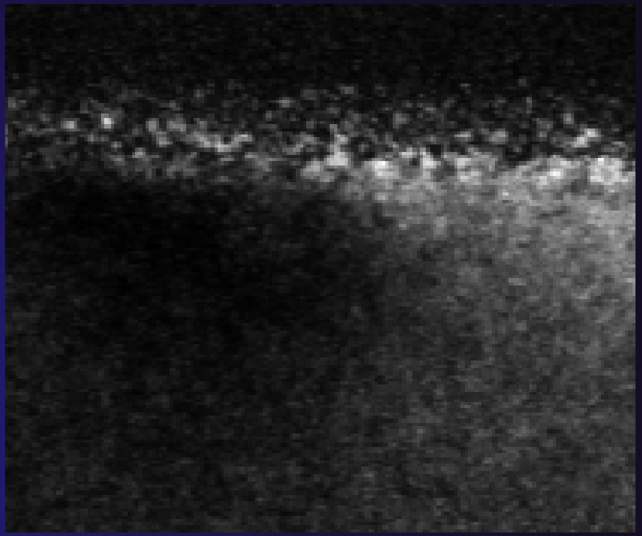
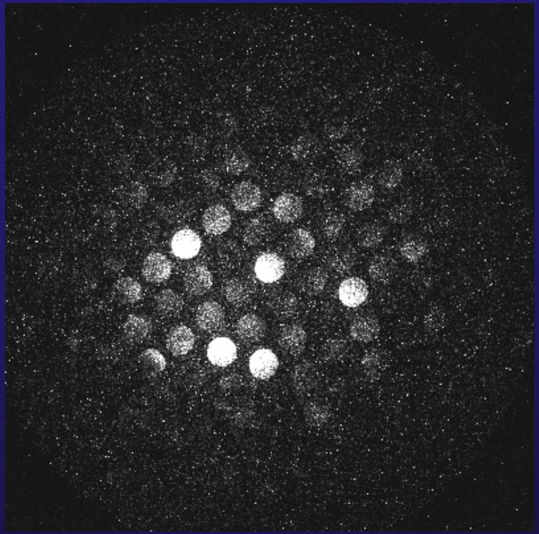
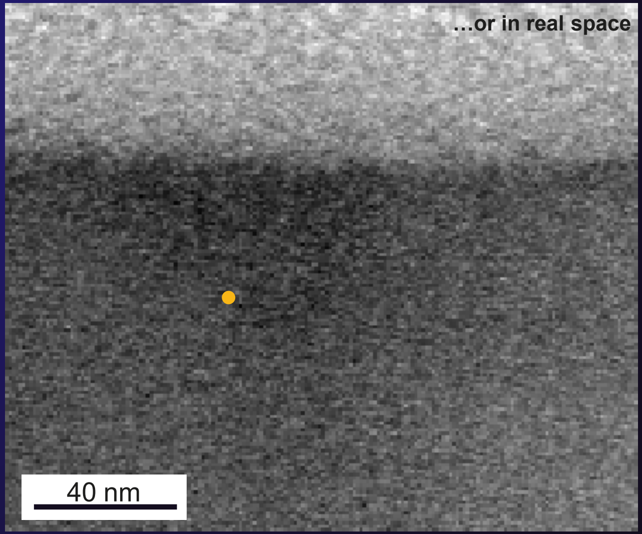
Results





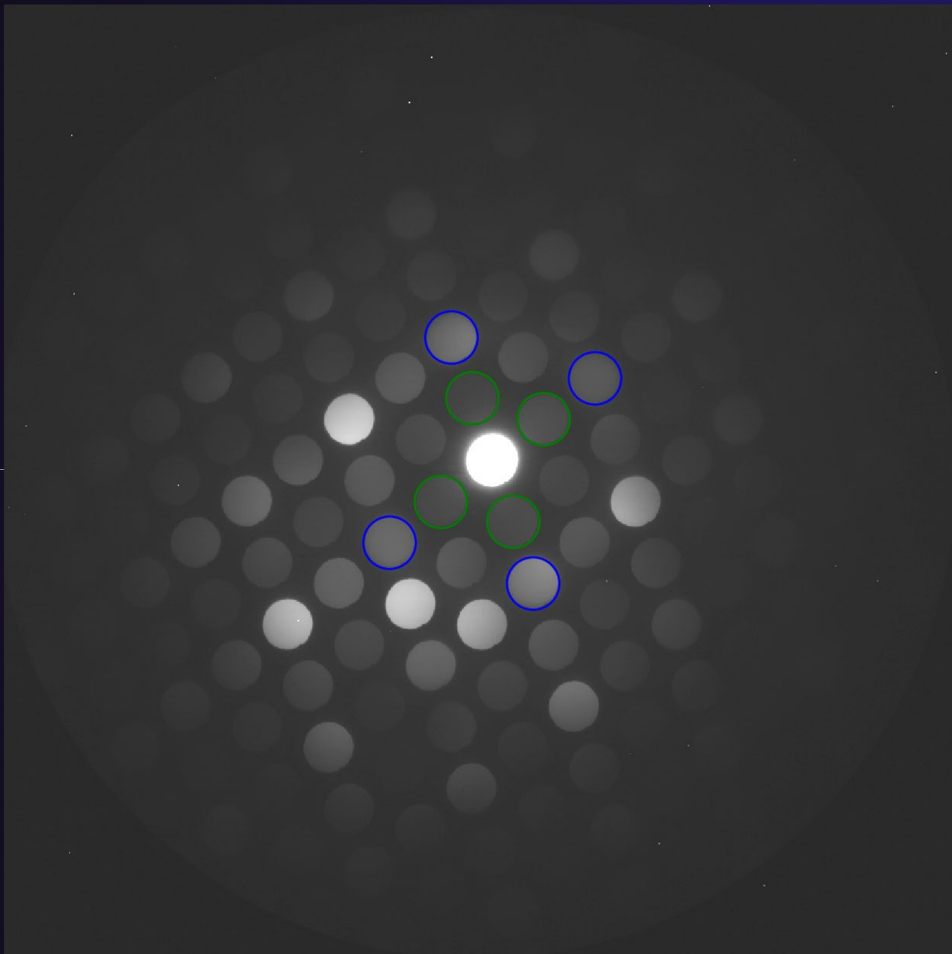


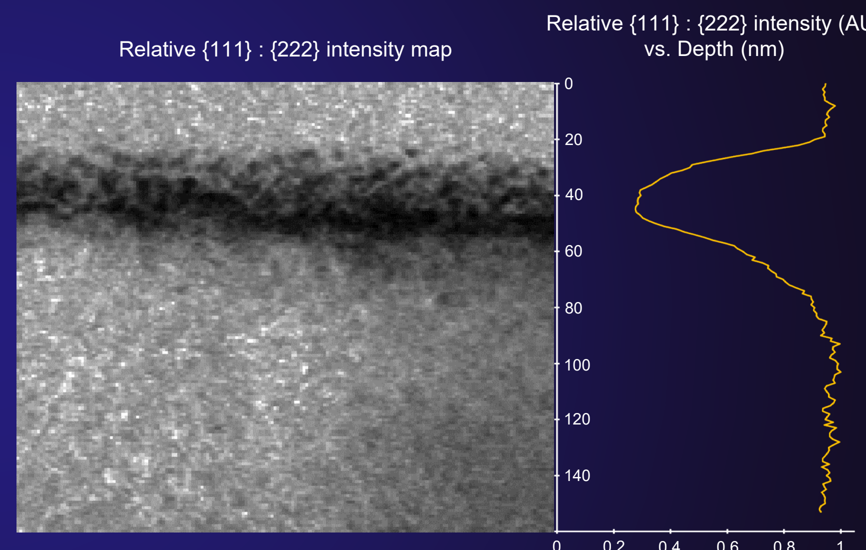




184 x 154 nm, 1 nm/px
28,336 diffraction patterns

Results

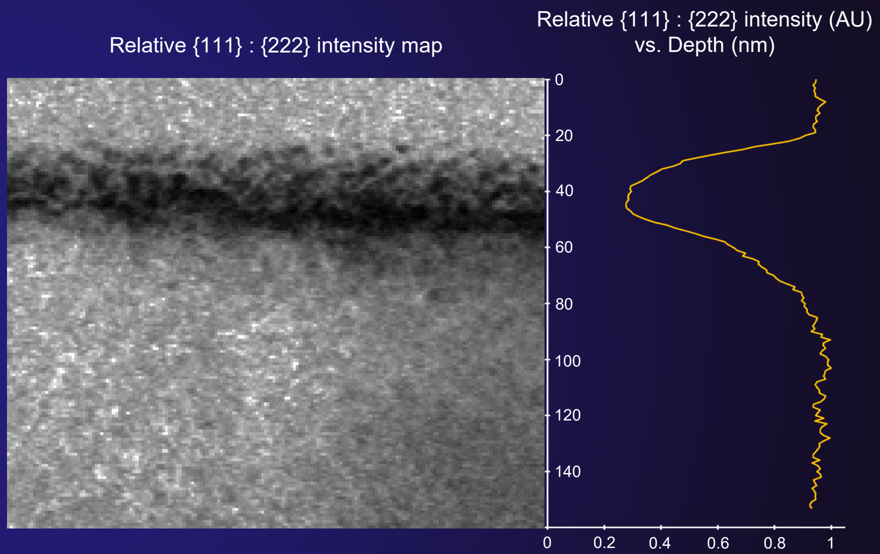




Relative {111} : {222} intensity map
Relative {111} : {222} intensity (AU)
vs. Depth (nm)
0
20
40
60
80
100
120
140
0
0.2
0.4
0.6
0.8
1

Results

- Areas of defect fluorite could almost be mistaken for bubbles
- Intensity in amorphous layer is high: noise/noise ≈ 1
  - Prior knowledge is important!
- Intensity drops over ~20 nm in transition from amorphous to fluorite layers
- Intensity rises over ~40 nm in transition from defect fluorite to pristine pyrochlore layers
- Some local orientation and thickness effects remain…



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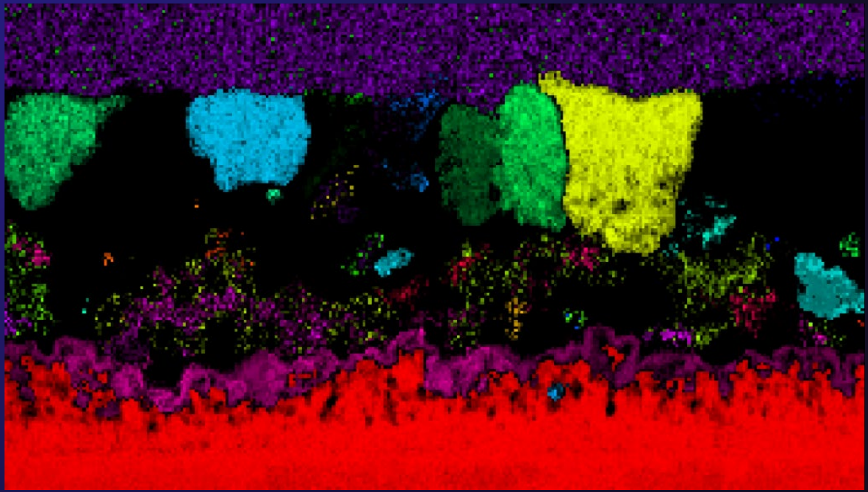
Future Directions: Pattern Matching

- Using CBED simulation software (MuSTEM), create a library of calculated diffraction patterns
- Goal: associate any given {111} : {222} intensity ratio to a specific percentage of cation mixing
  1. Determine local thickness and orientation so these effects can be removed
  2. Simulate pyrochlore structural models at various levels of cation disorder
  3. Normalize the experimental {111} : {222} intensity ratios by the expected ratio for pristine (fully-ordered) pyrochlore
  4. Map the fraction of measured intensity to expected intensity as percent cation mixing

Future Directions: Re-crystallization

- Some pyrochlores have a higher affinity than others for the defect fluorite structure- depends on chemistry
- Transformation from pyrochlore to amorphous passes through the defect fluorite structure
- Reverse is not predicted to be true for GTO
- In-situ XRD annealing experiments bear this hypothesis out, but…
- XRD is a bulk technique!
- Preliminary 4D-STEM results show evidence for a different phase at the very edge (~25 nm thick layer) of the re-crystallization front
- In-situ 4D-STEM heating experiments planned



Acknowledgements

- Ken McClellan – Single crystal growth
- Darrin Byler – Crystal orientation and sectioning
- Rafael Spillers – Polishing crystal sections
- James Valdez – GIXRD
- Ming Tang – AFM
- Di Chen and Yong Wang – Sample irradiation
- Ben Savitzky, Colin Ophus, and Jim Ciston – 4D-STEM on TEAM I
- Matt Schneider
- Terry Holesinger
- Blas Uberuaga

Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. JC and CO acknowledge support from the DOE Early Career Research Program. Project funding was provided by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division under award LANLE4BU. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is managed by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract 89233218CNA000001.