Toward *In Situ* Mapping of Crystal Selection during OFZ Crystal Growth

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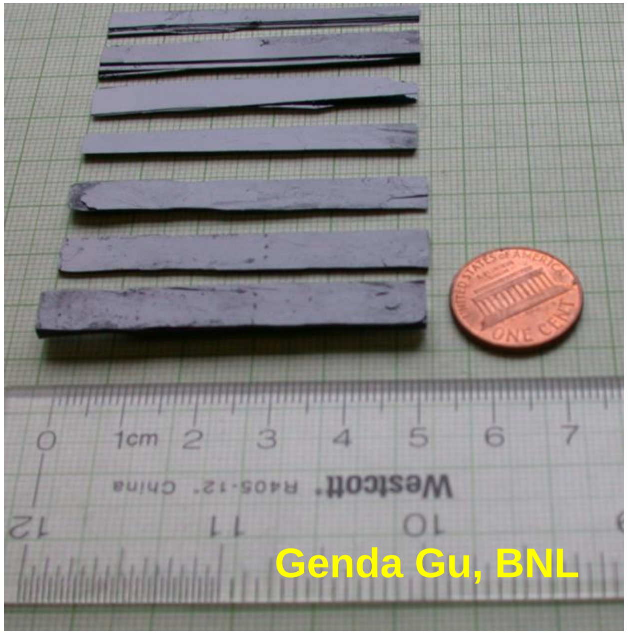
This work was supported as part of GENESIS: A Next Generation Synthesis Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0019212

A NEXT GENERATION SYNTHESIS CENTER

Large single crystals have been transformative



- Source of many key insights into high-T_c cuprate superconductors (inelastic neutron, ARPES, etc.)
- More recently being applied to other fields (solar fuels, catalysis, etc.)
- Key technology for producing crystals is optical floating zone furnace
- **OFZ growth is currently an art and not a science** – a quantitative understanding is lacking!

Some specific GENESIS goals

- Apply modern synchrotron methods to probe synthesis *in situ* in new ways and with unprecedented sensitivity
- Simultaneously probe polycrystalline, liquid, and crystal regions
- Obtain new insights into and greater control over crystal growth processes
- Gain access to important hard-to-grow phases

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OFZ furnace

Not easy to probe sample during growth!

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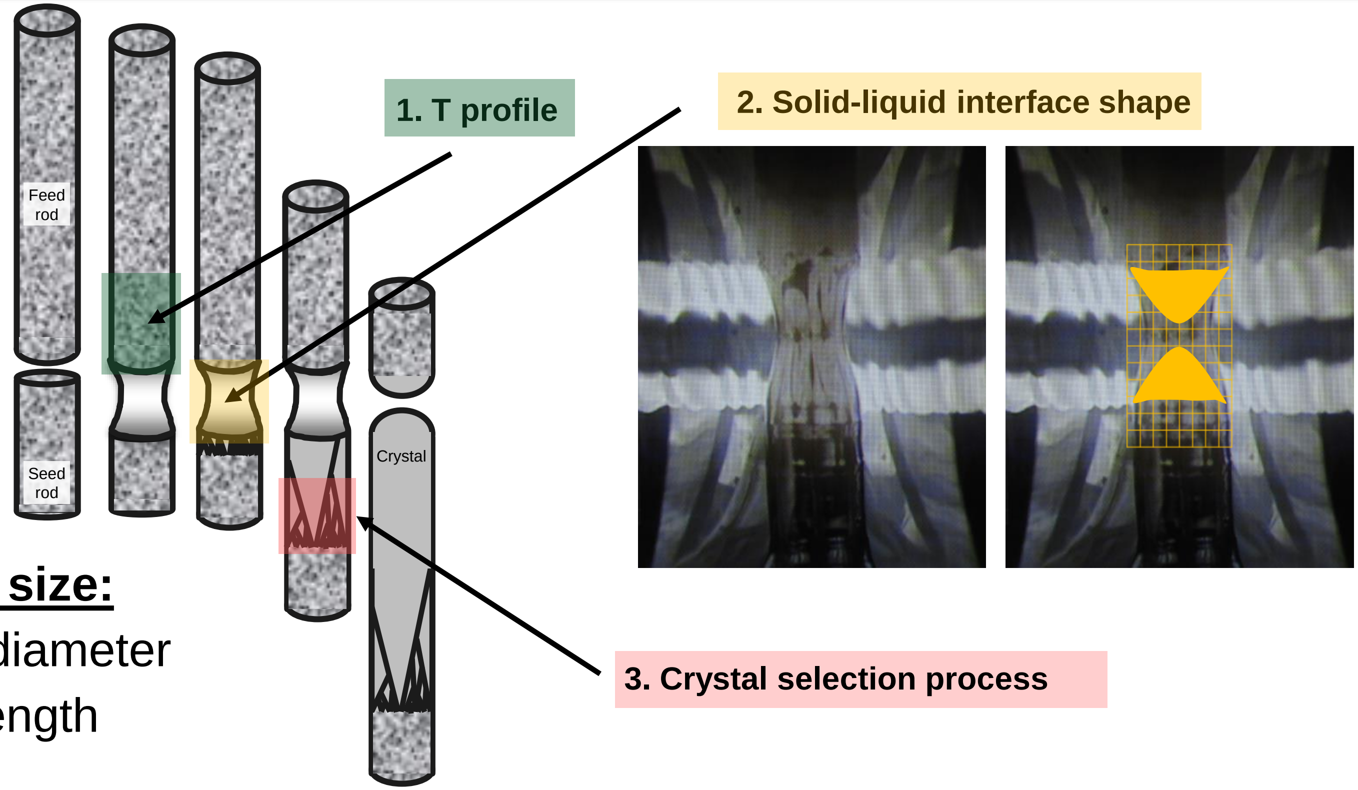
Opportunities to probe OFZ crystal growth



Sample size:

~5 mm diameter

~5 cm length

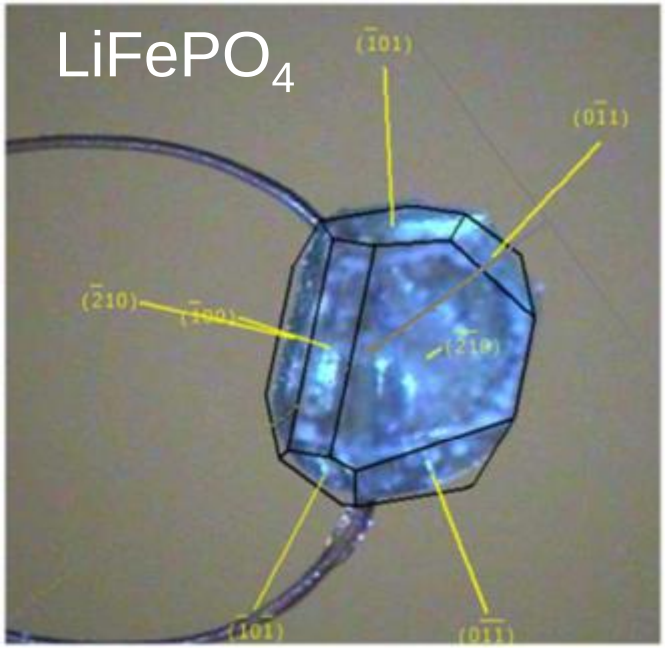
Crystal growth in OFZ furnace typically monitored using only video

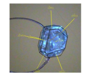
- Can roughly distinguish between solid and liquid regions
- Cannot monitor temperature / temperature profiles
- Cannot probe the interior of the crystal growth rods

New opportunities using a synchrotron, but **boules are not standard samples!**

(Mis)utilization of single crystal diffraction

~0.5 mm crystal





~10 mm crystal

Routine to characterize small xtals (< 0.5 mm) with SXRD to get 3 x 3 UB matrix

Very hard to characterize large crystals (5 – 10 mm) by Laue or SXRD

- Laue – works poorly when symmetry is low
- SXRD – transmission of beam is essentially zero; crystal larger than beam

(Mis)utilized high-energy synchrotron X-rays

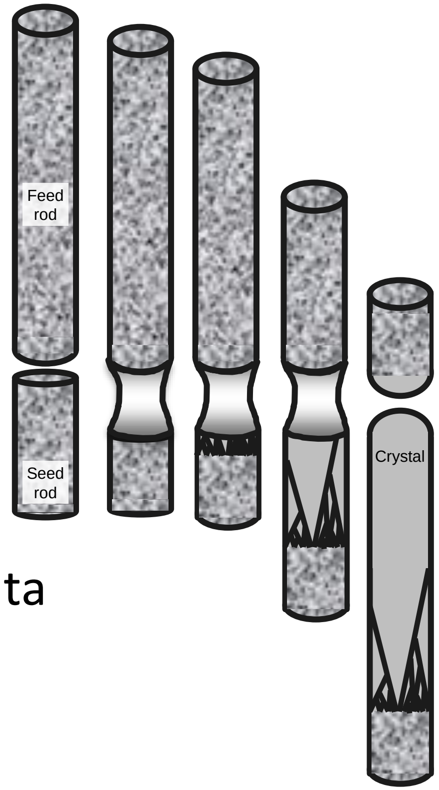
Experiments done at 28-ID powder diffraction beamlines of NSLS-II

- Suitable for mapping studies - detector / motors limit speed (≤ 1 sec)
- High energy X-rays can penetrate through (some) 5 mm thick samples
- Ongoing construction of HEX beamline (photons to ~200 keV)

1. Investigating the crystal selection process

Ideal growth product is a single crystal

- What is the pathway from powder to single crystal?
- What growth variables help/hinder selection process?
- Knowledge should improve crystal size and quality



It is possible but destructive / laborious to study *ex situ*

- What are opportunities to study this process *in situ*?
- Can optimize growths more rapidly when using *in situ* data

Initial *ex situ* synchrotron studies have been carried out

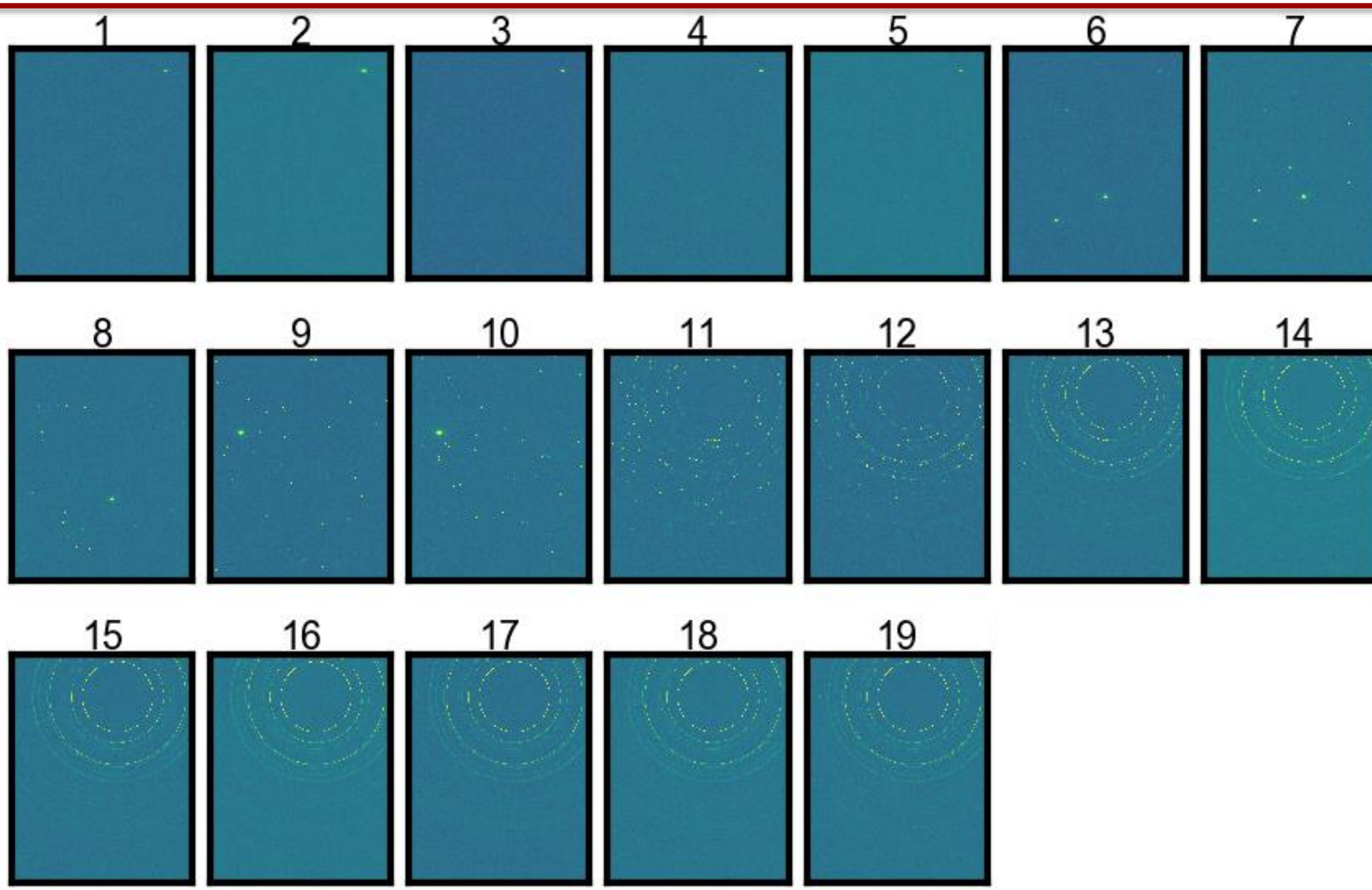
- Will be working to extend methods to *in situ* experiments
- May be applicable to processes other than just OFZ crystal growth

Ex situ data collection on powder beamline

Transmission measurements on TiO_2 boule grown in OFZ furnace

- Utilized high-energy X-rays (67 keV) and a 2D detector
- Sample scanned using a medium grid (0.2 x 0.2 mm spot size & step size)
  - Probe region about 5 mm x 40 mm, so about 25 x 400 = 10,000 grid points
- No rotation of sample was done in these proof-of-principle experiments
  - OFZ furnaces are designed to rotate samples during growth

Variation in diffraction patterns from crystal boule

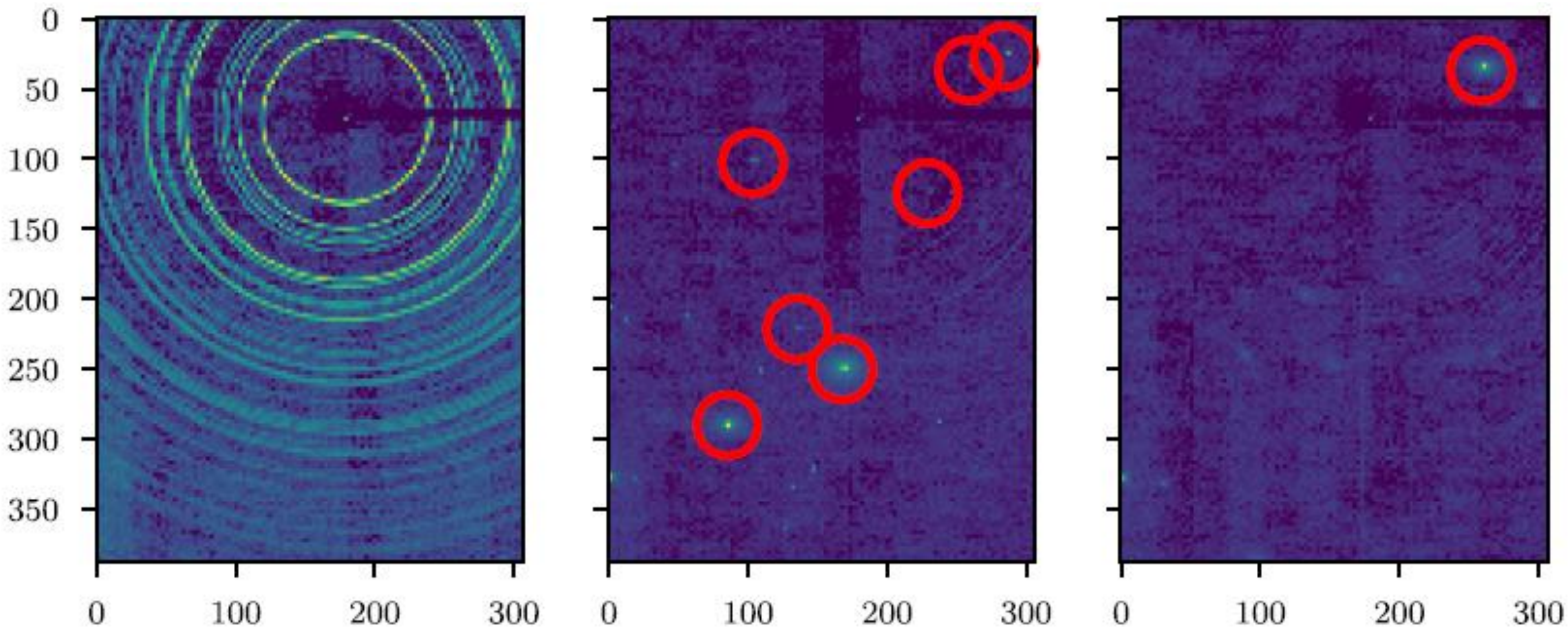


Diffraction patterns evolve from those of single crystal to multi-crystal to powder

- Existing software designed to deal with crystal spots or powder rings but not both

Analysis of crystal growth product – grain tracking

Boule 1



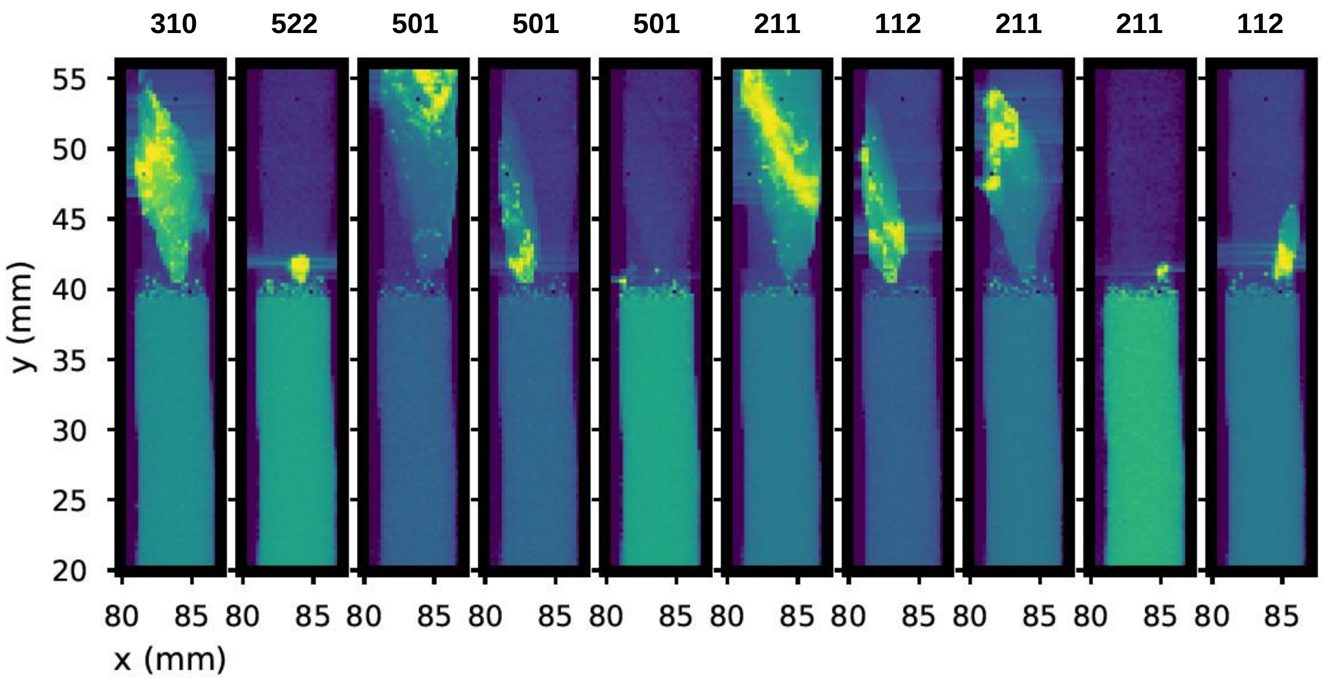
Single crystal diffraction spots used to extract info about grains in boule

- When beam scanned within a single crystal domain, same diffraction spots are seen
- For any one hkl reflection at a given azimuthal angle, can make a map of the grain
- Utilized existing peak finding functionality of trackpy package

Simple but effective approach

Analysis of crystal growth product – grain tracking

Boule 1



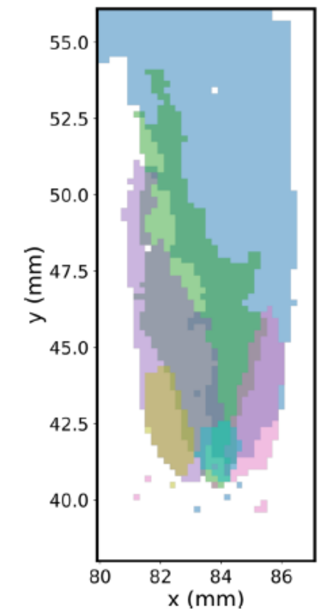


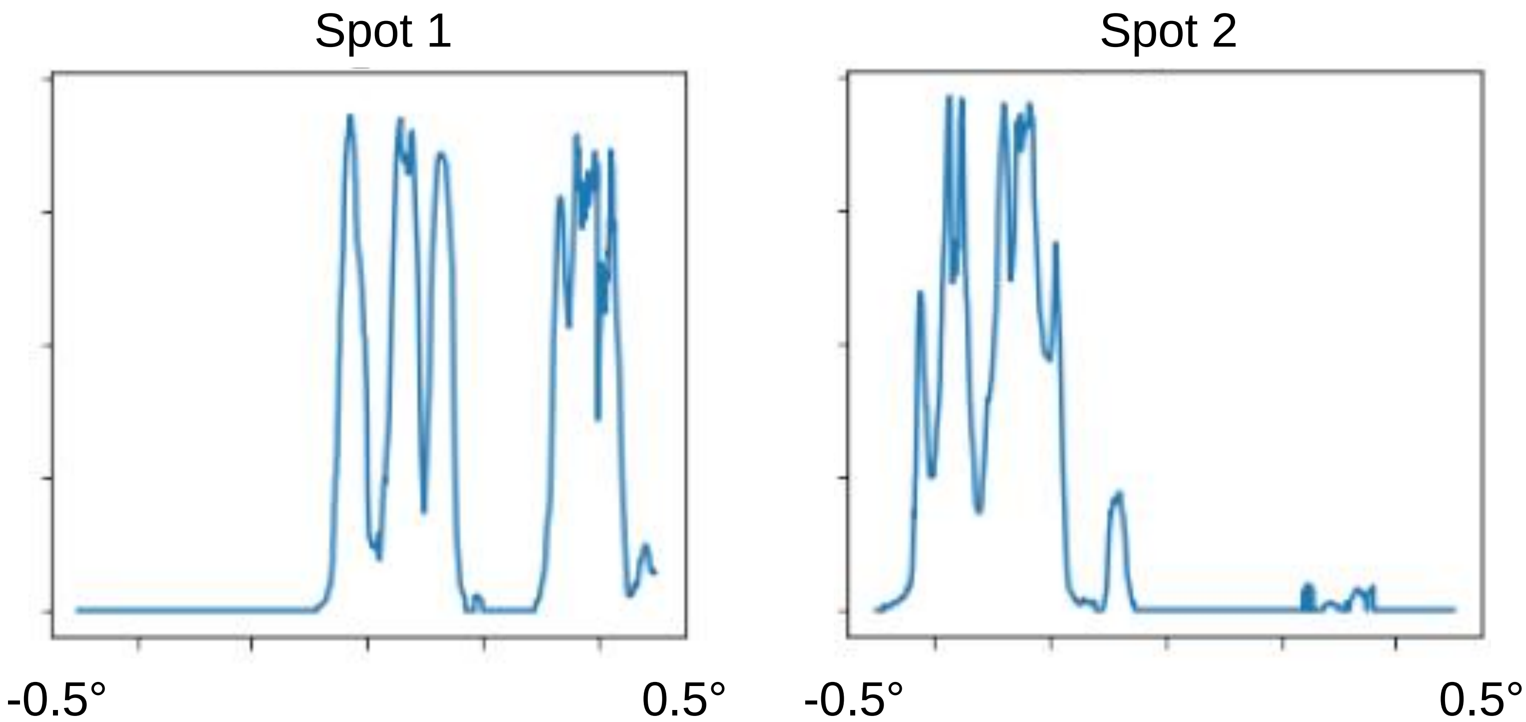
Image shows crystal domains which produce the 10 most intense diffraction spots

- Can see single crystal domains both expanding and terminating
- All major grains appear of have nucleated near the center of the boule
- Unexpected intensity bands commonly seen – ascribed to mosaicity effects

Next step: Calculate orientation-dependence of TiO_2 growth rate

Rocking curve measured at single spot

Boule 1

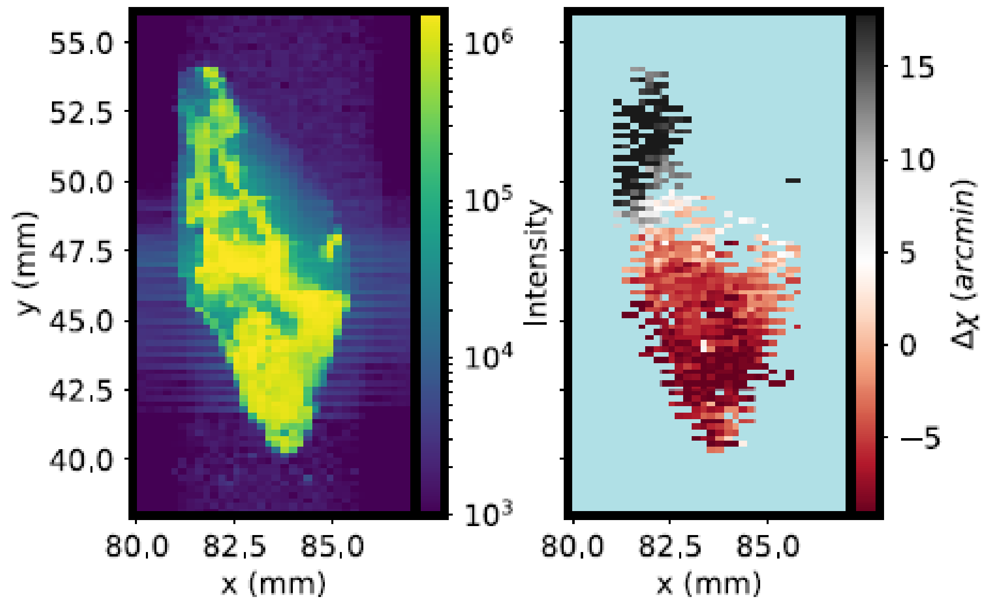


Rotated crystal by 1° in 0.01° steps

- Sharp onset and loss of intensity even with 0.01° rotation
- Presently testing precession methods to avoid intensity bands
- Suggests utility for investigating influence of growth parameters on quality

Mosaic spread variation across crystal

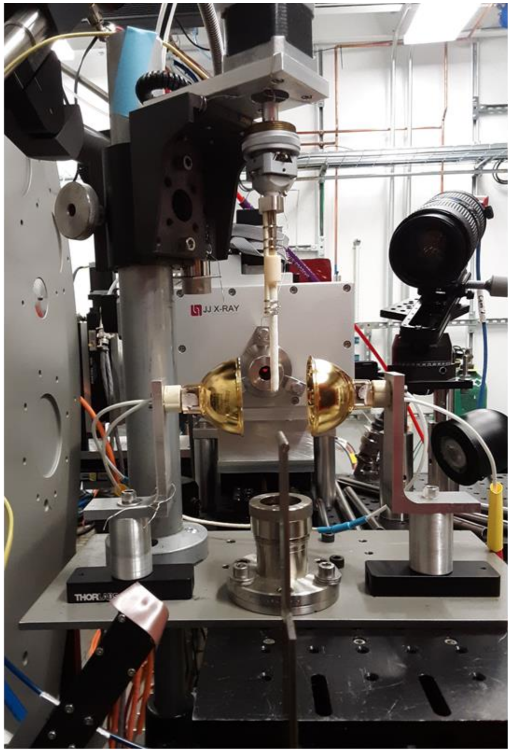
Boule 1



Can also probe mosaic spread in context of maps

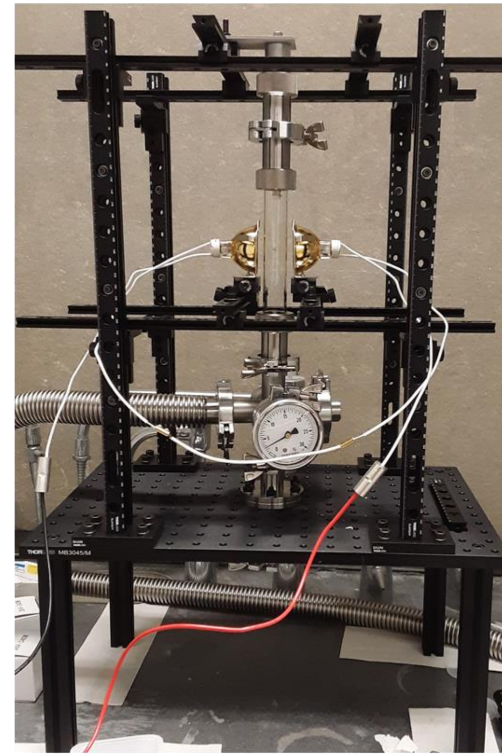
- Can extract position-dependent variation in azimuthal angle (right)
- More data needed to extract full mosaicity matrix (more spots, +rotation)
- Working to develop infrastructure needed to study crystal growth *in situ*

Development of infrastructure for *in situ* studies



Mark I – air only

Mark II – vacuum / gas

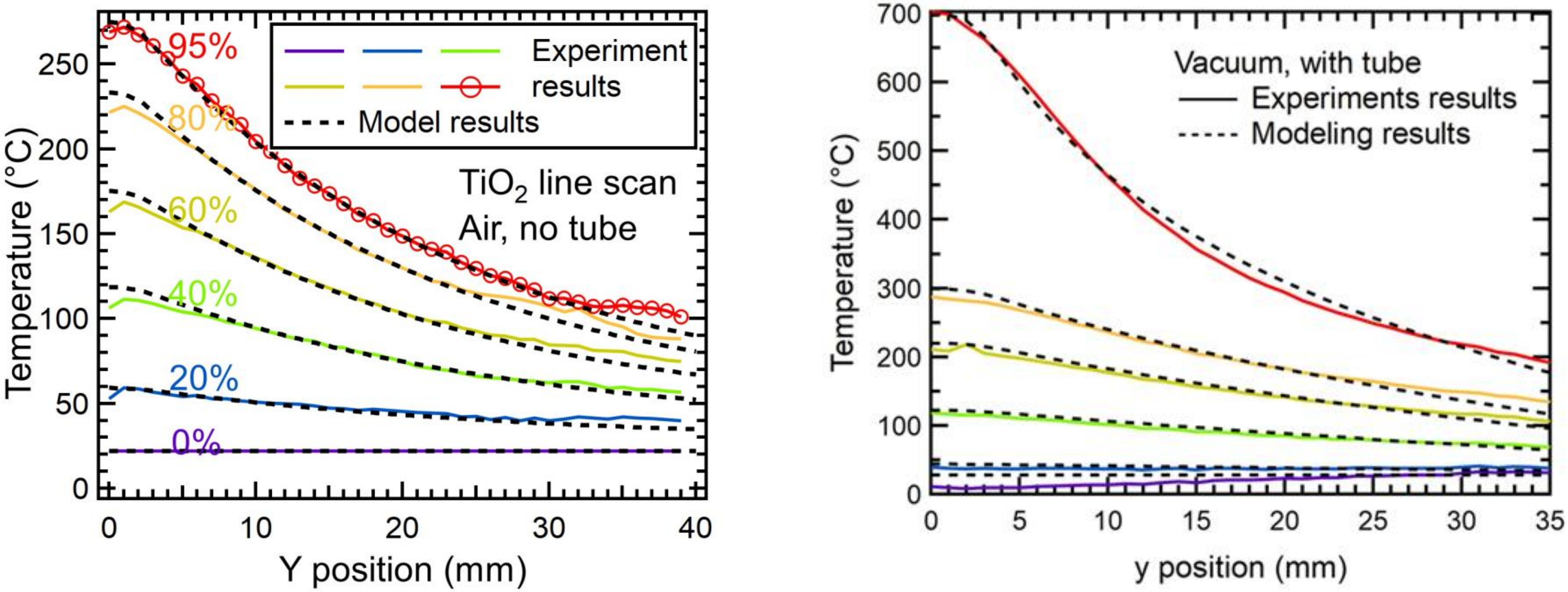


Mark III – dual-rod

Carrying out design and fabrication of "mini-FZ" furnaces for *in situ* studies

- Avoids limitations of commercial FZ furnaces (high cost, large mass)

Development of infrastructure for *in situ* studies

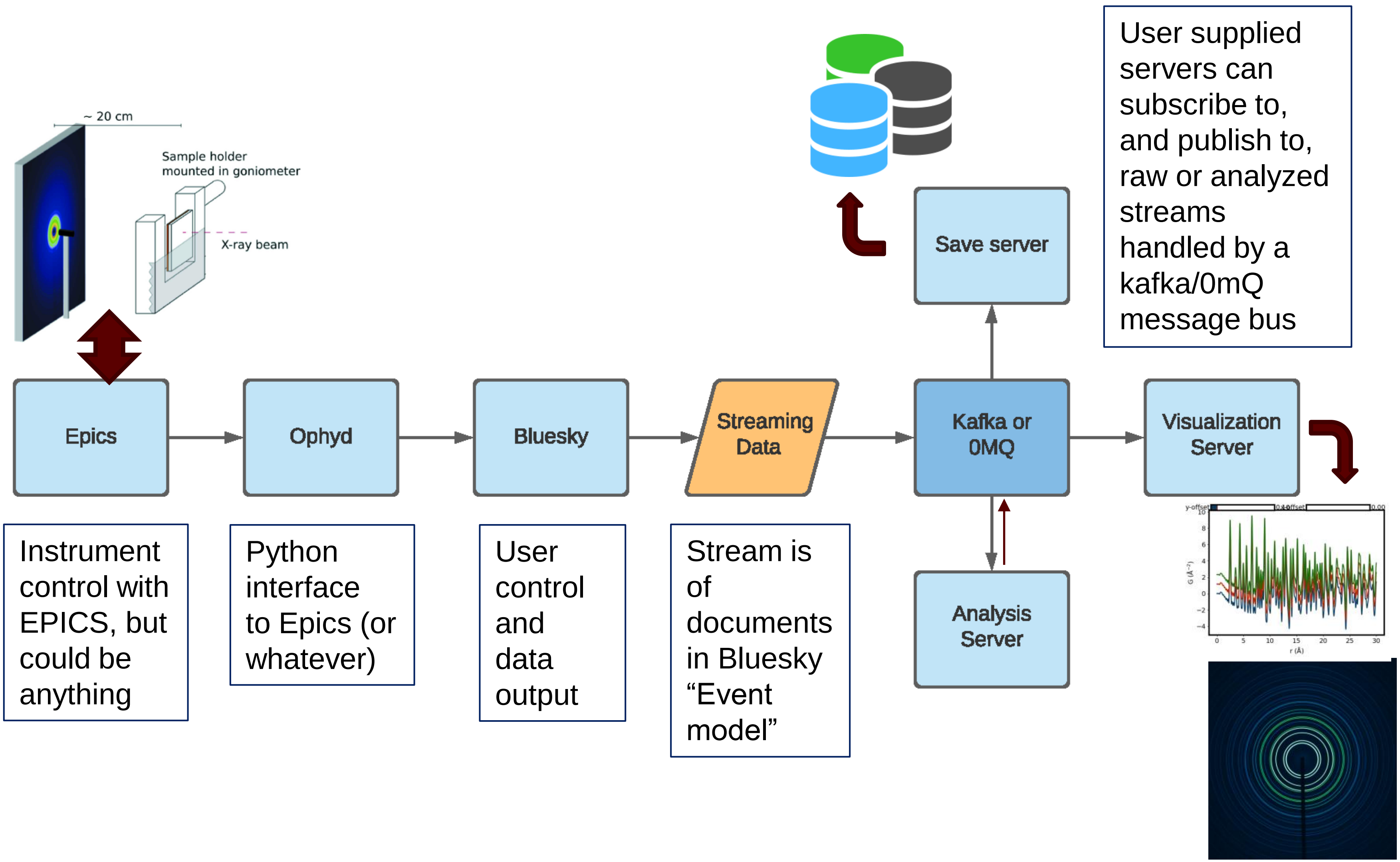


Have used powder diffraction data to extract temperature profiles of heated rods

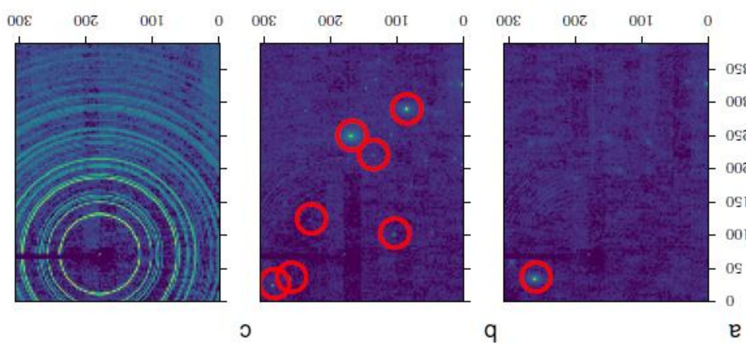
- From thermal expansion behavior (strain), can get T with precision < 0.25 °C
- Have developed physical models (dashed lines) that reproduce results
- First model for FZ environment parameterized and validated from expt. data

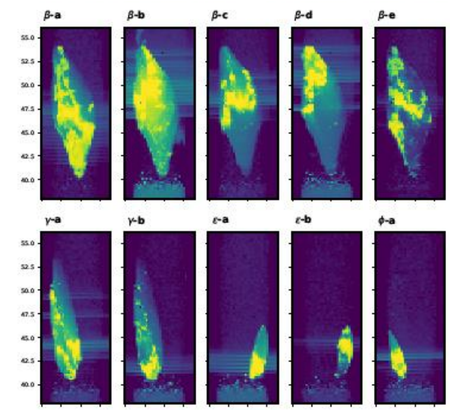
Next steps: (1) Inline analysis, (2) *in situ* crystal growth, (3) autonomation of growth

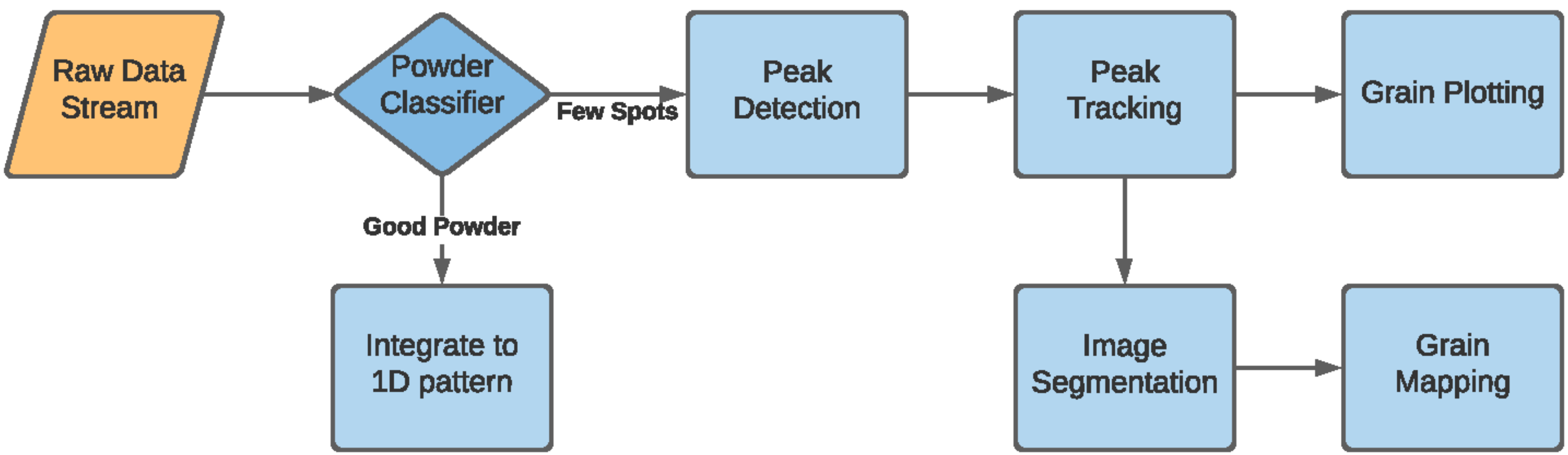
Automated data acquisition at NSLS-II, BNL

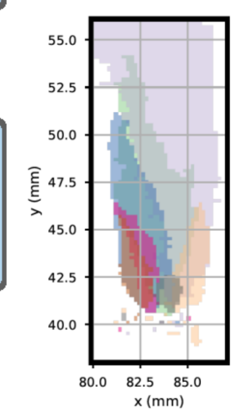


Analysis server for automated grain tracking









Conclusions / Acknowledgements

- Actively developing synchrotron methods to probe crystal growth
  - Temperature distributions https://doi.org/10.1107/S1600576720007062
  - Crystal grain distributions https://pubs.acs.org/doi/pdf/10.1021/acs.chemmater.1c00602
- Methods are or will be compatible with *in situ* crystal growth

DOE support: This work was supported as part of GENESIS: A Next Generation Synthesis Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0019212

NSF support: This material is based upon work supported by the National Science Foundation (Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-1539918.

User facility support: This research used the National Synchrotron Light Source-II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.