HOW HARDWARE CAN ACCELERATE MATERIALS SYNTHESIS AND DISCOVERY

ROLE OF AUTOMATION AND AUTONOMY IN PHASE EXPLORATION

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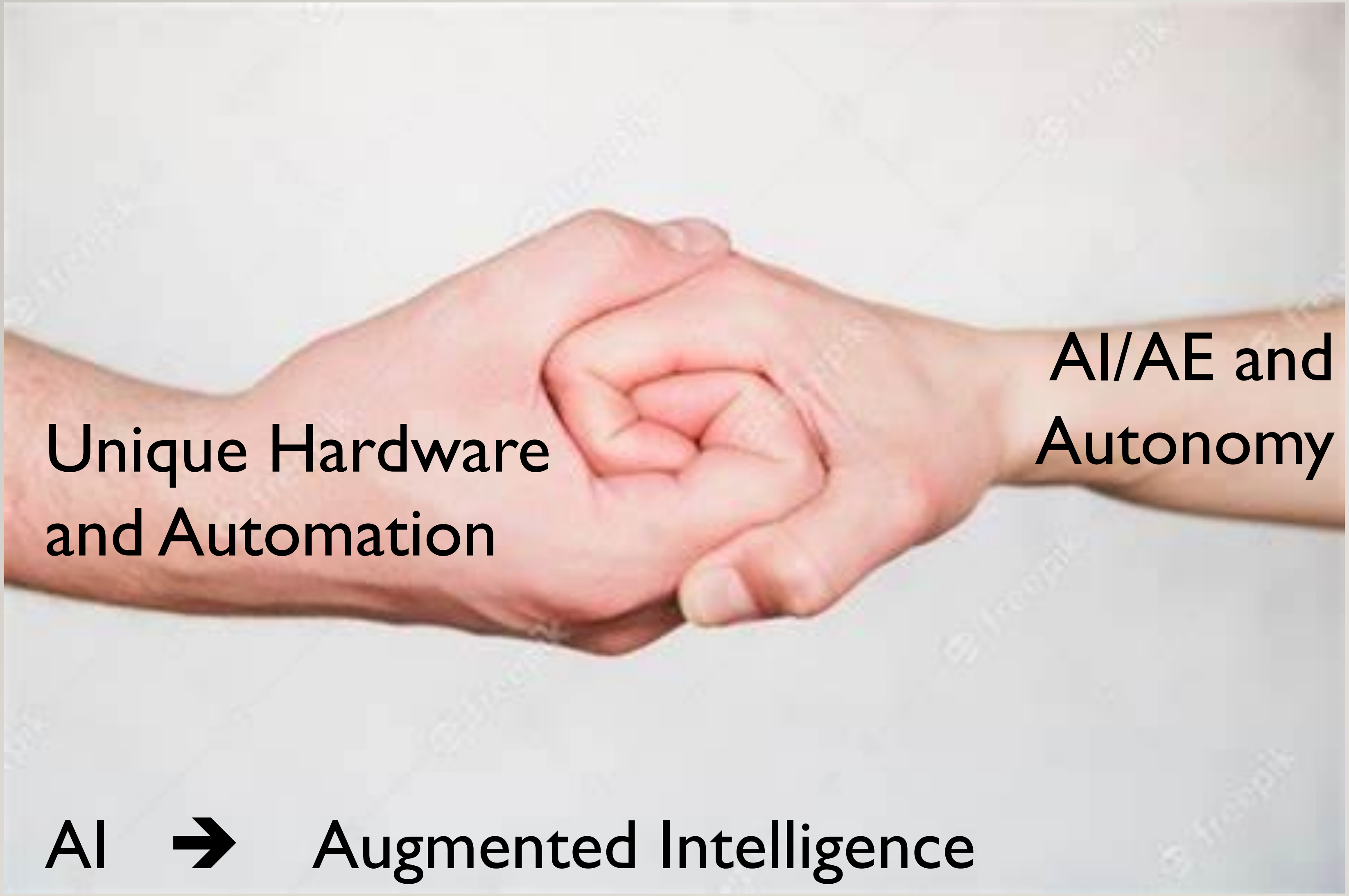
DEC. 6, 2024

CUSTOM HARDWARE $\Longrightarrow$ MATERIALS EXPLORATION

- Autonomous exploration has potential to dramatically accelerate discover
- Rate limiting steps still typical remains the experiments and analysis
- Need more in-operando characterization to provide understanding as well as optimization
- Critical to move synthesis and characterization onto time-scales that match autonomous decision making … then unique capabilities with AI
- Focus on transfer from small PI projects to centers
- **New experimental methods & new experimental hardware**
- **Highly automated and ideally linked to autonomous agents**
- **Advocate for mix of large facility and small-scale unique hardware**
- **Maximum potential when expensive / limited analysis fully utilized**

THE SYNERGISTIC LINK … AN INEVITABLE REVOLUTION



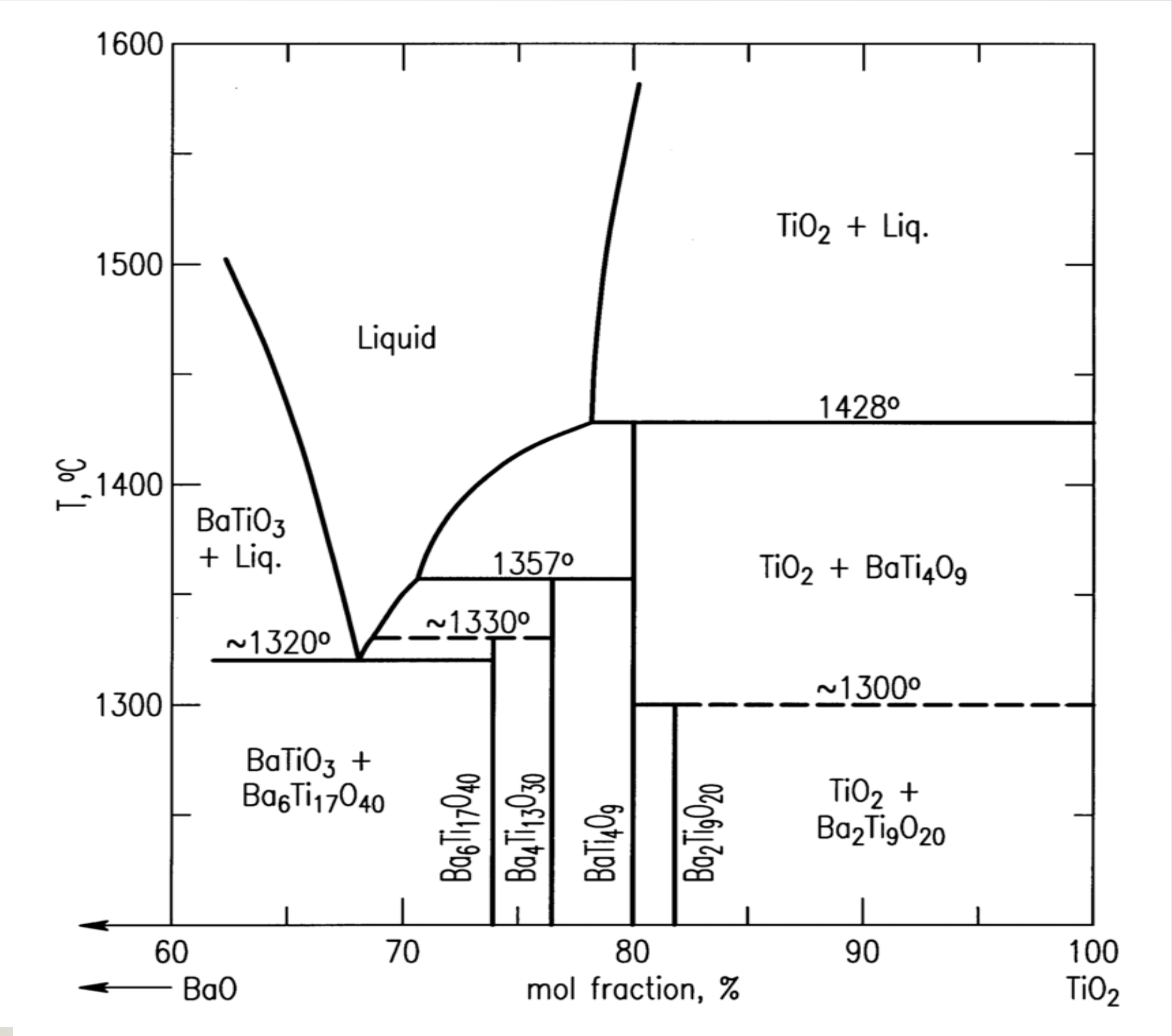
- In some cases, the ability to **do** experiments is outrunning our ability to intelligently analyze and synthesize the results
- Driven by advances in both the breadth of characterization and the speed of characterization
- Autonomous exploration requires new and highly automated experiments

EXAMPLE:
LATERAL GRADIENT LASER SPIKE ANNEALING

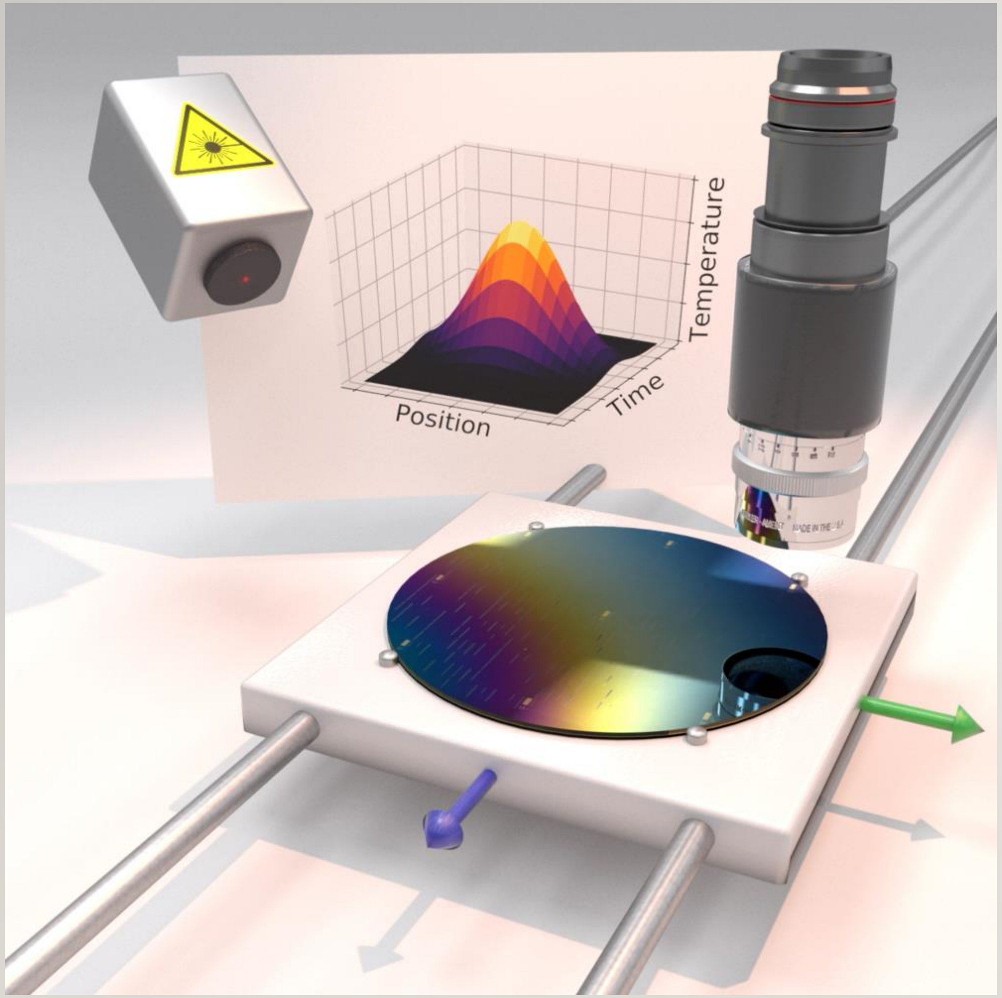
Rapid synthesis and characterization of phase behavior in complex alloys

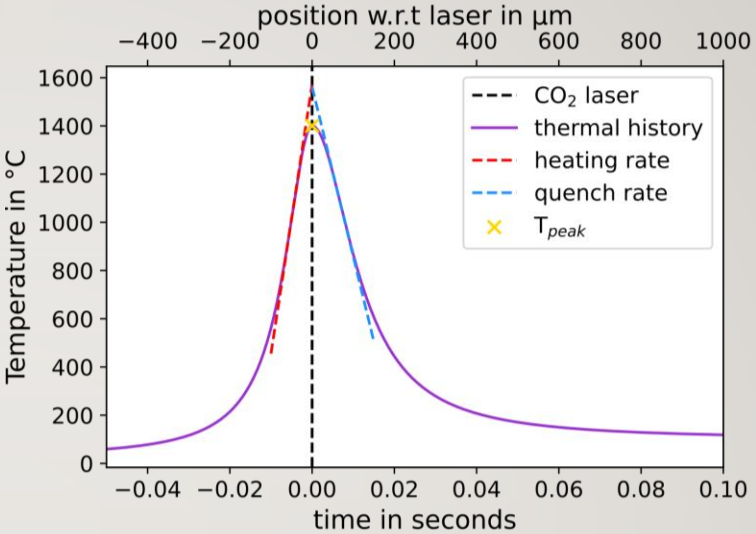
GOAL – GENERALIZED PHASE DIAGRAMS

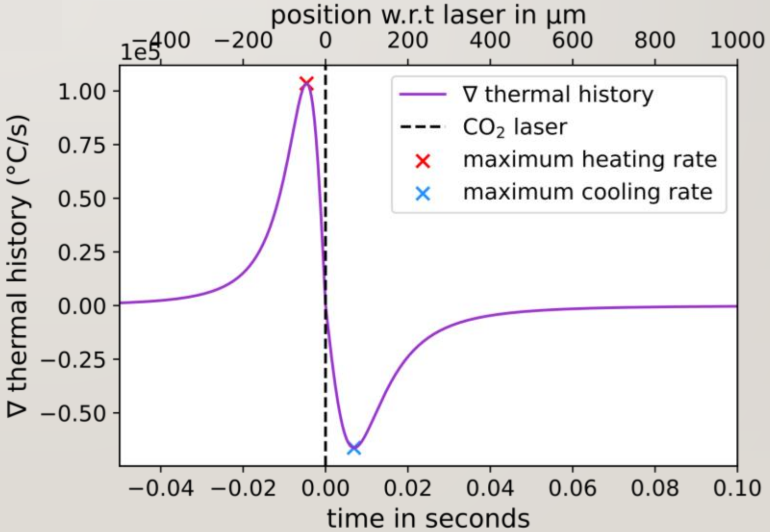
- Not all interesting phases are equilibrium
  - Both xT and μ/μ phase diagrams are still equilibrium
- Kinetics are at equally critical to formation
  - Time and temperature of anneals
- Kinetics pathway not necessarily reversible
- Both solid and liquid phase depend on nucleation phase
  - Competitive phase nucleation
  - Need to track nucleation especially in solid state



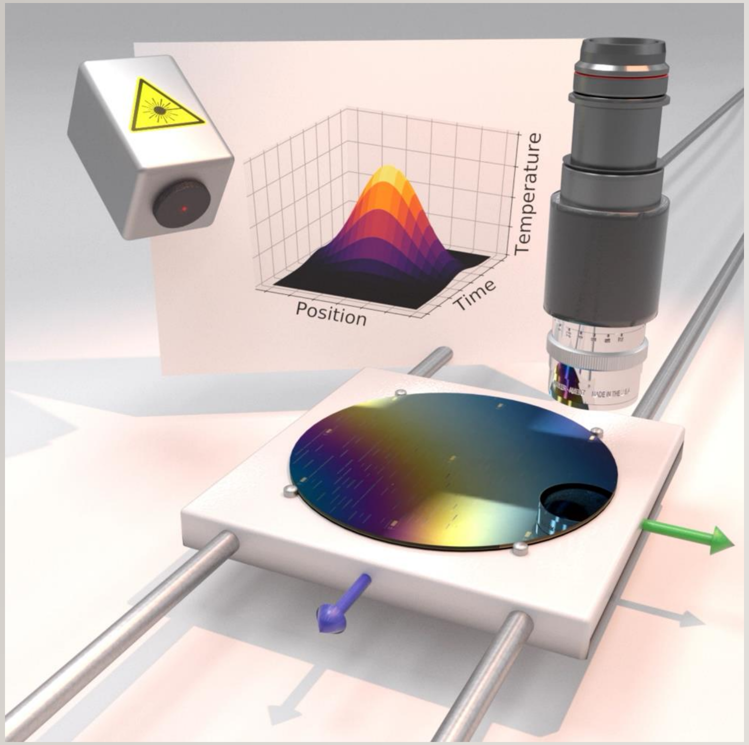
EXPERIMENTAL: LASER SPIKE ANNEALING

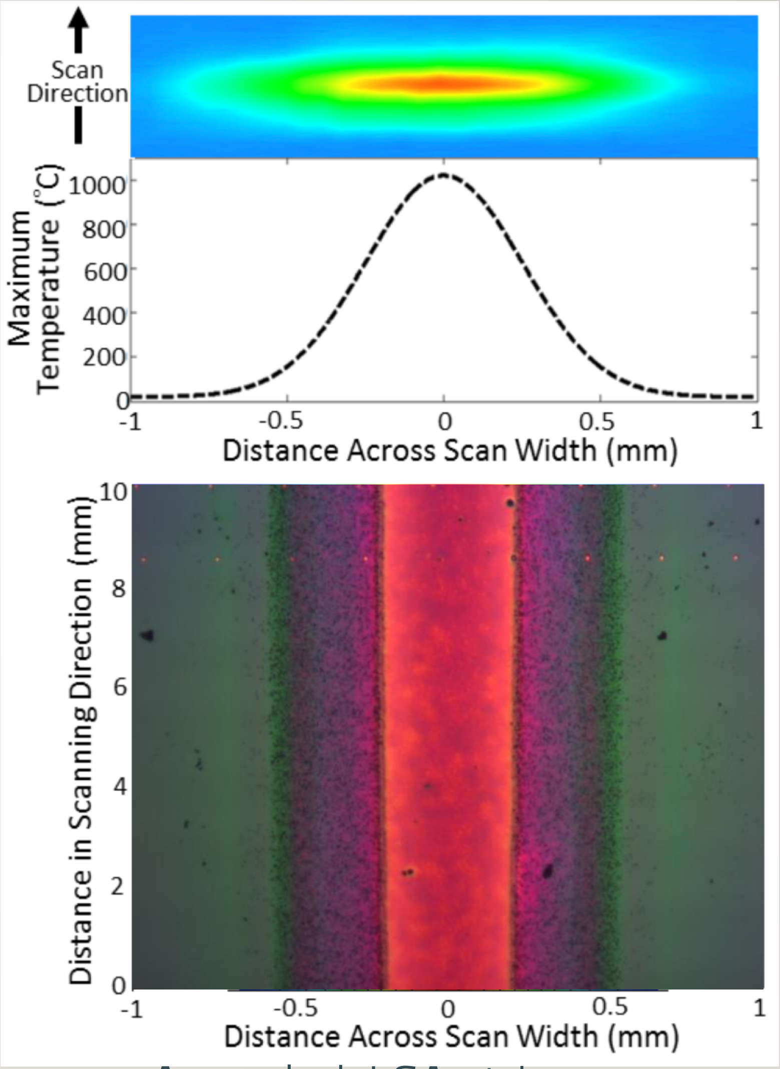






EXPERIMENTAL: METASTABLE PHASE SYNTHESIS



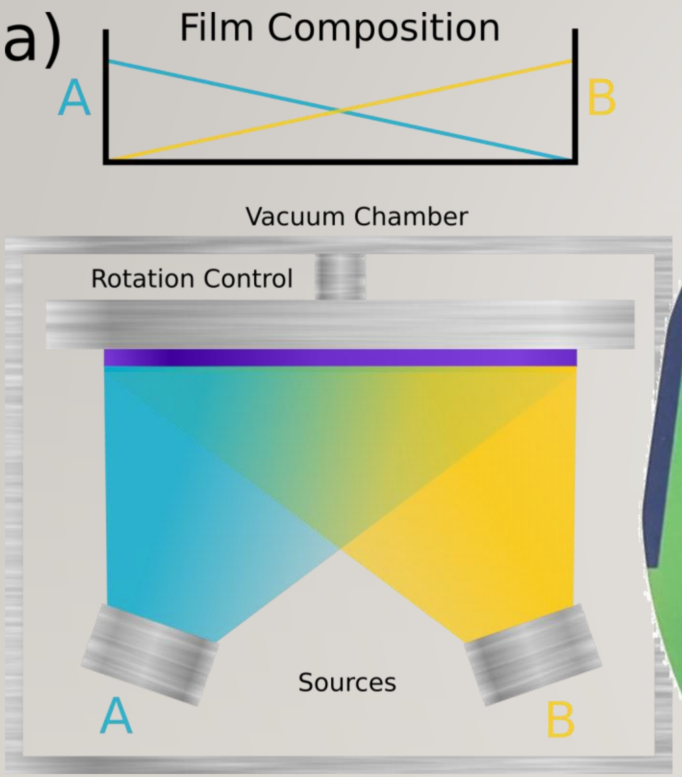


Annealed LSA stripe

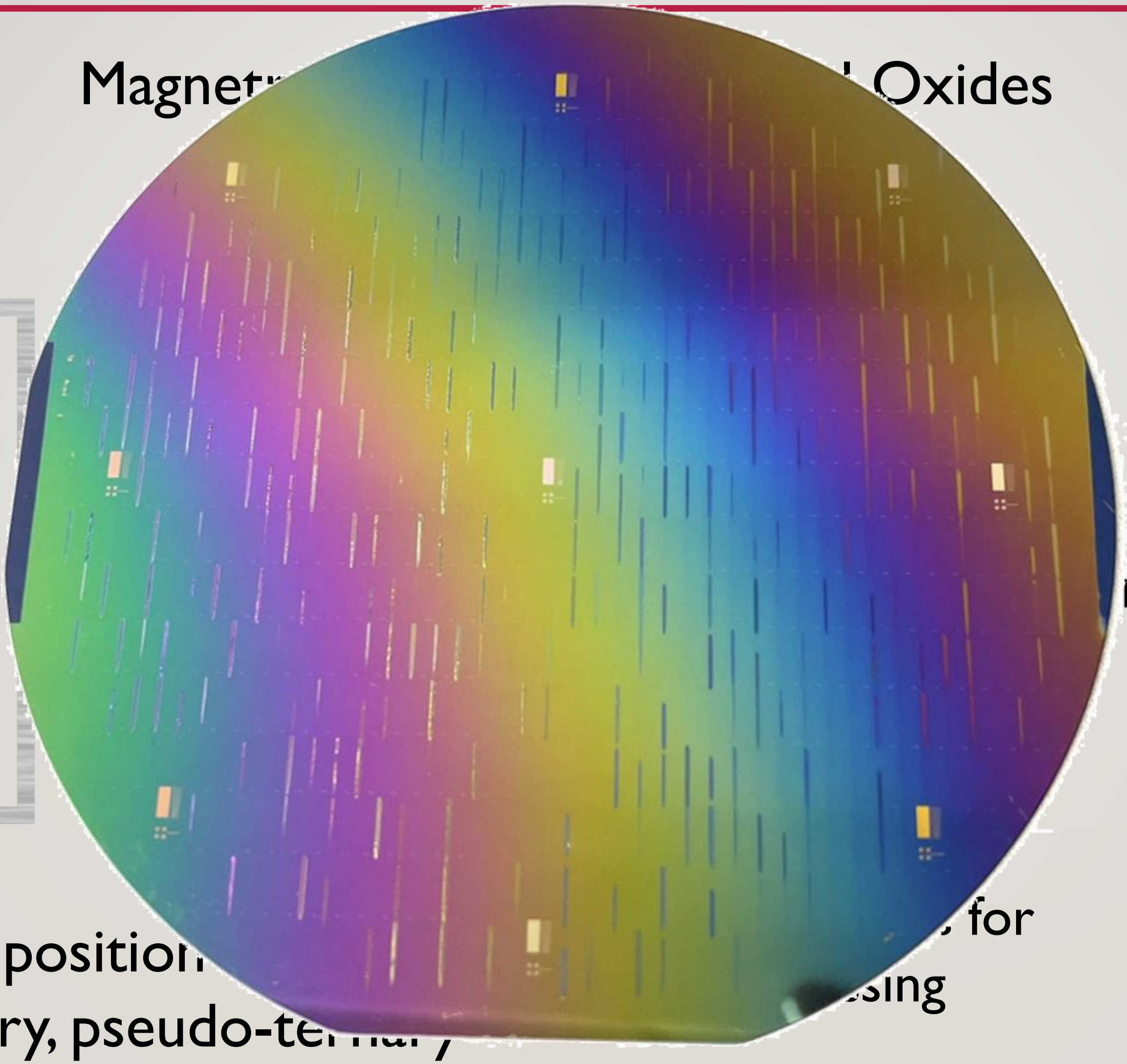
Processing + Composition Space (2D - 4+D)

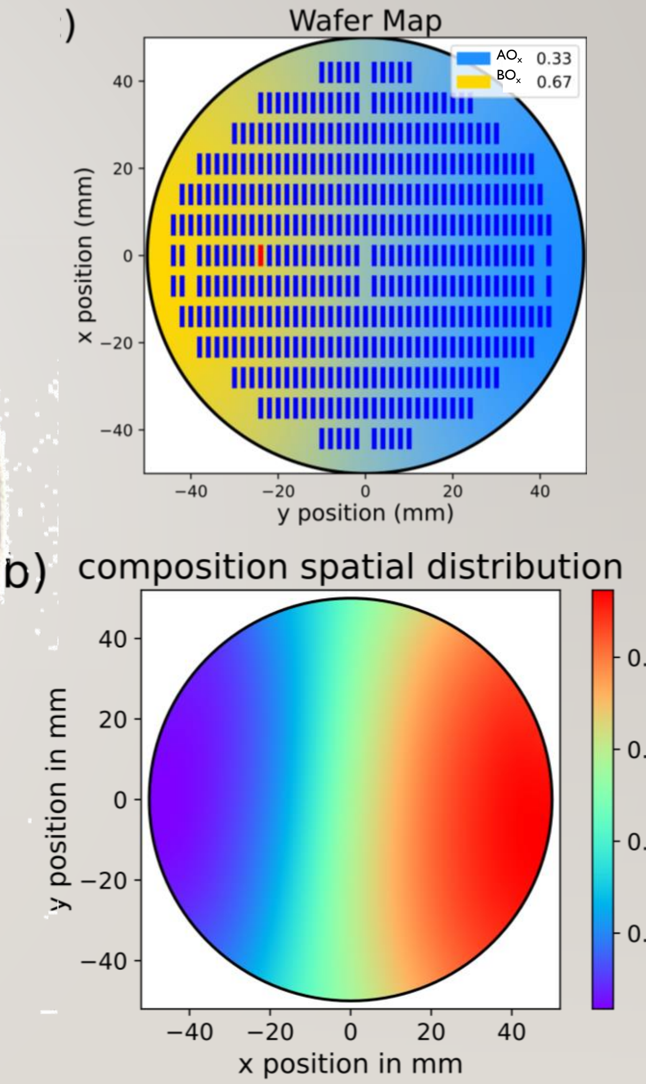
- Laser Power → peak temperature (T) + gradient
- Scan velocity → dwell time ($\tau \sim 100\ \mu s\ - 10$ ms)
  - Heat/Quench rates 10^4 - 10^7 K/sec
- Composition spread → chemical composition (X_A/X_B)

COMBINATORIAL THIN FILM SYNTHESIS



Magnet… …l Oxides

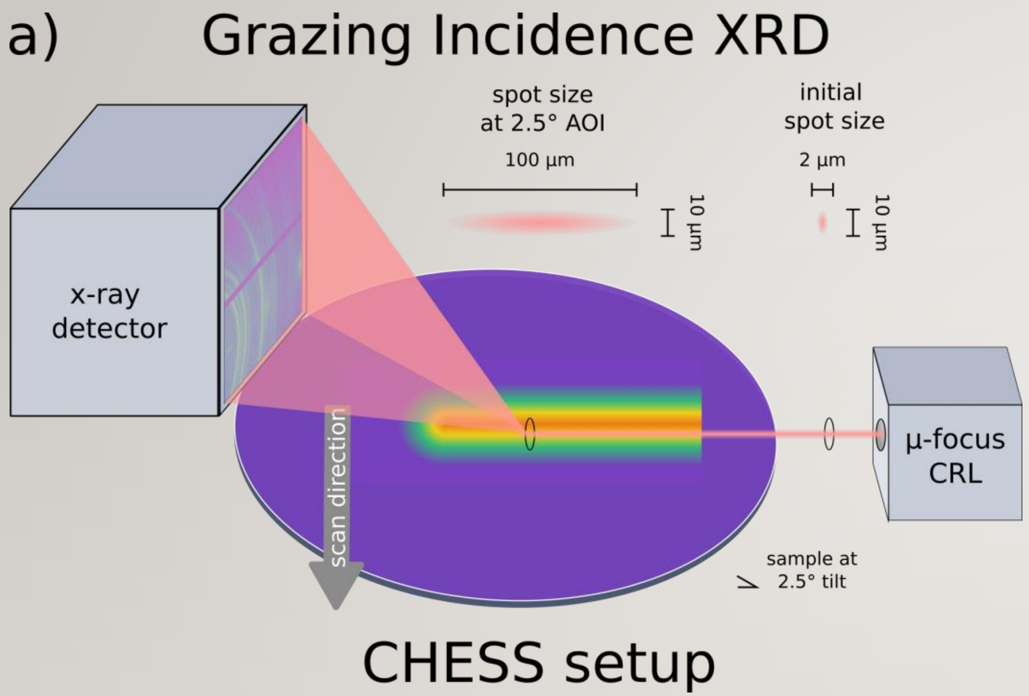


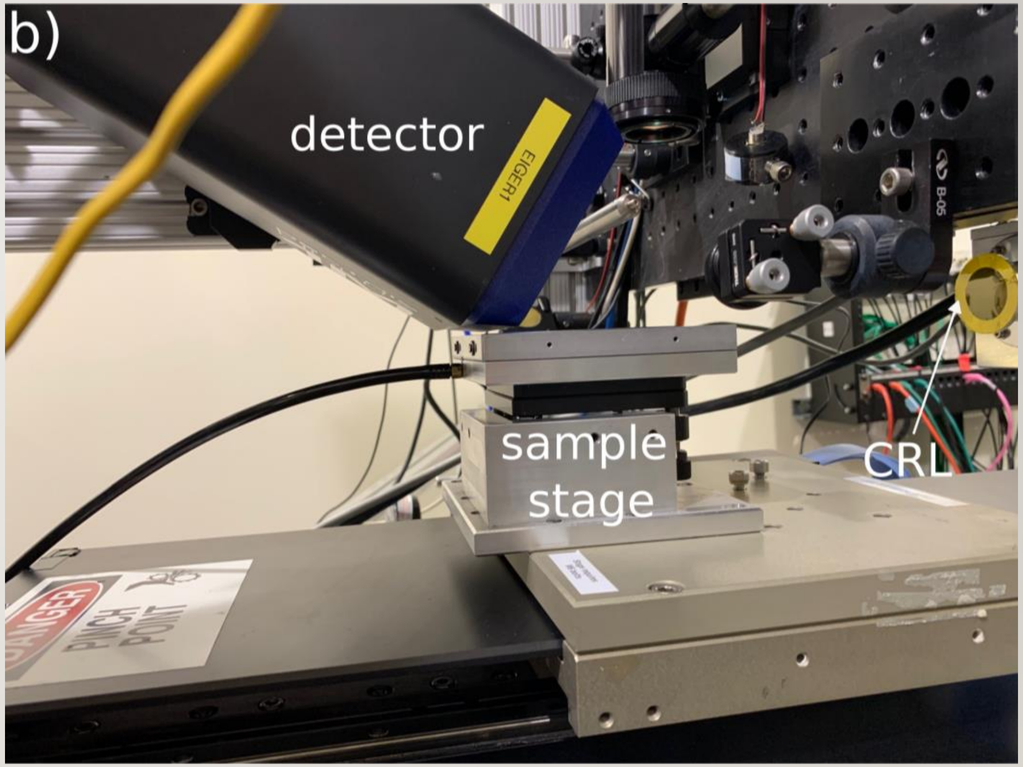


- Wide range of composition…
- Unary, binary, ternary, pseudo-te…

…for
…sing

SPATIALLY RESOLVED GRAZING INCIDENCE XRD



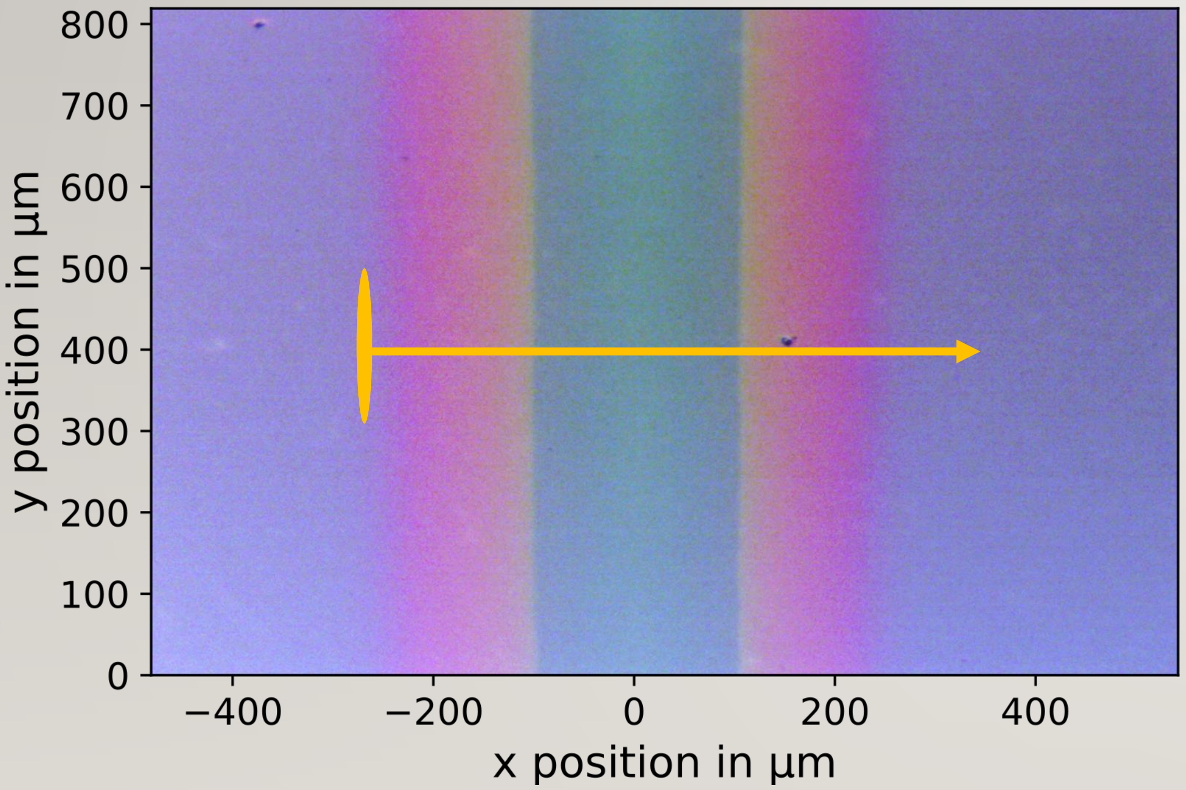


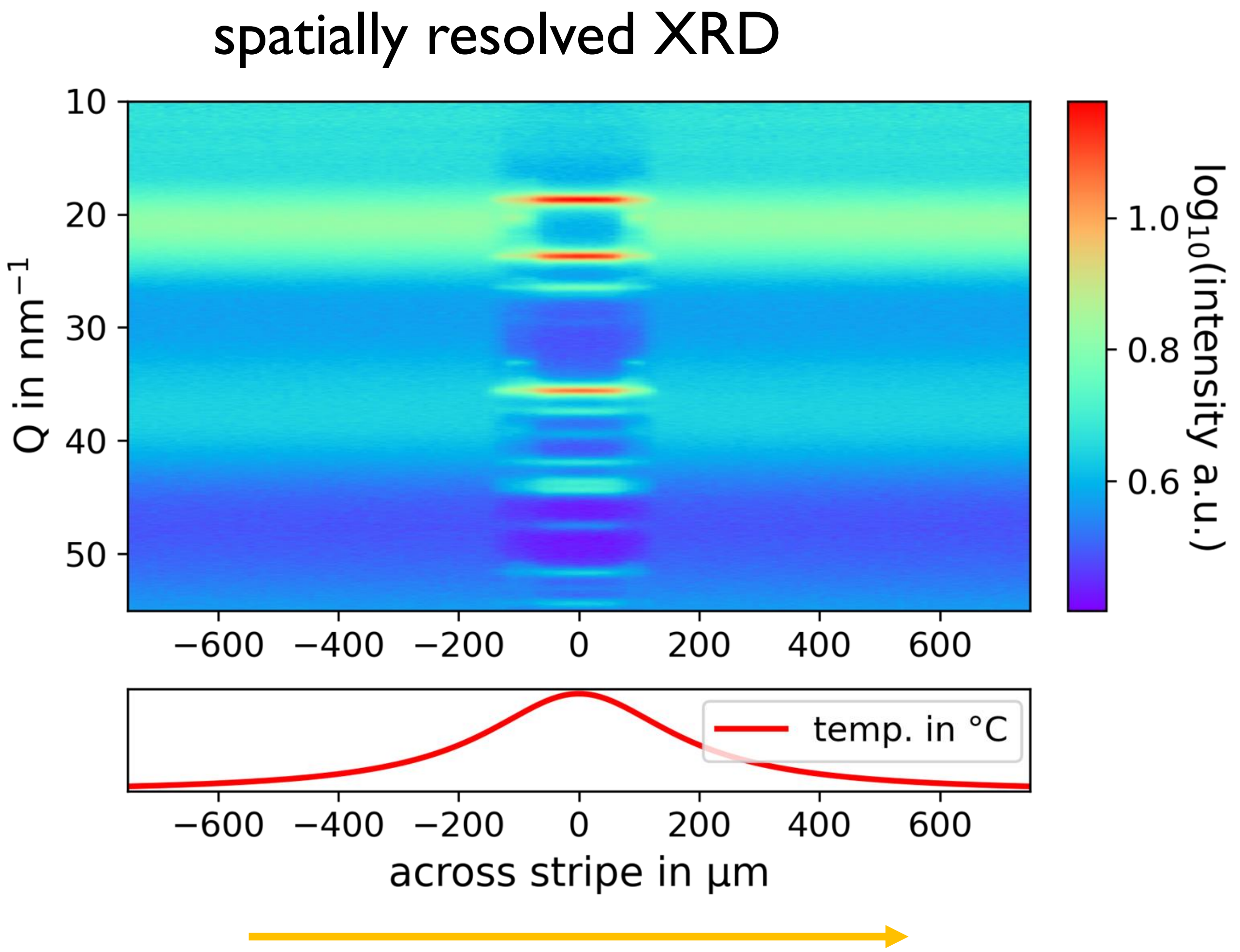
- 10 µm spatial resolution
- Crystallographic information (quantitative phase labeling)
- Synchrotron provides high throughput (50 ms/spectra)

- Generates enormous data ➔ demands fast reduction pipelines

CHESS
CORNELL HIGH ENERGY
SYNCHROTRON SOURCE

COLLECTING SPATIALLY RESOLVED GI XRD

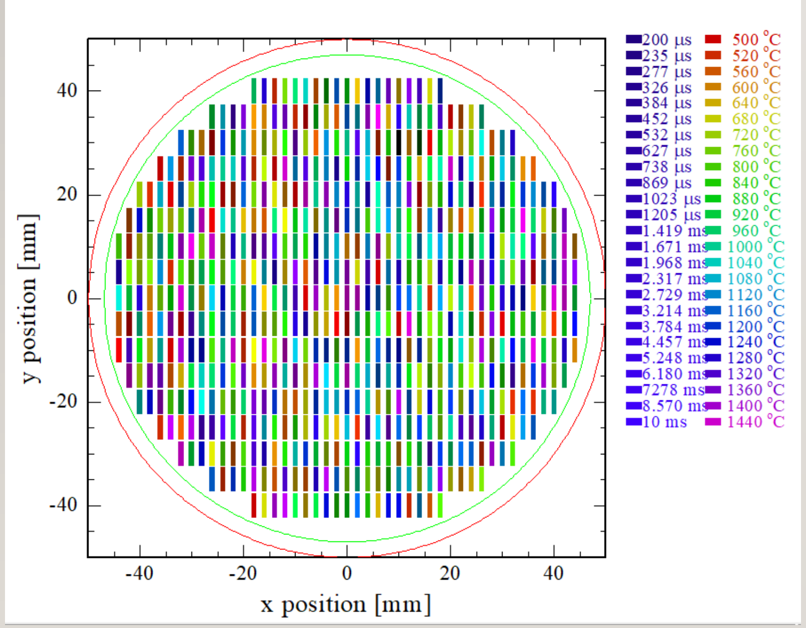


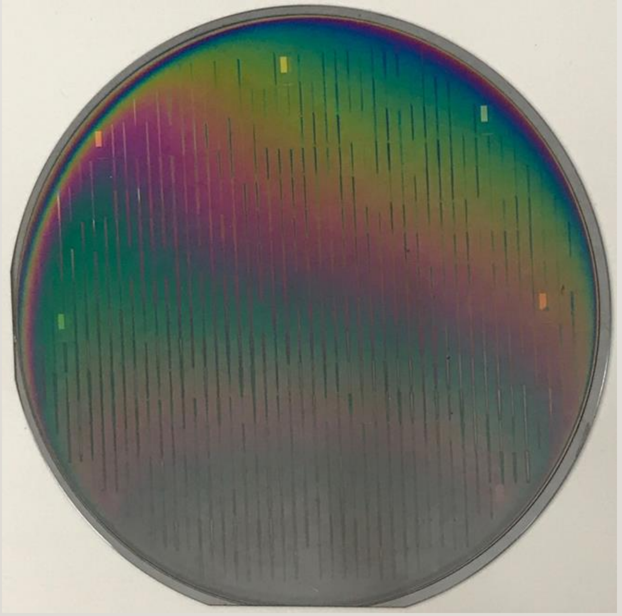


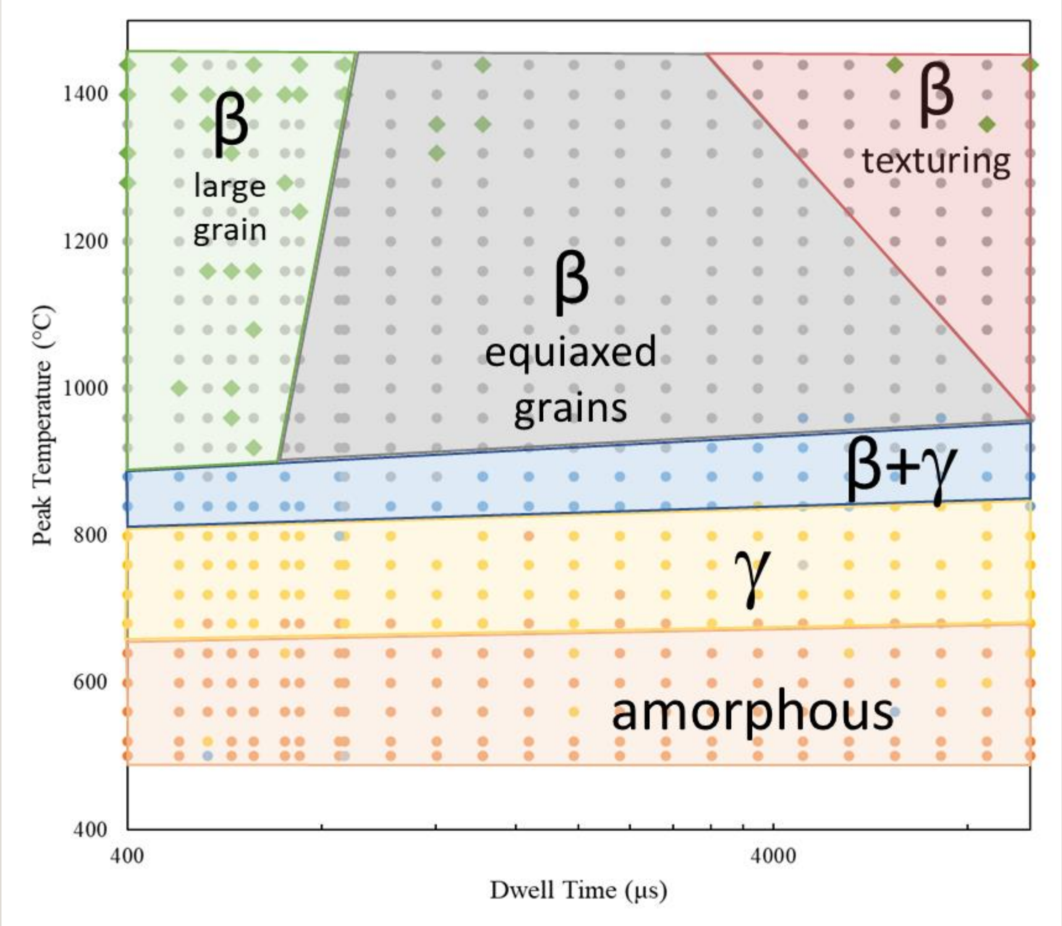
SIMPLE SYSTEMS … EXHAUSTIVE SEARCH … CAN'T EXTEND

- "Full Mesh" experiment:
  - 625 experimental combinations of T_{peak} / τ_{dwell}
  - 500 °C < T_{peak} < 1440 °C
  - 400 μs < τ_{dwell} < 10 ms
- 130,000 X-ray spectra over τ/T space

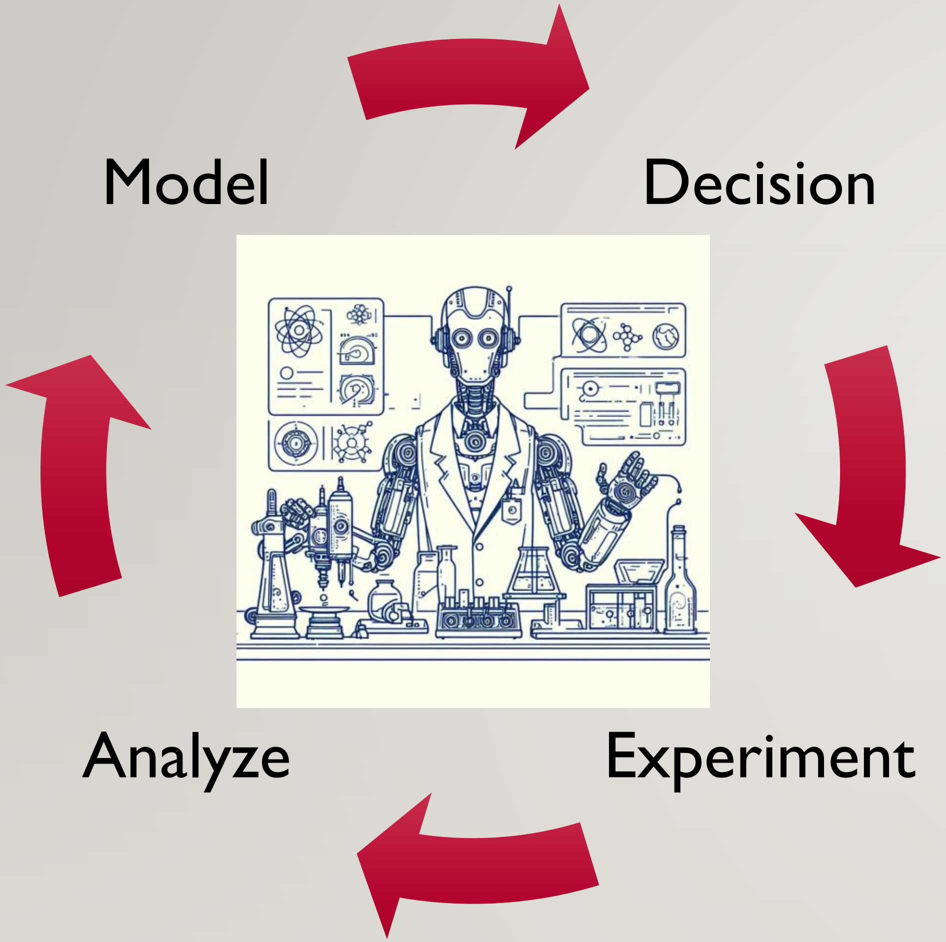
Amorphous Ga_2O_3 on SiO_2

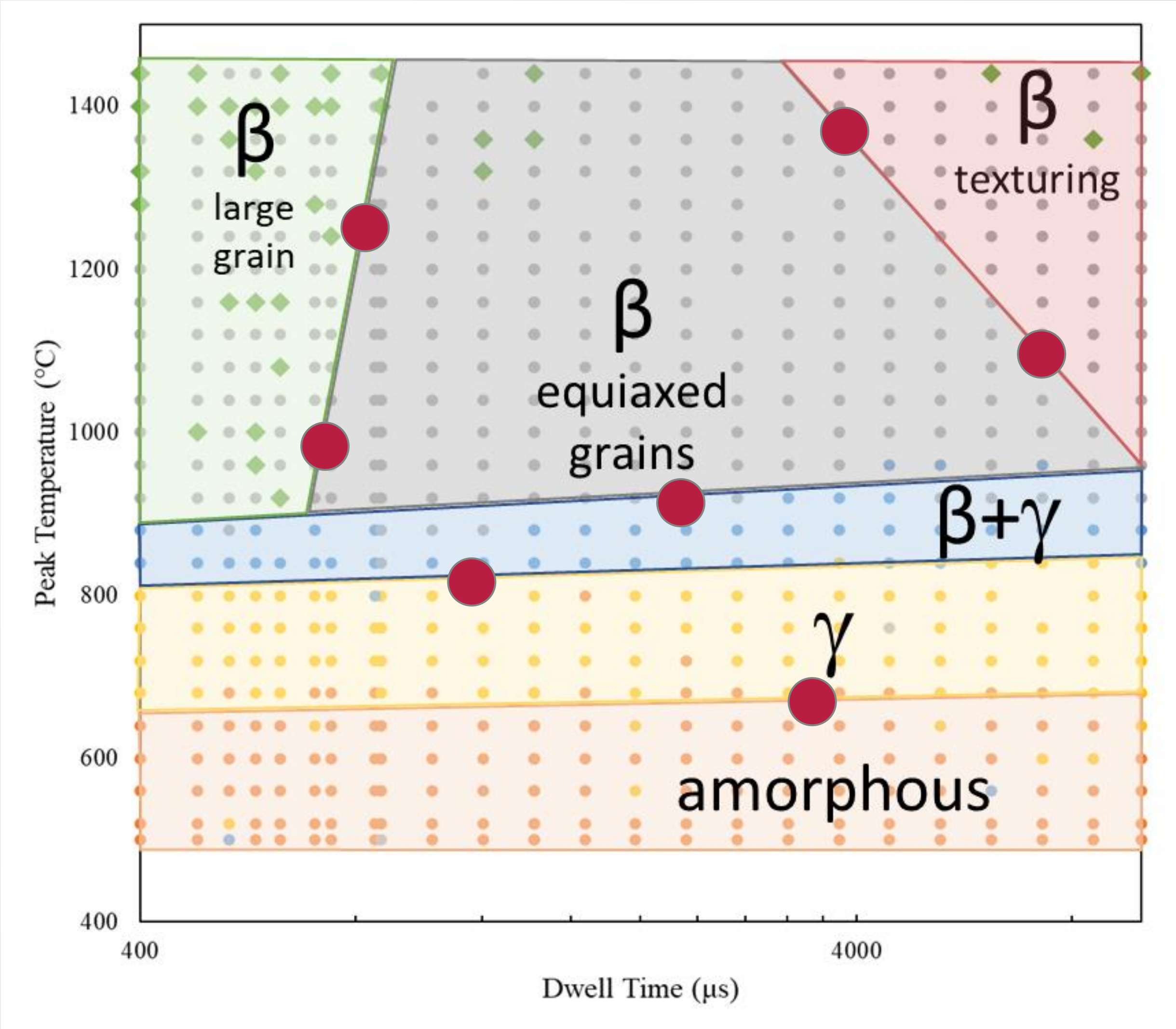






SARA: SCIENTIFIC AUTONOMOUS REASONING AGENT





Incorporating a-priori knowledge and physical constraints in model development

Ament et al., Sci. Adv.7, eabg4930 (2021)

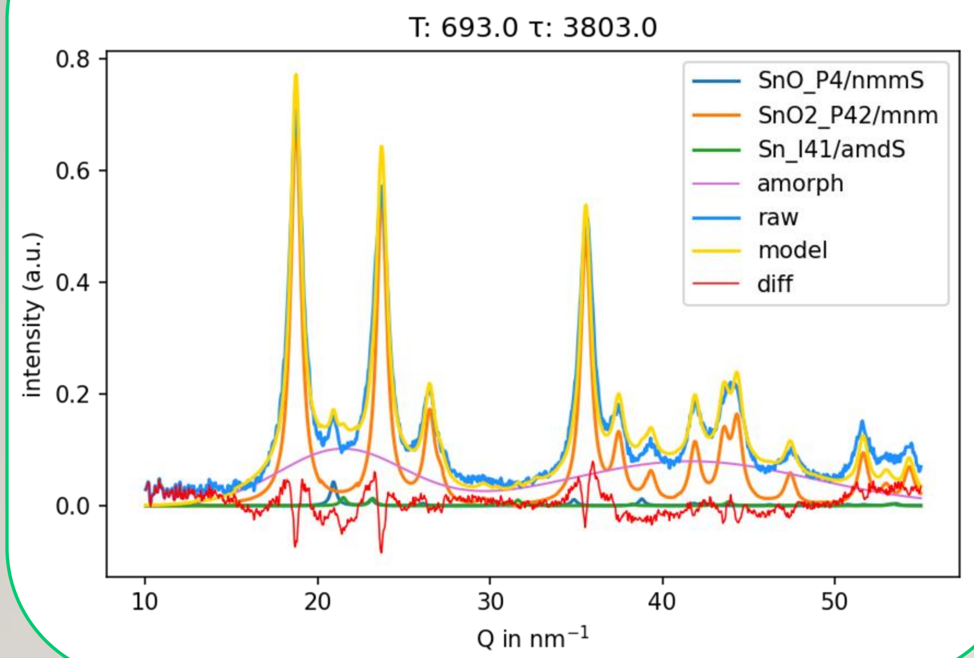
BUILD HARDWARE: FAST-LOOP EXPERIMENTS AT CHESS

Analysis required at comparable pace

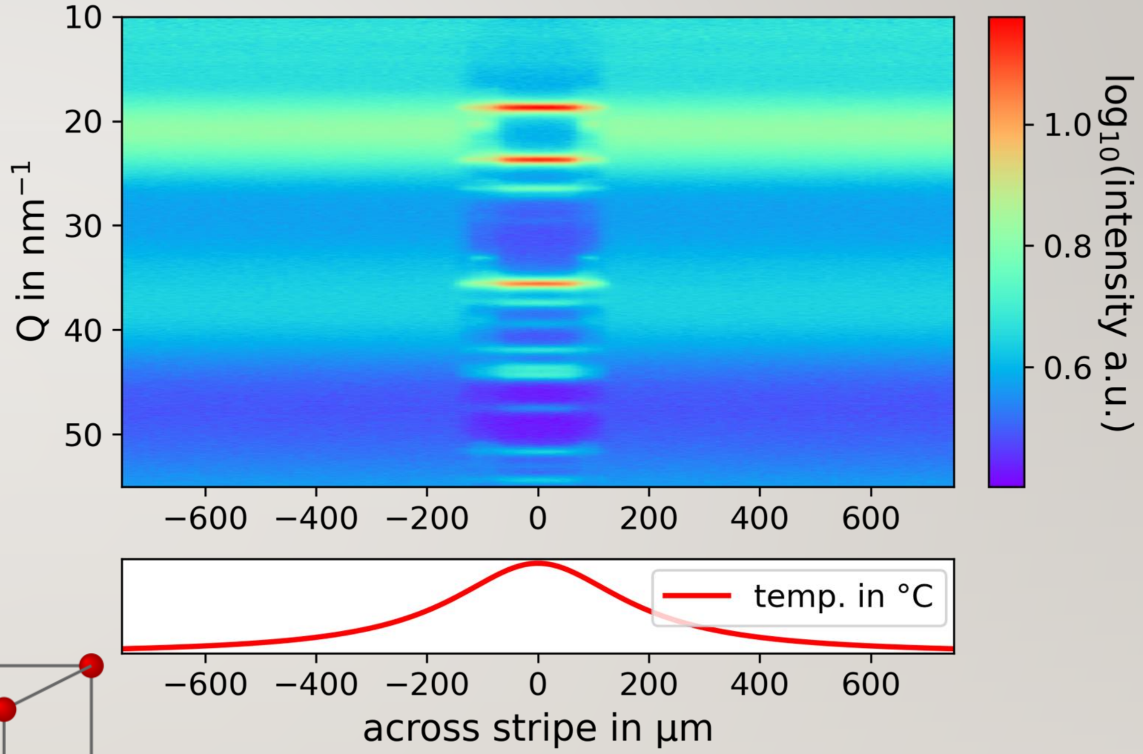
- Synthesis [illegible] including alignment and laser conditioning
- Analysis: 1 [illegible] for 201 X-ray spectra on 10 um centers
- Next experimental conditions needed within 20 seconds to fill pipeline

CRYSTAL SHIFT – RAPID PHASE IDENTIFICATION

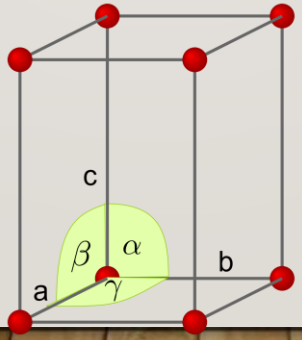
Quantitative Constituent Model



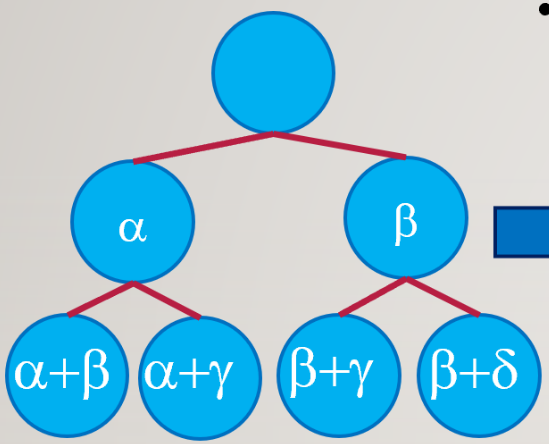
spatially resolved XRD



Ming-Chiang Chang



CRYSTALSHIFT: PHYSICALLY-REALISTIC, PROBABILISTIC LABELING



- Using matching pursuit heuristics

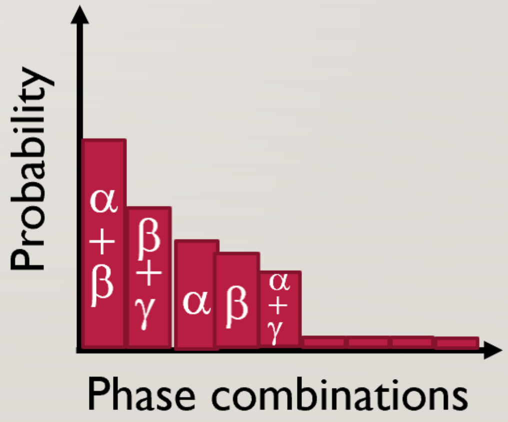
Best-first search algorithm

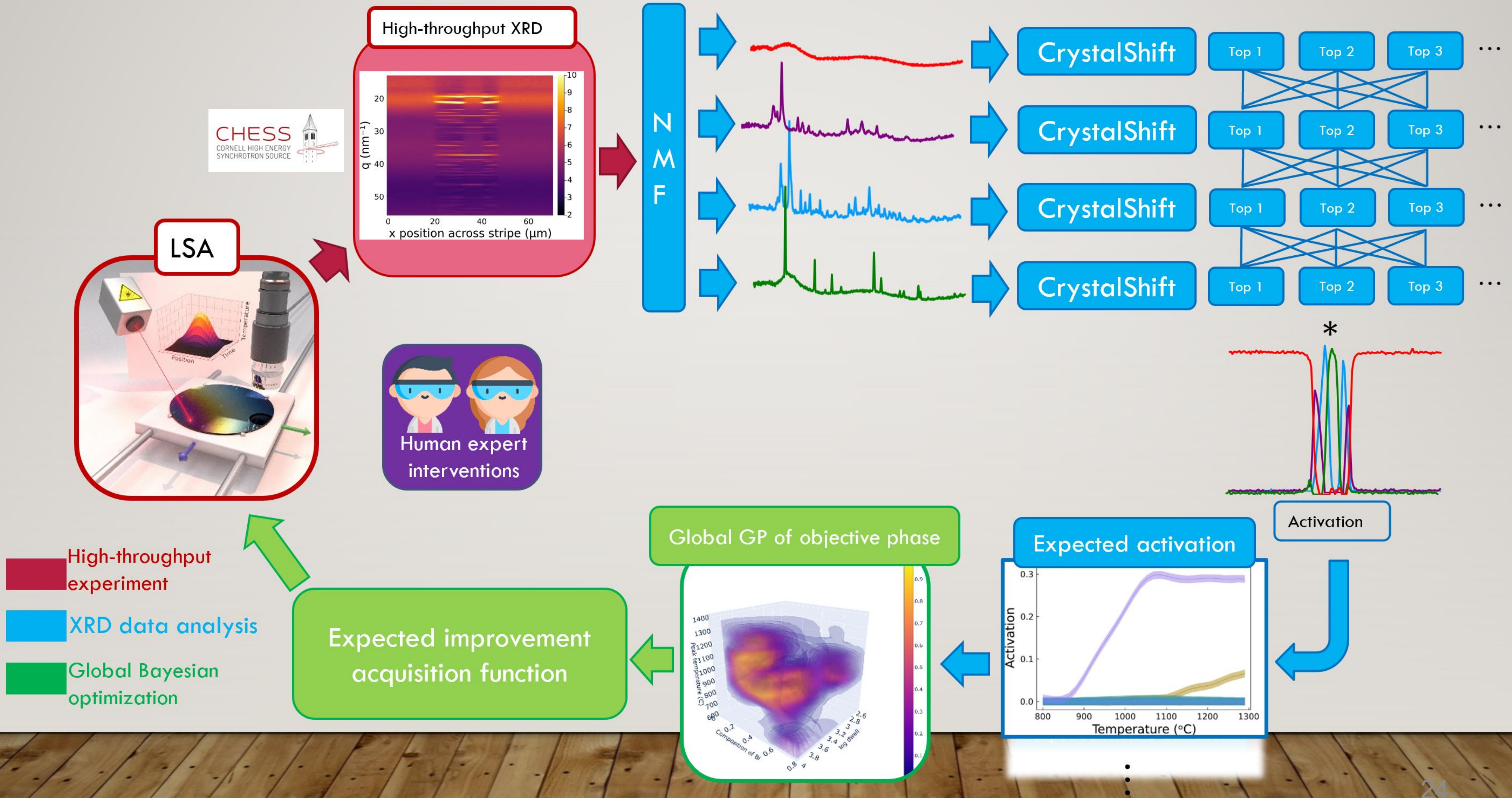
- Regularized LM optimization while preserving symmetry of the phase

Crystallographic-Realistic Optimization

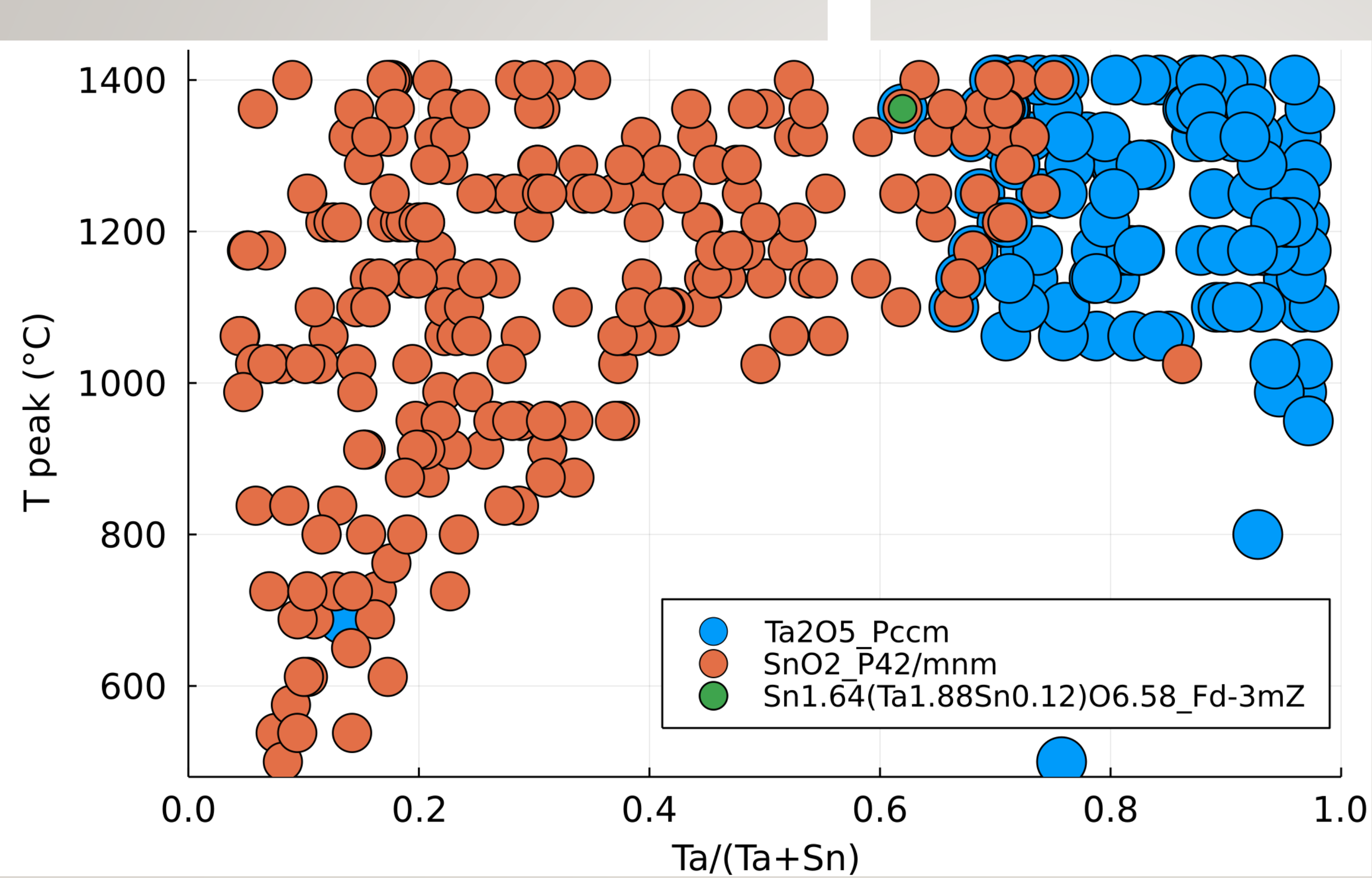
Estimate Probability of Presented Phases

- Based on Bayesian model comparison and Laplace approximation




High-throughput XRD
CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE
q (nm⁻¹)
x position across stripe (μm)
LSA
Position
Time
Temperature
N M F
CrystalShift
Top 1
Top 2
Top 3
Activation
Expected activation
Temperature (°C)
Global GP of objective phase
Peak temperature (°C)
Composition of Bi
log dwell
Expected improvement acquisition function
Human expert interventions
High-throughput experiment
XRD data analysis
Global Bayesian optimization

DOMAIN EXPERTISE … OR GARBAGE IN / GARBAGE OUT

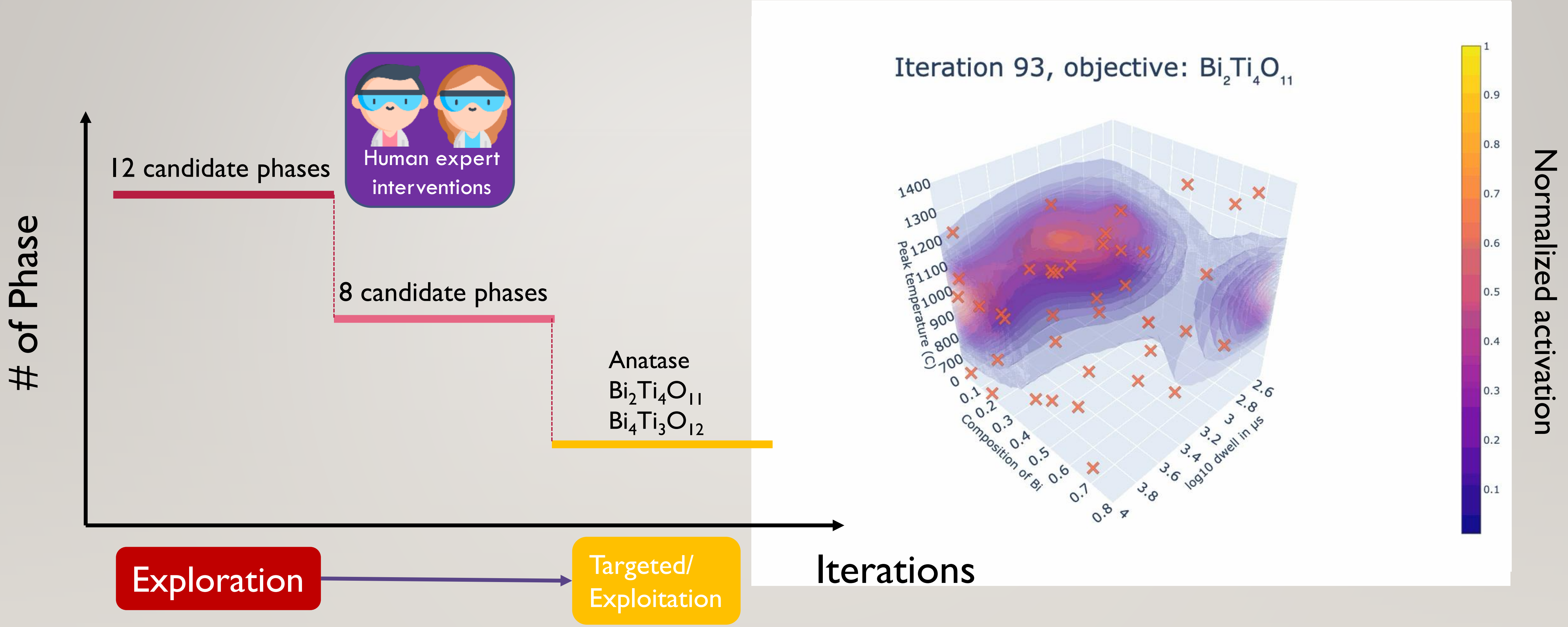


Physics based structural determination in-workflow

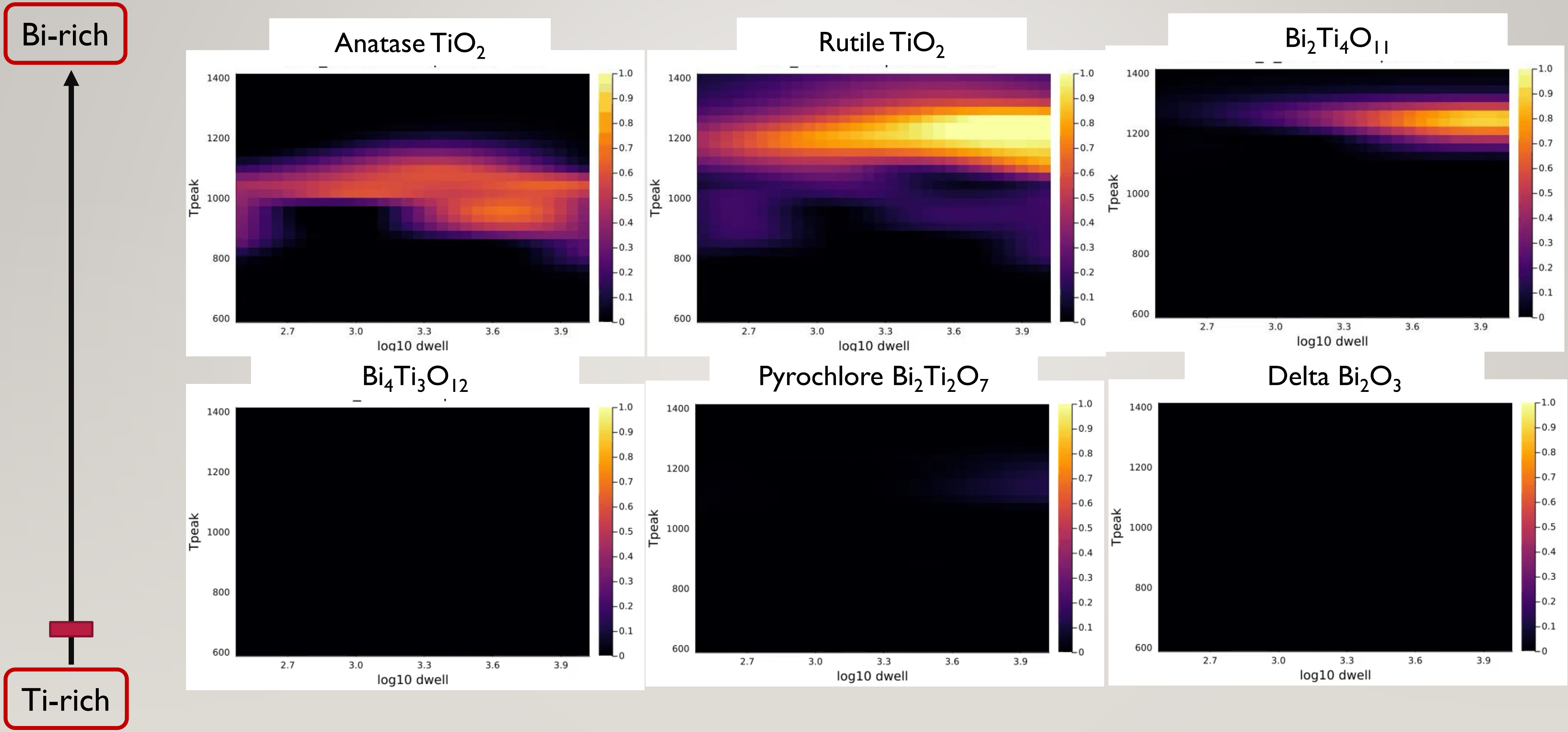
- Scan for mixtures of all known (Materials Project) structures with lattice distortion
- Automatic Processing Phase Diagram Generation

- Using XRD of center position only
- Dwell dependency suppressed from visualization

TARGETED SYNTHESIS IN Bi_2O_3-TiO_2 COMPOSITION SPREAD

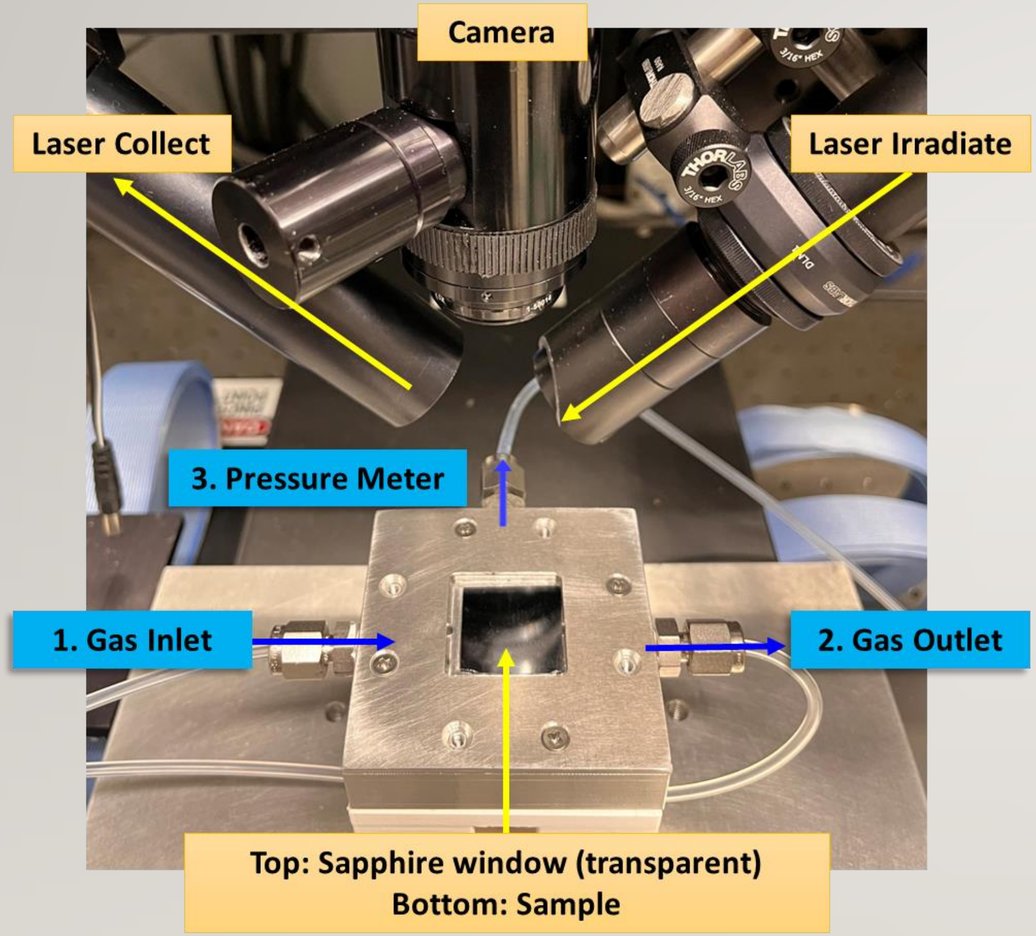


TARGETED SYNTHESIS IN BI_2O_3-TIO_2 COMPOSITION SPREAD



EXPANDING PROCESSING SPACE CONTROLLING GAS PHASE ACTIVITIES

LSA: AMBIENT-CONTROLLED CELL



Cross-sectional schematic of the cell

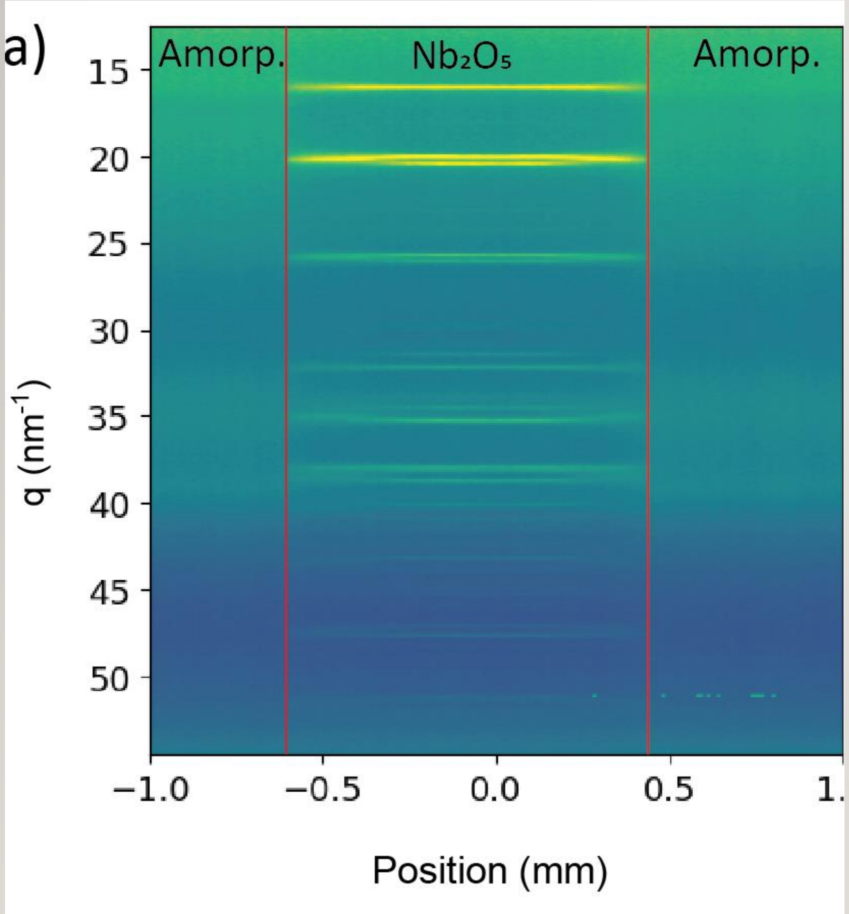
Ambients:

- Controlled p_{O2} / p_{H2O} from 10^{-7} to 1 bar
- Ammonia (ppm to 1 bar)
- Forming gas ($p_{O2} < 10^{-12}$ bar)
- Inert (Ar / He) or vacuum

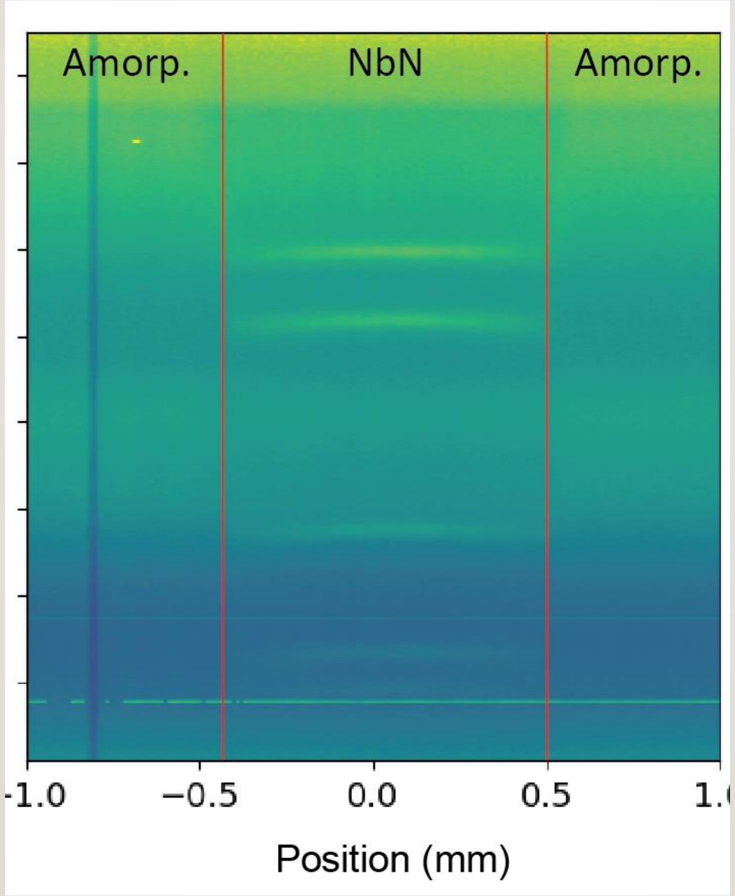
Currently limited to optical in-situ characterization with ex-situ structural and electrical properties

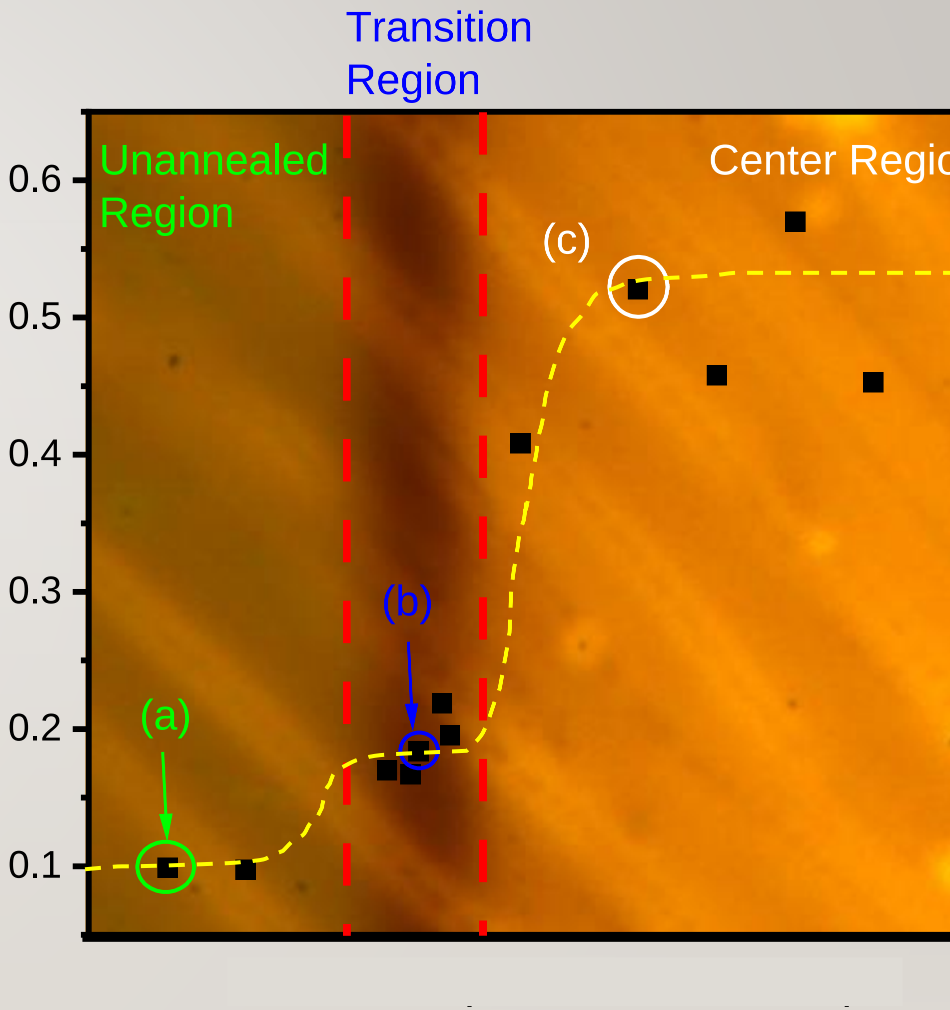
OXIDE TO NITRIDE CONVERSION: Nb_2O_5 TO NbN

1210 °C, 30 ms, Air



1050 °C, 30 ms, NH_3





SYSTEMS STUDIED: EXHAUSTIVELY OR VIA ACTIVE LEARNING

- $Bi2O3$
- $Al2O3$
- $CeO2$
- $Ga2O3$
- $In2O3$
- LaOx
- MnOx
- $MoO3$
- $Nb2O5$
- SnOx
- VOx
- WOx

- La-Mn-O
- Bi-Ti-O
- Ti-Cr-O
- Er-Y-O
- Mn-Ti-O
- Bi-Nb-O
- Bi-Ta-O
- Bi-Cr-O
- Bi-Y-O
- Bi-Zr-O
- Ce-In-O
- Ga-Zn-O
- Mo-Mg-N

- MoN-AlN
- Sb-Ni-O
- Sr-Ti-O
- Ta-Pb-O
- Rh-Pb-O
- Ta-Sn-O
- Ti-Sn-O
- Y-Pd-O
- Zn-Ti-O
- Zr-Si-O

- Al-Ga-In-O
- Al-Ga-Sc-O
- In-Ga-Zn-O (IGZO)
- Bi-V-Cu-O
- Ce-Er-Ta-O
- Er-Co-Cr-O
- La-Mn-Ca-O
- Ta-Sn-Co-O
- Pb-Sn-Bi-Sb-O
- ...and more....

Composition spreads potentially include 130,000 unique (χ, T, τ) XRD patterns on each 4" wafer!

Autonomy reduces the number of scans required to develop / optimize maps

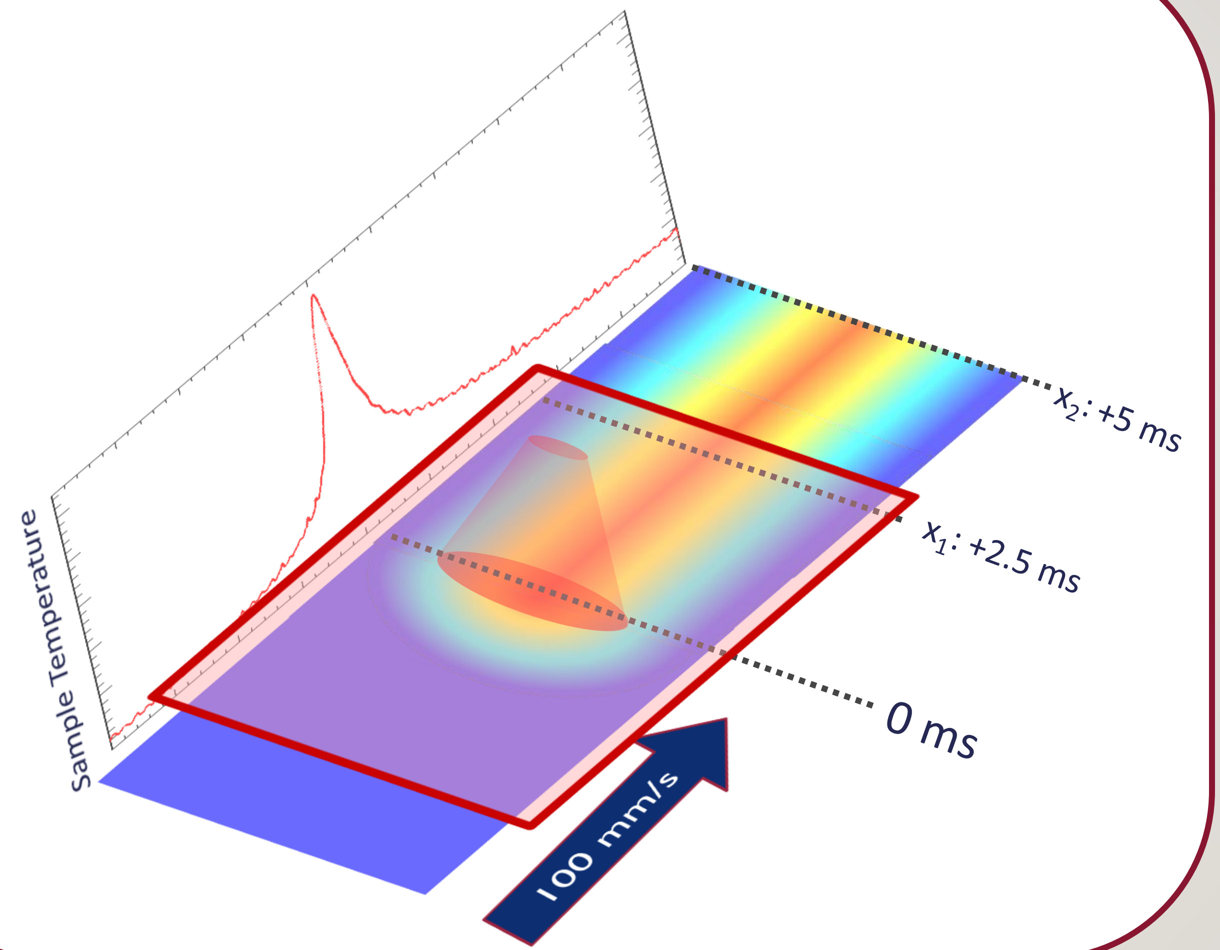
UNDERSTANDING FORMATION KINETICS:

Nucleation/transformation on sub-ms times

Aine Connolly

Katie Gann

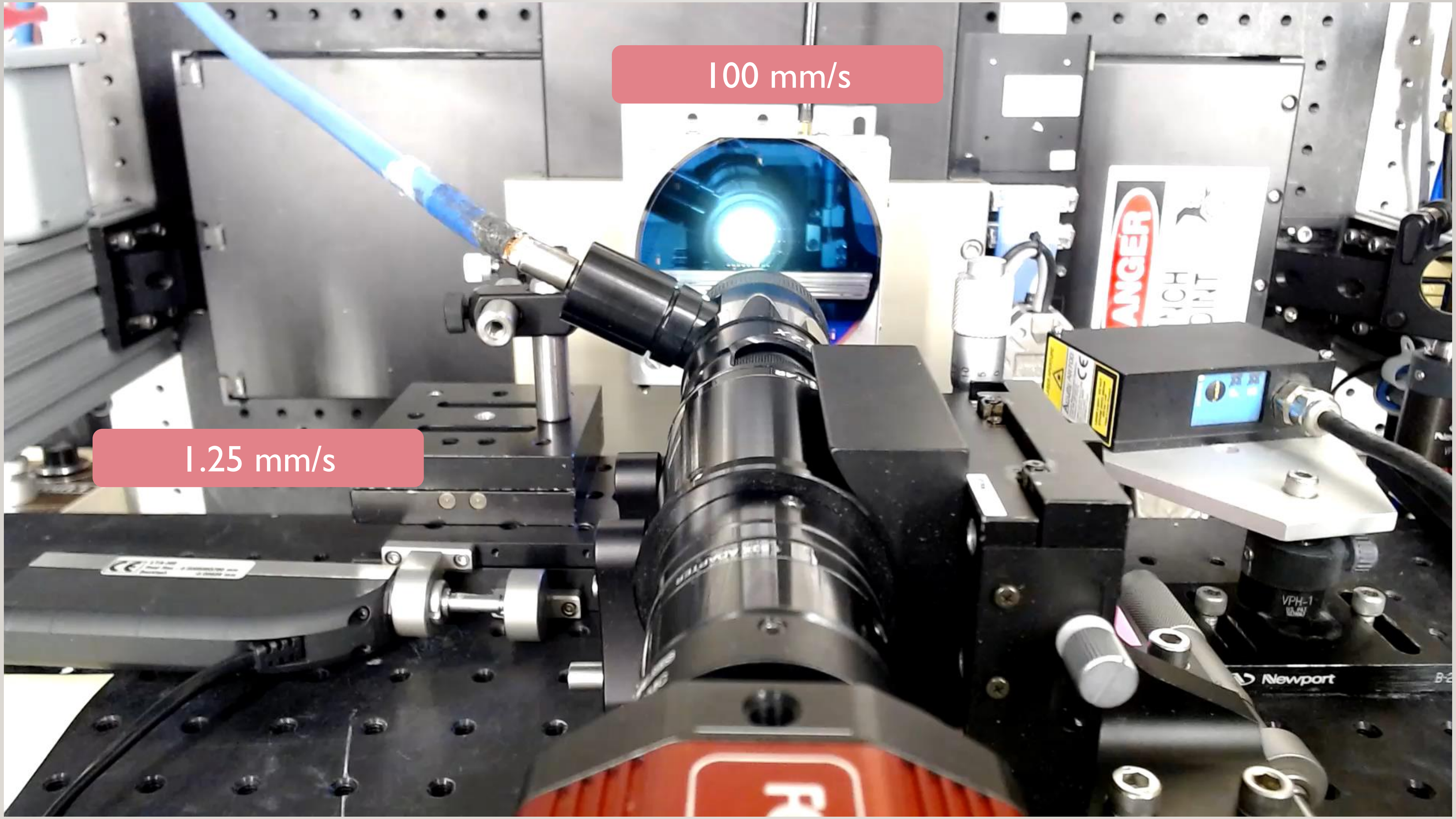
STATIONARY T FIELD ALLOWS TIME-RESOLVED ANALYSIS



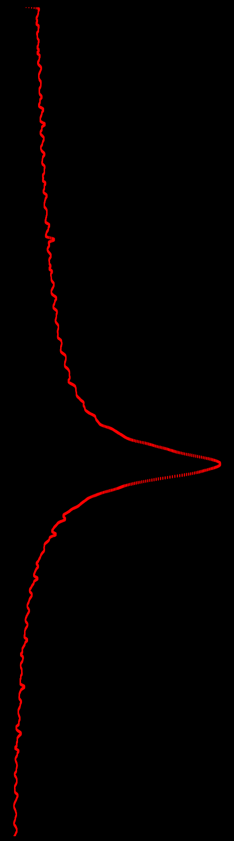
Time is translated to spatial dimension

Distances depend on speed of translation (dwell time of laser)

LIVE VIEW



Post anneal

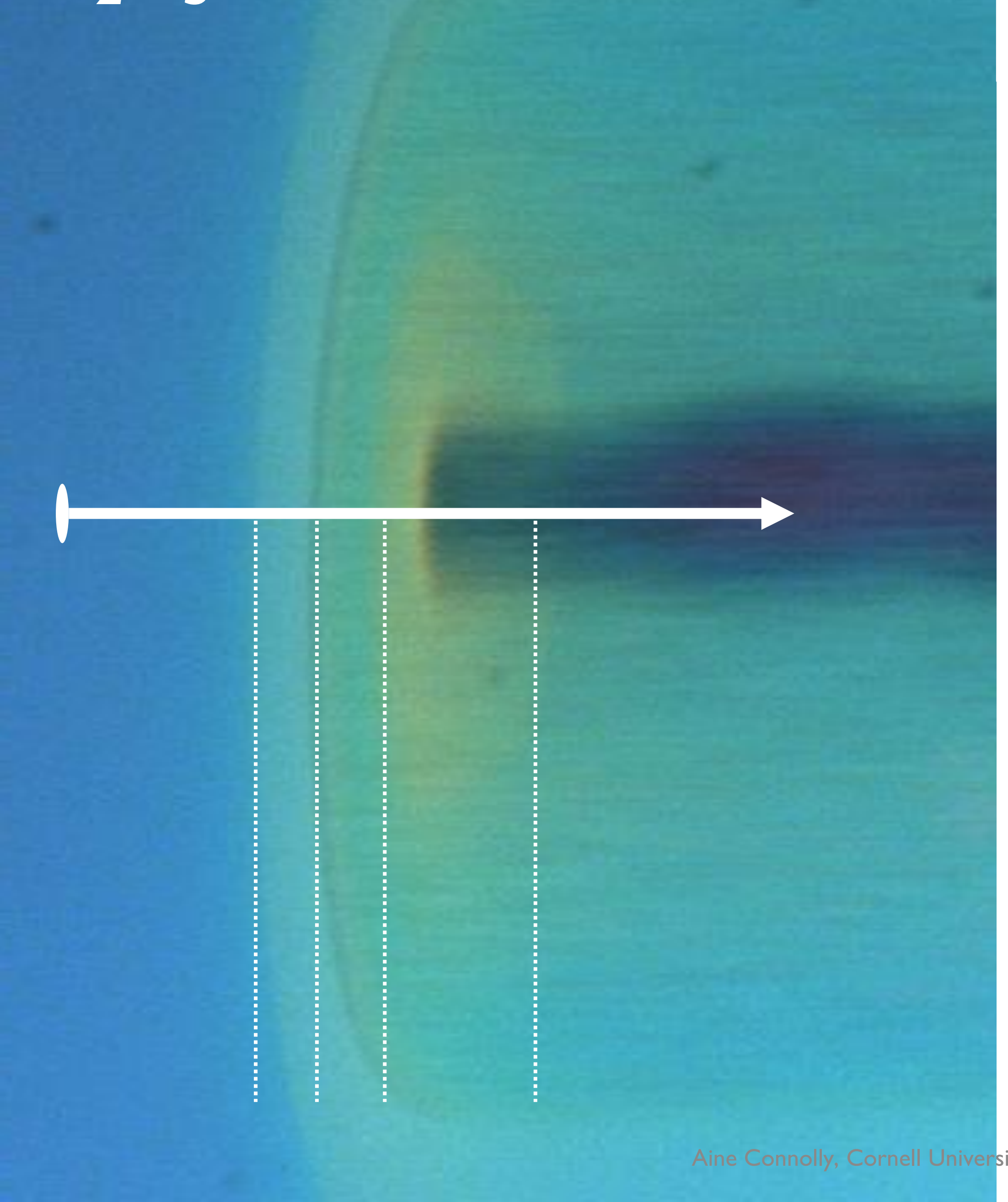


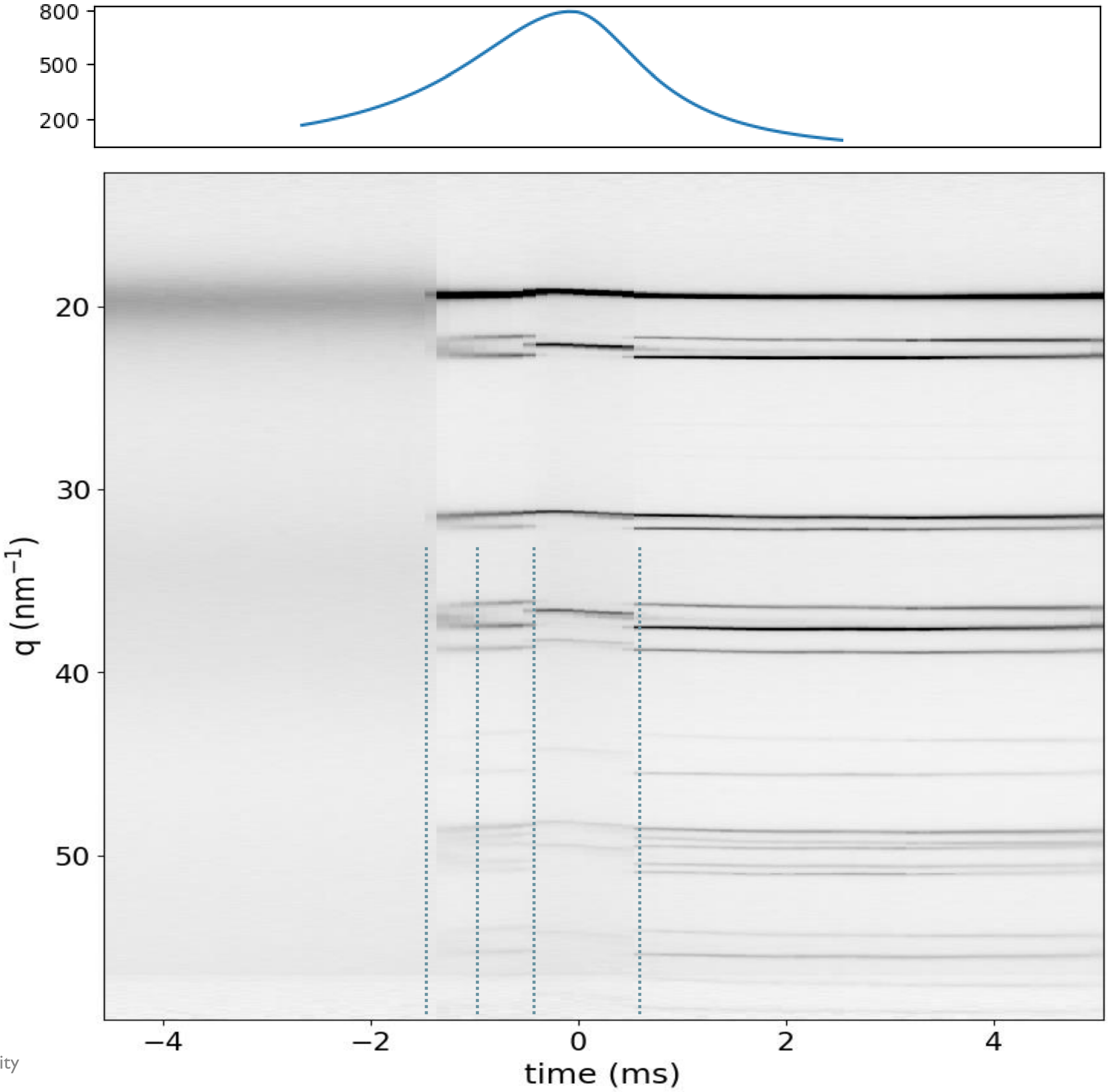
Unheated material

La2O3, 1400C, 40 mm/s

← X-ray spot

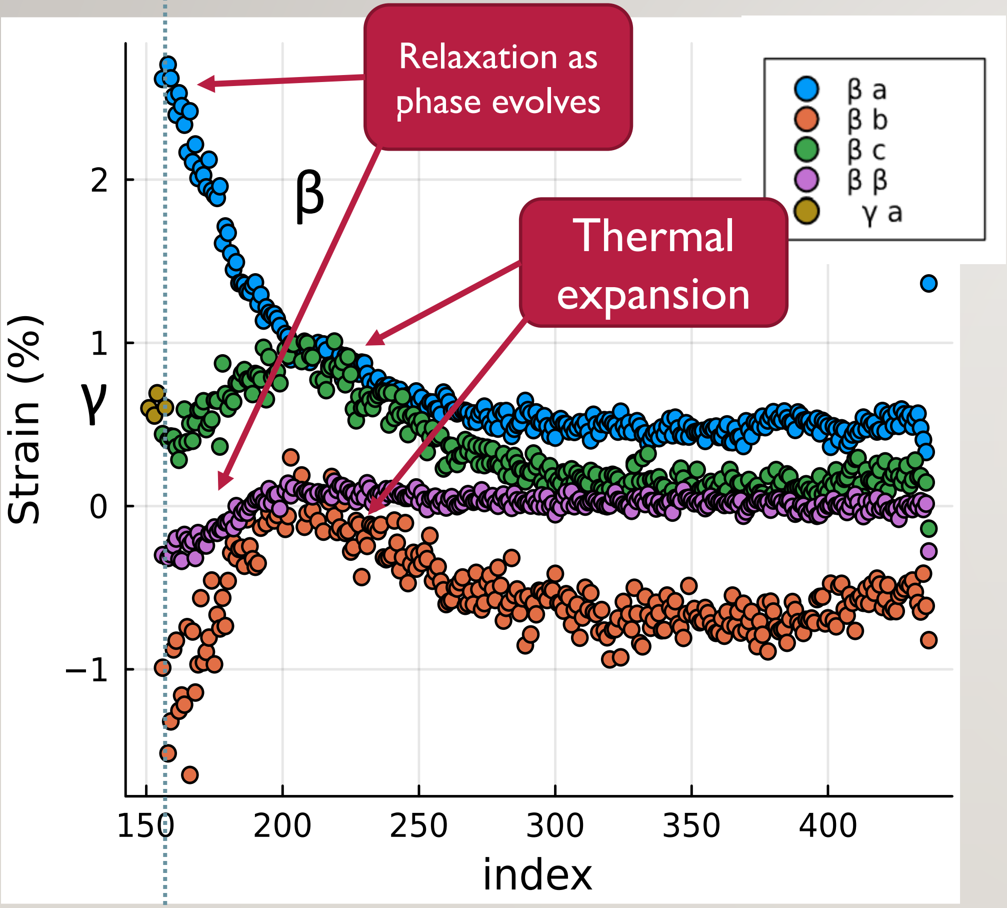
BI_2O_3 – 850 μS / 815 °C

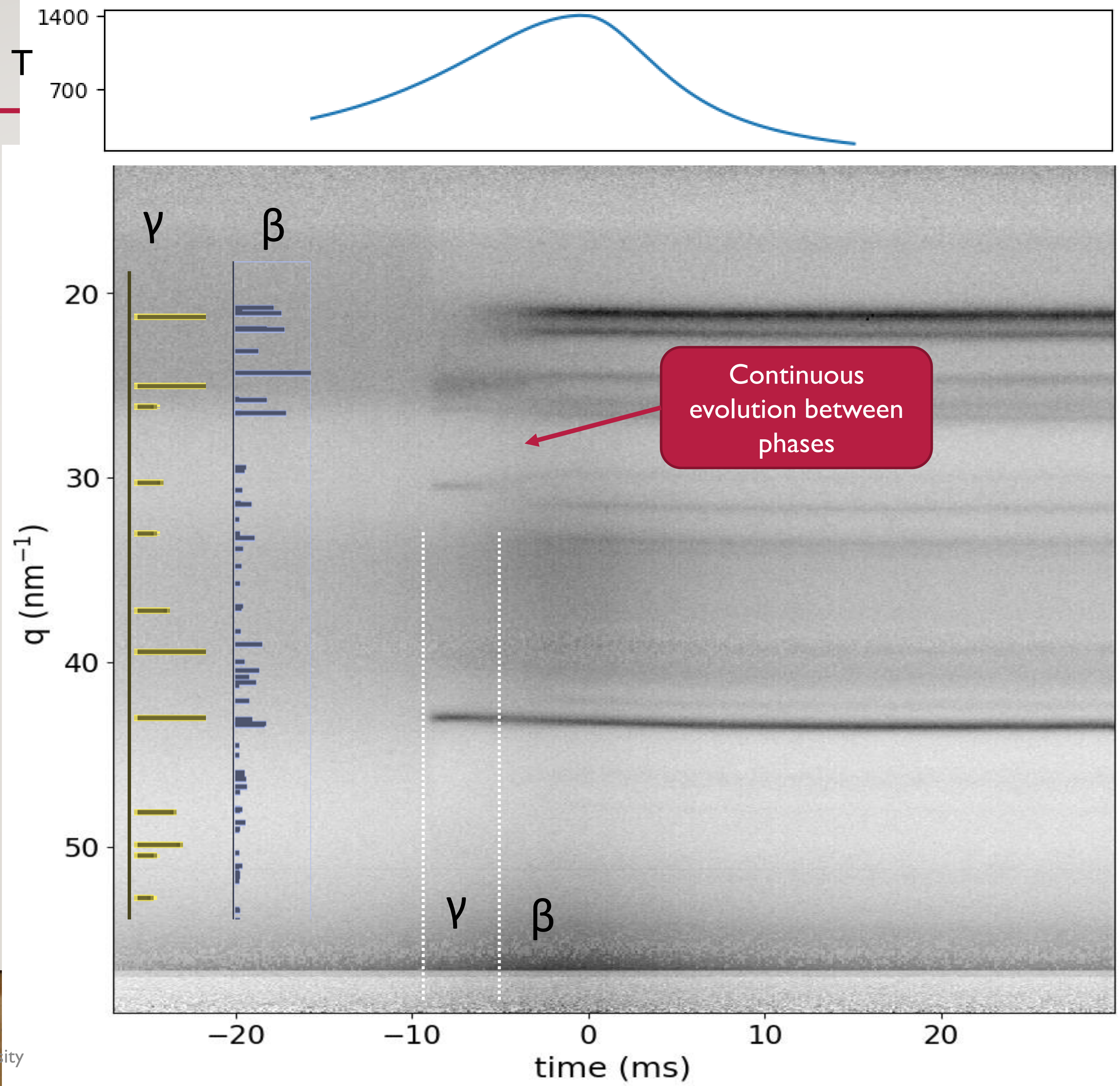




Aine Connolly, Cornell University

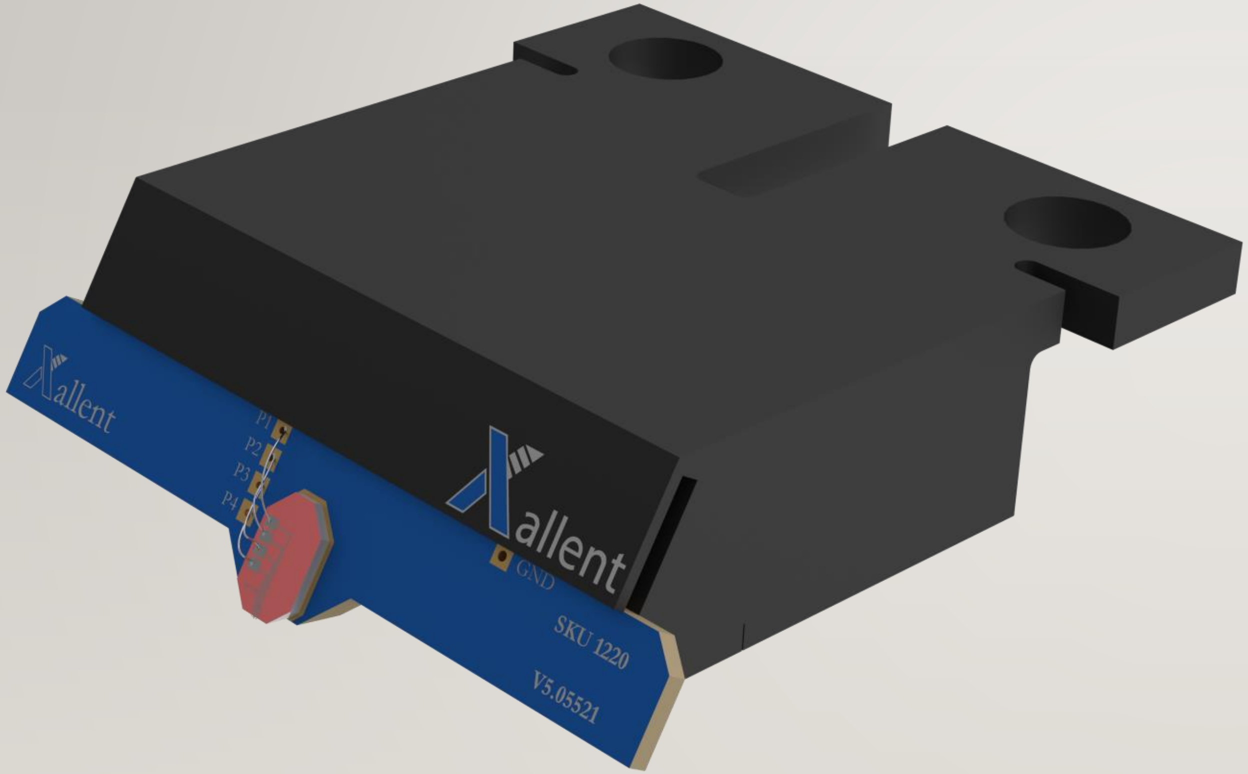
CONTINUOUS TRANSFORMS

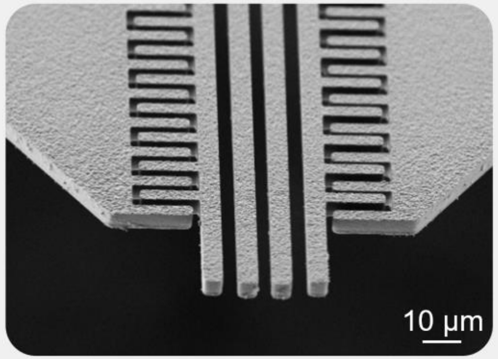




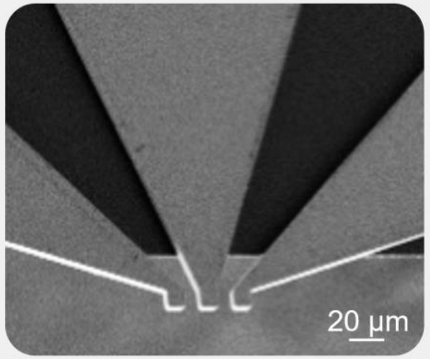
NEXT STEPS: MULTI-MODALITY ELECTRICAL CHARACTERIZATION

XALLENT: IN-SITU MICRO-CHARACTERIZATION

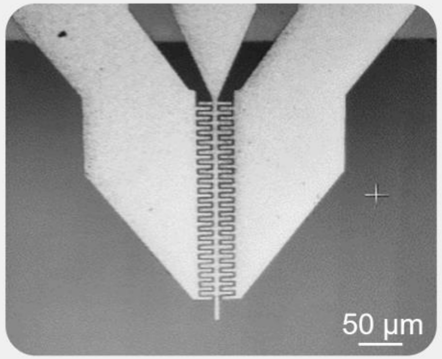




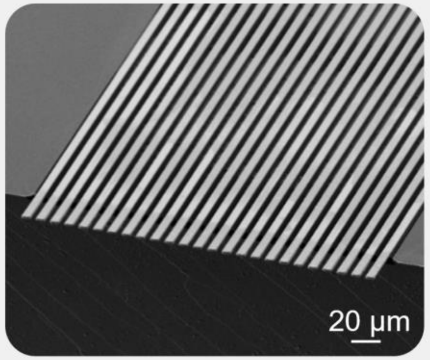
Sheet resistance and resistivity measurements



High frequency testing (DC-40 GHz)

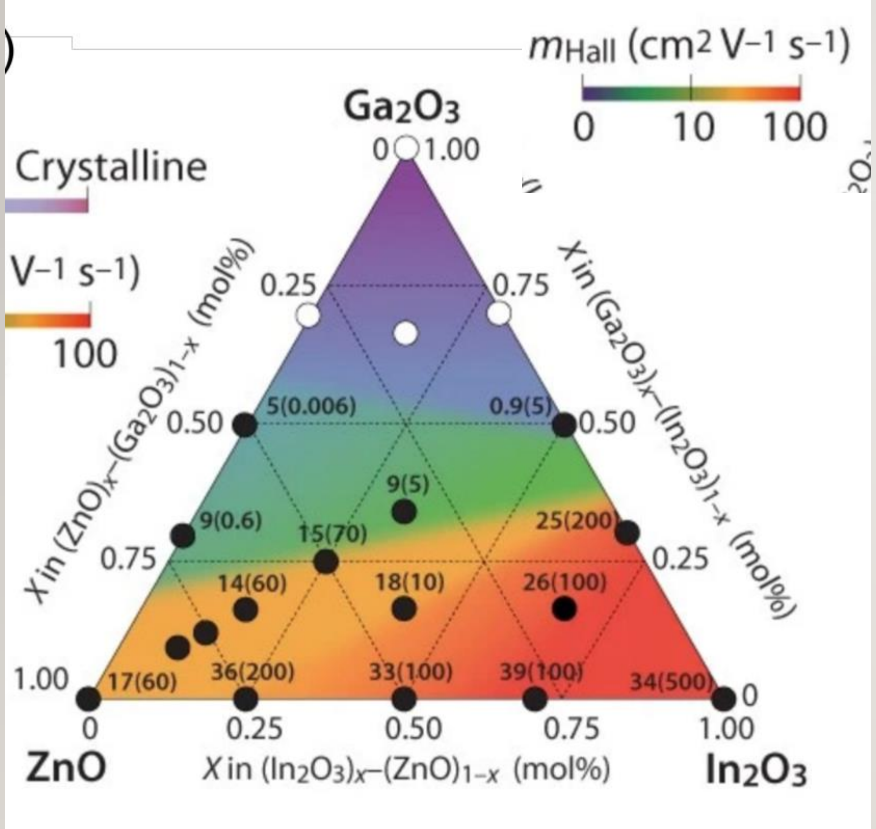


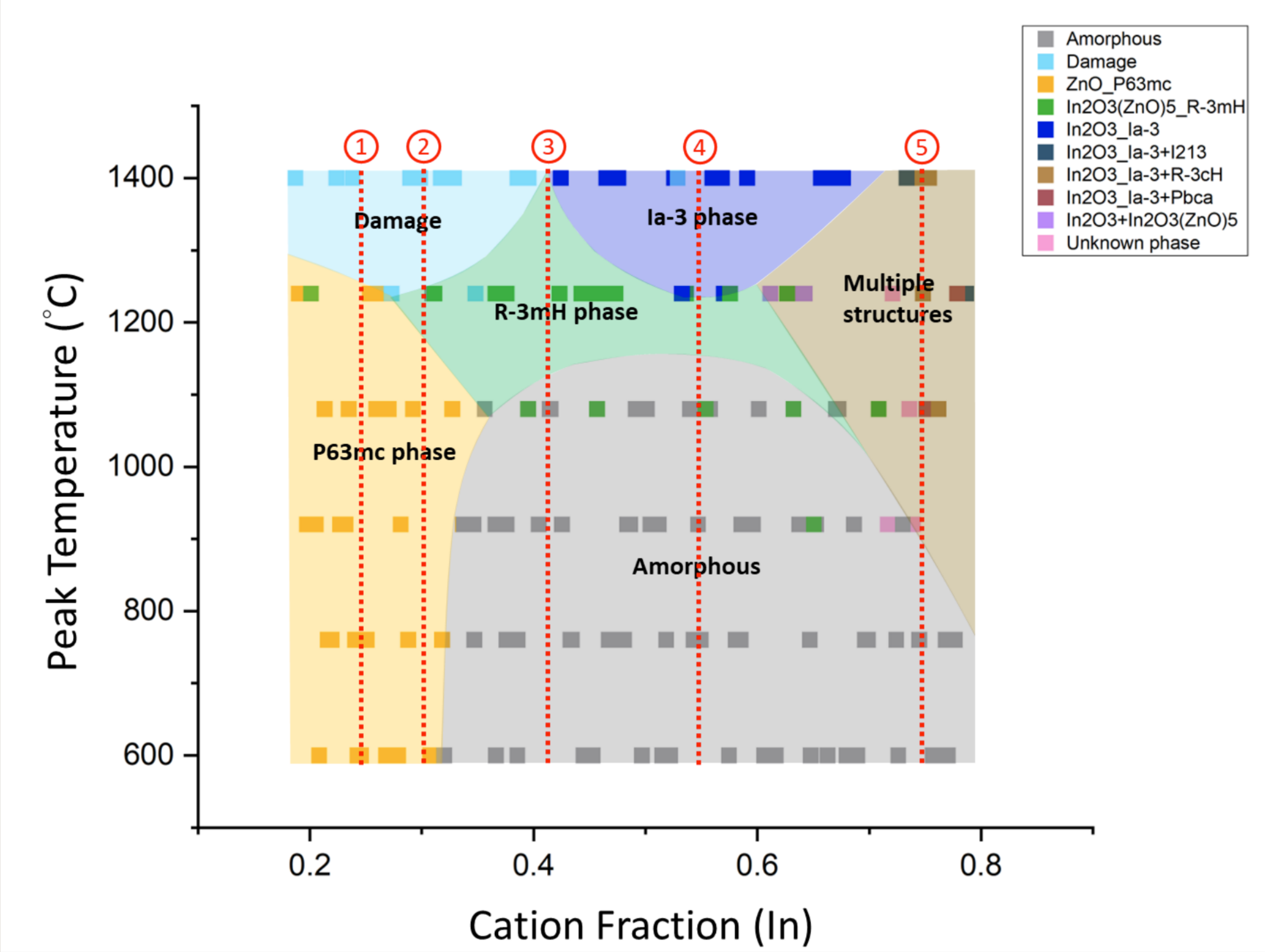
MEMS & NEMS cycle tests



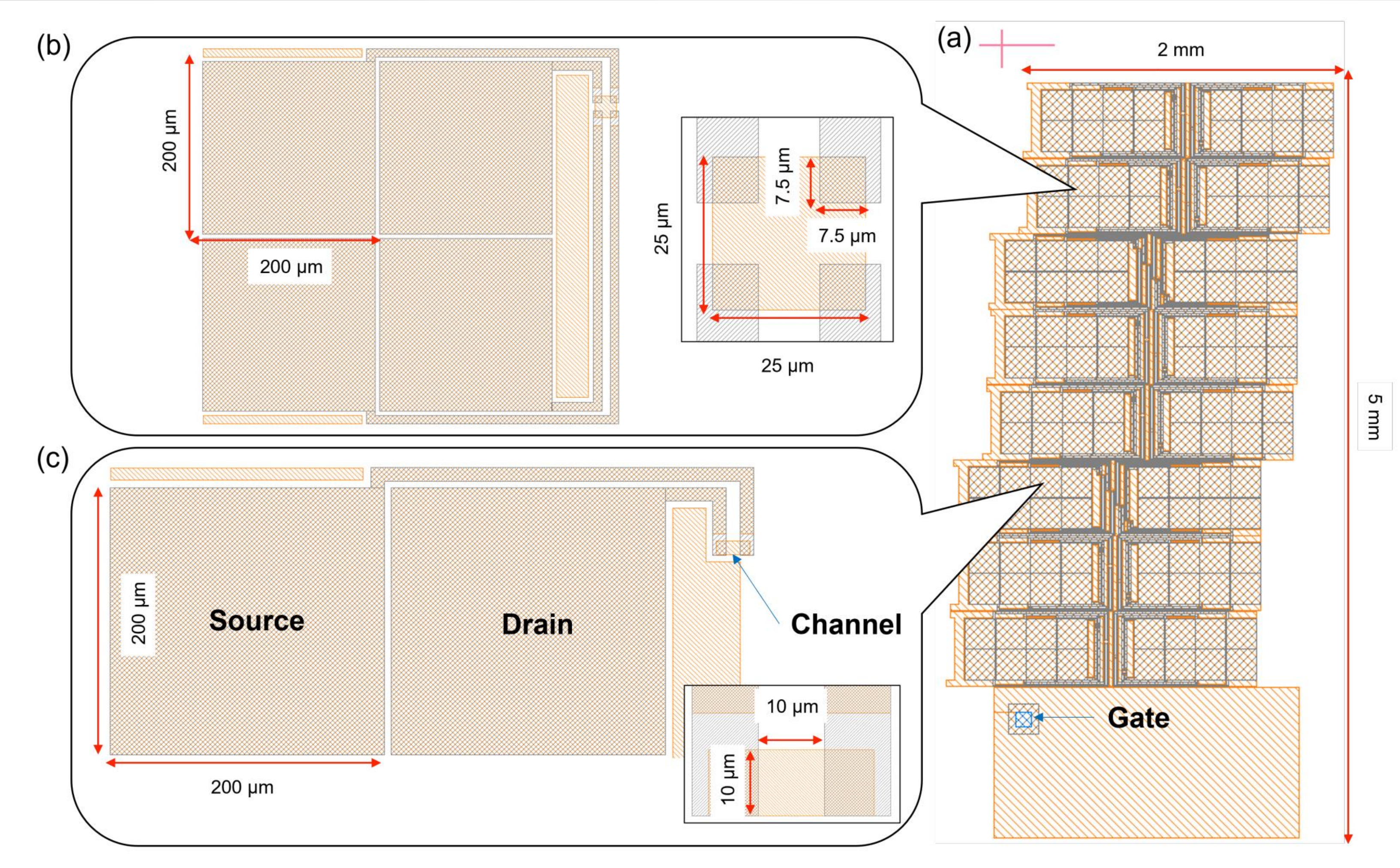
Mini & Micro LED testing

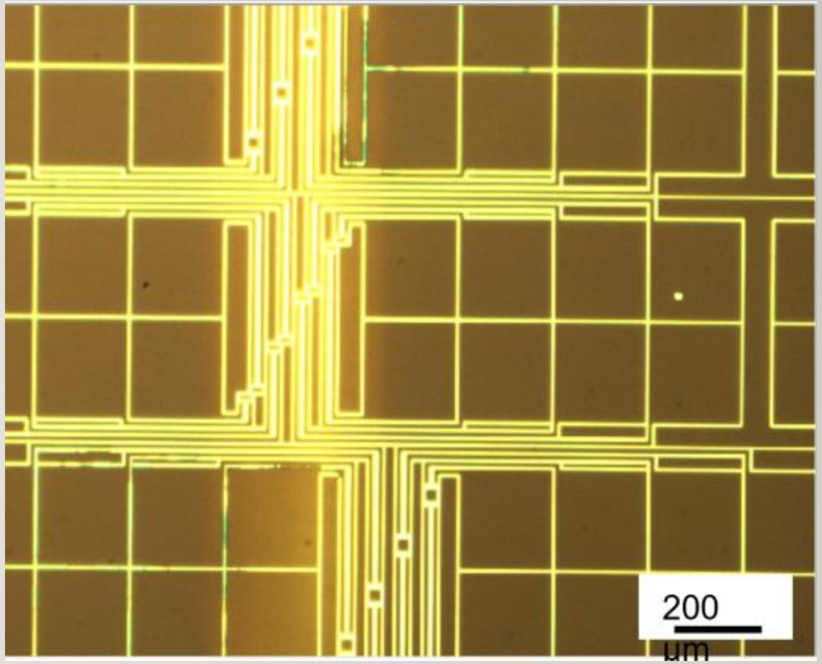
ELECTRICAL OPTIMIZATION IN CRYSTALLIZED IGZO





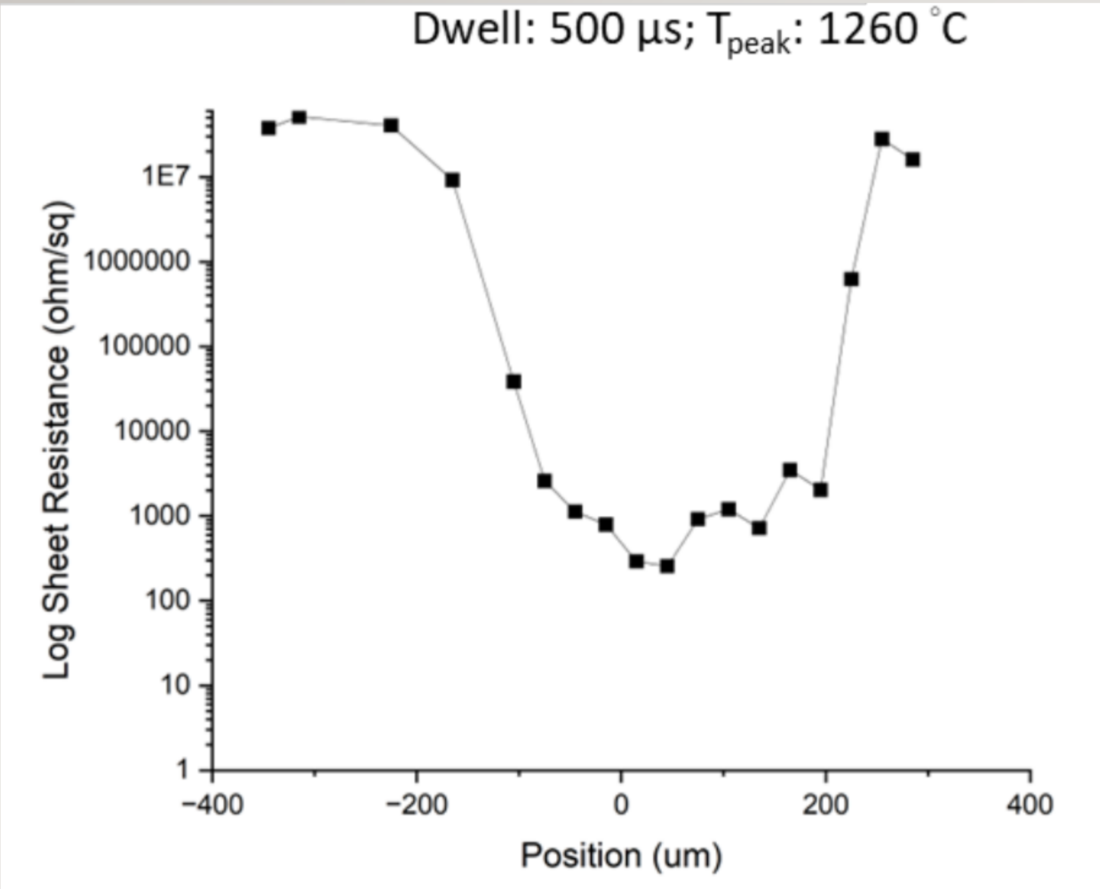
POST-ANNEAL PATTERNING FOR ELECTRICAL PROBES

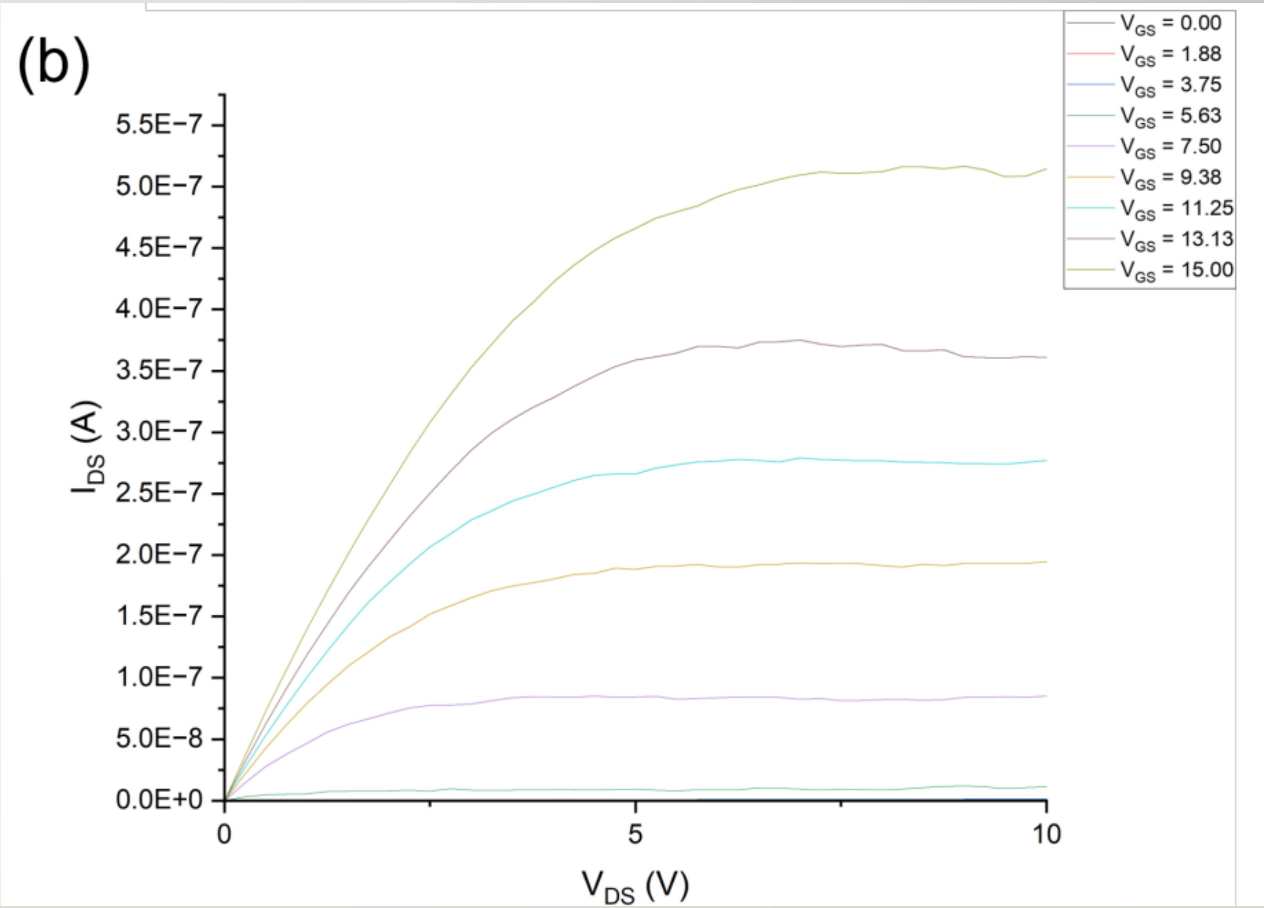




130,000 test conditions per wafer
… AI required

VAN DER PAUW AND TFT CHARACTERIZATION





FINAL THOUGHTS ON HARDWARE DEVELOPMENT FOR AE

DIRECTIONS FOR HARDWARE DEVELOPMENT

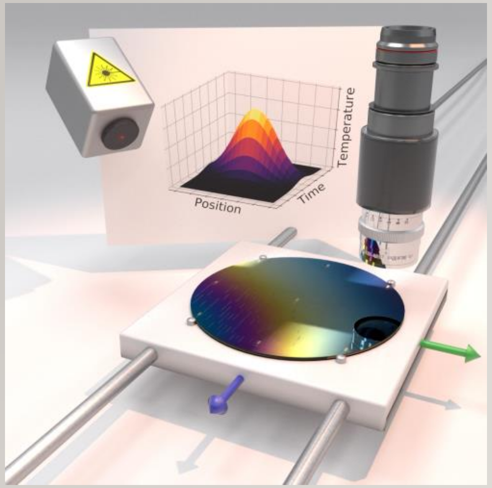
- Need critical mix of large facilities and small group developments
- Intensive design that enables / exploits AI and AE (autonomy)
  - in-operando experimental data acquisition
  - Tightly coupled synthesis and characterization
  - Capture of all available data
  - Development of surrogates for desired experimental objectives
- From conception, focus on metadata for eventual ML extraction
- Challenge of flexible / robust / exhaustive

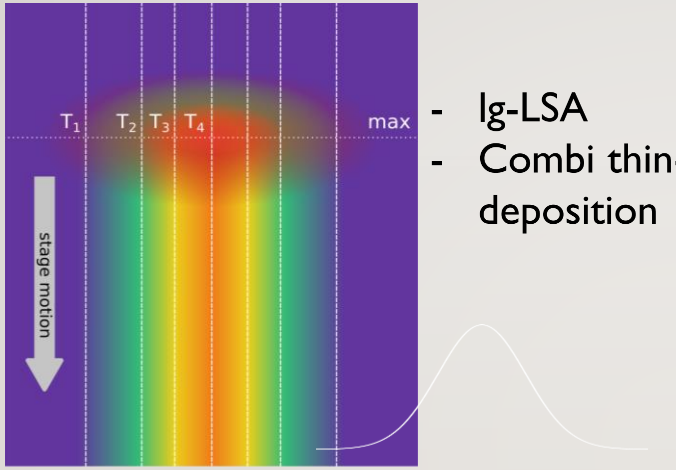
CHALLENGES ON HARDWARE EFFORTS

- Vendors:
  - Access to useful APIs to manage physical hardware
  - Paradigm shift from "solution" to "controllable platform"
- Experimental:
  - Need for well-structured metadata on synthesis and characterization
  - Well-defined set of descriptors for ML w/ flexibility for multiple lab/expertise and next modality
- Data explosion … practical issues of retaining all data acquired
  - Multiple TB per sample not sustainable with autonomy, but failures as valuable as successes
- Transferability
  - Hardware normally customized to experiment and facilities
  - How to retain expertise and capabilities
- Cost … and time …

SUMMARY

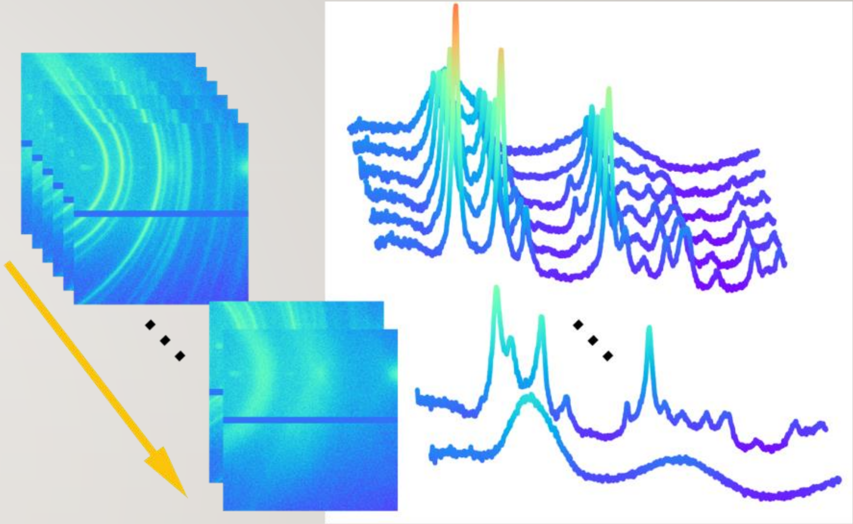
High Throughput combinatorial synthesis





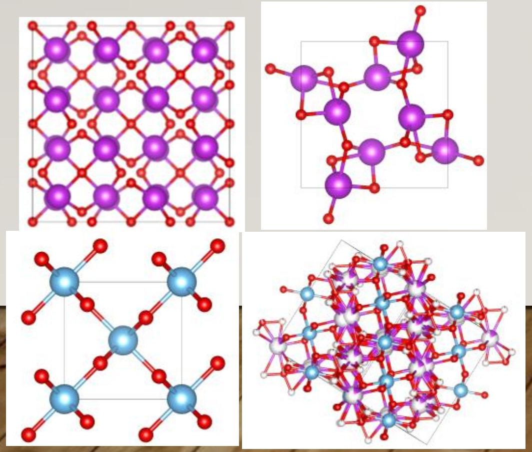
- lg-LSA
- Combi thin-film deposition

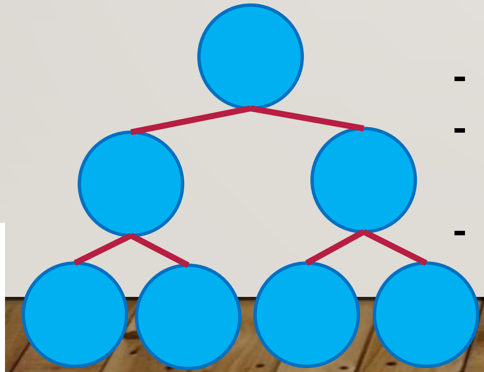
High Throughput Synchrotron XRD



Fast Quantitative Phase Determination

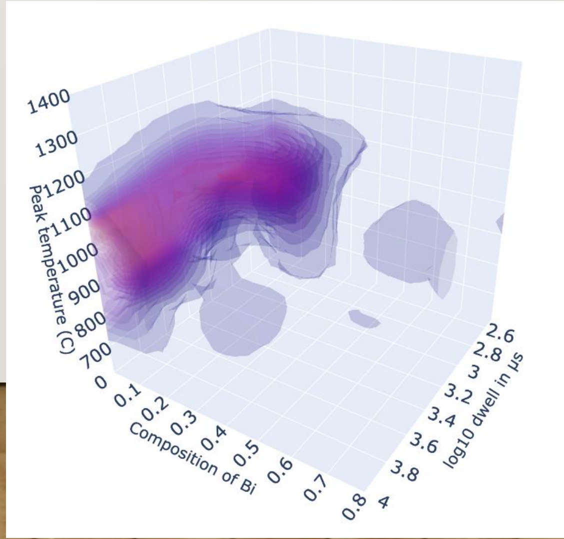
CIFs of Candidate Phases

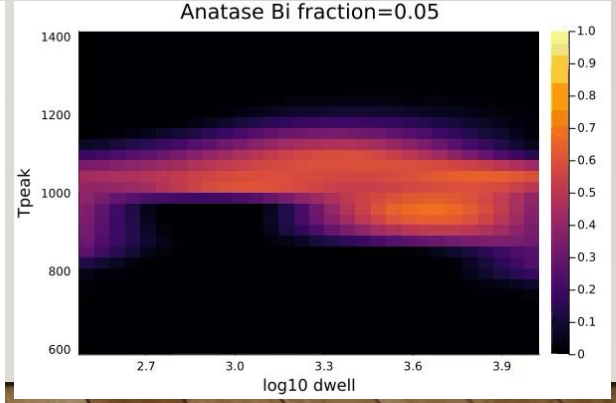




- Probabilistic
- Pseudo-refinement
- Fast

Active Learning on phase data





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