

Overview of Powder Diffraction at the APS and examples from the High-Resolution pXRD Beamline 11-BM

2012

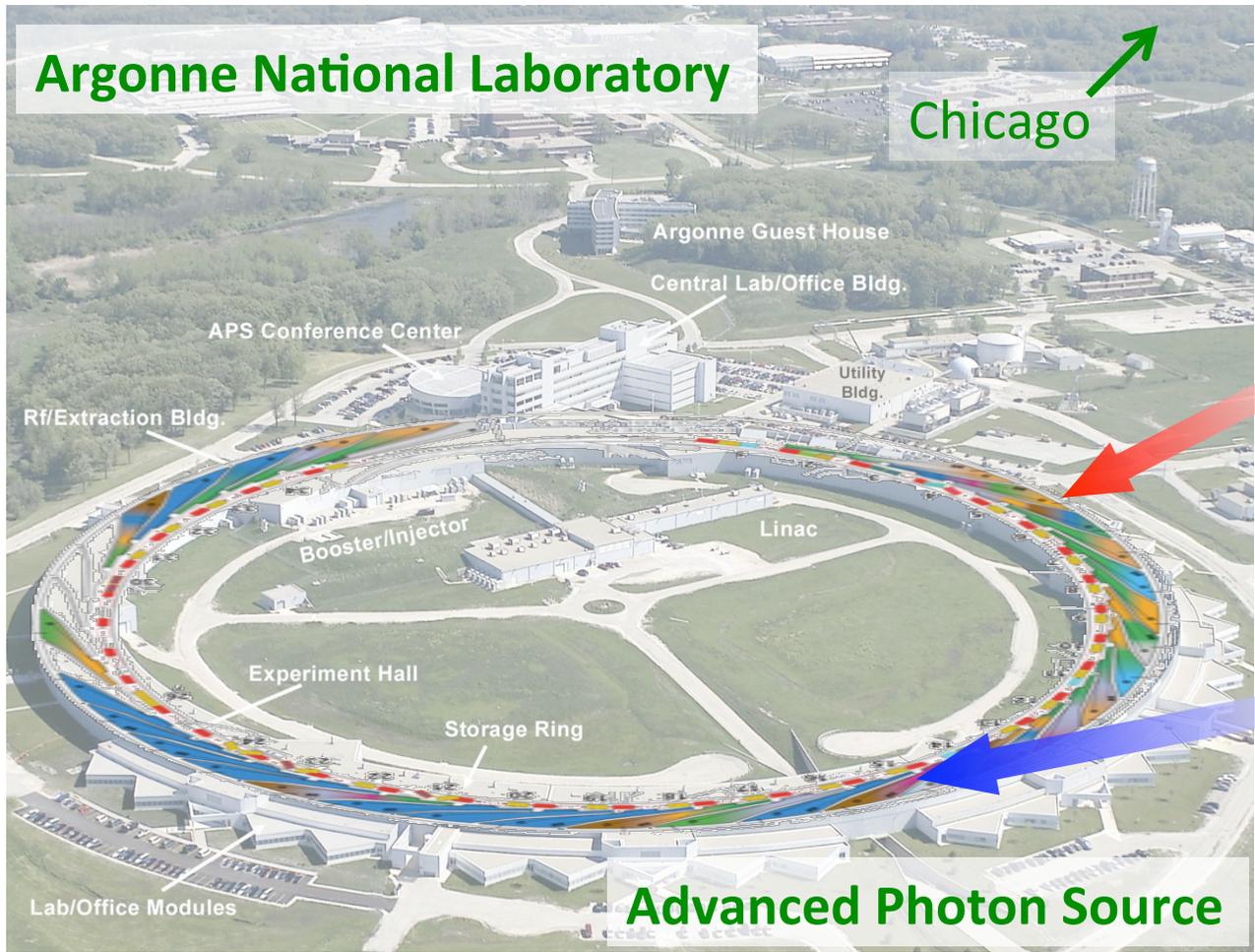
Matthew Suchomel

Advanced Photon Source (APS)

Argonne National Laboratory

Powder Diffraction at the APS

powder XRD is performed at multiple instruments (often called beamlines)



11-BM

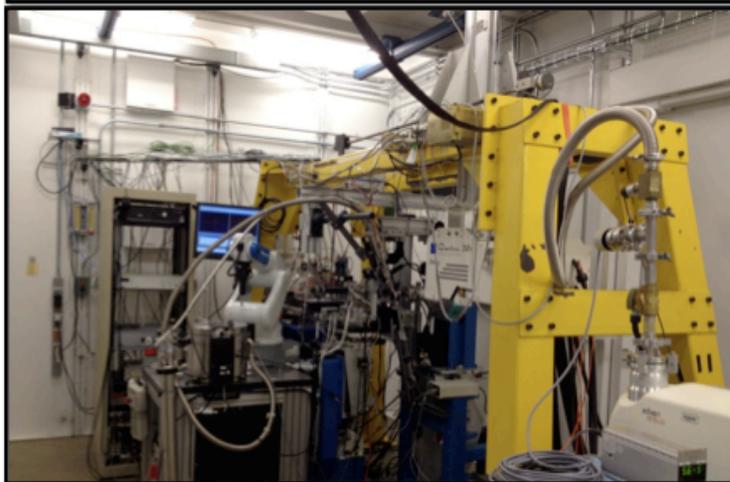
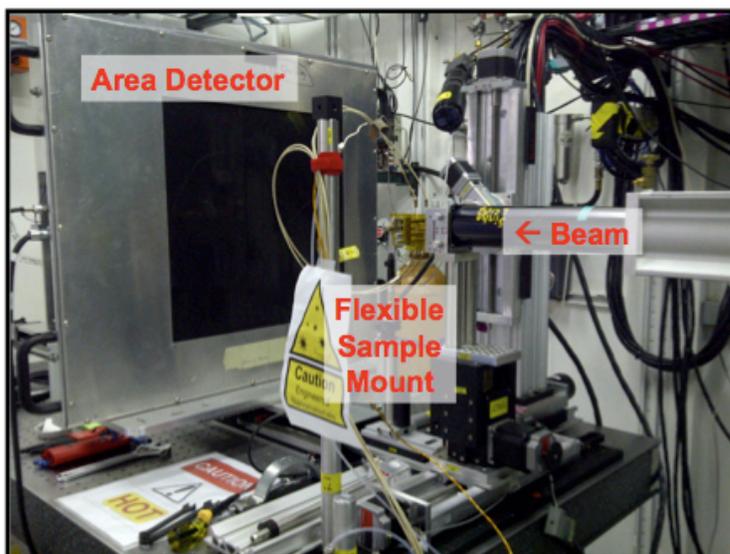
- Highest 2θ Resolution
- Superb Sensitivity
- Free Mail-In Program

~~1-BM~~ **17-BM***

- In-situ Studies
- Flexible Set-Up

* 1-BM moves to 17-BM in fall 2012

APS Powder Diffraction Beamlines



*Fast Area Detector (17-BM)**

17-BM is a powder diffraction instrument at the APS optimized for in-situ experiments under non-ambient conditions. A state-of-the-art area detector enables fast data acquisition, and on-site users benefit from a wide variety of flexible sample environments.

Instrument Specifications

- ✧ Energy Range: 7 – 20 keV
- ✧ Resolution: $\Delta d/d \approx 1 \times 10^{-2}$
- ✧ Scan Time: 0.1 - 60 seconds

Sample Environments

- ✧ Flowcell Reaction Furnace (<900 °C)
- ✧ Oxford Cryostream (100 - 450 K)
- ✧ In-Situ Controlled Atmospheres
- ✧ Diamond Anvil Cells (<10 GPa)

** Formerly 1-BM; moving to 17-BM Fall 2012*



APS Powder Diffraction Beamlines

High-Resolution (11-BM)

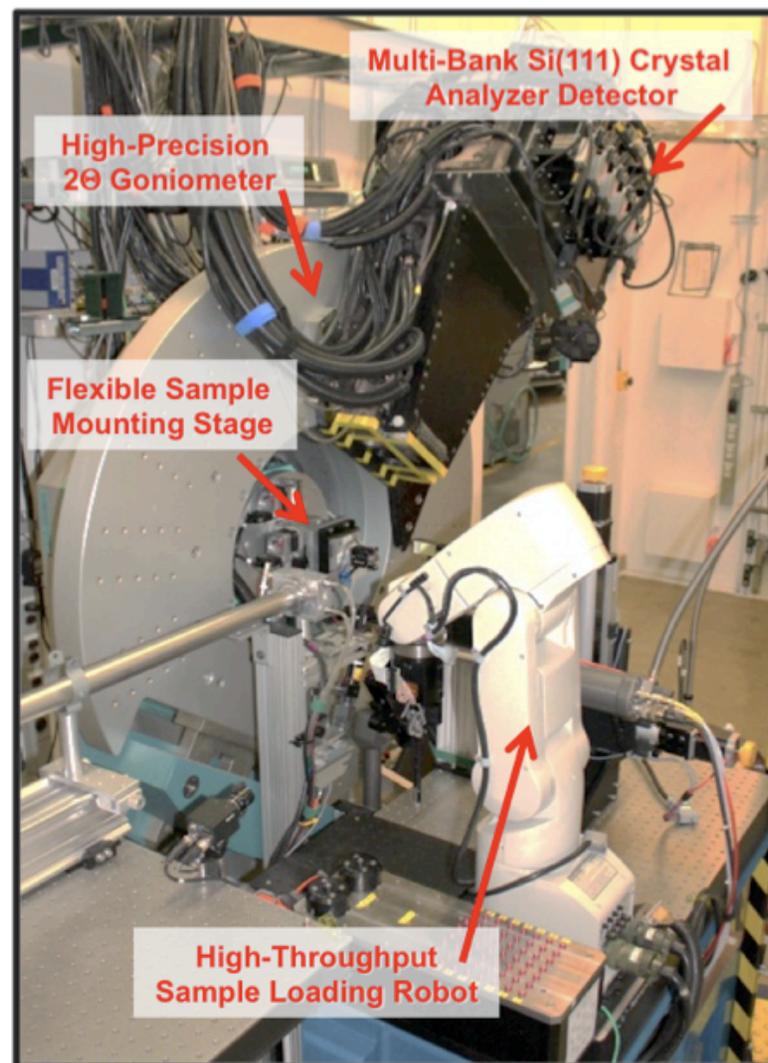
11-BM is a dedicated high resolution powder diffraction instrument at the APS. It affords powder diffraction data with world-class resolution and outstanding sensitivity. The beamline supports both on-site and rapid access mail-in user programs.

Instrument Specifications

- ✧ Energy Range: 15 – 35 keV
- ✧ Resolution: $\Delta d/d \approx 2 \times 10^{-4}$
- ✧ Scan Time: 10 - 60 minutes

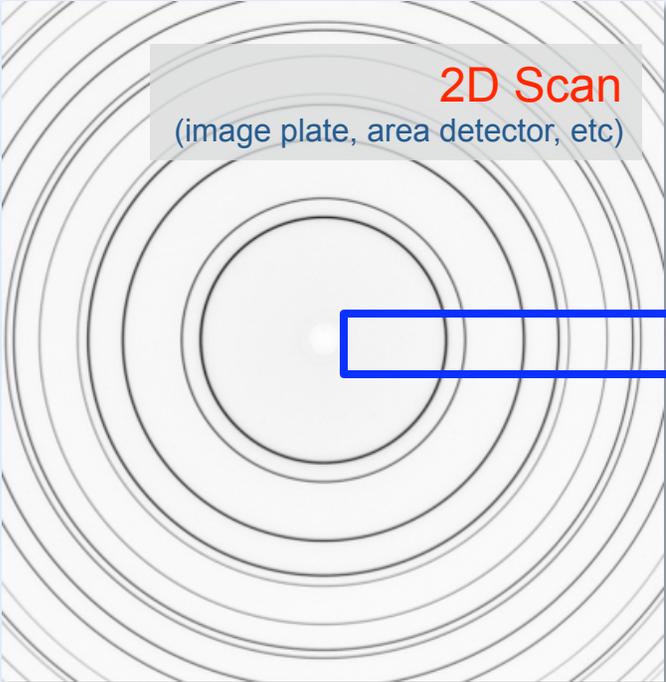
Sample Environments

- ✧ Oxford Cryostream (100 - 450 K)
- ✧ Cyberstar Hot Gas Blower (25 - 900 °C)
- ✧ Helium Flow Cryostat (5 - 150 K)
- ✧ Gas Reaction Cell (under development)
- ✧ High Temp (>1000 °C) furnace (planned)



Collecting Powder Diffraction Data

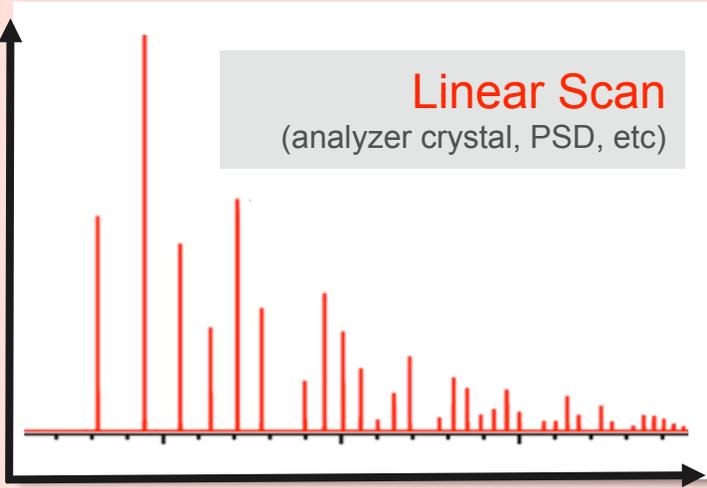
1-BM 17-BM



2D Scan
(image plate, area detector, etc)

- Sensitivity / Speed
 - Flexibility

11-BM



Linear Scan
(analyzer crystal, PSD, etc)

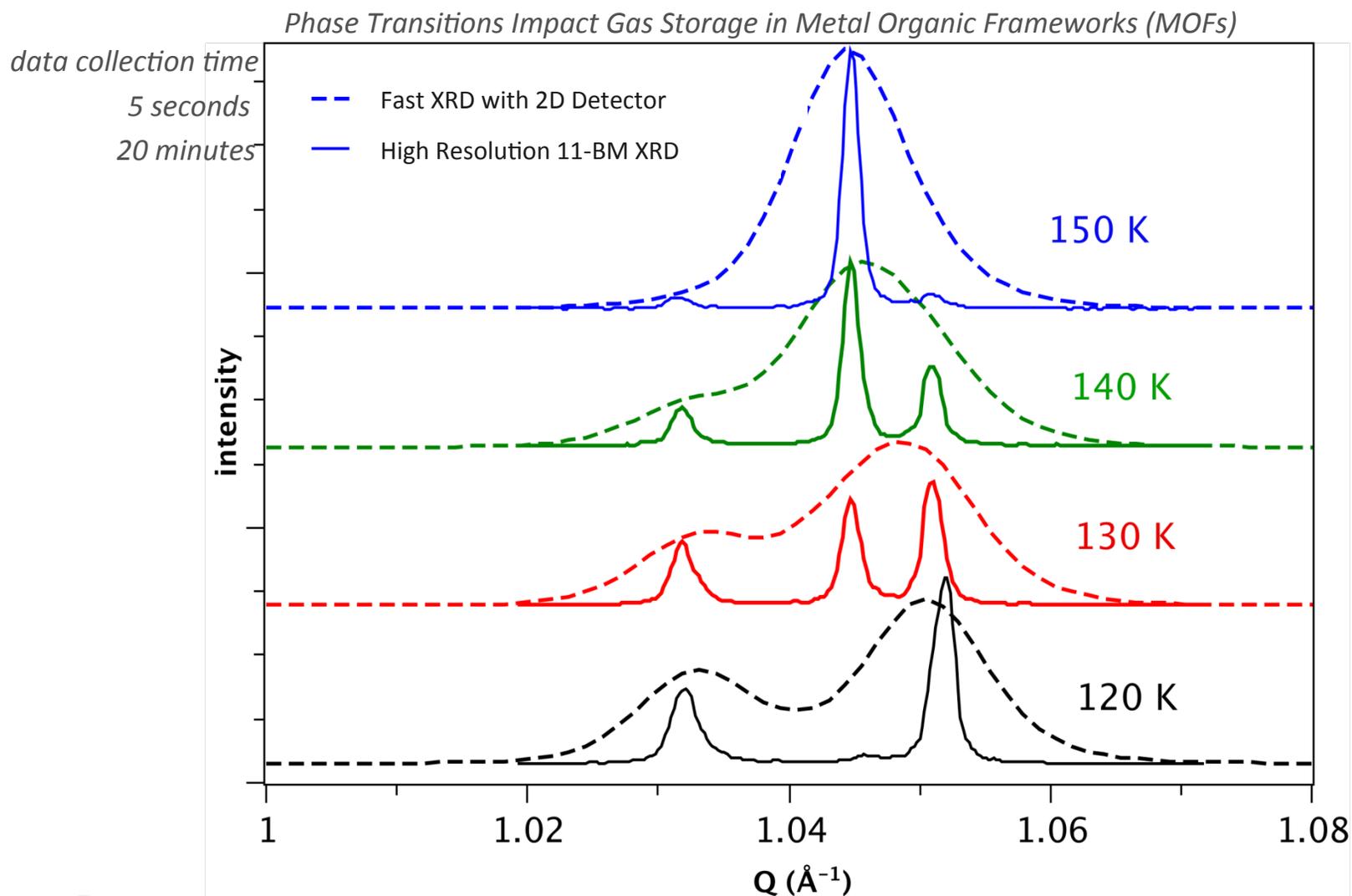
Intensity

angle (2θ)

- Resolution / Background
 - Extended 2θ Range

Which Beamline is 'Best'?

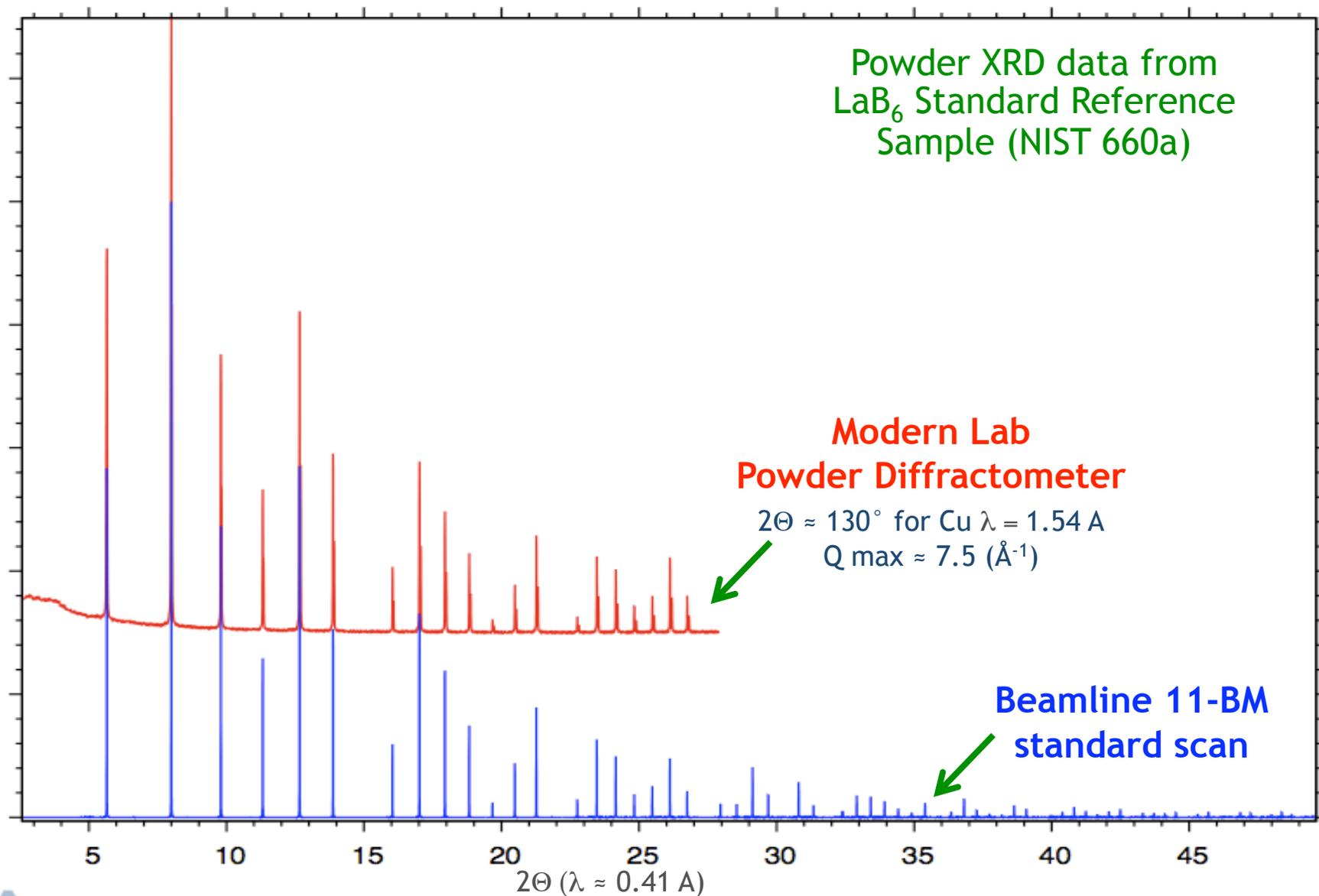
A: depends on your experiment !



The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory



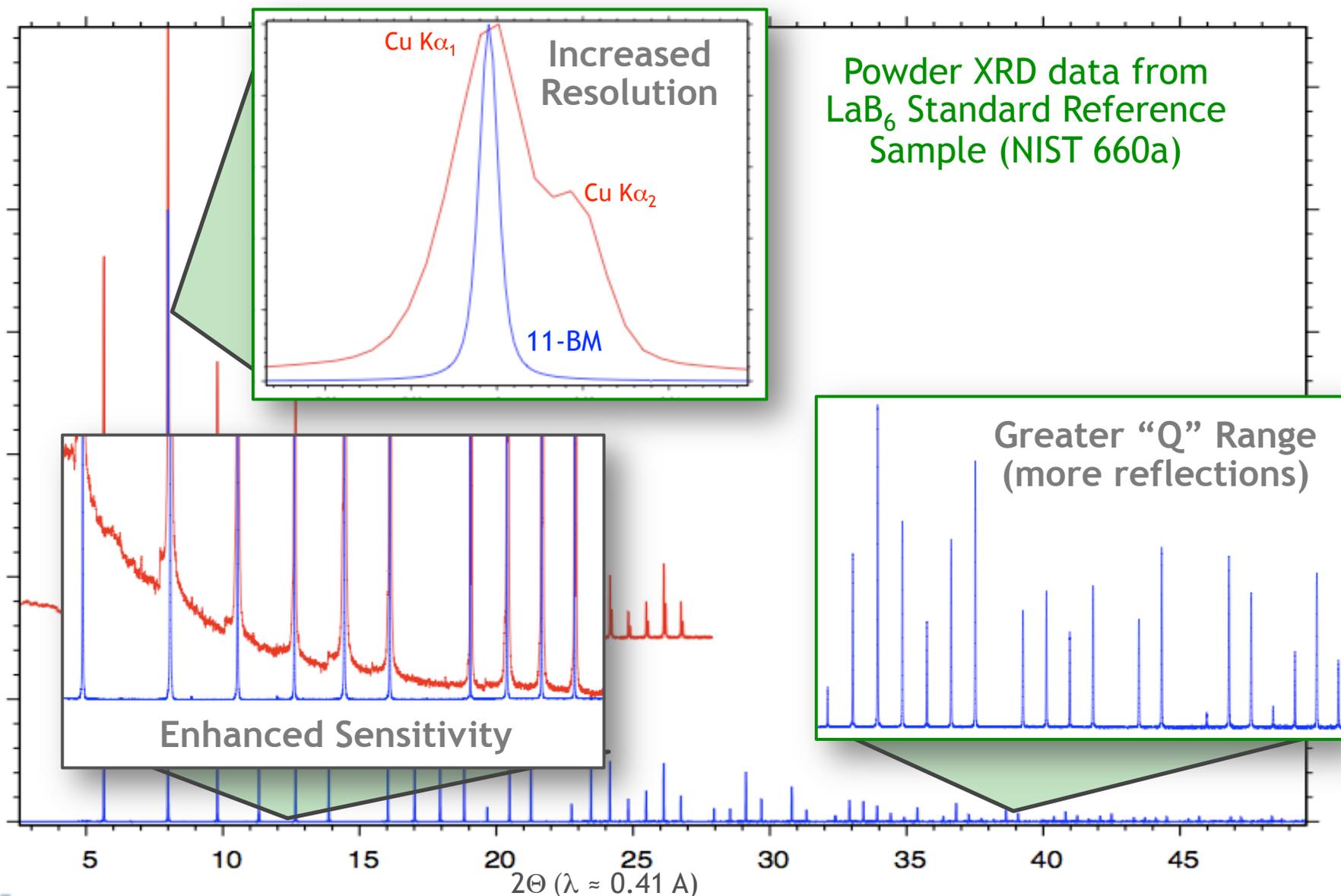
Why Use a Synchrotron for Powder Diffraction?



The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory



Why Use a Synchrotron for Powder Diffraction?



Powder XRD data from
LaB₆ Standard Reference
Sample (NIST 660a)

Greater "Q" Range
(more reflections)

Enhanced Sensitivity

Increased
Resolution

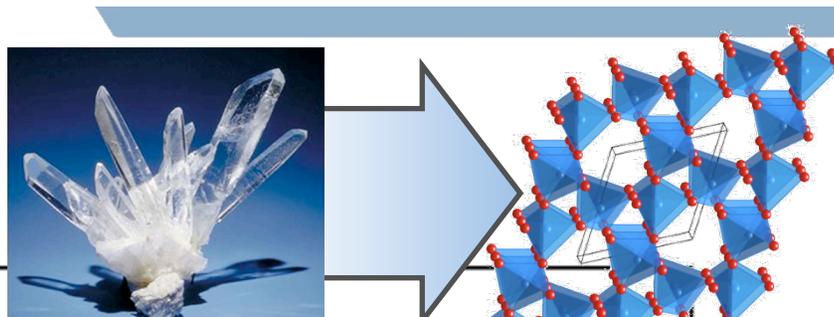
Cu $K\alpha_1$

Cu $K\alpha_2$

11-BM



High Resolution Performance Real Sample of SiO₂ Powder

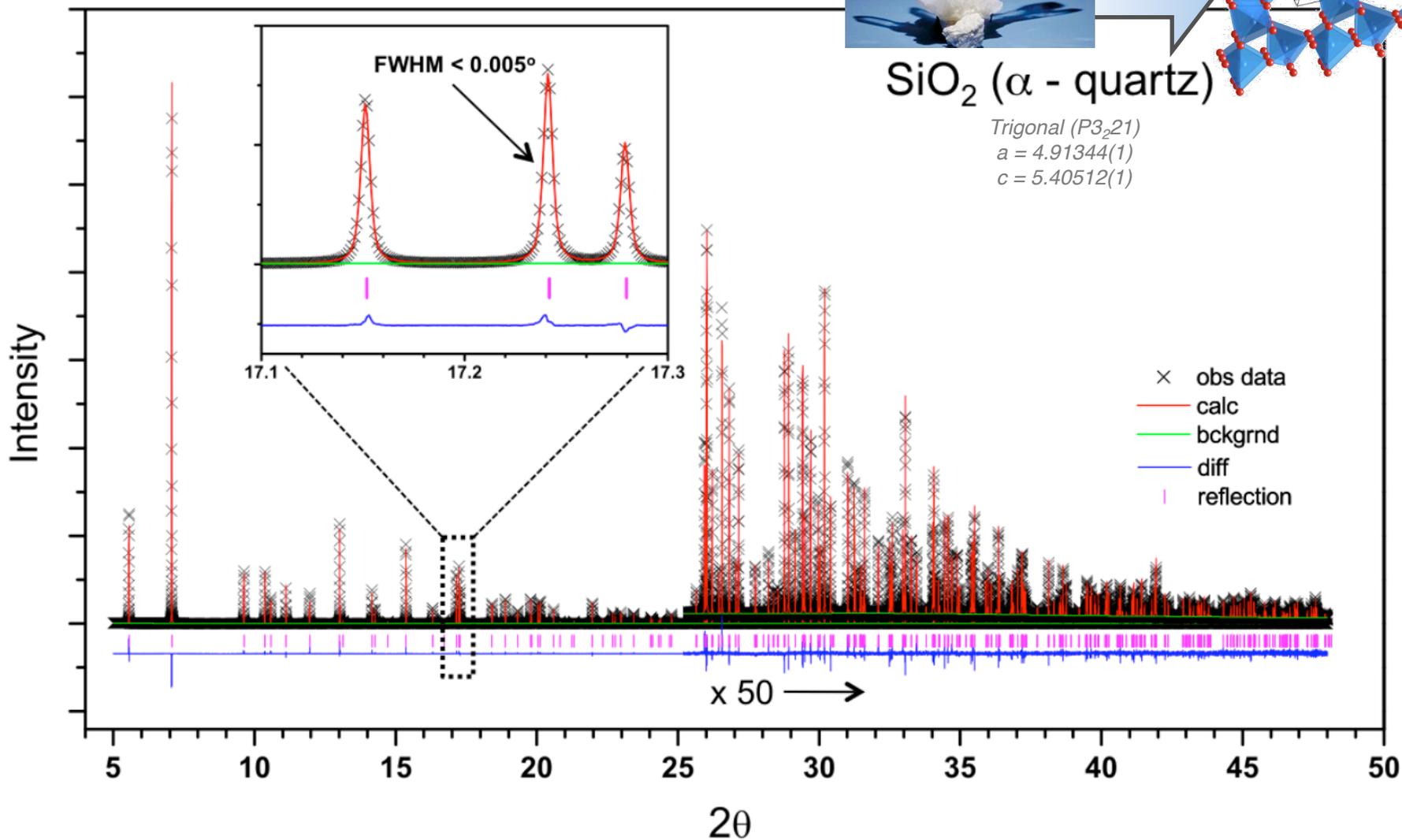


SiO₂ (α - quartz)

Trigonal ($P3_221$)

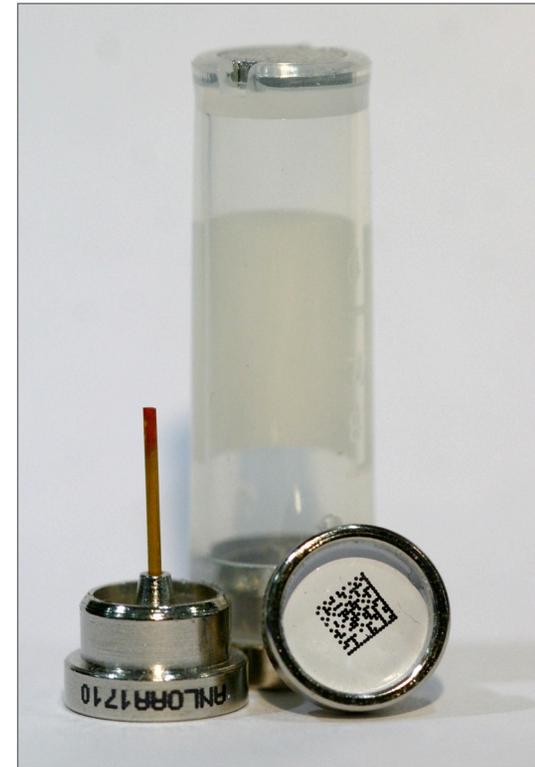
$a = 4.91344(1)$

$c = 5.40512(1)$



Rapid Access Mail-In Measurements @ 11-BM

- ✧ Short Proposal, Fast Review
- ✧ Open to US & International Users
- ✧ Limited to 8 Hours per Proposal
- ✧ **Free** (no cost!) for Non-Proprietary Work
- ✧ Sample Mounting Kits Provided
- ✧ Scans at Ambient or 100-450 K
- ✧ Fixed Energy 30 keV (0.41 Å)
- ✧ Download Data in ~ 4 weeks



more information

<http://11bm.xor.aps.anl.gov>

[email: 11bm@aps.anl.gov](mailto:11bm@aps.anl.gov)

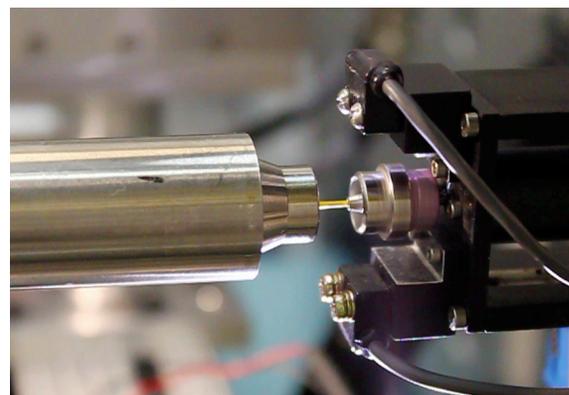
Robotic Data Collection

Check out 11-BM videos on YouTube : Google “11bm robot video” or use link below
<http://www.youtube.com/watch?v=sowojskY7c4>



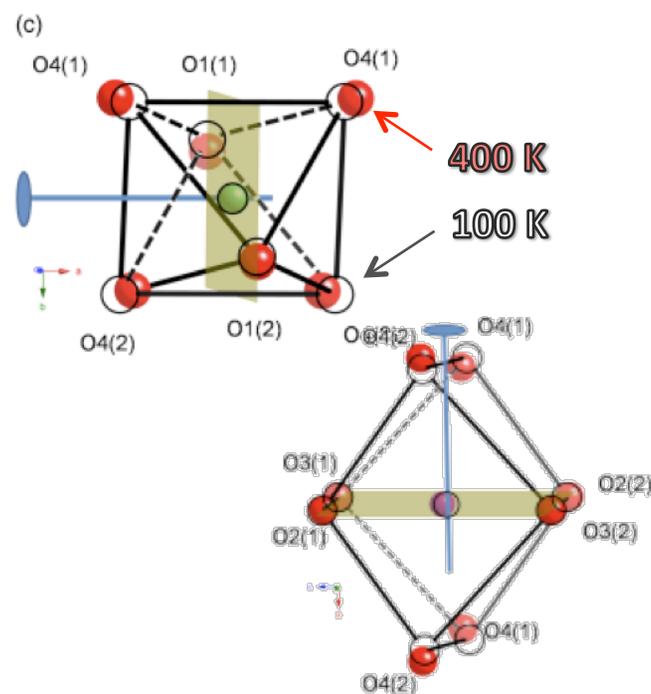
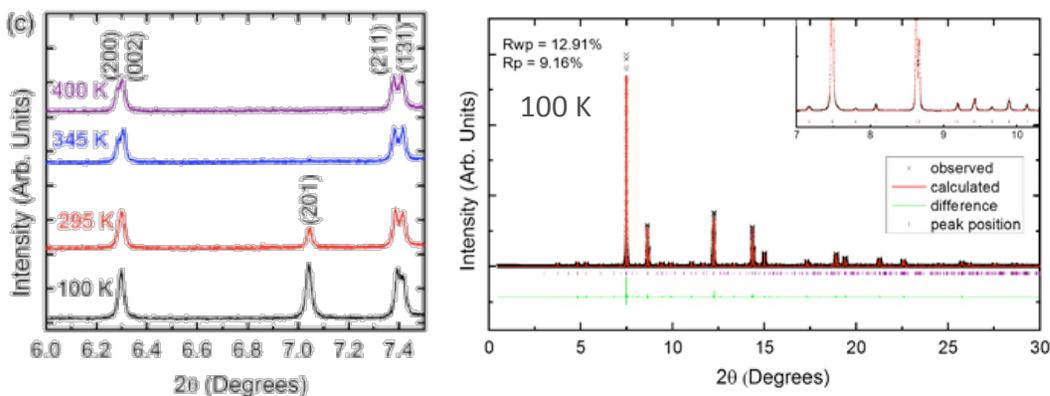
Mail-In @ Non-Ambient Temperatures

- Mail-in Service Integrates N₂ Cryostream
 - Select Temperatures over range 100 – 450 K
 - see 11-BM webpage for more information



Cai, Nino et al. *J Am. Cer. Soc.* (2010) v. 93 p. 875

- Used Mail-in Service to Study Phase Transitions in Gd₃NbO₇
- Multiple 11-BM Scans Collected Between 100 - 400 K
- High-Resolution Data Clarified *Cmcm* → *Cm2m* Transformation
- Refined Cation & Oxygen Shifts > Polyhedra Distortions

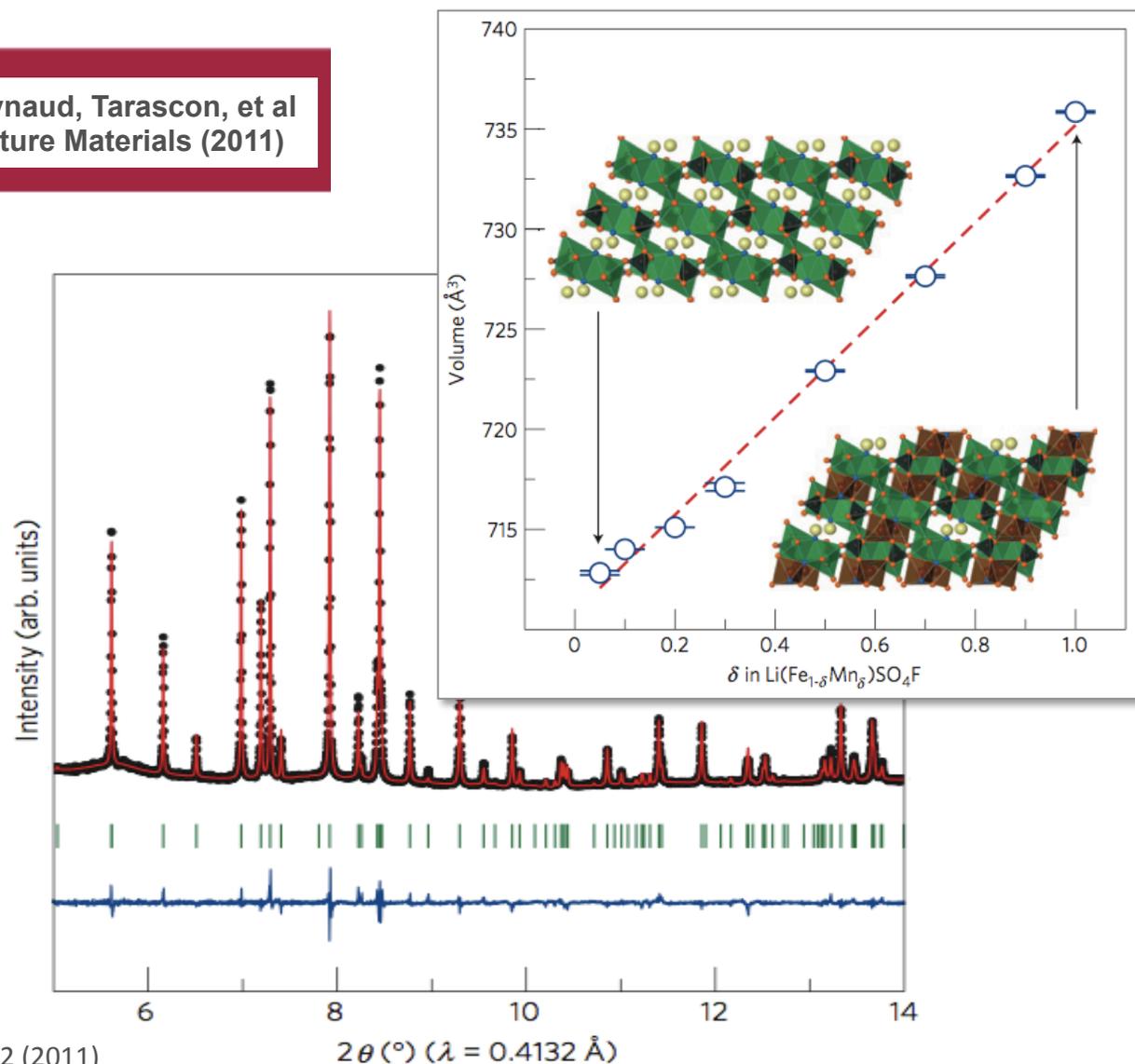


11-BM Mail-In = High Impact Science!

nature
materials

Reynaud, Tarascon, et al
Nature Materials (2011)

- Li-ion fluorosulphate electrode materials
- Track structural trends in $\text{Li}(\text{Fe}_{1-x}\text{Mn}_x)\text{SO}_4\text{F}$
- Quantify 0.6% volume change with Li -insertion



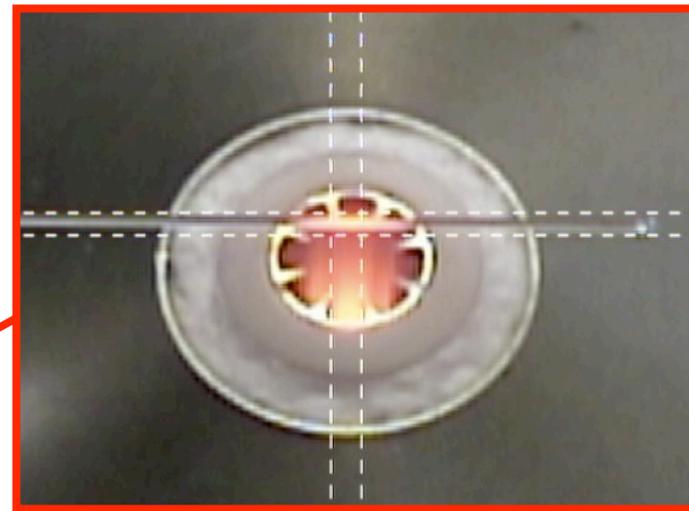
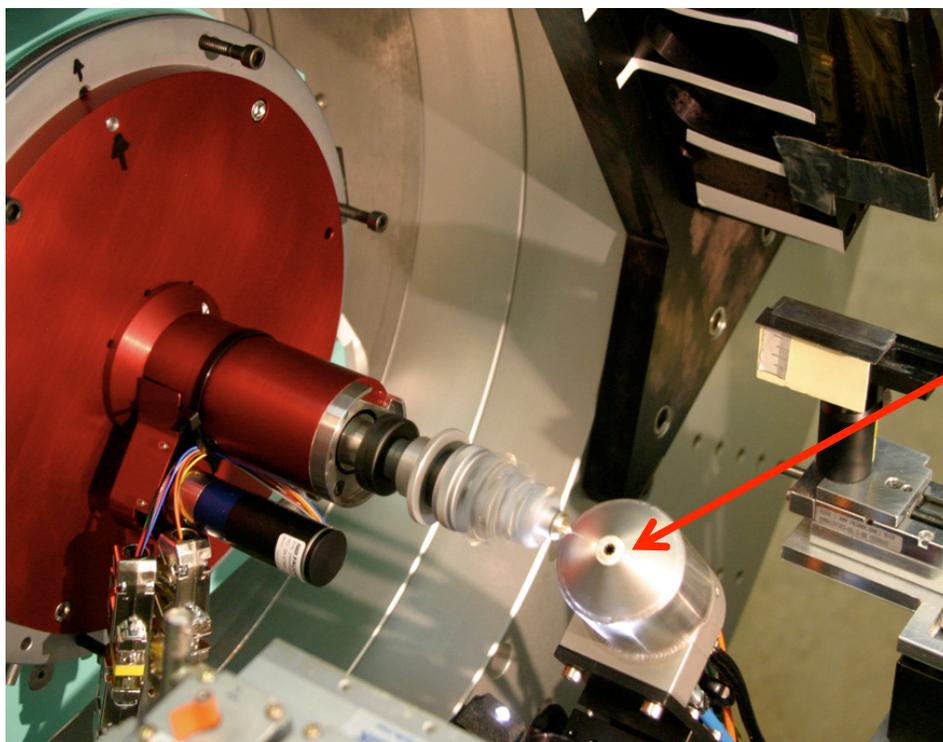
Barpanda, Tarascon et al, Nat. Mater. 10, 772 (2011)

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Not Just Mail-In: In-Situ Heating @ 11-BM

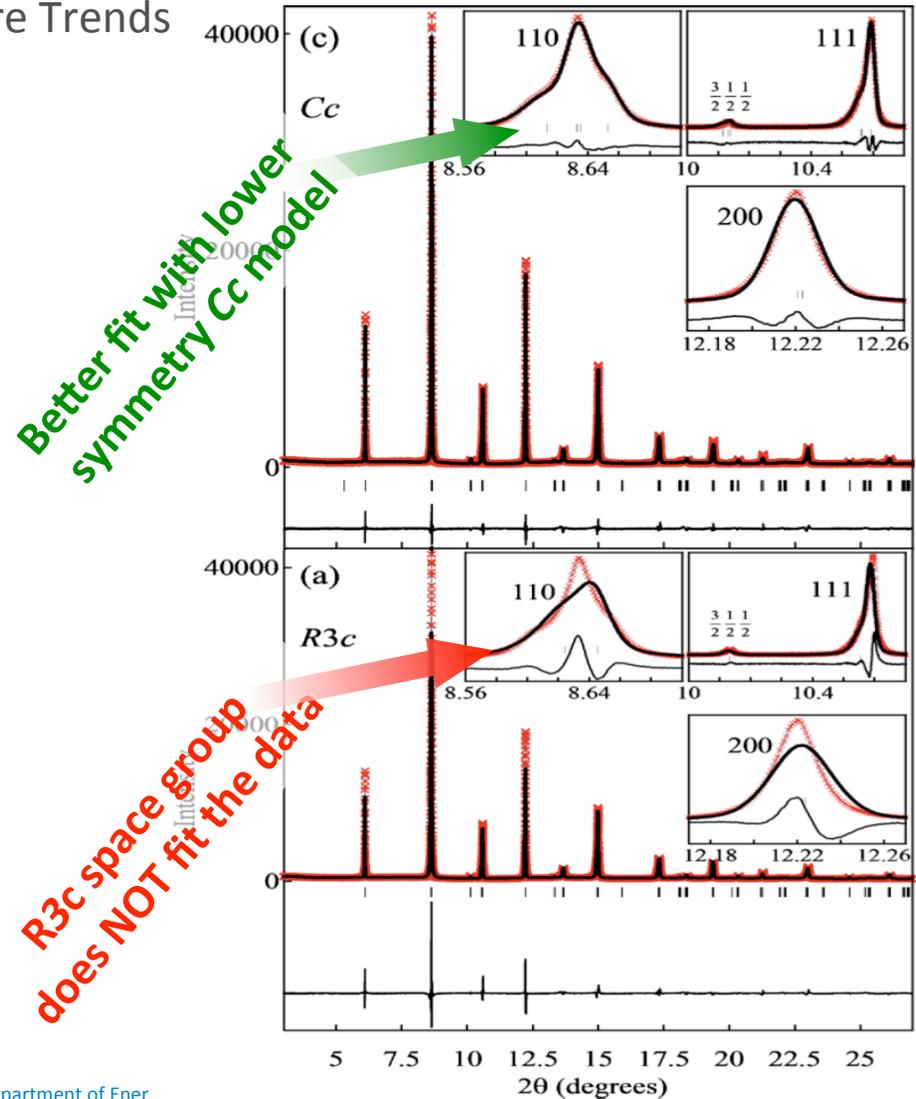
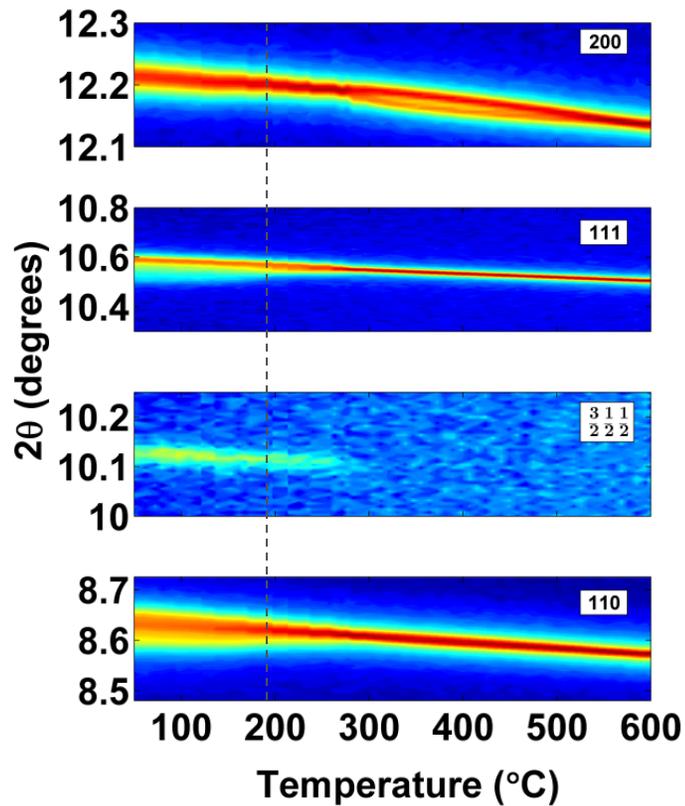
- Hot Air Blower
 - Room Temp \rightarrow 950 °C (> 1700 °F)
 - Optimized for small capillary samples
 - ONLY available for on-site user experiments



In Situ Heating @ 11-BM

- Synchrotron Sensitivity Reveals Detail in Subtle Splitting & Weak Reflections
- Connect Physical Response to Structure Trends

*In-Situ XRD & Property Measurements
Reveal Depoling Hysteresis Behavior in
Fe-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ Piezoelectrics*



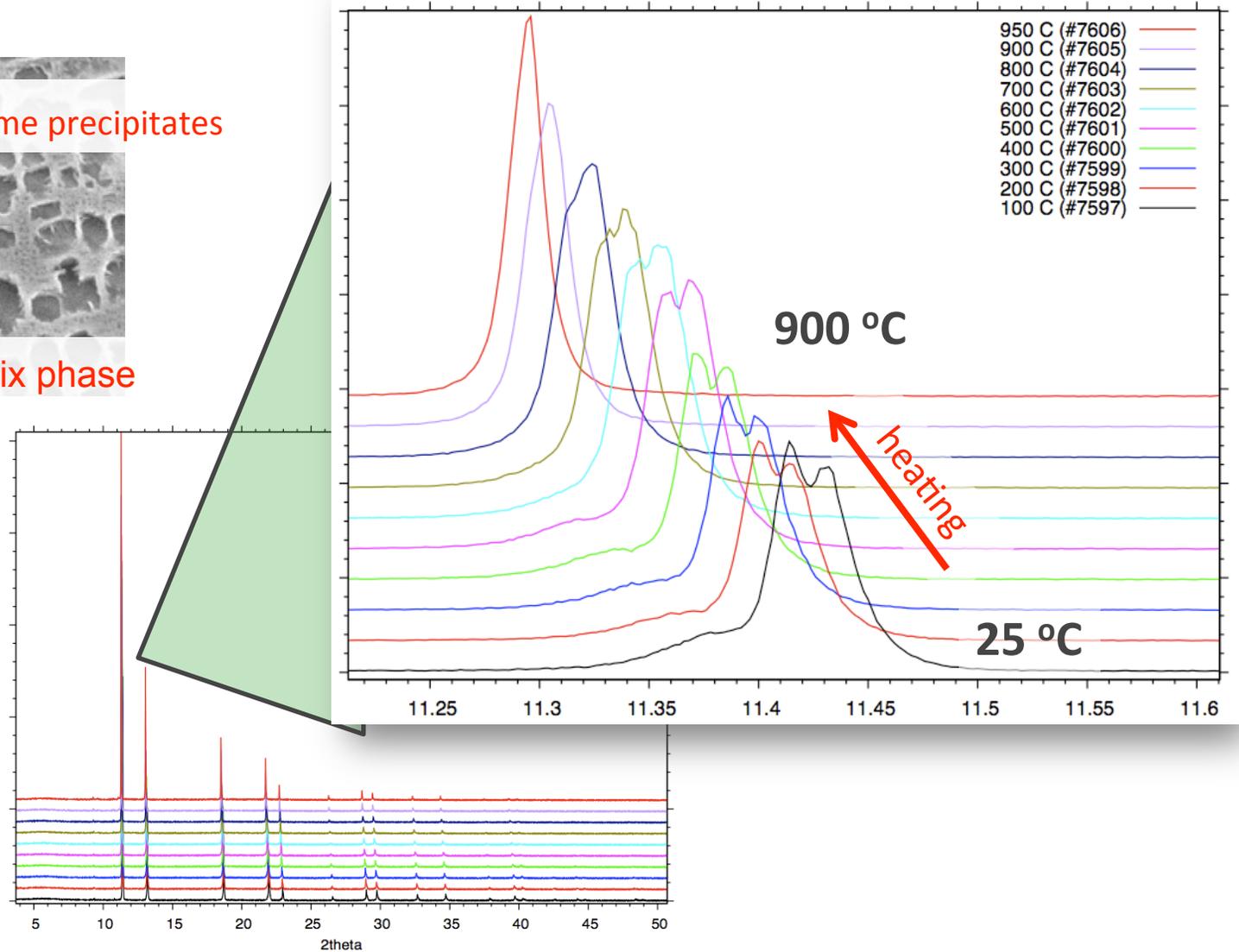
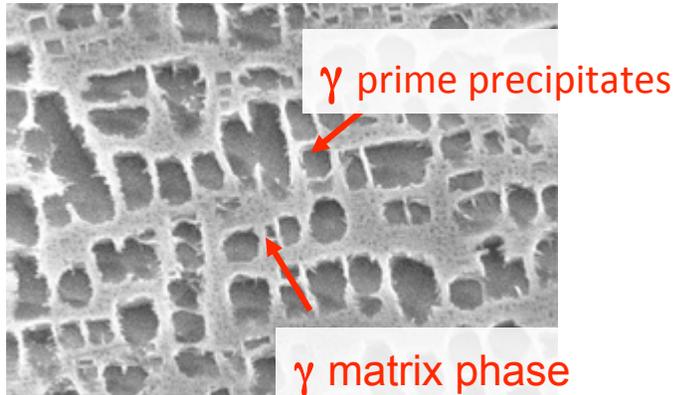
Aksel, Jones et al , Appl. Phys. Lett. 99, 222901 (2011)

The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Ener



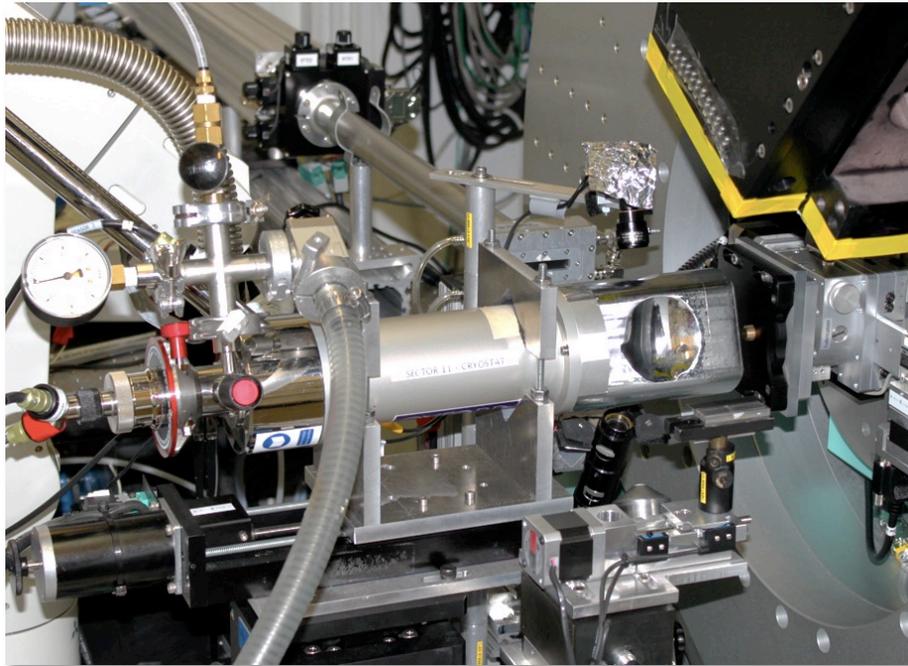
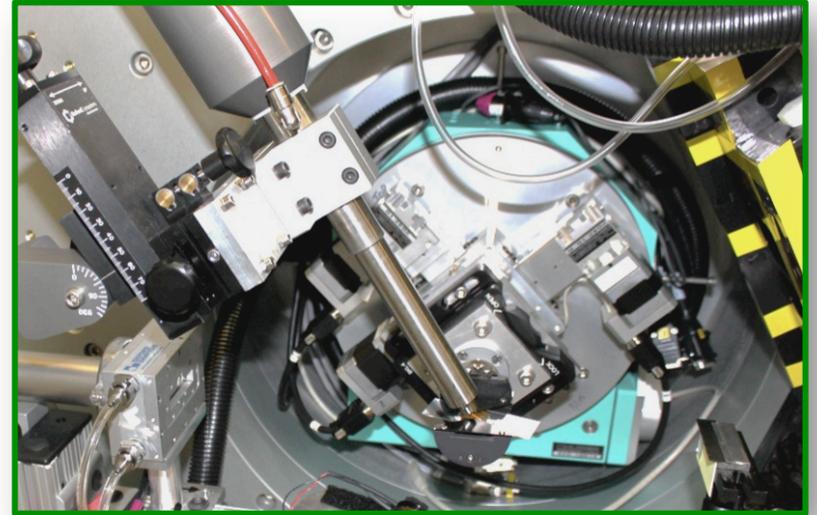
In-Situ Industrial Studies @ 11-BM

Superalloy Microstructure; Track small lattice mismatch vs. temperature at 11-BM



In Situ Cooling @ 11-BM

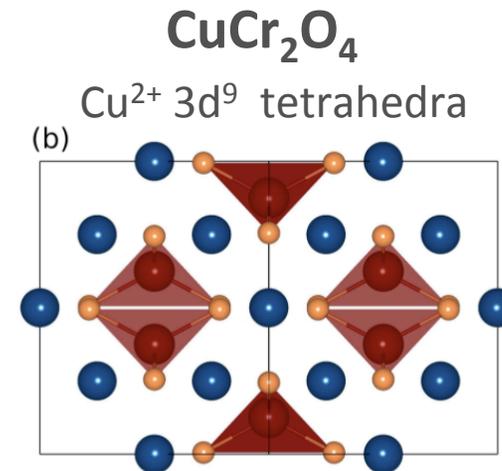
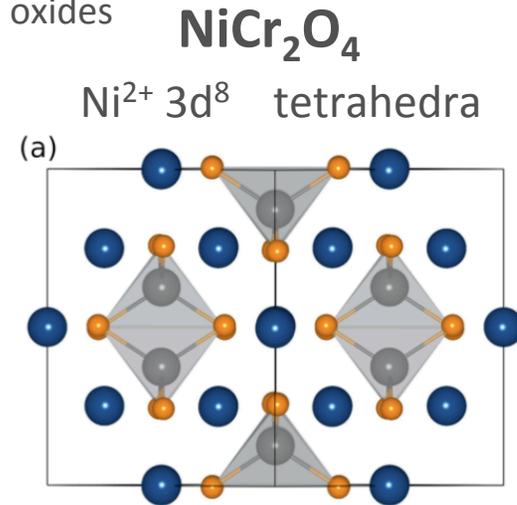
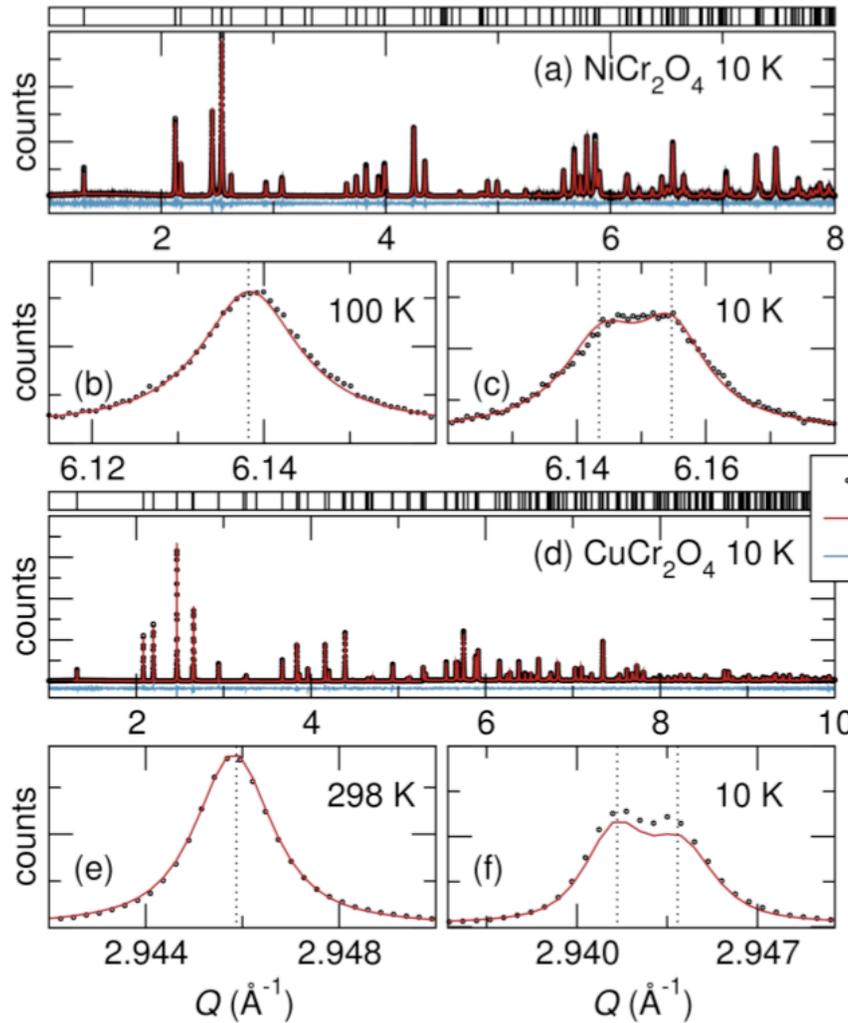
- Nitrogen Cryostream (+/- 200 C)
 - Flexible Open Flow Design
- Helium Cryostat (< 100 K)
 - Base Temp of approx. 5 K



Both sample mounts shown here are ONLY available for on-site user experiments

Magnetostructural Coupling in Jahn-Teller Spinels

High-Resolution cryogenic measurements at 11-BM help elucidate coupling between spin, lattice, and orbital ordering in spinel metal oxides



Suchomel, Kemei et al, Phys. Rev. B 86, 054406 (2012)



Magnetostructural Coupling in Jahn-Teller Spinels



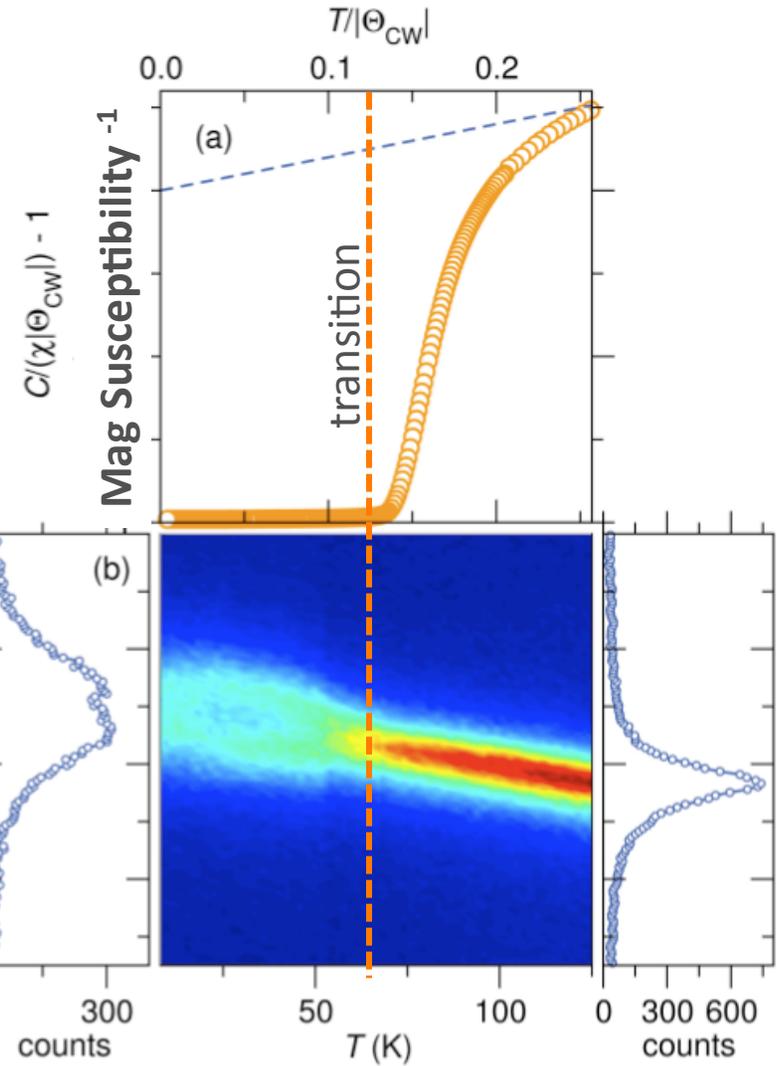
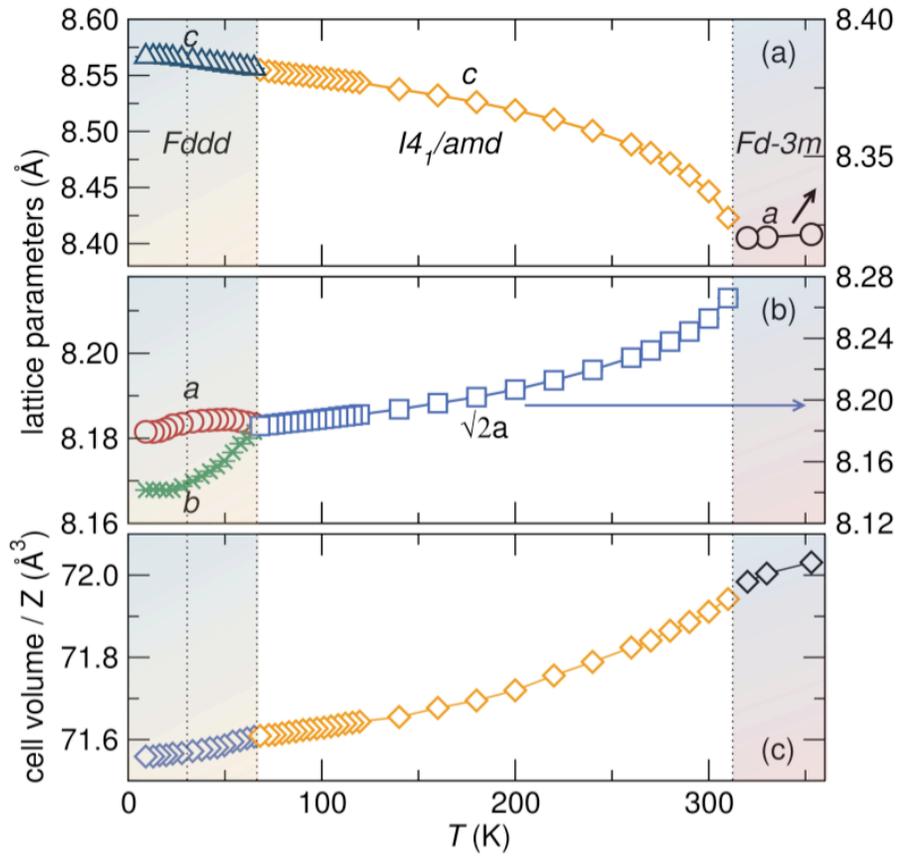
Ortho \longleftrightarrow Tetra \longleftrightarrow Cubic

65 K

320 K

Magnetic

J-T

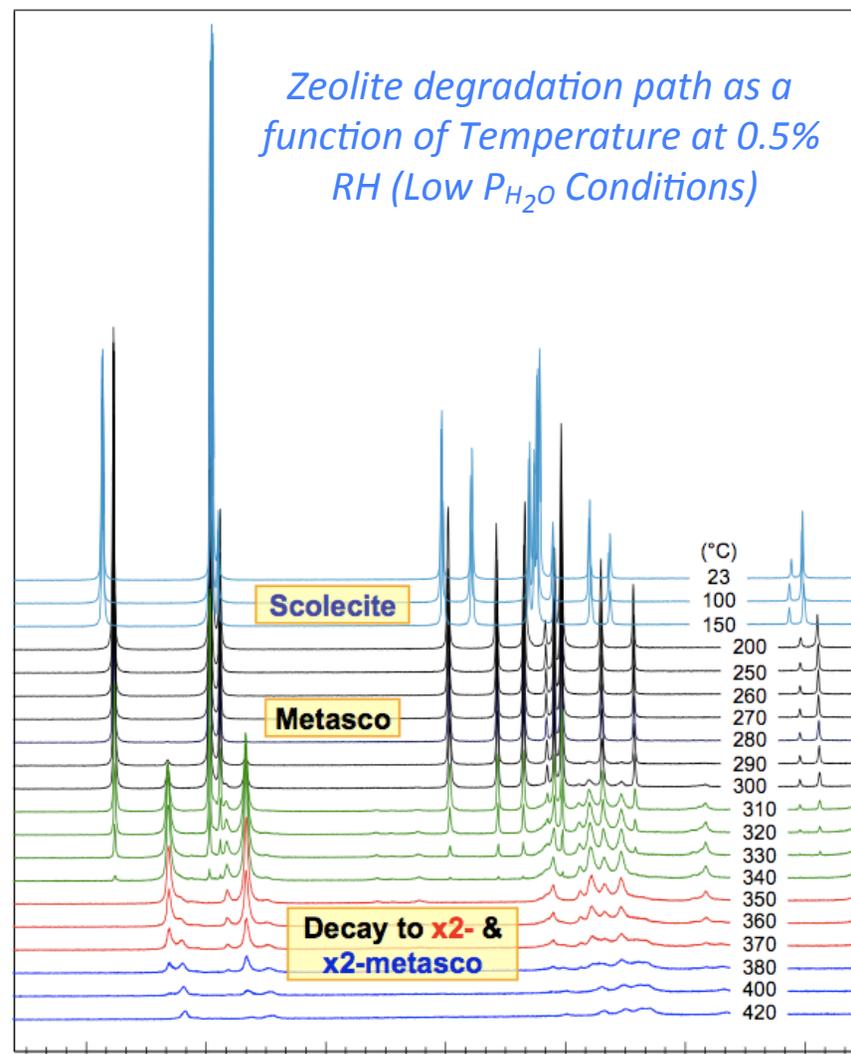


Suchomel, Kemei et al, Phys. Rev. B 86, 054406 (2012)



plus Temp & Atmosphere Control

- Reaction Cells & Gas Flow Meters
- Gas Reduction or Humidity Studies
- Only for On-Site Experiments

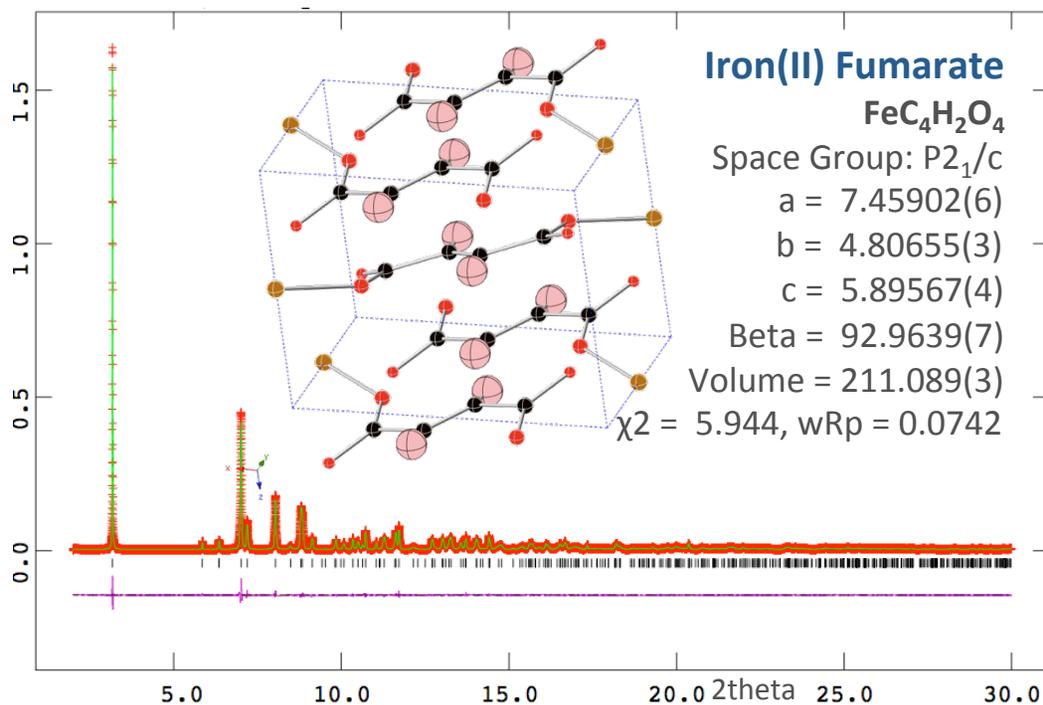


Hsiu-Wen Wang, Ph.D.-Thesis, Indiana University, 2011



Structure Solution with Powder Diffraction

- Use Powder Data to Solve & Refine Crystal Structure
 - easier than you think with modern software, computers, and data
 - variety of approaches viable for *ab initio* solution
- Even *In Situ* - e.g for sample with melting Temp below RT
 - Try Freezing Sample Capillary In-Situ at 11-BM, then Collect High Quality PD data



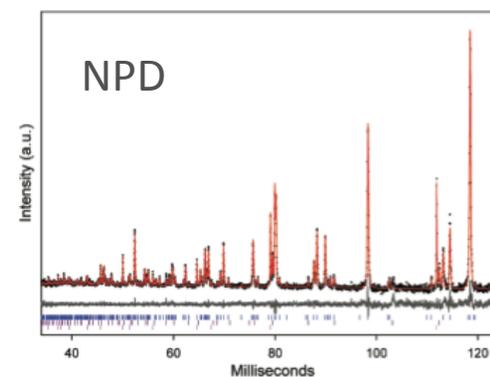
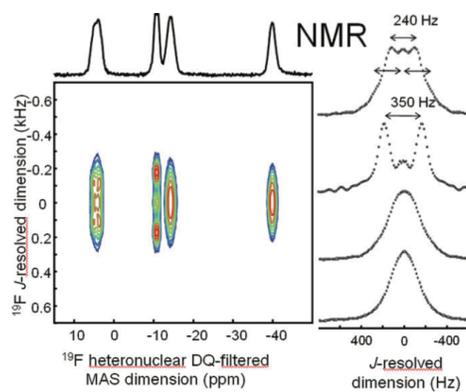
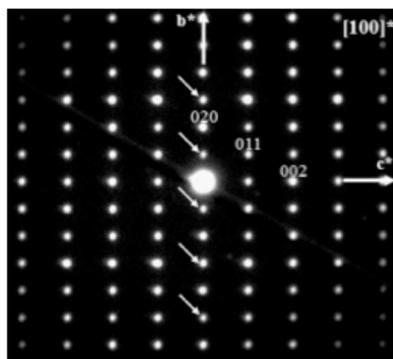
Iron Fumarate Example

1. pXRD data collected at 11-BM
2. molecular dynamics to model molecular unit
3. Index Unit Cell in EXPO2009
4. Solve Structure by Simulated Annealing in EXPO
4. Final Model Rietveld Refinement in GSAS

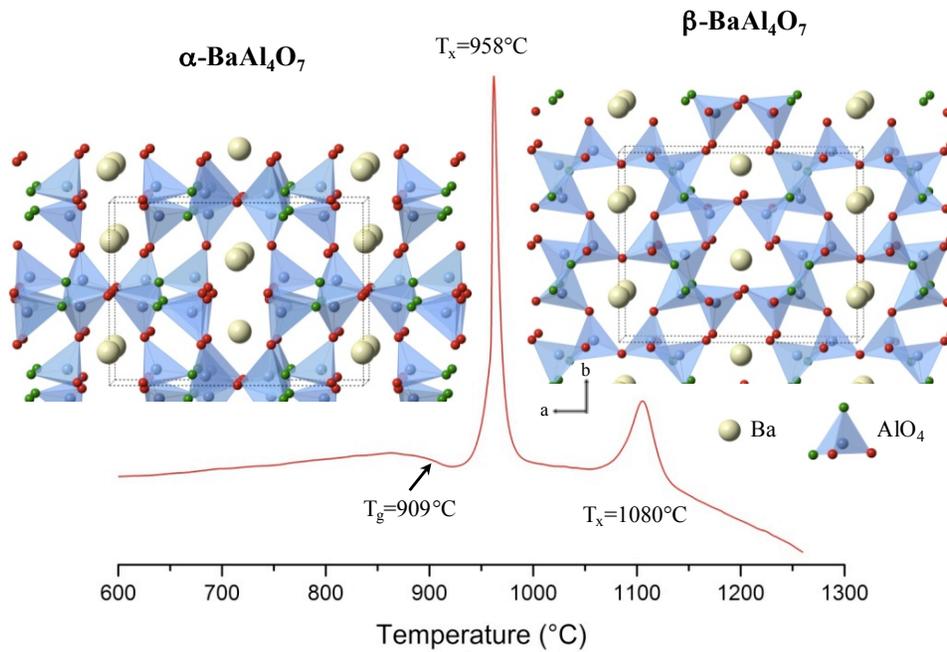
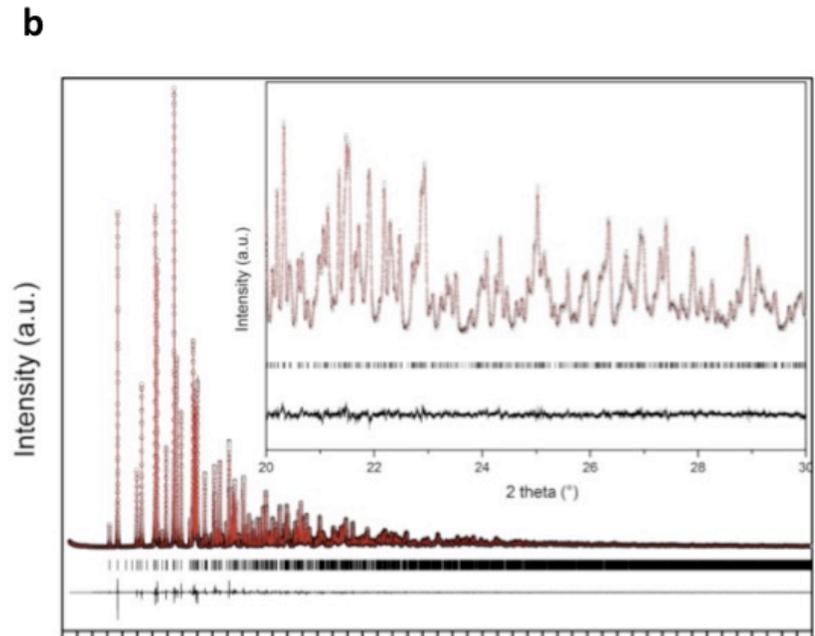
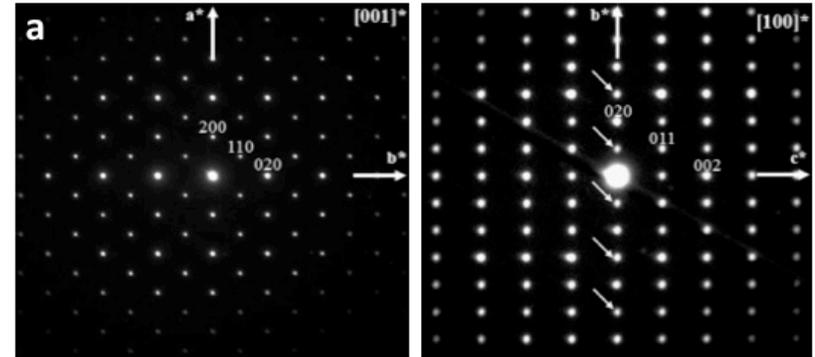
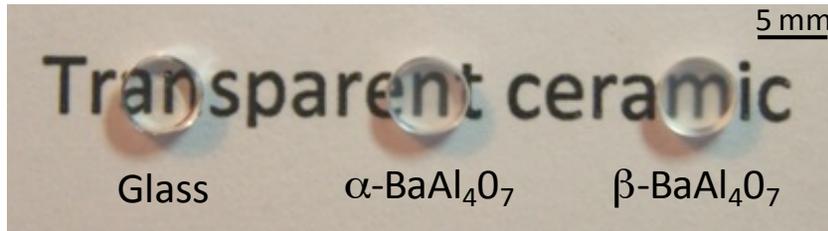
Suchomel, et al, unpublished

with a little help from your friends...

when high-resolution synchrotron powder diffraction is not enough...



Powder XRD + ED = new polycrystalline ceramics

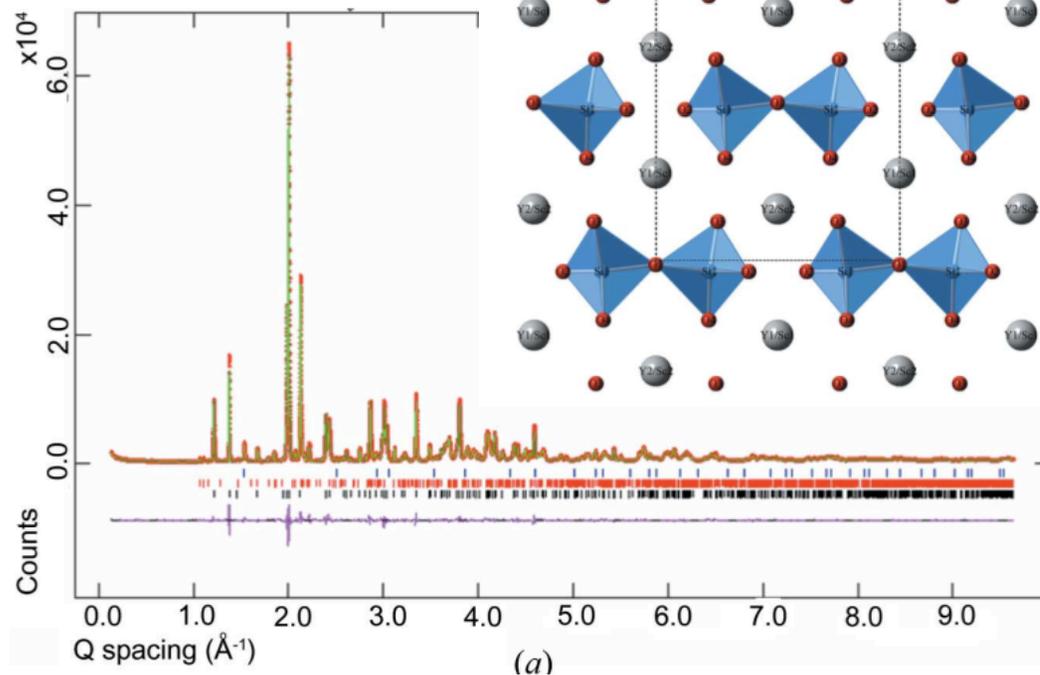
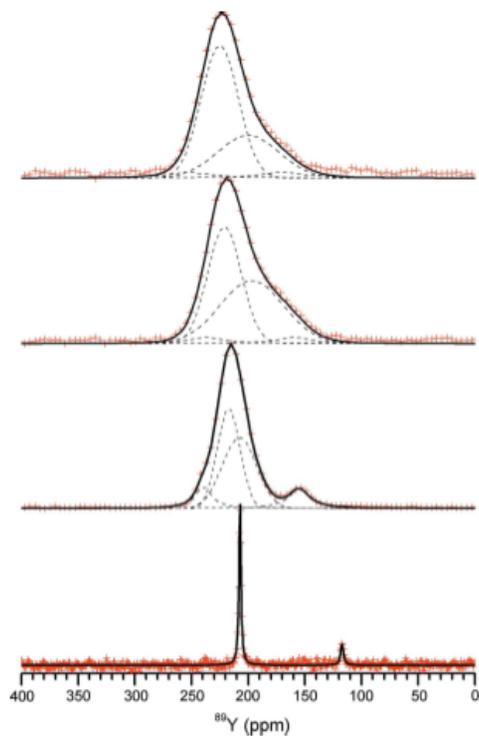


Allix, Suchomel et al *Adv Mat* 2012 *in press*



Powder XRD + solid state NMR for $Y_xSc_{2-x}Si_2O_7$

^{89}Y NMR => confirms 2 RE sites & lower symmetry in solid solution



Structure Solved; Rietveld Fit to Powder XRD

Allix, Becerro, et al, J App Crys (2011) vol. 44 pp. 846-852

Complementary X-ray & Neutron Powder Diffraction

New Program for Complementary Synchrotron XRD + Neutron
SNS contact Dr. Ashfia Huq huqa@ornl.gov

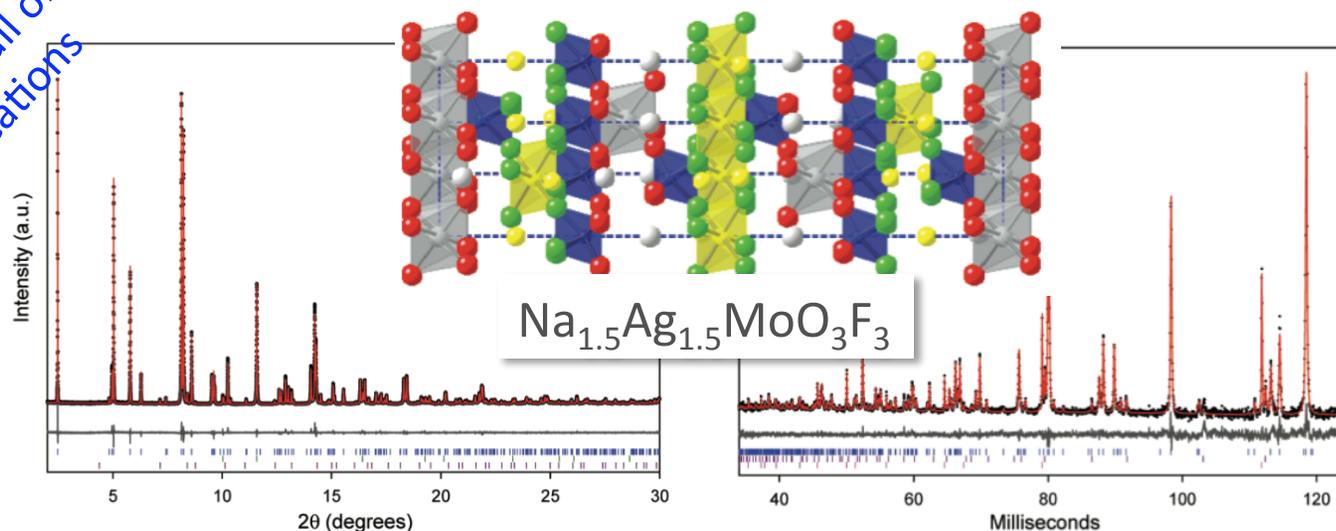


XRD @ APS 11-BM

+

NPD @ SNS POWGEN

XRD gives detail on
Ag + Mo cations



NPD gives detail
on O + F anions

Fry, Woodward, JACS (2012) vol. 134 pp. 2621

More Info for 11-BM Mail-In & On-Site Experiments

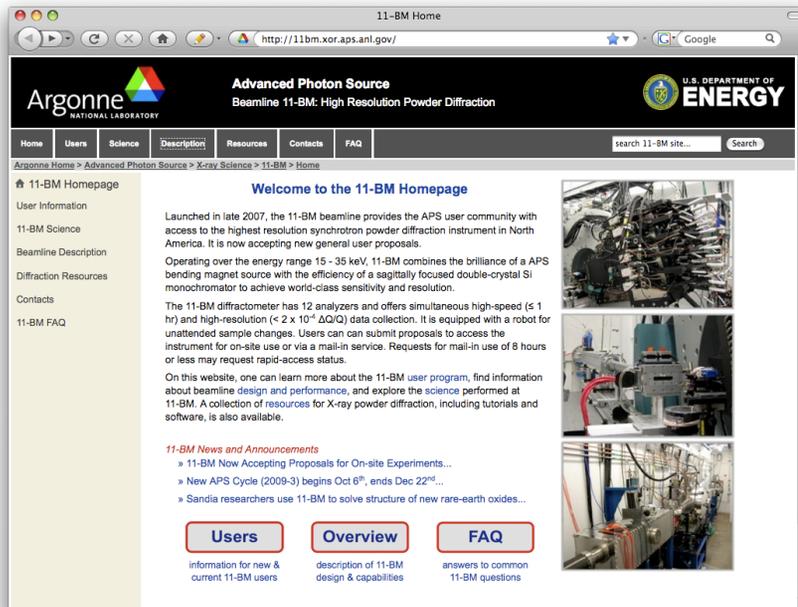
Google

11bm

Search

webpage: <http://11bm.xor.aps.anl.gov>

email contact: 11BM@aps.anl.gov



Rapid Access Mail-In
Proposals Accepted Anytime

Check APS webpage for
On-Site Proposal Call
(3x per year)

11-BM at the Advanced Photon Source at Argonne National Laboratory is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.