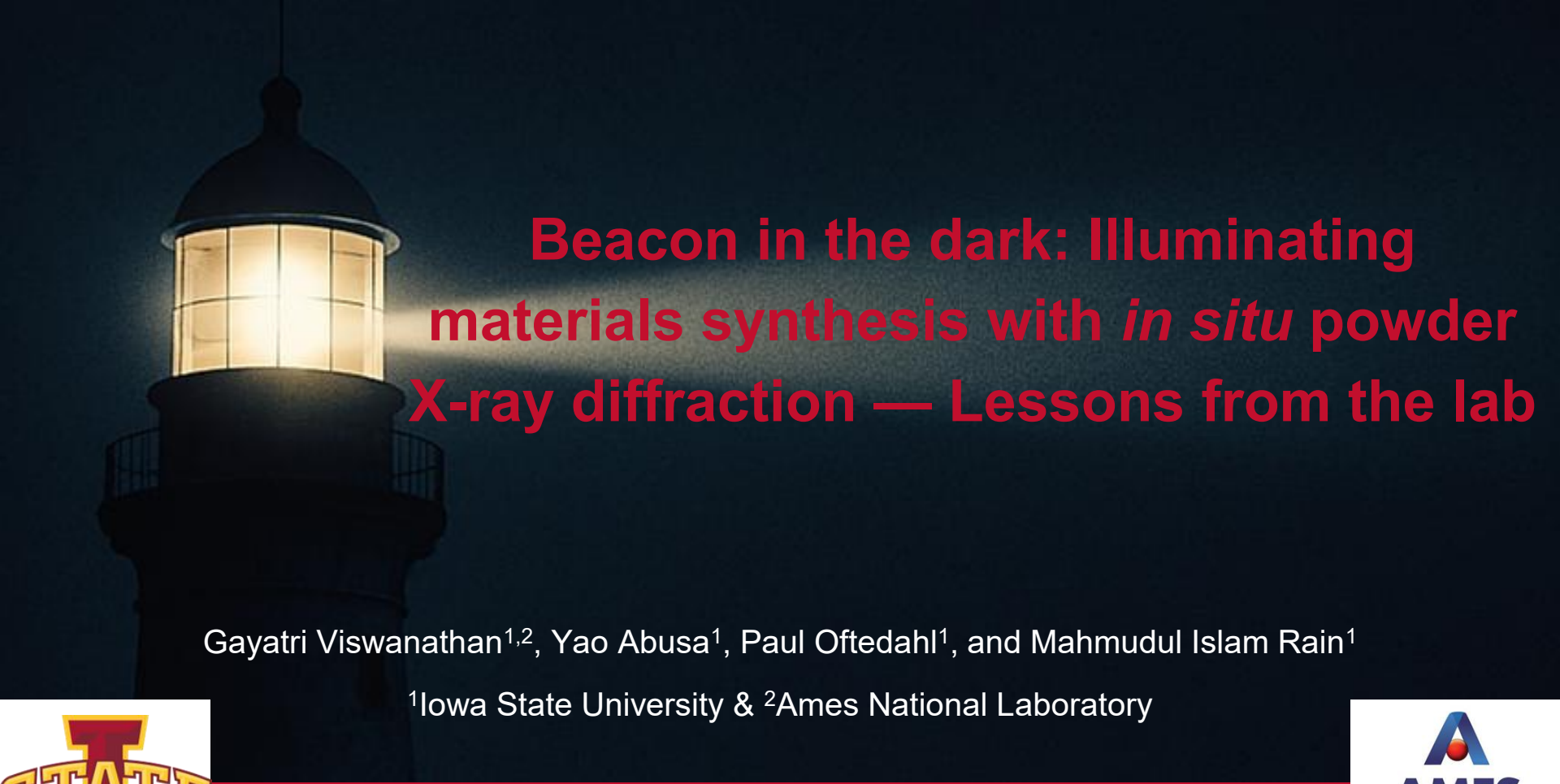


Beacon in the dark: Illuminating materials synthesis with *in situ* powder X-ray diffraction — Lessons from the lab

Gayatri Viswanathan[1,2], Yao Abusa[1], Paul Oftedahl[1], and Mahmudul Islam Rain[1]

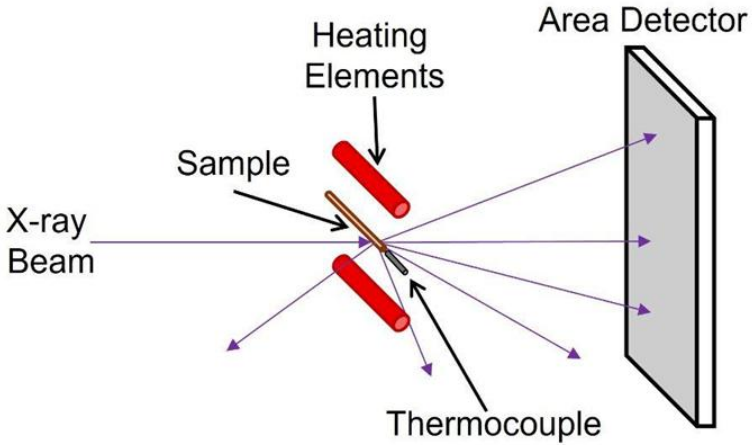
[1]Iowa State University & [2]Ames National Laboratory

In situ powder X-ray diffraction at user facilities

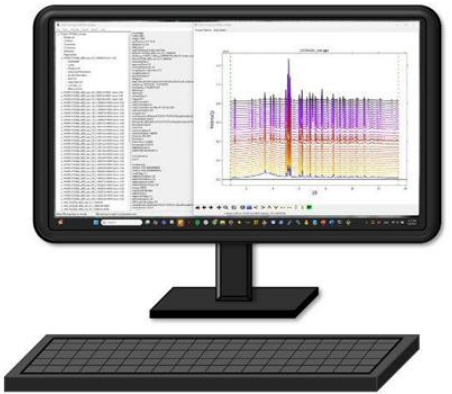
While diffraction and total scattering are primarily used to study structure, these techniques can also be leveraged to investigate materials synthesis.

In situ variable-temperature powder X-ray diffraction experiments are often conducted at user facilities.

Proposal Writing



Experiments



Data Analysis

What actually goes in the beam?

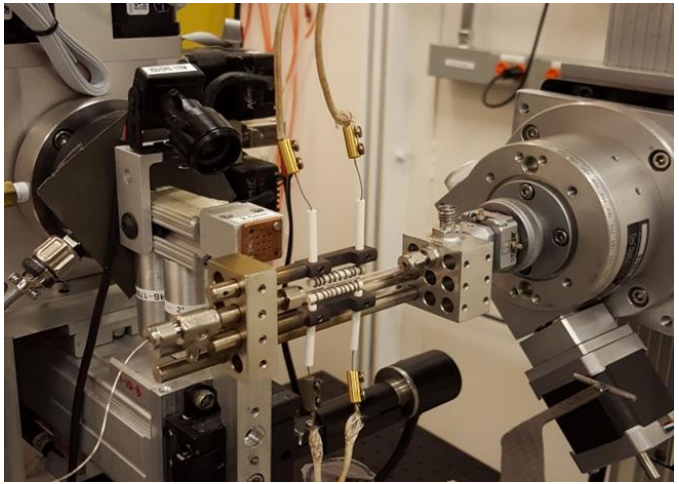
11mm OD sealed ampoule, ~7cm long

“make it mini”

0.7mm OD sealed capillary, ~3.5cm long

Considerations:

- Micron-size X-ray beam
- Need to minimize absorption
- *In situ* experiments are fast (kinetics-driven)

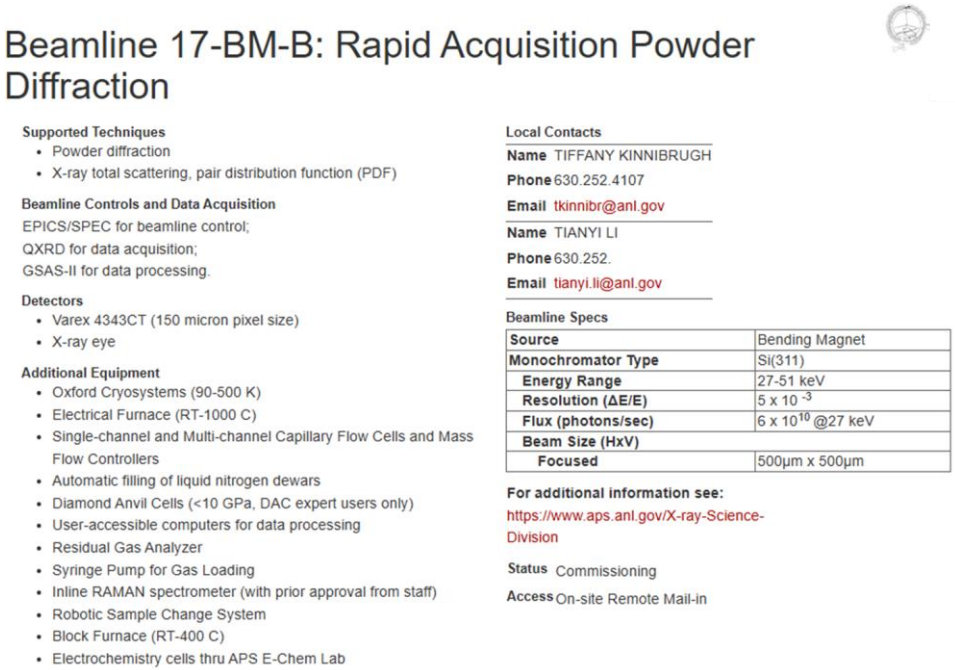


What equipment and set-ups are available?

Every beamline and facility is different!

Some beamlines and set-ups may allow for simultaneous spectroscopic measurements (ex: Raman/IR).

Advance planning and communication with beamline scientists are key to success!



Argonne NATIONAL LABORATORY | Advanced Photon Source

a U.S. Department of Energy Office of Science User Facility

Beamline 17-BM-B: Rapid Acquisition Powder Diffraction

Supported Techniques
- Powder diffraction
- X-ray total scattering, pair distribution function (PDF)

Beamline Controls and Data Acquisition
EPICS/SPEC for beamline control;
QXRD for data acquisition;
GSAS-II for data processing.

Detectors
- Varex 4343CT (150 micron pixel size)
- X-ray eye

Additional Equipment
- Oxford Cryosystems (90-500 K)
- Electrical Furnace (RT-1000 C)
- Single-channel and Multi-channel Capillary Flow Cells and Mass Flow Controllers
- Automatic filling of liquid nitrogen dewars
- Diamond Anvil Cells (<10 GPa, DAC expert users only)
- User-accessible computers for data processing
- Residual Gas Analyzer
- Syringe Pump for Gas Loading
- Inline RAMAN spectrometer (with prior approval from staff)
- Robotic Sample Change System
- Block Furnace (RT-400 C)
- Electrochemistry cells thru APS E-Chem Lab

Local Contacts

Name TIFFANY KINNIBRUGH
Phone 630.252.4107
Email tkinnibr@anl.gov

Name TIANYI LI
Phone 630.252.
Email tianyi.li@anl.gov

Beamline Specs

Source	Bending Magnet
Monochromator Type	Si(311)
Energy Range	27-51 keV
Resolution (ΔE/E)	5 x 10^{-3}
Flux (photons/sec)	6 x 10^{10} @27 keV
Beam Size (HxV)	
Focused	500μm x 500μm

For additional information see:
https://www.aps.anl.gov/X-ray-Science-Division

Status Commissioning
Access On-site Remote Mail-in

https://www.aps.anl.gov/Beamlines/Directory

Sample preparation: Choice of container

Capillary	T_{max}	Notes
kapton	400°C	semi-permeable
fused silica	1150°C	may be reactive to starting materials
alumina	1700°C	not X-ray invisible; internal temperature standard
sapphire	2000°C	expensive

When choosing an appropriate sample container, consider the following:

- Invisible to X-ray beam
- Inert to reactants
- Thermal stability
- Cost

Special requirements for neutron scattering experiments:

- Larger Sample Size
- Isotopic Enrichment
- Special Containers

A. Weiland, J. Chan, et al. *Chem. Mater.* **2021**, *33*, 7657–7664.

T.M. Kyrk, J. Chan, et al. *Chem. Mater.* **2025**, *37*, 2603−2610.

Sample preparation: Lab or On-site?

	Prep on-site?	Prep off-site?
flame-sealed	no	yes
epoxy-sealed	yes	yes
double-open-ended (gas flow/decomp)	yes	no
one-end open (solvothermal)	yes	no

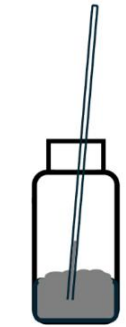
<u>For flame-sealed capillaries</u>

Prepare 3-4 replicates

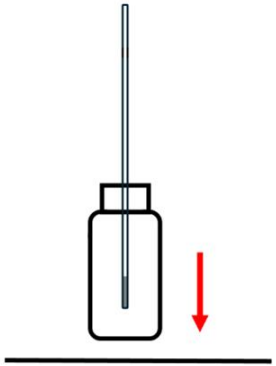
- 1 for *ex situ* test
- 1 to run
- 2 backups

0.7 mm OD capillary must fit inside shield capillary (1.1 OD or larger)

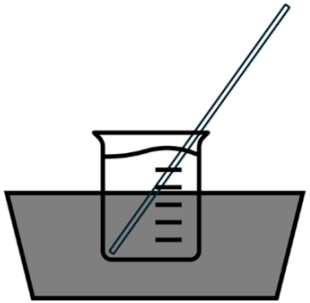
Sample preparation: Loading solid state reactions



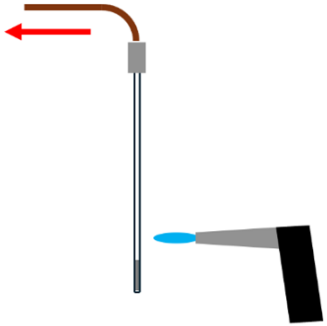
Load by capillary action



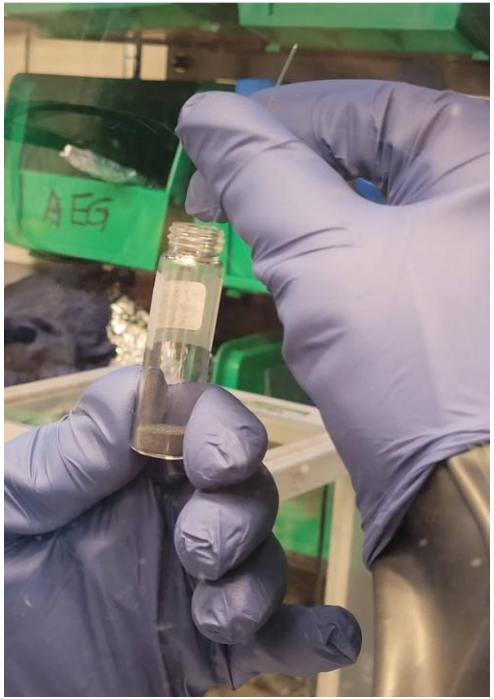
Tap to compact powders



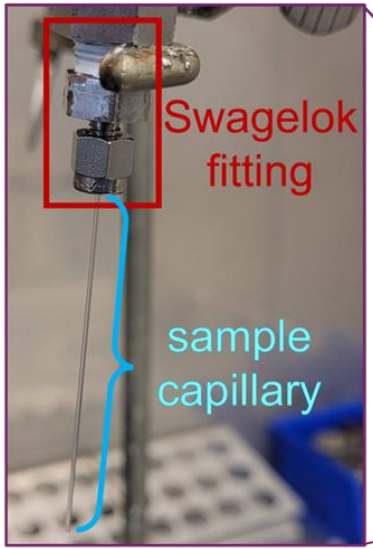
Sonicate to settle powders

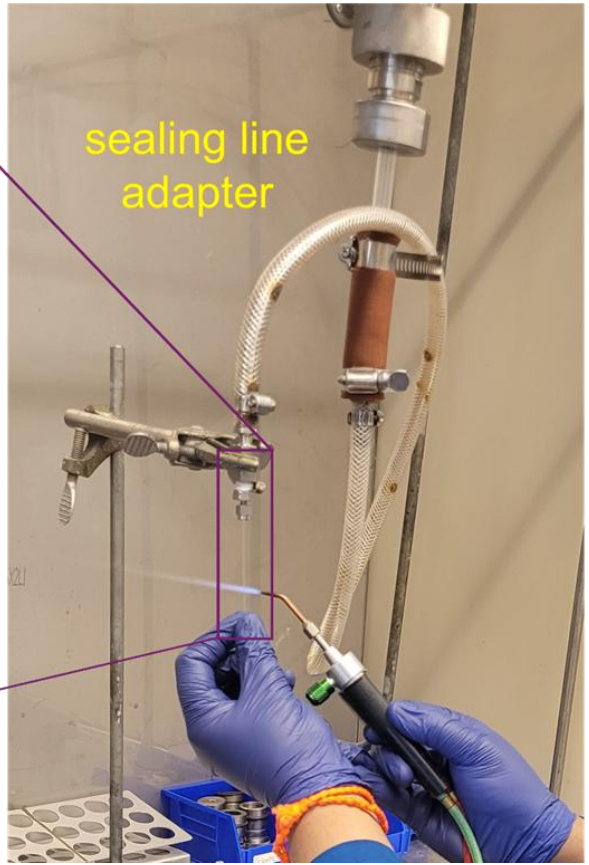


Evacuate and seal



Sample preparation: Sealing solid state reactions

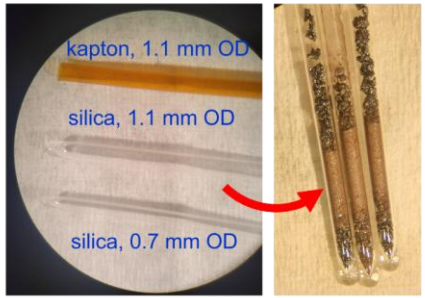




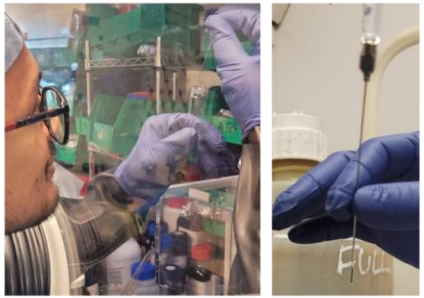
Sample preparation: Starting materials

Ideal starting materials enter the sample container easily, are well-homogenized, and will react under the experimental conditions (kinetics).

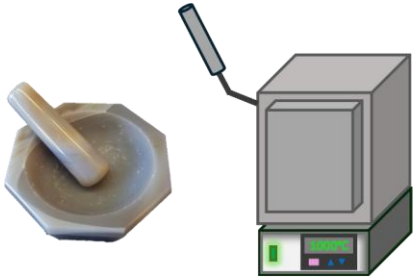
Sample Loading



particle size/morphology, air-sensitivity, liquids

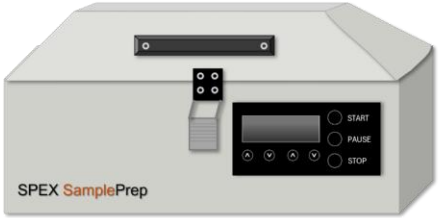


Homogenization

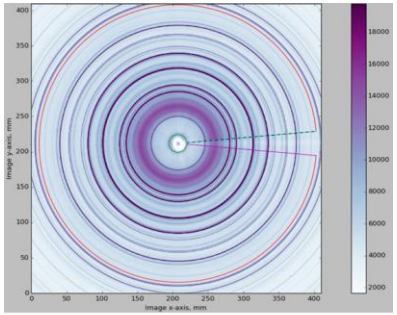


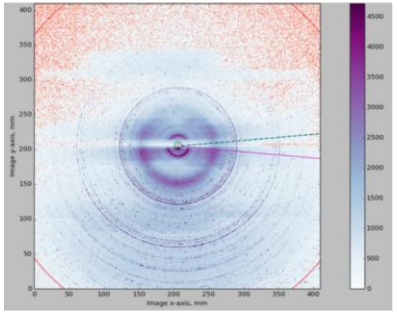
hand grinding

high-temperature pre-reaction



ball milling



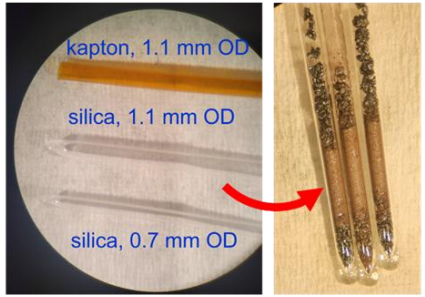


Importance of grinding samples well

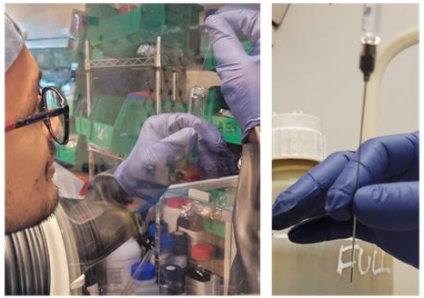
Sample preparation: Starting materials

Ideal starting materials enter the sample container easily, are well-homogenized, and will react under the experimental conditions (kinetics).

Sample Loading



particle size/morphology, air-sensitivity, liquids



Homogenization

hand grinding

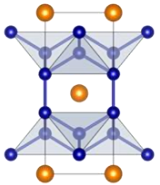
high-temperature pre-reaction

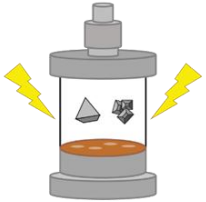
ball milling

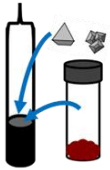
"Activation" of Reactants

hydride route – driven by decomposition

pre-form chemical bonds



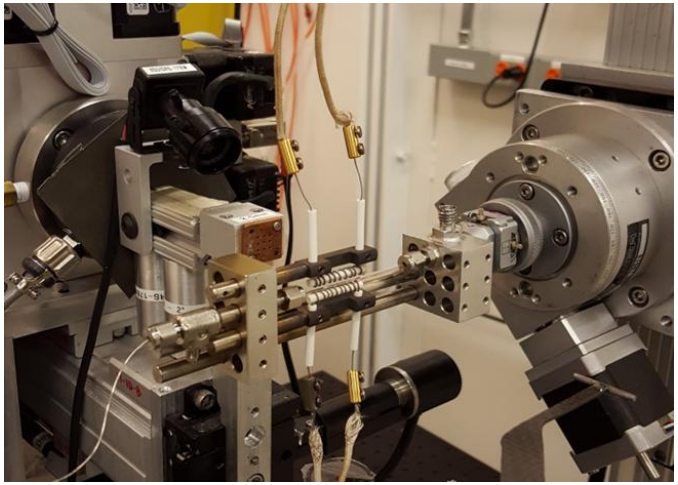


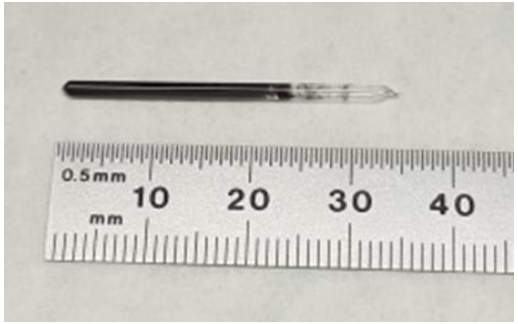


in-lab "first annealing"

activation of elemental Se

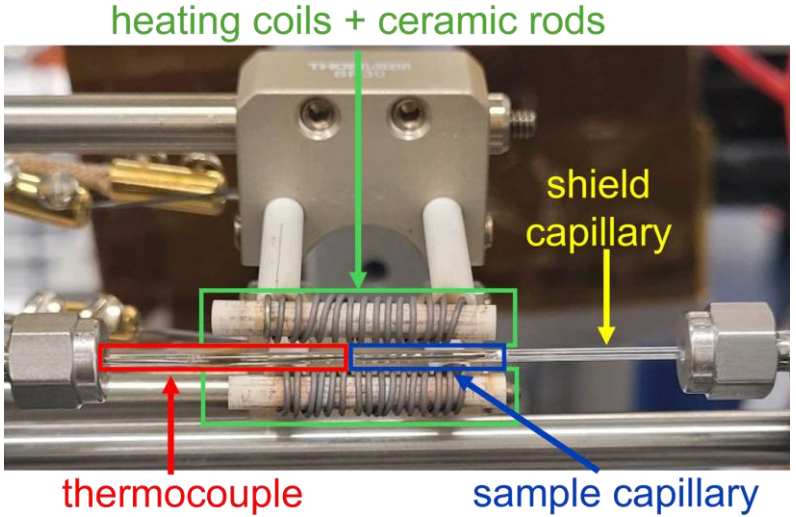
Traditional solid state synthesis





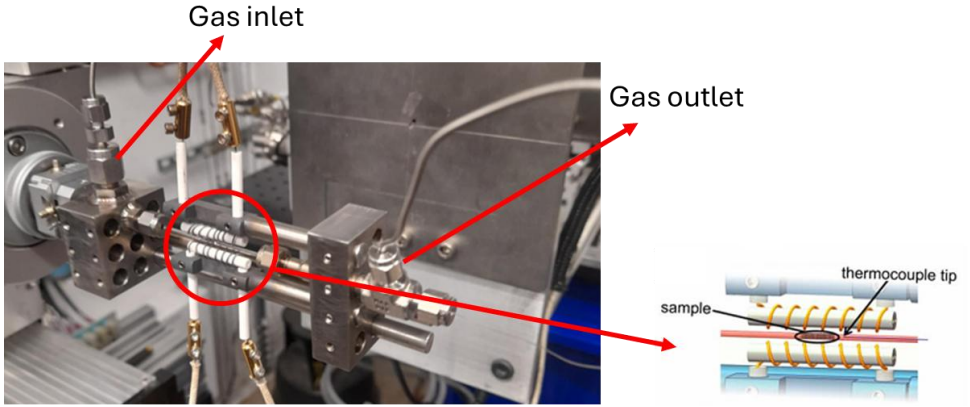
Study phase formation or decomposition.

Sealed capillaries are mounted in a flow cell between resistive coil heaters. Cell is typically mounted horizontally and reaches up to 1000°C.



Gas flow reactions

Study catalytic reactions (e.g., CO oxidation, methane reforming), gas adsorption/ desorption, and gas-induced phase transitions or reduction/oxidation processes.



The flow-cell supports diverse environments:

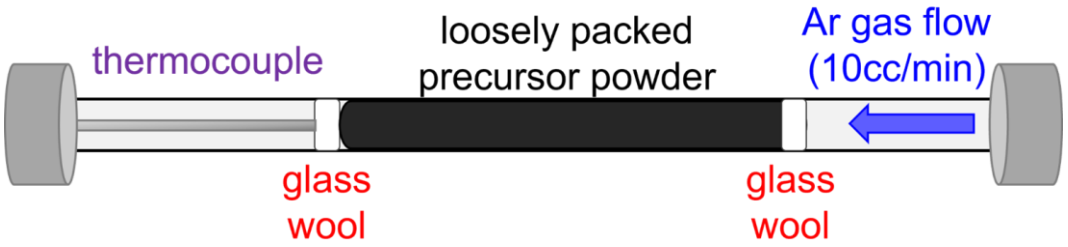
- Gas, vapor, and fluid under static or flow conditions
- Flow rates up to 100 mL/min
- Pressure range: vacuum to 2000 psi

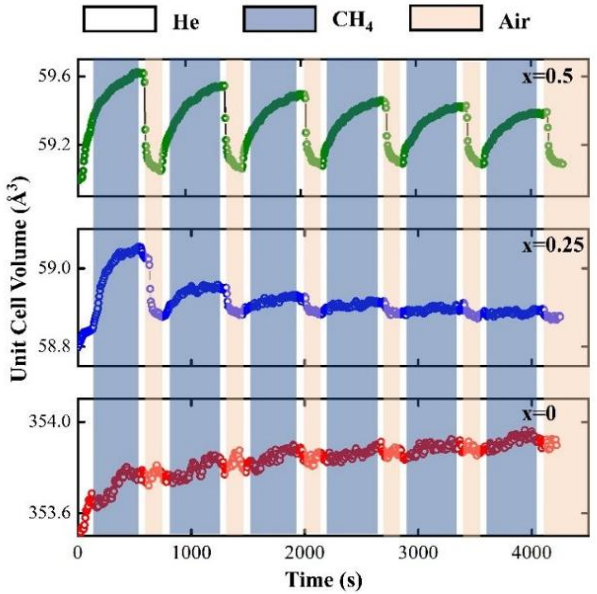
Under flow conditions, the exhaust can also be controlled and diverted for further analysis, such as residual gas analysis.

J.A. Rodriguez, J. Evans, et al. *Top. Catal.* **2007,** 44, 73–81.; K.W.Chapman, J.W. Richardson, et al. *Chem. Commun*. **2006**, 4013–4015.; D.D. Nguyen, A.M. Fry-Petit et al. *ACS Mater. Au* **2025**, 5, 3, 547–557; P.J. Chupas, C.P. Grey, et al. *J. Appl. Cryst.* **2008,** *41*, 822–824.

Gas flow reactions

Sample loaded at the center of a 1.1 mm OD double-open-ended capillary.
Glass wool is used to support the sample.
Gas flowed over powder toward thermocouple.





Refined cell volumes from *in situ* SXRD on $La_{1-x}Sr_xCoO_{3-\delta}$ after six chemical looping cycles at 800°C.

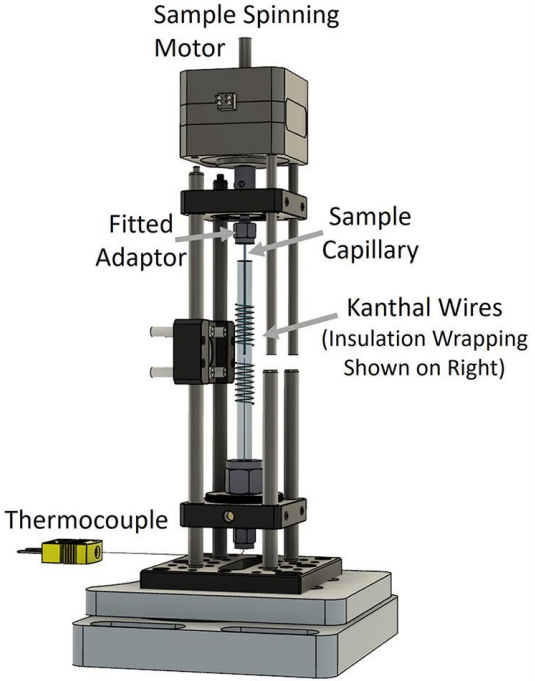
F.A. Perras, et al. J. *Am. Chem. Soc.* **2023**, 145, 27, 14660–14669.
T. Li, E.E. Rodriguez, et al. *Chem. Commun.* **2019**, *55*, 4929.

Hydride reactions

Closed systems where a liquid or gas component is evolved require special considerations.

Autogenous pressure can lead to rupture of capillaries – leave empty space when sealing.

Vertically-mounted capillaries may help mitigate sample movement out of the beam.



$$22NaH + 4Zn + 10Bi \rightarrow 2Na_{11}Zn_2Bi_5 + 11H_2$$

$$MgH_2 + 3Co + 2B \rightarrow MgCo_3B_2 + H_2$$

V. Gvozdetskyi, J. V. Zaikina, et al. *Chem. Eur. J.* **2021**, *27*, 15954–15966.
P. Oftedahl, J. V. Zaikina, et al. *Chem. Mater.* **2024**, *36*, 9834–9847.
A. Weiland, J. Chan, et al. *Chem. Mater.* **2021,** *33*, 7657–7664.

High vapor pressure and flux reactions

Vapor transport/high vapor pressure (e.g., iodine, mercury)

- Allow empty space
- Iodine as transport agent: sandwich powders between I_2

$$7Ni + 2BI_3 \rightarrow 2Ni_3B + NiI_2 + 2I_2$$

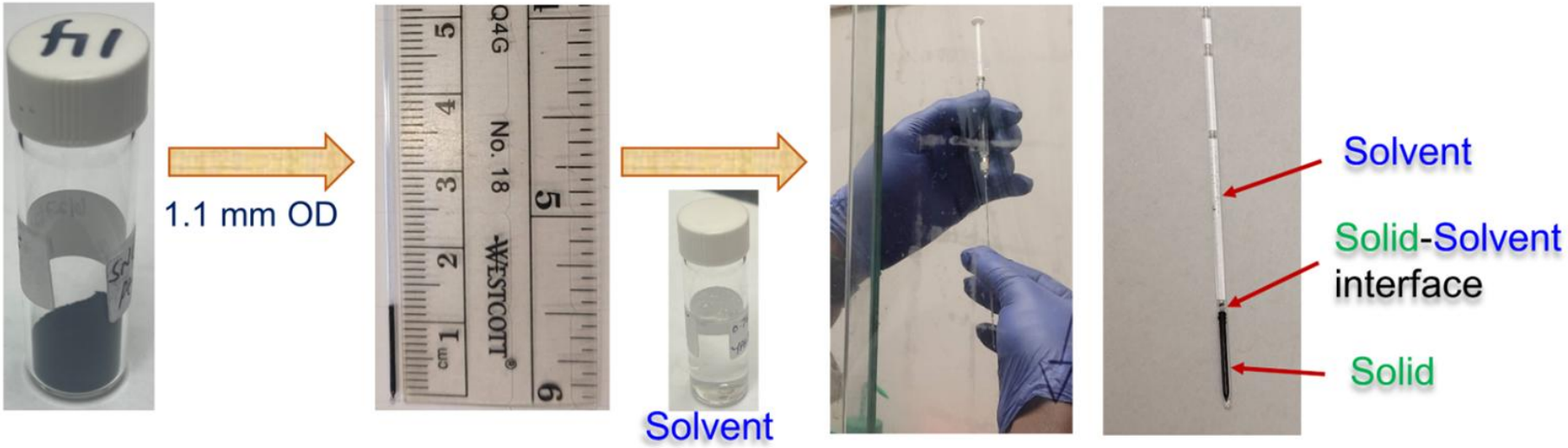
$$2Mo + 4Fe + 6B + 3I_2 \rightarrow 2MoFe_2B_2 + 2BI_3$$

Flux/crystal growth

- Can be run in horizontal or vertical setup
- Horizontal: if flux has low viscosity, it may spread and run out of the beam
- Vertical: flux and precursors may separate by density
- Choose appropriate flux to sample ratio

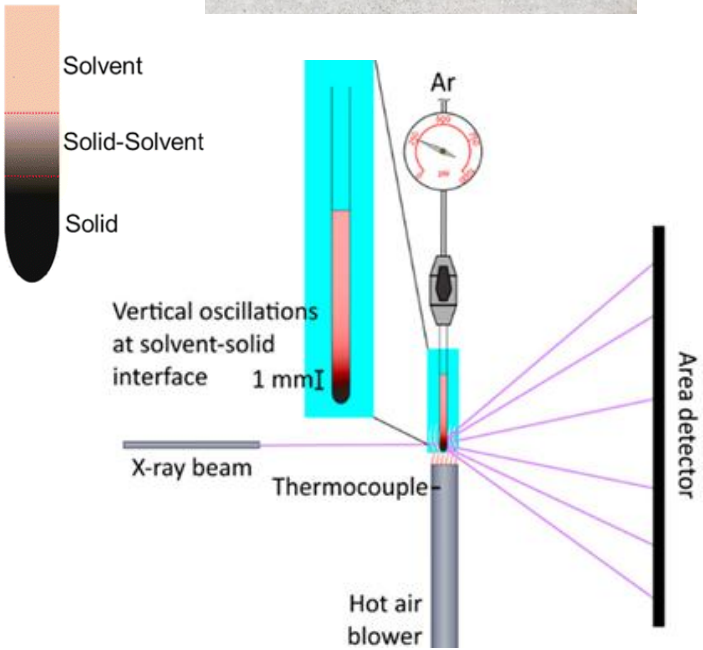
K.E. Woo, S. Kong, K. Kovnir, et al. *J. Mater. Chem. A* **2022**,10, 21738-21749.
E.H. Gamage, K. Kovnir, et al. *Submitted*.
A. Weiland, J. Chan, et al. Chem. Mater. **2021,** *33*, 7657–7664.

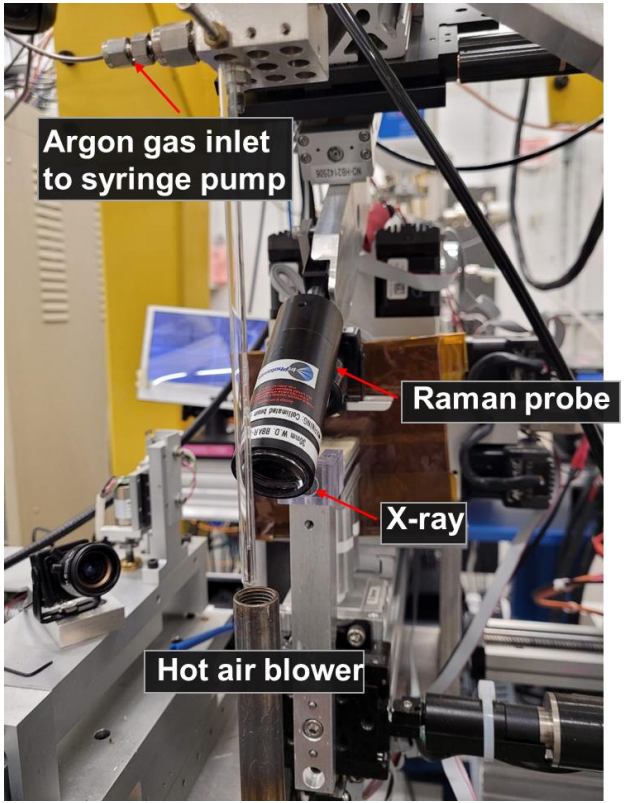
Working with powders and solvents

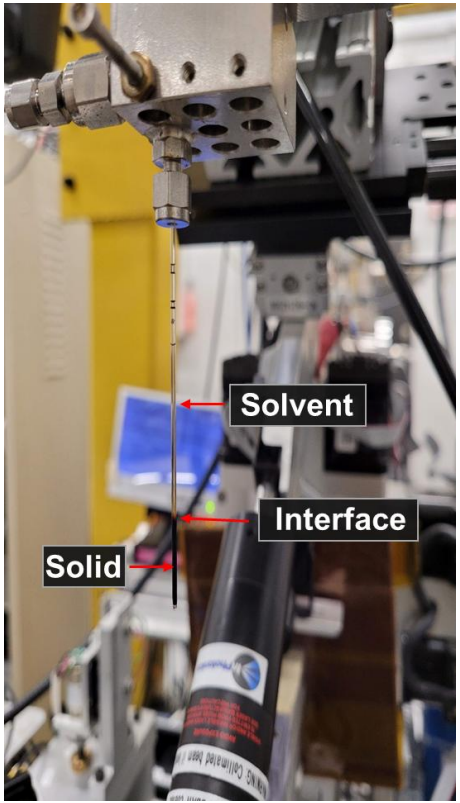


Solids and solvents are loaded in a fume hood of the designated lab space.

Solvothermal synthesis







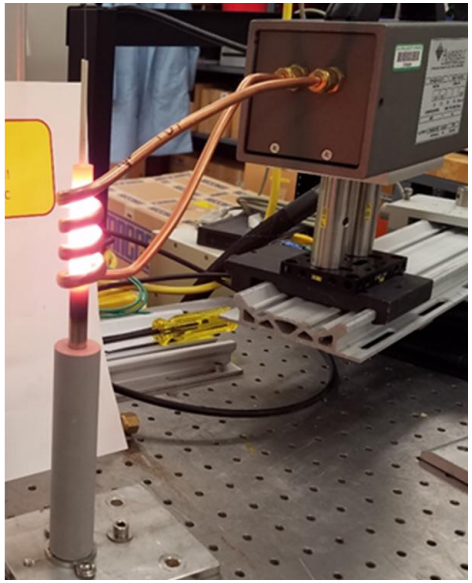
E. Gamage, K. Kovnir, et. al. *Inorg. Chem.* **2020**, *59*, 13353–13363.
D. Amarasinghe, K. Kovnir, et al. *Dalton Trans.* **2022**, 51, 16748-16756.

Other sample environments and scientific commissioning

These APS beamlines (and other facilities) may have other equipment available. Determine what environment is most suitable for your proposed experiments.

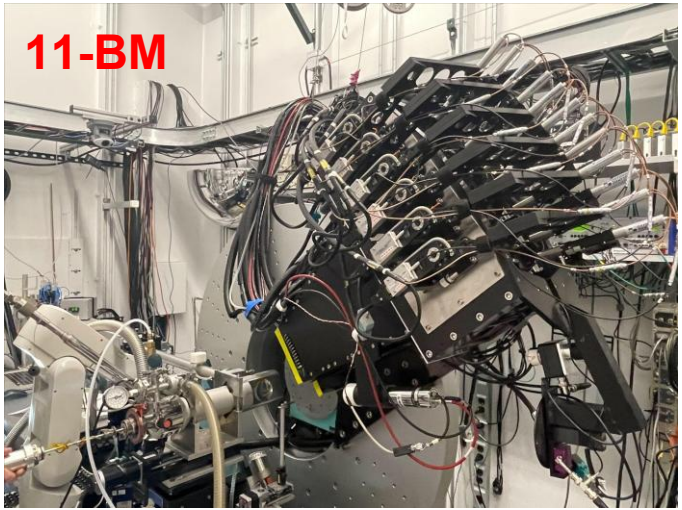
Users can bring their own set-up or collaborate with instrument scientists to commission a new sample environment.

For example, currently, an induction furnace (RF) set-up is not available at APS for powder diffraction/total scattering studies (beamline 17-BM or Sector 11).



Data collection: Resolution vs Speed

1D detector with many analyzer crystals



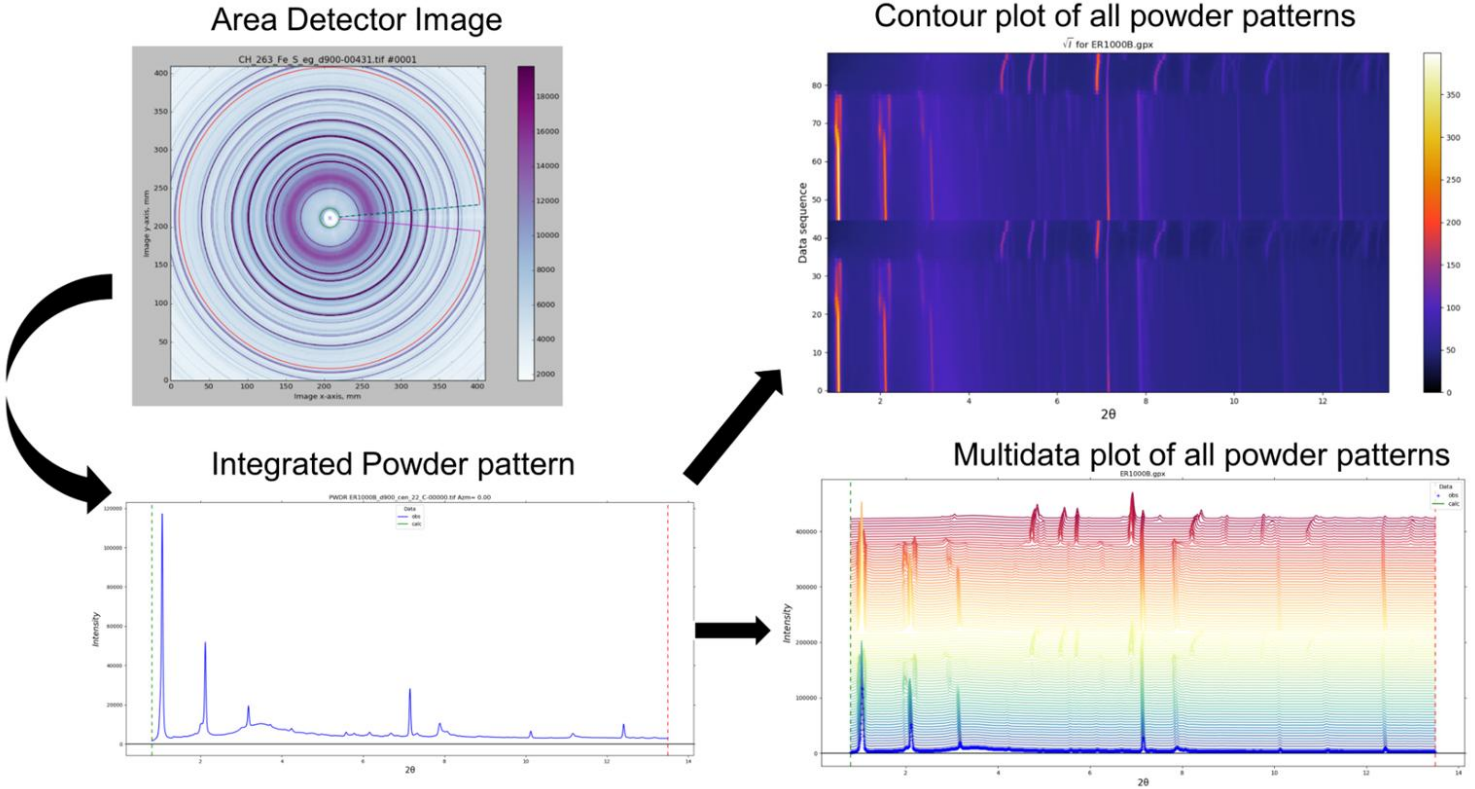
High angular resolution
Less flexibility in geometry
Longer acquisition time (10 min - 1 h)

2D area detector

Lower resolution, higher background
Requires image calibration and integration
Rapid data collection (< 30 s)

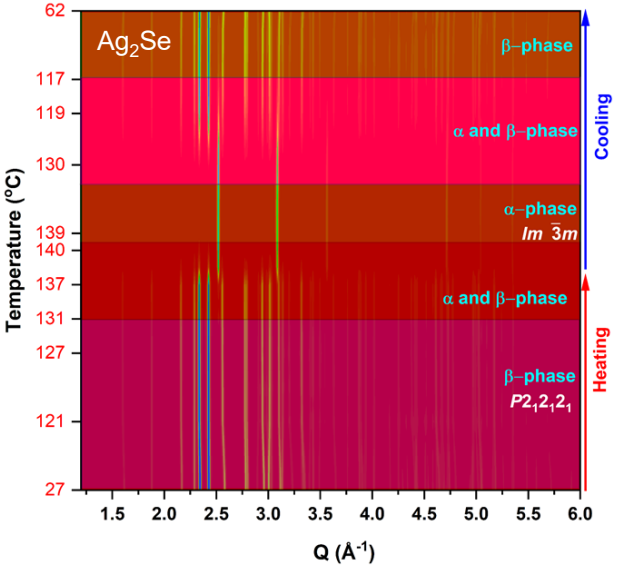
Integration and analysis

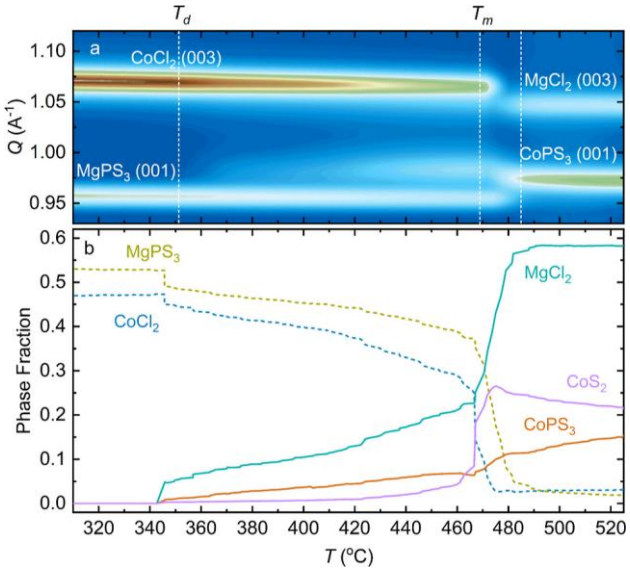
Images generated using GSAS II

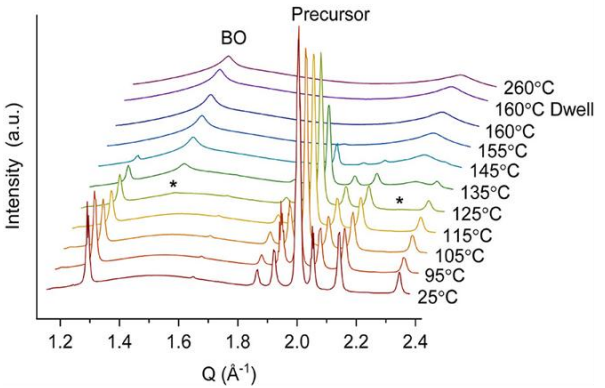


2D diffraction images are processed into 1D PXRD patterns, which can be visualized in different forms depending on the analysis needs.

Graphical representations of *in situ* data







These representations are helpful for tracking subsequent phase transitions and quantifying phase fractions through sequential Rietveld refinement.

Y. Abusa, K. Kovnir, et al. *J. Am. Chem. Soc.* **2024**, 146, 16, 11382–11391.
H.C. Mandujano, E.E Rodriguez, et al. *Chem. Mater.* **2024**, 36, 10, 5172–5183.
F.A. Perras, et al. J. *Am. Chem. Soc.* **2023**, 145, 27, 14660–14669.

Where do I start: Beamlines for *in situ* experiments

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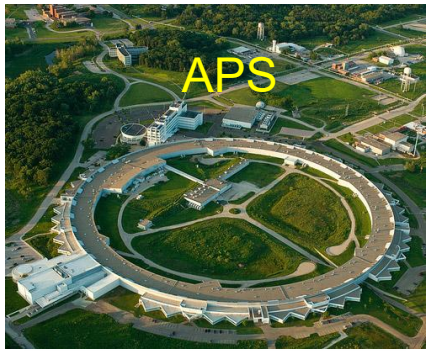


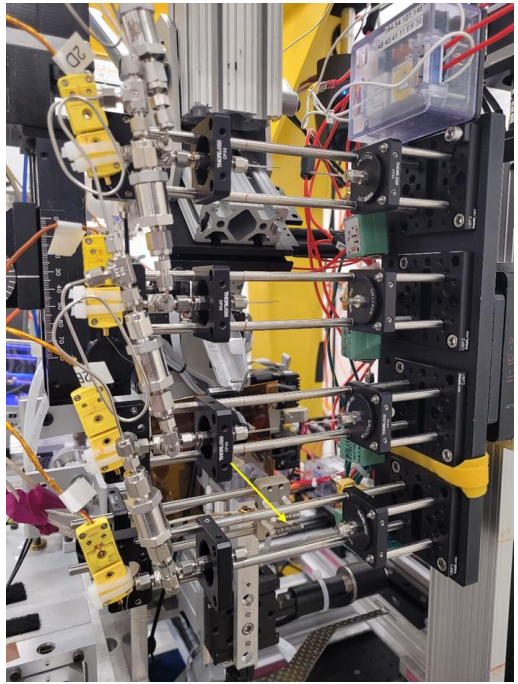
17-BM, 11-ID-B
11-ID-C, 11-BM

Brookhaven National Laboratory

NSLS-II 28-ID-1, 2

Canadian Light Source | Centre canadien de rayonnement synchrotron

BDXS-WLE, WHE



Mail-in options available
(17-BM, APS)

OAK RIDGE National Laboratory

ORNL SNS

POWGEN, NOMAD

SSRL

SSRL 2-1

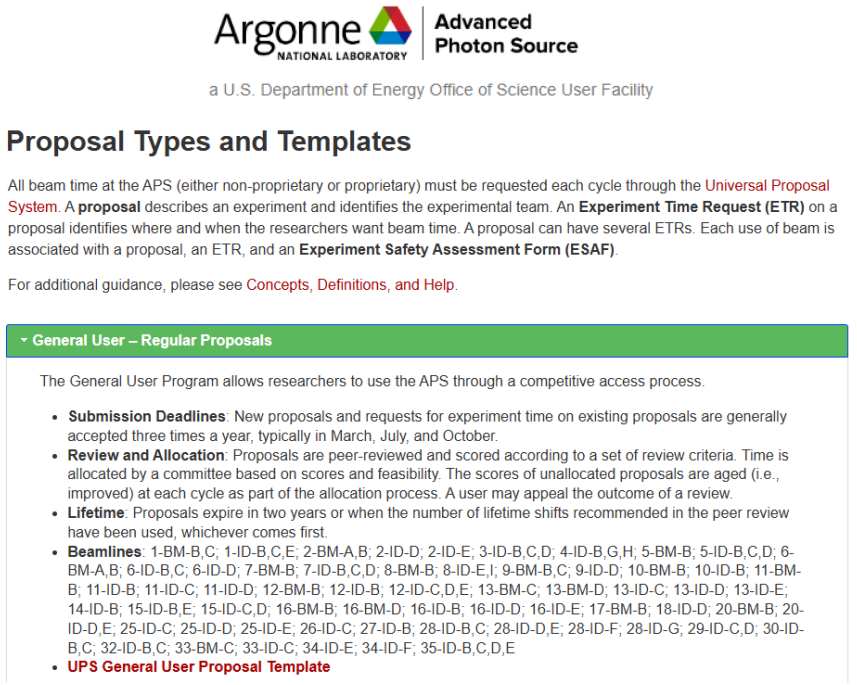
https://www.aps.anl.gov/Structural-Science

How do I get beamtime: The art of proposal writing

- ❑ Impact of research
- ❑ Quality of research plan
- ❑ Justification of need for facility resources

Develop a clear hypothesis and goals, then make a detailed experimental plan. Include preliminary results, if possible.

Seek feedback from beamline scientists (and don't wait for the last few days)! Pay attention to deadlines.



Argonne NATIONAL LABORATORY | Advanced Photon Source

a U.S. Department of Energy Office of Science User Facility

Proposal Types and Templates

All beam time at the APS (either non-proprietary or proprietary) must be requested each cycle through the Universal Proposal System. A **proposal** describes an experiment and identifies the experimental team. An **Experiment Time Request (ETR)** on a proposal identifies where and when the researchers want beam time. A proposal can have several ETRs. Each use of beam is associated with a proposal, an ETR, and an **Experiment Safety Assessment Form (ESAF)**.

For additional guidance, please see Concepts, Definitions, and Help.

General User – Regular Proposals

The General User Program allows researchers to use the APS through a competitive access process.

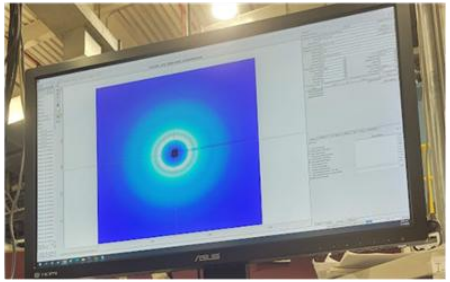
- **Submission Deadlines**: New proposals and requests for experiment time on existing proposals are generally accepted three times a year, typically in March, July, and October.
- **Review and Allocation**: Proposals are peer-reviewed and scored according to a set of review criteria. Time is allocated by a committee based on scores and feasibility. The scores of unallocated proposals are aged (i.e., improved) at each cycle as part of the allocation process. A user may appeal the outcome of a review.
- **Lifetime**: Proposals expire in two years or when the number of lifetime shifts recommended in the peer review have been used, whichever comes first.
- **Beamlines**: 1-BM-B,C; 1-ID-B,C,E; 2-BM-A,B; 2-ID-D; 2-ID-E; 3-ID-B,C,D; 4-ID-B,G,H; 5-BM-B; 5-ID-B,C,D; 6-BM-A,B; 6-ID-B,C; 6-ID-D; 7-BM-B; 7-ID-B,C,D; 8-BM-B; 8-ID-E,I; 9-BM-B,C; 9-ID-D; 10-BM-B; 10-ID-B; 11-BM-B; 11-ID-B; 11-ID-C; 11-ID-D; 12-BM-B; 12-ID-B; 12-ID-C,D,E; 13-BM-C; 13-BM-D; 13-ID-C; 13-ID-D; 13-ID-E; 14-ID-B; 15-ID-B,E; 15-ID-C,D; 16-BM-B; 16-BM-D; 16-ID-B; 16-ID-D; 16-ID-E; 17-BM-B; 18-ID-D; 20-BM-B; 20-ID-D,E; 25-ID-C; 25-ID-D; 25-ID-E; 26-ID-C; 27-ID-B; 28-ID-B,C; 28-ID-D,E; 28-ID-F; 28-ID-G; 29-ID-C,D; 30-ID-B,C; 32-ID-B,C; 33-BM-C; 33-ID-C; 34-ID-E; 34-ID-F; 35-ID-B,C,D,E
- **UPS General User Proposal Template**

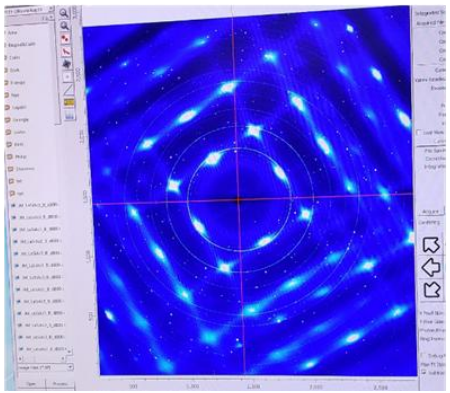
https://www.aps.anl.gov/Users-Information/About-Proposals/Apply-for-Time
https://www.aps.anl.gov/Users-Information/About-Proposals/Review-Criteria-for-General-User-Proposals
https://www.aps.anl.gov/Users-Information/About-Proposals/Proposal-Types

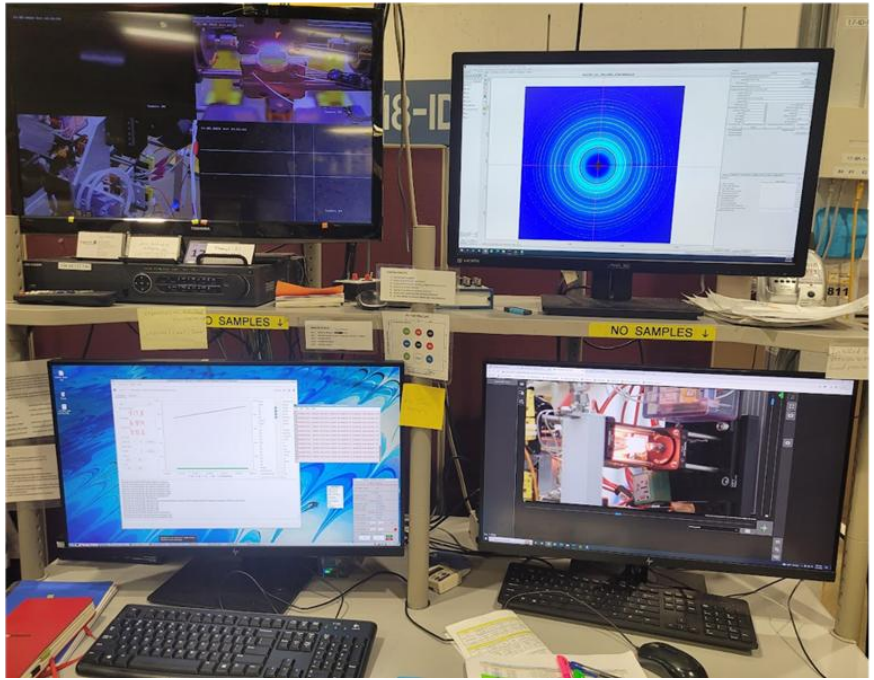
Conducting *in situ* PXRD experiments

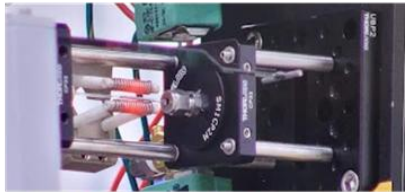
An experiment may last a little as an hour or as long as a few days. Regular monitoring is required as well as troubleshooting and flexibility.

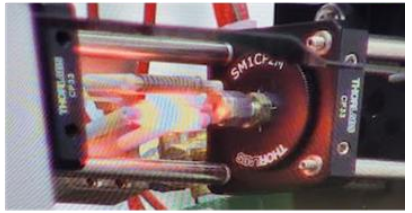
"Mission Control" – Yao Abusa

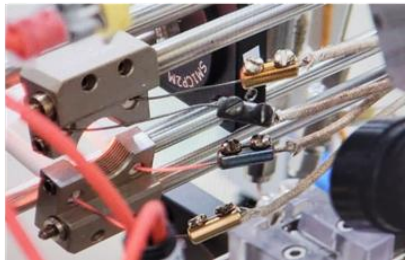








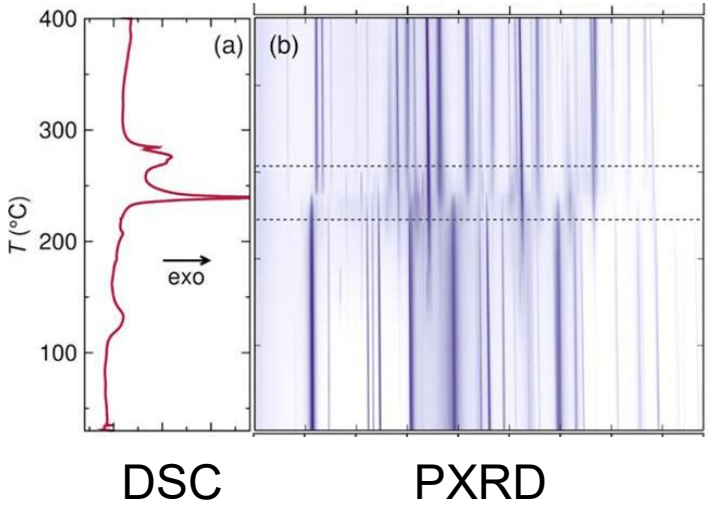




Preparation: Key to beamtime success!

Preliminary experiments:

- *Ex situ* reactions (in a capillary or other ampoule/crucible)
- DSC/DSC-TGA
- Mass spectrometry (especially for gas flow experiments)
- Capillary tests – does it survive???



Use every second of beamtime: calculate total time, prioritize samples

Know your systems: be prepared with CIFs/powder patterns of potential phases

- Powder databases (e.g. ICDD) may not be available on-site
- Plot data in Q-space

A.J. Martinolich and J.R. Neilson. *Chem. Mater.* **2017**, *29*, 479– 489.

Preparation: Key to beamtime success!

Questions to address with beamline staff:

- ❑ What sample cells are available?
- ❑ What temperature/heating rates are attainable in each setup?
- ❑ Sample environment setup: will beamtime be used, or can setup be done in advance?
- ❑ Sample environment changes: how long will it take?
- ❑ What challenges do you foresee with our experimental plan?
- ❑ Will lab space be required on-site?
- ❑ Will special components (e.g. reactive gases) have to be ordered in advance?

Flexibility is key! Be ready to change sample priorities and adapt based on incoming beamtime results

Tip: new users should avoid scheduling over a weekend if possible

Final remarks

In situ studies can offer valuable insight into materials synthesis to alleviate the bottleneck between materials prediction/discovery to realization.

- One successful *in situ* reaction saves significant time and effort in lab
- One beamtime may be up to 50 reactions (not all “successful” but informative)

Experimentation at user facilities requires proposal writing, good communication with instrument scientists, and a clear experimental plan.

- Be sure to acknowledge facilities and beamline scientists in resulting publications/dissertations!

Acknowledgements

Argonne NATIONAL LABORATORY

Advanced Photon Source

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Tianyi Li (11-ID-C)

Helpful resources: Overview of *in situ* studies + methods

General overview/applications

M.G. Kanatzidis and R. McClain. Panoramic (in beam) studies of materials synthesis. In Comprehensive Inorganic Chemistry III, Third Edition; Reedijk, J., Poeppelmeier, K. R., Eds.; Elsevier, **2023**; Vol. 1–10, pp 187–199.

P.J. Chupas, K.W. Chapman, G. Jennings, P.L. Lee, C.P. Grey. Watching Nanoparticles Grow: The Mechanism and Kinetics for the Formation of TiO_2-Supported Platinum Nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, 13822– 13824.

D. P. Shoemaker, Y.-J. Hu, D. Y. Chung, G. J. Halder, P. J. Chupas, L. Soderholm, J. F. Mitchell, M. G. Kanatzidis. In situ studies of a platform for metastable inorganic crystal growth and materials discovery. *PNAS* **2014**, *111*, 10922-10927.

R.B. Stubkjær, M. Kløve, A. Bertelson, A.B. Borup, M. Roelsgaard, B.B. Iversen. Reliability of pair distribution function analysis in in situ experiments. *J. App. Crystallogr.* **2025**, *58*, 495-503.

Helpful resources: Sample environments + examples

Sample environments

P.J. Chupas, K.W. Chapman, C. Kurtz, J.C. Hanson, P.L. Lee, C.P Grey. A versatile sample-environment cell for non-ambient X-ray scattering experiments *J. Appl. Crystallogr.* **2008**, 41, 822– 824

A. Weiland, M. Frith, S. Lapidus, J.Y. Chan. In Situ Methods for Metal-Flux Synthesis in Inert Environments. *Chem. Mater.* **2021**, *33*, 7657–7664.

D. Hu, M.L. Beauvais, B.G. Mullens, B.A.S. Monserrate, S.M. Vornholt, G.E. Kamm, J.J. Ferrari, P.J. Chupas, K.W Chapman. The RAPTR furnace: a rapid heating and cooling sample furnace for in situ X-ray scattering studies of temperature-induced reactions. *J. Appl. Crystallogr.* **2024**, *57*, 88-93.

S. Vornholt, J. Ferrari, B. Mullens, B.S. Monserrate, J. Hoffman, P. Chupas, K. Chapman. Bridging the gap between synchrotron and laboratory-based in situ powder diffraction. *ChemRxiv*, **2025**.

Metathesis/ion exchange reactions

Martinolich, A. J.; Neilson, J. R. Toward Reaction-by-Design: Achieving Kinetic Control of Solid State Chemistry with Metathesis. *Chem. Mater.* **2017**, *29*, 479– 489.

C.L. Rom, M. Jankousky, M.Q. Phan, S. O'Donnell, C.E. Regier, J.R. Neilson, V. Stevanović, A. Zakutayev. Ion Exchange Synthesizes a Metastable Layered Polymorph of $MgZrN_2$ and $MgHfN_2$ Semiconductors. *Chem. Mater.* **2025**, *37*, 2136–2144.

Helpful resources: Examples of “activated” precursors

Using products of high-temperature pre-reactions

P.Yox, F. Cerasoli, A. Sarkar, V. Kyveryga, G. Viswanathan, D. Donadio, K. Kovnir. New Trick for an Old Dog: From Prediction to Properties of “Hidden Clathrates” $Ba_2Zn_5As_6$ and $Ba_2Zn_5Sb_6$. *J. Am. Chem. Soc.* **2023***, 145*, 4638–4646.

Using arc-melted precursors

G. Akopov, J. Mark, G. Viswanathan, S.J. Lee, B.C. McBride, J. Won, F.A. Perras, A.L. Paterson, B. Yuan, S. Sen, A.N. Adeyemi, F. Zhang, C.Z. Wang, K.M. Ho, G.J. Miller, K. Kovnir. Third times the charm: Intricate non-centrosymmetric polymorphism in $LnSiP_3$ (Ln = La and Ce) induced by distortions of phosphorus square layers. *Dalton Trans.* **2021**, *50*, 6463-6476.

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Activation of elemental selenium for low-temperature synthesis

Y. Abusa, P. Yox, S. Cady, G. Viswanathan, J. Opare-Addo, E. Smith, Y. Mudryk, O.I. Lebedev, F. Perras, K. Kovnir. Make selenium reactive again: Activating elemental selenium for synthesis of metal selenides ranging from nanocrystals to large single crystals. *J. Am. Chem. Soc.* **2023**, *145*, 22762-22775.

Helpful resources: Working with gases and fluxes

Gas flow reactions

F. Perras, H. Thomas, P. Heintz, R. Behera, J. Yu, G. Viswanathan, D. Jing, S. Southern, K. Kovnir, L. Stanley, W. Huang. The Structure of Boron Monoxide. *J. Am. Chem. Soc.* **2023**, *145*, 14660-14669.

D. D. Nguyen, M. J. Milhander, E.M. Hitch, D. L.M. Cordova, J. L.G. Jimenez, J. Mora, D. Sandoval, M.Q. Arguilla, A.M. Fry-Petit. Direct Correlation of the Crystalline Phases of $La_{0.9}Sr_{0.1}Co_{1-y}Fe_yO_{3-\delta}$ with the Partial Oxidation of Methane via In Situ Neutron and Synchrotron Diffraction, *ACS Mater. Au* **2025**, *5*, 547–557.

Hydride synthesis

A.N Adeyemi, G.B. Bhaskar, T. Cox, S. Hong, V. Gvozdetskyi, J.V. Zaikina. Hydride Precursors in Materials Synthesis. In Comprehensive Inorganic Chemistry III, Third Edition; Reedijk, J., Poeppelmeier, K. R., Eds.; Elsevier, **2023**; Vol. 1–10, pp 128–146.

Iodide reactions

K.E. Woo, S. Kong, W. Chen, T.H. Chang, G. Viswanathan, A.M Diez, V. Sousa, Y.V. Kolen'ko, O.I Lebedev, M.C. Figueiredo, K. Kovnir. Topotactic BI_3-assisted borodization: Synthesis and electrocatalysis applications of transition metal borides. *J. Mater. Chem. A* **2022,** *10,* 21738-21749.

Z. Zhang, E.H Gamage, G. Amobi, S. Pradhan, A. Kutepov, K.D. Belashchenko, Y. Sun, K. Kovnir, V. Antropov. Discovery and Synthesis of a Family of Boride Altermagnets. *J. Am. Chem. Soc.* **2025**, *147*, 30117-30135.

Helpful resources: Solution chemistry and fluxes

In situ solvothermal synthesis

K.M.Ø. Jensen, C. Tyrsted, M. Bremholm, B.B. Iversen. In Situ Studies of Solvothermal Synthesis of Energy Materials. *ChemSusChem* **2014**, *7*, 1594-1611.

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Flux synthesis

D.P. Shoemaker, D.Y. Chung, J.F. Mitchell, T.H. Bray, L. Soderholm, P.J. Chupas and M.G. Kanatzidis. Understanding Fluxes as Media for Directed Synthesis: In Situ Local Structure of Molten Potassium Polysulfides. *J. Am. Chem. Soc.* **2012**, *134*, 9456-9463.

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Helpful resources: Neutron diffraction examples

J. Liu, P.S. Whitfield, M.R. Saccomanno, S.-H. Bo, E. Hu, X. Yu, J. Bai, C.P. Grey, X.-Q. Yang, P.G. Khalifah. In Situ Neutron Diffraction Studies of the Ion Exchange Synthesis Mechanism of $Li_2Mg_2P_3O_9N$: Evidence for a Hidden Phase Transition. *J. Am. Chem. Soc.* **2017**, *139*, 9192–9202.

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